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PROGRAMA DE DOCTORADO EN BIOTECNOLOGÍA ALIMENTARIA

**RECUPERACIÓN DE CONDENSADOS DE INDUSTRIAS LÁCTEAS MEDIANTE
TECNOLOGÍA DE MEMBRANAS. Evaluación técnica y económica**

Tesis Doctoral

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RESUMEN DEL CONTENIDO DE TESIS DOCTORAL

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RESUMEN (en español)

Los crecientes costes en el suministro y tratamiento de aguas y la tendencia hacia políticas de eficiencia energética están obligando a la industria alimentaria en general, y el sector lácteo en particular, a buscar alternativas de reaprovechamiento de recursos económicamente beneficiosas. En este sentido, CAPSA FOOD (Corporación Alimentaria Peñasanta S.A.) se ha planteado la recuperación de condensados de *flash cooler* generados en el tratamiento UHT directo, donde diferentes tipos de leches y derivados lácteos son procesados con el fin de alargar su vida útil. Estas aguas están consideradas como efluentes de baja carga contaminante, lo que hace que, junto con su temperatura (40–85°C), presenten unas características atractivas para su reutilización.

En este marco se desarrolla la presente tesis doctoral, donde se propone el tratamiento de estos condensados mediante técnicas de membranas con el objetivo principal de producción de agua de alta calidad para alimentación a calderas. El estudio, de carácter semi-industrial de acuerdo a los volúmenes manejados, se llevó a cabo *in situ* utilizando aguas reales de la factoría cuya naturaleza heterogénea hizo que su tratamiento mediante membranas implicase cierto desafío.

En la primera parte del estudio se realizó un análisis exhaustivo de los condensados obtenidos en los cuatro *flash coolers* operativos en la fábrica, para lo cual se tomaron muestras, durante semanas, en distintos momentos de sus ciclos observándose que, a pesar del bajo nivel de contaminación de las aguas, su heterogeneidad iba marcada tanto por el modo de funcionamiento de cada unidad así como por el momento del ciclo en el que se tomaba la muestra. De acuerdo con la composición media de los condensados se valoraron diferentes alternativas de tratamiento, utilizándose membranas de nanofiltración y ósmosis inversa de diferentes características. Ensayos en discontinuo permitieron seleccionar la opción más viable desde el punto de vista técnico y de cumplimiento de los objetivos propuestos. La ósmosis inversa con membranas de la gama Duratherm® (GE Water & Process Technologies, USA) junto con un post-tratamiento de carbón activo demostró ser la propuesta más adecuada. El uso de regresiones empíricas y modelos teóricos basados en la termodinámica irreversible facilitó la predicción de rechazos a diferentes grados de concentración, lo cual resultará de utilidad para una posible instalación industrial.

Los resultados obtenidos en la experimentación en discontinuo proporcionaron información suficiente para seleccionar las condiciones óptimas de trabajo en continuo. Los ensayos de larga duración determinaron el cumplimiento real de la calidad de agua objetivo para calderas y ayudaron a definir, por ejemplo, las



necesidades y rutinas de limpieza. Finalmente, toda la información y experiencia adquirida en continuo fue utilizada como base para un análisis económico completo, donde se demostró la rentabilidad del proceso.

RESUMEN (en Inglés)

The increasing costs of water supply and disposal and the current tendency towards energy efficiency policies are forcing the food industry in general, and the dairy sector in particular, to search for economically beneficial alternatives when reusing existing resources. With this in mind, CAPSA FOOD (Corporación Alimentaria Peñasanta S.A.) has contemplated the recovery of flash cooler condensates from the direct UHT treatment, where different types of milks and dairy products are processed in order to extend their shelf life. These wastewaters are considered low-pollutant effluents, which, along with their temperature (40–85°C), present attractive features for their reuse.

The thesis is developed in this context, where it is proposed to use membrane techniques to treat these condensates with the main objective of producing high-quality boiler water. The study, of semi-industrial character according to the volumes handled, was carried out *in situ* using real factory wastewaters whose heterogeneous nature made their membrane treatment a challenge.

In the first part of the study an exhaustive analysis of the condensates obtained from the four flash coolers operating at the factory was carried out, from which samples were taken for weeks at different times in their operational cycles. It was observed that, despite the low pollution level of these waters, their heterogeneity was conditioned by both the mode of operation of each unit and the time of the cycle at which the sample was taken. According to the average composition of the condensates various alternatives of treatment were evaluated, where several nanofiltration and reverse osmosis membranes of different characteristics were used. Discontinuous trials allowed the selection of the most viable option both from a technical point of view and from the fulfilment of the proposed objectives. The reverse osmosis by Duratherm® membranes (GE Water & Process Technologies, USA) along with an activated carbon post-treatment was shown to be the most suitable proposal. The use of empirical regressions and theoretical models based on the irreversible thermodynamics provided rejection predictions at different concentration levels, which will be useful for a possible industrial application.

The results obtained in batch experimentation supplied enough information to set the optimum conditions for continuous working. Long-term tests determined the real fulfilment of boiler quality requirements and helped to define the cleaning needs and routines. Finally, all the information and experience gained in continuous was applied as the basis of a complete economic analysis, where the profitability of the process was demonstrated.

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Resumen

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Abstract

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Capítulo 1: *Introducción*

1. Introducción

La industria alimentaria es, de entre todas las actividades industriales, una de las que presenta mayores consumos de agua y genera mayor volumen de efluentes por unidad de producción [1]. Debido al continuo incremento en el coste de abastecimiento de agua y en el coste de descarga, así como a la necesidad de una fuente de suministro de agua de buena calidad, fiable y asequible, su reutilización en el campo alimentario está siendo objeto de mucha atención aun existiendo estrictas limitaciones legislativas y preocupaciones higiénicas lógicas por parte de las empresas [2-4]. El objetivo es, en general, el desarrollo de políticas de cero descarga que sean económicamente ventajosas [5].

El consumo de agua en una industria de procesado lácteo es significativo en relación a la cantidad de leche tratada, siendo considerada además como una de las más contaminantes del sector alimentario [6]. Esta relación L agua/L leche tratada (generalmente entre 0,2 y 10 [7]) da una idea de las virtudes de la factoría en el uso racional del agua, correspondiendo bajos valores de este parámetro con políticas de reutilización de condensados y buenas prácticas en producción y limpiezas [8]. Además, antiguas prácticas de tratamiento colectivo de aguas de desecho tienden a ser sustituidas por operaciones de segregación y tratamiento individual optimizado en función de las características de la alimentación, lo que genera mejoras de eficiencia energética y ahorros económicos [9].

La industria láctea consume agua en la mayoría de sus procesos (limpiezas *in situ* (CIP) y aclarados, tratamientos térmicos, calderas, limpieza de camiones y superficies, etc.) y también en arranques, paradas intermedias y finales de producción. Estas corrientes de agua generadas contribuyen a la pérdida no accidental de fracciones lácteas y al incremento de la producción de aguas residuales [10, 11]. Las aguas residuales de una industria láctea, y en general las de cualquier industria alimentaria, se caracterizan por tener un alto contenido en materia orgánica, sales, sólidos en suspensión, aceites y grasas, nutrientes y agentes de limpieza [12, 13].

El agua de proceso en la industria alimentaria debe ser al menos de igual calidad a la estipulada para consumo humano [14]. La reutilización de aguas en este tipo de industrias está legislada en España [15, 16], siendo en muchos casos necesarias autorizaciones por parte de la autoridad sanitaria competente tras un análisis individualizado de cada situación. En todo caso ha de garantizarse su seguridad microbiológica, siendo esencial la aplicación de criterios basados en la metodología APPCC (análisis de peligros y puntos de control críticos) [2]. En general, la idoneidad del agua recuperada para la aplicación alimentaria considerada se establece en base al cumplimiento de los parámetros estipulados para dicho objetivo (aguas de proceso, de limpieza, de calderas, etc.) [3].

Los procesos de purificación de agua en general, y la filtración por membranas particularmente, no comercialmente viables en épocas pasadas, están adquiriendo viabilidad técnica y económica a medida que el desarrollo tecnológico avanza y los costes energéticos y de consumo de agua se incrementan [17-19]. Sin embargo, debido a las fluctuaciones y heterogeneidad de los efluentes industriales lácteos, estas operaciones aún implican cierto desafío [13].

Las técnicas con membranas, que representan una fuente primaria de separación para la industria alimentaria [20], presentan ciertas ventajas en relación a otros métodos tradicionales de separación debido a su consideración como procesos limpios (eliminación o reducción de productos químicos, bajo nivel de generación de residuos y efluentes, etc.), la gran flexibilidad en el diseño de los módulos, los cuáles son generalmente compactos (de todos los diseños, el espiral es el mayoritariamente utilizado por su elevada relación superficie/volumen, su control del ensuciamiento, su fácil operatividad y reemplazo y el amplio rango de materiales de fabricación [21, 22]), su alta eficiencia de separación, sus condiciones no severas de trabajo, su facilidad de implementación y automatización, su capacidad para ser fácilmente escalables, sus reducidos costes de operación y mantenimiento y su bajo consumo energético [23-25].

Tanto la nanofiltración (NF) como la ósmosis inversa (OI) han ampliado actualmente su aplicabilidad como técnicas de separación y purificación en el campo de la ingeniería medioambiental, no sólo siendo utilizadas en operaciones de desalinización sino también en separaciones selectivas y tratamiento de aguas residuales [26]. A su vez, estas técnicas han demostrado ser prometedoras en la producción de agua reutilizable a partir de efluentes lácteos [27]. Su principio de separación se basa en fenómenos de exclusión por tamaño, repulsión eléctrica e interacciones físico-químicas entre disolvente, soluto y membrana [28-30]. La OI es efectiva para la reducción de sales disueltas, siendo de todos los procesos con membranas el que mayor calidad de agua puede alcanzar [31], pero presenta limitaciones en la eliminación de compuestos orgánicos. El mayor inconveniente de éstas técnicas es el relacionado con la polarización de concentración y el ensuciamiento [32-34], requiriendo las membranas continuos ciclos de limpieza (rutinarios o no dependiendo de las circunstancias de cada aplicación y las características de la corriente de alimentación) que condicionan su vida útil. Además de esto, el ensuciamiento reduce la producción de permeado, aumenta las resistencias a la separación y altera la selectividad de la membrana [24, 35].

El ensuciamiento es el resultado de la unión, la acumulación y/o la adsorción de compuestos en la superficie de la membrana o en los poros de la misma [36]. En general, el ensuciamiento de las membranas en este tipo de aplicaciones lácteas viene usualmente determinado por la presencia de proteínas, que se adsorben y depositan sobre la superficie creando una capa de resistencia al flujo, y por la precipitación de iones solubles capaz de producir incrustaciones importantes [37], aunque el crecimiento microbiano también puede ser remarcable como forma de

ensuciamiento (*biofouling*) [38], adquiriendo importancia cuando los procesos de limpieza no se realizan de forma adecuada. Para prevenir estos fenómenos en la superficie del material, aparte de una óptima selección de la membrana, la generación de un nivel adecuado de turbulencia mediante el mantenimiento de un correcto flujo de alimentación serviría de ayuda, aunque han de evitarse altas velocidades que den lugar a una excesiva pérdida de carga y a fenómenos de erosión mecánica en la membrana [39]. Por otro lado, un diseño óptimo del sistema de bombeo podría limitar también la tendencia al ensuciamiento; adicionalmente, éste debería evitar una excesiva presión en la primera etapa, resultando en un empeoramiento de la calidad del permeado, y ser capaz de compensar el aumento de la presión osmótica en las siguientes [39].

El actual estado del arte en cuanto a NF y el desarrollo de procesos de OI a baja presión, que, manteniendo capacidades de rechazo similares, ha permitido mejoras en el flujo de permeado y ahorros energéticos frente a los procesos convencionales de OI, han hecho que estas técnicas sean frecuentemente utilizadas en el tratamiento de efluentes residuales [40, 41], siendo particularmente empleadas tanto de forma individualizada [10, 13, 42-45], como en combinación con otras operaciones de membranas [7, 36, 45, 46] en el campo del procesado de efluentes lácteos.

1.1. Definición de la aplicación

CAPSA FOOD (Corporación Alimentaria Peñasanta S.A.), industria de procesado lácteo, genera elevados caudales de condensados procedentes de su instalación UHT de leche (y otros derivados lácteos) los cuales presentan grandes fluctuaciones así como cierta heterogeneidad en su composición en función del ciclo de producción, incluso del tipo de producto lácteo tratado térmicamente en cada momento. Estas aguas, de baja carga contaminante en general, están siendo vertidas sin segregación a la planta de tratamiento de aguas, por lo que surgió una oportunidad de aprovechamiento, pareciendo apropiado su reutilización como agua de calderas de acuerdo a sus características y a la posibilidad de aprovechamiento energético [47], siendo los condensados normalmente vertidos en torno a 50°C. La opción más factible de reincorporación parece ser la etapa de desgasificación en el proceso de desmineralización y precalentamiento previo a calderas (ver apartado 1.1.3), al ser la pérdida energética nula.

La NF y la OI han demostrado ser técnicas efectivas para el tratamiento de este tipo de aguas residuales de baja carga contaminante (generalmente entran dentro de esta consideración aquellas con una DQO inferior a 700 mgO₂/L y una conductividad por debajo de 2200 µS/cm [1, 48]) con objetivos de reutilización en la propia industria láctea [49]. Además, el desarrollo de membranas compatibles con altas temperaturas supone una ventaja de eficiencia energética en el procesado de los condensados [47]. Aunque, a pesar de que ambas técnicas pueden generar altos rechazos de

materia orgánica, para aplicaciones en las que se exige una alta calidad de agua un único tratamiento de este tipo parece insuficiente, por lo que suelen requerir de etapas adicionales de procesado [50]. Concretamente, la adsorción mediante carbón activo puede considerarse una técnica atractiva para la eliminación de compuestos orgánicos que permanecen, en baja concentración, en los efluentes de industrias lácteas [51] y puede contribuir además a la reducción de olores y sabores indeseables [52]. Schreiber et al. [53] determinaron que la materia orgánica disuelta es preferiblemente absorbida por el carbón activo al aumentar la temperatura del agua.

La calidad del agua buscada en esta aplicación en concreto es aquella recomendada para su uso como agua de alimentación a calderas (pH 7–10, demanda química de oxígeno (DQO) <10 mgO₂/L, carbón orgánico total (TOC) <4 mgO₂/L, conductividad <40 μS/cm, aceites y grasas <1 mg/L, Ca²⁺ <0,4 mg/L [19, 49, 54]), que implica características más exigentes que las propias destinadas a consumo humano [10]. Además se requiere cierta calidad microbiológica, debiendo ser el recuento bacteriano de *Escherichia coli* y coliformes inferior a 100 unidades formadoras de colonias (UFC) por mL a sus temperaturas de incubación [49]. La calidad del agua de alimentación a calderas ha de ser asegurada para garantizar una alta eficiencia operativa y vida útil, limitar el uso de agentes químicos así como la frecuencia de purgado, y reducir los riesgos de corrosión y la presencia de incrustaciones que puedan dar lugar a sobrecalentamientos localizados [55, 56]. Ha de evitarse también la presencia de compuestos orgánicos que puedan generar espumas o puedan descomponerse en forma de ácido carbónico.

1.1.1.1. Proceso UHT directo en una industria láctea

El proceso *ultra high temperature* (UHT) es un tratamiento térmico de esterilización en continuo que tiene como objetivo asegurar una larga vida útil del producto incluso a temperatura ambiente. La combinación de una alta temperatura y un corto periodo de tiempo, usualmente 140°C durante 4s, permite minimizar el daño químico sobre los nutrientes e ingredientes funcionales de la leche u otros productos lácteos y reducir su sabor a tostado [57, 58]. El proceso directo (inyección o infusión de vapor) frente al indirecto (cambiadores de calor) presenta ventajas energéticas y mejor conservación del sabor [59].

En el proceso directo, el producto es precalentado hasta 75°C y bombeado a 4 bar para evitar la ebullición del líquido en la inyección. Posteriormente al tubo de mantenimiento, el producto es sometido a un enfriamiento *flash* y es homogenizado y nuevamente enfriado hasta la temperatura de envasado aséptico [60]. En la Fig. 1 se muestra un esquema simplificado de este proceso. La inyección de vapor, aproximadamente del 10–15% (p/p) [61], tiene lugar en una boquilla de tipo anular de forma coaxial al flujo del fluido a esterilizar. Este vapor se condensa a medida que tiene lugar el intercambio de calor con el fluido frío (leche), mezclándose con éste e incrementando su temperatura de

forma muy rápida [59]. La cantidad de vapor incorporado a la leche ha de ser posteriormente eliminado en la misma proporción de forma que no se comprometa la calidad del producto por dilución.

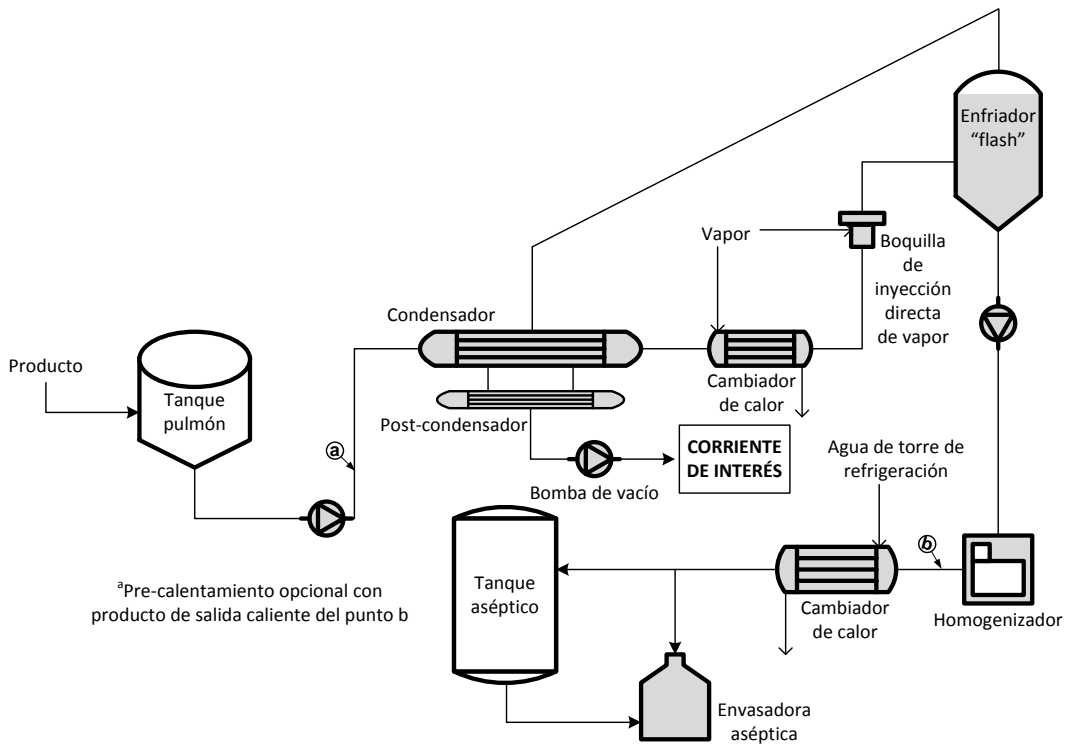


Fig. 1: Diagrama del proceso UHT directo de una industria láctea.

1.1.2. Enfriador “flash”

El enfriamiento *flash* tiene lugar en una cámara de expansión donde la temperatura del fluido desciende hasta aproximadamente 80°C y el contenido en sólidos original del producto es restablecido por eliminación del vapor previamente inyectado [62]. Dicha cámara opera bajo vacío parcial (0,5 bar) por acción de una bomba de vacío de anillo líquido, cuya presión de trabajo es regulada de tal forma que la cantidad de vapor inyectada en la boquilla de esterilización es la misma que la posteriormente eliminada. El equipo opera en torno al punto de ebullición del fluido tratado, de forma que, cuando la presión cae, gotículas del producto y ciertos compuestos volátiles son arrastrados por la fase vapor [61], contribuyendo de esta forma a una mayor carga orgánica en los futuros condensados. Este efecto puede incrementarse en el caso particular del equipo aquí estudiado, al no considerar en su diseño sistemas de retención de gotículas o ciclones.

En el sistema diseñado en la factoría el vapor eliminado en el enfriador *flash* es utilizado para precalentar el producto lácteo procesado, siendo posteriormente condensado y recogido en caliente a la salida de la bomba de vacío de anillo líquido, que es una bomba volumétrica rotativa con un agitador de paletas no concéntrico que utiliza agua de red como líquido auxiliar para transmitir la energía de compresión de las paletas al condensado. Este efecto de compresión se consigue mediante el anillo de líquido formado debido a la excentricidad entre la carcasa y las palas, generando, en huecos cada vez más pequeños, una acción de llenado y vacío que crea una respuesta de pistón en cada sección. La bomba actual está diseñada de tal manera que el vapor condensado se mezcla con el agua del anillo. Como resultado, la corriente de interés es una mezcla de condensados del enfriador *flash* y agua de red de la bomba que en su conjunto puede considerarse de baja carga contaminante.

La cantidad de agua de red usada en el anillo líquido controla la intensidad del vacío en el enfriador *flash*, pudiendo modificar en cierta medida la corriente de alimentación al proceso de membranas. Un mayor efecto de vacío requiere de una mayor entrada de agua de red al anillo (implicando una reducción en el tamaño de los huecos creados entre la carcasa y las paletas, y generando un mayor efecto de compresión como resultado), lo que produce dos efectos opuestos, uno de incremento de la carga contaminante y otro de dilución. En primer lugar, un mayor vacío incrementa el arrastre de partículas de leche aumentando la carga orgánica de los condensados, y en segundo lugar, como se requiere de una mayor cantidad de agua de red, y al ser ésta mezclada con los condensados, la carga orgánica se diluye. Además, como el agua de red es alimentada en frío, la temperatura de la mezcla se reduce.

El actual proceso UHT que existe en la factoría trabaja en ciclos, cuya distribución de tiempos típica se muestra en la **Fig. 2**, aunque esto puede variar dependiendo de las necesidades de producción o averías. Una serie de limpiezas asépticas intermedias, llevadas a cabo con un detergente de base alcalina y los respectivos aclarados, tienen lugar rutinariamente. De la misma forma, algunas horas después de la segunda limpieza intermedia se procede a una limpieza final con detergentes de base alcalina y ácida. Cuando el llenado aséptico de envases (botellas o *bricks*) no puede hacer frente al ritmo de producción, el producto estéril es acumulado en un tanque aséptico, y cuando éste se llena, el sistema empieza a trabajar con agua estéril hasta que la envasadora o el tanque aséptico son liberados y el producto puede entrar de nuevo en el proceso. Durante todo el ciclo (incluso cuando el equipo está cargado de agua estéril) se están produciendo condensados, salvo cuando se está realizando una limpieza final. Como resultado de esto, las características de los condensados son muy dependientes del momento del ciclo; por ejemplo, las aguas recogidas durante la limpieza intermedia son muy alcalinas, y las producidas en el arranque o tras una limpieza intermedia presentan una mayor carga orgánica, ya que el sistema está limpio y el grado de vacío es mayor y por tanto también lo es el arrastre de producto. Al contrario, aquellas aguas muestreadas con agua estéril en circulación dentro del sistema presentan una menor carga contaminante.

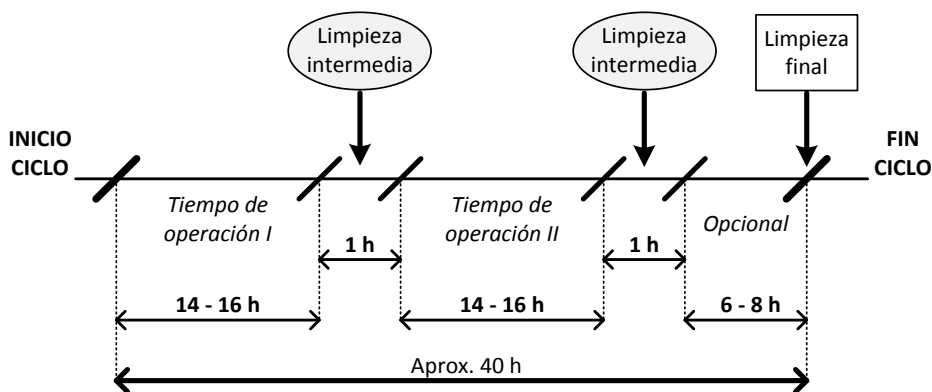


Fig. 2: Ciclo de funcionamiento estándar de los esterilizadores de la factoría.

La factoría cuenta con 4 equipos de esterilización UHT directo para productos lácteos líquidos (leches de diferentes tipos, batidos, etc.) que en su conjunto generan, cuando trabajan al mismo tiempo, un volumen medio de condensados (entendiendo por estos, la mezcla que incluye el agua auxiliar de la bomba) de 20 m³/h aproximadamente. Además, en la fábrica se pueden encontrar otras corrientes, procedentes de los esterilizadores UHT directos de nata y de los primeros efectos de los evaporadores del proceso de leche en polvo, que entrarían dentro de la consideración de aguas de baja carga contaminante y, aunque no han sido consideradas en este estudio, podrían ser susceptibles de un tratamiento conjunto. En general, las aguas procedentes de los 4 enfriadores *flash* presentan una heterogeneidad destacable de unos a otros y, lo que es más, el tipo de producto tratado y los parámetros de esterilización fijados pueden también condicionarlas en cierta medida. Todas estas circunstancias hacen que el agua de alimentación a la planta de membranas sea variable en cuanto a caudal y composición.

1.1.3. Tratamiento de agua para la producción de vapor

El agua que consume la factoría procede de CADASA (Consortio para el Abastecimiento de Aguas y Saneamiento en el Principado de Asturias, S.A.), siendo potable y no requiriendo nuevos tratamientos para su consumo directo en los procesos. Parte de esta agua sirve de abastecimiento al proceso de desmineralización previo a alimentación a calderas (ver **Fig. 3**). Al ser el cloro un elemento dañino para las resinas de intercambio iónico, el agua de red es en primer lugar declorada, alargando de esta forma la vida útil de dichos materiales. El agua es desmineralizada por acción de dos resinas catiónicas, de catión débil y fuerte, respectivamente, y una de carácter aniónico, siendo posteriormente desgasificada (CO₂) por aireación y almacenada en un depósito de 500 m³ en frío a 13–15°C, pudiendo presentar cierta variación estacional. Esta agua es ligeramente precalentada hasta aproximadamente 30°C mediante corrientes recuperadas de otros procesos, siendo ésta una medida de implantación actual y no teniéndose en cuenta en el momento de consideración del proyecto; posteriormente se almacena en un depósito de 250 m³. Desde este tanque se

bomba al desgasificador principal, donde tras una infusión de vapor, la temperatura de la corriente se incrementa hasta 105°C, reduciendo al mínimo la solubilidad del O₂ y favoreciendo principalmente su eliminación de la corriente. La cantidad de vapor alimentado es controlada por una válvula reductora de presión que mantiene la presión de ebullición del agua. En general, la eliminación de estos gases evita corrosiones en los elementos y tramos del circuito de vapor. Es en este equipo en donde se produce también la reincorporación de condensados. Finalmente, el agua es bombeada desde el desgasificador a 25 bar a un elemento economizador, donde, por contacto con los gases de salida de la caldera, la temperatura del agua se incrementa hasta aproximadamente 175°C, incorporándose posteriormente a las calderas, de tipo pirotubular donde los gases de combustión circulan por el interior de los tubos, y generándose en ésta un vapor saturado a 18 bar y 210°C que se distribuye por la fábrica.

Adicionalmente al tratamiento externo del agua de alimentación a calderas, se suele realizar un acondicionamiento interno de las aguas mediante dosificación en línea de diferentes reactivos químicos tales como agentes de ablandamiento (fosfatos y polifosfatos), que reducen la alcalinidad de las aguas y neutralizan su dureza mediante formación de compuestos insolubles, agentes anti-incrustaciones (taninos, poliácridatos, etc.), reactivos captadores de oxígeno (sulfito sódico, hidracina, etc.) y agentes anti-espumantes (tensoactivos) principalmente.

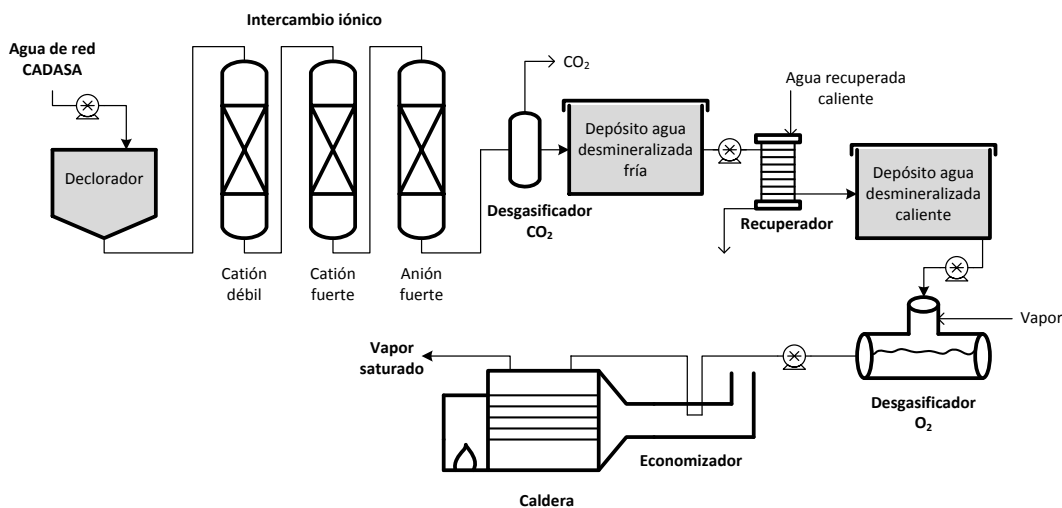


Fig. 3: Diagrama del proceso de desmineralización del agua de alimentación a calderas.

La compañía dispone de 5 calderas pirotubulares, cuyo funcionamiento viene condicionado por las necesidades de producción. Tres de ellas son convencionales, con capacidades de producción de vapor de 18, 10 y 8 t/h, respectivamente. Las otras dos restantes, de 20 t/h de producción cada una, son de recuperación y permiten una “tri-generación” energética, ya que por un lado el movimiento del vapor y los gases de la calderas están asociados a

turbinas, y por el otro aportan el calor necesario para el funcionamiento de un equipo de frío por absorción. El volumen medio de estas calderas es de 40 m³.

1.1.4. Normativa relativa a la reutilización de las aguas

La normativa española que regula los requisitos de calidad del agua de alimentación y del agua de calderas en aquellas de tipo piro-tubular es la UNE-EN 12953-10 [63], editada por AENOR (Asociación Española de Normalización y Certificación) y aprobada por el CEN (Comité Europeo de Normalización) en el año 2003. Con el objetivo de minimizar la corrosión, la formación de lodos y las incrustaciones, se establecen en esta norma tanto las concentraciones máximas y mínimas de los agentes químicos de acondicionamiento, así como las concentraciones admisibles de cierto número de impurezas. Para calderas de vapor con presión de trabajo entre 0,5 y 20 bar, como es el caso, se incluyen en la **Tabla I** los requisitos del agua de alimentación y de la caldera. En general, los requerimientos de purga vienen determinados por los ciclos de concentración de las impurezas, situándose la media actual en este caso en 50. La purga o sangrado se realiza normalmente, y de forma automática, una vez alcanzados los 1500 µS/cm de referencia, aunque pueden darse casos de purga por superación de cualquier otro límite paramétrico.

Tabla I: Requisitos del agua de alimentación y de la caldera según la norma UNE-EN 12953-10.

Agua de alimentación	
Apariencia	Clara, libre de sólidos en suspensión
Conductividad a 25°C, µS/cm	No especificada
pH a 25°C	< 9,2
Dureza total, mg CaCO ₃ /L	< 1
Hierro, mg/L	< 0,3
Cobre, mg/L	< 0,05
Sílice (SiO ₂), mg/L	No especificada
O ₂ , mg/L	< 0,05
Aceites/grasas, mg/L	< 1
COT, mg/L	Minimizar (recomendación)
Agua de la caldera, agua de alimentación de conductividad ≤ 30 µS/cm	
Apariencia	Clara, sin espuma estable
Conductividad a 25°C, µS/cm	< 1500
pH a 25°C	10 – 11
Alcalinidad compuesta, mg CaCO ₃ /L	10 – 100
Sílice (SiO ₂), mg/L	80 – 135 (función de la alcalinidad)
Fosfatos (PO ₄ ³⁻), mg/L	6 – 15
Sustancias orgánicas	Minimizar (recomendación)

El destino que se le da al vapor puede dar lugar a limitaciones adicionales. En la industria alimentaria, todo agua que pueda entrar en contacto con los alimentos ha de ser de calidad para consumo humano (Real Decreto (RD) 140/2003) [15]. Por tanto, la calidad higiénica del vapor es crítica y ha de ser garantizada, en primer lugar mediante una potabilidad del agua de partida garantizada por CADASA y en segundo lugar por un control organoléptico (ausencia de

color, olor y sabor) y microbiológico (*Escherichia coli*, *Enterococos*, *Clostridium perfringens*: 0 UFC en 100 mL) óptimo en la caldera, aunque el vapor generado sea virtualmente estéril.

En relación a la reutilización de las aguas, ésta viene legislada por el RD 1620/2007 [16] y viene condicionada por una autorización administrativa. Se prohíbe en todo caso la reutilización para fines propios de la industria alimentaria relacionados con la fabricación, tratamiento, conservación y comercialización de productos destinados al consumo humano, así como para la limpieza de superficies, objetos y materiales que puedan entrar en contacto con los alimentos; pero sí en aguas de proceso y limpieza generales en este tipo de industria pudiendo incluirse aquí la generación de vapor para contacto indirecto, siendo éste el objetivo buscado y requiriendo por lo tanto una diferenciación en fábrica de los diferentes tipos de vapor. Los requerimientos, son en todo caso menos estrictos que los propios del agua para consumo humano utilizada para la generación de vapor de contacto directo (ver Anexo I.A.3.calidad 3.1c del RD 1620/2007 [16]). Aunque, para evitar riesgos por contaminación cruzada, es aconsejable garantizar la máxima calidad microbiológica en todos los ámbitos de una factoría alimentaria.

1.2. Bibliografía general

- [1] V. Mavrov, E. Béliers, Reduction of water consumption and wastewater quantities in the food industry by water recycling using membrane processes, *Desalination*, 131 (2000) 75-86. [http://dx.doi.org/10.1016/S0011-9164\(00\)90008-0](http://dx.doi.org/10.1016/S0011-9164(00)90008-0).
- [2] S. Casani, S. Knöchel, Application of HACCP to water reuse in the food industry, *Food Control*, 13 (2002) 315-327. [http://dx.doi.org/10.1016/S0956-7135\(02\)00037-3](http://dx.doi.org/10.1016/S0956-7135(02)00037-3).
- [3] S. Casani, M. Rouhany, S. Knöchel, A discussion paper on challenges and limitations to water reuse and hygiene in the food industry, *Water Research*, 39 (2005) 1134-1146. <http://dx.doi.org/10.1016/j.watres.2004.12.015>.
- [4] S.A. Palumbo, K.T. Rajkowski, A.J. Miller, Current approaches for reconditioning process water and its use in food manufacturing operations, *Trends in Food Science & Technology*, 8 (1997) 69-74. [http://dx.doi.org/10.1016/S0924-2244\(97\)01014-5](http://dx.doi.org/10.1016/S0924-2244(97)01014-5).
- [5] W. Lee, M.R. Okos, Sustainable food processing systems - Path to a zero discharge: reduction of water, waste and energy, *Procedia Food Science*, 1 (2011) 1768-1777. <http://dx.doi.org/10.1016/j.profoo.2011.09.260>.
- [6] L.H. Andrade, F.D.S. Mendes, J.C. Espindola, M.C.S. Amaral, Nanofiltration as tertiary treatment for the reuse of dairy wastewater treated by membrane bioreactor, *Separation and Purification Technology*, 126 (2014) 21-29. <http://dx.doi.org/10.1016/j.seppur.2014.01.056>.
- [7] M. Vourch, B. Balanec, B. Chaufer, G. Dorange, Nanofiltration and reverse osmosis of model process waters from the dairy industry to produce water for reuse, *Desalination*, 172 (2005) 245-256. <http://dx.doi.org/10.1016/j.desal.2004.07.038>.
- [8] F.X. Milani, D. Nutter, G. Thoma, Invited review: Environmental impacts of dairy processing and products: A review, *Journal of Dairy Science*, 94 4243-4254. 10.3168/jds.2010-3955.
- [9] H. Miyaki, S. Adachi, K. Suda, Y. Kojima, Water recycling by floating media filtration and nanofiltration at a soft drink factory, *Desalination*, 131 (2000) 47-53. [http://dx.doi.org/10.1016/S0011-9164\(00\)90005-5](http://dx.doi.org/10.1016/S0011-9164(00)90005-5).
- [10] B. Balanec, G. Gésan-Guizoui, B. Chaufer, M. Rabiller-Baudry, G. Daufin, Treatment of dairy process waters by membrane operations for water reuse and milk constituents concentration, *Desalination*, 147 (2002) 89-94. [http://dx.doi.org/10.1016/S0011-9164\(02\)00581-7](http://dx.doi.org/10.1016/S0011-9164(02)00581-7).
- [11] J. Luo, L. Ding, Influence of pH on treatment of dairy wastewater by nanofiltration using shear-enhanced filtration system, *Desalination*, 278 (2011) 150-156. <http://dx.doi.org/10.1016/j.desal.2011.05.025>.

- [12] I.M.R. Sánchez, J.M.M. Ruiz, J.L.C. López, J.A.S. Pérez, Effect of environmental regulation on the profitability of sustainable water use in the agro-food industry, *Desalination*, 279 (2011) 252-257. <http://dx.doi.org/10.1016/j.desal.2011.06.015>.
- [13] B. Sarkar, P.P. Chakrabarti, A. Vijaykumar, V. Kale, Wastewater treatment in dairy industries – possibility of reuse, *Desalination*, 195 (2006) 141-152. <http://dx.doi.org/10.1016/j.desal.2005.11.015>.
- [14] Council Directive relating to the quality of water intended for human consumption 98/83/EC, *Official Journal of the European Communities*, L 330 (1998) 32-54.
- [15] Spanish legislation on health criteria for drinking quality water RD 140/2003, *BOE*, 45 (2003) 7228-7245.
- [16] Spanish legislation on legal system for reuse of treated water RD 1620 /2007, *BOE*, 294 (2007) 50639-50661.
- [17] G. Ciardelli, L. Corsi, M. Marcucci, Membrane separation for wastewater reuse in the textile industry, *Resources, Conservation and Recycling*, 31 (2001) 189-197. [http://dx.doi.org/10.1016/S0921-3449\(00\)00079-3](http://dx.doi.org/10.1016/S0921-3449(00)00079-3).
- [18] M. Clever, F. Jordt, R. Knaufl, N. Rübiger, M. Rübibusch, R. Hilker-Scheibel, Process water production from river water by ultrafiltration and reverse osmosis, *Desalination*, 131 (2000) 325-336. [http://dx.doi.org/10.1016/S0011-9164\(00\)90031-6](http://dx.doi.org/10.1016/S0011-9164(00)90031-6).
- [19] S. Judd, B. Jefferson, *Membranes for industrial wastewater recovery and re-use*, Elsevier Science Ltd, Oxford, 2003.
- [20] A. Hafez, M. Khedr, H. Gadallah, Wastewater treatment and water reuse of food processing industries. Part II: Techno-economic study of a membrane separation technique, *Desalination*, 214 (2007) 261-272. <http://dx.doi.org/10.1016/j.desal.2006.11.010>.
- [21] A. Bódalo-Santoyo, J.L. Gómez-Carrasco, E. Gómez-Gómez, M.F. Máximo-Martín, A.M. Hidalgo-Montesinos, Spiral-wound membrane reverse osmosis and the treatment of industrial effluents, *Desalination*, 160 (2004) 151-158. [http://dx.doi.org/10.1016/S0011-9164\(04\)90005-7](http://dx.doi.org/10.1016/S0011-9164(04)90005-7).
- [22] J. Schwinge, P.R. Neal, D.E. Wiley, D.F. Fletcher, A.G. Fane, Spiral wound modules and spacers: Review and analysis, *Journal of Membrane Science*, 242 (2004) 129-153. <http://dx.doi.org/10.1016/j.memsci.2003.09.031>.
- [23] G. Daufin, J.P. Escudier, H. Carrère, S. Bérot, L. Fillaudeau, M. Decloux, Recent and Emerging Applications of Membrane Processes in the Food and Dairy Industry, *Food and Bioproducts Processing*, 79 (2001) 89-102. <http://dx.doi.org/10.1205/096030801750286131>.
- [24] H. Li, V. Chen, Chapter 10 - Membrane Fouling and Cleaning in Food and Bioprocessing, in: Z.F. Cui, H.S. Muralidhara (Eds.) *Membrane Technology*, Butterworth-Heinemann, Oxford, 2010, pp. 213-254. <http://dx.doi.org/10.1016/B978-1-85617-632-3.00010-0>.
- [25] S.S. Madaeni, S. Koocheki, Application of taguchi method in the optimization of wastewater treatment using spiral-wound reverse osmosis element, *Chemical Engineering Journal*, 119 (2006) 37-44. <http://dx.doi.org/10.1016/j.cej.2006.03.002>.
- [26] K.O. Agenson, T. Urase, Change in membrane performance due to organic fouling in nanofiltration (NF)/reverse osmosis (RO) applications, *Separation and Purification Technology*, 55 (2007) 147-156. <http://dx.doi.org/10.1016/j.seppur.2006.11.010>.
- [27] J. Luo, L. Ding, Y. Wan, P. Paullier, M.Y. Jaffrin, Application of NF-RDM (nanofiltration rotating disk membrane) module under extreme hydraulic conditions for the treatment of dairy wastewater, *Chemical Engineering Journal*, 163 (2010) 307-316. <http://dx.doi.org/10.1016/j.cej.2010.08.007>.
- [28] J. Radjenović, M. Petrović, F. Ventura, D. Barceló, Rejection of pharmaceuticals in nanofiltration and reverse osmosis membrane drinking water treatment, *Water Research*, 42 (2008) 3601-3610. <http://dx.doi.org/10.1016/j.watres.2008.05.020>.
- [29] C. Bellona, J.E. Drewes, The role of membrane surface charge and solute physico-chemical properties in the rejection of organic acids by NF membranes, *Journal of Membrane Science*, 249 (2005) 227-234. <http://dx.doi.org/10.1016/j.memsci.2004.09.041>.
- [30] L. Malaeb, G.M. Ayoub, Reverse osmosis technology for water treatment: State of the art review, *Desalination*, 267 (2011) 1-8. <http://dx.doi.org/10.1016/j.desal.2010.09.001>.
- [31] C. García-Figueroa, B. Montag, A. Bes-Piá, J.A. Mendoza-Roca, E. Soriano-Costa, J. Lora-García, Study of the behaviour of a reverse osmosis membrane for wastewater reclamation – influence of wastewater concentration, *Desalination*, 222 (2008) 243-248. <http://dx.doi.org/10.1016/j.desal.2007.01.163>.
- [32] E.M. García-Castello, L. Mayor, S. Chorques, A. Argüelles, D. Vidal-Brotóns, M.L. Gras, Reverse osmosis concentration of press liquid from orange juice solid wastes: Flux decline mechanisms, *Journal of Food Engineering*, 106 (2011) 199-205. <http://dx.doi.org/10.1016/j.jfoodeng.2011.05.005>.

- [33] R. Gerard, H. Hachisuka, M. Hirose, New membrane developments expanding the horizon for the application of reverse osmosis technology, *Desalination*, 119 (1998) 47-55. [http://dx.doi.org/10.1016/S0011-9164\(98\)00102-7](http://dx.doi.org/10.1016/S0011-9164(98)00102-7).
- [34] B. Van der Bruggen, M. Mänttari, M. Nyström, Drawbacks of applying nanofiltration and how to avoid them: A review, *Separation and Purification Technology*, 63 (2008) 251-263. <http://dx.doi.org/10.1016/j.seppur.2008.05.010>.
- [35] S.S. Madaeni, S. Samieirad, Chemical cleaning of reverse osmosis membrane fouled by wastewater, *Desalination*, 257 (2010) 80-86. <http://dx.doi.org/10.1016/j.desal.2010.03.002>.
- [36] M. Turan, Influence of filtration conditions on the performance of nanofiltration and reverse osmosis membranes in dairy wastewater treatment, *Desalination*, 170 (2004) 83-90. <http://dx.doi.org/10.1016/j.desal.2004.02.094>.
- [37] G. Rice, A. Barber, A. O'Connor, G. Stevens, S. Kentish, Fouling of NF membranes by dairy ultrafiltration permeates, *Journal of Membrane Science*, 330 (2009) 117-126. <http://dx.doi.org/10.1016/j.memsci.2008.12.048>.
- [38] H.F. Ridgway, C.A. Justice, C. Whittaker, D.G. Argo, B.H. Olson, Biofilm Fouling of RO Membranes—Its Nature and Effect on Treatment of Water for Reuse, *Journal (American Water Works Association)*, 76 (1984) 94-102. 10.2307/41273154.
- [39] G. Al-Enezi, N. Fawzi, Design consideration of RO units: Case studies, *Desalination*, 153 (2003) 281-286. [http://dx.doi.org/10.1016/S0011-9164\(02\)01147-5](http://dx.doi.org/10.1016/S0011-9164(02)01147-5).
- [40] S.S. Madaeni, Y. Mansourpanah, COD Removal from Concentrated Wastewater Using Membranes, *Filtration & Separation*, 40 (2003) 40-46. [http://dx.doi.org/10.1016/S0015-1882\(03\)00635-9](http://dx.doi.org/10.1016/S0015-1882(03)00635-9).
- [41] M. Vourch, B. Balanec, B. Chaufer, G. Dorange, Treatment of dairy industry wastewater by reverse osmosis for water reuse, *Desalination*, 219 (2008) 190-202. <http://dx.doi.org/10.1016/j.desal.2007.05.013>.
- [42] R. Delbeke, Recovery of milk solids by hyperfiltration, *Milchwissenschaft*, 36 (1981) 669-672.
- [43] B. Balanec, M. Vourch, M. Rabiller-Baudry, B. Chaufer, Comparative study of different nanofiltration and reverse osmosis membranes for dairy effluent treatment by dead-end filtration, *Separation and Purification Technology*, 42 (2005) 195-200. <http://dx.doi.org/10.1016/j.seppur.2004.07.013>.
- [44] M. Frappart, M. Jaffrin, L.H. Ding, Reverse osmosis of diluted skim milk: Comparison of results obtained from vibratory and rotating disk modules, *Separation and Purification Technology*, 60 (2008) 321-329. <http://dx.doi.org/10.1016/j.seppur.2007.09.007>.
- [45] I. Koyuncu, M. Turan, D. Topacik, A. Ates, Application of low pressure nanofiltration membranes for the recovery and reuse of dairy industry effluents, *Water Science and Technology*, 41 (2000) 213-221.
- [46] Y.-W. Gong, H.-X. Zhang, X.-N. Cheng, Treatment of dairy wastewater by two-stage membrane operation with ultrafiltration and nanofiltration, *Water Science & Technology*, 65 (2012) 915-919.
- [47] A.-C. Valentin, Industrial water reuse opportunities and high temperature compatible membranes, *Water Science & Technology: Water Supply—WSTWS*, 10 (2010). doi:10.2166/ws.2010.083.
- [48] A. Fährnich, V. Mavrov, H. Chmiel, Membrane processes for water reuse in the food industry, *Desalination*, 119 (1998) 213-216. [http://dx.doi.org/10.1016/S0011-9164\(98\)00158-1](http://dx.doi.org/10.1016/S0011-9164(98)00158-1).
- [49] H. Chmiel, V. Mavrov, E. Belieres, Reuse of vapour condensate from milk processing using nanofiltration, *Filtration & Separation*, 37 (2000) 24-27.
- [50] C. Aydiner, U. Sen, S. Topcu, D. Ekinçi, A.D. Altınay, D.Y. Koseoglu-Imer, B. Keskinler, Techno-economic viability of innovative membrane systems in water and mass recovery from dairy wastewater, *Journal of Membrane Science*, 458 (2014) 66-75. <http://dx.doi.org/10.1016/j.memsci.2014.01.058>.
- [51] J.P. Kushwaha, V.C. Srivastava, I.D. Mall, Treatment of dairy wastewater by commercial activated carbon and bagasse fly ash: Parametric, kinetic and equilibrium modelling, disposal studies, *Bioresource Technology*, 101 (2010) 3474-3483. <http://dx.doi.org/10.1016/j.biortech.2010.01.002>.
- [52] A. Matilainen, N. Vieno, T. Tuhkanen, Efficiency of the activated carbon filtration in the natural organic matter removal, *Environment International*, 32 (2006) 324-331. <http://dx.doi.org/10.1016/j.envint.2005.06.003>.
- [53] B. Schreiber, T. Brinkmann, V. Schmalz, E. Worch, Adsorption of dissolved organic matter onto activated carbon—the influence of temperature, absorption wavelength, and molecular size, *Water Research*, 39 (2005) 3449-3456. <http://dx.doi.org/10.1016/j.watres.2005.05.050>.
- [54] V. Mavrov, H. Chmiel, E. Bélières, Spent process water desalination and organic removal by membranes for water reuse in the food industry, *Desalination*, 138 (2001) 65-74. [http://dx.doi.org/10.1016/S0011-9164\(01\)00246-6](http://dx.doi.org/10.1016/S0011-9164(01)00246-6).

- [55]** R.S. Dhodapkar, G.R. Pophali, T. Nandy, S. Devotta, Exploitation results of seven RO plants for recovery and reuse of treated effluents in textile industries, Desalination, 217 (2007) 291-300. <http://dx.doi.org/10.1016/j.desal.2007.02.015>.
- [56]** C.H. Koo, A.W. Mohammad, F. Suja, Recycling of oleochemical wastewater for boiler feed water using reverse osmosis membranes – A case study, Desalination, 271 (2011) 178-186. <http://dx.doi.org/10.1016/j.desal.2010.12.025>.
- [57]** H. Tran, N. Datta, M.J. Lewis, H.C. Deeth, Predictions of some product parameters based on the processing conditions of ultra-high-temperature milk plants, International Dairy Journal, 18 (2008) 939-944. <http://dx.doi.org/10.1016/j.idairyj.2008.01.006>.
- [58]** D.F. Newstead, G. Paterson, S.G. Anema, C.J. Coker, A.R. Wewala, Plasmin activity in direct-steam-injection UHT-processed reconstituted milk: Effects of preheat treatment, International Dairy Journal, 16 (2006) 573-579. <http://dx.doi.org/10.1016/j.idairyj.2005.11.011>.
- [59]** F. Innings, L. Hamberg, Steam condensation dynamics in annular gap and multi-hole steam injectors, Procedia Food Science, 1 (2011) 1278-1284. <http://dx.doi.org/10.1016/j.profoo.2011.09.189>.
- [60]** G. Bylund, T. Pak, Dairy processing handbook, Tetra Pak Processing Systems AB Lund, 2003.
- [61]** M.J. Lewis, Thermal Processing, in: Food Processing Handbook, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2006. 10.1002/3527607579.ch2.
- [62]** R. Early, Technology of dairy products, Springer, London, 1998.
- [63]** Spanish legislation on shell boilers. Part 10: Requirements for feedwater and boiler water quality UNE-EN 12953-10, AENOR, (2004) 17.

Capítulo 2: *Objetivo*

2. Objetivo

El continuo incremento en los costes energéticos, y de abastecimiento y vertido de agua, así como la adquisición de un compromiso creciente con el medio ambiente por parte de las compañías hace que las políticas de ahorro, reutilización y buenas prácticas vayan tomando relevancia y formando parte de los objetivos corporativos de las empresas. Dichos intereses, muy presentes en la industria alimentaria en general, dieron lugar al desarrollo de la presente tesis doctoral.

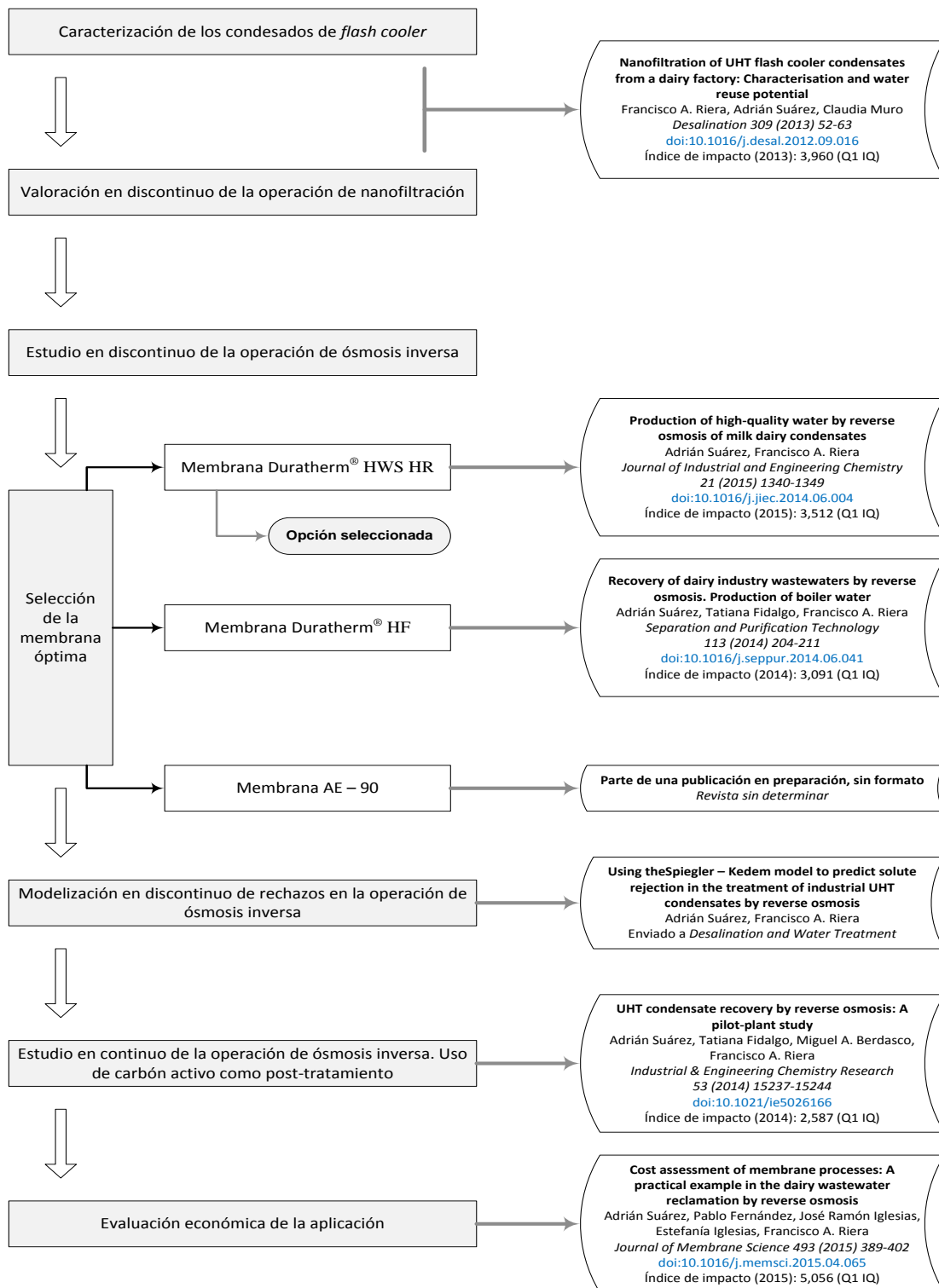
La compañía de procesado lácteo CAPSA FOOD (Corporación Alimentaria Peñasanta S.A.) con sede principal en Granda, Asturias, se planteó una acción de mejora en la recuperación de condensados del proceso UHT directo. Se valoró entonces el tratamiento de estas aguas de bajo carácter contaminante mediante membranas con objetivos de incorporación a las aguas desmineralizadas de alimentación a calderas para su reaprovechamiento como vapor de contacto indirecto, dado su potencial energético y de acuerdo a las posibilidades legislativas actuales.

El estudio y tratamiento *in situ* de estas aguas reales de proceso con objetivos de reutilización fue el propósito principal de la presente tesis doctoral. Para ello, se pilotaron, tanto en discontinuo como en continuo, plantas con capacidad de trabajo de hasta 2000 L/h, valorándose las características de las aguas de alimentación y determinándose la viabilidad técnica de diferentes membranas, tanto de NF como de OI, para la consecución de la calidad final de agua buscada. La predicción de rechazos mediante modelización, útil en la consideración de un escalado industrial, y la valoración económica de la aplicación fueron otros de los objetivos buscados.

Los resultados y conclusiones obtenidas pretenden ser aplicados, no sólo a la fábrica donde se llevaron a cabo los ensayos, sino también a otras factorías de la compañía o a cualquier otra industria láctea o alimentaria donde el tratamiento UHT directo esté presente o donde se generen aguas de características similares a las aquí estudiadas. Las circunstancias particulares de dichas factorías, y las propias de la zona en la que se encuentren, determinarían en gran medida las necesidades, así como los costes energéticos y de agua, y por tanto la viabilidad económica de implantación en cada caso.

Capítulo 3: *Organización de la memoria*

3. Organización de la memoria



Capítulo 4: *Resultados y discusión*

4. Resultados y discusión

4.1. Caracterización de los condensados de “flash cooler” y valoración de la operación de nanofiltración como alternativa para su tratamiento

La alternativa de tratamiento por nanofiltración de los condensados de *flash cooler* de esterilización UHT fue valorada en planta piloto con objetivos de recuperación de la corriente que permitieran tanto ahorros energéticos como de consumo y vertido de agua. Para ello se utilizó una membrana espiral de 200 Da de corte y se evaluó, tanto en ensayos discontinuos como en continuos de corta duración, la influencia de los parámetros de proceso sobre el rendimiento de la operación y la calidad del permeado obtenido, la cual condiciona en gran medida las posibilidades finales de reutilización. Las características de las aguas de alimentación fueron ampliamente estudiadas acorde al ciclo de trabajo clásico de los esterilizadores, siendo su propósito la obtención de unas recomendaciones de aprovechamiento. Por otro lado, se incluyó una evaluación económica preliminar que podría considerarse una aproximación a los resultados expuestos en el capítulo 4.5., donde los costes de la aplicación final fueron examinados con mayor profundidad. El detalle de la metodología de trabajo y de los resultados obtenidos en este apartado se incluye en la publicación:

Nanofiltration of UHT flash cooler condensates from a dairy factory: Characterisation and water reuse potential.

Francisco A. Riera, Adrián Suárez, Claudia Muro

Desalination 309 (2013) 52-63



Nanofiltration of UHT flash cooler condensates from a dairy factory: Characterisation and water reuse potential

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HIGHLIGHTS

- ▶ Flash cooler condensates were characterised to evaluate their potential reuse.
- ▶ A 200 Da nanofiltration unit was used to reduce the pollutant load of wastewater.
- ▶ The influence of operating conditions on permeate flux and quality was studied.
- ▶ The volume concentration ratio was a limiting factor on the final design proposed.
- ▶ An economic estimation, based on costs and savings, was carried out.

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ABSTRACT

The large consumption of water in the dairy industry makes water reuse a crucial issue. Flash Cooler (FC) condensates from direct ultra high temperature (UHT) treatments were characterised and nanofiltered in order to obtain potentially reusable water depending on the limitations of its end uses. A nanofiltration (NF) pilot plant (1.6 m² membrane area) with a SeIRO MPS-34 2540 B2X (Koch Membrane Systems) was used for these purposes. The influence of operating conditions (transmembrane pressure (TMP), temperature, time and water recovery) on permeate flow rate (J) and quality (conductivity, chemical oxygen demand (COD), total organic carbon (TOC) and Ca²⁺) was studied. Heating (taking into account the thermal potential of condensates) and other miscellaneous objectives were achieved, a volume concentration ratio (VCR) of 8 being set as a design parameter. The experimental data was used to design a NF plant with 20 m³/h feed capacity whose savings and operating costs were estimated at 2.807 and 0.777 €/m³, respectively.

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1. Introduction

Milk industries consume large amounts of water in different parts of their facilities (washing, rinsing, cleaning-in-place steps (CIPs), pasteurising, UHT processes, chilling, cooling, steam production, etc.). Water consumption varies between 1.5 and 5 L per litre of treated milk [1,2] depending on the type of industry.

Increasing water prices advise look for techniques not only to reduce water consumption, but also to reuse it in the plant. Industries with lower water/milk ratios correspond to those which recover different condensates, mainly from evaporation and drying. Spent cleaning CIP solutions are recommended for partial reuse since they represent one third of the total milk wastewater. Several techniques have been assayed to reduce the pollutant load of wastewaters generated by food industries in general, and dairy industries in particular: flocculation, deep filtration, coagulation, etc. Membrane technologies (MTs), ranging from microfiltration (MF) to reverse osmosis (RO),

are among the most promising techniques due to their consideration as “clean technologies”. Single MT steps have been used in many published research studies to produce water of different qualities [2,3]. One-step ultrafiltration (UF) experiments were performed by Sarkar et al. [4] and Chollangi and Hossain [5], but obtained permeates did not fulfil the quality levels to reuse the water. UF processes only reject proteins, passing lactose and other small molecules through the membrane, which leads to high values of COD in dairy wastewater permeates [6]. In other cases, a combination of different technologies has been adopted to obtain higher quality water [1,6–11]: pretreatment with cartridge filtration followed by ultraviolet (UV) disinfection and NF [1], an UF operation prior to a NF step [6], single NF or two-pass RO [10], pretreatment followed by nanofiltration (step 1) and nanofiltration or reverse osmosis (step 2) and ending with UV disinfection [12], NF followed by RO [13,14], etc. Vourch et al. [2] studied 11 dairy plants using RO as a technique to recover water. They reported the heterogeneity in composition and studied the negative effect of condensate storage on the final pollutant charge. In that study, RO allowed the reuse of permeates in the plant as cooling-heating waters. Water recoveries of 95% were possible with constant

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Nomenclature

Abbreviations

FC	Flash cooler
UHT	Ultra high temperature
NF	Nanofiltration
COD	Chemical oxygen demand
TOC	Total organic carbon
VCR	Volume concentration rate
CIP	Cleaning in place
MT	Membrane technology
MF	Microfiltration
RO	Reverse osmosis
UF	Ultrafiltration
UV	Ultraviolet
BOD ₅	Biological oxygen demand (five days)
NTU	Nephelometric turbidity unit
TSS	Total suspended solids
MWCO	Molecular weight cut-off
TS	Total solids
SDI	Silt density index
ASTM	American Society for Testing and Materials
I.C.	Intermediate cleaning
F.C.	Final cleaning
CFU	Colony forming unit
P.R.	Permeability reduction
R	Rejection
st	Short time
lt	Long time
NPV	Net present value
IRR	Internal rate of return

Symbols

TMP	Transmembrane pressure (bar)
J	permeate flow rate (L/h m ²)
V _f	Feed volume (m ³ or m ³ /h)
V _r	Retentate volume (m ³ or m ³ /h)
V _p	Permeate volume (m ³ or m ³ /h)
R	Rejection (%)
C _f	Feed concentration (mg/L)
C _p	Permeate concentration (mg/L)
h	Hours

permeate flow rates of 11 L/h m². Baskaran et al. [15] studied several Australian wastewaters from milk powder industries in order to reduce valuable organic products and reuse permeates after treatment with MTs.

One of the aspects to bear in mind when selecting the type of membrane treatment is that of deciding on the desired quality of the permeate, as this affects both the technology (MF-RO) and the process conditions used (effect of pressure, feed concentration, pH, etc., on membrane selectivity). Different water specifications depending on its end use can be seen in Table 1. The highest possible water quality is required when the aim is to reuse water to produce steam. Its main properties must include a low Ca²⁺ content as well as low conductivity and a low concentration of soluble solids. Water for boilers is only obtained using RO, combining two NF steps or sequences of NF and RO. The characteristics of water that is to be used in cleaning and watering are less restrictive and, in these cases, simple processes can be sufficient to achieve the purpose. Bacteriological control is of paramount importance when the reused water may come into contact with food (heat exchangers, etc.).

Table 1

Water specifications according to end uses.

Parameter	Boiling water ^m	Cooling–heating water ^a	Water for cleaning ^{a,b}	Process ^{a,b}	Other uses ^{a,c}
pH	7–10	6.9–9.0	6.5–9.0	6.5–9.5	6–9
Conductivity (25 °C), μS/cm	<40	1000	<200	2500 (20 °C)	/
COD, mg O ₂ /L	<10	75	/	<5	43 ^d
TOC, mg O ₂ /L	<4	14 ^d	<4	<4	16 ^d
BOD ₅ , mg O ₂ /L	1–50	25	/	/	30
Ca ²⁺ , mg/L	<0.4	240	<1	<400	/
Total suspended solids, mg/L	0.5–10	100	35	/	<20
Turbidity, NTU	/ ^e	50	/	<5	<10
Colony count/1 mL	/	/	<100	<100	/
<i>E. coli</i> /100 mL	/	/	ND ^f	ND	<200
Coliform bacteria/100 mL	/	/	ND	ND	<200

^a Adapted from Mavrov et al. [11], Judd and Jefferson [16], Spanish legislation [17,18] and the US Environmental Protection Agency [19].

^b Water used in the industry for production processes, equipment cleaning, heat-exchangers, etc., which could be in contact with food (must be drinking quality water).

^c Watering, fire protection systems, industrial washing of vehicles, etc.

^d Using the most unfavourable correlation between COD, TOC and BOD₅ (BOD₅/COD = 0.7 and BOD₅/TOC = 1.85).

^e No limitation found.

^f Not detected.

The heterogeneity of dairy industry wastewaters is summarised in Table 2, in which values of conductivity, pH, COD, TOC, total suspended solids (TSS) and residual hardness are used as the main properties to define the pollution load of the wastewater and permeates. Condensates from evaporation and drying may be considered low pollutant waters according to Chmiel et al. [1] and Mavrov and Bélières [12], while end pipe wastewaters need intense treatment to obtain clean water.

Segregating wastewater streams or “in situ” wastewater treatment before mixing with other currents can be a wise practice. It has the advantages of optimizing water use and the treatments to reuse the water produced by MT, adapting the water composition to the most suitable technology to obtain a certain water quality. Automatic online monitoring of each stream for pH, conductivity and turbidity is recommended to control and isolate water streams with a similar composition which could be processed using similar technology.

FCs are present in all food industries when direct UHT treatment is used and consist in a vacuum chamber into which the sterilised product is sprayed. The degree of vacuum is regulated to remove the amount of vapour which was previously diluted into the product through direct heat treatment.

Water streams from FCs and condensates from evaporation and drying processes represent an important percentage of the total wastewater generated in the factory (between 20 and 40%) [2]. These streams can be considered as having a low pollutant load [1]. However, their composition fluctuates strongly depending on several factors such as the type of product that is being treated, the stability of the operation and the moment at which the FC is working (cleaning, production, etc.), making it necessary to continuously inspect and monitor condensate quality.

The benefits of water recovery from FCs may be twofold, providing savings in water consumption as well as in the recovery of heat energy. Steam condensates can be reused in numerous areas of the plant such as boiler and cooling tower feed water, CIP systems, reconstitution of powdered products, cheese curd wash water, dryer wet scrubbers, indirect heating (via heat exchange) and pump seal water, depending on the quality of the water. Recovering the steam condensate from boilers and steam distribution systems can significantly reduce operating costs, the use of chemical and the amount of makeup water required by the boiler. A condensate return system also reduces

Table 2
Summary of several industry wastewater characteristics.

Wastewater	COD (ppm)	TSS (ppm)	pH	Conductivity (µS/cm)	TOC (ppm)	Ca ²⁺ (ppm)	Reference
Effluent from a municipal treatment	68–214	1340–2730	7.5–8.2	/	9–55	/	del Pino and Durham [20]
Condensates (different sources)	2–720	/	4.1–8.5	6–190	/	0.4–1.5	Chmiel et al. [11]
General wastewater ^a	50–500	85	/	1800	/	1200	Koyuncu et al. [10]
Steam condensates	5–45	/	4.0–8.0	6–190	1.6–10	0.4–1.0	Mavrov and Béliers [12]
Wastewater from washing bottles	210	/	11.8	3160	92	/	Scharnagl et al. [21]
Effluent from a biological treatment	55–500	85	/	1750	/	1200	Turan [14]
Model milk wastewater	8200	/	6.6	700	/	/	Vourch et al. [13]
Surface water	/	/	7.7	407	3.2	/	Costa and de Pinho [22]
General wastewater ^a	1500–3000	250–600	5.5–7.5	/	/	/	Sarkar et al. [4]
General wastewater ^a	380–59,100	31–796	6.6–7.2	350–46,400	96–2460	7.6–238	Vourch et al. [2]
General wastewater ^a	2500–3900	500–750	6.2–6.9	/	/	/	Gong et al. [6]

Additional information in Danalewich et al. [23].

^a End pipe food industry wastewaters.

energy costs, seeing as the already hot condensate requires less energy to reheat.

In this study, flash cooler condensates from a dairy factory (1.5 · 10⁹ L processed per day) were characterised and then processed using a nanofiltration membrane (molecular weight cut-off (MWCO) 200 Da) in a single step pilot plant (1.6 m² surface area) to study the effect of the main process parameters (pressure, temperature, recovery rate) on the quality of the permeate thus obtained. An economic study based on a number of starting hypotheses and on the results obtained in this research study was performed to provide information on the savings of the proposed process depending on the end use of the permeates. Previously, a nanofiltration membrane plant was designed and set up to carry out the application.

2. Materials and methods

2.1. Feed source characterisation

The effluent used in this study was taken from a Spanish dairy factory. The wastewater source was collected at the output of four FCs used in a direct UHT process. The FCs generate about 20 m³/h of condensates originating from different dairy products (milks, shakes, etc.).

The feed was characterised according to the main parameters monitored in wastewater recycling and reuse for quality control. The measurements routinely analyzed were thus pH, electrical conductivity, COD, TOC and residual hardness (expressed as Ca²⁺), while total solids (TS), TSS, fat and oils, chlorine, total microorganisms and Enterobacteriaceae were determined sporadically. The silt density index (SDI) was also measured in order to verify the fulfilment of the requirements from the membrane manufacturer.

2.2. Analytical methods

Physicochemical and chemical analyses were carried out on feed, concentrate and permeate samples. The measurements of COD (sulphuric oxidation and Cr³⁺ determination at 605 nm), TOC (absorption measurement of a CO₂-indicator complex at 605 nm), residual hardness (determination of a coloured phthalein complex at 565 nm) and chlorine (measurement of a free chlorine and dipropyl-p-phenylenediamine compound at 550 nm) were determined by means of cell tests using a Spectroquant NOVA 60 photometer (Merck, Germany).

Conductivity and pH were monitored using an HQ40d multimeter (Hach Lange, Belgium), both sensors presenting automatic correction of the measurements with temperature. Total and suspended solids were measured according to standard methods [24]. Fat and oils were analyzed by infrared spectrophotometry. Finally, the automated tools TEMPO TVC and EB (bioMérieux, France) were used to count the aerobic mesophilic total flora at 40–48 h and the Enterobacteriaceae at 24 h, respectively.

The SDI fouling index is a parameter that provides information on the water fouling potential and is critical in NF and RO processes. SDI determination is standardized in the ASTM Standard Test Method D 4189-95. This method evaluates the quantity of matter in water, based on fouling variation of a 0.45 µm membrane after a 15 minute filtration time. It is usually applied to low fouling potential waters such as pre-treated water feeding RO or NF [25], and could become a good parameter to measure the fouling potential of water with low turbidity and suspended solids. This method is not useful to measure the fouling potential trend of raw dairy wastewaters, such as the effluent used in this work, due to the high values of SDI obtained. For this reason, the feed wastewater SDI was determined after 5 min instead of after the fifteen specified in the method.

2.3. Membrane

A commercial spiral wound SeIRO MPS-34 2540 B2X (Koch Membrane Systems, USA) NF membrane was used in this study. Its main characteristics are given in Table 3.

Membrane permeation properties were checked with tap water that had been previously prefiltered in order to obtain water with a SDI lower than three [25]. For preservation between runs, the membrane was stored after being cleaned in a 2500 ppm sodium metabisulfite solution. Normally, this requirement was further exploited to clean the membrane following the protocol presented in Table 4. The sodium metabisulfite was also added to the nanofiltration feed to protect the membrane from attack by free chlorine (generally between 0.04–0.21 mg/L for FC condensates and 0.28–0.36 mg/L for prefiltered cleaning water).

The cleaning efficiency was assessed by plotting the graph of the permeate flow rate (J) versus the transmembrane pressure (TMP) at 30 °C for prefiltered water.

Table 3
Membrane characteristics.

Material: proprietary composite	
MWCO, Da	200
Glucose/sucrose rejection ^a , %	95/97
NaCl rejection ^a , %	35
Permeate flow ^a , L/h	95.83
Membrane area, m ²	1.6
Maximum operating pressure, bar	35
Maximum temperature, °C	70
pH operating range	0–14
Maximum feed turbidity, NTU	1
Maximum feed SDI	5

^a Test conditions: RO water at 30 bar and 30 °C. Feed solution for rejection tests: 3% glucose/3% sucrose or 5% NaCl.

Table 4
Cleaning protocol followed.

Stage	Product ^a	Dosage	pH	Time (min)	Temperature (°C)	Pressure (bar)
Initial discontinuous rinsing	Cold tap water	/	/	15	/	5
Alkaline cleaning	NaOH	2.5% w/v	12.0–12.6	45	50	15
Discontinuous rinsing	Cold tap water	/	/	5	/	5
Continuous rinsing	Cold tap water	/	/	Until achieving tap water pH	/	5
Acid cleaning	HNO ₃	1.0% v/v	0.6–1.0	45	50	15
Discontinuous rinsing	Cold tap water	/	/	5	/	5
Continuous rinsing	Cold tap water	/	/	Until achieving tap water pH	/	5

^a Prefiltered water used for cleaning purposes.

2.4. Nanofiltration setup

The experiments were performed in a pilot-scale plant equipped with a 2540 spiral wound membrane.

Fig. 1 shows a scheme of the pilot plant. The raw water is taken from the feed tank (50 L capacity) and passes through a 100 µm prefilter in order to protect the pumps and the membrane against large particles before being pumped into the spiral wound module. Three level switches installed in the feed tank are used to enable the possibility of continuous operation. A flow detector is used to avoid the pump system working under vacuum. The product is impelled towards the nanofiltration membrane by means of the volumetric and pressure pumps, while the recirculation pump generates high speeds over the membrane surface, thus improving filtration performance. Two manometers at each side of the membrane module monitor the TMP. Three flowmeters measure the volumetric flow rate in the feed, retentate and permeate lines. The TMP is regulated by means of a needle valve located on the retentate side. A heat exchanger (steam fed) and a cooler (cold tap water fed) are also used to control the feed solution temperature, when necessary. To obtain high quality water, a prefiltration system consisting of a bag filter and three deep cartridge prefiltrators of 5, 1 and 0.2 µm, respectively, is available.

2.5. Operating conditions

The pilot plant was operated in closed-loop mode in the first part of the trials, during which both the permeate and concentrate streams were recirculated to the feed tank.

The membrane was first characterised with prefiltered tap water. After stabilization, the permeate flow rate was plotted versus temperature, TMP and time. Condensates from industrial FCs were nanofiltered at pressures between 15 and 30 bar and temperatures between 30 and 50 °C. Feed flow rates varied between 3.5 and 5 m³/h. The permeate flow rate was measured continuously and permeate samples were analyzed each hour.

In the second part of this research work, the influence of VCR on membrane permeability and permeate characteristics was studied in 6-hour-long experiments at 25 bar and 50 °C. The permeate flow rate values at a given VCR (2, 3, 8, 12 and 15) was monitored over time once the steady-state was reached.

VCR was defined as:

$$VCR = \frac{V_f}{V_r} = \frac{V_f}{V_f - V_p} \tag{1}$$

where V_f, V_r and V_p are the feed, retentate and permeate volumes, respectively.

In order to calculate the separation efficiency and to monitor the analyzed parameters, the rejection of the membrane was defined as:

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{2}$$

where C_p and C_f are the permeate and feed concentration, respectively.

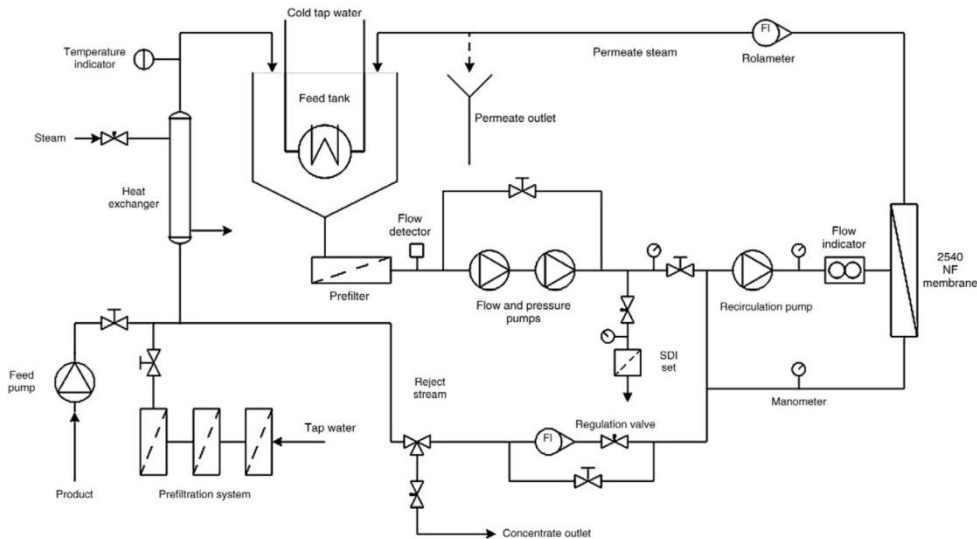


Fig. 1. Scheme of the NF rig.

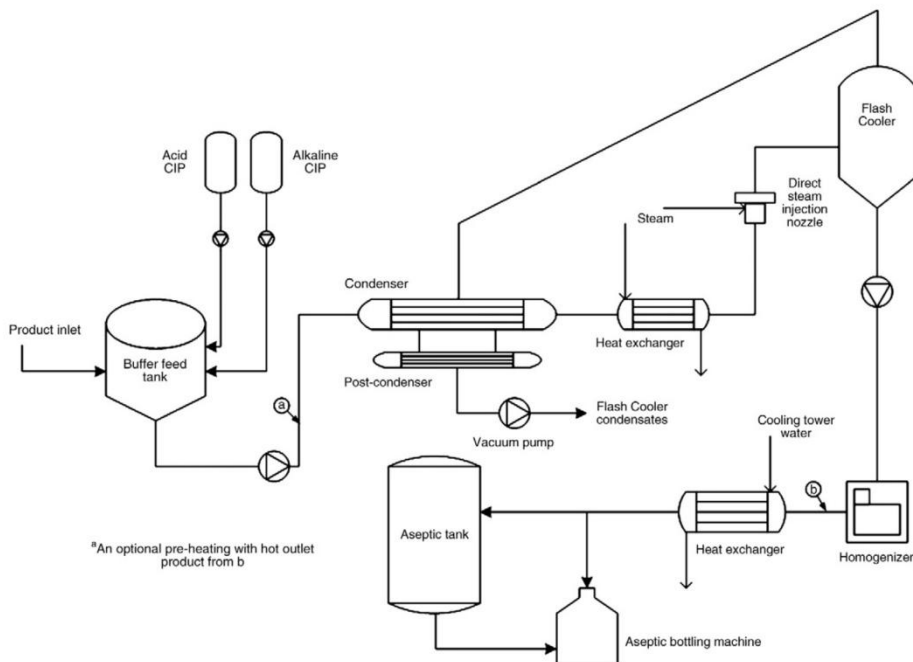


Fig. 2. UHT process: direct steam injection and flash cooler drainage.

2.6. Economic estimation

The costs associated with nanofiltration treatment can be divided in capital costs corresponding to membranes, pressure vessels, pumps, piping, controls, tanks, etc., and operating costs corresponding to pre-treatments, maintenance, chemicals, concentrate disposal, membrane replacement, energy and amortization of capital costs.

Membrane capital costs are highly dependent on flux, as this parameter determines the number of membrane modules and their related equipment. Therefore, capital costs typically decrease as

plant capacity increases due to the economies of scale associated with manufactured equipment and other facilities [26].

The model of Sethi and Wiesner [26] was used to estimate the main capital costs of the designed nanofiltration operation presented in this paper. Correlations, in the form of a power law, between equipment costs and membrane area constitute the basis for the calculation of these costs. An original model from Pickering and Wiesner [27], slightly modified by Sethi and Wiesner [26], was also applied for the purpose of estimating operating costs.

The future savings related to the implementation of this study were mainly calculated in terms of energy and water savings, taking

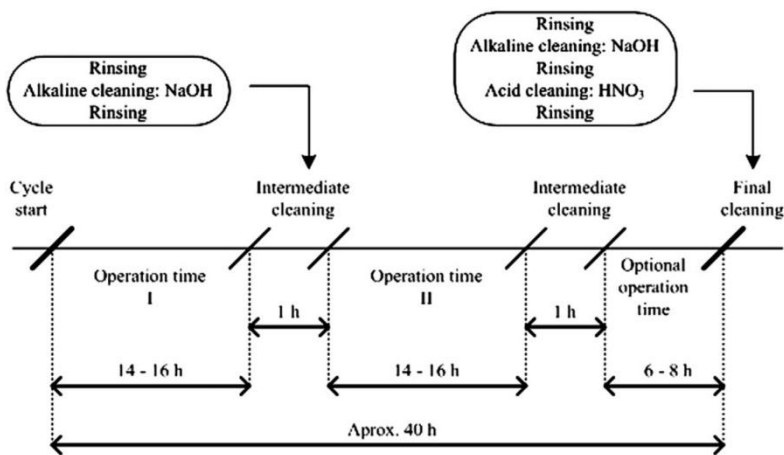


Fig. 3. Operating cycle of the milk sterilization flash coolers.

into account the supplied water, steam generation and water disposal costs for the company.

3. Results and discussion

3.1. Flash cooler condensate characterisation

Fig. 2 shows a diagram of the direct UHT treatment in the industrial plant considered here. Injected steam is removed from the FCs by means of an ejector (identified as a vacuum pump in Fig. 2). The vapour is condensed through two condensers in a row and then mixed with the tap water used in the ejector. The average flow rate of the FC wastewater condensates is around 20 m³/h (for the four FCs existing in the industrial plant) and the temperature of the condensates normally varies between 40 and 85 °C.

The heterogeneity found in the analyzed condensates depends on the moment at which the samples are taken with respect to the FC step. Fig. 3 shows a simplified scheme of the way in which the FC

work. The complete FC cycle is about 40 h, although this can vary slightly depending on production needs. Intermediate cleaning (I.C.), which mainly consists in an alkaline pass with two interspersed rinsings, is performed or not depending on the type of product manufactured at each moment (milk, skimmed milk, different flavoured shakes, etc.). Additionally, a final cleaning (F.C.) is always carried out between operating cycles. When the system is not operating, it is loaded with sterile water.

Fig. 4 shows the results from the condensate analysis (for the four FCs studied) carried out at different moments of the cycles. Results for FC#3 contained in this figure are represented on the right y-axis as are the Ca²⁺ results for FC#4.

The performance of FC#1, #2 and #4 is quite similar for all the parameters measured, although FC#3 shows higher values of TOC, COD and Ca²⁺, which suggests that this machine is performing poorly. Maximum values of pH are found for samples taken during intermediate cleaning (cleaning with NaOH). The differences in COD and TOC for FC#4 compared to FC#1 and #2 are probably due to its higher

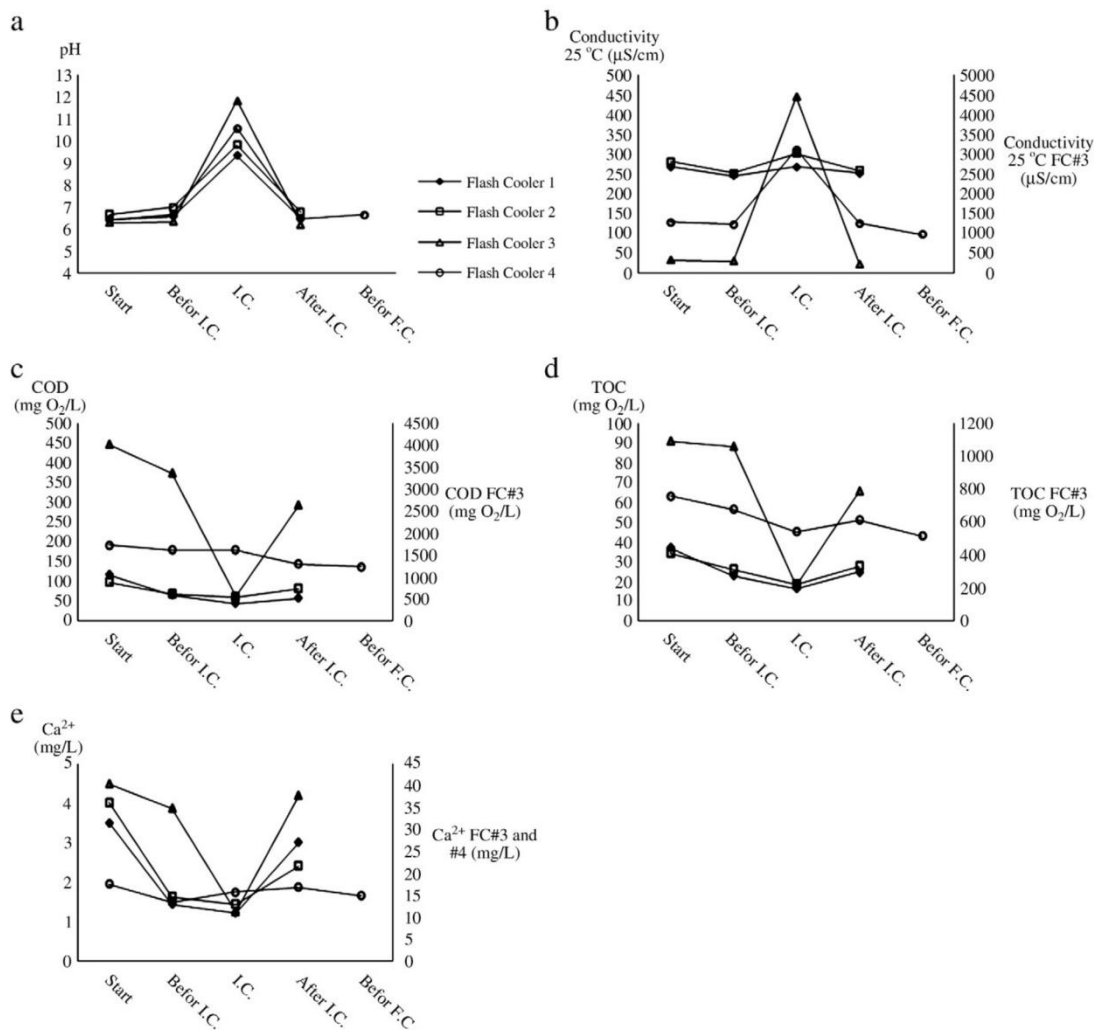


Fig. 4. Characterisation of the flash cooler condensates. (a) pH, (b) conductivity, (c) chemical oxygen demand, (d) total organic carbon and (e) residual hardness of condensates.

energy efficiency, which may increase the drag by increasing the effectiveness of the vacuum pump operation. It should also be noted that none of the FCs has either demisters or cyclones to reduce the drag of milk particles.

COD values are higher than TOC values due to the presence of inorganic compounds (not analysed), as has been previously described [2,28]. These authors detected more than 100 small volatile molecules in condensates from FC, drying and evaporation stages. These compounds originate from the degradation of proteins, fat and lactose [29].

In line with the analytical results, the waters from FC#3 were segregated from the rest and the condensates from FC#1, #2 and #4 were treated with membranes. The average composition of the treated condensates is presented in Table 5. The values shown are similar to those reported by other authors [1,2].

Additional analyses (apart from those shown in Table 5) were carried out to obtain an enhanced condensate characterisation: TS (76–208 mg/L), TSS (1.5–3.5 mg/L), fat and oils (5.61–21.8 mg/L), total microorganisms (<1 colony forming unit (CFU)/g) and Enterobacteriaceae (<1 CFU/g). These analyses were performed non-routinely.

Condensates from flash coolers and from milk evaporation processes are usually quite similar, the differences are found (lower values of conductivity, COD and pH in case of Chmiel et al. [1]) depending on the moment at which samples are taken and on the correct performance of the equipment used at the plants. This leads to the need to carry out experiments with each wastewater so as to check the membrane permeability and rejection based on the main parameters (pressure, temperature, and recovery rate) and, ultimately, to estimate the economy of the process taking into account the quality of permeates obtained. The results shown in Table 5 can be compared with the values presented in Table 1. As the condensate parameters do not fulfil the values for reuse as water in the plant, their treatment is justified.

3.2. Membrane experiments

3.2.1. Membrane permeability and rejection at VCR 1

The nanofiltration membrane was characterised using prefiltered tap water (SDI after 15 min between 2.5 and 3) at different transmembrane pressures and temperatures (results not shown) in order to obtain clean water with a low SDI according to the recommendations given by Mosset et al. [25]. The membrane permeability at 30 °C was 3.32 L/h m² bar, slightly higher than the values suggested by the manufacturer.

FC condensates were collected in a 1000 L tank and immediately nanofiltered to avoid natural acidification, as recommended by Vourch et al. [2]. When condensates are stored for several hours, pH decreases due to degradation of organic matter and its conversion into small organic molecules. Additionally, this way of operating also contributes to reducing heating costs (the average temperature of condensates is typically around 75 °C [30]) as reported by Chmiel et al. [1], who propose the use of the thermal energy of condensates at roughly 50 °C. The permeate flow rates of condensates were thus measured at different module inlet pressures (between 5 and 30 bar) and temperatures (30 and 50 °C). Fig. 5 shows the differences

between water and flash cooler condensate permeabilities after 10 and 20 min.

The condensate permeate flow rate is lower than the values obtained for water at pressures higher than 10 bar, which means that a certain tendency to fouling arises when condensates are processed. The differences between measurements at 10 and 20 min are negligible.

Fouling effects are studied in Fig. 6. It can be seen that after 6 h of experimentation, J reductions are between 5.5 and 20.0%, being slightly higher at increasing transmembrane pressures. However, permeate flow rate reductions occur mainly in the first part of the experiments (first 2 h), after which the flux becomes stabilized. The permeabilities obtained employing a 200 Da MWCO membrane are substantially higher than those obtained with nanofiltration in other published studies [3,31], which opens up the possibility of a smaller nanofiltration plant to treat these types of condensates. The effect of temperature on J is very important (increase of about 3% per °C), as previously reported by Valentin [30] and Snow et al. [32]. Given that the working temperature of 50 °C is quite far from the limit temperature of the membrane used (70 °C), this is unlikely to suffer thermal damage. An increase of 15 bar (from 15 to 30) increases the J value 35.6%, although it is advisable to work at medium pressure to reduce possible pressure membrane damage over long operating times.

Analyses of the main parameters studied (conductivity, COD, TOC and Ca²⁺) were carried out in the permeate stream to determine the influence of operating time and process conditions (pressure and temperature) on the characteristics of the permeates. The results are shown in Fig. 7, in which the rejection (R) is also presented as a function of these parameters. Membrane rejection for the measured parameters increases in all cases with transmembrane pressure, whereas temperature has a negligible influence. Operating time does not affect the rejection either, which means that fouling effects are of minor importance. This behaviour has been previously reported in other published papers studying other types of wastewater and membranes [10,12,33]. The results agree with mathematical models proposed for nanofiltration of diluted feeds [34,35].

Permeate conductivities are lower than maximum permissible values for all possible water reuses except for reuse as boiling water. COD and TOC only satisfy the requirements for cooling, heating and service uses. In addition to the aforementioned requirements, the obtained concentration of Ca²⁺ also complies with the process needs, which correspond to drinking quality objectives. In light of these results, only cooling, heating and services conditions were met. However, consistent with the thermal potential of permeate condensates, their first use has to be related to heating purposes.

Permeate pH has also been plotted versus operating time (at VCR 1) in Fig. 8. Slightly increasing values of pH are detected at approximately 15 bar TMP. However, during concentration with membranes, the evolution of the pH of the permeate had not been studied in depth in the

Table 5 Average analyses of nanofiltered condensates.

Parameter	Value range
pH	5.93–7.03
Conductivity (µS/cm)	199.5–287.0
COD (mg O ₂ /L)	61–125
TOC (mg O ₂ /L)	23.2–46.0
Ca ²⁺ (mg/L)	0.97–1.75
SDI ^a	5.59–6.54

^a Measured after 5 min.

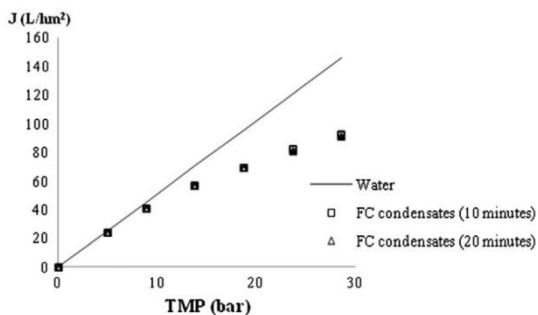


Fig. 5. Membrane permeability vs. transmembrane pressure at 50 °C.

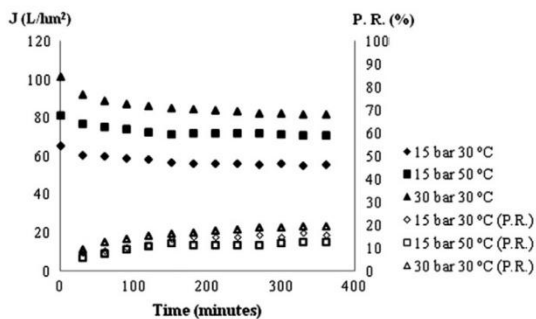


Fig. 6. Membrane permeability (and permeability reduction (P.R.)) as a function of operating time at different transmembrane pressures and temperatures.

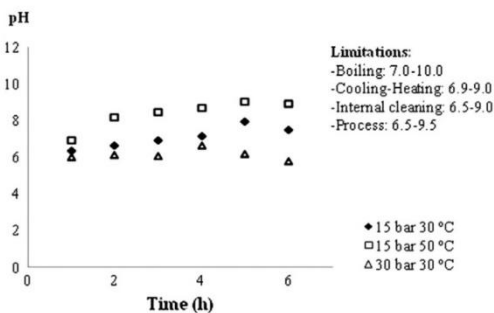


Fig. 8. Evolution of permeate pH as a function of temperature, pressure and time (6 h).

previous work. An increase in pH on the permeate side was also found at different VCRs (see the following experiments in Section 3.2.2.) and the reasons for this behaviour will be subsequently explained. Notwithstanding, it can be seen in Fig. 8 that permeate pH fulfils the specifications for all waters regardless of the desired end use.

3.2.2. Membrane behaviour at different VCRs

In the second part of the NF experiments, condensates were concentrated at different volume concentration ratios (from 2 to 15) in accordance with the aforementioned definition. Experiments were performed at 50.0 ± 0.1 °C and 25 bar of inlet module pressure (23.7 bar TMP).

3.2.2.1. Evolution of permeate pH. A similar evolution of permeate pH values was found during water concentration at different VCRs, as

can be seen in Fig. 9. The results presented in these two figures (and in Fig. 8) correspond to different experiments. In all cases, permeate pH increases with VCR and during full recycling experiments at constant VCR. This behaviour was also observed in other previous studies [22,36] using different membranes and feed, even though the results were not clearly explained. If the pH is higher in the permeate stream than in the concentrated stream, different H^+ and OH^- ion rejections must occur [37]. The SelRO MPS-34 membrane used in this study is recommended for recovering caustic products (CIP chemicals) in the permeate stream. Hence, the passage of alkaline compounds is preferential, probably due to the positive membrane charge in a wide interval of feed pH. However this point has not been demonstrated as the composition of the active layer of the membrane is not available.

During the concentration step (working in continuous mode operation), the increase in pH is not very pronounced and is almost linear

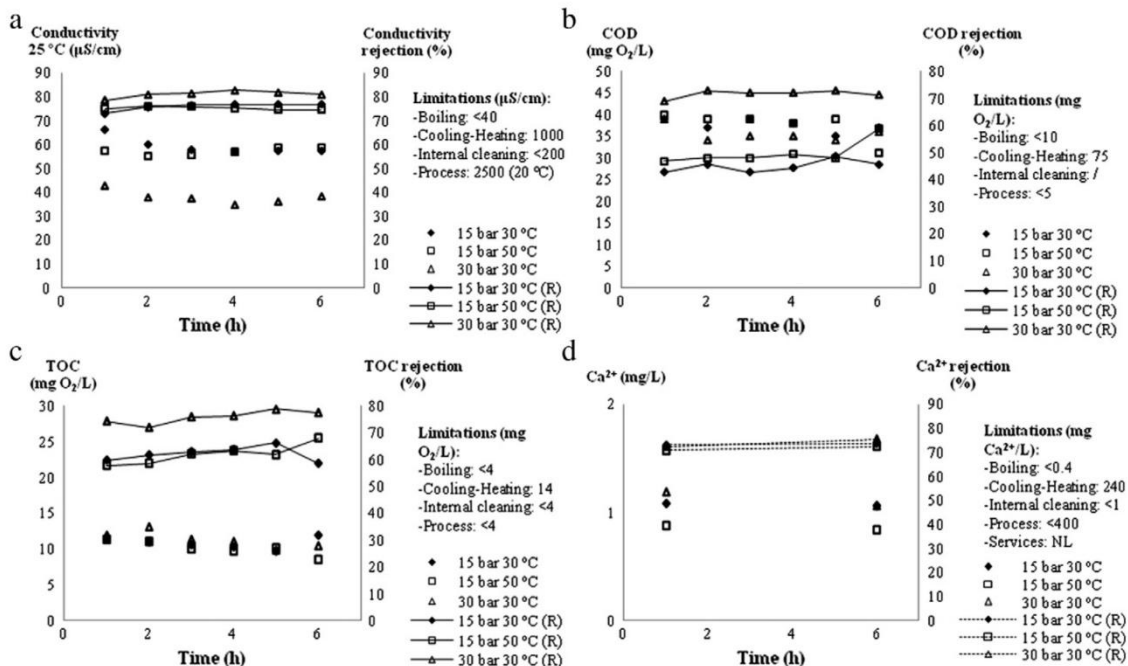


Fig. 7. Permeate characteristics at different temperatures, pressures and time (6 h). (a) Conductivity, (b) chemical oxygen demand, (c) total organic carbon and (d) residual hardness of permeates.

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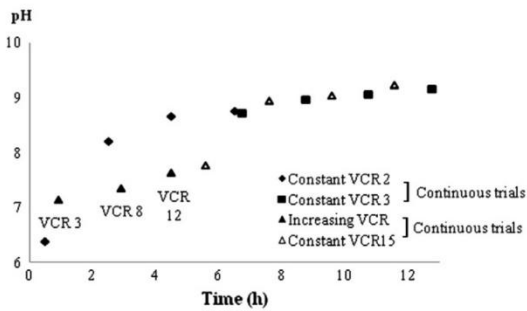


Fig. 9. Permeate pH changes with VCR and time.

with time. However, after reaching the desired VCR and beginning to work in full recirculation mode at fixed VCR, the pH rises sharply at first, subsequently remaining unchanged and reaching similar final values in both cases. However, the increase in permeate pH is less acute when the pH is higher and the positive membrane charge is probably lower. These results facilitate the reuse of the permeate as its pH falls within the limits for different water uses (see Table 1) and there is no need to add acidic compounds to neutralize it.

3.2.2.2. Membrane permeate flow rate and rejection at different VCRs. Multiple authors have studied the influence of VCR on the membrane performance for dairy wastewater reuse applications, achieving maximum values from 3 to 6 for high concentrated feed water [3,38,39], while 6 to 17 for less fouled feeds as used in the present work [1,10]. A key factor to design a NF plant for condensates recovery is to know how the membrane behaves at different VCR values. This is shown in Fig. 10. The two lines correspond to permeate flow rates measured once the VCR was achieved (short time (st)) and 15 min later (long time (lt)).

Average permeabilities (around 4 L/h m² bar) are similar to those published by other authors who studied milk condensates and wastewaters employing nanofiltration membranes (average permeability between 3.5 and 4.5 L/h m² bar) [1] and higher than those for milk wastewaters treated by means of RO (0.5 L/h m² bar) [2] and UF (approximately 0.5 L/h m² bar) [6]. The reduction in permeability at VCR 15 (93.3% condensates recovery) is low (3.8%). Additionally, operating stability at VCR 15 was tested after 6 h of operation (results not shown), obtaining a reduction in permeability of less than 4.4%. This result would suggest the possibility of recovering practically all the condensates treated at good permeation rates (around 100 L/h m²) under a stable permeate flow rate.

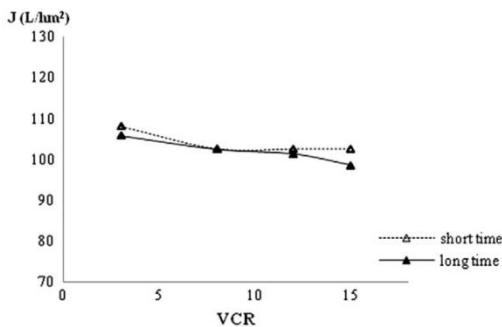


Fig. 10. Membrane permeability at different VCRs. TMP: 23.7 bar and temperature: 50 ± 1 °C.

As regards permeate quality, rejection of the main parameters studied is represented versus VCR under fixed process conditions in Fig. 11. The results included in this figure correspond to the analysis of samples taken at the previously described short and long times, except for VCR 15, the long-time value of which corresponds to a 6-hour full recirculation experiment after achieving the VCR values. Closed symbols correspond to the analysis of a duplicate experiment.

The general trend is an increase in COD and TOC rejection with increasing VCR (TOC rejection from 67.6% at VCR 3 to 82.1% at VCR 15 and COD rejection from 59.0% at VCR 3 to 76.2% at VCR 15). Both curves are parallel, which means that all compounds (organic for TOC and organic/inorganic for the COD) are similarly rejected. The low molecular weight compounds present in condensates have been described by several authors. These compounds (acetone, acetoin, diacetyl, dimethylsulfide, etc., between 60 and 100 Da) account for 20–70% of the final TOC and COD and are partially retained by the membrane (for the membrane used, R_{NaCl} = 35% and R_{Glucose} = 95%). The increase in rejection for these compounds is due to the polarization concentration layer on the membrane surface (however, they do not apparently foul the membrane). In the case of conductivity, the effect of VCR on rejection is negligible. Permeate characteristics at different VCRs are summarised in Table 6, in which it can be seen that permeates for VCR higher than 8 afford similar conductivities to that of the feed, while permeate COD and TOC values are lower than the analyzed values in the feed. For example, the conductivity limits for cleaning water are around 200 µS/cm; hence a degree of concentration above VCR 8 is not recommended in the final plant design, which limits the recovery rate consistent with this end use. With respect to COD and TOC values, all the permeates obtained (in the interval of VCRs studied) fall within the limits. The permeate Ca²⁺ concentration is very low and this ion concentration in the concentrate for VCR8 is too low to be detected with the analytical method followed.

3.3. Nanofiltration plant design

Using the experimental results included in this study, a nanofiltration membrane plant was designed based on a configuration suggested by Nilsson et al. [40]. A scheme of the facility is shown in Fig. 12. Feed pretreatments are not included in this scheme.

The FC condensate output stream is used as the feed for the plant, entering at 50 °C and pumping at 25 bar pressure and an approximate flow rate of 20 m³/h. The inlet temperature could be higher, bearing in mind the average temperature of the condensates and the physical limitations of the membranes, which would imply an increase in the permeate flow, hence generating a decrease in membrane area and in capital and operating costs. The savings would be also affected if the primary use of the permeate was indirect heating, a secondary use also being possible. The feed is concentrated at VCR 8,

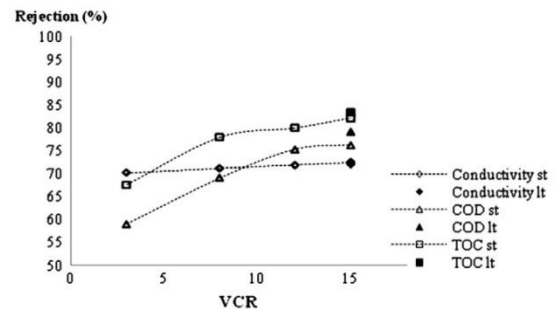


Fig. 11. Influence of time on the parameter rejection at different VCRs. TMP: 23.7 bar and temperature: 50 ± 1 °C.

Table 6
Permeates quality at different VCRs.

	VCR 1	VCR 2	VCR 3	VCR 8	VCR 12	VCR 15
Assay conditions	30 bar, 30 °C	25 bar, 50 °C	25 bar, 50 °C	25 bar, 50 °C	25 bar, 50 °C	25 bar, 50 °C
pH	5.80–6.65	6.37–8.74	8.71–9.15	6.73–9.16	7.62–9.23	7.75–9.23
Conductivity 25 °C (µS/cm)	34.7	88.5	123.0	204.1	213.3	220.0
COD (mg O ₂ /L)	34.0	32.0	29.0	37.0	55.0	52.0
TOC (mg O ₂ /L)	9.8	10.3	8.3	9.9	19.6	17.5
Ca ²⁺ mg/L	1.06	0.42	0.44	0.3	ND ^a	ND

^a Not detectable.

representing a recovery of 87.5% and resulting in a permeate stream of 17.5 m³/h. The permeate flow was adjusted to 102.4 L/h m² (measured at 25 bar, 50 °C and VCR 8). This value was chosen on the basis of the experimental results obtained for the selected membrane and the real water used. As VCR 8 is the largest volume concentration ratio the membranes could operate under, this permeate flow would thus be the lowest J and provide the maximum installed area. The membranes will not usually work at VCR 8, but will have to do so at a slightly lower VCR. As this involves a smaller permeate flow and membrane area, oversizing is thus guaranteed with this J at VCR 8.

The proposed plant is equipped with sanitary grade SeIRO MPS-34 8040 B2X (Koch Membrane Systems, USA) in a spiral wound configuration with a surface area of 20.6 m² and 57 mil (1.4 mm) spacers, as recommended for food industry applications. The total membrane area of the facility is 171 m², comprising nine spiral wound elements distributed in three series of feed and bleed loops, the first and the second one consisting of two parallel pressure vessels with two membranes inside each one, and the third one with only one membrane inside its corresponding pressure vessel.

The recirculation pumps have to feed the maximum flow suggested by the membrane manufacturer (17.1 m³/h) in order to ensure sufficient velocities for each element in the setup. Furthermore the pressure losses in the modules (0.7 bar per membrane) have to be also compensated for these pumps.

3.4. NF costs and savings estimation

A preliminary economic assessment was conducted considering the designed nanofiltration plant to process the condensates from the FCs. The basic assumptions considered in the calculations are summarised in Table 7 (information in bold).

Table 7
Economic assessment of FC condensate treatment to produce reusable water using nanofiltration (MWCO 200 Da).

<i>General data</i>	
Plant capacity, m³/h	20
Permeate flux, L/h m²	102.4
Operating hours, h/y	8640
Membrane area, m ²	171
Recovery rate, %	87.5
Feed pressure, kPa	2500
Pump efficiency, %	70
Power demand, kWh/m ³	1.21
Energy costs, €/kWh	0.1018
Membrane lifespan, y	3
Amortization period, y	15
Interest rate, %	7
Membrane replacement costs, €/m²	165
Outlet permeate temperature, °C	50
Steam cost ^a , €/t	25.5
Supplied water cost ^a , €/m ³	0.2859
Water disposal cost ^a , €/m ³	1.591
<i>Capital costs, €</i>	
Pipes and valves	64,600
Instruments and controls	54,100
Tanks and frames	58,500
Miscellaneous	185,500
Pumps	58,600
Membranes	28,200
Pressure vessels	3300
Total capital costs	452,800
<i>Operating costs, €/m³</i>	
Amortization	0.288
Concentrate disposal	0.199
Energy	0.123
Pre-treatment	0.101
Maintenance	0.010
Chemicals	0.006
Membrane replacement	0.051
Total operating costs	0.777
<i>Savings, €</i>	
Steam generation	201,200
Supplied water	43,200
Water disposal	240,600
Total savings, €/m³	2,807
NPV, €	2,742,100
IRR, %	77.45
Payback period, y	1.29

^a Data from the company.

The total membrane area is a function of the designed plant capacity and was determined using the permeate flux measured at 50 °C, 25 bar and VCR 8. The costs of pipes and valves, instruments and

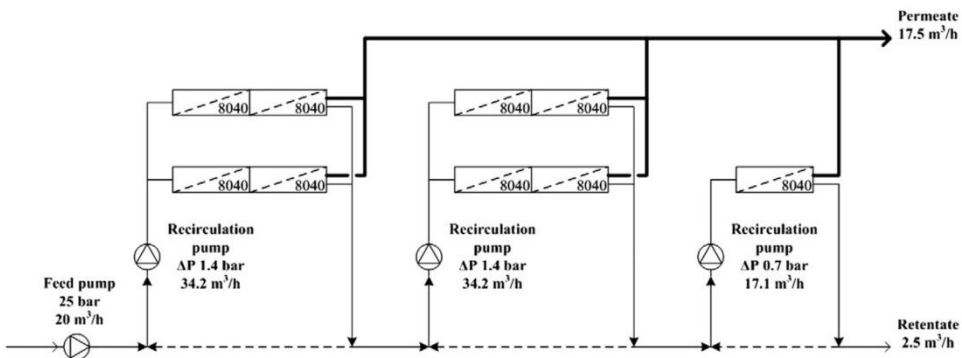


Fig. 12. Multistage nanofiltration scheme for continuous processing of FC condensates.

controls, tanks and frames and miscellaneous were calculated on the basis of this area. A correlation from Perry and Chilton [41] was used to determine the costs of the feed and recirculation pumps taking into account their work pressure and flow. The data provided in 1996 US\$ by the model of Sethi and Wiesner [26] was converted by applying the average exchange rate for that year (US\$1 = €0.81) and corrected to represent current values using the Chemical Engineering Plant Cost Index.

The cost of membranes and pressure vessels was provided by the membrane manufacturer in terms of €/m² membrane area for each concept. This membrane price also represents the membrane replacement cost. Operating costs were expressed as cost per m³ of treated water. The investment cost was annualized considering a 7% interest rate and a design life of the plant of 15 years. The costs of disposing of the concentrate were calculated assuming only the price paid by the company for disposal, which includes an on-side physical treatment and a discharge to an external sewage plant. Energy costs are only based on the energy requirements for pumping and were proportional to the pressure and flow of the designed permeate stages. The cost of energy for the company is an important parameter to consider. The chemicals costs were based on a monthly alkaline and acidic cleaning of the membrane and equipment at a price of 0.369€/kg and 0.330€/kg for the alkaline and acidic detergents, respectively. The cost of membrane replacement was determined assuming a 3-year lifespan for the membranes based on the operating conditions of the plant (high temperature and pressure). Maintenance costs were referenced from Costa and de Pinho [22]. A value of 15% of the total operating costs presented by Bergman [42] was used to estimate pre-treatment costs.

The following assumptions were made to calculate the savings of this project: the permeate exits the plant at 50 °C without heat losses, the ground or tap water used by the company is supplied at 15 °C, the steam used in the industry is saturated steam at 18 bar and 218 °C. The costs of water and energy for the company must also be taken into consideration.

The NPV (Net Present Value), the IRR (Internal Rate of Return) and the payback period were also estimated taking into account the calculated costs and savings per m³ and the designed plan capacity.

The results obtained in terms of operating costs (0.777€/m³) are in keeping with other nanofiltration facilities, although the final application of the plant varies. Chmiel et al. [1] obtained a cost of 1.25 US\$/m³ (1.36€/m³) in a nanofiltration plant for industrial vapour condensate to produce boiler makeup water. Blöcher et al. [43] give a value of 0.97€/m³ for treatment costs associated with a nanofiltration step of 5 m³/h capacity to obtain drinking quality water with a membrane bioreactor as pre-treatment. Bergman [44] reports costs of 0.15–0.91 US\$/m³ (0.12–0.74 €/m³) for plant capacities between 3800 and 56,000 m³/d. Wiesner et al. [45] also report costs between 0.30 and 0.75 US\$/m³ (0.25–0.63 €/m³). Other studies by Gorenflo et al. [46] and Costa and de Pinho [22] determined values of 0.23 and 0.214€/m³ for 27,000 and 100,000 m³/d nanofiltration plant capacity, respectively. All the results found show that the greater the plant capacity, the lower the overall cost, thus demonstrating the aforementioned economies of scale [47].

4. Conclusions

The analysis of FC condensates from a direct UHT treatment at a dairy factory shows that this water cannot be reused in the plant due to its high conductivity, TOC and COD values. The heterogeneity of different wastewaters in the food industry counsels segregating waters with a similar pollutant load in order to recover them by means of a specific treatment.

The nanofiltration membrane (200 Da MWCO) used in this study allows permeates be obtained that can be reused in the industry with high permeate flow rates (around 100 L/h m²).

At the selected temperature and inlet pressure of 50 °C and 25 bar, respectively, the influence of VCR on membrane separation efficiency was also examined. Permeabilities around 4 L/h m² bar were obtained, the design limit VCR being 8 depending on the end quality of the permeates. The permeate analysis at this VCR was 204.1 µS/cm conductivity, 37 mg O₂/L COD, 9.9 mg O₂/L TOC and 0.3 mg/L Ca²⁺. According to these data and bearing in mind the limitations of their end use, the generated permeates could be used first for indirect heating purposes, taking advantage of the thermal potential of condensates. A subsequent secondary reuse would also be possible in other miscellaneous services.

A NF plant has been proposed (171 and 185.4 m² theoretical and real membrane areas, respectively) to treat 20 m³/h of condensates with 87.5% water recovery. The economic estimation of costs (0.777€/m³) and savings (2.807 €/m³) allow recovery of the investment in a period of 1.29 years.

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References

- [1] H. Chmiel, V. Mavrov, E. Bélières, Reuse of vapour condensate from milk processing using nanofiltration, *Filtr. Sep.* 37 (2000) 24–27.
- [2] M. Vourch, B. Balanec, B. Chaufer, G. Dorange, Treatment of dairy wastewater by reverse osmosis for water reuse, *Desalination* 219 (2008) 190–202.
- [3] B. Balanec, M. Vourch, M. Rabiller-Baudry, B. Chaufer, Comparative study of different nanofiltration and reverse osmosis membranes for dairy effluent treatment by dead-end filtration, *Sep. Purif. Technol.* 42 (2005) 195–200.
- [4] B. Sarkar, P.P. Chakrabarti, A. Vijaykumar, V. Kale, Wastewater treatment in dairy industries – possibility of reuse, *Desalination* 195 (2006) 141–152.
- [5] A. Chollangi, M.M. Hossain, Separation of proteins and lactose from dairy wastewater, *Chem. Eng. Process.* 46 (2007) 398–404.
- [6] Y.M. Gong, H.X. Zhang, X.N. Cheng, Treatment of dairy wastewater by two-stage membrane operation with ultrafiltration and nanofiltration, *Water Sci. Technol.* 65 (2012) 915–919.
- [7] R. Delbeke, Recovery of milk by hyperfiltration, *Milchwissenschaft* 36 (11) (1981) 669–672.
- [8] B.D. Blanchard, Plant effluents dairy waste streams recovery, *Dairy Food Environ. Sanitation* 11 (9) (1991) 494–496.
- [9] V. Yip, S.D. Arntfield, A.W. Hydamaka, Potential for stainless steel microfiltration processing to reduce effluent from a fluid milk and ice cream processing plant, *J. Dairy Sci.* 79 (1996) 710–716.
- [10] I. Koyuncu, M. Turan, D. Topacik, A. Ates, Application of low pressure nanofiltration membranes for the recovery and reuse of dairy industry effluents, *Water Sci. Technol.* 41 (1) (2000) 213–221.
- [11] V. Mavrov, H. Chmiel, E. Bélières, Spent process water desalination and organic removal by membranes for water reuse in the food industry, *Desalination* 138 (2001) 65–74.
- [12] V. Mavrov, E. Bélières, Reduction of water consumption and wastewater quantities in the food industry by water recycling using membrane processes, *Desalination* 131 (2000) 75–86.
- [13] M. Vourch, B. Balanec, B. Chaufer, G. Dorange, Nanofiltration and reverse osmosis of model process waters from the dairy industry to produce water for reuse, *Desalination* 172 (2005) 245–256.
- [14] M. Turan, Influence of filtration conditions on the performance of nanofiltration and reverse osmosis membranes in dairy wastewater treatment, *Desalination* 170 (2004) 83–90.
- [15] K. Baskaran, L.M. Palmowski, B.M. Watson, Wastewater reuse and treatment options for the dairy industry, *Water Sci. Technol.: Water Supply* 3 (2003) 85–91.
- [16] S. Judd, B. Jefferson, *Membrane for Industrial Wastewater Recovery and Reuse*, Elsevier Science Ltd., Oxford, UK, 2003.
- [17] Spanish legislation on health criteria for drinking quality water RD 140/2003, *BOE* 45 (2003) 7228–7245.
- [18] Spanish legislation on legal system for reuse of treated water RD 1620 /2007, *BOE* 294 (2007) 50639–50661.
- [19] U.S. Environmental Protection Agency, Guidelines for Water Reuse, EPA/625/R-04/108, 2004.
- [20] M.P. del Pino, B. Durham, Wastewater reuse through dual-membrane processes: opportunities for sustainable water resources, *Desalination* 124 (1999) 271–277.
- [21] N. Scharnagl, U. Bunse, K. Peinemann, Recycling of washing waters from bottle cleaning machines using membranes, *Desalination* 131 (2000) 55–63.
- [22] A.R. Costa, M.R. de Pinho, Performance and cost estimation of nanofiltration for surface water treatment in drinking water production, *Desalination* 196 (2006) 55–65.
- [23] J.R. Danalewich, T.G. Papagiannis, R.L. Belyea, M.E. Tumbleson, L. Raskin, Characterization of dairy waste streams, current treatment practices, and potential for biological nutrient removal, *Water Res.* 32 (1998) 3555–3568.

- [24] American Public Health Association/American Water Works Association/Water Environment Federation, Standard Methods for the Examination of Water and Wastewater, 19th edition, 1995. American Public Health Association (APHA), Washington DC, USA.
- [25] A. Mosset, V. Bonnelye, M. Petry, M.A. Sanz, The sensitivity of SDI analysis: from RO feed water to raw water, *Desalination* 222 (2008) 17–23.
- [26] S. Sethi, M.R. Wiesner, Cost modeling and estimation of crossflow membrane filtration processes, *Environ. Eng. Sci.* 17 (2) (2000) 61–79.
- [27] K.D. Pickering, M.R. Wiesner, Cost model for low-pressure membrane filtration, *J. Env. Eng. ASCE* 119 (5) (1993) 772–797.
- [28] A. Stroem, The quality, treatment and use of condensate and reverse osmosis permeates, *Bull. Internat. Dairy Fed.* 232 (1988) 2–18.
- [29] L. Moio, J. Dekimpe, P. Etievant, F. Addeo, Neutral volatile compounds in the raw milks from different species, *J. Dairy Res.* 60 (2) (1993) 199–213.
- [30] A.C. Valentin, Industrial water reuse opportunities and high temperature compatible membranes, *Water Sci. Tech.: Water Supply* 10 (1) (2010) 113–120.
- [31] B. Van der Bruggen, M. Mänttari, M. Nyström, Drawbacks of applying nanofiltration and how to avoid them: a review, *Sep. Purif. Technol.* 63 (2008) 251–263.
- [32] M.J.H. Snow, D. de Winter, R. Buckingham, J. Campbell, J. Wagner, New techniques for extreme conditions: high temperature reverse osmosis and nanofiltration, *Desalination* 105 (1996) 57–61.
- [33] V. Mavrov, A. Fähnrich, H. Chmiel, Treatment of low-contaminated waste water from the food industry to produce water of drinking quality for reuse, *Desalination* 113 (1997) 197–203.
- [34] X.L. Wang, T. Tsuru, S. Nakao, S. Kimura, The electrostatic and steric-hindrance model for the transport of charged solutes through nanofiltration membranes, *J. Membr. Sci.* 135 (1997) 19–32.
- [35] B. Van der Bruggen, C. Vandecasteele, Modelling of the retention of uncharged molecules with nanofiltration, *Wat. Res.* 36 (2002) 1360–1368.
- [36] L.C. Juang, D.H. Tseng, H.Y. Lin, Membrane processes for water reuse from effluent of industrial park wastewater treatment plant: a study on flux and fouling of membrane, *Desalination* 202 (2007) 302–309.
- [37] J.J. Qin, M.H. Oo, H. Lee, B. Coniglio, Effect of feed pH on permeate pH and ion rejection under acidic conditions in NF process, *J. Membr. Sci.* 232 (2004) 153–159.
- [38] B. Balannec, G. Gésan-Guizou, B. Chaufer, M. Rabiller-Baudry, G. Daufin, Treatment of dairy process waters by membranes operations for water reuse and milk constituents concentration, *Desalination* 147 (2002) 89–94.
- [39] J. Luo, L. Ding, B. Qi, M.Y. Jaffrin, Y. Wan, A two-stage ultrafiltration and nanofiltration process for recycling dairy wastewater, *Bioresour. Technol.* 102 (2011) 7437–7442.
- [40] M. Nilsson, F. Lipnizki, G. Trägårdh, K. Ostergren, Performance, energy and cost evaluation of a nanofiltration plant operated at elevated temperatures, *Sep. Purif. Technol.* 60 (2008) 36–45.
- [41] R.H. Perry, C.H. Chilton, *Chemical Engineers' Handbook*, McGraw-Hill, New York, USA, 1991.
- [42] R.A. Bergman, Membrane softening versus lime softening in Florida: a cost comparison update, *Desalination* 102 (1995) 11–24.
- [43] C. Blöcher, M. Noronha, L. Fünfroeken, J. Dorda, V. Mavrov, H.D. Janke, H. Chmiel, Recycling of spent process water in the food industry by an integrated process of biological treatment and membrane separation, *Desalination* 144 (2002) 143–150.
- [44] R.A. Bergman, Cost of membrane softening in Florida, *J. AWWA* 88 (1996) 32–43.
- [45] M.R. Wiesner, J. Hackney, S. Sethi, J.G. Jacangelo, J.M. Laïne, Cost estimates for membrane filtration and conventional treatment, *J. AWWA* 86 (1994) 33–41.
- [46] A. Gorenflo, D. Velázquez-Padrón, F.H. Frimmel, Nanofiltration of a German groundwater of high hardness and NOM content: performance and costs, *Desalination* 151 (2002) 253–265.
- [47] S.S. Adham, J.G. Jacangelo, J.M. Laïne, Characteristics and costs of MF and UF plants, *J. AWWA* 88 (1996) 22–31.

Conclusiones particulares del apartado 4.1.

Los condensados de *flash cooler* resultaron ser una corriente muy heterogénea (con valores máximos 3–4 veces superiores a los mínimos en términos de conductividad, DQO y COT, por ejemplo), variando su composición y características en los diferentes equipos de esterilización, con bases de funcionamiento muy similares, y en función del momento del ciclo de trabajo. Los condensados recogidos durante las limpiezas intermedias presentaron un carácter muy alcalino (pH: 9,4–12,3), lo que hizo que fueran descartados para el tratamiento con membranas, no obviando por otro lado sus posibilidades de reutilización en primeros aclarados de otros equipos, incluso pudiendo ser considerados como una alternativa de limpieza de las propias membranas.

La corriente procedente del equipo número 3 destacó por su elevado contenido en materia orgánica (hasta 4010 mgO₂/L), con una media aproximadamente 25 veces superior al del resto de esterilizadores, ofreciendo síntomas de funcionamiento defectuoso del equipo, lo que hizo que fuera segregada para evitar su procesamiento mediante membranas. En cuanto al aprovechamiento energético, y aunque las temperaturas de salida de los condensados pueden alcanzar hasta los 85°C, la temperatura de trabajo en el pilotaje fue reducida hasta un máximo de 50°C previo enfriamiento, lo que redujo los posibles ahorros. Sin embargo, esto permitió evitar un excesivo daño térmico de las membranas, aún situándose su limitación térmica en torno a los 70°C a las presiones de trabajo ensayadas, e incluso mejorar la calidad de los permeados por razones de modificación de viscosidad, difusividad e incluso tamaño de poro.

La operación de nanofiltración no permitió obtener la calidad de agua buscada para su reutilización como alimentación a calderas al presentar los permeados a VCR 8 valores de 204,1 µS/cm, 37 mgO₂/L, 9,9 mgO₂/L y 0,3 mg/L en conductividad, DQO, COT y Ca²⁺, respectivamente, sí pudiendo encontrarle otros usos menos exigentes. Por otro lado, el comportamiento del sistema con el factor de concentración de volumen es primordial en el diseño de plantas de filtración, ya que determina el grado de recuperación máximo, en este caso del 87,5%, y permite simular el funcionamiento de las últimas etapas de una operación en cascada, las cuáles serían críticas al delimitar los ciclos de limpieza y las posibilidades de reutilización en función del permeado producido. En ocasiones es necesario llegar a un compromiso entre la eficiencia de recuperación y la calidad final.

4.2. Estudio de la operación de ósmosis inversa en discontinuo. Selección de la membrana óptima

Tras descartar la nanofiltración como alternativa de tratamiento, se evaluó el estudio de la ósmosis inversa para la aplicación considerada. De todas las operaciones con membranas, la ósmosis inversa es la que mejor calidad de agua podría generar, siendo los requisitos en la producción de agua de calderas muy demandantes. Se valoraron técnica y económicamente membranas de diferentes características, aún compartiendo un mismo fabricante, con el objetivo de seleccionar la más adecuada para el proceso. Las membranas consideradas en el estudio (membranas Duratherm® HWS HR, Duratherm® HF y AE – 90) fueron propuestas por el propio fabricante de acuerdo a las características de la alimentación y a los objetivos de calidad de agua buscados. Ensayos de diversa índole, aunque principalmente discontinuos, fueron llevados a cabo a escala piloto con este propósito de selección. La información aquí obtenida permitió además seleccionar las condiciones del proceso para una producción continua de larga duración que satisficiera los exigentes requerimientos fijados. La obtención de una alta calidad en el agua de alimentación a calderas permite principalmente reducir la frecuencia de purgado y la presencia de incrustaciones y corrosión en el circuito. La metodología de trabajo y los resultados experimentales obtenidos con cada una de las membranas se incluyen en sus publicaciones correspondientes, a excepción de los concernientes a la membrana AE – 90, que se muestran como parte de una publicación sin formato, y en elaboración, pendiente de ser considerada para envío a una revista científica sin determinar.

4.2.1. Membrana Duratherm® HWS HR

Production of high-quality water by reverse osmosis of milk dairy condensates

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Production of high-quality water by reverse osmosis of milk dairy condensates



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ABSTRACT

Low-pollution flash cooler (FC) condensates from the direct heat treatment of milk and milk-based products were treated by means of reverse osmosis (RO) in order to obtain high-quality water for use in boilers. The behaviour of the spiral-wound membranes at the pilot-plant scale (8.2 m² surface area) was tested in terms of the permeate flow rate (J) and quality (conductivity and chemical oxygen demand (COD)) as a function of the operation conditions, including the pressure, temperature and volume concentration rate (VCR). Response surfaces were drawn with the aim of obtaining information regarding the permeate flow rate as well as conductivity and COD reduction in the range of the studied parameters. Based on the experimental data, a plant with a 90% recovery rate (RR) was proposed with the objective of carrying out a preliminary economic assessment, which yielded a payback of 1.16 years.

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Introduction

Increasing prices of water supply and disposal, the availability and quality of water, and strict legal environmental controls have increased concerns about sustainable development and the preservation of the public image of companies. It has therefore been advised that industries internally reclaim and reuse process waters in order to reduce water consumption and effluent production.

Dairy factories are characterised by high consumption of water, generating from 0.2 to 10 L of effluent per litre of treated milk [1]. Washing, rinsing, cleaning-in-place (CIP), pasteurising, ultra-high temperature (UHT) processes, chilling, cooling, steam production, etc. are the main processes in which large amounts of water are consumed. The wastewater streams of this type of industry show variable composition, often containing different concentrations of organic matter (proteins, carbohydrates and lipids), suspended solids and oils/fats. According to the levels of these contaminants, the wastewater is considered to be a low-, medium- or high-pollution stream. The heterogeneity of dairy industry wastewaters is one of the problems with treating these effluents [2].

As a general rule, water streams with different levels of pollution are collected and treated on-site or in municipal sewage-treatment plants [3]. However, low-pollution wastewater streams

(such as boiler steam condensates, evaporation and drying condensates, cooling tower feed water, CIP washes, water for indirect heating, pump seal water, etc.), characterised by chemical oxygen demands (CODs) lower than 700 mg/L [4] and conductivities below 2200 $\mu\text{S}/\text{cm}$ [5], should be separated and treated individually.

Membrane technologies (MTs), mainly nanofiltration (NF) and reverse osmosis (RO), have shown satisfactory behaviour in the treatment of these low-pollution streams and are promising techniques due to their advantages as “clean technologies”. The good quality of water obtained with these techniques, the high recovery rates, space savings, chemical dosage savings, continuous and simple operation without phase changes, easy transportation and reduced cost [6–8] are important advantages. However, MTs undergo a decline in permeate flux due to the problems of particle blocking, concentration polarisation and fouling after continuous long-term operation [7]. Biofouling problems can cause frequent shutdowns [8] and are related to the discontinuity of production cycles [9]. Several researchers have used MTs to produce water of different qualities using single or combination membrane stages (with or without pre- and post-treatments), which include one-step processes such as ultrafiltration (UF) [10,11], NF [6,12] or RO [12,13], and combinations of UF+NF [14], NF+NF [3,4], NF+RO [4,15], or RO+RO [6,15].

Several factors should be taken into account when selecting the type of membrane treatment. Primary aspects to bear in mind are the process conditions used (pressure, temperature, feed and permeate flow, recovery rate, etc.), the operation mode

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Nomenclature

Abbreviations

ASTM	American Society for Testing and Materials
BOD ₅	Biological oxygen demand (five days)
CFU	Colony forming unit
CIP	Cleaning-in-place
COD	Chemical oxygen demand
FC	Flash cooler
MT	Membrane technology
NF	Nanofiltration
NTU	Nephelometric turbidity unit
RO	Reverse osmosis
RR	Recovery rate
SDI	Silt density index
TDS	Total dissolved solids
TKN	Total Kjeldahl nitrogen
TOC	Total organic carbon
TS	Total solids
TSS	Total suspended solids
UF	Ultrafiltration
UHT	Ultra-high temperature
VCR	Volume concentration rate

Symbols

A	Membrane permeability (L/hm ² bar)
C _f	Feed concentration (μS/cm or mg O ₂ /L)
C _p	Permeate concentration (μS/cm or mg O ₂ /L)
J	Permeate flow rate (L/hm ²)
R	Reduction (%)
TMP	Transmembrane pressure (bar)
V _f	Feed volume (m ³ or m ³ /h)
V _p	Permeate volume (m ³ or m ³ /h)
V _r	Retentate volume (m ³ or m ³ /h)

(continuous or discontinuous), the physicochemical properties of the membrane, the feed composition (which will determine the tendency for fouling because of its organic, inorganic-mineral and/or microbial content) and the desired permeate quality, which depends on the requirements for reuse (CIP, cooling, heating, boiler feed, external cleaning of floor and trucks, etc.) [16]. Boiler water specifications (pH 7–10, conductivity (25 °C) <40 μS/cm, COD <10 mg O₂/L, total organic carbon (TOC) <4 mg O₂/L, biological oxygen demand after 5 days (BOD₅) 1–50 mg O₂/L, Ca²⁺ <0.4 mg/L and total suspended solids (TSS) 0.5–10 mg/L) [17,18] are the most restrictive reuse parameters of all these possibilities. From a legal standpoint, the water used in the food industry (including process water that could come into contact with food or with surfaces subsequently exposed to the product) must be at least equal to the highest standard for drinking water required by the local authorities [19,20] and, in some cases, special permission is required. Thus, the microbiological quality of reusable water must be continuously ensured and monitored.

In the direct UHT process, flash coolers (FCs) are vacuum chambers in which the water content of the product is sterilised and partially removed to maintain the original dry matter content of the final product. Liquid ring vacuum pumps consume tap water, which mixes with the condensates to generate wastewaters that are considered to have a low pollutant load [3]. However, the characteristics are dependent on several variables, such as the treated product, the sterilisation parameters and the moment of the cycle when the FC is working; these data are completely

necessary to maintain continuous quality control [2]. The reuse of FC condensates in boilers and steam distribution systems can provide water and energy savings since hot condensates need less energy to reheat. This also reduces operating costs by cutting down the amount of chemicals and make-up water demanded by the boiler [2].

If a high-purity feed water is achieved, the blowdown frequency and the possibility of scaling and/or corrosion will be reduced. As a result, the efficiency and the service lifetime will be improved. So, in order to maintain these properties, the quality of water in terms of conductivity, pH, hardness and organic matter must be guaranteed. The presence of dissolved solids inside the boiler could eventually cause deposition, leading to scale formation and may result in localised overheating. In addition, hardness is another factor related to incrustations. Low or high feed pH values may cause corrosion or increase the scaling potential [8]. Organic substances can decompose to form carbonic acid, thereby changing the pH and causing corrosive issues or deposits and leading to the formation of foams. Organic matter present in the steam negatively affects the organoleptic properties of the product when direct UHT treatments are used.

In this study, FC condensates from the dairy industry were processed using an RO pilot-plant rig to obtain permeates with similar quality to boiler feed water. The experiments performed at the laboratory scale permitted the selection of the best operation parameters, taking into account the permeate quality. Response surfaces obtained from these experiments enabled prediction of the permeate quality and flux when working within the studied process values. Finally, a preliminary economic evaluation was made using, as a reference, energy, water and wastewater treatment costs.

Experimental

Analytical methods

The water treated in this study was the effluent from some of the FCs operating in a direct UHT process at a Spanish dairy factory. Whole and skimmed milk as well as milkshakes of different flavours were sterilised using similar UHT processes. The volume of wastewater generated by all the FCs was 20 m³/h.

To characterise the main parameters of the feed waters, some routine analyses were performed (pH (accuracy ±0.05), electrical conductivity (accuracy ±0.5%) and COD (accuracy ±3 mg O₂/L)). Other analyses included: TOC, silt density index (SDI), residual hardness (expressed as Ca²⁺), chlorine, total solids (TS), TSS, total microorganisms and Enterobacteriaceae, BOD₅, total dissolved solids (TDS), Mg²⁺, K⁺ and Na⁺ ions, phosphates, sulphates, fat and oils, total Kjeldahl nitrogen (TKN), and turbidity; these were performed only to characterise the condensates and were not performed during RO tests.

Spectrophotometric measurements of COD (sulphuric oxidation and Cr³⁺ determination at 605 nm), TOC (absorption measurement of a CO₂-indicator complex at 605 nm), residual hardness (determination of a coloured phthalein complex at 565 nm) and chlorine (measurement of a free chlorine and dipropyl-p-phenylenediamine compound at 550 nm) were carried out by means of cell tests using a Spectroquant NOVA 60 photometer (Merck, Germany).

An HQ40d multimeter (Hach Lange, Belgium) was used to monitor electrical conductivity (referenced at 25 °C) and pH (automatic correction of the measurement with temperature). Total and suspended solids were measured according to standard methods [21]. Fats and oils were analysed by infrared spectrophotometry. Electrometry was used to determine BOD₅ and TKN. Sulphates, phosphates, Mg²⁺, K⁺ and Na⁺ were measured by ionic chromatography. TDS was estimated through gravimetry and

Table 1
Membrane characteristics.

Material: proprietary composite (thin-film membrane)	
Average salt rejection ^a , %	99.5
Maximum crossflow, m ³ /h	4.5
Average permeate flow ^a , m ³ /d	8.7
Active area, m ²	8.2
Maximum operating pressure, bar	
5–50 °C	41.4
51–70 °C	20.7
Maximum operating temperature, °C	70
Maximum cleaning temperature, °C	50
Maximum sanitization temperature, °C	90
pH operating range	4.0–11.0
pH cleaning range	2.0–11.5
Maximum feed turbidity, NTU	1
Maximum feed SDI	5

^a Testing conditions: 2000 mg/L NaCl solution at 15.5 bar operating pressure, 25 °C, pH 7.5 and 15% recovery before any hot water sanitization.

turbidity by using nephelometry. Finally, the automated tools TEMPO TVC and EB (bioMérieux, France) were used to count the aerobic mesophilic total flora at 40–48 h and the Enterobacteriaceae at 24 h, respectively.

The SDI fouling index is a critical parameter when processing water by NF and RO, and is commonly applied to low-pollution waters [22]. The SDI determination is standardised in the American Society for Testing and Materials (ASTM) Standard Test Method D 4189–4195, which evaluates the quantity of matter in water, based on fouling variation of a 0.45 µm membrane after 15 min of filtration time. In the present work, a modified SDI was determined after 5 min instead of the time specified in the method.

Membrane

For the RO experiments, a spiral-wound thin-film Duratherm[®] HWS 4040 HR membrane was recommended by the manufacturer (GE Water & Process Technologies, USA) to treat this type of

effluent. The main specific properties of the membrane used are given in Table 1.

For preservation between runs, the membrane was stored after being cleaned using two alternative methods: an acid soak with Divos 2 (Diversey, The Netherlands) at pH 3.0–4.0 or an enzymatic soak with Divos 95 and Divos 80-2 (Diversey) at pH 9.2–9.8. An acid-alkaline-based protocol with Divos 2 and Divos 123 (Diversey), respectively, was applied when necessary in order to clean the membrane using prefiltered tap water in order to obtain cleaning water with an SDI lower than 3 [22].

The membrane cleaning efficiency was assessed by measuring the permeate flow rate (*J*) at 5 bar and 30 °C with prefiltered water (SDI <3).

Reverse osmosis setup

The pilot-scale plant used, made of stainless steel, was equipped with two 4040 spirally-wound membranes. The scheme of the pilot plant is shown in Fig. 1. The condensates from the FCs were pumped to an intermediate feed tank (1000-L capacity). A set of high-pressure pumps fed the RO membranes. To avoid working under vacuum, a flow detector was installed before the pumps. Transmembrane pressure (TMP), which was regulated using a needle valve located on the retentate line, was monitored by means of two manometers. The feed, retentate and permeate flow rates were controlled by flow meters. To modify the temperature of the feed solution, a heat exchanger was used. Finally, a prefiltration system consisting of a bag filter and three deep cartridge prefiltrators of 5, 1 and 0.2 µm, respectively, was available in order to maintain low values of water SDI for the rinsing and cleaning steps.

Operation conditions and data analysis

The pilot plant was operated in semi-closed-loop mode, during which the concentrate stream was recirculated to the feed tank and the permeate was stored in another 1000-L tank. Meanwhile, the

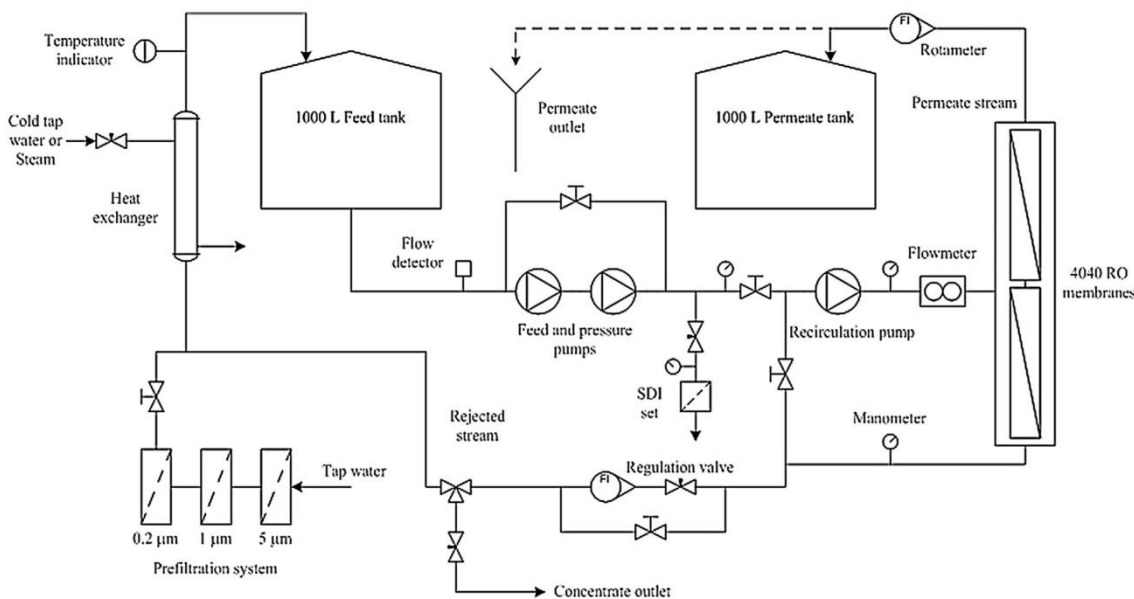


Fig. 1. Scheme of the RO rig.

permeate was removed from the rig as the feed stream was being concentrated. To assess the degree of concentration, the volume concentration rate (VCR) was defined as:

$$VCR = \frac{V_f}{V_r} = \frac{V_f}{V_f - V_p} \quad (1)$$

where V_f , V_r and V_p are the feed, retentate and permeate volumes, respectively.

The VCR is directly related to the recovery rate (RR) by means of Eq. (2). This term expresses the percentage of feed flow that is recovered as permeate.

$$RR(\%) = \frac{VCR - 1}{VCR} \times 100 \quad (2)$$

Condensates were fed to the RO rig at pressures between 10 and 20 bar and temperatures between 50 °C and 70 °C. Feed flow rates were fixed at 2.5 m³/h. The permeate flow rate was measured continuously and permeate samples were analysed at different VCR values (between 1 and 10). Thus, the influence of pressure, temperature and VCR on permeate flux and quality was studied.

The reduction (R) in the main parameters studied, *i.e.* COD and conductivity, in the permeate stream was expressed as:

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (3)$$

where C_p and C_f are the permeate and feed values of both parameters considered, respectively.

In order to obtain response surfaces and to process the results, Statgraphics (Centurion XV version) statistical analysis and data visualisation software (StatPoint Technologies Inc., USA) was used. The software also determines multivariate correlations and regression analysis. The level of significance was set at $P=0.05$.

Economic estimation

The calculation method used here was previously reported by Riera et al. [2], and was slightly modified for the RO process.

Investment costs (membranes and pressure vessels, pumps, piping, tanks, control devices, etc.) of the large-scale RO plant were estimated by using the model of Sethi and Wiesner [23], which is based on the power laws between equipment costs and membrane area. Most operating costs (amortisation, membrane replacement, energy, cleaning chemicals and concentrate disposal) were determined by applying the model of Pickering and Wiesner [24], slightly modified by Sethi and Wiesner [23].

The savings and the payback period estimated in this work take the prices of water vapour and energy for medium-sized dairy Spanish companies as the basis of calculation.

Results and discussion

Flash cooler condensate characterisation

In direct UHT treatment, injected steam is removed from the FCs by means of an ejector, in which the tap water used to create the vacuum is mixed with the condensed vapour. The resultant wastewater from the FCs produces an average flow of around 20 m³/h and the temperature usually varies between 40 °C and 85 °C.

In order to obtain feed characterisation, routine and non-routine analyses were performed. The average composition of the water that fed the membranes was as follows (minimum and maximum values found): pH (5.85–6.30), conductivity (127.2–258.0 μS/cm), COD (24–102 mg O₂/L), TOC (23.2–46.0 mg O₂/L), BOD₅ (27–68 mg O₂/L), SDI_{15 min} (5.6–6.5), TS (76–208 mg/L),

TSS (1.5–3.5 mg/L), TDS (<226 mg/L), Ca²⁺ (1.08–22.72 mg/L), Mg²⁺ (<1.1 mg/L), K⁺ (<1.6 mg/L), Na⁺ (2.6–42.9 mg/L), phosphates (<2.5 mg/L), sulphates (<6.8 mg/L), fat and oils (5.6–21.8 mg/L), TKN (<0.5 mg/L), turbidity (1.4–15.2 nephelometric turbidity unit (NTU)), total microorganisms (<1 colony forming unit (CFU)/g) and Enterobacteriaceae (<1 CFU/g). Furthermore, to prevent attack of the membrane by harmful compounds, the concentration of free chlorine was measured (generally between 0.04 and 0.21 mg/L). Analysis of conductivity, COD, pH and hardness were selected as the parameters used to follow membrane efficiency.

The first aspect found was the heterogeneity of condensates obtained from the four FCs studied. The water composition was dependent on the point in the cycle at which the FC was operating and also between different FCs, so the membrane experiments were influenced by the characteristics of the feed. Condensates from FC 3 were excluded from this study due to the unexpectedly high values of COD (up to 4010 mg O₂/L), TOC (up to 1091.7 mg O₂/L) and Ca²⁺ (up to 40.34 mg/L). For the other FCs studied (1, 2 and 4), the analysis results were similar to those reported by other authors [3,13], and showed normal values common to dairy industry condensates. The average analysis of the condensates demonstrates that these streams did not fulfil the requirements for boiler water reuse (pH 7–10, conductivity at 25 °C <40 μS/cm, COD <10 mg O₂/L, Ca²⁺ <0.4 mg/L).

Membrane experiments

Membrane characterisation

The permeate flux values of the RO membranes (L/hm²) at different transmembrane pressures and 50 °C are shown in Fig. 2. FC condensates were collected in a 1000-L tank, and were immediately treated in the RO pilot plant in order to avoid natural acidification [13] and temperature losses. The solid line corresponds to the permeation with prefiltered tap water with a low SDI (<3). The membrane permeability (A) at 50 °C was 6.9 L/h m² bar, obtained as the slope of the water line in Fig. 2 ($J=A \times \text{TMP}$).

The membrane permeability was higher than the values suggested by the manufacturer and slightly higher than those obtained by other authors that used similar cut-off membranes. Correcting the permeability by the temperature, the value (0.138 L/h m² bar °C) can be compared, for example, with 0.125 L/h m² bar °C from the Desal AG used by Akoum et al. [25], or with 0.067, 0.115 and 0.107 L/h m² bar °C from the Desal 3 SF, TFC HR and BW 30, respectively, used by Balanec et al. [1]. Differences in permeabilities between previously published results can be explained due to the different type of membranes tested. However, in this work, the membrane skin layer and structure were not supplied by the manufacturer (proprietary material).

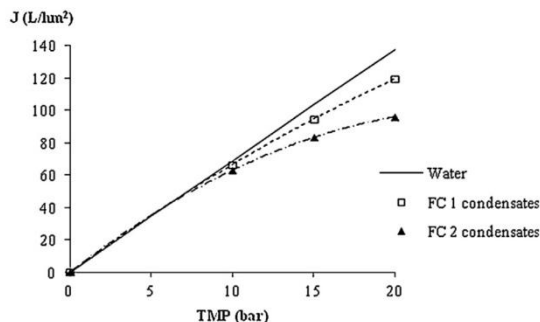


Fig. 2. Membrane permeate flow rate vs. transmembrane pressure at 50 °C.

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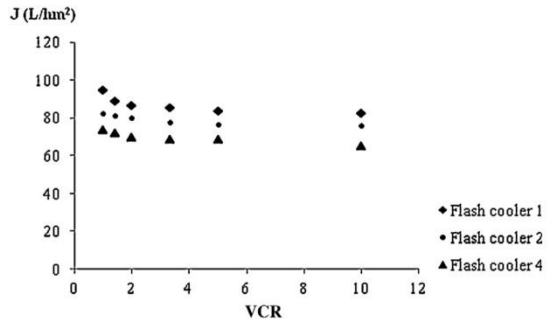


Fig. 3. Membrane permeate flow rate as a function of VCR for different feeds under constant operation conditions (inlet pressure: 15 bar, temperature: 50 °C).

In Fig. 2, the dotted lines represent the permeate flow rates of condensates from FCs 1 and 2. As observed in the figure, mild fouling effects arose when condensates were processed at pressures higher than approximately 10 bar. At 20 bar of pressure, the condensate permeability was estimated to be 6.0 and 4.8 L/h m² bar for FC 1 and 2, respectively. The differences between FC waters were significant as condensates from FC 2 were usually more polluted in terms of COD and suspended milk particles.

Membrane behaviour at different VCRs

The VCR is a relevant parameter to obtain information about the RR of RO processes, since in a large-scale installation with stages in series and in parallel, each membrane is subjected to different VCRs depending on its position in the cascade. As a general rule, higher feed concentrations produce lower permeate quality and greater membrane fouling [26]. The permeate quality and productivity, and therefore the size of the industrial plant, are not only conditioned by the VCR but also by the characteristics of the feed and the operation conditions.

Influence of the feed characteristics. As indicated in previous sections, the heterogeneity of the condensates from the different FCs is important, as they are not similar in design, configuration, vacuum pump, operation cycle, etc., and they do not work with the same operation parameters (work flow, sterilisation temperature, flash cooler level, etc.). For this reason, the behaviour of the membrane was tested with waters from FCs 1, 2 and 4; the main results are shown in Figs. 3–5, in which the permeate flow (Fig. 3) and permeate quality in terms of conductivity (Fig. 4) and COD (Fig. 5) are plotted vs. VCR, respectively. The experiments were

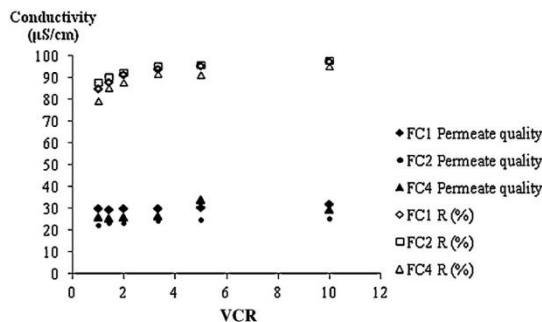


Fig. 4. Permeate conductivity and its reduction (R, %) as a function of VCR for different feeds under constant operation conditions (inlet pressure: 15 bar, temperature: 50 °C).

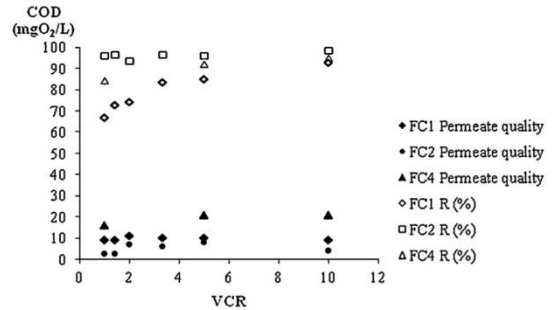


Fig. 5. Permeate COD and its reduction (R, %) as a function of VCR for different feeds under constant operation conditions (inlet pressure: 15 bar, temperature: 50 °C).

carried out under the same conditions of inlet pressure (15 bar) and temperature (50 °C).

In Fig. 3, it can be seen that the permeate flow rate decreased noticeably at low values of VCR for the three FC waters studied. The permeate flux decrease for FC 1 condensates was 9.7% from VCR 1 to VCR 3.33 and 3.6% from VCR 3.33 to VCR 10. Similar results were obtained for waters from FC 2 and 4, where the values were 5.9% and 1.7%, and 6.6% and 5.1%, respectively. After this initial decrease, the flux tended to stabilise. Permeate flux vs. VCR can be plotted using a logarithmic equation [26]:

$$J = a - b \ln(\text{VCR}) \tag{4}$$

After omitting the value of permeate flow at VCR 1, as the membrane usually needs some stabilisation time, the coefficients of Eq. (4) for each FC were determined to be 89.4 and 3.1, 82.1 and 2.8, and 72.6 and 3.0 for the a and b coefficients and for FC 1, 2 and 4, respectively. However, if the permeate flow rate was plotted vs. the time at which a particular VCR was reached (data not shown), the trend was toward a linear decrease (it is necessary to bear in mind that, in the case of FC 1 for example, the elapsed time between VCR 1 and 1.43 was 0.19 h, while the time between VCR 1.43 and 2 was 0.14 h, so the considerable decrease between permeate flow at VCR 1 and 1.43 could be explained based on the increased processing time).

A relevant difference in permeate flux, under the same operation conditions, was observed between the condensates. This could be explained according to their characteristics since, in general, condensates from FC 1 were less polluted than those from FC 2, and these were in turn less polluted than those from FC 4. These differences agree with the trend of the coefficients of Eq. (4),

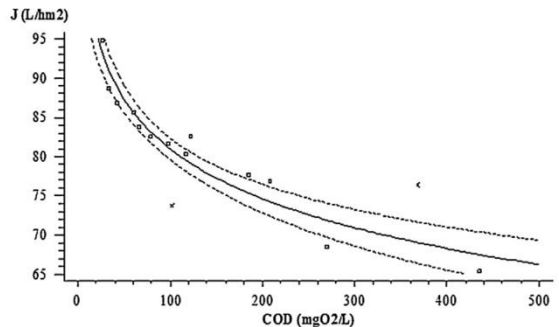


Fig. 6. Permeate flow rate vs. feed COD (inlet pressure: 15 bar, temperature: 50 °C). Dotted lines represent the 95% confidence level.

where FC 4 showed the lowest value of coefficient a , which approximately determines the initial permeate flow at VCR 1; however, the tendency of fouling, determined by coefficient b , was similar in all cases. For this batch of tests, the feed composition changed from 201.9 $\mu\text{S}/\text{cm}$ at VCR 1 to 1200.0 $\mu\text{S}/\text{cm}$ at VCR 10 in terms of conductivity, and from 27 $\text{mg O}_2/\text{L}$ at VCR 1 to 122 $\text{mg O}_2/\text{L}$ at VCR 10 in terms of COD for the water from FC 1. In the same way, this was reduced from 190.3 to 1183.0 $\mu\text{S}/\text{cm}$ and from 79 to 368 $\text{mg O}_2/\text{L}$ for FC 2 and from 127.2 to 668.0 $\mu\text{S}/\text{cm}$ and from 102 to 435 $\text{mg O}_2/\text{L}$ for FC 4 regarding conductivity and COD, respectively. The influence of feed COD on permeate flow rate can be observed in Fig. 6. Pairs of values were correlated using statistical software through a logarithmic equation ($J = 123.2 - 9.2 \ln(\text{COD})$; $R^2 = 92.7\%$). The continuous line represents the model and dotted lines the 95% confidence level; meanwhile, the x-shaped points correspond to atypical residues. J values were reduced by more than 25% when passing from 27 to 435 $\text{mg O}_2/\text{L}$.

The COD and conductivity values of the permeates in Figs. 4 and 5, respectively, show that, in most cases, permeate quality was below the requirements for boiler feed water for the FC 1 and 2 condensates. In terms of conductivity, the standard was always fulfilled, even at VCR 10. As expected, due to the constant quality control performed on the permeates obtained in these experiments, the percentage of reduction in these parameters increased with the VCR, considering that the feed was more concentrated. The achieved reductions went from minimum values of 79.6% at low VCRs to a maximum of 97.8% at high VCRs. This tendency was repeated for the COD values (66.7–98.9%). Considering that the R values were due to the rejection of a group of compounds present in the condensates, not due to a single compound, it was not possible to correlate the membrane reduction with the physical properties of the rejected solutes (molecular weight, size, charge, etc.). Permeates from FC 4 showed COD values higher than the requirements ($< 10 \text{ mg O}_2/\text{L}$) at all the VCRs studied. With respect to the residual hardness (expressed as Ca^{2+}), the values found at VCR 10 were 0.61 mg/L and 0.61 mg/L for FC 1 and 2, respectively, similar to the requirements, and 1.31 mg/L for FC 4, which is higher than the required 0.4 mg/L . Note that these values were measured in permeates at VCR 10 and the values will be lower at lower VCRs.

The reduction in COD and conductivity increased with VCR for all condensates and, in the case of FC 2, the values were close to 100%. These values are in good agreement with those obtained by other authors [1,13] who published organic matter and conductivity reductions of 99.9% and 97.0%, respectively, working at different VCRs and using RO membranes to process real dairy effluents. The R values for conductivity and COD can be correlated with their respective concentration values in the feed through reverse independent variable-type equations ($Y = a + b/X$), where the a

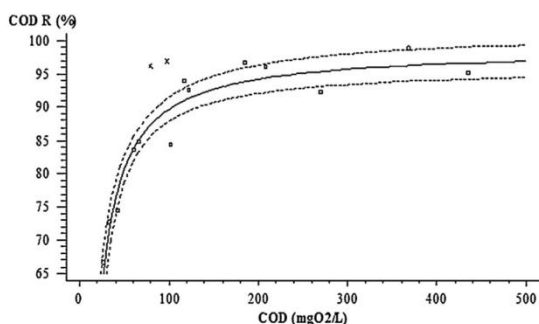


Fig. 8. COD reduction vs. feed COD (inlet pressure: 15 bar, temperature: 50 °C). Dotted lines represent the 95% confidence level.

factor can be fixed at the maximum reduction of 100%. Figs. 7 and 8 show the conductivity (conductivity $R = 99.4 - 2500.1/\text{conductivity}$; $R^2 = 96.2\%$) and COD ($\text{COD } R = 98.7 - 902.1/\text{COD}$; $R^2 = 93.2\%$) correlations, respectively. As previously described, dotted lines represent the 95% confidence level, while the x-shaped points correspond to atypical residues, which were discarded. With this information, the reductions could be predicted for the conditions of pressure and temperature studied here, based on feed characteristics.

For the case of FC 4 condensates, the most polluted in terms of organic matter and the stream with the worst permeate quality, it would be recommended to segregate this stream and to perform individual treatments in order to obtain a permeate applicable to reuse in other, less restrictive applications. On the other hand, since, in the future large-scale application, the water from different sterilisers will be mixed (approximately 31% water from FC 4) together in a buffer tank prior to the filtration step, the feed to the membrane will be weakly polluted due to the dilution effect, so the quality of the permeates would presumably be closer to those from FC 1 and 2. Furthermore, permeates obtained in this application would be mixed with demineralised water (approximately 40/60) to feed the steam boiler, so a second dilution effect will be considered.

Since the best results were obtained for the FC 1 and 2 condensates, the rest of the experiments were performed using these wastewaters.

Pressure and temperature influence on the membrane permeate flow rate. Permeate fluxes ($\text{L}/\text{h}\text{m}^2$) for the FC 1 and 2 condensates were obtained at different temperatures (50 °C, 65 °C and 70 °C), pressures (10, 15 and 20 bar) and VCRs (between 1 and 10). The

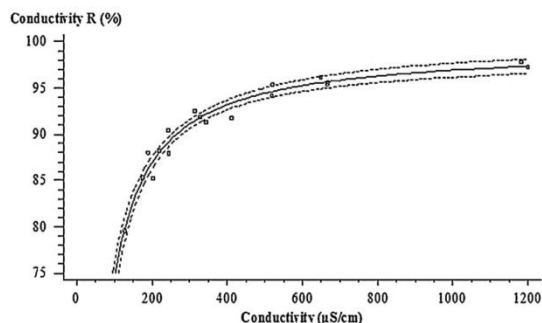


Fig. 7. Conductivity reduction vs. feed conductivity (inlet pressure: 15 bar, temperature: 50 °C). Dotted lines represent the 95% confidence level.

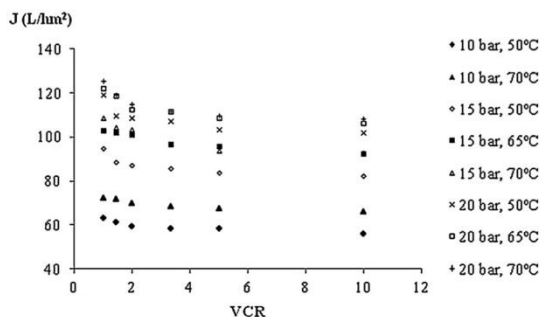


Fig. 9. Effect of VCR on the permeate flux at different pressures and temperatures.

results are shown in Fig. 9. As expected, increased pressure increased the permeate flux. At VCR 1 (average 201.6 $\mu\text{S}/\text{cm}$), for example, the flux increased by 33.3% from 10 to 15 bar and 20.6% from 15 to 20 bar at a fixed temperature of 50 °C. This influence was less acute at high VCRs and the effect of temperature decreased at higher pressures. As reported by Valentin [27] and Snow et al. [28], the effect of temperature on permeate flow rate is important, with an increase of around 3% per °C. A higher temperature decreases the viscosity of the fluids, and increases the diffusivity and the membrane pore size. Only considering the values at VCR 1, as previously explained, the increase of permeate flow rate per °C varied between 0.15% and 1.20%; at different pressures and taking into account only the change from 50 °C to 70 °C, the percentages were 0.73%, 0.74% and 0.26% at 10, 15 and 20 bar, respectively. Fouling was more important at high pressures (the drop in flux was 11.1%, 13.0% and 14.7% at 10, 15 and 20 bar, respectively, at 50 °C), although there were no large differences between the results obtained at 10 and 15 bar. The optimum process parameters (transmembrane pressure and temperature) do not depend only on the permeate flux rate but also the permeate quality. Usually, it is necessary to reach a compromise between several parameters.

The conclusions reached here can be reinforced by the information obtained from the coefficients of Eq. (4), which were calculated for the different applied treatments. According to the initial permeate flow, given by coefficient *a*, the value was higher at a higher temperature and pressure, as previously observed. The tendency of fouling, determined by the coefficient *b*, fits with the behaviour described above. For each individual pressure, this trend increased with temperature, and at a particular temperature, it increased with pressure.

Based on these experimental results, the permeate flow rate could be predicted at different combinations of temperature and pressure using response surfaces. The data obtained from the experiments were adjusted to a second-order polynomial equation. The prediction mesh constructed can be seen in Fig. 10, where the permeate flow rate is represented vs. temperature (between 50 °C and 75 °C) and TMP (between 10 and 20 bar) and where the experimental data are represented over the surface, shown as the distance between the real points tested and the predictive net indicated by the straight line. The adjustment achieved was good ($R^2 = 94.5\%$), although it could be improved (up to $R^2 = 97.8\%$) by including feed characterisation variables such as conductivity and COD. The increase in *J* with temperature was linear, and was 0.62 L/h m² per °C, independent of the TMP. In percentages, and taking into account that the initial permeate flow rate was higher with pressure, the increase in permeate flow per °C, with reference to the initial *J* at 50 °C, was 1.02, 0.69 and 0.59 at 10, 15 and 20 bar, respectively, which fits with previously reported percentages.

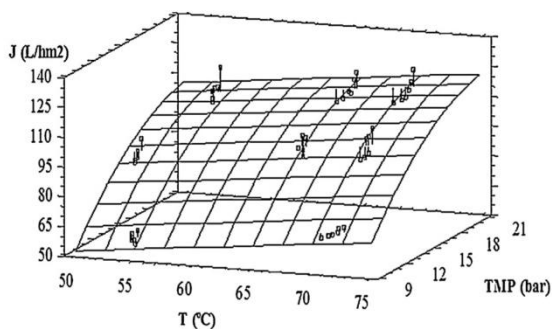


Fig. 10. Predictive permeate flow rate response surface based on temperature and TMP variables.

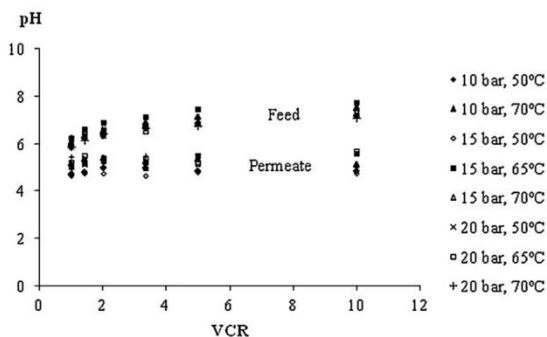


Fig. 11. Effect of VCR on pH at different pressures and temperatures.

However, the influence of pressure seemed to be more important than that of temperature; a non-linear trend could be observed, as the fouling phenomenon was more significant with pressure, as shown in Fig. 2.

Pressure and temperature influence permeate characteristics and quality. The membrane behaviour in terms of quality (permeate conductivity and COD) and characteristics (concentrate and permeate pH) at different pressures, temperatures and VCRs is shown in Figs. 11–13 respectively.

With regard to the pH of the concentrate and permeate, the values were barely altered by the temperature, pressure and VCR. At the working feed pH, most RO membranes are negatively charged [29]. However, this point cannot be demonstrated as the composition of the active layer of the membranes was not available (proprietary material). The permeate acidification observed in Fig. 11 (the permeate pH was always lower than the feed pH) can be explained by the favourable passage of H⁺ ions through the membrane; meanwhile, OH⁻ ions were rejected [30]. Although the permeate pH was lower than the minimum value recommended for use as boiler water (between 7 and 10), it is necessary to take into account that post-treatments carried out after RO can increase these values. Although it has not been performed in the present work, the permeate is usually degassed after RO in order to reduce the concentration of O₂ and CO₂, causing, in the case of CO₂, an increase in pH. Furthermore, this water is also treated with antiscaling and antifouling compounds (generally phosphates) to fulfil the pH requirements inside the boiler.

Permeate hardness was also measured at VCR 10 with the objective of testing the fulfilment of the water requirements even under the worst conditions. The values obtained were always near the limits or slightly above (between 0.41 and 0.75 mg/L in all cases). The permeate obtained at VCR 10 will be mixed with other permeates from previous steps (at lower VCR), which would be presumably low charged in hardness, so the dilution effect will reduce the final content. No influence of temperature or pressure on this parameter was found.

The influence of VCR on permeate conductivity at different pressures (10, 15 and 20 bar) and temperatures (50 °C, 65 °C and 70 °C) is shown in Fig. 12. The figure represents the values of conductivity (bars) compared with the requirement for boiler water and the reduction in this parameter under the different conditions (lines). In Fig. 13, similar results are plotted for permeate COD. The general trend was an increase in the reduction of both parameters when VCR increased, under all conditions studied.

In some cases, the absolute values of conductivity and COD surpassed the limits (horizontal dotted line) established for boiler

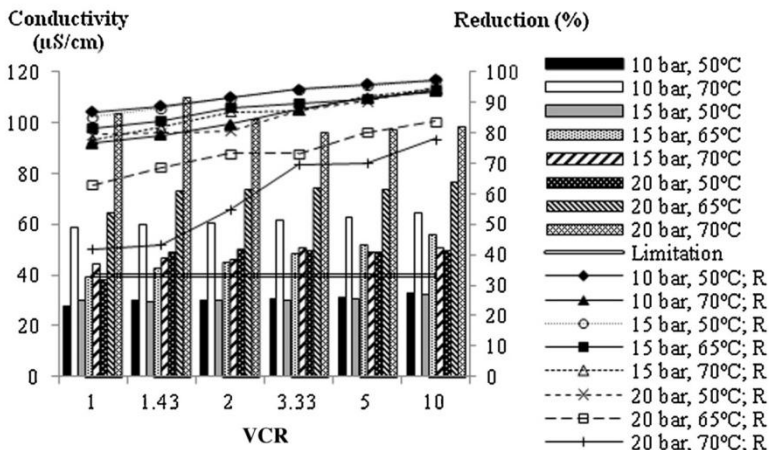


Fig. 12. Effect of VCR on conductivity quality of permeates and its reduction (R, %) at different pressures and temperatures.

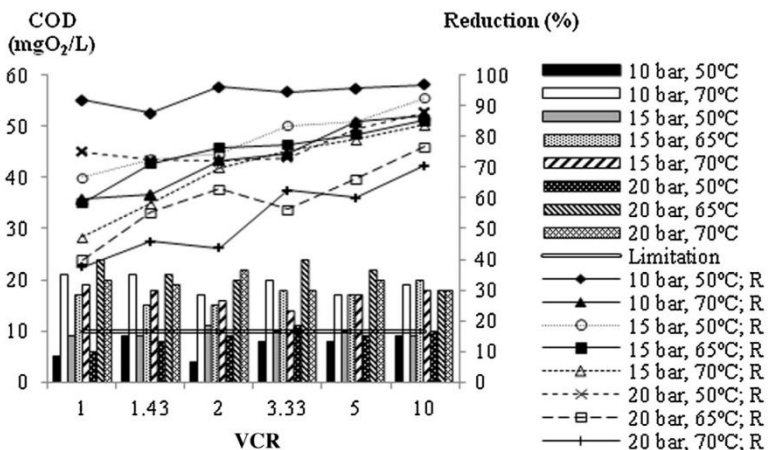


Fig. 13. Effect of VCR on COD quality of permeates and its reduction (R, %) at different pressures and temperatures.

feed water, especially in experiments at higher pressures and temperatures. When the temperatures exceeded 50 °C, as the diffusivity and pore size increased with the temperature, the species that contribute to conductivity and COD passed more readily through the membranes, such that the limits of 40 µS/cm for conductivity and 10 mg O₂/L for COD were clearly surpassed when the condensates were treated at 65 °C and 75 °C. As the quality was reduced with temperature, parameter reductions showed the same proportional effect, and the VCR had little impact. Working at 50 °C implies that all the demineralised water currently used in the company could be completely substituted by permeates. If the condensates need to be treated at a higher temperature in order to increase energy savings, it will be necessary to use new mixing ratios between permeates and demineralised water. For example, at 15 bar, 65 °C and VCR 10 (55.7 µS/cm and 20 mg O₂/L in the permeate stream), the mixing ratio should be 72% and 53% permeate for conductivity and COD, respectively. In the case of working at 70 °C and 20 bar (worst

permeates obtained: 101.5 µS/cm and 22 mg O₂/L), the mixing ratio should be 30% and 48% permeate for conductivity and COD, respectively, at VCR 2. From the results obtained in these experiments, the maximum temperature to achieve boiler water

Table 2
Water quality parameters when processing flash cooler condensates by RO with boiler water production purposes.

Parameter	Initial feed water	Feed water at VCR 10	RO permeate at VCR 10 ^a	Boiler water ^b
pH	6.00	7.36	4.74	7–10
Conductivity (25 °C), µS/cm	201.9	1200.0	32.1	<40
COD, mg O ₂ /L	27	122	9	<10
Ca ²⁺ , mg/L	–	–	0.61	<0.4

^a At 15 bar and 50 °C of pressure and temperature operation conditions, respectively.

^b Adapted from Mavrov et al. [17] and Judd and Jefferson [18].

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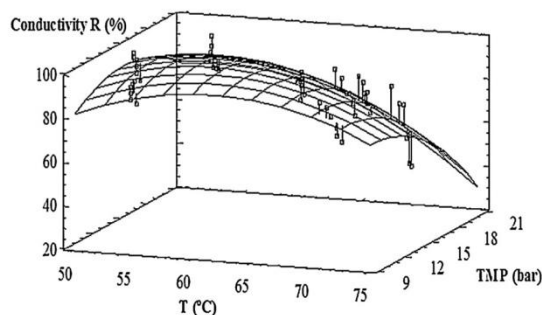


Fig. 14. Predictive conductivity *R* response surface based on temperature and TMP variables.

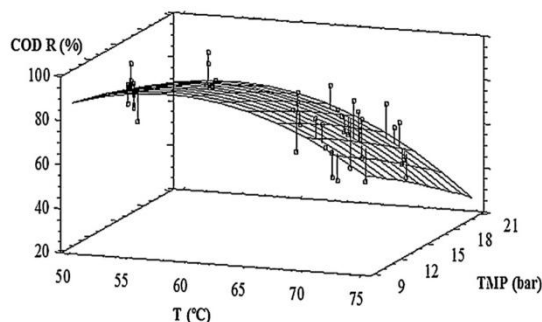


Fig. 15. Predictive COD *R* response surface based on temperature and TMP variables.

specifications was 50 °C, and pressures higher than 15 bar led to values of conductivity and COD higher than the limits at a high VCR. This conclusion can be reinforced with the information included in Table 2, where the permeate quality from the RO optimum operation conditions, the feed water characteristics of this specific trial (at VCR 1 and 10) and the boiler water limitations were compared. Under these conditions, it was possible to work at the maximum VCR studied.

The reduction in both parameters as a function of temperature and TMP could be predicted by using response surfaces. The statistically predicted meshes of conductivity and COD reductions are displayed in Figs. 14 and 15, respectively. The adjustment could be improved up to 85.4% (R^2) and 80.1% (R^2) for conductivity and COD, respectively, by introducing feed wastewater characteristics. The general trend was in good agreement with the conclusions previously obtained in Figs. 12 and 13, i.e. high temperatures and pressures result in lower reductions. The maximum conductivity reduction took place at a moderate pressure (approximately 15 bar). However, the COD reduction clearly decreased with pressure, so low pressures and temperatures are recommended.

Economic evaluation

With the information obtained in these experiments, a preliminary economic evaluation was carried out in order to determine the costs and savings of a large-scale plant for processing condensates. The RO conditions must assure that the permeate quality fulfils the characteristics required for steam boilers. Once this condition is accomplished, other factors such as the maximum permeate flow rate and process conditions (temperature and pressure) might be sufficient and not far from the optimum values for the membrane material, respectively. The

permeate flow rate determines the membrane area and therefore the size of the equipment. On the other hand, and due to the rules of economies of scale, operating costs decrease as plant capacity increases [23].

The economic assessment was performed considering the classical design, widely used for NF/RO applications, using a Christmas tree (single pass) design where the permeates from different steps were mixed. From the previous experiments at the pilot-plant scale, the main parameters for the industrial plant economic assessment can be fixed: volumetric flow rate 20 m³/h; temperature 50 °C; pressure 15 bar; permeate flow rate 82.5 L/h m². The selected permeate flow rate corresponds to the value found at maximum VCR (10), which means the worst-case scenario possible. Under these conditions, the permeate can be used in boilers and the permeate flow rate and energy costs will be reasonable.

Real FC waters are usually at a higher temperature than 50 °C, so a heat exchanger (the capital and operation costs of this equipment were not included in the economic evaluation) should be placed before the membrane. The feed is concentrated in the plant until VCR 10, which means a recovery rate of 90%. Working at VCR 10 means that the latter membranes are subjected to high feed concentrations, so this step will limit the performance of the installation, and therefore, to simplify the economic calculations, the evaluation will be completely based on this module.

The plant needs an RO membrane surface area of 218 m². The costs of pipes, valves, instruments, controls, tanks and miscellaneous items were calculated on the basis of this total area. Regarding pump costs, they were determined by using a correlation from Perry and Chilton [31]. The data provided in 1996 US\$ according to the model of Sethi and Wiesner [23] was converted by applying the average exchange rate for that year (US \$1 = €0.81) and corrected to represent current values using the Chemical Engineering Plant Cost Index.

Membranes (investment and replacement) and pressure vessel costs were provided by the membrane manufacturer in terms of actualised €/m². The investment cost was annualised considering a 7% interest rate and a design life of the plant of 15 years [32]. To estimate the concentrate disposal and energy costs (pumping requirements), the real price paid for the company was used. Chemical costs were based on an alkaline and acidic cleaning, performed every 2 days, at a price of 3.040 and 1.687 €/L for the Divos 123 and Divos 2 (Diversey), respectively. Membrane life was fixed at 1 year. Maintenance costs were taken from Costa and de Pinho [33]. A value of 15% of the total operating costs published by Bergman [34] was used to estimate pre-treatment costs. The savings of the project were estimated from disposal, energy and tap water savings.

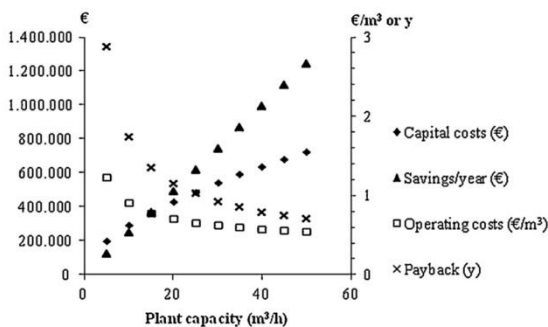


Fig. 16. Evolution of cost and saving indexes as a function of the plant capacity.

With this information, the capital costs, the operation costs (expressed as € per m³ of treated water), the savings per year, the savings per m³ of treated water and the payback period were estimated; these values were 435,300 €, 0.710 €/m³, 498,800 €, 2.887 €/m³ and 1.16 years, respectively.

The influences of the main parameters (plant capacity, recovery rate (or VCR), permeate flux, feed pressure and temperature, membrane lifespan, amortisation period, interest rate, membrane replacement costs and cleaning frequency) on these indices were studied. If water with similar characteristics was intended to be incorporated in the near future for treatment in the RO plant, it would be appropriate to study the behaviour of costs and savings with the size of the plant. To this end, the influence of plant capacity on final costs, savings and payback is shown in Fig. 16. The greater the plant capacity, the lower the operation costs (although they tend to stabilise) and the shorter the payback period (since cash flow increases with size), thus showing an economy of scale. As expected, the savings of the project, due to an increase in the volume of water handled, and the investment costs, because they are related to the membrane area, are higher with the plant size.

The conditions of 15 bar and 50 °C were considered as optimum, using the results obtained at the pilot-plant scale; however, 10 bar was considered as an alternative for the TMP, taking into account the small differences in terms of permeate quality at these two pressures. Lower TMPs would mean savings in pump costs and would probably extend the membrane life. Assuming a membrane life of 2 years (manufacturer recommendations) and with the rest of variables held constant, working at a pressure of 10 bar, a permeate flow rate of 56.2 L/h m² (at VCR 10) and a surface area of 320 m² was obtained. In this case, the new values obtained were 530,300 €, 0.743 €/m³ and 1.43 years for the capital costs, the operation costs and the payback period, respectively, which means an increase of 21.8%, 4.6% and 23.3% in capital costs, operation costs and payback, respectively, when changing from 15 to 10 bar of pressure.

Conclusions

Condensates from FCs can be considered as containing low levels of pollution, but their heterogeneity complicates the treatment of them as a whole. The treated condensates do not fulfil the characteristics of water if they are to be reused in boilers. Thus, the general recommendation is to characterise each condensate and to treat them separately if necessary. RO under controlled conditions of pressure and temperature allow the production of high-quality permeates with the appropriate membrane.

The permeate flow rate increased with temperature and transmembrane pressure (in this case, the evolution was linear) as expected, but the permeate quality decreased with these two parameters. Thus, it was necessary to find a compromise between the two main operating conditions. Predictive response surfaces obtained by adjusting the results were able to describe the behaviour of the studied membranes when processing industry

wastewaters between conductivity values of 174.3 and 1200 μS/cm and COD values of 24 and 284 mg O₂/L for a range of conditions between 50 °C and 75 °C and 10 and 20 bar of pressure.

With the information obtained in the pilot plant, the operation parameters were fixed at 50 °C, inlet pressure of 15 bar and at VCR 10. The industrial equipment designed to treat condensates at 20 m³/h gave a permeate flux of 82.5 L/h m² (at the maximum VCR assayed), such that the permeates were suitable for boiler water purposes (conductivity 32.1 μS/cm, COD 9 mg O₂/L and a residual hardness of 0.61 mg/L, meaning a 97.3% and 92.6% reduction in conductivity and COD, respectively). The resultant membrane area was 218 m², and the payback period was estimated to be 1.16 years based on the costs and savings balance.

These estimations and assumptions need confirmation through long-term continuous assays in order to determine more precisely the frequency of cleaning and the membrane life. An evaluation of the necessity for pre- and post-treatments should also be considered.

References

- [1] B. Balanec, M. Vourch, M. Rabiller-Baudry, B. Chaufer, *Sep. Purif. Technol.* 42 (2005) 195.
- [2] F.A. Riera, A. Suárez, C. Muro, *Desalination* 309 (2013) 52.
- [3] H. Chmiel, V. Mavrov, E. Bélières, *Filtr. Sep.* 37 (2000) 24.
- [4] V. Mavrov, E. Bélières, *Desalination* 131 (2000) 75.
- [5] A. Fährlich, V. Mavrov, H. Chmiel, *Desalination* 119 (1998) 213.
- [6] I. Koyuncu, M. Turan, D. Topacik, A. Ates, *Water Sci. Technol.* 41 (1) (2000) 213.
- [7] L.C. Juang, D.H. Tseng, H.Y. Lin, *Desalination* 202 (2007) 302.
- [8] C.H. Koo, A.W. Mohammad, F. Suja', *Desalination* 271 (2011) 178.
- [9] B. Farizoglu, S. Uzuner, *Biochem. Eng. J.* 57 (2011) 46.
- [10] B. Sarkar, P.P. Chakrabarti, A. Vijaykumar, V. Kale, *Desalination* 195 (2006) 141.
- [11] A. Chollangi, M.M. Hossain, *Chem. Eng. Process* 46 (2007) 398.
- [12] M. Turan, *Desalination* 170 (2004) 83.
- [13] M. Vourch, B. Balanec, B. Chaufer, G. Dorange, *Desalination* 219 (2008) 190.
- [14] Y.M. Gong, H.X. Zhang, X.N. Cheng, *Water Sci. Technol.* 65 (2012) 915.
- [15] M. Vourch, B. Balanec, B. Chaufer, G. Dorange, *Desalination* 172 (2005) 245.
- [16] B. Balanec, G. Gésan-Guizieu, B. Chaufer, M. Rabiller-Baudry, G. Daufin, *Desalination* 147 (2002) 89.
- [17] V. Mavrov, H. Chmiel, E. Bélières, *Desalination* 138 (2001) 65.
- [18] S. Judd, B. Jefferson, *Membrane for Industrial Wastewater Recovery and Reuse*, Elsevier Science Ltd., Oxford, 2003.
- [19] Directive 98/83/EC, Official Journal of the European Communities L 330 (1998) 32.
- [20] S. Casani, S. Knöchel, *Food Control* 13 (2002) 315.
- [21] American Public Health Association/American Water Works Association/ Water Environment Federation, Standard Methods for the Examination of Water and Wastewater, 19th edition, American Public Health Association (APHA), Washington DC, 1995.
- [22] A. Mosset, V. Bonnellye, M. Petry, M.A. Sanz, *Desalination* 222 (2008) 17.
- [23] S. Sethi, M.R. Wiesner, *Environ. Eng. Sci.* 17 (2) (2000) 61.
- [24] K.D. Pickering, M.R. Wiesner, *J. Environ. Eng.-ASCE* 119 (5) (1993) 772.
- [25] O. Akoum, M.Y. Jaffrin, L.H. Ding, M. Frappart, *J. Membrane Sci.* 235 (2004) 111.
- [26] C. Sagne, C. Fargues, R. Lewandowski, M. Lameloise, M. Gavach, M. Decloux, *Chem. Eng. Process.* 49 (2010) 331.
- [27] A.C. Valentin, *Water Sci. Tech.: Water Supply* 10 (1) (2010) 113.
- [28] M.J.H. Snow, D. de Winter, R. Buckingham, J. Campbell, J. Wagner, *Desalination* 105 (1996) 57.
- [29] R. Gerard, H. Hachisuka, M. Hirose, *Desalination* 119 (1998) 47.
- [30] J. Qin, M.H. Oo, H. Lee, B. Coniglio, *J. Membrane Sci.* 232 (2004) 153.
- [31] R.H. Perry, C.H. Chilton, *Chemical Engineers' Handbook*, McGraw-Hill, New York, 1991.
- [32] A. Gorenflo, D. Velázquez-Padrón, F.H. Frimmel, *Desalination* 151 (2002) 253.
- [33] A.R. Costa, M.R. de Pinho, *Desalination* 196 (2006) 55.
- [34] R.A. Bergman, *Desalination* 102 (1995) 11.

4.2.2. Membrana Duratherm® HF

Recovery of dairy industry wastewaters by reverse osmosis. Production of boiler water

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Recovery of dairy industry wastewaters by reverse osmosis. Production of boiler water



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ABSTRACT

Low-pollutant dairy condensates from flash coolers of a direct UHT plant were processed through a RO spiral-wound membrane (8.4-m² surface area) in a pilot plant in order to obtain high-quality boiler water. Conductivity, chemical oxygen demand and pH were used as the main parameters to evaluate the permeate quality. Firstly, discontinuous tests were performed with the objective of checking the membrane behaviour under different process conditions. Then, the information obtained was used to perform long-term continuous trials. Conductivity and chemical oxygen demand reductions up to 98.2% and 97.8%, respectively were achieved. To improve the organic matter removal, an activated carbon column at the outlet of the permeate line was used. A post-treatment would be necessary to adjust the permeate to the final pH. The return of investment of an installation to treat 20 m³/h condensates was estimated as being within 2.2 years.

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1. Introduction

Membrane processes have become major tools in the food-processing industry, in which the majority of the industrial developments of membrane technologies have originated from the dairy industry [1]. The use of membranes in dairy processing is widely accepted as an alternative to some unit operations [2]. In addition, the implementation of this technology in the treatment of dairy effluents for water recovery can have a great impact on decreasing water intake and disposal by dairy plants [3].

The food sector has one of the highest consumptions of water (mainly from continuous cooling and heating systems and cleaning processes) and is one of the biggest producers of effluent per unit of production [4]. Within this sector, the dairy industry is the biggest consumer, presenting ratios from 0.2 to 10 L of effluent per litre of processed milk [5]. Most of the end wastewaters from the food industry in general, and the dairy industry particularly, are characterised by high organic content, suspended solids, salts, oils, fats and cleaning agents if they are not previously segregated, along with seasonal changes in flow and composition [6].

This large consumption of water, the stricter quality discharge regulations, the rise of the true cost of water for use in food processing – mainly involving the cost of supply and the cost of wastewater treatment and disposal – and the feasibility of better

purification processes [7] could act as an incentive to reduce water, or even to decrease the amount of energy and waste associated, which would mean environmental and economical advantages [8]. Furthermore, the need for a safe, reliable and affordable supply of water by the food-processing industry reinforces the interest in both reconditioning and recycling of water [9].

Reverse osmosis (RO) is a common technology used in chemical and environmental engineering separations, where wastewater treatment is a well-established example [10]. The suitability of RO for such applications depends on the feasibility of satisfying the following requirements: high permeate flux at moderate transmembrane pressure (TMP); good retention capability; proper mechanical strength; inertness (and bio-inertness), and chemical and thermal stability; resistance to cleaning and sanitising agents; resistance to microbial action; high fouling protection; compliance with safety requirements; long service life; and affordable cost [11].

RO is the process that ensures the highest water quality [12], reducing high levels of dissolved salts and suspended solids, but RO encounters certain limitations when used for the removal of organic compounds [10]. Fouling is the limiting factor – both technically and economically – when membrane processes are applied in the dairy industry [13]. RO has been used in dairy wastewater treatments to produce water of different qualities by making use of one-step processes [5,14] or in combination with nanofiltration (NF) [15,16] or another RO stage [16,17].

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Nomenclature

Abbreviations

RO	reverse osmosis
NF	nanofiltration
HACCP	hazard analysis critical control point
COD	chemical oxygen demand
BOD ₅	biological oxygen demand after 5 days
TSS	total suspended solids
UHT	ultra high temperature
FC	flash cooler
TK	tank
P	pump
F	filter
FCV	flow control valve
PI	pressure indicator
FI	flow indicator
SDI	silt density index
VCR	volume concentration rate

RR	recovery rate
CR	conductivity reduction
CODR	chemical oxygen demand reduction
ACC	activated carbon column
UF	ultrafiltration

Symbols

TMP	transmembrane pressure (bar)
J	permeate flow rate (L/h m ²)
V_f	feed volume (m ³ or m ³ /h)
V_r	retentate volume (m ³ or m ³ /h)
V_p	permeate volume (m ³ or m ³ /h)
R	reduction (%)
C_f	feed concentration (μS/cm or mgO ₂ /L)
C_p	permeate concentration (μS/cm or mgO ₂ /L)
A	membrane permeability (L/h m ² bar)

Traditionally, effluents from the different dairy processes are collected and treated simultaneously on-site or in municipal sewage treatment plants [18]. However, optimal treatments could be achieved by segregating streams, where separation of low-concentration wastewaters would result in energy savings, lower costs and improved efficiency regarding treatment, discharge and reuse [7]. The suitability of recovering water for any food operation is dictated by the required quality of water, the standard of the used water, the recovery and the ability to recondition the water to the level demanded [7]. Water used in the food industry should be at least equal to the highest standard for drinking water [19], and hazard analysis critical control point (HACCP) systems are recommended in order to ensure optimum microbiological quality [20]. From all the possibilities of reuse, the most restrictive parameters are given by boiler water specifications (pH 7–10, conductivity (25 °C) < 40 μS/cm, chemical oxygen demand (COD) < 10 mgO₂/L, biological oxygen demand after 5 days (BOD₅) 1–50 mgO₂/L, Ca²⁺ < 0.4 mg/L and total suspended solids (TSS) 0.5–10 mg/L) [21,22].

Wastewaters treated in this research came from a direct ultra-high-temperature (UHT) process of a dairy factory. The feed of the RO was a mixture of condensates from the flash cooler (FC) vacuum chamber and tap water from the liquid ring vacuum pump, and can be considered as low-pollutant wastewater (CODs < 700 mgO₂/L [15] and conductivity < 2200 μS/cm [23]). Real wastewater was treated in discontinuous and continuous modes at a medium temperature by means of a RO membrane in a pilot plant in order to reach boiler feed water specifications.

2. Materials and methods

2.1. Reverse osmosis setup

The scheme of the pilot plant used is shown in Fig. 1. The plant was made of stainless steel and had a capacity for two in-parallel 4040 spiral-wound membranes. An external 1000-L tank (TK-02) was used to receive the wastewaters from the FC vacuum system; meanwhile the smaller tank (TK-01) was only used for cleaning purposes. The pilot plant had two pumps (P-02 and P-03 (Grundfos, Denmark); 7.5 and 2.2 kW, respectively) to feed the RO membranes. To protect these membranes against coarse particles, a 125-μm prefilter (F-01) was installed. The combination of a pump frequency regulator and a needle valve (FCV-03) located on the

retentate line allowed to fix the pressure and the feed flow conditions. TMP and feed flow were monitored by means of manometers PI-03 and PI-05, and a flow meter FI-01, respectively. Permeate and concentrate fluxes were measured with FI-03 and FI-04 flow meters. Finally, a prefiltration system, consisting of a bag filter and a series of cartridge prefilters (5, 1 and 0.2 μm, respectively), was used to maintain low water silt density index (SDI) values (lower than 3) for the rinsing and cleaning steps [24].

2.2. Membrane

A spiral-wound thin-film membrane Duratherm[®] HF (proprietary composite), recommended by the manufacturer (GE Water & Process Technologies, USA), was used for the experiments. Average salt rejection for this membrane was 99.5% (2000 mg/L NaCl at 15.5 bar, 25 °C and pH 7). The active area was 8.4 m². The membrane was designed to work at low-medium pressures (up to 27.6 bar at 50–70 °C). The permeate flow rate (J) recommended by the manufacturer is around 40 L/h m² and so process conditions (feed flow rate, temperature and TMP) were selected to produce this value.

The membrane cleaning protocol applied was suggested by a detergent manufacturer (Diversey, The Netherlands) according to the condensates characteristics. The cleaning step consisted of an acid pass to remove mineral deposits (Divos 2, pH 1.9–2.1, 20 min, 45 °C) and then an alkaline cleaning to remove organic matter (Divos 123, pH 11.0–11.5, 45 min, 45 °C) with intermediate rinsing [25]. For preservation between runs, membranes were stored in their own pressure vessel after cleaning in an acid soak with Divos 2 at pH 3.0–4.0. Cleaning efficiency, represented as flux recovery, was assessed by measuring the permeate flow rate at 10.7 bar of TMP, 1 m³/h of feed flow and approximately 10.5 °C of temperature with prefiltered water.

2.3. Analytical methods

Wastewaters to be processed came from real condensates of a direct UHT process in a Spanish dairy factory. Condensates came from four FCs that worked independently. When they work at the same time, the wastewater generated is about 20 m³/h.

In order to characterise feed wastewaters, concentrates and permeates from the RO process, pH (accuracy ± 0.05), electrical conductivity (accuracy ± 0.5%) and COD (accuracy ± 3 mgO₂/L) were routinely measured, as well as residual hardness expressed

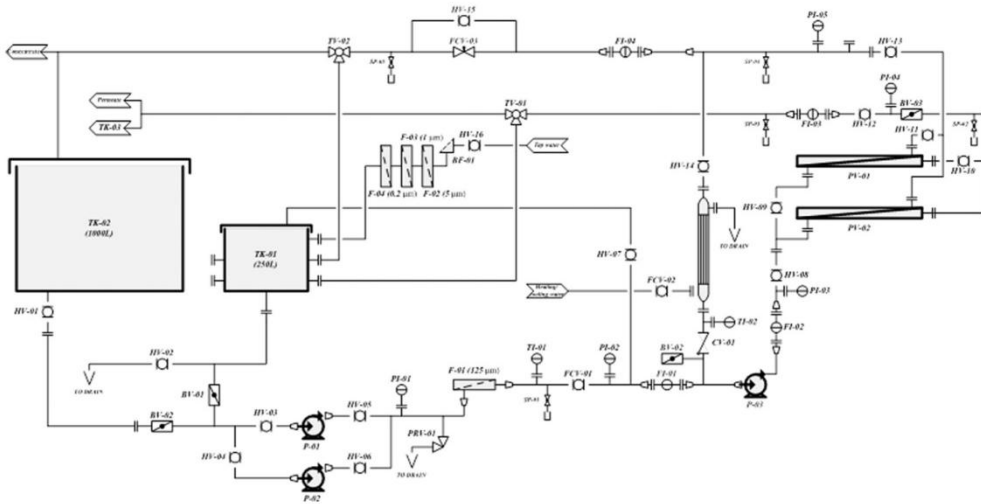


Fig. 1. Scheme of the RO rig.

as Ca²⁺ (accuracy ± 0.10 mg/L), which was sporadically measured. pH (with automatic correction of temperature) and electrical conductivity (referenced at 25 °C) were monitored by using an HQ40d multimeter (Hach Lange, Belgium). A Spectroquant NOVA 60 photometer (Merck, Germany) was utilised for the spectrophotometric measurements of COD (by sulphuric oxidation and Cr³⁺ determination at 605 nm) and residual hardness (by determination of a coloured phthalein complex at 565 nm).

2.4. Operating conditions

The tests were performed in two different operation modes, the first mode was a discontinuous mode through a semi-closed loop where the permeate stream was returned to the feed tank in order to reach the desired degree of concentration or volume concentration rate (VCR) through the following equation:

$$VCR = \frac{V_f}{V_r} = \frac{V_f}{V_f - V_p} \tag{1}$$

where V_f, V_r and V_p are the feed, retentate and permeate volumes, respectively. The experiments in discontinuous mode were performed at VCR values between 1 and 10.

The recovery rate (RR), which is a parameter that determines the size and the economy of the installation, is directly related to the VCR by means of Eq. (2).

$$RR(\%) = \frac{VCR - 1}{VCR} \times 100 \tag{2}$$

The discontinuous trials were performed at different pressures, temperatures and feed flow rates, and permeate flow rate was continuously measured. Membrane rejection (or reduction) (R) to conductivity (CR) and COD (CODR) was calculated at different VCR values by means of the equation:

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{3}$$

where C_p and C_f are the permeate and feed values of both parameters considered, respectively.

Some experiments (tests 9–11) were performed with a double RO. Permeates obtained after the first RO step were collected in a 1000-L tank and immediately fed to a second RO step using the

same membranes and conditions to obtain an initial permeate flow rate of about 40 L/h m².

The second operation mode consisted of a continuous mode where feed waters were continuously pumped to an intermediate 1000-L tank, which was directly connected to the pilot plant. A heat exchanger was installed after this tank with the objective of regulating the inlet temperature to the plant when necessary. Continuous trials at constant permeate flow rate (~40 L/h m²) were performed in two sets of tests. Firstly, short-term continuous experiments (~8 h) were carried out at different TMPs and temperatures to reach initial permeate flow rate, and at different feed flow rates (1000–2000 L/h). In the second step, a long-term continuous test (~60 h) was performed.

Some of the continuous tests were performed by coupling an activated carbon column (ACC) FCA-355 model (Sefiltra S.A., Spain) to treat permeates. The ACC was made from polyester reinforced with fibreglass with a capacity of 1800 L/h, 0.355 m in diameter, 1.117 m high and approximately 110 L of internal volume. The ACC was filled with 50 kg of activated carbon GAC MG - 1050 (density ~0.5 g/cm³) (Sefiltra S.A., Spain).

2.5. Scale-up

With the information obtained from the experimental trials, a simple economic estimation was made to evaluate the economic viability of this application. The pay-back period of a RO plant to process 20 m³/h of real FC condensates was estimated by means of the calculation method previously used by Riera et al. [26], which is based on the model of Pickering and Wiesner [27] (slightly modified by Sethi and Wiesner [28]) to determine the majority of operating and investment costs. Membrane and pressure vessel investment costs were supplied by membrane manufacturer and the cost of steam and energy for Spanish medium-sized dairy companies were used in the economic estimation.

3. Results and discussion

3.1. Characterisation of condensates

FCs generate condensates continuously – however, they work in cycles mode (production and rinsing) and thus the level of

pollution of condensates depends on the timing of the cycle in which the condensates are analysed. The condensates obtained in the production and rinsing steps were not segregated in the industrial plant. Condensates collected to perform the discontinuous RO processes were taken only during the production step (in those periods, the UHT plant mainly produced whole milk and skimmed milk). In the continuous experiments, condensates from the production and rinsing steps were treated regardless of their compositions.

In all cases, conductivity, COD and pH were routinely measured to characterise the condensates. The values obtained varied between 156.2 and 285.0 $\mu\text{S}/\text{cm}$ (average: 192.4 $\mu\text{S}/\text{cm}$), COD values were between 5 and 89 mgO_2/L (average: 47 mgO_2/L) and pH varied between 5.0 and 7.3 (average: 5.7). Total solids in condensates varied between 76 and 208 mg/L . These values are slightly higher than those published for steam condensates in food industries [18,21]. The wide range of values obtained depends on the step of the FC cycle (production or rinsing) as well as the type of product being manufactured at that time (whole milk, skimmed milk, natural or fruit shakes, etc.). Conductivities and CODs of condensate samples from FC rinsing steps showed values between 156.2 and 211.7 $\mu\text{S}/\text{cm}$, and 5 and 42 mgO_2/L , respectively, which were lower than the values obtained in condensates from production steps (conductivities between 185 and 285 $\mu\text{S}/\text{cm}$ and CODs between 42 and 89 mgO_2/L). This variability between condensates has been previously published by several authors [15,26]. Detailed analysis of this type of wastewaters is complex and the information is scarce. Stroem [29] detected organic molecules including ethanol, acetone, acetoin and diacetyl in vapour condensates. The number of volatile compounds was found to be over 100 in milk [30].

3.2. Membrane characterisation

The water permeability of the RO membranes was measured at 10.7 bar of TMP and 11 °C using prefiltered tap water with low SDI (<3). The value obtained was 19.6 $\text{L}/\text{h m}^2$, which is within the values suggested by the manufacturer.

The membrane permeability (A), given by the equation $J = A$ TMP and corrected for the temperature, was 0.168 $\text{L}/\text{h m}^2 \text{bar } ^\circ\text{C}$, which was higher than the reference given by the manufacturer (0.111 $\text{L}/\text{h m}^2 \text{bar } ^\circ\text{C}$), but it was similar to values obtained by other authors that used RO membranes (0.125 $\text{L}/\text{h m}^2 \text{bar } ^\circ\text{C}$ from the Desal AG used by Akoum et al. [31], or 0.067, 0.115 and 0.107 $\text{L}/\text{h m}^2 \text{bar } ^\circ\text{C}$ from the Desal 3 SF, TFC HR and BW 30, respectively,

used by Balannec et al. [32]). As the total solids in condensates were very low, osmotic pressure was considered negligible.

3.3. Operation mode

3.3.1. Discontinuous trials

Experiments to estimate the membrane permeate flow rates and rejections at different VCR values are of paramount importance to know the viability of a RO application. In large-scale installations, RO plants are designed in stages and the endings steps work at higher VCR. In these conditions, the membrane fouling is greater, the membrane permeability is reduced and the rejection properties of the membrane change [33]. When the objective is to produce permeates of high quality (boiler water quality in this work), the most important point is to ensure that permeates meet the desired requirements at all stages.

In the discontinuous trials, the main process parameters (TMP and temperature) were adjusted to get the initial permeate flow rate suggested by the membrane manufacturer as optimum (maximum of 40 $\text{L}/\text{h m}^2$), and this determines the initial TMP used in the trials where the temperature of fresh condensates was not modified by the heat exchanger.

Fig. 2 shows the conductivities of permeates (open symbols) at a VCR of 2, 5 and 10, concentrates (bars) at a VCR of 1, 2, 5 and 10 and conductivity reduction (CR) (closed symbols) at a VCR of 2, 5 and 10 at different conditions of feed rate, temperature and TMP (see Table 1). The tests were performed with real-time FC condensates, which explains the different initial values of COD for each experiment, i.e. between 22 and 89 mgO_2/L (see COD values of each

Table 1
Process conditions for tests 1–11. Discontinuous RO tests.

	Feed flow rate (L/h) (± 50 L/h)	Temperature (°C) (± 3.0 °C)	TMP (bar) (± 0.5 bar)
Test 1	2000	46.4	6.7
Test 2	1250	49.0	6.2
Test 3	1550	47.3	7.3
Test 4	1550	46.9	8.5
Test 5	1450	48.6	9.4
Test 6	2000	32.2	9.3
Test 7	2000	38.8	11.2
Test 8	2000	30.6	13.5
Test 9	1600	42.2	8.3
Test 10	1550	42.5	8.7
Test 11	1500	43.4	9.6

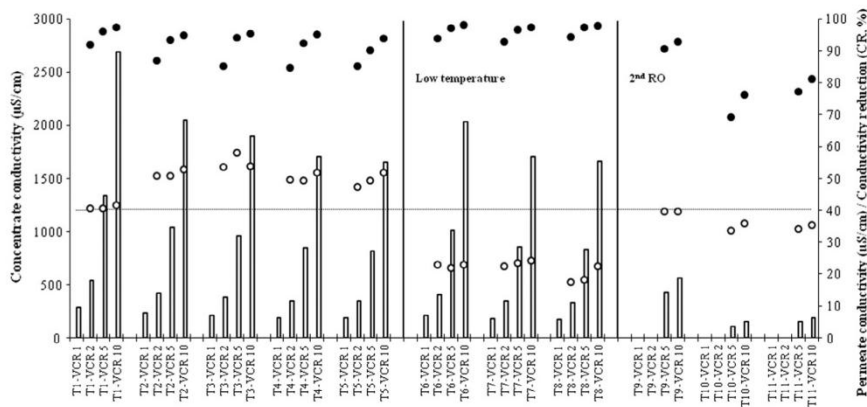


Fig. 2. Discontinuous RO. Permeate and concentrate conductivities ($\mu\text{S}/\text{cm}$) and conductivity reduction (CR, %) as a function of VCR at different operating conditions (tests 1–11; see Table 1).

Table 2
Initial and final (permeate at VCR 10) COD for tests 1–11. Discontinuous RO tests.

Test	1	2	3	4	5	6	7	8	9	10	11
Initial COD (mgO ₂ /L)	69	65	74	89	89	24	22	23	41	82	76
Permeate COD at VCR 10 (mgO ₂ /L)	21	25	24	22	23	19	22	21	15	16	10

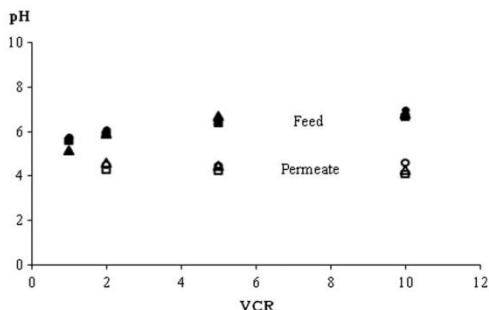


Fig. 3. Discontinuous RO. pH of membrane feed and permeate vs. VCR under different process conditions: feed: ● 9.3 bar, 32.2 °C; ▲ 11.2 bar, 38.8 °C; ■ 13.5 bar, 30.6 °C, permeate: ○ 9.3 bar, 32.2 °C; △ 11.2 bar, 38.8 °C; □ 13.5 bar, 30.6 °C.

experiment at VCR 1 in Table 2). The dotted horizontal line in Fig. 2 corresponds to the maximum value of conductivity allowed for using permeates for boiler water purposes. Tests 1–5 were performed at temperatures between 46 and 49 °C and pressures between 6.2 and 9.4 bar. The CR varied from 84.7% at VCR 1 to 97.5% at VCR 10 and the differences between experiments were not significant in spite of the different process conditions essayed.

Tests 6–8 were performed at lower temperature (between 32 and 39 °C). The influence of temperature on RO rejection for low-pollutant wastewaters was previously studied [31]. Permeate conductivity was lower at lower temperature since solute transport through the RO membrane is mainly diffusive and diffusivity decays when temperature is reduced. The permeate quality in conductivity for this group of tests was below 24.2 μS/cm in all cases.

Tests 9–11 correspond to experiments performed using a double RO. The permeate obtained in the first RO was filtered again using the same membranes and similar process conditions as in the first step. As can be seen, the CRs were lower in these experiments (between 69.2% and 92.9%) due to that most ionic compounds were removed in the first RO, but the final permeate quality was improved (between 33.8 and 39.7 μS/cm) after two RO steps. Combined membrane processes (RO + RO, NF + RO, ultrafiltration (UF) + RO, etc.) have been suggested by several authors for the treatment of condensates and wastewaters [16,17,21,34]. In most of these studies, the permeate quality accomplished the final requirements after the second step but economic implications of this second step were not evaluated in these studies.

In all tests (1–11) CR increased with VCR. This behaviour can be explained by considering that RO processes are dominated by diffusion. At higher VCR, the solutes concentration difference across both sides of the membrane increases. Although CR values increased with VCR, permeate conductivities were also slightly increased in some cases due to the higher values of feed conductivities at higher VCR. The best permeate quality was obtained at lower working temperatures – however, this implies lower permeate flow rates and a higher TMP to achieve the recommended *J* value when working at constant permeate flow rate. The effect of temperature on plant costs can be estimated using experimental information about *T* (°C) vs. *J* (L/h m²). For RO of low polluted dairy wastewater a reduction of 10 °C in feed leads to an increase of about 20% on payback for these types of applications.

COD measurements were made at the beginning (feed) and at the end (permeate) of each test, and the results are shown in Table 2. None of the final permeate COD values obtained were lower than the value required (10 mgO₂/L). The COD reduction was almost negligible for experiments with double RO treatment as most of the dissolved solids that produce COD were removed in the first RO step [23]. When comparing the permeate COD at VCR 10 with the initial feed COD, reductions were between 61.5% and 75.3% for experiments 1–5, between 0% and 20.8% for double RO tests and between 63.4% and 86.8% for experiments 9–11 (low temperatures) were obtained.

Fig. 3 shows the evolution of pH in permeates and concentrated feeds with VCR under different process conditions. Fresh FC condensates showed pHs between 5.0 and 7.3 and these values are out of the range required for their use as boiler waters (between 7 and 10). After RO treatment, the permeates showed lower pHs than the concentrated streams. Acidification of RO permeates is due to the electrostatic repulsion between the membrane and solutes. Duratherm® HF membranes are negatively charged at working pH, and electrostatic repulsion between negative solutes and membrane surface leads to permeate acidification, which is more marked at higher pH [35]. Cationic compounds and H⁺ are less rejected by the membrane. Post-treatment of the permeate will be necessary to correct the final pH (degassing) if they are to be used as boiler waters.

Permeate flow rates for tests 1–11 are shown in Fig. 4. The initial values of the permeate flow rates were adjusted as much as possible to the value recommended by the manufacturer (40 L/h m²) except for test 6, which was at a lower temperature. The permeate flow rates decreased between 6.7% (for test 6) and 23.2% (for test 2) when passing from VCR 1 to VCR 10. At lower feed flow the fouling and concentration polarisation were responsible for the permeate flow rate decreasing; however, both phenomena were not quantified. In all experiments performed, the permeate flow rates (between 25 and 43 L/h m²) at maximum VCR studied can be considered as good for a RO application.

3.3.2. Continuous trials

Continuous trials were performed in constant permeate flux mode. As the condensates temperatures (between 41 °C and 56 °C) depend on the FC step, initial TMP of each assay must be adjusted to get the recommended permeate flow rate (40 L/h m²). The evolution of TMP vs. operation time is shown in Fig. 5 for several tests. The maximum TMP recommended by the membrane manufacturer is 30 bar. Tests 3 and 4, which were performed at a lower feed flow (~1000 L/h), showed that the maximum TMP was achieved after 8 and 3 h of running, respectively. This means that lower feed flow is responsible for the decrease in permeate flow rate (membrane fouling). Feed flow in tests 1, 2 and 5 (performed at 56, 54 and 47 °C, respectively, and at the same feed flow: 2000 L/h) maintained low TMP (13.3, 11.8 bar and 17.2 bar, respectively) after 8 h running.

Figs. 6 and 7 show CR (Fig. 6) and permeate conductivities (Fig. 7) for continuous short-term tests (8 h) 1, 2 and 5. Condensates collected over 8 h came from FC production (UHT whole and skimmed milk) and from the rinsing steps. Both types of condensates showed different conductivities, as previously explained. Noticeable differences were found in the CR values depending on

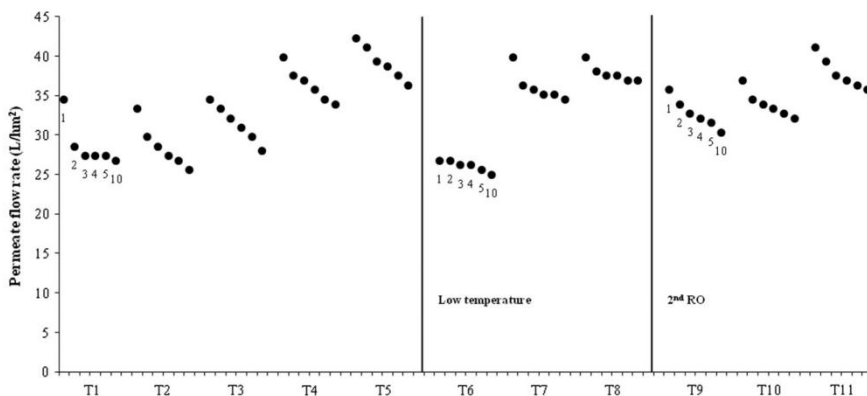


Fig. 4. Discontinuous RO. Membrane permeate flow rate (L/h m²) vs. VCR (1,2,...,10) at different operating conditions (tests 1–11; see Table 1).

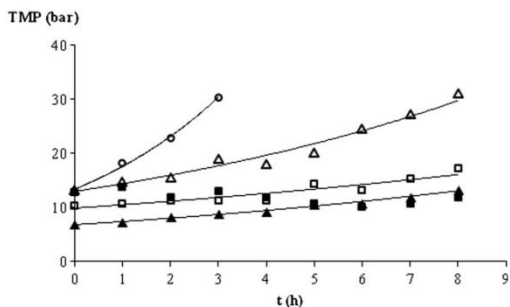


Fig. 5. Continuous short-term RO treatments at VCR 1. TMP (bar) evolution vs. time (h) under different process conditions and at constant permeate flow rate ($J = 40$ L/h m²). Average temperature and feed flow for processing time: ▲ test 1: 55.9 °C, 2000 L/h; ■ test 2: 53.7 °C, 2000 L/h; △ test 3: 41.3 °C, 1000 L/h; ○ test 4: 48.0 °C, 1000 L/h; □ test 5: 46.9 °C, 2000 L/h.

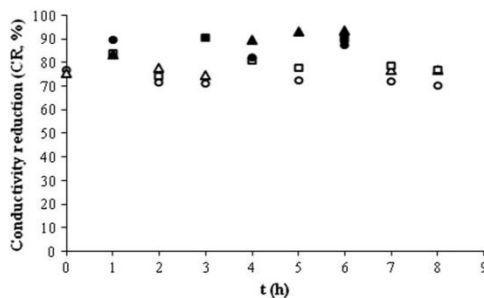


Fig. 6. Conductivity reduction (CR, %) in continuous short-term RO treatments vs. time (h). Influence of condensate quality (averaged temperature, feed flow and TMP for processing time): condensates from FC production steps: ○ 55.9 °C, 2000 L/h, 9.7 bar; △ 53.7 °C, 2000 L/h, 11.9 bar; □ 46.9 °C, 2000 L/h, 12.8 bar, condensates from FC rinsing steps: ● 55.9 °C, 2000 L/h, 9.7 bar; ▲ 53.7 °C, 2000 L/h, 11.9 bar; ■ 46.9 °C, 2000 L/h, 12.8 bar.

the type of condensates. When condensates came from rinsing steps, CR values were higher (between 81.9% and 93.7%) and permeate conductivity values were, in general, lower than the limit (40 μ S/cm) (see Fig. 7). However, when condensates came from production steps, the CRs were lower (between 70.3 and 83.9%). For example, in test 1, CR varied between 81.9% and 89.5% for rinsing condensates and between 70.3% and 77.0% for condensates in production steps. A similar trend was found in tests 2 and 5. The CR values for all tests were approximately constant with time, and no clear trend was observed during the 8 h run. Permeate conductivities were above the limit when processed condensates from milk UHT production. Only in test 5 (47 °C and 2000 L/h feed flow) were the values lower than the limit in any of the analysed samples. Tests 1 and 2 were performed at the same feed flow as test 5, but at higher temperatures (56 and 54 °C, respectively) and showed lower CR, as was demonstrated in previous discontinuous trials.

With respect to the COD values in continuous RO, some samples of tests 1 and 2 were analysed. As in the case of conductivities, the condensates' CODs from the rinsing steps were lower (between 5 and 32 mgO₂/L) than the values obtained for condensates from production steps (between 31 and 86 mgO₂/L), but both were over the limit (10 mgO₂/L) before membrane treatment. CODRs were 100% for rinsing condensates and between 65% and 78% for production steps. Final CODs of the permeates for the samples ana-

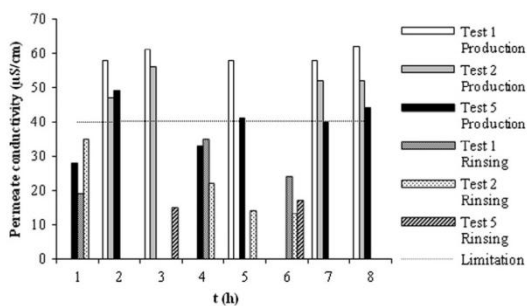


Fig. 7. Continuous RO treatments. Permeate conductivities (μ S/cm) vs. time (h) for different treatments: condensates from FC production steps: test 1: 55.9 °C, 2000 L/h, 9.7 bar; test 2: 53.7 °C, 2000 L/h, 11.9 bar; test 5: 46.9 °C, 2000 L/h, 12.8 bar, condensates from FC rinsing steps: test 1: 55.9 °C, 2000 L/h, 9.7 bar; test 2: 53.7 °C, 2000 L/h, 11.9 bar; test 5: 46.9 °C, 2000 L/h, 12.8 bar.

lysed were over the limit for the production step. Therefore, it must be concluded that the membrane used cannot remove all compounds that produce COD.

Fig. 8(a–d) shows the main results of a 60-h continuous trial using real FC condensates as feed. Because organic compounds of

low molecular weight are not easily rejected by RO membranes [10], permeates obtained in this test were passed through an ACC with the aim of reducing the organic matter of the final permeates. ACC treatments (alone or in combination with other processes such as coagulation, etc.) have been used by several authors to reduce organic matter in high or medium polluted food industry wastewaters [36,37]. Fig. 8a shows the process conditions (feed temperatures between 41.9 and 49.8 °C) as well as the evolution of TMP vs. running time. The test was performed at constant permeate flow rate (40 L/h m²) and feed flow (2000 L/h). Two cleaning steps (at 10 h and 35 h) were performed during the experiments and after the initial permeability was recovered. Membrane cleaning steps were made each weekend regardless of whether the TMP was lower than 30 bar. Fig. 8b shows the evolution of pH in feed and permeate streams before and after the ACC treatment. As in the discontinuous tests, the permeate pH was lower than the feed. The pH after ACC was slightly lower than the permeate before ACC treatment, probably due to some organic compounds retained by ACC being charged. Fig. 8c shows the feed and permeate conductivities along the experiment. Feed conductivity varied between 159.4 and 217.3 μS/cm. Lower values correspond to condensates from rinsing steps. Permeate conductivities are represented in left y-axis and, as can be seen in the figure, most of the samples showed lower conductivities than the maximum limit. In Fig. 8c, the values of permeate conductivity after the ACC treatment are also represented. The effect of the ACC on this parameter was negligible as it can be seen in the figure, where the CR and CR after ACC values are represented (right y-axis), with the reductions achieved being between approximately 70% and 95% in both cases.

With respect to the COD, values of feed and permeate are presented in Fig. 8d. Feed COD values varied between 16 and 45 mgO₂/L. Low feed COD values correspond to rinsing steps. CODR

varied between 72.2% and 100.0%, and all permeate samples showed lower CODs than the limit. In all the permeates analysed, COD values were zero. However, some permeates showed odours. This behaviour has been noted previously by several authors [5,30]. According to these researchers, compounds such as ethanol, acetone, acetoin, 2-butanone, 2-pentanone and others at very small concentrations including 2,3-butanodione, hexanal, octanal, dimethylsulfide, and 2 and 3 methylbutanal, etc., can be present, among other compounds (more than 100 small volatile molecules), in different dairy industry condensates. These compounds come from milk fat and some protein degradation, their presence in milk being induced by intense heat treatments [38,39]. According to these researchers, these compounds are responsible for 20–70% of total organic carbon and they are responsible for the permeate odours too (even those present in very small concentrations), because their concentrations usually are above their threshold in water [40]. After the ACC treatment, the permeate odour was reduced but not completely removed (compounds were not quantified).

3.4. Scale-up

Based on previous experimentation, scale-up was carried out to process 20 m³/h of condensates from the vacuum system of a UHT process by a medium–low pressure RO continuous plant. Permeate flow rate was set at 40 L/h m² and the RR at 90% (VCR 10). Average feed pressure was set at 21 bar, which was the average TMP in running periods between cleaning steps, and the temperature was fixed at 45 °C. According to the previous assumptions and considering 8040 spiral-wound membranes (33 m² per element), the filtration area was estimated as being 450 m² (14 elements). Similar plant sizes were obtained by Vourch et al. [5], who designed a

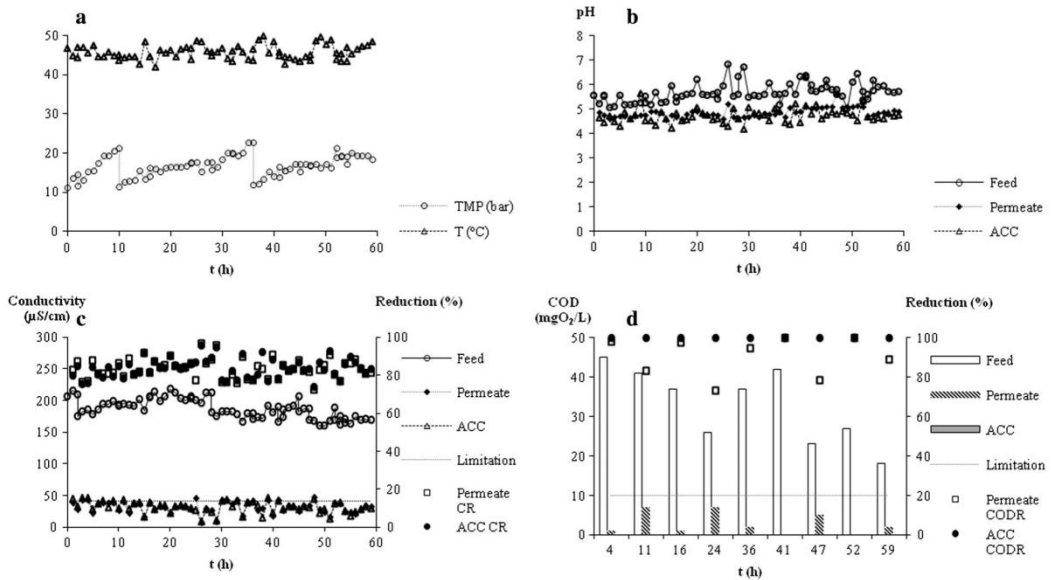


Fig. 8. (a) Feed temperature (Δ) (°C) and TMP (○) (bar) vs. time (h) in a continuous RO-ACC. Constant permeate flow rate ($J = 40 \text{ L/h m}^2$). Feed flow: 2000 L/h. Long-term experiment (b), pH evolution of feed (○), permeate (◆) and after activated carbon treatment (Δ) vs. time (h) in a continuous RO-ACC. Constant permeate flow rate ($J = 40 \text{ L/h m}^2$). Feed flow: 2000 L/h. Long-term experiment (c), Conductivities of the long-term continuous experiment vs. time. Constant permeate flow rate ($J = 40 \text{ L/h m}^2$), feed flow = 2000 L/h. Conductivity (μS/cm) vs. time (h): feed (○), permeate (◆) and after activated carbon treatment (Δ). Conductivities reduction (CR, %): permeate (□) and after activated carbon treatment (●) (d). Feed and permeate (before and after ACC) COD (mgO₂/L) of the long-term continuous experiment vs. time (h) and COD reduction (CODR, %) in permeates (before (□) and after activated carbon treatment (●)). Permeate flow rate ($J = 40 \text{ L/h m}^2$), feed flow = 2000 L/h.

540-m² RO plant to process 6.3 m³/h of dairy wastewaters assuming 11 L/h m² of permeate flow rate and 95% of RR, and Nilsson et al. [41], who proposed a 300-m² NF plant to treat 10 m³/h of meat industry wastewaters at 30 L/h m² of permeate flow rate and VCR 10. The final plant payback was estimated as being 2.2 years.

4. Conclusions

High-quality water with low conductivity (up to 17.5 µS/cm) and COD (up to 10 mgO₂/L) can be obtained after discontinuous RO (Duratherm[®] HF membranes) of low-pollutant direct UHT milk condensates (156.2–285.0 µS/cm conductivity and 5–89 mgO₂/L COD). Reductions up to 98.2% and 97.8% in conductivity and COD, respectively, were achieved when working at increased VCR (up to 10). Permeate conductivities and CODs lower than 40 µS/cm and 10 mgO₂/L, respectively, were obtained by single RO couple with an activated carbon column when working in continuous mode. However, as permeate pH was lower than required for use as boiler water, a permeate post-treatment is necessary. A scale-up proposed to process 20 m³/h with a 90% recovery rate needed a 450-m² membrane surface and the economic payback was estimated as 2.2 years.

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References

- G. Daufin, J.-P. Escudier, H. Carrère, S. Bérot, L. Fillaudeau, M. Decloux, Recent and emerging applications of membrane processes in the food and dairy industry, *Trans. IChemE (C)* 79 (2001) 89–102.
- Y. Pouliot, Membrane processes in dairy technology – from a simple idea to worldwide panacea, *Int. Dairy J.* 18 (2008) 735–740, <http://dx.doi.org/10.1016/j.jidairy.2008.03.005>.
- F.X. Milani, D. Nutter, G. Thoma, Environmental impacts of dairy processing and products: a review, *J. Dairy Sci.* 94 (2011) 4243–4254, <http://dx.doi.org/10.3168/jds.2010-3955>.
- V.B. Brião, C.R.G. Tavares, Effluent generation by the dairy industry: preventive attitudes and opportunities, *Braz. J. Chem. Eng.* 24 (4) (2007) 487–497.
- M. Vourch, B. Balanec, B. Chaufer, G. Dorange, Treatment of dairy industry wastewater by reverse osmosis for water reuse, *Desalination* 219 (2008) 190–202, <http://dx.doi.org/10.1016/j.desal.2007.05.013>.
- I.M. Román Sánchez, J.M. Molina Ruiz, J.L. Casas López, J.A. Sánchez Pérez, Effect of environmental regulation on the profitability of sustainable water use in the agro-food industry, *Desalination* 279 (2011) 252–257, <http://dx.doi.org/10.1016/j.desal.2011.06.015>.
- S. Casani, M. Rouhany, S. Knochel, A discussion paper on challenges and limitations to water reuse and hygiene in the food industry, *Water Res.* 39 (2005) 1134–1146, <http://dx.doi.org/10.1016/j.watres.2004.12.015>.
- W. Lee, M.R. Okos, Sustainable food processing systems – path to a zero discharge: reduction of water, waste and energy, *Proc. Food Sci.* 1 (2011) 1768–1777, <http://dx.doi.org/10.1016/j.profoo.2011.09.260>.
- S.A. Palumbo, K.T. Rajkowski, A.J. Miller, Current approaches for reconditioning process water and its use in food manufacturing operations, *Trends Food Sci. Technol.* 8 (1997) 69–74.
- A. Bódalo-Santoyo, J.L. Gómez-Carrasco, E. Gómez-Gómez, M.F. Máximo-Martín, A.M. Hidalgo-Montesinos, Spiral-wound membrane reverse osmosis and the treatment of industrial effluents, *Desalination* 160 (2004) 151–158.
- Z. Berk, *Food Process Engineering and Technology*, first ed., Elsevier Inc., Oxford, UK, 2009.
- C. García-Figueroa, B. Montag, A. Bes-Plá, J.A. Mendoza-Roca, E. Soriano-Costa, J. Lora-García, Study of the behaviour of a reverse osmosis membrane for wastewater reclamation – influence of wastewater concentration, *Desalination* 222 (2008) 243–248, <http://dx.doi.org/10.1016/j.desal.2007.01.163>.
- J.J. Bryony, Y. Jing, X.D. Chen, Membrane fouling during filtration of milk – a microstructural study, *J. Food Eng.* 60 (4) (2003) 431–437, [http://dx.doi.org/10.1016/S0260-8774\(03\)00066-9](http://dx.doi.org/10.1016/S0260-8774(03)00066-9).
- M. Turan, Influence of filtration conditions on the performance of nanofiltration and reverse osmosis membranes in dairy wastewater treatment, *Desalination* 170 (2004) 83–90, <http://dx.doi.org/10.1016/j.desal.2004.02.094>.
- V. Mavrov, E. Bélières, Reduction of water consumption and wastewater quantities in the food industry by water recycling using membrane processes, *Desalination* 131 (2000) 75–86.
- M. Vourch, B. Balanec, B. Chaufer, G. Dorange, Nanofiltration and reverse osmosis of model process waters from the dairy industry to produce water for reuse, *Desalination* 172 (2005) 245–256, <http://dx.doi.org/10.1016/j.desal.2004.07.038>.
- I. Koyuncu, M. Turan, D. Topacik, A. Ates, Application of low pressure nanofiltration membranes for the recovery and reuse of dairy industry effluents, *Water Sci. Technol.* 41 (1) (2000) 213–221.
- H. Chmiel, V. Mavrov, E. Bélières, Reuse of vapour condensate from milk processing using nanofiltration, *Filtr. Sep.* 37 (2000) 24–27.
- Directive 98/83/EC, Off. J. Eur. Commun. L 330 (1998) 32–54.
- S. Casani, S. Knochel, Application of HACCP to water reuse in the food industry, *Food Control* 13 (2002) 315–327.
- V. Mavrov, H. Chmiel, E. Bélières, Spent process water desalination and organic removal by membranes for water reuse in the food industry, *Desalination* 138 (2001) 65–74.
- S. Judd, B. Jefferson, *Membrane for Industrial Wastewater Recovery and Reuse*, first ed., Elsevier Science Ltd., Oxford, UK, 2003. doi:<http://dx.doi.org/10.1016/B978-185617389-6/50001-1>.
- A. Fährnich, V. Mavrov, H. Chmiel, Membrane processes for water reuse in the food industry, *Desalination* 119 (1998) 213–216.
- A. Mosset, V. Bonnellye, M. Petry, M.A. Sanz, The sensitivity of SDI analysis: from RO feed water to raw water, *Desalination* 222 (2008) 17–23, <http://dx.doi.org/10.1016/j.desal.2007.01.125>.
- Z.F. Cui, H.S. Muralidhara, *Membrane Technology*, first ed., Elsevier Inc., Oxford, UK, 2010. doi:<http://dx.doi.org/10.1016/B978-1-85617-632-3.00010-0>.
- F.A. Riera, A. Suárez, C. Muro, Nanofiltration of UHT flash cooler condensates from a dairy factory: characterisation and water reuse potential, *Desalination* 309 (2013) 52–63, <http://dx.doi.org/10.1016/j.desal.2012.09.016>.
- K.D. Pickering, M.R. Wiesner, Cost model for low-pressure membrane filtration, *J. Environ. Eng. ASCE* 119 (5) (1993) 772–797.
- S. Sethi, M.R. Wiesner, Cost modeling and estimation of crossflow membrane filtration processes, *Environ. Eng. Sci.* 17 (2) (2000) 61–79.
- A. Stroem, Quality, treatment and use of condensate and reverse osmosis permeates, *Bull. Int. Dairy Fed.* 232 (1988) 2–18.
- L. Moio, J. Dekimpe, P. Etievant, F. Addeo, Neutral volatile compounds in the raw milks from different species, *J. Dairy Res.* 60 (1993) 199–213.
- O. Akoum, M.Y. Jaffrin, L.H. Ding, M. Frappart, Treatment of dairy process waters using a vibrating filtration system and NF and RO membranes, *J. Membr. Sci.* 235 (2004) 111–122, <http://dx.doi.org/10.1016/j.memsci.2004.01.026>.
- B. Balanec, M. Vourch, M. Rabiller-Baudry, B. Chaufer, Comparative study of different nanofiltration and reverse osmosis membranes for dairy effluent treatment by dead-end filtration, *Sep. Sci. Technol.* 42 (2005) 195–200, <http://dx.doi.org/10.1016/j.seppur.2004.07.013>.
- G. Brans, C.G.P.H. Schröen, R.G.M. van der Sman, R.M. Boom, Membrane fractionation of milk: state of the art and challenges, *J. Membr. Sci.* 243 (2004) 263–272, <http://dx.doi.org/10.1016/j.memsci.2004.06.029>.
- Y.M. Gong, H.X. Zhang, X.N. Cheng, Treatment of dairy wastewater by two-stage membrane operation with ultrafiltration and nanofiltration, *Water Sci. Technol.* 65 (2012) 915–919, <http://dx.doi.org/10.2166/wst.2012.937>.
- E. Morin, B. Salgado, M.L. Lameloise, M. Decloux, Usefulness of reverse osmosis in the treatment of condensates arising from the concentration of distillery vinasses, *Desalination* 196 (2006) 306–317, <http://dx.doi.org/10.1016/j.jclepro.2007.02.009>.
- W. Qasim, A.V. Mane, Characterization and treatment of selected food industrial effluents by coagulation and adsorption techniques, *Water Res. Ind.* 4 (2013) 1–12, <http://dx.doi.org/10.1016/j.wri.2013.09.005>.
- J.P. Kushwaha, V.C. Srivastava, I.D. Mall, Treatment of dairy wastewater by commercial activated carbon and bagasse fly ash: parametric, kinetic and equilibrium modelling, disposal studies, *Bioresour. Technol.* 101 (2010) 3474–3483, <http://dx.doi.org/10.1016/j.biortech.2010.01.002>.
- E. Valero, M. Villamiel, B. Miralles, J. Sanz, I. Martínez-Castro, Changes in flavour and volatile components during storage of whole and skimmed UHT milk, *Food Chem.* 72 (2001) 51–58.
- J. Pereda, D.P. Jaramillo, J.M. Quevedo, V. Ferragut, B. Guamis, A.J. Trujillo, Characterization of volatile compounds in ultra-high-pressure homogenized milk, *Int. Dairy J.* 18 (2008) 826–834, <http://dx.doi.org/10.1016/j.idairyj.2007.12.002>.
- P.A. Vazquez-Landaverde, G. Velazquez, J.A. Torres, M.C. Qian, Quantitative determination of thermally derived off-flavour compounds in milk using solid-phase microextraction and gas chromatography, *J. Dairy Sci.* 88 (2005) 3764–3772.
- M. Nilsson, F. Lipnizki, G. Trägårdh, K. Östergren, Performance, energy and cost evaluation of a nanofiltration plant operated at elevated temperatures, *Sep. Purif. Technol.* 60 (2008) 36–45, <http://dx.doi.org/10.1016/j.seppur.2007.07.051>.

4.2.3. Membrana AE – 90

4.2.3.1. Introduction

Using a reverse osmosis (RO) AE – 90 membrane (GE Water & Process Technologies, USA) was another alternative contemplated by suggestion of the membrane manufacturer regarding the application considered (the RO pilot plant, membrane configuration, analytical methods and operating conditions are the same than those described in Suárez et al. [1]). The main characteristics of this type of membrane are summarized in **Table I**, where a comparison with other project membranes is also offered.

Table I: Comparing characteristics of the different membranes evaluated in the application considered.

	Duratherm® HWS HR	Duratherm® HF	AE – 90
Membrane type	RO	RO	RO
Size	4040	4040	4040
Cost (8040), €	1063	1930	900
Active area, m ²	8.2	8.4	8.4
Material	Proprietary composite (Thin-film membrane)	Proprietary composite (Thin-film membrane)	Proprietary composite (Thin-film membrane)
Average salt rejection, %	99.5 ^a	99.5 ^a	99.8 ^b
Maximum crossflow, m ³ /h	4.5	4.5	/
Average permeate flow, m ³ /d	8.7 ^a	8.7 ^a	7.6 ^b
Typical operating flux, Lmh	17-31	17-31	12-19
Outer grap	Cage	Cage	Fiberglass
Maximum operating pressure, bar	/	/	82.7
5-50 °C	41.4	41.4	/
51-70 °C	/	27.6	/
Maximum operating temperature, °C	70	70	50
Maximum cleaning temperature, °C	50	50	50
Maximum sanitization temperature, °C	90	90	/
pH operating range	4.0-11.0	4.0-11.0	4.0-11.0
pH cleaning range	2.0-11.5	2.0-11.5	2.0-11.5
Maximum feed turbidity, NTU	1	1	1
Maximum feed SDI	5	5	5
Chlorine tolerance	500 ppm-hours	500 ppm-hours	1000+ ppm-hours
Dimensions, inches	40 (A), 0.75 (B), 3.9 (C)	40 (A), 0.75 (B), 3.9 (C)	40 (A), 0.75 (B), 3.9 (C)
Perfect mechanical fit with housing	NO	NO	YES

^aTesting conditions: 2000 mg/L NaCl solution at 15.5 bar operating pressure, 25 °C, pH 7.5 and 15% recovery.

^bTesting conditions: 32000 mg/L NaCl solution at 55.2 bar operating pressure, 25 °C, pH 8 and 10% recovery.

The water flux of the AE – 90 membrane was evaluated by measuring its permeation with prefiltered tap water with low silt density index (SDI) (<3). A value of 9.52 L/hm² at 10.7 bar of transmembrane pressure (TMP) and 13.2°C was obtained. The membrane permeability corrected for the temperature, was calculated in 0.168, 0.138 and 0.068 L/hm²bar°C for Duratherm® HF, Duratherm® HWS HR and AE – 90 membranes, respectively, being the values higher than the references suggested by the manufacturer (0.111, 0.114 and 0.027 L/hm²bar°C, respectively). Regarding the AE – 90 membrane, this value was in the order of the obtained by Balannec et al [2] (0.067

L/hm²bar°C) when using a Desal 3 SF RO membrane (Osmonics, France).

Although these differences found in permeability between the studied membranes could be based on membrane skin layer and structure, there is a lack of information about the membrane composition (proprietary material). On the other hand, it is assumed that, according to their respective salt rejection (99.5% for Duratherm® HF/Duratherm® HWS HR and 99.8% for AE – 90 membranes), the cut-off of the AE – 90 membrane may be lower and therefore the water permeability, even though the separation of components in RO is not based entirely on size, but in charge exclusion and physicochemical interactions between solute, solvent and membrane too [3]. This circumstance means that achieving the same permeate flow rate in these membranes requires a higher pressure to be applied in case of the AE – 90 membrane.

In general, and as recommended by membrane manufacturer, these membranes have to be operated at maximum of 40 L/hm² for Duratherm® HF/Duratherm® HWS HR and 33 L/hm² for AE – 90 membranes. These values reported have to be respected in continuous trials when processing real wastewaters, but not necessarily in short-term discontinuous tests.

4.2.3.2. Discontinuous trials

The behaviour of the AE – 90 membrane in discontinuous trials as a function of volume concentration rate (VCR) was studied in order to study its technical feasibility for producing high quality boiler water from low polluted wastewaters. The feed flow was fixed at 2000 L/h to avoid fouling issues and selectivity losses. The permeate flow rate was set approximately 33 L/hm² as previously reported. The different tests, listed in **Table II** (averaged values between VCR 1 and 10), were performed at various combinations of pressure and temperature (T) to satisfy a wide range of *Wagner* units ($TMP \times T$). The pressure was not corrected to compensate the concentration polarization and fouling phenomena, remaining constant and allowing the plant to operate at decreasing permeate flow rate (constant pressure mode). Wastewaters from flash cooler (FC) 2 and 4, which showed to be significantly different in feed wastewater characteristics as evidenced by Riera et al. [4], were processed. Results in the form of permeate flow rate (J) versus VCR and time (t), and permeate conductivity quality (and its reduction/rejection (R)) at different VCRs are given in **Fig. 1** and **Fig. 2**, respectively.

Table II: Averaged operation conditions for AE – 90 membrane discontinuous testing.

	T (°C)	TMP (bar)	FC	Wagner units (bar°C)
Test 1	32.5	15.3	4	497
Test 2	41.2	18.4	4	758
Test 3	45.7	24.5	4	1120
Test 4	49.6	23.9	4	1185
Test 5	32.6	18.1	2	590
Test 6	40.4	21.3	2	860
Test 7	45.2	25.6	2	1157
Test 8	49.0	26.1	2	1279

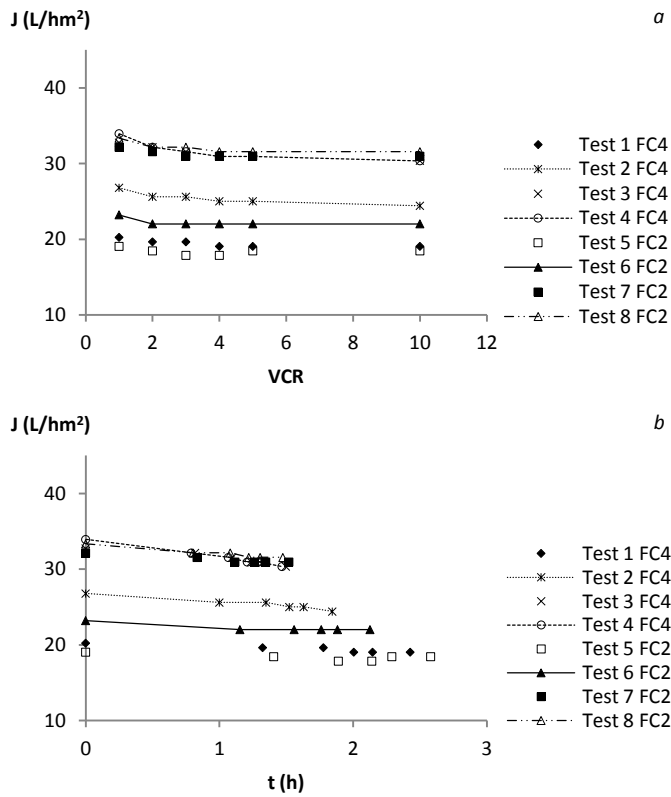


Fig. 1: AE – 90 membrane permeate flow rate as a function of VCR (a) and time (b) at different operation conditions.

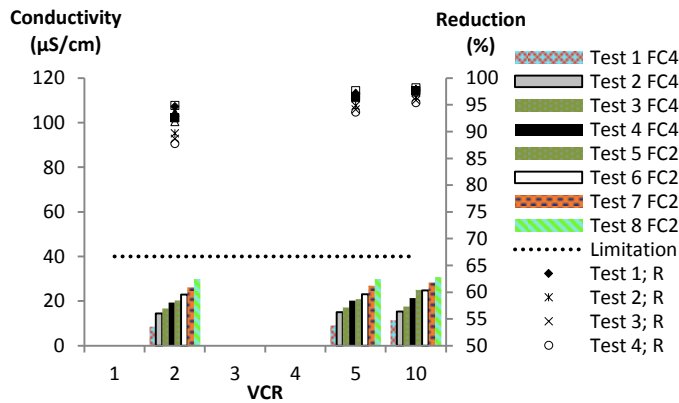


Fig. 2: AE – 90 permeate conductivity and its reduction (R, %) as a function of VCR at different operation conditions.

In **Fig. 1** and considering each FC individually, higher permeate flow rates corresponded to high *Wagner* unit values according to the combined influence of pressure and temperature. Although this effect was not present between FCs, at least for the tests performed at values of *Wagner* units lower than 1000 bar^oC, since Test 5 and 6 (FC 2) should be located above Test 1 and 2 (FC 4), respectively, and the situation was the opposite. A different effectiveness of the membrane cleaning cycles performed could clarify this situation as the membrane could start in not identical conditions. These differences could not be attributed to the different feed characteristics of wastewaters from FC 2 and 4, as it would be reasonable that waters from FC 4 were situated below those from FC 2 considering that the organic matter presence was lower in this latter case [4] and it is feasible that the largest contributor to the decline of permeate flux was the COD [5]. Although the flow reduction (FR), regarding to the values at VCR 2, was hardly noticeable (the maximum FR for all tests was 5.6%), the greatest effect was observed when wastewaters from FC 4 were processed, demonstrating this last organic matter related hypothesis. The permeate flow rate decreased with VCR following a logarithmic equation ($J = a - b \ln[VCR]$) [6]. However, this decrease was linear with time, the assays with lower J being the ones with the longest processing time as expected.

A permeate flow rate prediction mesh can be constructed based on these experimental results through adjusting the data from the different combinations of pressure and temperature to a second order polynomial equation. **Fig. 3** shows the response surface obtained when the permeate flow rate is represented versus temperature (30–55°C) and TMP (15–30 bar). Experimental data is represented over the surface as square spots, representing the distance between the real points tested and the net by dashed straight lines. A good adjustment ($R^2 = 91.4\%$) was achieved, being able to be improved (up to 97.1%) by including feed characteristics (feed conductivity and COD). J increased with temperature linearly, and independently of the TMP, in the order of 0.65 L/hm² per °C. Furthermore, J decreased 3.51% and increased 6.18 and 28.75% when working at 20, 25 and 30 bar, respectively, and taking as

reference the permeate flow rate at 50°C and 15 bar. No effects of membrane compaction or concentration polarization, characterised by a decrease in the slope (in a fixed plane) when increasing the pressure, were observed. In fact, a negligible contrary tendency was presented, but maybe associated to the statistical model.

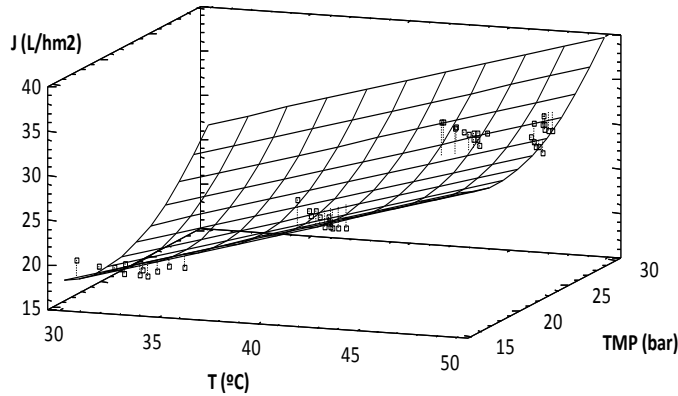


Fig. 3: Predictive permeate flow rate response surface according to temperature and TMP effects.

The permeate conductivity, shown in **Fig. 2**, fulfilled in all cases the boiler water requirement, being the values reached (8.6–30.8 $\mu\text{S}/\text{cm}$) below those obtained for the Duratherm® HF and HWS HR membranes, since the AE – 90 membrane presented an improved salt rejection capacity (see **Table II**). Although the requirement was satisfied at even high temperatures, the quality was poorer the higher the *Wagner* units were for each FC. Wastewaters from FC 4, which presented the lowest initial feed conductivity [4], were concentrated to a lesser extent, resulting in an improved permeate quality. This behaviour is reflected in **Fig. 4** where feed conductivity was plotted versus its respective VCR. The tendency was given by a potential equation ($\text{Feed conductivity } (\mu\text{S}/\text{cm}) = c (\text{VCR}^d)$; averaged $R^2 = 99.5\%$), being the coefficient c the initial feed conductivity and d the parameter which represents the concentration tendency. The averaged coefficient c was calculated to be 91.7 and 214.1 $\mu\text{S}/\text{cm}$ for FC 4 and 2, respectively, which shows the lower initial feed conductivity of FC 4 previously reported. The coefficient d is very similar in both cases (0.716 and 0.795 for FC 4 and 2, respectively), being the tendency almost identical, although the concentration degree reached is clearly more important where working with FC 2 wastewaters, as the coefficient c is 2.3 times higher. With regard to the chemical oxygen demand (COD), the permeate values at VCR 10 were between 12 and 33 mgO_2/L , not satisfying in any case the boiler water requirement ($<10 \text{ mgO}_2/\text{L}$) and not finding any clear tendency with increasing the *Wagner* units. Anyway, less polluted in organic matter wastewaters (FC 2) showed the best averaged permeate quality (17.5 mgO_2/L), versus the 25.2 mgO_2/L obtained when processing FC 4 wastewaters. Future working at low temperature or considering a second RO pass would not have sense, since good results in terms of conductivity could be obtained without energy losses (until 50°C) and the second RO pass did not demonstrate to be a good option for COD remove [1], so the use of an activated carbon column (ACC) would be necessary.

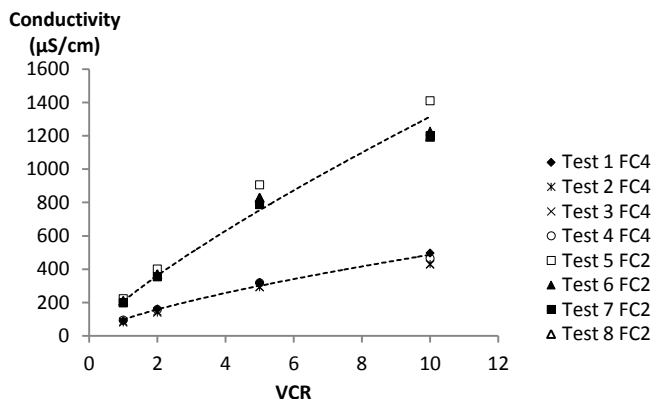


Fig. 4: Feed conductivity evolution when increasing the VCR: concentration effect.

A maximum reduction of 98.2% in conductivity was achieved, which demonstrated to be higher than those obtained with the Duratherm® HF and HWS HR membranes. Conductivity R values could be correlated with their respective feed concentration by using reverse independent variable type equations ($Conductivity\ R\ (\%) = e - f / feed\ conductivity\ (\mu S/cm)$, $R^2 = 94.1\%$), being the coefficient e estimated in 98.9%, which could correspond to the maximum reduction of 100%. With the correlation shown in Fig. 5, where dotted lines represent the 95% confidence level while the x-shaped spots corresponds to discarded atypical residues, R values could be predicted regarding the feed conductivity of the wastewaters

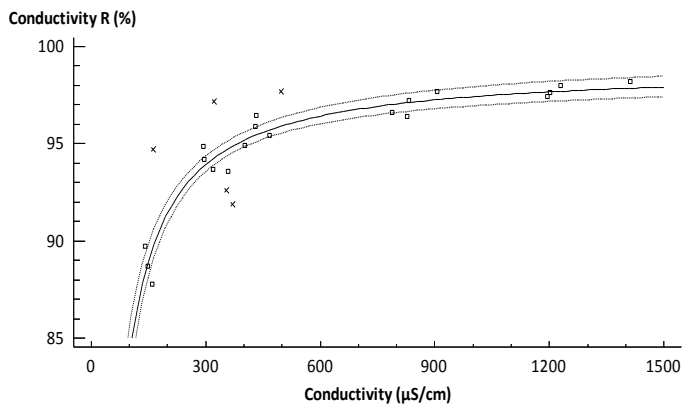


Fig. 5: Conductivity reduction versus feed conductivity (TMP 15.3–26.1 bar; Temperature 32.5–49.6 °C).

4.2.3.3. Continuous trials

Short-term continuous trials were performed in order to evaluate the feasibility of the membrane for long-term experiments. Discontinuous and previous experience was used to set the variables; temperature was fixed at

approximately 50°C and feed flow was maintained in 1500 L/h with the objective of satisfying the same feed/permeate flux ratio (40 L/hm²/2000 L/h versus 33 L/hm²/1500 L/h for Duratherm® HF/Duratherm® HWS HR and AE – 90 membranes, respectively) used with the previous membranes. The pilot was operated without concentration (VCR 1); if this stage works, higher VCRs will be tested, if it fails additional testing will not be necessary. The trials were carried out in a different way as shown in **Fig. 6**, one at constant J (increasing TMP) and another at constant TMP (decreasing J). In both cases the membrane did not reach the proposed objectives. At constant J , the limitation of 30 bar of pressure was achieved after 5 hours and the system had to be stopped. In view of the results it is necessary to bear in mind two things: first of all the AE – 90 membrane required a higher initial TMP to reach equivalent permeate flow rate than Duratherm® HF/Duratherm® HWS HR, so the pressure limitation is closer. On the other hand, its maximum operating pressure is higher (as typical in desalination membranes), so in this case the pressure limitation could be higher, although 30 bar is the maximum pressure that the pilot plant can withstand. This means that the limitation of pressure could be raised, but it could not be tested in the pilot plant used. For this reason it was decided to operate the installation at constant TMP, an unusual circumstance in continuous operation at industrial scale. J decreased by 25.5% after 6 hours of operation. A usual cleaning recommendation is given when flux decreases below 15% of its initial J ; this value was achieved after 3 hours (even if the more stable J value after one hour is taken as the initial reference, the 15% decrease is reached after 5 hours).

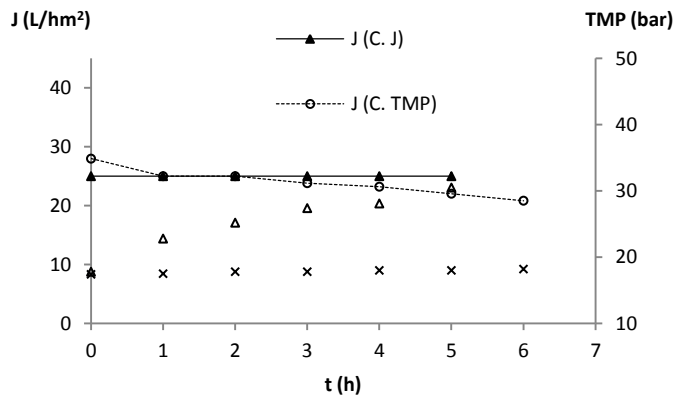


Fig. 6: TMP and permeate flow rate behaviour as a function of time in continuous tests (AE – 90 membrane) at VCR 1 (C. = constant).

In view of the results, the membrane did not reach the searched goal as the lost of technical viability is palpable when a complete cleaning has to be carried out each 3–5 hours, even at VCR 1 (at higher values the cleaning frequency would be greater). Additional testing (permeate quality evaluation, CAC coupling, long-term continuous trials at VCR 1

and future long-term tests with improved RR) will not be necessary as the AE – 90 membrane was discarded for the concrete implementation in boiler water production from dairy low polluted wastewaters.

Although the AE – 90 membrane was technically discarded, its economy was also calculated by using the scale-up recommendations given by Suarez et al. [1] in order to serve as a comparison. The recovery rate was established based on the more appropriate VCR according to the experimental results since the high tendency of fouling observed even at low VCRs. The payback period was estimated to be approximately 15 years. The suitability of this membrane for the application considered (boiler water production) was not proved, neither technically nor economically, since the operating costs of the process was weighed down by the lower recovery rate considered and the high frequency of cleaning estimated, which in turn could produce a lower membrane durability [7].

4.2.3.4. Particular references

- [1] A. Suárez, T. Fidalgo, F.A. Riera, Recovery of dairy industry wastewaters by reverse osmosis. Production of boiler water, *Separation and Purification Technology*, 133 (2014) 204-211, <http://dx.doi.org/10.1016/j.seppur.2014.06.041>.
- [2] B. Balanec, M. Vouch, M. Rabiller-Baudry, B. Chaufer, Comparative study of different nanofiltration and reverse osmosis membranes for dairy effluent treatment by dead-end filtration, *Separation and Purification Technology*, 42 (2005) 195-200, <http://dx.doi.org/10.1016/j.seppur.2004.07.013>.
- [3] J. Radjenović, M. Petrović, F. Ventura, D. Barceló, Rejection of pharmaceuticals in nanofiltration and reverse osmosis membrane drinking water treatment, *Water Research*, 42 (2008) 3601-3610, <http://dx.doi.org/10.1016/j.watres.2008.05.020>.
- [4] F.A. Riera, A. Suárez, C. Muro, Nanofiltration of UHT flash cooler condensates from a dairy factory: Characterisation and water reuse potential, *Desalination*, 309 (2013) 52-63, <http://dx.doi.org/10.1016/j.desal.2012.09.016>.
- [5] A. Suárez, F.A. Riera, Production of high-quality water by reverse osmosis of milk dairy condensates, *Journal of Industrial and Engineering Chemistry*, 21 (2015) 1340-1349, <http://dx.doi.org/10.1016/j.jiec.2014.06.004>.
- [6] C. Sagne, C. Fargues, R. Lewandowski, M.-L. Lameloise, M. Gavach, M. Decloux, A pilot scale study of reverse osmosis for the purification of condensate arising from distillery stillage concentration plant, *Chemical Engineering and Processing: Process Intensification*, 49 (2010) 331-339, <http://dx.doi.org/10.1016/j.cep.2010.03.002>.
- [7] H. Li, V. Chen, Chapter 10 - Membrane Fouling and Cleaning in Food and Bioprocessing, in: Z.F. Cui, H.S. Muralidhara (Eds.) *Membrane Technology*, Butterworth-Heinemann, Oxford, 2010, pp. 213-254, <http://dx.doi.org/10.1016/B978-1-85617-632-3.00010-0>.

Conclusiones particulares del apartado 4.2.

De todas las membranas ensayadas, las Duratherm® fueron las únicas que pudieron dar lugar a un permeado de calidad cercana al necesario para ser utilizado como agua de calderas. En cuanto a la AE – 90, aparte de no alcanzar el objetivo propuesto, al dar lugar a permeados a VCR 10 de hasta 33 mgO₂/L de DQO, se encontraron inconvenientes técnicos (baja permeabilidad, 9,52 L/hm², con relación a las otras membranas, un menor flujo de permeado admisible en continuo, 33L/hm², y una mayor tendencia al ensuciamiento, 3–5 horas, incluso a bajas concentraciones) que condicionaron además la economía preliminar del proceso, por lo que fue descartada. Al ser los resultados obtenidos con ambas Duratherm® muy similares, aunque ligeramente ventajosos en el caso de la membrana HWS HR al presentar rechazos máximos de hasta el 97,8 y el 98,9% en conductividad y materia orgánica respectivamente, se seleccionó ésta para ensayos continuos de larga duración, simplemente por criterios económicos, al presentar un precio comercial del orden de la mitad al de la Duratherm® HF.

Los ensayos discontinuos con la membrana Duratherm® HWS HR permitieron fijar las condiciones de trabajo para los estudios piloto de larga duración en continuo. Se incluyó además una predicción a través de datos empíricos tanto de flujos de permeado como de rechazos en función de las condiciones de trabajo; dichas predicciones podrían ser mejoradas al considerar las características de la alimentación. Temperaturas de tratamiento de condensados por encima de 50°C dieron lugar a un incumplimiento de requisitos, y por debajo a una reducción de los ahorros energéticos. Hipotéticamente, a 50°C, el porcentaje de sustitución de agua desmineralizada por permeados de este tipo podría ser de hasta el 100%.

Por otro lado, el grado de recuperación se fijó en un máximo del 90%, aunque a altos valores de éste parámetro y a presiones por encima de 15 bar, las limitaciones se vieron ligeramente sobrepasadas. Como resultado, y para evitar picos indeseados de materia orgánica por encima de 10 mg/L, se consideraría la instalación de una columna de carbón activo como post-tratamiento formando parte de los ensayos continuos de larga duración.

Otra de las recomendaciones obtenidas en este capítulo es el mantenimiento de altos flujos de alimentación, encontrándose un óptimo en torno a 2000 L/h (para 16,8 m² de membrana, es decir, 2 membranas de tamaño 4040 como es el caso en esta parte del estudio), al retrasar los fenómenos de ensuciamiento en flujo tangencial, reduciendo las pérdidas en selectividad, y evitar descensos acusados en el flujo de permeado.

El uso de un doble paso por ósmosis inversa demostró mejorar las características finales del permeado, aunque de forma no muy importante, lo que no justificaría una inversión al multiplicarse los costes de operación.

4.3. Modelización de rechazos de la operación de ósmosis inversa en base a la termodinámica irreversible

Con la membrana seleccionada (Duratherm® HWS HR), y mediante una experimentación en discontinuo, se ajustaron los resultados experimentales de rechazos a modelos teóricos de filtración ya conocidos como son el modelo de *Spiegler–Kedem* y el *film theory–Spiegler–Kedem*. A diferencia de otros estudios de este tipo donde se suelen utilizar disoluciones modelo, en este caso se pretendió modelizar una corriente real de carácter multi-componente. La información aquí obtenida aportaría una predicción aproximada del comportamiento del sistema de membranas en una instalación futura. La polarización por concentración fue considerada, al ser uno de los fenómenos que podría condicionar el diseño del proceso. Aunque de carácter reversible, la presencia de este efecto podría dar lugar a formas de ensuciamiento más importantes en el procesado en continuo, condicionando tanto el rendimiento del proceso como la vida útil de las membranas. También se determinó la contribución relativa del mecanismo de transporte, difusivo o convectivo, sobre la transferencia de los solutos. Los resultados de este estudio aparecen publicados en el trabajo que se incluye a continuación y que se encuentra en fase de revisión:

**Using the Spiegler–Kedem model to predict solute rejection in the treatment of industrial UHT
condensates by reverse osmosis**

Adrián Suárez, Francisco A. Riera

Enviado a *Desalination and Water Treatment*

Using the Spiegler–Kedem model to predict solute rejection in the treatment of industrial UHT condensates by reverse osmosis

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Abstract

Flash cooler condensates from the ultra-high-temperature process of a commercial dairy were treated in situ by reverse osmosis at a semi-industrial scale with the objective of modelling the membrane rejection. These multi-component streams, unlike the synthetic solutions used in theoretical studies, proved to be strongly heterogeneous. Their inorganic and organic loads were measured in terms of conductivity and chemical oxygen demand, respectively, and membrane rejection for these parameters was evaluated at different permeate fluxes (between 55 and 105 L/hm², approximately) and concentrations (between 197.5 and 1143.0 μS/cm conductivity and 67 and 289 mgO₂/L chemical oxygen demand). The Spiegler–Kedem and film theory–Spiegler–Kedem models were brought face to face and their precision was checked. Although no significant differences were found when modelling conductivity rejection, the latter model produced the lowest relative error (1.82%) when comparing the observed and estimated rejections of organic matter, which provided evidence of the advantages of considering the concentration polarisation phenomenon.

Keywords

Modelling; Concentration polarisation; Reverse osmosis; Commercial dairy; Wastewater reclamation

1. Introduction

Predicting the performance of high-pressure membrane applications leads to process optimisation [1]. Modelling provides a reliable prediction of the membrane system behaviour in terms of flux and rejection [2, 3]. Several review works can be found in the literature regarding nanofiltration (NF) and reverse osmosis (RO) modelling by mechanistic or mathematical development [4-8]. The models are generally classified into those based on transport mechanisms/hydrodynamics (solution-diffusion, Kimura-Sourirajan, extended Nerst-Plank models, etc.), which can be further divided into porous and nonporous or homogeneous models, and those derived from the irreversible thermodynamics or nonequilibrium (Kedem-Katchalsky, Spiegler-Kedem (SK) models, etc.) [8, 9]. Although most of them are strongly related, some models show complex mathematic equations and require sophisticated solution techniques [1, 10]. Furthermore, the information which must be enter for the model, such as the pore geometry, solute diffusion coefficients, etc., is frequently unknown and its determination complex and impractical for use in industrial conditions [11, 12].

Membrane processes (mainly RO and NF) are becoming fairly common in the production of drinking water, wastewater treatment and other industrial applications [13-17]. RO membranes have proved to be effective in the removal of ions and organic chemicals, but suffer from fouling and concentration polarisation (CP) problems [18]. Although new proprietary thin-film-composite (TFC) membranes could add electrostatic and steric functionality, solute transport in traditional semi-permeable RO membranes is most likely to be caused by diffusion or diffusion/advection (sterically and chemically conditioned) through a membrane pore [1].

In order to describe the performance of RO, the phenomenological SK model [19] has been extensively recommended [5]. It is based on the consideration that the solvent and solute fluxes are both dependent on the differences in chemical potential, caused either by concentration or pressure gradients (driving forces) between the sides of the membrane [9]. The membrane is considered a black box by neglecting its porosity and where no specific knowledge of transport mechanisms and membrane structure is required [20], making the methodology more accessible but providing no insight into the mechanism of separation [21, 22]. Additionally, the electrostatic potential of the system is not taken into account as the model assumes the membrane to be uncharged [23]. Not only has the SK model been used to predict salt [24] and organic compound [25] transport across the membrane in single and binary solute systems, but it has also been applied in the field of multi-component separation description, and for this reason it is very useful in RO industrial processes [9].

The SK model defines the membrane transport as a combination of convection, resulting from the applied transmembrane pressure (ΔP), and diffusion, a consequence of the concentration gradient (dC/dx) [26]. It is a two-parameter model described by the solute permeability (P_s) and the reflection coefficient (σ), both obtained by a fitting procedure in rejection trials [27]. The relevant equation for the SK model defines the solute flux (J_s) across the membrane as follows:

$$J_s = P_s \Delta x \frac{dC}{dx} + (1 - \sigma) J_v C \quad (1)$$

where C represents the solute concentration and J_v the permeate flux, which is defined by the following equation [28]:

$$J_v = L_p (\Delta P - \sigma \Delta \pi) \quad (2)$$

the L_p being the membrane permeability and $\Delta \pi$ the osmotic pressure, which can be determined, if necessary, using the Van't Hoff's equation in the case of diluted solutions [29]. Integrating Eq. (1) over the membrane thickness (Δx) and introducing the rejection definition (supposing the concentration at the membrane surface (C_m), difficult to obtain experimentally, equal to that of the feed (C_f)), an expression to relate the estimated rejection (R_{est}) and J_v is obtained [30]:

$$R_{est} = 1 - \frac{1 - \sigma}{1 - \sigma e^{-\frac{(1 - \sigma) J_v}{P_s}}} \quad (3)$$

P_s is a measure of the diffusive transport, while σ , which influences the convective term, is the maximum rejection possible for a given component, and corresponds with the rejection at the idealised condition of infinite solvent flux [31]. Convective solute transport does not take place when σ reaches a value of 1 (ideal RO membranes with no pores available) and becomes zero in the case of an entirely unselective membrane [32].

One of the main drawbacks when applying the standard SK model is that there is no consideration of the CP effect, so a correction of the model should be provided as this phenomenon is one of the most important factors influencing the membrane design process [33, 34]. CP, which is considered a reversible effect, occurs within a boundary film facing the membrane/feed solution interface when an increase in the local concentration is created by the retained species which accumulate at the membrane surface [30, 35]. This effect causes an increase in the osmotic pressure and, consequently, a reduction in the net driving forces of the system [36]. Neglecting this phenomenon may result in inaccurate determinations of L_p and σ , and could lead to overestimation of water quality and recovery in case of wastewater reclamation applications [37].

In order to take into account the CP effect, the SK model has been coupled to the film theory (resulting in the combined film theory–Spiegler–Kedem or CFSK model [22]), which assumes that, at steady state, the thickness of the polarisation layer (δ) is established at the equilibrium of the convective fluxes towards and through the membrane and the back diffusive flux. The mass balance generated is solved within the boundary conditions by Eq. (4), which could be combined with the SK model to obtain a relationship between R_{est} and J_v (Eq. 5) [30].

$$\frac{c_m - c_p}{c_f - c_p} = e^{\frac{\delta}{D} J_v} \quad (4)$$

$$R_{est} = 1 - \frac{1}{1 + \frac{\sigma}{1 - \sigma} \left[e^{-\frac{\delta}{D} J_v} - e^{-\frac{(1 - \sigma) J_v}{P_s} - \frac{\delta}{D} J_v} \right]} \quad (5)$$

The permeate concentration and the solute diffusivity are C_p and D , respectively. The D/δ ratio corresponds with the mass transfer coefficient (k), usually determined by mass transfer correlations available in the literature [38, 39], but which may not hold well with differences in equipment geometry and hydrodynamic entrance effects [40]. At any rate, k could be simultaneously calculated (and specifically for the membrane configuration selected) with P_s and σ through experimental data of observed rejection (R_{obs}) and J_v by a fitting procedure as well. The major deficiencies found when applying this model are the assumption that k is constant, when it is often concentration-dependent, and the consideration of concentration linearity in the boundary layer [32].

The mathematical models previously described have been frequently tested with synthetic solutions; however, their usefulness has not been studied in depth in the case of industrial processes where feed composition and heterogeneity introduce extra difficulty in the prediction of fluxes and rejections [41]. Some previous works published by the authors [15-17] have demonstrated the possibility of reusing low polluted flash cooler (FC) condensates, from the direct ultra-high-temperature (UHT) process of a commercial dairy, with the purpose of boiler water production by RO. In this technical paper the SK and CFSK models have been tested to this application at a semi-industrial scale, and the model parameters estimated experimentally. Due to the complexity of the composition of these condensates, membrane selectivity of salts and organic matter has been measured indirectly in terms of conductivity and chemical oxygen demand (COD), respectively.

2. Materials and methods

2.1. Reverse osmosis pilot plant

Two spiral-wound TFC Duratherm® HWS 4040 HR membranes (GE Water & Process Technologies, USA) were installed in series as part of the RO rig described in **Fig. 1**, the properties of this specific RO membrane being given in **Table 1**. The RO plant was fed with condensates from one of the four FCs operating in a Spanish commercial dairy, the RO trials being performed in situ. The established membrane cleaning protocol was a sequence of acid (20 min, 45°C) and alkali (45 min, 45°C) steps with Divos 2 and Divos 123 (Diversey, The Netherlands), respectively. Cleaning was carried out between each set of experiments, the reference permeability being fully recovered in all cases. On the other hand, and in order to maintain low values of water silt density index (SDI) for rinsing and cleaning purposes, a prefiltration system, consisting of a bag filter (BF-01) and three cartridge prefilters F-01, F-02 and F-03 of 5, 1 and 0.2 µm, respectively, was installed.

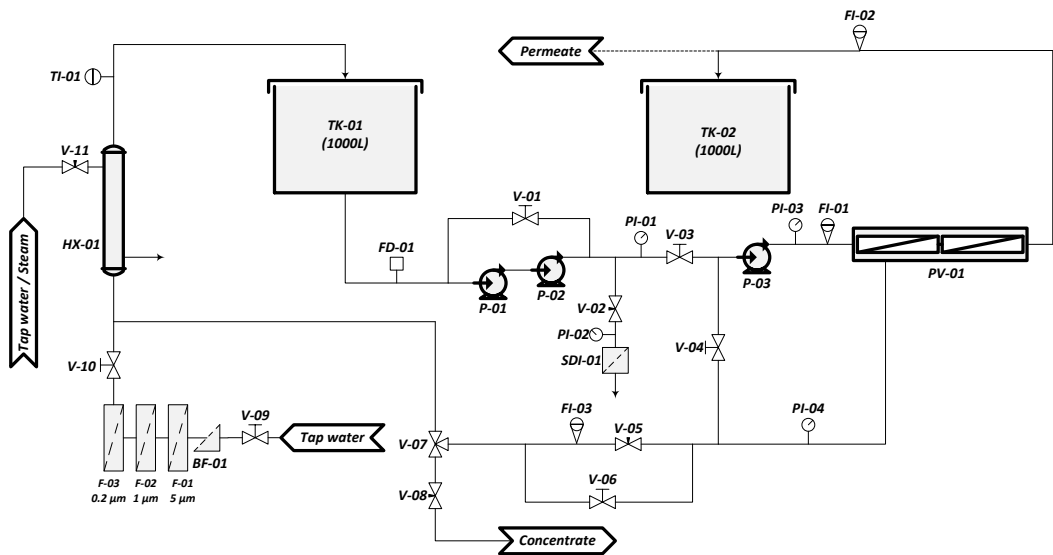


Fig. 1: Scheme of the RO pilot plant.

The FC condensates were collected in a 1000 L feed tank (TK-01) and fed to the RO pressure vessel (PV-01) through a set of high pressure pumps (P-01 and P-02 (Lowara, Italy); 2.2 and 3.0 kW, respectively). A flow detector (FD-01) was installed before the pumps to avoid the system working under vacuum. The ΔP was controlled by regulating the needle valve (V-05) located on the concentrate line and monitored by the pressure indicators (PI) of the system. The flow in the feed, concentrate and permeate channels was measured by their respective flow meters (FI), and the temperature

controlled and adjusted by a temperature indicator (TI-01) and a heat exchanger (HX-01), respectively.

Table 1: Duratherm® HWS 4040 HR membrane characteristics.

Material: Proprietary composite (TFC membrane)	
Average salt rejection ^a , %	99.5
Maximum crossflow, m ³ /h	4.5
Spacer thickness, mil	31
Active area, m ²	8.2
Maximum operating pressure (5–50°C), bar	41.4
Maximum operating temperature, °C	70
pH operating range	4.0–11.0

^aTesting conditions: 2000 mg/L NaCl solution at 15.5 bar operating pressure, 25 °C, pH 7.5 and 15% recovery before any hot water sanitization.

2.2. Operating procedure and conditions

The trials were performed discontinuously through a semi-closed loop where the permeate produced in the RO pilot plant was stored in an external 1000 L tank (TK-02, **Fig. 1**) and the concentrate returned to the feed tank. In this way, a certain degree of concentration was achieved as the system worked at increasing values of the volume concentration ratio (VCR), a parameter defined as follows:

$$VCR = \frac{V_f}{V_c} = \frac{V_f}{V_f - V_p} \quad (6)$$

where V_f , V_c and V_p are the feed, concentrate and permeate volumes, respectively.

The feed flow rate and temperature were fixed at approximately 2.5 m³/h and 50°C, respectively, and the different tests performed at variable VCRs (1–10) and ΔP s (10–20 bar). The J_v was continuously measured and the R_{obs} for the main parameters, i.e. COD and conductivity, studied, determined at different operating conditions by means of the equation

$$R_{obs} = \left(1 - \frac{C_p}{C_f}\right) \cdot 100 \quad (7)$$

where C_p and C_f are the permeate and feed concentration values of both parameters considered, respectively.

2.3. Analytical methods

The fresh FC condensates and resultant RO permeates were characterised in terms of pH (accuracy ± 0.05), electrical conductivity (accuracy $\pm 0.5\%$) and COD (accuracy ± 3 mgO₂/L). A more complete analysis of these streams was previously published by Riera et al. [14] and Suárez & Riera [17]. pH, corrected with temperature, and electrical conductivity, referenced at 25°C, were measured by an HQ40d multimeter (Hach Lange, Belgium). COD was determined spectrophotometrically by previous Cr³⁺ determination at 605 nm using a Spectroquant NOVA 60 photometer (Merck, Germany) after a sulphuric oxidation in a cell test.

2.4. Determination of model parameters

The two parameters P_s and σ of the SK model, and the three of the CFSK model (P_s , σ and k) were estimated by a non-linear fitting procedure linked to a least-squares algorithm (*Solver* tool, Microsoft Excel) of the pairs of values (J_v , R_{obs}) obtained for each concentration (VCR). So, these experimental data were fitted to Eq. (3) when considering the SK model and Eq. (5) regarding the CFSK model, the respective model parameters being those that minimised the squared differences between the observed and predicted rejections, $(R_{obs} - R_{est})^2$.

3. Results and discussion

Discontinuous tests performed at increasing VCRs (1–10), different pressures (10, 15 and 20 bar, approximately) and at constant temperature (52.5 ± 1.5 °C) allowed to obtain the pairs of values (J_v , R_{obs}) required to test the mathematical models at different feed concentrations. The heterogeneity of the real industrial water hindered the repeatability of the initial starting conditions and, as a result, the feed composition of the different trials showed certain variability (pH: 6.02 ± 0.15 ; conductivity: 197.5 ± 10.6 μ S/cm; COD: 67 ± 10 mgO₂/L; at VCR 1). The standard deviation gained importance, in general, with growing concentration (pH: 7.27 ± 0.07 ; conductivity: 1143.0 ± 79.0 μ S/cm; COD: 289 ± 76 mgO₂/L; at VCR 10).

The permeability of the membrane with prefiltered tap water (SDI <3) at 50 °C was previously measured giving a value of 6.9 L/hm²bar [17]. When processing condensates in a batch, the permeate flux showed a linear dependency with ΔP up to 15 bar, the flux percentage improvement being almost constant ($33.3 \pm 2.4\%$) in all cases when increasing the pressure from 10 to 15 bar at the different VCRs studied. However, this linearity was lost at higher pressures, as observed by Turan [42], as the flux increment when changing from 15 to 20 bar was only maintained at VCR 1 (29.8%). Moreover, this flux increment was reduced when increasing the concentration of the feed solution (20.2, 17.5,

16.0 and 14.9% at VCR 2, 3.3, 5 and 10, respectively). Higher salt concentration increases the osmotic pressure, thus reducing the driving pressure and therefore the permeate flux [20], although, at the low concentrations used in this work, the osmotic contribution can be neglected. The decreasing slope of the curve J_v vs. ΔP at certain pressures could be associated with the occurrence of CP phenomena [43], the resistance to permeation being higher with the increased concentration of solutes at the surface of the membrane [35, 44]. Other authors associate it to membrane compaction at high working pressures [45].

The experimental R_{obs} at each J_v was used to determine the parameters P_s , σ and k of the SK and the CFSK models, the main results being collected in **Table 2**. Theoretical rejections were calculated based on these values and plotted in **Figs. 2** and **3** regarding conductivity and COD, respectively, and the effect of neglecting or not neglecting the CP phenomenon was studied at different concentrations (VCRs). A comparison between model predictions and experimental results was also included.

No experimental points were obtained at low permeate fluxes due to the physical limitations of the RO rig when working at the conditions tested, but several authors have demonstrated the model compliance in this part of the curve for experiments at laboratory scale [12, 26, 30, 46]. However, in spite of the fact that both models predict very low rejections at low permeate flux regardless of the feed concentration, the theoretical rejections, specifically those of COD, are very high even for low solute concentrations at low permeate fluxes. This could be considered as a limitation of the models and generate a point of controversy [23]. What is more, there are some examples in the literature where the rejection predicted by the models did not converge towards zero at low permeate flux [45, 47].

Table 2: Model parameter estimation when neglecting concentration polarisation (CP) (Spiegler–Kedem (SK) model) and when considering CP (film theory–Spiegler–Kedem (CFSK) model).

	VCR	Concentration	SK model		CFSK model		
			P_s , L/hm ²	σ , %	P_s , L/hm ²	σ , %	k , L/hm ²
Conductivity, $\mu\text{S}/\text{cm}$	1	197.5±10.6	3.810	88.79	5.209	99.97	106.474
	2	335.0±22.1	2.046	92.59	2.819	99.99	92.253
	3.3	499.3±55.9	0.743	94.55	1.359	99.89	67.291
	5	681.3±63.1	0.583	95.95	1.096	99.96	71.997
	10	1143.0±79.0	0.597	97.61	0.759	99.98	81.541
COD, mgO ₂ /L	1	67±10	0.373	94.07	0.050	99.98	17.167
	2	105±12	0.239	95.12	0.146	99.91	23.651
	3.3	147±36	0.287	95.62	0.083	99.92	20.536
	5	177±36	0.193	95.90	0.073	99.78	23.566
	10	289±76	0.131	97.87	0.167	99.52	40.875

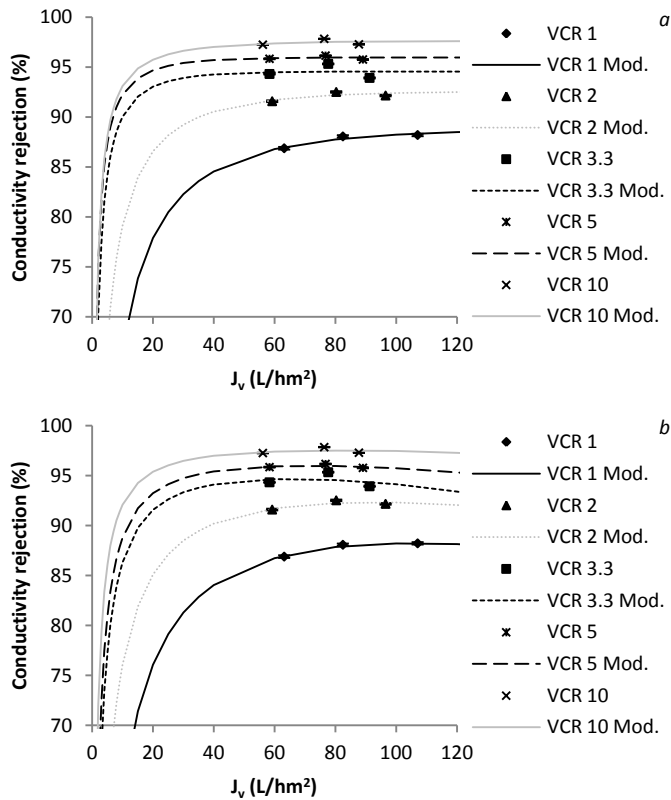


Fig. 2: Experimental and theoretical conductivity rejections vs. permeate flux (J_v) at different volume concentration ratios (VCRs) when considering the Spiegler–Kedem (SK) model (a) or the film theory–Spiegler–Kedem (CFSK) model (b) (symbols: experimental rejections; lines: model predictions).

When neglecting CP (Figs. 2a and 3a), the SK model predicted the whole range of conductivity rejections and those of COD at low pressures well, but failed to predict the COD rejection values at permeate fluxes higher than approximately 80 L/hm², which corresponds to a value of ΔP exceeding 15 bar. The existence of this critical pressure has been previously observed in other NF and RO applications [48]. Above a given pressure, the drag forces (convective transport), conditioned by the flux into pores, become important and the solute transfer grows, decreasing its rejection [49, 50]; until that pressure, the drag forces can be neglected and rejection increases as the solutes are retained by the surface forces (diffusive transport) which are pressure independent [51, 52]. The SK theory predicts an increase in solute rejection (up to an asymptotic value) with flux until the drag forces become dominant [53], but it is unable to predict this maximum rejection observed.

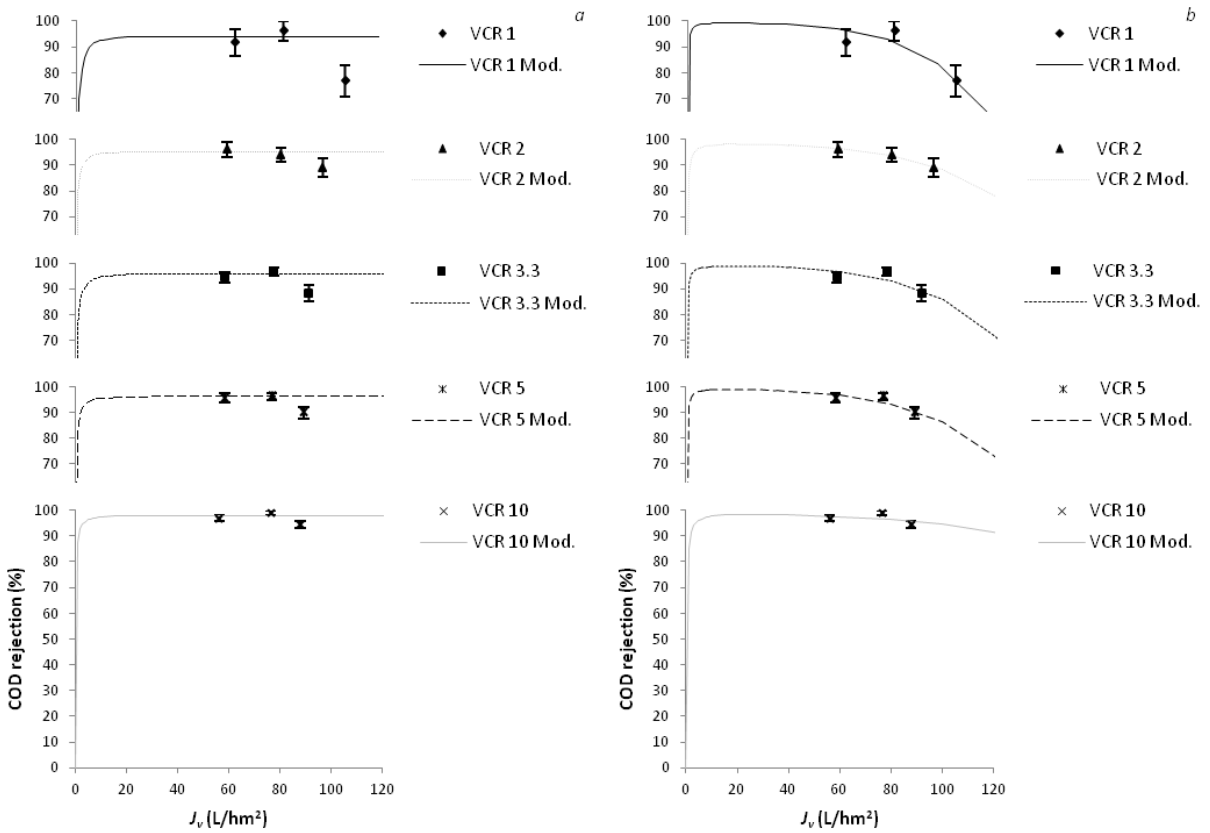


Fig. 3: Experimental and theoretical chemical oxygen demand (COD) rejections vs. permeate flux (J_v) at different volume concentration ratios (VCRs) when considering the Spiegler–Kedem (SK) model (a) or the film theory–Spiegler–Kedem (CFSK) model (b) (symbols: experimental rejections; lines: model predictions).

The σ values of the SK model (**Table 2**) ranged from 88.79 to 97.61% and from 94.07 to 97.87% regarding conductivity and COD, respectively, and showed very little concentration dependence. The P_s values varied between $0.16 \cdot 10^{-6}$ and $1.06 \cdot 10^{-6}$ m/s, and between $0.04 \cdot 10^{-6}$ and $0.10 \cdot 10^{-6}$ m/s for conductivity and COD, respectively. The conductivity P_s values were in the order of those determined by Chaabane et al. [30] ($0.35 \cdot 10^{-6}$ – $2.94 \cdot 10^{-6}$ m/s) when studying Ca/Cu/Cd(NO₃)₂ and ZnCl₂ salt passage (10–100 mg/L) in NF, Gilron et al. [33] ($1.60 \cdot 10^{-6}$ – $6.10 \cdot 10^{-6}$ m/s) when modelling NaCl rejection (150–1500 mg/L), and Rice et al. [26] ($1.58 \cdot 10^{-6}$ – $2.47 \cdot 10^{-6}$ m/s) when modelling KCl transport (5–10 mM at pH 7.0–7.5), but well below the values given by Levenstein et al. [24] ($16.16 \cdot 10^{-6}$ – $27.36 \cdot 10^{-6}$ m/s) who also modelled NaCl passage (0.5–2.5%). Considering the organic matter P_s , the values are slightly below those calculated by Wadley et al. [54] ($0.87 \cdot 10^{-6}$ m/s) when modelling organics rejection by NF. These data are included for reference; however, it is difficult to draw final conclusions by comparing the values obtained by different authors as these parameters are strongly influenced by the conditions used (temperature, pressure range, etc.), the

type of solute-solvent-membrane interactions and the membrane material as, for example, a smaller pore size implies a greater contribution of the diffusion mechanism conditioning the P_s value.

In this work, the increase in feed concentration caused a rise in the reflection coefficient and a reduction in the salt permeability, contrary to the trend observed in other studies [12, 24, 33, 49]. This opposed effect, characteristic of charged membranes, was explained by these authors as an increase in the ionic strength with concentration producing a shielding phenomenon which neutralises the membrane charge and decreases the repulsion forces. However, although it may be considered an atypical behaviour, there are certain examples in the literature where the authors also observed an increase in the rejection [55-59] and a reduction in the salt permeability [60] with concentration. Symmetric salts (NaCl, KCl, etc.) usually showed a rejection decrease with concentration, while non-symmetric ones (MgCl₂, CaCl₂, etc.) tended to behave in the opposite way [55]. However, as the rejection and the salt permeability are conditioned by the specificity of the membrane, the solute species involved and the concentration range, a general behaviour cannot be established [46]. In fact, it should be borne in mind that, due to the low solute concentrations used in this work, the possibility of reaching the concentration from which the rejection starts to decrease has not yet been put in evidence. On the other hand, this modification in the charge density of the membrane may result in swelling of the pores and lead to a reduction in the rejection of neutral organic compounds [61]. Nevertheless, there was neither evidence about that in this work nor in others, like Garcia-Aleman et al. [20], for example, who studied the rejection of lactose in a mixed solute system with NaCl.

The relative contribution of diffusive ($J_{diffusive}$) and convective flux ($J_{convective}$) on solute transport was also calculated by using Eq. (8), the main results being shown in **Table 3**. This calculation methodology was proposed by Gilron et al. [33], being applied in the study of monovalent salt-polyvalent ion mixture passage through NF membranes.

$$J_s = J_{diffusive} + J_{convective} = P_s(C_m - C_p) + J_v C_{lm}(1 - \sigma) \quad (8)$$

where C_{lm} is the log mean average between C_m and C_p . C_m was approximated to a C_f value recalculated by applying the model R_{est} .

According to these data, organic transport proved to be dominated by convection, its contribution being around 80%, a circumstance previously observed by Geens et al. [62], who modelled the organic transport in non-aqueous NF. Kim et al. [63] also obtained similar results when studying the transport of organic species through NF and RO membranes and they stated that convection is dominant in most cases except in the passage of hydrophobic non-polar compounds where the diffusion term can be more important. Moreover, they found that permeability in NF

membranes seemed to be dominated more by convection than in RO, as expected. In these cases, the reflection coefficient can be approximated to the solute rejection as the diffusive term hardly contributes to solute transport [31]. Regarding the transport of charged species and in general, the convective term represented at least half of the salt flux, which is in good agreement with the results obtained by Gilron et al. [33]. It could be observed that the convective contribution increased with the pressure applied as expected and was at a minimum at the higher feed concentration (VCR 10) as the concentration gradient gained relevance [50].

Table 3: Contribution of convective flux ($J_{convective}$) to solute transport at different volume concentration ratios (VCRs) and pressures (the diffusive influence is given by the difference).

	VCR	$J_{convective}$, %		
		10 bar	15 bar	20 bar
Conductivity	1	47.70	53.55	59.46
	2	46.31	53.28	57.60
	3.3	59.64	66.21	69.71
	5	55.98	62.50	65.89
	10	38.32	45.36	48.71
COD	1	78.06	82.29	85.78
	2	80.00	84.43	86.70
	3.3	74.00	79.12	81.66
	5	79.54	83.64	85.57
	10	70.36	76.34	78.76

The CFSK model, which considers the concentration polarisation effect, was evaluated (Figs. 2b and 3b, and Table 2). CP increases with pressure and can modify the membrane separation properties leading to a decrease in rejection [49, 52]. In this work the COD rejection was reduced by 4.5–19.9% when ΔP increased from 15 to 20 bar. For this model, the estimated P_s values were in the order of those obtained by the SK model, and the σ values, which were near 100%, could be closer to representing an RO membrane than those calculated by using SK. Regarding the study of k values, they were compared in Table 4 with those obtained by the graphical method described by Murthy & Gupta [64] and Wang et al. [65] considering the assumptions of the film theory–solution–diffusion (CFSD) model. This method lies in plotting $\ln[(1-R_{obs})J_v/R_{obs}]$ vs. J_v and evaluating the slope of the corresponding straight line, which corresponds with the reciprocal of the mass transfer coefficient (k^{-1}). As can be seen in Table 4, both the data obtained by the CFSK model and those obtained by the CFSD methodology are strongly consistent. The effect of CP seemed to be more significant in the case of organics (lower k values), the performance of this specific application being powerfully controlled by the organic load [17]. Although, as the mass transfer coefficient was defined by D/δ and assuming a polarisation layer only of equivalent thickness, the discrepancy observed in the k values when modelling inorganic and organic matter could be associated with the difference in the diffusivities of the species involved. It should be also noted in Figs. 2b and 3b that the maximum rejections for the different concentrations (VCRs) were approximately reached when the J_v acquired the same value as the corresponding k , a circumstance

previously observed by other researchers [22, 40, 64]. This condition is characteristic of the model; that is to say, if the CFSD model equation is differentiated with respect to J_v and the derivative set to zero, the result is that the J_v which produces the maximum rejection matches with the mass transfer coefficient, and this fact is independent of the membrane transport parameters.

Table 4: Comparison between the mass transfer coefficients (k) obtained by the film theory–Spiegler–Kedem (CFSK) and the film theory–solution–diffusion (CFSD) models.

	$k, L/hm^2$		
	VCR	CFSK	Graphical CFSD
Conductivity	1	106.474	107.527
	2	92.253	91.743
	3.3	67.291	66.667
	5	71.997	71.429
	10	81.541	80.645
COD	1	17.167	23.697
	2	23.651	23.310
	3.3	20.536	28.818
	5	23.566	24.630
	10	40.875	40.984

Finally, the precision of both the SK and the CFSK models for predicting the conductivity and COD rejections was checked and compared as shown in **Table 5**, where the relative error between R_{obs} and the R_{est} was calculated.

When using the SK model the errors varied in the range of 0.05–0.84% and 0.26–18.09% for the conductivity and COD, respectively. On the other hand, they moved in the range of 0.01–0.79% and 0.16–4.84% for the conductivity and COD, respectively, when applying the CFSK model. No significant differences were found when modelling the conductivity rejection; however, in the case of COD, the average error was decreased (from 3.57 to 1.82%), as well as the maximum error (from 18.09 to 4.84%), when checking the SK results against those of the CFSK model, which reveals the predictive advantages offered by the latter. In the case of COD, it should be noticed that the error estimated when applying the CFSK model was highly improved at high pressure regarding those values calculated for the SK model.

Table 5: Relative errors calculated between the observed rejection (R_{obs}) and predicted rejection (R_{est}) when considering Spiegler–Kedem (SK) or film theory–Spiegler–Kedem (CFSK) modelling.

VCR	J_w , L/hm ²	Conductivity					COD				
		R_{obs} , %	R_{est} SK, %	^a E1, %	R_{est} CFSK, %	^b E2, %	R_{obs} , %	R_{est} SK, %	E1, %	R_{est} CFSK, %	E2, %
1	63.22	86.89	86.99	0.12	86.99	0.12	91.94	94.07	2.27	96.62	4.84
	82.54	88.07	87.84	0.27	87.92	0.17	96.20	94.07	2.27	92.15	4.40
	107.12	88.21	88.34	0.15	88.23	0.01	77.05	94.07	18.09	77.79	0.96
2	59.27	91.59	91.69	0.11	91.70	0.12	96.23	95.12	1.16	96.53	0.31
	80.34	92.52	92.20	0.34	92.26	0.28	94.02	95.12	1.16	93.57	0.47
	96.58	92.16	92.38	0.23	92.31	0.16	89.25	95.12	6.18	89.39	0.16
3.3	58.39	94.32	94.48	0.17	94.63	0.33	94.48	95.62	1.19	96.91	2.50
	77.71	95.33	94.54	0.84	94.58	0.79	96.76	95.62	1.19	93.74	3.22
	91.31	93.92	94.55	0.66	94.34	0.44	88.39	95.62	7.56	89.55	1.29
5	58.39	95.84	95.88	0.05	95.91	0.08	95.65	95.90	0.26	96.97	1.36
	76.83	96.15	95.93	0.23	95.97	0.19	96.15	95.90	0.26	94.11	2.18
	89.13	95.77	95.94	0.19	95.87	0.11	89.86	95.90	6.31	90.75	0.98
10	56.20	97.24	97.33	0.09	97.36	0.12	96.83	97.87	1.06	97.68	0.87
	76.39	97.84	97.49	0.35	97.50	0.34	98.91	97.87	1.06	96.61	2.38
	87.81	97.28	97.54	0.26	97.49	0.22	94.44	97.87	3.50	95.71	1.32

^aE1: relative error associated with the SK model

^bE2: relative error associated with the CFSK model

4. Conclusions

Unlike synthetic solutions, industrial streams involve complex multi-component mixtures which usually undergo a strong variability in their composition. The condensates, which can be considered low polluted wastewaters, showed characteristics in the range of 197.5 ± 10.6 – 1143.0 ± 79.0 $\mu\text{S}/\text{cm}$ for conductivity and 67 ± 10 – 289 ± 76 mgO_2/L for COD, when working at increasing VCR (1–10).

The SK model failed to predict those COD rejections at permeate fluxes higher than 80 L/hm^2 , in other words, those values reached when exceeding 15 bar of pressure. The P_s and σ values varied in the range of $0.16 \cdot 10^{-6}$ – $1.06 \cdot 10^{-6}$ m/s and $0.04 \cdot 10^{-6}$ – $0.10 \cdot 10^{-6}$ m/s , and 88.79 – 97.61% and 94.07 – 97.87% regarding conductivity and COD, respectively; these parameters being in the order of those found in the literature. On the other hand, the solute transport was shown to be dominated ($\approx 80\%$) by convection when modelling COD rejection, but the diffusion term acquired relevance in the case of conductivity ($\approx 50\%$).

The consideration of concentration polarisation by the film theory explained the maximum rejection observed regarding COD. As a result, the relative error between the observed and predicted rejection was decreased from 3.57 to 1.82% when introducing the mass transfer coefficient as a third fitting parameter. The k values of the CFSK model, which were between 81.5 and 106.5 L/hm^2 , and between 17.2 and 40.9 L/hm^2 for conductivity and COD, respectively, were shown to be in good agreement with those calculated by the CFSK graphical methodology.

References

- [1] C. Bellona, J.E. Drewes, P. Xu, G. Amy, Factors affecting the rejection of organic solutes during NF/RO treatment—a literature review, *Water Research*, 38 (2004) 2795-2809, <http://dx.doi.org/10.1016/j.watres.2004.03.034>.
- [2] H. Mehdizadeh, K. Molaiee-Nejad, Y.C. Chong, Modeling of mass transport of aqueous solutions of multi-solute organics through reverse osmosis membranes in case of solute–membrane affinity: Part 1. Model development and simulation, *Journal of Membrane Science*, 267 (2005) 27-40, <http://dx.doi.org/10.1016/j.memsci.2005.03.059>.
- [3] B. Van der Bruggen, M. Mänttari, M. Nyström, Drawbacks of applying nanofiltration and how to avoid them: A review, *Separation and Purification Technology*, 63 (2008) 251-263, <http://dx.doi.org/10.1016/j.seppur.2008.05.010>.
- [4] M. Soltanieh, W.N. Gill, Review of reverse osmosis membranes and transport models, *Chemical Engineering Communications*, 12 (1981) 279-363, 10.1080/00986448108910843.
- [5] E.A. Mason, H.K. Lonsdale, Statistical-mechanical theory of membrane transport, *Journal of Membrane Science*, 51 (1990) 1-81, [http://dx.doi.org/10.1016/S0376-7388\(00\)80894-7](http://dx.doi.org/10.1016/S0376-7388(00)80894-7).
- [6] J.G. Wijmans, R.W. Baker, The solution-diffusion model: a review, *Journal of Membrane Science*, 107 (1995) 1-21, [http://dx.doi.org/10.1016/0376-7388\(95\)00102-1](http://dx.doi.org/10.1016/0376-7388(95)00102-1).
- [7] N. Hilal, H. Al-Zoubi, N.A. Darwish, A.W. Mohamma, M. Abu Arabi, A comprehensive review of nanofiltration membranes: Treatment, pretreatment, modelling, and atomic force microscopy, *Desalination*, 170 (2004) 281-308, <http://dx.doi.org/10.1016/j.desal.2004.01.007>.
- [8] L. Malaeb, G.M. Ayoub, Reverse osmosis technology for water treatment: State of the art review, *Desalination*, 267 (2011) 1-8, <http://dx.doi.org/10.1016/j.desal.2010.09.001>.
- [9] A.L. Ahmad, M.F. Chong, S. Bhatia, Mathematical modeling and simulation of the multiple solutes system for nanofiltration process, *Journal of Membrane Science*, 253 (2005) 103-115, <http://dx.doi.org/10.1016/j.memsci.2005.01.005>.
- [10] W.R. Bowen, J.S. Welfoot, P.M. Williams, Linearized transport model for nanofiltration: Development and assessment, *AIChE Journal*, 48 (2002) 760-773, 10.1002/aic.690480411.
- [11] A.A. Merdaw, A.O. Sharif, G.A.W. Derwish, Water permeability in polymeric membranes, Part I, *Desalination*, 260 (2010) 180-192, <http://dx.doi.org/10.1016/j.desal.2010.04.042>.
- [12] L. Suárez, M.A. Diez, R. García, F.A. Riera, Recovery of Na₄EDTA from aqueous solutions using nanofiltration, *Separation and Purification Technology*, 118 (2013) 144-150, <http://dx.doi.org/10.1016/j.seppur.2013.06.046>.
- [13] W.S. Ang, S. Lee, M. Elimelech, Chemical and physical aspects of cleaning of organic-fouled reverse osmosis membranes, *Journal of Membrane Science*, 272 (2006) 198-210, <http://dx.doi.org/10.1016/j.memsci.2005.07.035>.
- [14] F.A. Riera, A. Suárez, C. Muro, Nanofiltration of UHT flash cooler condensates from a dairy factory: Characterisation and water reuse potential, *Desalination*, 309 (2013) 52-63, <http://dx.doi.org/10.1016/j.desal.2012.09.016>.
- [15] A. Suárez, T. Fidalgo, M.A. Berdasco, F.A. Riera, UHT Condensate Recovery by Reverse Osmosis: A Pilot-Plant Study, *Industrial & Engineering Chemistry Research*, 53 (2014) 15237-15244, <http://dx.doi.org/10.1021/ie5026166>.
- [16] A. Suárez, T. Fidalgo, F.A. Riera, Recovery of dairy industry wastewaters by reverse osmosis. Production of boiler water, *Separation and Purification Technology*, 133 (2014) 204-211, <http://dx.doi.org/10.1016/j.seppur.2014.06.041>.
- [17] A. Suárez, F.A. Riera, Production of high-quality water by reverse osmosis of milk dairy condensates, *Journal of Industrial and Engineering Chemistry*, 21 (2015) 1340-1349, <http://dx.doi.org/10.1016/j.jiec.2014.06.004>.
- [18] J.M. Ochando-Pulido, S. Rodríguez-Vives, G. Hodaifa, A. Martínez-Ferez, Impacts of operating conditions on reverse osmosis performance of pretreated olive mill wastewater, *Water Research*, 46 (2012) 4621-4632, <http://dx.doi.org/10.1016/j.watres.2012.06.026>.
- [19] K.S. Spiegler, O. Kedem, Thermodynamics of hyperfiltration (reverse osmosis): criteria for efficient membranes, *Desalination*, 1 (1966) 311-326, [http://dx.doi.org/10.1016/S0011-9164\(00\)80018-1](http://dx.doi.org/10.1016/S0011-9164(00)80018-1).
- [20] J. Garcia-Aleman, J. Dickson, A. Mika, Experimental analysis, modeling, and theoretical design of McMaster pore-filled nanofiltration membranes, *Journal of Membrane Science*, 240 (2004) 237-255, <http://dx.doi.org/10.1016/j.memsci.2004.05.009>.

- [21] S. Mandale, M. Jones, Membrane transport theory and the interactions between electrolytes and non-electrolytes, *Desalination*, 252 (2010) 17-26, <http://dx.doi.org/10.1016/j.desal.2009.11.007>.
- [22] S. Jain, S.K. Gupta, Analysis of modified surface force pore flow model with concentration polarization and comparison with Spiegler–Kedem model in reverse osmosis systems, *Journal of Membrane Science*, 232 (2004) 45-62, <http://dx.doi.org/10.1016/j.memsci.2003.11.021>.
- [23] Y. Garba, S. Taha, N. Gondrexon, G. Dorange, Ion transport modelling through nanofiltration membranes, *Journal of Membrane Science*, 160 (1999) 187-200, [http://dx.doi.org/10.1016/S0376-7388\(99\)00085-X](http://dx.doi.org/10.1016/S0376-7388(99)00085-X).
- [24] R. Levenstein, D. Hasson, R. Semiat, Utilization of the Donnan effect for improving electrolyte separation with nanofiltration membranes, *Journal of Membrane Science*, 116 (1996) 77-92, [http://dx.doi.org/10.1016/0376-7388\(96\)00029-4](http://dx.doi.org/10.1016/0376-7388(96)00029-4).
- [25] B. Van der Bruggen, C. Vandecasteele, Modelling of the retention of uncharged molecules with nanofiltration, *Water Research*, 36 (2002) 1360-1368, [http://dx.doi.org/10.1016/S0043-1354\(01\)00318-9](http://dx.doi.org/10.1016/S0043-1354(01)00318-9).
- [26] G. Rice, A.R. Barber, A.J. O'Connor, G.W. Stevens, S.E. Kentish, Rejection of dairy salts by a nanofiltration membrane, *Separation and Purification Technology*, 79 (2011) 92-102, <http://dx.doi.org/10.1016/j.seppur.2011.03.022>.
- [27] C. Bellona, M. Marts, J.E. Drewes, The effect of organic membrane fouling on the properties and rejection characteristics of nanofiltration membranes, *Separation and Purification Technology*, 74 (2010) 44-54, <http://dx.doi.org/10.1016/j.seppur.2010.05.006>.
- [28] O. Kedem, A. Katchalsky, Thermodynamic analysis of the permeability of biological membranes to non-electrolytes, *Biochimica et Biophysica Acta*, 27 (1958) 229-246, [http://dx.doi.org/10.1016/0006-3002\(58\)90330-5](http://dx.doi.org/10.1016/0006-3002(58)90330-5).
- [29] T.N. Shah, Y. Yoon, C.L. Pederson, R.M. Lueptow, Rotating reverse osmosis and spiral wound reverse osmosis filtration: A comparison, *Journal of Membrane Science*, 285 (2006) 353-361, <http://dx.doi.org/10.1016/j.memsci.2006.09.004>.
- [30] T. Chaabane, S. Taha, M. Taleb Ahmed, R. Maachi, G. Dorange, Coupled model of film theory and the Nernst–Planck equation in nanofiltration, *Desalination*, 206 (2007) 424-432, <http://dx.doi.org/10.1016/j.desal.2006.03.577>.
- [31] J. Geens, K. Boussu, C. Vandecasteele, B. Van der Bruggen, Modelling of solute transport in non-aqueous nanofiltration, *Journal of Membrane Science*, 281 (2006) 139-148, <http://dx.doi.org/10.1016/j.memsci.2006.03.028>.
- [32] S. Shirazi, C.-J. Lin, D. Chen, Inorganic fouling of pressure-driven membrane processes – A critical review, *Desalination*, 250 (2010) 236-248, <http://dx.doi.org/10.1016/j.desal.2009.02.056>.
- [33] J. Gilron, N. Gara, O. Kedem, Experimental analysis of negative salt rejection in nanofiltration membranes, *Journal of Membrane Science*, 185 (2001) 223-236, [http://dx.doi.org/10.1016/S0376-7388\(00\)00639-6](http://dx.doi.org/10.1016/S0376-7388(00)00639-6).
- [34] S. Kim, E.M.V. Hoek, Modeling concentration polarization in reverse osmosis processes, *Desalination*, 186 (2005) 111-128, <http://dx.doi.org/10.1016/j.desal.2005.05.017>.
- [35] T. Mohammadi, M. Kazemimoghadam, M. Saadabadi, Modeling of membrane fouling and flux decline in reverse osmosis during separation of oil in water emulsions, *Desalination*, 157 (2003) 369-375, [http://dx.doi.org/10.1016/S0011-9164\(03\)00419-3](http://dx.doi.org/10.1016/S0011-9164(03)00419-3).
- [36] V. Alvarez, S. Alvarez, F.A. Riera, R. Alvarez, Permeate flux prediction in apple juice concentration by reverse osmosis, *Journal of Membrane Science*, 127 (1997) 25-34, [http://dx.doi.org/10.1016/S0376-7388\(96\)00285-2](http://dx.doi.org/10.1016/S0376-7388(96)00285-2).
- [37] E.M.V. Hoek, J. Allred, T. Knoell, B.-H. Jeong, Modeling the effects of fouling on full-scale reverse osmosis processes, *Journal of Membrane Science*, 314 (2008) 33-49, <http://dx.doi.org/10.1016/j.memsci.2008.01.025>.
- [38] S. Lee, C.-H. Lee, Effect of operating conditions on CaSO₄ scale formation mechanism in nanofiltration for water softening, *Water Research*, 34 (2000) 3854-3866, [http://dx.doi.org/10.1016/S0043-1354\(00\)00142-1](http://dx.doi.org/10.1016/S0043-1354(00)00142-1).
- [39] E. Matthiasson, B. Sivik, Concentration polarization and fouling, *Desalination*, 35 (1980) 59-103, [http://dx.doi.org/10.1016/S0011-9164\(00\)88604-X](http://dx.doi.org/10.1016/S0011-9164(00)88604-X).
- [40] I. Sutzkover, D. Hasson, R. Semiat, Simple technique for measuring the concentration polarization level in a reverse osmosis system, *Desalination*, 131 (2000) 117-127, [http://dx.doi.org/10.1016/S0011-9164\(00\)90012-2](http://dx.doi.org/10.1016/S0011-9164(00)90012-2).
- [41] A.L. Ahmad, M.F. Chong, S. Bhatia, Mathematical modeling of multiple solutes system for reverse osmosis process in palm oil mill effluent (POME) treatment, *Chemical Engineering Journal*, 132 (2007) 183-193, <http://dx.doi.org/10.1016/j.cej.2006.12.022>.
- [42] M. Turan, Influence of filtration conditions on the performance of nanofiltration and reverse osmosis membranes in dairy wastewater treatment, *Desalination*, 170 (2004) 83-90, <http://dx.doi.org/10.1016/j.desal.2004.02.094>.

- [43] B. Wendler, B. Goers, G. Wozny, Regeneration of process water containing surfactants by nanofiltration—investigation and modelling of mass transport, *Water Science & Technology*, 46 (2002) 287-292.
- [44] L. Song, M. Elimelech, Theory of concentration polarization in crossflow filtration, *Journal of the Chemical Society, Faraday Transactions*, 91 (1995) 3389-3398, [10.1039/FT9959103389](https://doi.org/10.1039/FT9959103389).
- [45] H.C. van der Horst, J.M.K. Timmer, T. Robbertsen, J. Leenders, Use of nanofiltration for concentration and demineralization in the dairy industry: Model for mass transport, *Journal of Membrane Science*, 104 (1995) 205-218, [http://dx.doi.org/10.1016/0376-7388\(95\)00041-A](http://dx.doi.org/10.1016/0376-7388(95)00041-A).
- [46] D. Van Gauwbergen, J. Baeyens, Modelling reverse osmosis by irreversible thermodynamics, *Separation and Purification Technology*, 13 (1998) 117-128, [http://dx.doi.org/10.1016/S1383-5866\(97\)00065-8](http://dx.doi.org/10.1016/S1383-5866(97)00065-8).
- [47] M. Nyström, L. Kaipia, S. Luque, Fouling and retention of nanofiltration membranes, *Journal of Membrane Science*, 98 (1995) 249-262, [http://dx.doi.org/10.1016/0376-7388\(94\)00196-6](http://dx.doi.org/10.1016/0376-7388(94)00196-6).
- [48] B. Cancino-Madariaga, C.F. Hurtado, R. Ruby, Effect of pressure and pH in ammonium retention for nanofiltration and reverse osmosis membranes to be used in recirculation aquaculture systems (RAS), *Aquacultural Engineering*, 45 (2011) 103-108, <http://dx.doi.org/10.1016/j.aquaeng.2011.08.002>.
- [49] L. Paugam, S. Taha, G. Dorange, P. Jaouen, F. Quéméneur, Mechanism of nitrate ions transfer in nanofiltration depending on pressure, pH, concentration and medium composition, *Journal of Membrane Science*, 231 (2004) 37-46, <http://dx.doi.org/10.1016/j.memsci.2003.11.003>.
- [50] P.-Y. Pontalier, A. Ismail, M. Ghoul, Mechanisms for the selective rejection of solutes in nanofiltration membranes, *Separation and Purification Technology*, 12 (1997) 175-181, [http://dx.doi.org/10.1016/S1383-5866\(97\)00047-6](http://dx.doi.org/10.1016/S1383-5866(97)00047-6).
- [51] P.-Y. Pontalier, A. Ismail, M. Ghoul, Specific model for nanofiltration, *Journal of Food Engineering*, 40 (1999) 145-151, [http://dx.doi.org/10.1016/S0260-8774\(99\)00041-2](http://dx.doi.org/10.1016/S0260-8774(99)00041-2).
- [52] A. Sorin, A. Favre-Réguillon, S. Pellet-Rostaing, M. Sbaï, A. Szymczyk, P. Fievet, M. Lemaire, Rejection of Gd(III) by nanofiltration assisted by complexation on charged organic membrane: Influences of pH, pressure, flux, ionic strength and temperature, *Journal of Membrane Science*, 267 (2005) 41-49, <http://dx.doi.org/10.1016/j.memsci.2005.05.022>.
- [53] A. Dobrak, B. Verrecht, H. Van den Dungen, A. Buekenhoudt, I.F.J. Vankelecom, B. Van der Bruggen, Solvent flux behavior and rejection characteristics of hydrophilic and hydrophobic mesoporous and microporous TiO₂ and ZrO₂ membranes, *Journal of Membrane Science*, 346 (2010) 344-352, <http://dx.doi.org/10.1016/j.memsci.2009.09.059>.
- [54] S. Wadley, C.J. Brouckaert, L.A.D. Baddock, C.A. Buckley, Modelling of nanofiltration applied to the recovery of salt from waste brine at a sugar decolourisation plant, *Journal of Membrane Science*, 102 (1995) 163-175, [http://dx.doi.org/10.1016/0376-7388\(94\)00284-6](http://dx.doi.org/10.1016/0376-7388(94)00284-6).
- [55] C. Mazzoni, S. Bandini, On nanofiltration Desal-5 DK performances with calcium chloride–water solutions, *Separation and Purification Technology*, 52 (2006) 232-240, <http://dx.doi.org/10.1016/j.seppur.2006.04.004>.
- [56] G. Hagemeyer, R. Gimbel, Modelling the salt rejection of nanofiltration membranes for ternary ion mixtures and for single salts at different pH values, *Desalination*, 117 (1998) 247-256, [http://dx.doi.org/10.1016/S0011-9164\(98\)00109-X](http://dx.doi.org/10.1016/S0011-9164(98)00109-X).
- [57] W.R. Bowen, J.S. Welfoot, Modelling the performance of membrane nanofiltration—critical assessment and model development, *Chemical Engineering Science*, 57 (2002) 1121-1137, [http://dx.doi.org/10.1016/S0009-2509\(01\)00413-4](http://dx.doi.org/10.1016/S0009-2509(01)00413-4).
- [58] C. Labbez, P. Fievet, A. Szymczyk, A. Vidonne, A. Foissy, J. Pagetti, Retention of mineral salts by a polyamide nanofiltration membrane, *Separation and Purification Technology*, 30 (2003) 47-55, [http://dx.doi.org/10.1016/S1383-5866\(02\)00107-7](http://dx.doi.org/10.1016/S1383-5866(02)00107-7).
- [59] T. Van Gestel, C. Vandecasteele, A. Buekenhoudt, C. Dotremont, J. Luyten, R. Leysen, B. Van der Bruggen, G. Maes, Salt retention in nanofiltration with multilayer ceramic TiO₂ membranes, *Journal of Membrane Science*, 209 (2002) 379-389, [http://dx.doi.org/10.1016/S0376-7388\(02\)00311-3](http://dx.doi.org/10.1016/S0376-7388(02)00311-3).
- [60] P. Lipp, R. Gimbel, F.H. Frimmel, Parameters influencing the rejection properties of FT30 membranes, *Journal of Membrane Science*, 95 (1994) 185-197, [http://dx.doi.org/10.1016/0376-7388\(94\)00124-3](http://dx.doi.org/10.1016/0376-7388(94)00124-3).
- [61] G. Bargeman, J.M. Vollenbroek, J. Straatsma, C.G.P.H. Schroën, R.M. Boom, Nanofiltration of multi-component feeds. Interactions between neutral and charged components and their effect on retention, *Journal of Membrane Science*, 247 (2005) 11-20, <http://dx.doi.org/10.1016/j.memsci.2004.05.022>.

[62] J. Geens, A. Hillen, B. Bettens, B. Van der Bruggen, C. Vandecasteele, Solute transport in non-aqueous nanofiltration: effect of membrane material, *Journal of Chemical Technology & Biotechnology*, 80 (2005) 1371-1377, [10.1002/jctb.1337](https://doi.org/10.1002/jctb.1337).

[63] T.-U. Kim, J.E. Drewes, R. Scott Summers, G.L. Amy, Solute transport model for trace organic neutral and charged compounds through nanofiltration and reverse osmosis membranes, *Water Research*, 41 (2007) 3977-3988, <http://dx.doi.org/10.1016/j.watres.2007.05.055>.

[64] Z.V.P. Murthy, S.K. Gupta, Sodium cyanide separation and parameter estimation for reverse osmosis thin film composite polyamide membrane, *Journal of Membrane Science*, 154 (1999) 89-103, [http://dx.doi.org/10.1016/S0376-7388\(98\)00280-4](http://dx.doi.org/10.1016/S0376-7388(98)00280-4).

[65] R. Wang, Y. Li, J. Wang, G. You, C. Cai, B.H. Chen, Modeling the permeate flux and rejection of nanofiltration membrane separation with high concentration uncharged aqueous solutions, *Desalination*, 299 (2012) 44-49, <http://dx.doi.org/10.1016/j.desal.2012.05.014>.

Nomenclature

Abbreviations

NF: Nanofiltration

RO: Reverse osmosis

SK: Spiegler–Kedem

CP: Concentration polarization

TFC: Thin film composite

CFSK: Film theory–Spiegler–Kedem

FC: Flash cooler

UHT: Ultra high temperature

COD: Chemical oxygen demand

SDI: Silt density index

BF: Bag filter

F: Prefilter

TK: Tank

PV: Pressure vessel

P: Pump

FD: Flow detector

V: Valve

PI: Pressure indicator

FI: Flow meter

TI: Temperature indicator

HX: Heat exchanger

VCR: Volume concentration ratio

CFSD: Film theory–solution–diffusion

Symbols

ΔP : Transmembrane pressure

dC/dx : Concentration gradient

P_s : Solute permeability

σ : Reflection coefficient

J_s : Solute flux

C : Solute concentration

J_v : Permeate flux

L_p : Membrane permeability

$\Delta\pi$: Osmotic pressure

Δx : Membrane thickness

C_m : Membrane surface concentration

C_f : Feed concentration

R_{est} : Estimated rejection

δ : Polarization layer thickness

C_p : Permeate concentration

D : Diffusivity

k : Mass transfer coefficient

R_{obs} : Observed rejection

V_f : Feed volume

V_c : Concentrate volume

V_p : Permeate volume

$J_{convective}$: Convective flux

$J_{diffusive}$: Diffusive flux

C_m : Log mean average concentration

Conclusiones particulares del apartado 4.3.

El modelo de *film theory–Spiegler–Kedem* demostró ser más ventajoso desde el punto de vista de la precisión en la predicción de rechazos al ser el error cometido entre el valor teórico y el experimental inferior al obtenido mediante el modelo de *Spiegler–Kedem* (1,82% vs. 3,57%). La consideración del fenómeno de polarización por concentración permitió explicar los máximos valores de rechazo observados en la práctica. Sin embargo, el modelo de *Spiegler–Kedem* falló en las predicciones a presiones por encima de 15 bar, principalmente en relación a la materia orgánica, cuyo transporte demostró estar gobernado por la convección (70,36–86,70%). Por su parte, la difusión, que en teoría es un fenómeno más característico de un proceso de filtración por ósmosis inversa, sólo adquirió relevancia suficiente en el transporte de material inorgánico, donde su porcentaje de influencia se situó en torno al 50%.

La recomendación de trabajo para éste tipo de membranas en cuanto al flujo de permeado para una operación en continuo es de fijar la producción en torno a 40 L/hm² estables, trabajando a presión creciente. Para este valor, las predicciones de rechazos del modelo de *film theory–Spiegler–Kedem* entre el mínimo (1) y el máximo (10) factor de concentración de volumen se situarían entre el 84 y el 97% para la conductividad, respectivamente, y alrededor del 98%, en ambos casos, para la demanda química de oxígeno, lo que correspondería con una buena calidad de permeado incluso a altas tasas de recuperación de agua.

4.4. Estudio en continuo de la operación de ósmosis inversa utilizando carbón activo como post-tratamiento

Los resultados obtenidos en discontinuo con la membrana seleccionada, aunque satisfactorios, necesitan de confirmación mediante experimentación en continuo. La información resultante permitiría validar técnicamente la aplicación y sentaría las bases para una estimación económica completa. Los parámetros de procesado fueron fijados en relación a las recomendaciones del fabricante para una operación en continuo y en base a los resultados obtenidos en el pilotaje en discontinuo, siendo la alimentación bombeada a 1000 L/h (al utilizar una única membrana de 8,2 m²) y a temperaturas inferiores a 50°C, aunque suficientemente elevadas para una buena recuperación energética, el flujo de permeado fijado a 40 L/hm² y la presión creciente hasta un límite de corte para limpieza de 30 bar. Aunque un grado de recuperación del 90% resultó ser un compromiso óptimo entre ahorro y calidad, esto necesitó de una validación/comprobación en semi-continuo con el objetivo de fijar el valor definitivo para los ensayos continuos de larga duración. Como parte de este proceso se incluyó una etapa final de tratamiento por carbón activo con el propósito de asegurar el límite máximo de materia orgánica establecido para la aplicación considerada. Por otro lado, es de importancia determinar si las predicciones teóricas previamente realizadas se cumplen, a pesar de que los modelos teóricos utilizados no tienen en cuenta fenómenos de ensuciamiento característicos de operaciones continuas de larga duración, como es el caso, que podrían condicionar la selectividad de la membrana. Tanto la metodología de trabajo como los resultados obtenidos en los experimentos realizados en continuo se muestran en la publicación:

UHT condensate recovery by reverse osmosis: A pilot-plant study

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UHT Condensate Recovery by Reverse Osmosis: A Pilot-Plant Study

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ABSTRACT: Real ultrahigh-temperature (UHT) flash cooler (FC) condensates obtained in the dairy industry were processed in situ using a reverse-osmosis (RO) membrane (Duratherm HWS 4040 HR; 8.2 m² filtration area). Semicontinuous trials were performed to estimate the maximum volume concentration rate (VCR) that fulfils the permeate specifications for reuse as boiler water. Then, long-term continuous experiments (100 h in duration) were carried out at a constant permeate flow rate (40 L h⁻¹ m⁻²), and the conductivity, chemical oxygen demand (COD), pH, and Ca²⁺ concentration were monitored. An activated carbon column (ACC) was used to reduce the organic charge of the permeate.

1. INTRODUCTION

The food industry is one of the most extensive water-using industries,¹ and the dairy industry can be considered one of the most polluting because of its high water consumption (up to 10 L of water per liter of processed milk) and its status as the largest producer of food processing wastewater.^{2,3} These dairy wastewaters are characterized by wide fluctuations in pollutant charge and flow rate.^{4,5} In most cases, wastewaters generated in different individual operations are mixed and neutralized prior to discharge into the municipal sewage system; however, it seems that segregating streams would enable optimal treatment for each type of wastewater, as well as energy and cost savings.^{6,7}

Because of this extensive water consumption; stricter pollution control legislation regarding waste disposal; growing concerns for sustainable development; and the need for a safe, reliable, and affordable supply of quality water, interest in developing a zero-discharge process has gained relevance, and the practice of reconditioning, recycling, and reusing water is becoming an objective of study and research.^{8–12} In this scenario, membrane processes are useful technologies in wastewater reclamation and reuse and are currently well integrated in the dairy industry, as the decreasing costs of installation and operation in continuous processing favor their use.^{13–16} More specifically, reverse osmosis (RO) has been found to be a promising separation technique for the treatment of dairy wastewaters.^{2,11,17–24}

Ultrahigh-temperature (UHT) treatment of milk and milk-based products involves a heating process that ensures a sterile product with a shelf life at room temperature of at least 6 months, while minimizing cooked flavors.^{25,26} A typical UHT treatment consists of treatment at 140 °C for 4 s,²⁶ which could be achieved by direct or indirect heating. The benefit of the direct process lies in higher rates of heat transfer and lower changes in taste compared to the indirect process.²⁷ In direct steam injection (DSI) contact, the product is preheated and pressurized to approximately 4 bar, in order to prevent boiling of the liquid. After passing through the holding tube, the product is flash-cooled, homogenized, cooled again, and aseptically packaged.²⁸ The flash cooling takes place in an expansion chamber, known as the flash cooler (FC), which operates under a partial vacuum, obtained using a vacuum

pump, where the pressure is controlled to restore the product's original dry matter.²⁹ Flash cooling also permits the removal of some volatile compounds.³⁰ As the FC operates at the liquid boiling point, when the pressure drops, some milk droplets could be entrained in the vapor phase, contributing to an increase in the pollution load of the condensates.

In the dairy company considered in this work as a case study, the vapor from the FCs is used to preheat the dairy product to be processed and subsequently condensed and collected after the vacuum pump. This rotary volumetric pump uses tap water as an auxiliary liquid that is mixed with the condensates to generate the vacuum. As a consequence, the feed wastewater used in the present work is a mixture of condensates from the FCs and tap water used in the vacuum pump. This effluent can be considered to have a low pollutant load.^{21,31}

The amount of tap water used in the vacuum pump determines, to some extent, the characteristics of the stream that feeds the RO process. In general, a higher degree of vacuum requires greater consumption of tap water, which causes two effects: an increase in the pollution load (at a higher degree of vacuum, more milk drops pass into the vapor) and a dilution effect.

Among all possibilities for water reuse, including drinking-water standards, the most restrictive specifications are given by boiler-water usage [pH 7–10, conductivity at 25 °C < 40.0 μS/cm, chemical oxygen demand (COD) < 10 mg of O₂/L, total organic carbon (TOC) < 4 mg of O₂/L, Ca²⁺ concentration < 0.40 mg/L].^{32,33} These parameters must be guaranteed to improve the efficiency and service lifetime of the boiler; control the blow-down frequency; and avoid potential scaling, corrosion, and formation of foams.

The aim of this study was to evaluate the effectiveness of an RO continuous pilot process at a moderate temperature to obtain high-quality water for boiler reuse from real dairy condensates of a UHT vacuum system. Preliminary tests were performed in semicontinuous mode to determine the optimum volume concentration rate (VCR) for long-term processing. An

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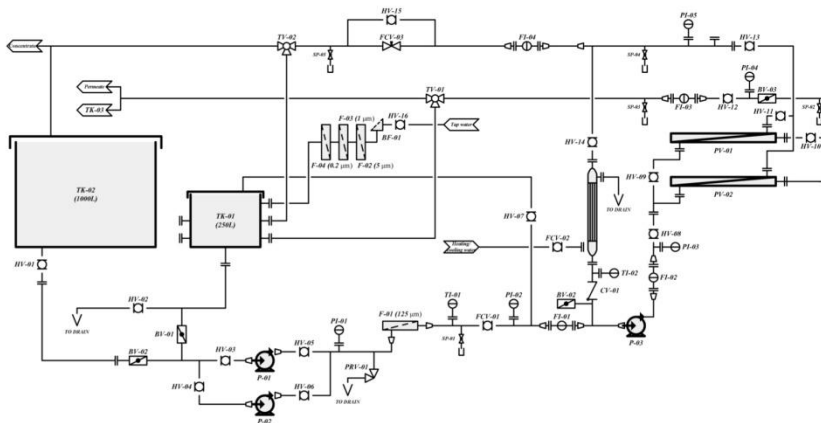


Figure 1. Scheme of the RO equipment.

activated carbon column (ACC) was coupled after the RO step to correct the limit on organic matter in the final permeate.

2. MATERIALS AND METHODS

2.1. Flash Cooler Performance. In the Spanish factory where the trials were carried out, four FCs operate simultaneously but at different stages of the production cycle. When working at the same time, they generate $\sim 20 \text{ m}^3$ of condensates per hour with different pollution loads.

The UHT system works in a cyclic manner, although some steps can vary depending on production needs or breakdowns. Aseptic intermediate cleanings (AICs), consisting of the use of an alkaline-based detergent with two intermediate rinsing steps, are performed routinely. In the same way, depending on the variability of the production schedule, a final cleaning (alkaline and acid) is carried out. On the other hand, when the aseptic bottle-filling step cannot handle the production rate, the product is sent to an aseptic tank; when this tank becomes full, the system starts to work with sterile water until the aseptic packaging system can again allow product to enter.

Condensates are continuously produced during the cycle (even when the equipment is loaded with sterile water), except when final cleaning is performed. As a result, their characteristics are highly dependent on the instant in the cycle; for example, condensates collected during the intermediate cleaning show high pH, whereas those accumulated during the start of or after the AICs are more concentrated and have a higher organic load, and those occurring when sterile water is circulating have low pollution levels. Finally, the type of product sterilized (milk, shakes, etc.) and the sterilization parameters also have some influence on the condensate characteristics.

2.2. Analytical Methods. In this work, pH (accuracy ± 0.05), electrical conductivity (accuracy $\pm 0.5\%$), and COD (accuracy $\pm 3 \text{ mg of O}_2/\text{L}$) were measured continuously, whereas residual hardness, expressed as Ca^{2+} concentration (accuracy $\pm 0.10 \text{ mg/L}$), was analyzed occasionally. pH and electrical conductivity were measured by means of an HQ40d multimeter (Hach Lange, Mechelen, Belgium). Spectrophotometric measurements of COD (in which samples were oxidized with a hot sulfuric solution of potassium dichromate using silver

sulfate as the catalyst and Cr^{3+} ions were then determined photometrically at 605 nm) and residual hardness (in which calcium and magnesium ions were reacted with phthalein purple in alkaline solution to form a violet colorant that was determined photometrically at 565 nm) were carried out by means of Spectroquant cell test kits (Merck, Darmstadt, Germany) using a NOVA 60 photometer (Merck, Darmstadt, Germany).

2.3. Reverse-Osmosis Pilot Plant. A scheme of the membrane pilot plant is shown in Figure 1. Although the plant had the capacity for two in-parallel 4040 spiral-wound membranes, only one was used, and the other pressure vessel was kept closed. Tank TK-01 was used exclusively for cleaning purposes, and an additional external 1000-L capacity tank (TK-02) was available to collect the condensates from the FC vacuum system. The RO rig was fed using two consecutive pumps [P-02 and P-03, 7.5 and 2.2 kW, respectively (Grundfos, Bjerringbro, Denmark)]. A $125\text{-}\mu\text{m}$ prefilter (F-01) was installed to remove coarse particles that could damage these pumps and the membrane. The pressure and feed flow rate were fixed by regulating a needle valve (FCV-03) placed on the retentate side. Transmembrane pressure (TMP) was controlled by means of manometers PI-03 and PI-05, whereas the feed, permeate, and concentrate fluxes were measured by flow meters FI-01, FI-03, and FI-04, respectively. Finally, to maintain low water silt density index (SDI) values (<3)³⁴ for the rinsing and cleaning steps, a prefiltration system consisting of a bag filter and 5-, 1-, and $0.2\text{-}\mu\text{m}$ cartridge prefiltration was used.

2.4. Membrane. A spiral-wound thin-film (proprietary composite) RO Duratherm HWS 4040 HR membrane (GE Water & Process Technologies, Trevose, PA) was selected on the basis of the recommendation of the membrane manufacturer to treat the type of effluent studied. The specific membrane properties are listed in Table 1. The maximum TMP and permeate flow rate (J) were set to 30 bar and $40 \text{ L h}^{-1} \text{ m}^{-2}$, respectively, according to the manufacturer.

The cleaning protocol followed was suggested by a detergent manufacturer (Diversey, Utrecht, The Netherlands) according to the characteristics of the wastewater processed. Standard membrane cleanings consisted of acid (Divos 2, pH 1.9–2.1, 20 min, 45°C) and alkaline (Divos 123, pH 11.0–11.5, 45 min, 45°C) steps with intermediate water rinsings. However, only

Table 1. Main Membrane Characteristics

RO Duratherm HWS 4040 HR	
average salt rejection ^a (%)	99.5
active area (m ²)	8.2
spacer thickness (mil)	31
maximum operating pressure (bar)	
5–50 °C	41.4
51–70 °C	20.7
maximum operating temperature (°C)	70
maximum cleaning temperature (°C)	50
pH operating range	4.0–11.0
pH cleaning range	2.0–11.5

^aTesting conditions: 2000 mg/L NaCl solution at 15.5 bar operating pressure, 25 °C, and pH 7.5.

alkaline cleaning was carried out when intermediate cleanings were required. To avoid microbiological growth, the membrane was stored between runs in acid solution (Divos 2 at pH 3.0–4.0). The flux recovery was evaluated to determine the cleaning efficiency by measuring *J* at an inlet pressure of 10 bar, a feed flow rate of 1 m³/h, and a temperature of approximately 15 °C with prefiltered tap water (SDI < 3).

2.5. Operating Procedure. Trials were carried out in two different modes of operation. In the first mode, after the 1000-L feed tank had been filled, semicontinuous operation of the plant was started, with the permeate being drained and the concentrate returned to the feed tank until the desired VCR was reached. Once this degree of concentration was achieved, the permeate stream was sent back to the feed tank, and the system began to run in a discontinuous closed loop for several hours. The VCR was estimated as

$$VCR = \frac{V_f}{V_r} = \frac{V_f}{V_f - V_p} \tag{1}$$

where *V_f*, *V_r*, and *V_p* are the feed, retentate, and permeate volumes, respectively. The concentration tests in semicontinuous mode were performed at VCRs of 2, 6, and 10.

Regarding the VCR, the recovery rate (RR), defined as

$$RR (\%) = \frac{VCR - 1}{VCR} \times 100 \tag{2}$$

is an essential parameter for determining the size and economy of a large-scale membrane installation.

In the second part of the work, the rig was operated in continuous mode. The degree of concentration in the feed tank was maintained by regulating the entrance of fresh feed and controlling the amount of concentrate returned to the rig. The surplus concentrate stream was drained out to the factory's sewage system. On the other hand, the permeate stream was continuously drained out. To verify the desired VCR, the conductivity inside the feed tank was continuously measured.

When working in continuous mode, a model FCA-355 activated carbon column (ACC; Sefiltra S.A., Madrid, Spain) with 110-L capacity was coupled to the permeate outlet to reduce the organic matter content (RO-ACC). This ACC, made of polyester reinforced with fiberglass and having a capacity of 1800 L/h, was filled with 50 kg of GAC MG 1050 activated carbon (density ≈ 0.45 g/cm³) (Sefiltra S.A., Madrid, Spain).

In both semicontinuous and continuous trials, a cooler was used to regulate the inlet temperature, which was fixed at approximately 45 °C in all tests. The feed flow rate was

maintained at 1000 L/h [with the cross-flow velocity (CFV) estimated to be 0.35 m/s], the permeate flow rate was fixed at 40 L h⁻¹ m⁻², and the system was run at increasing TMP to compensate for fouling. Feed and permeate characteristics such as temperature, TMP, feed flow rate, and permeate flow rate (*J*) were continuously recorded, as was the membrane rejection (or reduction) (*R*) in terms of conductivity and COD, which can be calculated by means of the equation

$$R (\%) = \left(1 - \frac{C_p}{C_f} \right) \times 100 \tag{3}$$

where *C_p* and *C_f* are the permeate and feed (concentrated) values, respectively, of both parameters considered.

3. RESULTS AND DISCUSSION

3.1. Flash Cooler Performance and Condensate Characterization. A complete characterization of the condensates used in this work was previously published by Riera et al.⁴ The values correspond to samples taken during several complete operating cycles of the FCs (eight cycles per FC), and their variability reflects the different steps explained before. The compositions of fresh condensates (and condensates at a VCR of 6) are presented in Table 2. As can be

Table 2. Compositions of Initial and Concentrated Feed Condensates for RO Processing

parameter	initial value range	average	concentration value range ^a	average
<i>T</i> (°C)	40.5–59.9	50.2	–	–
pH	5.31–6.49	5.83	6.34–8.24	7.14
conductivity (μS/cm)	76.1–245.0	184.1	447.0–1017.0	728.2
COD (mg of O ₂ /L)	4–240	70	30–360	153
TOC (mg of O ₂ /L)	–	–	32.1–85.4	56.8
Ca ²⁺ concentration (mg/L)	–	–	1.22–2.38	1.67

^aAt VCR 6 for continuous processing.

seen, the condensates, before and after any previous concentration, did not fulfill the requirements for boiler water (pH 7–10, conductivity at 25 °C < 40.0 μS/cm, COD < 10 mg of O₂/L, TOC < 4 mg of O₂/L, Ca²⁺ concentration < 0.40 mg/L),^{32,33} so its treatment by RO was justified.

The characteristics of the fresh condensates are in agreement with those reported by Chmiel et al.,³⁵ slightly higher than those published by Mavrov and Bélières,²¹ and well above those described by Verheyen et al.^{36,37} for steam condensates in the dairy industry. Detailed analyses of condensates from UHT FCs are scarce, although odors due to thermal treatment and produced by the presence of volatile compounds from milk fat and some protein degradation have previously been reported. However, in-depth analyses of these compounds are available. Some major organic compounds found in previous research suggested that acetone, ethanol, acetoin, dimethylsulfide, diacetyl, and so on are mainly responsible for organic matter and odors.^{23,38–40}

3.2. Reverse-Osmosis Treatment. 3.2.1. Semicontinuous Trials. The RO membrane was characterized using prefiltered tap water with an SDI of <3.³⁴ The membrane permeability at a feed flow rate of 1000 L/h, temperature of 40 °C, and TMP of

4–19 bar was calculated to be $5.7 \text{ L h}^{-1} \text{ m}^{-2} \text{ bar}^{-1}$. After the temperature correction, the calculated value, $0.143 \text{ L h}^{-1} \text{ m}^{-2} \text{ bar}^{-1} \text{ } ^\circ\text{C}^{-1}$, was comparable to those published by other authors who used RO for dairy wastewater processing.^{2,17,19,20}

The water recovery capacity, that is, the amount of permeate recovered as a percentage of the volume of condensates fed, determines the size of a large-scale membrane installation and is dependent on the VCR. RO plants are designed in stages, and membranes face the highest concentration in the final stages. As the feed concentration increases, the permeate flow rate is reduced, the quality of the permeate is poorer, and the membrane cleaning frequency increases.⁴¹ For this reason, the maximum VCR (or RR) at which the permeate satisfies the requirements must be estimated.

Semicontinuous trials were performed to determine the behavior of the RO membrane at different VCRs, for experiments that were 12 h in duration. The trials were carried out at a constant feed flow rate of 1000 L/h and a fixed permeate flow rate of $40 \text{ L h}^{-1} \text{ m}^{-2}$, which was the value recommended by the membrane manufacturer. The TMP was increased during the experiments to compensate for the permeate flux decay due to polarization concentration and fouling. The temperature was maintained at an average of $45.2 \pm 1.7 \text{ } ^\circ\text{C}$ by using a cooler, as the condensates come from FCs at temperatures between 47.8 to $55.1 \text{ } ^\circ\text{C}$.

The permeate and feed conductivities and their R values are plotted for VCRs of 2, 6, and 10 in Figure 2 (the conductivity

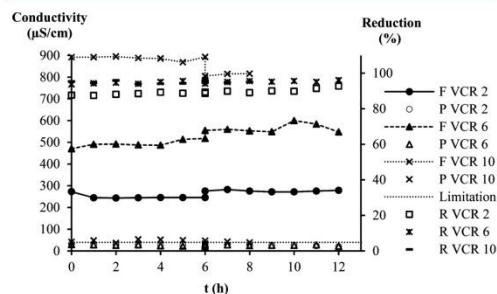


Figure 2. Semicontinuous RO. Feed (F) and permeate (P) conductivities ($\mu\text{S}/\text{cm}$) and conductivity reduction (R , %) at different operating VCRs. Boiler-water limit = $40.0 \mu\text{S}/\text{cm}$.

requirement for boiler water is represented by the horizontal dotted line at $40 \mu\text{S}/\text{cm}$). The experiments were conducted on different days, with different condensate characteristics, which explains the discontinuity in conductivity observed at 6 h. The R value for conductivity remained almost constant after 12 working hours, and the average values were estimated to be 89.5%, 95.0%, and 95.0% for VCRs of 2, 6, and 10, respectively; this means that the conductivity R value increased slightly with increasing VCR. At higher VCR, the difference in solute concentration across the two sides of the membrane increased, and as a result, the reduction increased as well (see eq 3).⁴² The permeate conductivity varied from 20.3 to $53.5 \mu\text{S}/\text{cm}$.

The conductivity requirements were satisfied (permeate values were lower than $30 \mu\text{S}/\text{cm}$ in most cases) at VCRs of 2 and 6. However, the limit was exceeded at a VCR of 10, reaching permeate values up to $53.5 \mu\text{S}/\text{cm}$; for this reason, the trial was stopped after 8 h.

The evolutions of the TMP and COD were also studied as functions of time at the three VCRs tested (2, 6 and 10) (data not shown). The greater the VCR, the higher the pressure required to reach the same permeate flow rate, as the increase in the concentration of solutes had a negative impact on the performance of the process;⁴¹ however, the difference was not significant (TMP increased from 8.1 to 10.1 bar as VCR was increased from 2 and 10). During these experiments, the TMP remained constant, and fouling effects were not observed.

Irrespective of the VCR, the permeate exhibited COD values between 0 and $14 \text{ mg of O}_2/\text{L}$, which exceeded the limit for boiler-water reuse ($10 \text{ mg of O}_2/\text{L}$) in some cases. These results suggest the need to install an ACC to treat the RO permeate.

Considering that the permeate conductivities at a VCR of 10 exceeded the requirements for boiler water, continuous trials were designed at a VCR of 6, which means an RR value of 83.3% of the water fed.

3.2.2. Continuous Trials. Continuous 100-h long-term trials were performed at a constant VCR of 6 to simulate the last stages of an industrial RO installation. Such tests provide information about the membrane behavior in terms of rejection and fouling frequency. When the industrial UHT sterilization system was undergoing cleaning and no other FC was producing condensates, the RO pilot plant worked with condensates that had been previously accumulated in the 1000-L feed tank, which remained at a VCR of 6; during this period, both the permeate and the concentrate were sent back to the tank. The ACC coupled to the permeate line was not used when the permeate and concentrate were recirculated. The experiment was performed at a feed flow rate of 1000 L/h, a constant permeate flow rate of $40 \text{ L h}^{-1} \text{ m}^{-2}$, and an increasing pressure to compensate for the flux decay. The feed temperature was maintained at an average of $44.9 \pm 3.3 \text{ } ^\circ\text{C}$.

Figure 3 shows some of the results of the long-term continuous experiment, where the temperature, TMP, con-

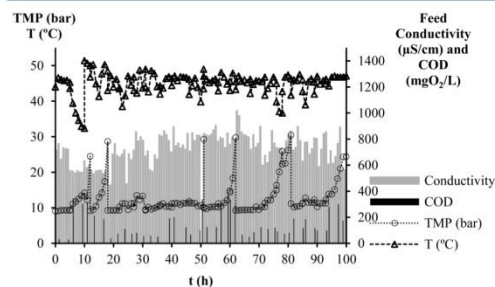


Figure 3. Long-term continuous RO-ACC test. Conditions: Constant permeate flow rate ($f = 40 \text{ L h}^{-1} \text{ m}^{-2}$), feed flow rate = 1000 L/h (CFV = 0.35 m/s). TMP (bar) and temperature (T , $^\circ\text{C}$) vs time at a VCR of 6 and as functions of feed conductivity ($\mu\text{S}/\text{cm}$) and COD ($\text{mg of O}_2/\text{L}$).

ductivity, and COD of the condensates fed are plotted as functions of time. The temperature variability during the first part of the experiment (first 10 h) was due to the mode of operation. During the periods in which the system was working in recirculation mode (see 6–10 h, 23 h, 49–51 h, etc.), the temperature control was difficult, and a drop in temperature was recorded. During these periods, the membrane perme-

ability was lower because of an increase in fluid viscosity and a decrease of diffusivity; then, an increase in TMP was necessary to maintain a permeate flow rate of $40 \text{ L h}^{-1} \text{ m}^{-2}$. Except in the situations described above, the average temperature was $45 \text{ }^\circ\text{C}$, with the loss of temperature inside the equipment estimated to be $2.5 \text{ }^\circ\text{C}$ by comparing the inlet and RO-ACC outlet temperatures.

The evolution of TMP in Figure 3 provides information about membrane fouling. Each time the rig reached the maximum TMP (30 bar), an alkaline cleaning step was performed. Further, complete (alkaline- and acid-based) cleaning was carried out each weekend to avoid microbiological growth during the weekend shutdowns (the UHT system was stopped on weekends as well). During the entire continuous test, seven complete cleanings and three alkaline cleanings were performed. The original membrane permeate flow rate was recovered after both cleaning protocols.

The COD values in Figure 3 (black columns) demonstrate the heterogeneity of the inlet condensates, with values from 30 to $360 \text{ mg of O}_2/\text{L}$, corresponding to the original values (at a VCR of 1) of 4 and $117 \text{ mg of O}_2/\text{L}$, respectively. After 12, 18, 51, 62, and 81 h of operation, the maximum TMP was reached. However, the pressure peaks at 12, 18, 51, and 62 h were due to a momentary increase in concentrated feed COD (black bars). COD values higher than approximately $300 \text{ mg of O}_2/\text{L}$ caused a very rapid increase in TMP. On the contrary, when COD remained low (as in the period from 67 to 81 h), the increase in TMP was slower, and the membrane worked for 14 h without any cleaning or rinsing step.

Values of concentrated feed conductivity during the test were approximately $728 \pm 113 \text{ } \mu\text{S}/\text{cm}$. Conductivity did not show any influence on fouling as, in general, there was neither significant heterogeneity nor momentary peaks of high conductivity.

In Figure 4, the conductivity and COD values of the permeate before and after ACC treatment, as well as the reductions of these two parameters, are plotted as functions of time. As expected, the differences in conductivity before and after ACC were negligible (Figure 4a), and only some permeate samples showed values higher than the limit. Conductivity RO-ACC reductions were between 90.1% and 98.3% (average = 95.4%) and remained almost constant throughout the tests.

It has been well demonstrated that fouling affects membrane selectivity and that a rise in pressure both increases the hydraulic resistance of the membrane and decreases the membrane selectivity.⁴³ This behavior was observed from 76 to 81 h, when the permeate quality in terms of conductivity worsened as the TMP increased. As a result, the RO-ACC outlet conductivity changed from 18.6 to $47.1 \text{ } \mu\text{S}/\text{cm}$, and the reduction decreased from 97.5% to 94.4%. This behavior was also observed in the last part of the tests, from 90 h onward, although it is difficult to determine whether this stepwise increase was related to the previous statement or was influenced by the observed rise in feed conductivity, given that, although the permeate conductivity increased from 22.8 to $39.2 \text{ } \mu\text{S}/\text{cm}$, the decrease in reduction was negligible (0.5%).

With respect to the COD (Figure 4b), permeates showed significant differences with time due to the variability of the feed characteristics. (In Figure 4, if a permeate or an ACC vertical bar does not appear for a given feed, this means that the value reached was $0 \text{ mg of O}_2/\text{L}$.) In most cases, high COD values corresponded to momentary inlets of highly polluted organic matter, where the concentrated feed reached values

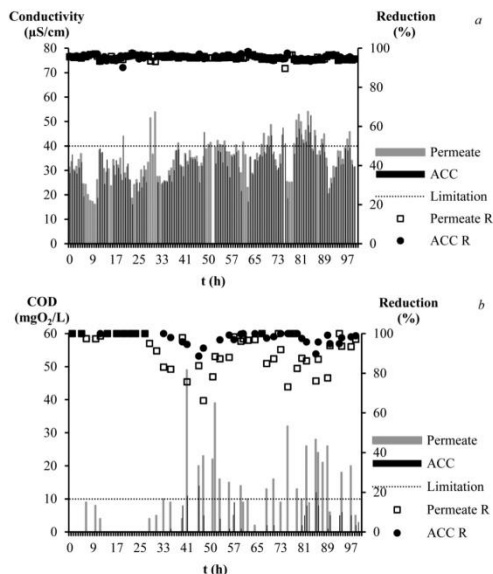


Figure 4. Long-term continuous RO-ACC processing. Conditions: Constant permeate flow rate ($J = 40 \text{ L h}^{-1} \text{ m}^{-2}$), feed flow rate = 1000 L/h ($\text{CFV} = 0.35 \text{ m/s}$), temperature = $44.9 \pm 3.3 \text{ }^\circ\text{C}$. (a) Conductivity ($\mu\text{S}/\text{cm}$) and reduction ($R, \%$) and (b) COD ($\text{mg of O}_2/\text{L}$) and reduction ($R, \%$) at a VCR of 6 of permeate and after activated carbon (ACC) treatment.

between 185 and $360 \text{ mg of O}_2/\text{L}$, which are far from the average COD for concentrated feed, estimated to be $85 \text{ mg of O}_2/\text{L}$. As a result, these fleeting high feed CODs or the combination of various consecutive high values were strongly associated with the fouling observed and, thus, with the rapid increase in TMP. Regarding the nature of the fouling observed, it has been demonstrated that inorganic fouling is negligible at working pH values (neutral to alkaline), as soluble calcium, which appears to be the main promoter of inorganic fouling, is complexed with phosphate and citrate at these pH values.⁴⁴ On the other hand, organic fouling, mainly caused by proteins, is the major factor responsible for membrane fouling in dairy applications.^{3,22,45} However, the TMP peak at 81 h was not due to an increase in the organic load of the feed. In that case, the membrane was run for 14 h without cleaning.

There were several significant drops in the COD reduction of the RO permeate that matched the fouling periods corresponding to peaks at 51 and 81 h. As reported by Brans et al.,⁴⁶ the fouling and increase in associated pressure reduced the selectivity of the membrane, leading to a lower permeate quality in terms of organic matter. Furthermore, in some cases, the decreases in COD reduction corresponded to peaks in feed COD, such as that at 41 h, where the R value was reduced by up to 75.6%, which matched with a momentary COD inlet of $201 \text{ mg of O}_2/\text{L}$. Figure 4b demonstrates the inability of RO membranes to completely remove the organic matter, as stated by Bódalo-Santoyo et al.,⁴⁷ who showed the limited ability of RO to reject low-molecular-weight organic compounds. On the other hand, the effectiveness of the ACC in reducing the organic charge of permeates is well demonstrated in the figure.

The maximum COD reduction achieved after the RO–ACC process was 100.0%, although the average was established as 97.9%.

During the continuous trial, 25.9 m³ of permeate was fed into the ACC. No information was found with respect to the maximum organic load for the commercial column used, as it is highly dependent on the contaminant type, the characteristics of the effluent, the feed concentration, and the type of activated carbon.⁴⁸ The average COD removal of the ACC was calculated to be 76.8% by comparing the concentrations of the inlet (RO permeate) and outlet streams. The total organic load supported was 0.0057 kg of COD per kilogram of activated carbon. At this rate, the breakthrough for this particular case, defined as the point at which the COD in the RO–ACC outlet stream continuously exceeded the limit required and, therefore, the ACC exhaustion point, was not reached. The ACC required some maintenance during the trials: retro-washing with tap water at high flow rate was performed weekly. In the case of reaching irreversible saturation, the activated carbon should be regenerated in an oven or completely removed and replaced.

The average conductivity and COD of the RO–ACC outlet stream were 33.3 $\mu\text{S}/\text{cm}$ and 3 mg of O₂/L, respectively. Some samples reached maximum values of 52.6 $\mu\text{S}/\text{cm}$ and 14 mg of O₂/L, respectively. Although these values were above the restriction, the permeate obtained in an industrial plant will be diluted before entering the boiler. Permeates obtained in RO steps with high VCRs and those from low VCRs (with better permeate quality) will be mixed in the final current^{49,50} and the RO–ACC outlet stream will be mixed with fresh demineralized water to satisfy the current necessity of the factory. This behavior could also be applied to Ca²⁺, which showed values of up to 0.67 mg/L, even though the average, 0.36 mg/L, was located below the limit (0.40 mg/L).

The heterogeneity in organic matter found when processing wastewaters from the vacuum system of the UHT sterilization process by RO advised that possible momentary high-organic-load streams should be controlled and segregated to reduce the cleaning frequency and avoid unexpected rapid periods of fouling. If this segregation is not taken into account, the membrane behavior is not easily predictable and intermediate cleanings would take place when necessary, reducing the economic interest of the application.

Finally, the pH performance during the continuous test as a function of time for the concentrated feed, the permeate, and the ACC output stream are shown in Figure 5. The feed pH values (at a VCR of 1) varied between 5.3 and 6.9, and those for the concentrated feed (at a VCR of 6) showed values between 6.3 and 8.2. In the figure, some pH drops (clearly observed after 18, 40, 51, 78, and 93 h) can be noted due to the variability in the inlet waters (as a function of the degree of vacuum, the timing in the FC cycle, the product treated, and the sterilization parameters of the UHT system) for different working days. Permeate acidification with respect to the feed was previously observed by Suárez and Riera,⁴² and it was attributed to the membrane and feed characteristics. The permeate was acidified, generally always to the same extent (it was reduced in all cases by 1.9 ± 0.2 pH units), as a result of electrostatic repulsion/attraction effects between the solutes and the membrane surface, which is negatively charged at working pH values, as are most RO membranes,⁵¹ promoting the favorable passage of H⁺ ions.⁵² The acidification observed is common in RO wastewater processing.^{53–55} Organic or

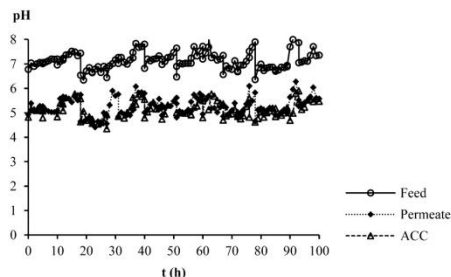


Figure 5. Long-term continuous RO–ACC processing. pH evolution with time of feed and permeate and after activated carbon (ACC) treatment. Conditions: Constant permeate flow rate ($J = 40 \text{ L h}^{-1} \text{ m}^{-2}$), feed flow rate = 1000 L/h (CFV = 0.35 m/s).

inorganic compounds adsorbed on the membrane surface can influence its charge.⁵⁶ In these experiments, there was no evidence of this effect, as the pH of the permeate remained practically constant (5.3 ± 0.4). No significant differences were found between pH samples before and after the ACC.

When permeate pH values were outside the range required for boiler-water reuse (7–10), then some treatments, such as degassing steps to reduce the content of CO₂, or the addition of alkalizing or antiscalant/antifouling chemicals, should be taken into consideration as a final step before the reuse of permeates as boiler waters.

4. CONCLUSIONS

The main difficulties when treating real UHT condensates in the dairy industry are related to the heterogeneity of the feed in terms of conductivity and, especially, COD. The conductivities of concentrated condensates treated when working in continuous mode (at a VCR of 6) varied between 447 and 1017 $\mu\text{S}/\text{cm}$ (average = 728 $\mu\text{S}/\text{cm}$), and the reduction obtained was between 90.1% and 98.3% (average = 95.4%). In general, the permeate conductivities were lower than the fixed limit (40 $\mu\text{S}/\text{cm}$). Momentary values higher than the boiler-water requirement were obtained when the membrane was fouled (maximum TMP) as a result of an increase of organic matter in the feed. COD was considered to be the most important parameter that affected the permeate quality because, when the organic load was significant (about 300 mg of O₂/L in this work), rapid membrane fouling took place, and an additional cleaning had to be done. The feed COD at a VCR of 6 varied between 30 and 360 mg of O₂/L, and the RO membrane was not able to reduce the permeate content to satisfy the limit established when the feed presented high COD values. The ACC was demonstrated to be effective in reducing the organic load, and the RO–ACC outlet stream fulfilled the boiler-water specifications (10 mg of O₂/L) in most of the samples analyzed. When permeate pH was acidified (outside the limit), then a post-treatment was advisable to adjust it.

A general recommendation for treating these types of wastewaters with the objective of producing boiler water is to segregate condensates when COD reached values higher than 300 mg of O₂/L. In the rest of the cases, RO followed by ACC was shown to be effective.

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Notes

The authors declare no competing financial interest.

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NOMENCLATURE

Abbreviations

ACC = activated carbon column
 AIC = aseptic intermediate cleaning
 CFV = cross-flow velocity
 COD = chemical oxygen demand
 DSI = direct steam injection
 F = filter
 FC = flash cooler
 FCV = flow control valve
 FI = flow indicator
 P = pump
 PI = pressure indicator
 RO = reverse osmosis
 RR = recovery rate
 SDI = silt density index
 TK = tank
 TMP = transmembrane pressure (bar)
 TOC = total organic carbon
 UHT = ultrahigh temperature
 VCR = volume concentration rate

Symbols

C_f = feed concentration ($\mu\text{S}/\text{cm}$ or mg of O_2/L)
 C_p = permeate concentration ($\mu\text{S}/\text{cm}$ or mg of O_2/L)
 J = permeate flow rate ($\text{L h}^{-1} \text{m}^{-2}$)
 R = reduction (%)
 V_f = feed volume (m^3 or m^3/h)
 V_p = permeate volume (m^3 or m^3/h)
 V_r = retentate volume (m^3 or m^3/h)

REFERENCES

- (1) Salehi, F. Current and future applications for nanofiltration technology in the food processing. *Food Bioprod. Process.* **2014**, *92* (2), 161–177.
- (2) Vourch, M.; Balanec, B.; Chaufer, B.; Dorange, G. Nanofiltration and reverse osmosis of model process waters from the dairy industry to produce water for reuse. *Desalination* **2005**, *172* (3), 245–256.
- (3) Andrade, L. H.; Mendes, F. D. S.; Espindola, J. C.; Amaral, M. C. S. Nanofiltration as tertiary treatment for the reuse of dairy wastewater treated by membrane bioreactor. *Sep. Purif. Technol.* **2014**, *126*, 21–29.
- (4) Riera, F. A.; Suárez, A.; Muro, C. Nanofiltration of UHT flash cooler condensates from a dairy factory: Characterisation and water reuse potential. *Desalination* **2013**, *309*, 52–63.
- (5) Farizoglu, B.; Uzuner, S. The investigation of dairy industry wastewater treatment in a biological high performance membrane system. *Biochem. Eng. J.* **2011**, *57*, 46–54.
- (6) Noronha, M.; Britz, T.; Mavrov, V.; Janke, H. D.; Chmiel, H. Treatment of spent process water from a fruit juice company for

purposes of reuse: Hybrid process concept and on-site test operation of a pilot plant. *Desalination* **2002**, *143* (2), 183–196.

(7) Casani, S.; Rouhany, M.; Knochel, S. A discussion paper on challenges and limitations to water reuse and hygiene in the food industry. *Water Res.* **2005**, *39* (6), 1134–1146.

(8) Sánchez, L. M. R.; Ruiz, J. M. M.; López, J. L. C.; Pérez, J. A. S. Effect of environmental regulation on the profitability of sustainable water use in the agro-food industry. *Desalination* **2011**, *279* (1–3), 252–257.

(9) Morin-Couallier, E.; Fargues, C.; Lewandowski, R.; Decloux, M.; Lameloise, M.-L. Reducing water consumption in beet distilleries by recycling the condensates to the fermentation phase. *J. Cleaner Prod.* **2008**, *16* (5), 655–663.

(10) Lee, W.; Okos, M. R. Sustainable food processing systems—Path to a zero discharge: Reduction of water, waste and energy. *Proc. Food Sci.* **2011**, *1*, 1768–1777.

(11) Sarkar, B.; Chakrabarti, P. P.; Vijaykumar, A.; Kale, V. Wastewater treatment in dairy industries—Possibility of reuse. *Desalination* **2006**, *195* (1–3), 141–152.

(12) Palumbo, S. A.; Rajkowski, K. T.; Miller, A. J. Current approaches for reconditioning process water and its use in food manufacturing operations. *Trends Food Sci. Technol.* **1997**, *8* (3), 69–74.

(13) Juang, L.-C.; Tseng, D.-H.; Lin, H.-Y. Membrane processes for water reuse from the effluent of industrial park wastewater treatment plant: A study on flux and fouling of membrane. *Desalination* **2007**, *202* (1–3), 302–309.

(14) Pouliot, Y. Membrane processes in dairy technology—From a simple idea to worldwide panacea. *Int. Dairy J.* **2008**, *18* (7), 735–740.

(15) Coskun, T.; Debik, E.; Demir, N. M. Treatment of olive mill wastewaters by nanofiltration and reverse osmosis membranes. *Desalination* **2010**, *259* (1–3), 65–70.

(16) Koyuncu, I.; Turan, M.; Topacik, D.; Ates, A. Application of low pressure nanofiltration membranes for the recovery and reuse of dairy industry effluents. *Water Sci. Technol.* **2000**, *41*, 213–221.

(17) Akoum, O.; Jaffrin, M. Y.; Ding, L. H.; Frappart, M. Treatment of dairy process waters using a vibrating filtration system and NF and RO membranes. *J. Membr. Sci.* **2004**, *235* (1–2), 111–122.

(18) Balanec, B.; Gésan-Guizoui, G.; Chaufer, B.; Rabiller-Baudry, M.; Daufin, G. Treatment of dairy process waters by membrane operations for water reuse and milk constituents concentration. *Desalination* **2002**, *147* (1–3), 89–94.

(19) Balanec, B.; Vourch, M.; Rabiller-Baudry, M.; Chaufer, B. Comparative study of different nanofiltration and reverse osmosis membranes for dairy effluent treatment by dead-end filtration. *Sep. Purif. Technol.* **2005**, *42* (2), 195–200.

(20) Frappart, M.; Jaffrin, M.; Ding, L. H. Reverse osmosis of diluted skim milk: Comparison of results obtained from vibratory and rotating disk modules. *Sep. Purif. Technol.* **2008**, *60* (3), 321–329.

(21) Mavrov, V.; Bélières, E. Reduction of water consumption and wastewater quantities in the food industry by water recycling using membrane processes. *Desalination* **2000**, *131* (1–3), 75–86.

(22) Turan, M. Influence of filtration conditions on the performance of nanofiltration and reverse osmosis membranes in dairy wastewater treatment. *Desalination* **2004**, *170* (1), 83–90.

(23) Vourch, M.; Balanec, B.; Chaufer, B.; Dorange, G. Treatment of dairy industry wastewater by reverse osmosis for water reuse. *Desalination* **2008**, *219* (1–3), 190–202.

(24) Aydiner, C.; Sen, U.; Topcu, S.; Ekinci, D.; Altinay, A. D.; Koseoglu-Imer, D. Y.; Keskinler, B. Techno-economic viability of innovative membrane systems in water and mass recovery from dairy wastewater. *J. Membr. Sci.* **2014**, *458*, 66–75.

(25) Tran, H.; Datta, N.; Lewis, M. J.; Deeth, H. C. Predictions of some product parameters based on the processing conditions of ultra-high-temperature milk plants. *Int. Dairy J.* **2008**, *18* (9), 939–944.

(26) Newstead, D. F.; Paterson, G.; Anema, S. G.; Coker, C. J.; Wewala, A. R. Plasmin activity in direct-steam-injection UHT-processed reconstituted milk: Effects of preheat treatment. *Int. Dairy J.* **2006**, *16* (6), 573–579.

- (27) Innings, F.; Hamberg, L. Steam condensation dynamics in annular gap and multi-hole steam injectors. *Proc. Food Sci.* **2011**, *1*, 1278–1284.
- (28) Gösta, B.; López, A. *Manual de Industrias lácteas TETRA PAK*; Ediciones Mundi Prensa: Madrid, Spain, 1994.
- (29) Early, R. *Technology of Dairy Products*; Springer: London, 1998.
- (30) Lewis, M. J. Thermal Processing. In *Food Processing Handbook*; Brennan, J. G., Ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2006; Chapter 2; pp 33–70.
- (31) Fährnich, A.; Mavrov, V.; Chmiel, H. Membrane processes for water reuse in the food industry. *Desalination* **1998**, *119* (1–3), 213–216.
- (32) Judd, S.; Jefferson, B. *Membranes for Industrial Wastewater Recovery and Re-Use*; Elsevier Science Ltd.: Oxford, U.K., 2003.
- (33) Mavrov, V.; Chmiel, H.; Bélières, E. Spent process water desalination and organic removal by membranes for water reuse in the food industry. *Desalination* **2001**, *138* (1–3), 65–74.
- (34) Mosset, A.; Bonnelly, V.; Petry, M.; Sanz, M. A. The sensitivity of SDI analysis: From RO feed water to raw water. *Desalination* **2008**, *222* (1–3), 17–23.
- (35) Chmiel, H.; Mavrov, V.; Belieres, E. Reuse of vapour condensate from milk processing using nanofiltration. *Filtr. Sep.* **2000**, *37* (3), 24–27.
- (36) Verheyen, V.; Cruickshank, A.; Wild, K.; Heaven, M. W.; McGee, R.; Watkins, M.; Nash, D. Soluble, semivolatile phenol and nitrogen compounds in milk-processing wastewaters. *J. Dairy Sci.* **2009**, *92* (7), 3484–3493.
- (37) Verheyen, V.; Cruickshank, A.; Wild, K.; Heaven, M. W.; McGee, R.; Watkins, M.; Nash, D. Characterization of organic particulates present in milk factory process waters used for reuse along with aerobically digested effluent wastewater. *Bioresour. Technol.* **2011**, *102* (2), 2118–2125.
- (38) Moio, L.; Dekimpe, J.; Etievant, P.; Addeo, F. Neutral volatile compounds in the raw milks from different species. *J. Dairy Res.* **1993**, *60* (2), 199–213.
- (39) Pereda, J.; Jaramillo, D. P.; Quevedo, J. M.; Ferragut, V.; Guamis, B.; Trujillo, A. J. Characterization of volatile compounds in ultra-high-pressure homogenized milk. *Int. Dairy J.* **2008**, *18* (8), 826–834.
- (40) Valero, E.; Villamiel, M.; Miralles, B.; Sanz, J.; Martínez-Castro, I. Changes in flavour and volatile components during storage of whole and skimmed UHT milk. *Food Chem.* **2001**, *72* (1), 51–58.
- (41) Sagne, C.; Fargues, C.; Lewandowski, R.; Lameloise, M.-L.; Gavach, M.; Decloux, M. A pilot scale study of reverse osmosis for the purification of condensate arising from distillery stillage concentration plant. *Chem. Eng. Process.: Process Intensif.* **2010**, *49* (4), 331–339.
- (42) Suárez, A.; Riera, F. A. Production of high-quality water by reverse osmosis of milk dairy condensates. *J. Ind. Eng. Chem.*, published online Jun 10, 2014, <http://dx.doi.org/10.1016/j.jiec.2014.06.004>.
- (43) Gésan-Guizoiu, G.; Daufin, G.; Boyaval, E. Critical stability conditions in skimmed milk crossflow microfiltration: Impact on operating modes. *Lait* **2000**, *80* (1), 129–138.
- (44) Rabiller-Baudry, M.; Bouzid, H.; Chaufer, B.; Paugam, L.; Delaunay, D.; Mekmene, O.; Ahmad, S.; Gaucheron, F. On the origin of flux dependence in pH-modified skim milk filtration. *Dairy Sci. Technol.* **2009**, *89* (3–4), 363–385.
- (45) Madaeni, S. S.; Mansourpanah, Y. Chemical cleaning of reverse osmosis membranes fouled by whey. *Desalination* **2004**, *161* (1), 13–24.
- (46) Brans, G.; Schroën, C. G. P. H.; van der Sman, R. G. M.; Boom, R. M. Membrane fractionation of milk: State of the art and challenges. *J. Membr. Sci.* **2004**, *243* (1–2), 263–272.
- (47) Bódalo-Santoyo, A.; Gómez-Carrasco, J. L.; Gomez-Gomez, E.; Maximo-Martin, M. F.; Hidalgo-Montesinos, A. M. Spiral-wound membrane reverse osmosis and the treatment of industrial effluents. *Desalination* **2004**, *160* (2), 151–158.
- (48) Nguyen, L. N.; Hai, F. I.; Kang, J.; Price, W. E.; Nghiem, L. D. Removal of trace organic contaminants by a membrane bioreactor–granular activated carbon (MBR–GAC) system. *Bioresour. Technol.* **2012**, *113*, 169–173.
- (49) Jirjis, B. F.; Luque, S. Practical Aspects of Membrane System Design in Food and Bioprocessing Applications. In *Membrane Technology: A Practical Guide to Membrane Technology and Applications in Food and Bioprocessing*; Cui, Z. F., Muralidhara, H. S., Eds.; Butterworth-Heinemann: Oxford, U.K., 2010; Chapter 9, pp 179–212.
- (50) Schwinge, J.; Neal, P. R.; Wiley, D. E.; Fletcher, D. F.; Fane, A. G. Spiral wound modules and spacers: Review and analysis. *J. Membr. Sci.* **2004**, *242* (1–2), 129–153.
- (51) Gerard, R.; Hachisuka, H.; Hirose, M. New membrane developments expanding the horizon for the application of reverse osmosis technology. *Desalination* **1998**, *119* (1–3), 47–55.
- (52) Qin, J.-J.; Oo, M. H.; Lee, H.; Coniglio, B. Effect of feed pH on permeate pH and ion rejection under acidic conditions in NF process. *J. Membr. Sci.* **2004**, *232* (1–2), 153–159.
- (53) Qin, J.-J.; Oo, M. H.; Wai, M. N.; Wong, F.-S. Effect of feed pH on an integrated membrane process for the reclamation of a combined rinse water from electroless nickel plating. *J. Membr. Sci.* **2003**, *217* (1–2), 261–268.
- (54) Prats, D.; Chillon-Arias, M. F.; Rodriguez-Pastor, M. Analysis of the influence of pH and pressure on the elimination of boron in reverse osmosis. *Desalination* **2000**, *128* (3), 269–273.
- (55) Kang, M.; Kawasaki, M.; Tamada, S.; Kamei, T.; Magara, Y. Effect of pH on the removal of arsenic and antimony using reverse osmosis membranes. *Desalination* **2000**, *131* (1–3), 293–298.
- (56) Childress, A. E.; Elimelech, M. Effect of solution chemistry on the surface charge of polymeric reverse osmosis and nanofiltration membranes. *J. Membr. Sci.* **1996**, *119* (2), 253–268.

Conclusiones particulares del apartado 4.4.

Los ensayos en semi-continuo determinaron un grado máximo de recuperación del 83,3% de acuerdo al cumplimiento de los requerimientos marcados, principalmente en conductividad, ya que la columna de carbón activo permitiría controlar los límites máximos de materia orgánica. Dicho porcentaje fue fijado como parámetro de diseño de la operación en continuo de larga duración.

Aunque los ciclos de limpieza de la membrana no fueron reproducibles debido a la heterogeneidad de la alimentación, que influyó en gran medida la tendencia al ensuciamiento y por tanto la frecuencia de limpieza, sí que se pudo determinar un valor medio, situándose éste en torno a las 12 h. Picos de materia orgánica por encima de 300 mg de O₂/L produjeron un rápido incremento en la presión de trabajo, demostrando ser el principal responsable del ensuciamiento. En vista a estos resultados, se aconsejaría segregar éste tipo de entradas de alta carga contaminante que pudieran dar en concentración valores por encima del aquí recomendado.

Salvo valores puntuales, las características exigidas al agua de alimentación a calderas se cumplieron para las 100 h de trabajo en continuo con el proceso combinado de ósmosis inversa y carbón activo. Es necesario tener en cuenta además que al trabajar a un factor de concentración de volumen de 6 se estaría operando en las condiciones de alimentación más exigentes, siendo de suponer que las etapas previas del proceso de membranas, con alimentaciones menos concentradas, darían lugar a permeados de mejor calidad. Salvo en periodos de ensuciamiento, los rechazos se mantuvieron cerca de las predicciones teóricas para altos grados de concentración, no teniendo efecto ninguno la columna de carbón activo en la conductividad del permeado como se suponía, pero sí en la materia orgánica, donde se obtuvieron rechazos de hasta el 100%.

De acuerdo al volumen de permeados que se podría generar y conociendo el volumen total de agua desmineralizada actual de aporte a calderas en la factoría, los permeados generados no podrían suplir el total de la alimentación, sólo un 43%, por lo que habría que considerar un efecto de dilución al mezclarse estos permeados con agua desmineralizada en la proporción comentada. Ésta mezcla no solo ha de respetar los límites de agua de calderas tomados como referencia a lo largo del trabajo, que lo hace, sino también los requisitos establecidos en la norma UNE-EN 12953-10. De esta forma se incluye una tabla comparativa (**Tabla I**) entre el agua desmineralizada actual y la pretendida mezcla al 43% con permeados en relación a los parámetros objetivo de referencia considerados en la factoría para el cumplimiento de la normativa. Como se observa, el aporte de permeados no compromete la calidad del agua de alimentación a calderas.

Tabla I: Comparativa entre el agua desmineralizada objetivo y la posible mezcla con permeados incorporados.

	Agua desmineralizada	43% permeados
Turbidez, NTU	< 1	< 1
Alcalinidad total, mg CaCO ₃ /L	< 0,5	< 0,5
Alcalinidad compuesta, mg CaCO ₃ /L	11,2	11,2
Cloruros, mg Cl ⁻ /L	< 0,7	< 0,7
Conductividad a 25°C, μS/cm	< 20	< 20
Dureza total, mg CaCO ₃ /L	1,01	0,96
Fosfatos, mg PO ₄ ³⁻ /L	< 0,04	< 0,04
Hierro, mg/L	< 0,02	< 0,02
Sílice (SiO ₂), mg/L	1,92	1,31
pH a 25°C	5,12	5,58

En cuanto al pH, que en ambas corrientes presentó un valor ácido, y otros parámetros como el O₂ disuelto, los tratamientos previos a la caldera, véase desgasificación e incorporación de aditivos, permitirán su corrección. Microbiológicamente y desde el punto de vista higiénico, los permeados, incluso la propia alimentación a membranas, se encontraron por debajo de 1 UFC/g en coliformes y presentaron una ausencia total de patógenos.

4.5. Evaluación de costes en las operaciones tradicionales de membrana. Desarrollo de un modelo económico para la aplicación estudiada

Validada técnicamente la aplicación, el siguiente paso fue determinar la viabilidad económica del proceso. Para ello, y de acuerdo a los datos experimentales obtenidos en continuo, se utilizó como base un modelo económico (Sethi and Wiesner, 2000) que fue mejorado y completado con aspectos relacionados con la aplicación concreta. Este modelo de cálculo de costes, junto con una estimación de ahorros, permitió obtener un valor del periodo de recuperación de la inversión. En este capítulo se dan además las bases para una completa evaluación económica, basada en un balance costes-ahorros, de cualquier proceso de membranas tradicional donde la presión es la fuerza impulsora. Con el objetivo de conocer las variables que controlan la rentabilidad del proceso se llevó a cabo un análisis de sensibilidad, que además permitió estudiar el efecto sobre la economía de variables que no pudieron ser evaluadas en profundidad durante el pilotaje. La explicación del modelo así como los resultados obtenidos para la aplicación se detallan en la publicación:

Cost assessment of membrane processes: A practical example in the dairy wastewater reclamation by reverse osmosis

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Cost assessment of membrane processes: A practical example in the dairy wastewater reclamation by reverse osmosis

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ABSTRACT

The profitability of a reverse osmosis application has been evaluated by using a well-known economic model based on experimental data, where additional operating costs were considered to represent a more realistic estimation. A calculation template was included to provide an easy-access to a preliminary economic evaluation of a specific membrane installation. The response of the model was checked with a real reverse osmosis application as this is the condensate recovery from a dairy ultra-high-temperature plant. A sensitivity analysis was performed to show the model behaviour when subjected to some process parameter fluctuations. The base case, which considers a design flow of 20 m³/h, produced a payback period of 3.3 years, being a cost-effective facility for the amortization period studied. The recovery rate proved to be a relevant parameter of influence in the economic viability of the process, as an increase of 20% produced an improvement of 48.6% in the net present value estimated.

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1. Introduction

Membrane treatment can be considered a primary source of separation in food processing plants, being particularly well integrated in the dairy industry and becoming quite popular in wastewater treatment and reclamation [1–3]. Compared to conventional separation techniques, membrane technology offers easy implementation, considerable flexibility, compactness and good automation, which, together with the decreasing installation and operation costs, make membrane processes a reliable, environmentally friendly, competitive and economically profitable alternative to other techniques [4–7]. When selecting and designing a membrane operation both economical and technical objectives have to be borne in mind. The cost of a membrane application is largely dependent on the flux, module design, plant capacity and operating conditions, while the yield and purity finally achieved are functions of the rejection or reduction (R , %) and the volume concentration rate (VCR) [8,9].

Of all membrane technologies, reverse osmosis (RO) is the method which is gaining the greatest worldwide acceptance in water treatment as well as in desalination applications due to its competitive cost, simplicity and membrane performance [10–13]. Moreover, the development of low-pressure RO processes could

provide improved flux and solute separations at wide temperature and pH ranges [14]. Conversely, RO shows limitations when used for the removal of organic compounds and is susceptible to fouling, a major problem which implies permeate flow rate (J , L/m² h) reduction, irreversible membrane damage and increased operating costs from frequent chemical cleaning [15–18].

Cost is the major factor when implementing membrane technologies [8]. An economic analysis provides the basis for justifying a project in monetary terms and allows comparisons between alternatives based on the total costs and associated benefits [17]. Several factors affect the unit product cost for membrane facilities, such as the mass balance of the target separation in terms of stream flow rates and quality, the operating conditions, the system and module design, the mode of operation and the company on-site conditions (cost of water supply, energy, steam, wastewater treatment and disposal, availability of qualified manpower, financing conditions, etc.) [19–22]. Of all these parameters, membrane flux is broadly the most influential for the application costs as it is a direct measure of productivity and determines the pressure (and hence the energy requirements) and the membrane area (A_m , m²). Therefore, an accurate estimation of the permeate flow rate is essential [23–25].

Pilot studies are critical to the success of a membrane project as they provide a reliable basis for evaluating the effect of the operating parameters on the cost and performance of a large-scale installation. This information makes it possible to determine the influence of feed variability on the permeate flow rate – and thus

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the membrane area – the optimum recovery rate (RR, %), average transmembrane pressure (TMP, kPa) and pressure drop along the housings [17,19,23,26]. Discontinuous testing at increasing VCR allows to obtain information on the permeate flow rate and rejection to the solutes of interest. On the other hand, continuous testing, performed at the optimum conditions to fulfil the permeate quality requirements, gives information about the lifespan of the membranes as well as the impact of fouling and cleaning frequency. Optimal pilot testing can save up to 30% in investment and the accuracy of economic evaluation can be estimated to have an effect of ± 20 –30%, which could make the error significant when carrying out a preliminary economic balance [17,27].

The economic evaluation of a membrane process and its production cost comprises the calculation of both the capital expenditure or investment (CAPEX), which can involve direct and indirect capital costs, and the operating and maintenance cost (OPEX), which can be divided into fixed and variable (dependent on plant production) costs [8,20,23,28]. The concept of capital cost employed may produce differences in the results obtained depending on the items included in its estimation [29]. This could also be applied to operating costs, although it is well-known that they are those expenditures incurred after plant commissioning and during operation [30]. CAPEX can be composed of land, construction (civil investments), engineering services, project development, financing, auxiliary equipment, pre- and post-treatment, framework, membranes and pressure vessels, stocking tanks, automation and control, piping, valves and fittings, pumps, cleaning in place (CIP), miscellaneous costs (building, electrical supply and distribution, treated water storage and pumping, etc.) and indirect costs (freight and insurance, construction overhead, owner's cost and contingency). OPEX can cover amortization, electrical energy, labour, maintenance and spares, chemicals (cleaning and disposal), membrane replacement, pre- and post-treatment (and replacement), concentrate disposal, quality control and insurance costs [8,20,21,29,31–39].

The benefits of a membrane project depend on the application considered. They can be based on the revenue given by the recovery and valorization of any specific compound [40], the exploitation of whole concentrates [41], the production of desalinated water [42], the economic advantages conferred by an equipment (or conventional technology) replacement [43], the water supply and disposal savings or even energy savings obtained from wastewater treatment and reuse [44–46], etc. The profitability of a project can be estimated by measuring three typical economic indicators, the net present value (NPV), the internal rate of return (IRR) and the payback period (PB), evaluated using cash flow analysis.

Cost modelling is usually applied to estimate the cost of investment. Most cost models have been established according to published historical data of real membrane facilities and tender provided by supplier and vendor [24,47]. Examples of such types of models are those developed by Sethi and Wiesner [24], which were based on data from real microfiltration (MF) and ultrafiltration (UF) installations, and which were used by Costa and de Pinho [35] to estimate the cost of a surface water nanofiltration (NF) plant for drinking water production. Gorenflo et al. [37] used the same models in an NF installation for groundwater treatment, while Guerra et al. [48] and Suárez et al. [49] employed them to study a surface water UF process and to evaluate the economics of a NF process to recover detergents in a dairy industry, respectively. Verberne and Wouters [50] proposed another model which was utilized by Ali et al. [47] in general NF selection and cost analysis, Mohammad et al. [51] on NF optimization and Van der Bruggen et al. [21] to evaluate economically an NF application for the removal of pesticides, nitrate and hardness from groundwater. Other authors have made their economic calculations using the simple six-tenths power rule [30,38], taking literature references as the basis of estimation [34], using specific equipment costs obtained from manufacturers [13,28,52–54], or a combination

of these [55]. Finally, another option consists of using process design software equipped with cost estimation modules [8,41].

The model of Sethi and Wiesner [24] presents some advantages regarding to those found in the literature: it is based on real published data and it considers an economy of scale; it is useful to preliminary estimations or those based on previous experimentation; it includes running costs of pre- and post-treatments; it differentiates the components of the capital costs; and it has proved to be valid for different configurations [56]. Regarding the downsides of other existing economic models, Adham et al. [57] used the feed flow as key parameter and no information about other operating parameters involved (permeate flux, recovery rate) was considered. Pickering and Wiesner [58] correlated the costs with the number of modules, which is too specific. The six-tenths power rule fails when the plants under study have different final objectives, membrane characteristics, etc. The model of Verberne and Wouters [50] is developed based on the feed flow and number of modules, which presents the drawbacks of aforementioned models. Finally, regarding to the calculation method used by Nilsson et al. [27], the membrane costs seems to be overestimated.

The objective of this work was to provide a basis for the economic evaluation of a membrane process, supplying cost-related membrane information, which is usually dispersed, and developing the hypotheses, variables and calculations required to obtain a complete cost-revenue balance. Although the model of Sethi and Wiesner [24] has been applied to represent cross-flow pressure-driven processes as the parameters which could differentiate them (J , TMP, membrane cost, durability, surface area, etc.) are taking part in the model calculations, as far as the authors know, no examples have been published regarding RO. To illustrate this, the process economics of a low-pressure RO plant to treat condensates from an ultra-high-temperature (UHT) installation in a dairy factory was studied and evaluated through pilot plant information in order to perform a sensitivity analysis and identify crucial parameters for the profitability of the membrane application.

2. Materials and methods

2.1. General considerations

When considering a preliminary economic evaluation of a membrane process, numerous factors and variables have to be borne in mind. Some of these, such as factors related to feed flow and composition, or the membrane best suited to attaining the objectives of the final application, should be considered beforehand. However, other parameters, such as the permeate flow rate, RR, cleaning frequency, etc., which could be taken as basic assumptions, need further confirmation through pilot plant studies. Fig. 1 shows a scheme in which the main variables involved in the economics of a membrane process are collected in order to serve as a simple starting point for future research studies and business projects. The variables essential for the calculation are highlighted in bold, their most common units being displayed in brackets. In general, the variables included here are mostly quantitative and could vary as a function of process specificity.

2.2. Description of the economic model

The model described by Sethi and Wiesner [24] was used as a basis to determine the CAPEX of the membrane application. These authors segregate the total capital cost of the installation in non-membrane equipment and facilities (pipes and valves (C_{PV}), instruments and controls (C_{IC}), tanks and frames (C_{TF}), miscellaneous (C_{MI}) and pumps (C_P)) on the one hand and membrane investment (membrane and pressure vessel costs, C_m and C_v ,

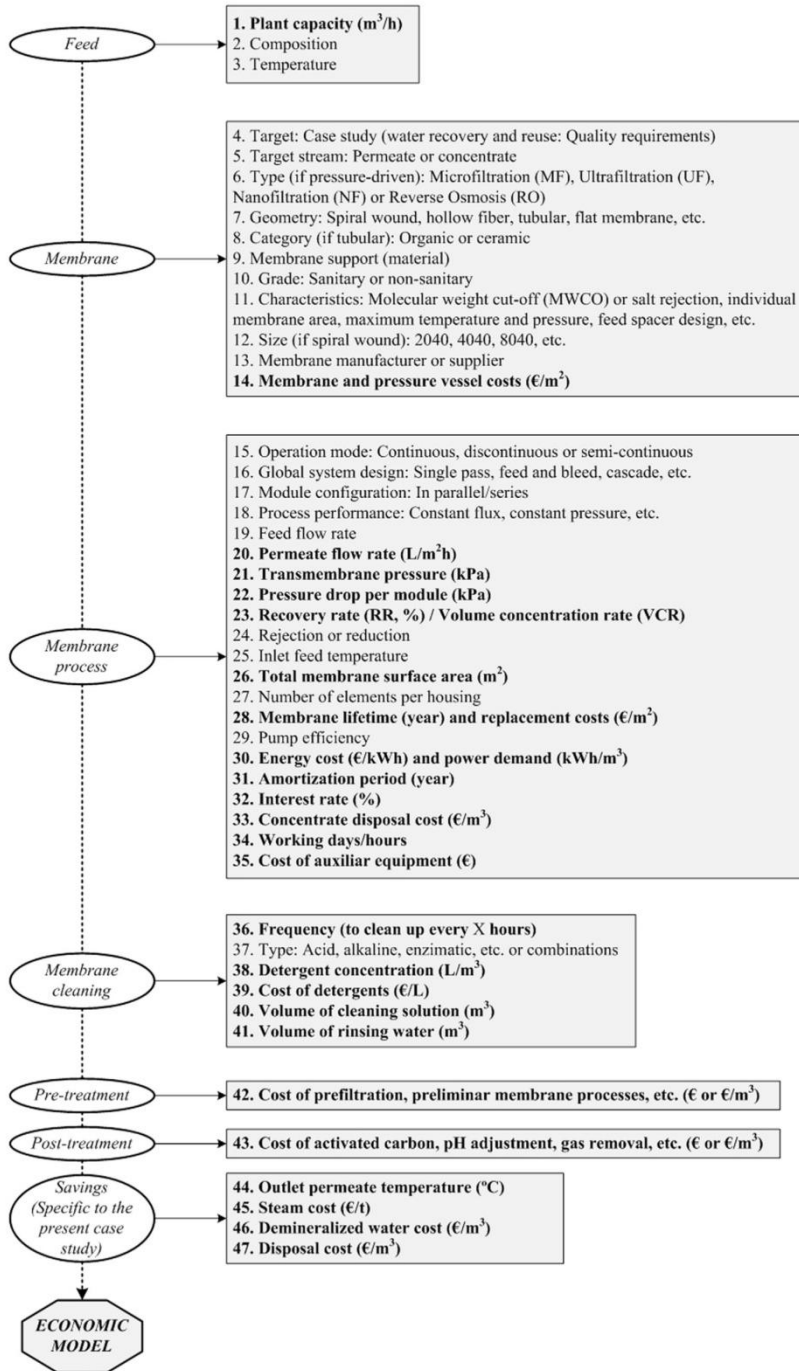


Fig. 1. Variables involved in cross-flow membrane economics.

respectively) on the other. The equations applied in the calculation, which are based on the total membrane area of the installation, are shown below. To estimate the total A_m (m^2) it is necessary to consider the plant capacity (Q , m^3/h), the permeate flow rate (L/m^2h) and the RR (%).

$$C_{PV} = 5926.13(A_m)^{0.42} \quad (1)$$

$$C_{IC} = 1445.50(A_m)^{0.66} \quad (2)$$

$$C_{TF} = 3047.21(A_m)^{0.53} \quad (3)$$

$$C_{MI} = 7865.02(A_m)^{0.57} \quad (4)$$

When solving these equations, the results obtained are expressed in 1996 US\$, and they should first be converted into 1996 € (\$1 = €0.81) and then actualized to represent current values by applying the Chemical Engineer Plant Cost Index (CEPCI) ratio, which can be considered equal to 572.8/381.7 (January 2014/full-year 1996).

The membrane (C_m) and pressure vessel (C_v) costs were estimated in actualized values by multiplying the total membrane area by the membrane (P_m) and pressure vessel (P_v) price per unit area ($€/m^2$) or membrane module, respectively. Another option could be to determine the number of elements by using the individual membrane area per element and applying the global cost of an integral element. C_p is calculated using a pump cost correlation for general-purpose centrifugal pumps [59]

$$C_p = 622.59(Q \cdot P)^{0.39} \quad (5)$$

where the first factor is the result of multiplying the correlation factor (81.27) by the labour factor (1.4), the material factor (1.5 for type 316 stainless steel), the suction pressure range factor (1.6 for suction pressures between 1030 and 3520 kPa) and the cost index ratio to update the cost to 1996 (2.28); Q is the total feed flow (plant capacity) in m^3/h and P is the inlet pressure in kPa.

As a result, the global CAPEX was determined as the sum of these actualized concepts (non-membrane and membrane constituents) plus a factor considering the cost of installation (C_i) and representing around 25% of the total capital costs (purchased equipment costs) [34,60].

On the other hand, the OPEX was estimated basically through the elements offered by Sethi and Wiesner [24] to calculate the concepts which involve amortization, membrane replacement, energy, chemicals and concentrate disposal. Furthermore, some additional factors were included to make the economic balance as precise as possible such as the costs of chemical and rising disposal, maintenance and feed pre-treatment. As the values are given per unit of volume of inlet feed in an annualized form ($€/m^3$), the annual plant capacity ($m^3/year$) should be considered as the divisor. The amortization constituent (A_c) is the result of multiplying the total capital costs or CAPEX by the amortization factor (AF), which is defined as

$$AF = \frac{i(1+i)^{DL}}{(1+i)^{DL} - 1} \quad (6)$$

where i represents the interest rate in decimal percentage and DL the design life of the plant in years.

The membrane replacement costs (M_c) are given by the amortization of the capital costs associated exclusively with the membrane modules considering that when a substitution takes place, the total area of the installation is replaced. However, in practice, the membrane modules are individually or stepwise substituted. In this case, the amortization factor of the membrane replacement (AF_m) is described as follows:

$$AF_m = \frac{i_m}{(1+i_m)^{ML} - 1} \quad (7)$$

where i_m and ML mean the interest rate for membrane

replacement in decimal percentage and the membrane lifetime in years, respectively.

The total cost of energy (E_c) mainly involves the pumping requirements for the feed, omitting the requirements related to recycling or recirculation (to compensate the head-loss across the length of the membrane) as further plant design information would be necessary to incorporate the operating costs of this secondary pumping system as part of the E_c . Using the following calculation formula, the annual plant capacity can be avoided, the result being expressed in $€/m^3$:

$$E_c = \frac{Q_1 P_1 c_e}{\eta Q} \quad (8)$$

where Q_1 is the plant capacity in m^3/s , P_1 is the inlet pressure in Pa, c_e is the energy cost in $€/Wh$, η is the efficiency of the feed pump in decimal % and Q is the plant capacity in m^3/h .

To estimate the cost of chemicals (C_c) it is necessary to know the type of cleaning performed and the estimation is obtained by multiplying the frequency of cleaning in times per year by the volume of the cleaning solution used (m^3), the concentration of the detergents applied (L/m^3 if the product is supplied in liquid state) and the price of the detergents ($€/L$). If further concentrate exploitation is not carried out, the concentrate disposal cost (CD_c) is determined by considering the production of concentrate per year and the factory disposal cost (d_c) in $€/m^3$. In the same way, the disposal costs of the cleaning and rinsing solutions (CRD_c) can be evaluated by calculating the cleaning solution volume as three times the internal volume (typically $1.5 L/m^2$ of membrane area) per flush [19]. In addition and in order to count the death volume and the CIP tank volume, this calculation is oversized by 50%. The rinsing volume per cleaning step can be estimated taking as reference the volume of 500 L per membrane module given by Liikanen et al. [23], who considered in their calculations membranes with a surface area of $37 m^2$.

Finally, according to Van der Bruggen et al. [21], the maintenance costs (MA_c) can be fixed at 2% of the total investment costs and the pre-treatment costs (PT_c), calculated as 15% of the total OPEX minus the maintenance costs; as defined by Bergman [61], this percentage includes pre-treatment (primarily cartridge filter replacement if necessary) and maintenance costs.

Regarding the major indicators of investment analysis, the NPV, IRR and PB evaluation methods are suitable both for determining the economic viability of new investments and the comparison of alternatives. Thus, the most favourable option is associated with a higher NPV and IRR and a lower PB. The NPV allows the estimation of the current value of a specified number of cash flows (CFs, €) resulting from an initial investment, whereas the IRR is the average of the expected future yields obtained from such investment. The PB determines the time required to recover the initial investment in its entirety. In general and when there is constant annual CF, these can be described as follows:

$$NPV = \sum_{t=1}^n \frac{CF_t}{(1+r)^t} - I_0 \quad (9)$$

$$\sum_{t=1}^n \frac{CF_t}{(1+IRR)^t} - I_0 = 0 \quad (10)$$

$$PB = \frac{I_0}{CF} \quad (11)$$

where n represents the holding period of investment evaluation in years, I_0 is the initial investment in € and r is the discount rate of the invested capital in decimal %.

2.3. Case study description

The RO recovery of flash cooler (FC) condensates from the UHT process of a dairy factory was used as a case study to apply the economic model. The flow diagrams that represent the UHT process and consequently, the origin of the condensates, as well as the pilot plant used to process these condensates have been previously published by the authors [44,62]. The objective of the application was to produce high quality water to satisfy boiler requirements (pH 7–10, conductivity (25 °C) < 40 µS/cm, chemical oxygen demand (COD) < 10 mgO₂/L, total organic carbon (TOC) < 4 mgO₂/L, biological oxygen demand after 5 days (BOD₅) between 1 and 50 mgO₂/L, Ca²⁺ < 0.4 mg/L and total suspended solids (TSS) between 0.5 and 10 mg/L [63,64]. Previous pilot plant trials were performed to obtain the necessary information for entry in the model. In these studies, different membranes (RO and NF) and conditions were tested, finally selecting the RO followed by an activated carbon post-treatment alternative as the optimum [44–46,62].

2.3.1. Specific economic terms of the case study

For the specific case study selected, additional specific information was considered in the CAPEX and OPEX estimations as an activated carbon column (ACC) was set up as a permeate post-treatment in order to satisfy the organic matter requirements for boiler water production. The investment cost of the ACC (C_{acc}) could be obtained by knowing the quantity (kg) of activated carbon required and its price (P_{ac}) in an actualized value (€/kg). As part of the OPEX, the activated carbon replacement costs (AC_c) are given by the amortization of the ACC CAPEX, simulating Eq. (7) for this purpose and taking i_c and ACL as the activated carbon replacement (decimal %) and the activated carbon lifetime (years), respectively.

As can be seen, the C_{Ml} equation was not included in the calculations of the case study as the terms that it represents (previously described) are generally already available or considered by the factory.

To evaluate the profit of this specific application it is necessary to consider the savings provided in energy recovery (condensate streams leave the UHT system at high temperature) and those in fresh demineralized water and wastewater disposal. With the purpose of determining the savings in € per m³, the following three terms were taken into account: the energy savings (E_s), which are obtained in terms of saturated steam water (1.8 MPa and 210 °C) saved per year and calculated through a heat transfer balance, and using the factory steam cost (s_c) (€/t); the fresh demineralized water savings (DW_s), determined by considering the permeate production (m³/year) and the factory demineralized water cost (dw_c) (€/m³); and the water disposal savings (WD_s) based on the information concerning the plant capacity (m³/year) and the factory water disposal cost (d_c) (€/m³) (if CD_c were not taken into account in the OPEX, only the permeate production (m³/year) would be considered).

2.3.2. Basic assumptions of the case study

The plant capacity was designed to treat 20 m³/h, the maximum feed flow peak with all the FCs of the dairy factory operating simultaneously. The membrane installation was considered to run 350 days per year and 20 h per day as the UHT system of the dairy factory usually operates in continuous mode, except for some hours at the end of the week. The cleaning periods, maintenance shutdowns, etc., of the membrane plant were also taken into account to estimate this running time. The permeate flow rate was fixed at 39 L/m²h according to the values recommended by the membrane manufacturer (< 40 L/m²h).

Based on previous pilot runs [46,62], a fixed VCR of 6 was selected. In these conditions, the permeate satisfies the boiler water requirements and the membrane fouls moderately. VCR 6 corresponds to an

RR of 83% (a recovery of 16.6 m³/h per 20 m³/h fed). As the system was performing at a constant permeate flow rate, increasing TMP must be applied to compensate the flow loss due to concentration polarization and fouling. The average TMP used in the estimations, 1300 kPa, came from long-term continuous trials at VCR 6 [62]. The cleaning steps were carried out when a value of 3000 KPa of maximum TMP was reached. The cleaning and rinsing volumes were estimated to be 3 and 6.5 m³, respectively, by using the information detailed in Section 2.2. The cleaning protocol, previously optimized by pilot experimentation, was based on an alkaline cleaning (Divos 123; Diversey, the Netherlands) performed every 12 h and a weekly acid cleaning (Divos 2; Diversey, the Netherlands) at 0.25% and 0.38% v/v, respectively, both performed at 45 °C. The detergent prices, supplied by the manufacturer, were €3.04/L and €1.69/L, respectively. The pump efficiency was set to be 70% and the energy costs of the factory (€/kWh) were omitted due to confidentiality agreements.

The cost of the 8040 spiral-wound RO membranes (33 m² membrane area each and common 31 mils feed spacers) and their respective pressure vessels were supplied by the membrane manufacturer. For this particular application, 2600 kg of GAC MG 1050 activated carbon (Sefiltra S.A., Madrid, Spain) were calculated to be necessary, the price being established at €3.43/kg according to the supplier's information. The durability or the lifetime of both the membranes and the activated carbon was initially fixed at 1 year. It has been reported that the membrane lifetime in dairy applications can be as short as 18 months to 3 years depending on several factors as the cleaning regimes used (chemicals, extreme pHs, and high temperatures) [19,65], the tendency of RO membranes to foul [66], the absence of an efficient pre-treatment method [10] and the operating conditions. As a result, the membrane life was established in 1 year taking into account the cleaning frequency (each 12 h) and the strong operating conditions set. Regarding the activated carbon

Table 1
Basic assumptions in the economic calculation.

RO membrane installation general data	
Plant capacity, m ³ /h	20
Operating hours, h/year	7000
Permeate flow rate, L/m ² h	39
Recovery rate, %	83
Feed pressure, kPa	1300
Pump efficiency, %	70
Energy costs, €/kW h	- ^a
Membranes cost (including replacement), €/m ²	- ^b
Pressure vessels cost, €/m ²	- ^b
Activated carbon, kg	2600
Cost of activated carbon (including replacement), €/kg	3.43
Membrane lifespan, year	1
Activated carbon life-time, year	1
Amortization period, year	15
Interest rate, %	7
Cleaning volume, m ³	3
Rinsing volume, m ³	6.5
Alkaline cleaning cycle	Every 12 h
Acid cleaning cycle	Weekly
Alkaline detergent concentration, L/m ³	2.5
Acid detergent concentration, L/m ³	3.8
Alkaline detergent cost, €/L	3.04
Acid detergent cost, €/L	1.69
Outlet permeate temperature, °C	45
Tap water temperature, °C	15
Saturated steam enthalpy (1.8 MPa and 210 °C), kJ/kg	2800
Water specific heat, kJ/kg °C	4.19
Water density, kg/m ³	995.3
Steam cost ^a , €/t	- ^a
Supplied demineralized water cost ^a , €/m ³	- ^a
Water disposal cost ^a , €/m ³	- ^a

^a Confidential data from the company.

^b Confidential data from the membrane supplier.

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Table 2

Concept	Parameters	Calculation equations	Results
Membrane area (m²)			
A _m	Q = 20 m ³ /h J = 39 L/m ² h RR = 83%	$A_m = \frac{20 \frac{\text{m}^3}{\text{h}} \cdot \frac{1000 \text{ L}}{1 \text{ m}^3} \cdot 0.83}{39 \frac{\text{L}}{\text{m}^2 \text{ h}}} \quad (12)$	≈ 426 m ²
CAPEX (€)			
C _{PV}	A _m = 426 m ²	$C_{PV} = 5962.13 \cdot (426 \text{ m}^2)^{0.42} \cdot \frac{€0.81}{\$1} \cdot \frac{572.8}{381.7} \quad (1)$	€/
C _{IC}	1996; \$1 = €0.81	$C_{IC} = 1445.50 \cdot (426 \text{ m}^2)^{0.66} \cdot \frac{€0.81}{\$1} \cdot \frac{572.8}{381.7} \quad (2)$	€/
C _{TF}	CEPCI = 572.8/381.7	$C_{TF} = 3047.21 \cdot (426 \text{ m}^2)^{0.53} \cdot \frac{€0.81}{\$1} \cdot \frac{572.8}{381.7} \quad (3)$	€/
C _m	A _m = 426 m ² P _m = €/m ²	$C_m = 426 \text{ m}^2 \cdot P_m \left(\frac{€}{\text{m}^2} \right) \quad (13)$	€/
C _v	A _m = 426 m ² Membrane module area = 33 m ² P _v = €/membrane module	$C_v = \frac{426 \text{ m}^2}{33 \text{ m}^2 / \text{membrane module}} \cdot P_v \left(\frac{€}{\text{membrane module}} \right) \quad (14)$	€/
C _p	Q = 20 m ³ /h P = 1300 kPa 1996; \$1 = €0.81 CEPCI = 572.8/381.7	$C_p = 622.59 \cdot \left(20 \frac{\text{m}^3}{\text{h}} \cdot 1300 \text{ kPa} \right)^{0.39} \cdot \frac{€0.81}{\$1} \cdot \frac{572.8}{381.7} \quad (5)$	€/
C _{acc}	Quantity of activated carbon = 2600 kg P _{ac} = €3.43/kg	$C_{acc} = 2600 \text{ kg} \cdot \frac{€3.43}{\text{kg}} \quad (15)$	€/
C _l	C _{PV} ; C _{IC} ; C _{TF} ; C _m ; C _v ; C _p ; C _{acc}	$C_l = 0.25 \cdot (C_{PV} + C_{IC} + C_{TF} + C_m + C_v + C_p + C_{acc}) \quad (16)$	€/
Total CAPEX			≈ €432,500
OPEX (€/m³) per year			
A _c	CAPEX = €432,500 i = 7% DL = 15 years Q = 20 m ³ /h 350 d; 20 h	$A_c = \frac{0.07 \cdot (1 + 0.07)^{15} \cdot €432,500}{(1 + 0.07)^{15} - 1} \cdot \frac{20 \frac{\text{m}^3}{\text{h}} \cdot \frac{20 \text{ h}}{1 \text{ d}} \cdot \frac{350 \text{ d}}{1 \text{ year}}}$	/ $\frac{€}{\text{m}^3}$
M _c	C _m = € i _m = 7% ML = 1 year Q = 20 m ³ /h 350 d; 20 h	$M_c = \frac{0.07}{(1 + 0.07)^1 - 1} \cdot C_m (\text{€}) \cdot \frac{20 \frac{\text{m}^3}{\text{h}} \cdot \frac{20 \text{ h}}{1 \text{ d}} \cdot \frac{350 \text{ d}}{1 \text{ year}}}$	/ $\frac{€}{\text{m}^3}$
E _c	c _e = €/Wh Q _l = 0.0055 m ³ /s P _l = 1,270,000 Pa η = 70% Q = 20 m ³ /h	$E_c = \frac{0.0055 \frac{\text{m}^3}{\text{s}} \cdot 1,270,000 \text{ Pa} \cdot c_e \left(\frac{€}{\text{Wh}} \right)}{0.7 \cdot 20 \frac{\text{m}^3}{\text{h}}} \quad (8)$	/ $\frac{€}{\text{m}^3}$
C _c	Alkaline cleaning frequency = every 12 h (700 times/year) Alkaline detergent concentration = 2.5 L/m ³ Alkaline detergent price = €3.04/L Acid cleaning frequency = weekly (52 times/year) Acid detergent concentration = 3.8 L/m ³ Acid detergent price = €1.69/L Cleaning volume = 3 m ³ Q = 20 m ³ /h 350 d; 20 h	$C_c = \frac{3 \text{ m}^3 \cdot \left((700 \cdot 2.5 \frac{\text{L}}{\text{m}^3} \cdot \frac{€3.04}{\text{L}}) + (52 \cdot 3.8 \frac{\text{L}}{\text{m}^3} \cdot \frac{€1.69}{\text{L}}) \right)}{20 \frac{\text{m}^3}{\text{h}} \cdot \frac{20 \text{ h}}{1 \text{ d}} \cdot \frac{350 \text{ d}}{1 \text{ year}}} \quad (16)$	/ $\frac{€}{\text{m}^3}$
CD _c	d _c = €/m ³ RR = 83% Q = 20 m ³ /h 350 d; 20 h	$CD_c = \frac{(1 - 0.83) \cdot \left(20 \frac{\text{m}^3}{\text{h}} \cdot \frac{20 \text{ h}}{1 \text{ d}} \cdot \frac{350 \text{ d}}{1 \text{ year}} \right) \cdot d_c \left(\frac{€}{\text{m}^3} \right)}{20 \frac{\text{m}^3}{\text{h}} \cdot \frac{20 \text{ h}}{1 \text{ d}} \cdot \frac{350 \text{ d}}{1 \text{ year}}} \quad (17)$	/ $\frac{€}{\text{m}^3}$
CRD _c	d _c = €/m ³ Alkaline cleaning frequency = every 12 h (700 times/year) Acid cleaning frequency = weekly (52 times/year) Cleaning volume = 3 m ³ Rinsing volume = 6.5 m ³ Q = 20 m ³ /h 350 d; 20 h	$CRD_c = \frac{(700 + 52) \cdot (3 \text{ m}^3 + 6.5 \text{ m}^3) \cdot d_c \left(\frac{€}{\text{m}^3} \right)}{20 \frac{\text{m}^3}{\text{h}} \cdot \frac{20 \text{ h}}{1 \text{ d}} \cdot \frac{350 \text{ d}}{1 \text{ year}}} \quad (18)$	/ $\frac{€}{\text{m}^3}$
AC _c	C _{acc} = € i _c = 7% ACL = 1 year Q = 20 m ³ /h 350 d; 20 h	$AC_c = \frac{0.07}{(1 + 0.07)^1 - 1} \cdot C_{acc} (\text{€}) \cdot \frac{20 \frac{\text{m}^3}{\text{h}} \cdot \frac{20 \text{ h}}{1 \text{ d}} \cdot \frac{350 \text{ d}}{1 \text{ year}}}$	/ $\frac{€}{\text{m}^3}$
MA _c	CAPEX = 432,500 € Q = 20 m ³ /h 350 d; 20 h	$MA_c = \frac{0.02 \cdot €432,500}{20 \frac{\text{m}^3}{\text{h}} \cdot \frac{20 \text{ h}}{1 \text{ d}} \cdot \frac{350 \text{ d}}{1 \text{ year}}}$	/ $\frac{€}{\text{m}^3}$
PT _c	A _c ; M _c ; E _c ; C _c ; CD _c ; CRD _c ; AC _c ; MA _c	$PT_c = (0.15 \cdot (A_c + M_c + E_c + C_c + CD_c + CRD_c + AC_c + MA_c)) - MA_c \quad (19)$	/ $\frac{€}{\text{m}^3}$

Table 2 (continued)

Concept	Parameters	Calculation equations	Results
			TOTAL OPEX
			≈ €1.16/m³
Savings (€)			
E_s	$s_c = \text{€}/t$ Outlet permeate temperature = 45 °C Tap water temperature = 15 °C Saturated steam enthalpy (1.8 MPa and 210 °C) = 2800 kJ/kg Water specific heat = 4.19 kJ/kg °C Water density = 995.3 kg/m ³ RR = 83% Q = 20 m ³ /h 350 d; 20 h	$E_s = \frac{0.83 \cdot \left(20 \frac{\text{m}^3}{\text{h}} \cdot \frac{20 \text{ h}}{1 \text{ d}} \cdot \frac{350 \text{ d}}{1 \text{ year}}\right) \cdot 995.3 \frac{\text{kg}}{\text{m}^3} \cdot 4.19 \frac{\text{kJ}}{\text{kg} \cdot \text{C}} \cdot (45^\circ\text{C} - 15^\circ\text{C})}{2800 \frac{\text{kJ}}{\text{kg}} \cdot \frac{1000 \text{ kg}}{1 \text{ t}} \cdot \frac{1}{s_c} \left(\frac{\text{€}}{\text{m}^3}\right)} \quad (20)$	$/ \frac{\text{€}}{\text{y}}$
DW_s	RR = 83% Q = 20 m ³ /h 350 d; 20 h $dw_c = \text{€}/\text{m}^3$	$DW_s = 0.83 \cdot \left(20 \frac{\text{m}^3}{\text{h}} \cdot \frac{20 \text{ h}}{1 \text{ d}} \cdot \frac{350 \text{ d}}{1 \text{ year}}\right) \cdot dw_c \left(\frac{\text{€}}{\text{m}^3}\right) \quad (21)$	$/ \frac{\text{€}}{\text{y}}$
WD_s	$d_c = \text{€}/\text{m}^3$ Q = 20 m ³ /h 350 d; 20 h	$WD_s = \left(20 \frac{\text{m}^3}{\text{h}} \cdot \frac{20 \text{ h}}{1 \text{ d}} \cdot \frac{350 \text{ d}}{1 \text{ year}}\right) \cdot d_c \left(\frac{\text{€}}{\text{m}^3}\right) \quad (22)$	$/ \frac{\text{€}}{\text{y}}$
			TOTAL savings
			≈ €291,900/year
Savings per m³ (€/m³)			
Savings = 350,700 €/year Q = 20 m ³ /h 350 d; 20 h		$= \frac{291,900 \frac{\text{€}}{\text{year}}}{20 \frac{\text{m}^3}{\text{h}} \cdot \frac{20 \text{ h}}{1 \text{ d}} \cdot \frac{350 \text{ d}}{1 \text{ year}}} \quad / \frac{\text{€}}{\text{m}^3}$	
			TOTAL Savings per m³
			≈ €2.09/m³
			NPV (€)
			≈ 751,400
			IRR (%)
			≈ 29.4
			PB (year)
			≈ 3.3

lifetime, it is conditioned by the application and the contaminant type, the characteristics of the effluent, the feed concentration, and the type of activated carbon used [67]. In the case study, the activated carbon column exhaustion point was not reached, so an accurate durability cannot be offered. So, a value of 1 year was set to work at the most demanding conditions. In addition, the design life of the plant was considered to be 15 years and the investment, membrane and activated carbon replacement costs were annualized by taking into account a 7% interest rate.

To calculate the savings of the application, the outlet permeate temperature was established at 45 °C, with the factory tap water temperature averaged at 15 °C (note that this temperature could suffer seasonal changes, which could condition the balance). The saturated steam enthalpy was set at 1.8 MPa and 210 °C, the water specific heat and density at the average temperature were 2800 kJ/kg, 4.19 kJ/kg °C and 995.3 kg/m³, respectively. The factory steam (€/t), demineralized water and disposal costs (€/m³) were included in the model, but the figures are not shown in this work as they correspond to company private data.

3. Results and discussion

3.1. Development of the economic calculation of the base case study

The economic assessment of the RO plant for processing dairy condensates was performed in order to determine its economic viability based on essential assumptions, tested technically and validated in previous works [46,62]. All these previous assumptions considered are collated in Table 1. In the same way, a complete description of the calculations is shown in Table 2. In Fig. 2, a calculation template is also included to illustrate the paths to obtain the results shown in Table 2. With this information, the capital and the operating costs, the savings per year, the savings

per m³ of treated water and the PB obtained were €432,500, €1.16/m³, €291,900, €2.09/m³ and 3.3 years, respectively. The capital cost calculated by the described model is of the same order as the commercial offer provided by the membrane manufacturer for a membrane installation of similar characteristics and objectives, the deviation obtained being 13.7%, which gives an idea of the accuracy of the calculation. In addition, the differences in capital costs could be estimated at 33.9% and 29.1% when applying the six-tenths power rule model using the data of Elazhar et al. [8] and Shen et al. [26], respectively, or 57.3% and of greater importance using the model applied by Nilsson et al. [27].

The OPEX value (€1.16/m³) is in good agreement with those values reported by other authors who have treated food industry wastewaters using membrane processes (US\$1.25/m³ (€1.36/m³) and €0.97/m³ estimated by Chmiel et al. [68] and Blöcher et al. [69], respectively). However, they are higher than the average operating costs for RO desalination applications, established at US \$0.50/m³ (€0.38/m³) [30,70] (The \$/€ conversion, applied when necessary, is given for each respective date of research publication). The CAPEX for RO desalination being given for guidance only as these values are dependent on economies of scale and technical and economic local particularities.

The relative distribution and the ratio of influence of the different contributors to the CAPEX, OPEX and savings are shown in Fig. 3. It should be pointed out the small relevance that the membrane investment has for the total capital cost. Usually, its relative weight would vary between 20% and 30% in the case of small plants (4000–8000 m³/d), being of greater importance in the case of a larger installation size [23]. However, this factor is highly dependent on the type of membrane selected, its associated cost and the total plant area [31]. For example, the price of spiral-wound elements is one third of the cost of corresponding tubular membranes and the organic membranes will probably show a lower permeate flux [9].

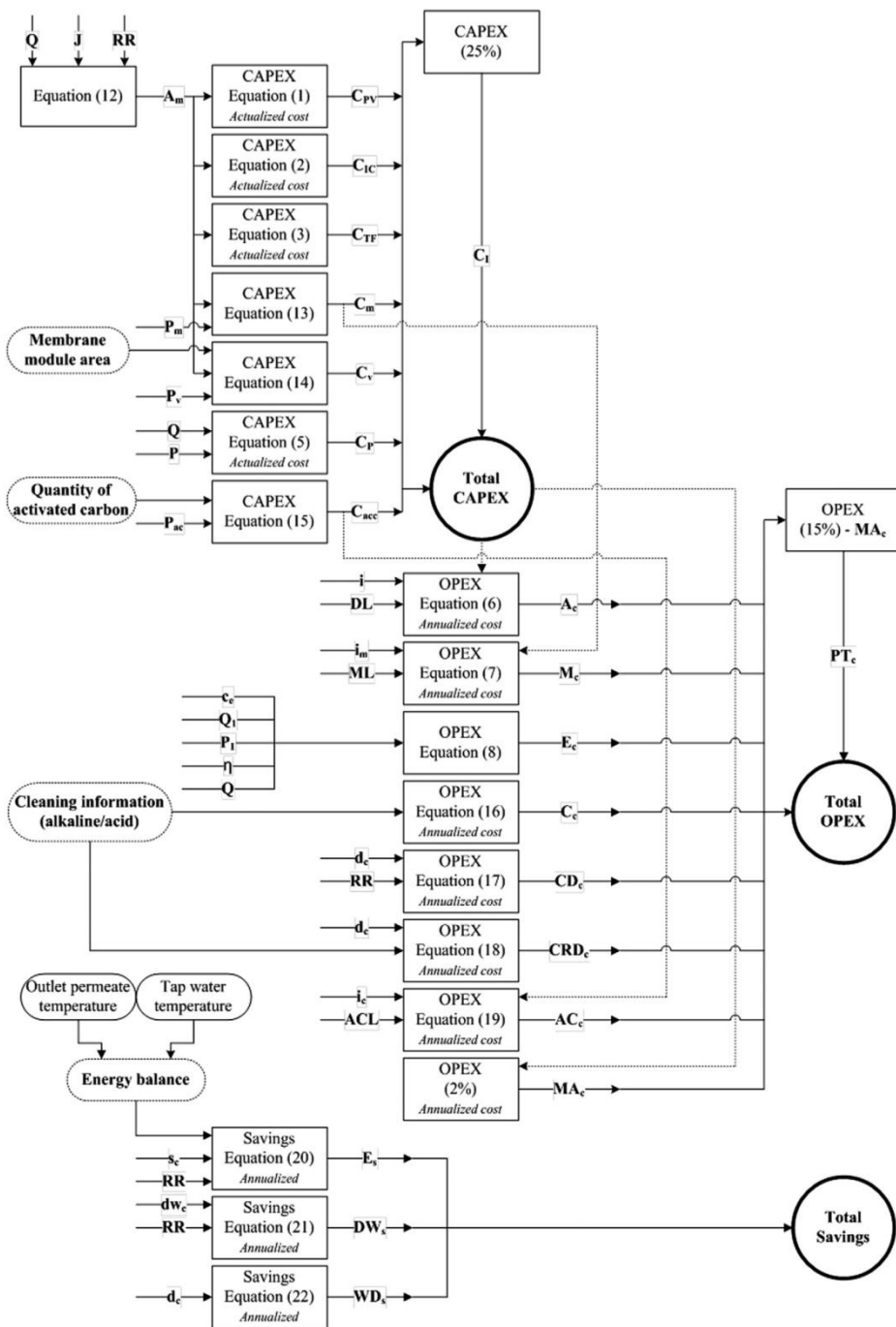


Fig. 2. Calculation template of the economic model for the specific case study considered. Abbreviations: A_c : amortization constituent, AC_c : activated carbon replacement costs, C_{acc} : investment cost of the activated carbon column, C_c : cost of chemicals, C_i : cost of installation, G_c : instruments and controls capital cost, C_m : membranes capital cost, C_P : pumps capital cost, C_{pv} : pipes and valves capital cost, C_{TF} : tanks and frames capital cost, C_v : pressure vessels capital cost, CAPEX: capital expenditure or investment, CD_c : concentrate disposal cost, CRD_c : disposal costs of the cleaning and rinsing solutions, DW_s : demineralized water savings, E_c : total cost of energy, E_s : energy savings, M_c : membrane replacement costs, MA_c : maintenance costs, OPEX: operating and maintenance costs, PT_c : pre-treatment costs, RR : recovery rate, and WD_s : water disposal savings. Symbols: A_m : membrane area, ACL : activated carbon lifetime, c_e : energy cost, d_c : factory disposal cost, DL : design life of the plant, d_w : factory demineralized water cost, i : interest rate, i_c : interest rate for activated carbon replacement, i_m : interest rate for membrane replacement, J : permeate flow rate, ML : membrane lifetime, η : pump efficiency, P : inlet pressure in kPa, P_1 : inlet pressure in Pa, P_{ac} : activated carbon price, P_m : membrane price per unit area, P_v : pressure vessel price per membrane module, Q : plant capacity in m^3/h , Q_1 : plant capacity in m^3/s , and s_c : factory steam cost.

When comparing the OPEX distribution to the data previously published, it is necessary to bear in mind that the major factors affecting the costs vary according to the types of applications and sites [23]. Although the initial purchase of membranes is a relatively small component of the facility investment [25], their replacement is a relevant part of the operating costs in RO, together with the energy consumption [10]. Its influence is higher at lower driving pressures [23], as in this study in which low-pressure RO membranes were used. In general, the largest single-cost component is the annualized capital cost [38]. The value of 29.3% obtained in this work is similar to those values of 32%, 34% and 39% obtained by Van der Bruggen et al. [21], Mohammad et al. [51] and Lapuente [29], respectively.

Regarding the benefits, they are entirely conditioned by the savings on water disposal, showing that the factory circumstances exert a relevant influence on these values. As a result, the distribution could vary considerably if distinct cost data are taken into account.

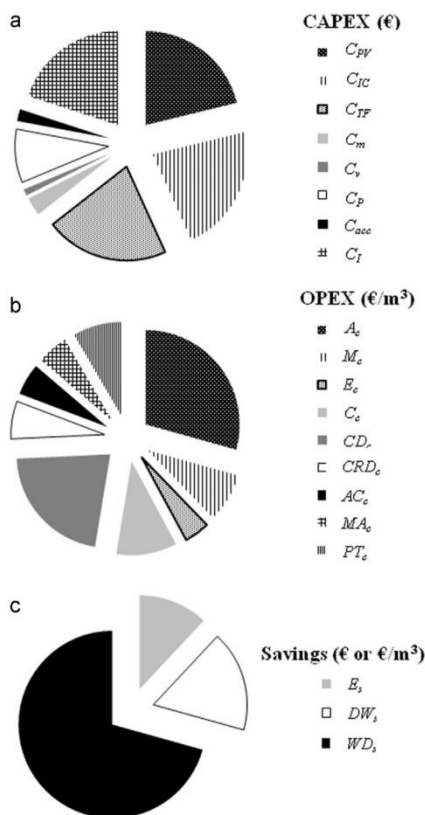


Fig. 3. Proportion of contribution of the different cost elements to the CAPEX (a), OPEX (b) and savings (c) in the membrane project considered. Abbreviations: A_c : amortization constituent, AC_c : activated carbon replacement costs, C_{acc} : investment cost of the activated carbon column, C_c : cost of chemicals, C_I : cost of installation, C_{IC} : instruments and controls capital cost, C_m : membranes capital cost, C_P : pumps capital cost, C_{PV} : pipes and valves capital cost, C_{TF} : tanks and frames capital cost, C_v : pressure vessels capital cost, CAPEX: capital expenditure or investment, CD_c : concentrate disposal cost, CRD_c : disposal costs of the cleaning and rinsing solutions, DW_s : demineralized water savings, E_c : total cost of energy, E_s : energy savings, M_c : membrane replacement costs, MA_c : maintenance costs, OPEX: operating and maintenance costs, PT_c : pre-treatment costs, and WD_s : water disposal savings.

3.2. Base case sensitivity analysis

A sensitivity analysis was carried out to determine the most important parameters involved in a membrane process and their influence on the economy of the installation. In this analysis, the original values of most relevant process parameters were modified by approximately $\pm 20\%$ and the impact of these changes on the economic indicators was evaluated. The parameters subjected to changes were:

1. The plant capacity and the number of working hours to take into account possible increases or decreases in production capacity, breakdowns, etc.
2. The permeate flux and the feed pressure to take into account possible fluctuations in feed temperature (which also determines the outlet temperature, the latter also being lower or higher in connection with the plant heat tracing) or to compensate irreversible fouling.
3. The RR which – in the specific situation of the case study application – could be enough for later reutilization in the case of a lower permeate quality, or which could, according to factory steam necessities, condition the amount of demineralized water.
4. The membrane lifetime, dependent on the heterogeneity of the feed composition, the module emplacement in the cascade, the temperature and pressure selected, the cleaning frequency and the strength of detergents, the clogging effects, etc.
5. In this particular application, the activated carbon lifetime, influenced by the content of organic matter of the permeate, the retro-washing frequency, the type of activated carbon used, the effectiveness of the active sites and their distribution.
6. The amortization period due to the different design life of the plant offered by the manufacturer according to previous experience in similar country, to represent the financing costs for the current year.
7. Membrane cost as this could change due to market influence, etc.

The results of this variability study are shown in Table 3, in which the influence (percentage) on the base case economic indicators is displayed. Positive values mean an increase with respect to the reference value (base case study) and the negative values a decrease. As can be seen, the plant capacity, the permeate flux and the RR exert a strong influence on the CAPEX as they directly affect the membrane area. Most of the studied parameters, although to a greater or lesser extent, directly impact on the operating costs, although the differentiation is complex as all of them are composed of several terms. The savings are mainly conditioned by the volume of inlet water managed, although as observed in the outlet temperature row, the degree of influence of the energy recovered could be of importance, particularly when the factory cost of steam is raised. Finally, and according to the payback periods calculated (affected by costs and savings variations), the application remained viable for all fluctuations studied.

Two of the parameters studied in Table 3, RR and membrane lifetime, were selected to study their influence on the main indicators that determine the economic balance (PB, IRR, NPV, savings per m^3 , total savings, OPEX and CAPEX). The study of the membrane life performance on the economy of the installation is important for this application, as after 145 working hours and 14 cleaning cycles, no membrane deterioration evidences were observed. As a result, since the real lifetime is unknown, it is necessary to determine the membrane duration at which the system acquires certain viability. The data used for the parameters selected RR (a) or membrane lifetime (b) were obtained from Table 3 and are summarized in Fig. 4,

Table 3

Percentage of influence on the economic indicators of a membrane installation as a function of the process parameter fluctuation.

		CAPEX	OPEX	Savings	Savings per m ³	NPV	IRR	PB
Plant capacity, m ³ /h	^a 20	–	–	–	–	–	–	–
	^b 24	10.8	–4.9	20.0	0.0	36.9	15.9	–13.0
	^c 16	–11.6	7.5	–20.0	0.0	–36.7	–19.7	22.0
Permeate flux, L/m ² h	^a 39	–	–	–	–	–	–	–
	^b 47	–8.6	–5.4	0.0	0.0	15.5	17.9	–14.3
	^c 31	12.1	8.3	0.0	0.0	–23.2	–21.9	24.9
Recovery, %	^a 83	–	–	–	–	–	–	–
	^b 100	10.2	–16.9	6.0	6.0	48.6	23.6	–18.1
	^c 66	–10.9	17.1	–6.0	–6.0	–48.5	–29.7	36.6
Feed pressure, kPa	^a 1300	–	–	–	–	–	–	–
	^b 1560	0.8	1.3	0.0	0.0	–3.0	–2.6	2.5
	^c 1040	–1.0	–1.3	0.0	0.0	3.2	2.8	–2.6
Membrane lifetime, year	^a 1.0	–	–	–	–	–	–	–
	^b 1.2	0.0	–1.7	0.0	0.0	3.3	2.3	–2.0
	^c 0.8	0.0	2.5	0.0	0.0	–4.9	–3.4	3.2
Activated carbon lifetime, year	^a 1.0	–	–	–	–	–	–	–
	^b 1.2	0.0	–1.1	0.0	0.0	2.1	1.5	–1.3
	^c 0.8	0.0	1.6	0.0	0.0	–3.2	–2.2	2.1
Amortization period, year	^a 15	–	–	–	–	–	–	–
	^b 18	0.0	–3.2	0.0	0.0	23.4	5.4	–3.8
	^c 12	0.0	4.9	0.0	0.0	–28.6	–9.9	6.6
Interest rate, %	^a 7.0	–	–	–	–	–	–	–
	^b 8.4	0.0	3.0	0.0	0.0	–18.5	–4.1	3.9
	^c 5.6	0.0	–2.9	0.0	0.0	21.2	3.9	–3.5
Membrane replacement costs, €/m ²	^a X	–	–	–	–	–	–	–
	^b X+0.2X	0.8	2.2	0.0	0.0	–4.8	–3.8	3.7
	^c X–0.2X	–0.8	–2.2	0.0	0.0	4.8	3.9	–3.5
Cleaning frequency, alkaline/acid (every x hours/every x weeks)	^a 12/1	–	–	–	–	–	–	–
	^b 10/1.2	0.0	3.9	0.0	0.0	–7.7	–5.3	5.1
	^c 15/0.8	0.0	–3.9	0.0	0.0	7.7	5.2	–4.6
Outlet temperature, °C	^a 45	–	–	–	–	–	–	–
	^b 54	0.0	0.0	3.6	3.6	12.6	8.6	–7.4
	^c 36	0.0	0.0	–3.6	–3.6	–12.7	–8.7	8.7
Working hours, h	^a 20	–	–	–	–	–	–	–
	^b 16	0.0	17.5	–20.0	0.0	–59.0	–42.2	59.9

Abbreviations: CAPEX: capital expenditure or investment, IRR: internal rate of return, NPV: net present value, OPEX: operating and maintenance costs, and PB: payback period.

^a Parameters of the base case.

^b Base case + 20% base case, approximately.

^c Base case – 20% base case, approximately.

where the grey bars mean that the original value of the basic assumption (83% of RR, or 1 year of membrane lifetime) has been increased by 20%, while the white ones denote a reduction of 20%. The effect of this fluctuation can increase the y-axis economic indicators, the bars being displaced to the positive area of the x-axis, or decrease them and displace the bars towards the x-axis negative area. It is also necessary to bear in mind that, for instance, a positive displacement on the PB is considered a negative issue, as it represents that the PB has increased with regards to the value determined in the base case study. Note that there is no direct relation between the increased parameter value and the percentage obtained. For instance, an increment of 20% in the RR produced an increase of 48.6% in the NPV; in the same way, a decrease of 20% caused a reduction of 10.9% in the CAPEX. Moreover, the importance of the percentage differed when the indicators changed in a positive or negative way. To highlight this, it can be observed that a 20% longer membrane lifetime caused a decrease of 1.7% in the OPEX, while increasing it by 2.5% when the durability of the membrane was reduced by the same percentage. The changes in the total savings and those per m³ were affected by the same proportion, as these two parameters are strongly connected. Finally, as the NPV, IRR and PB are conditioned by the balance in costs and savings and their respective rate of change, the total proportion is accumulated in these indicators by showing the higher percentages of increase/decrease depending on the fluctuation. For example, the unfavourable accumulative percentage of

36.6% in the PB generated when the RR was modified to represent a 20% lower value was the result of a positive influence of 10.9% due to the reduction of the CAPEX and the negative influences of 17.1% and 6.0% produced by both the increase in the OPEX and the decrease in the savings of the application, respectively.

The influence of both RR and membrane lifetime on the individual elements obtained from the breakdown of the economic indicators is shown in Table 4. Regarding the CAPEX and in the case of the RR change, the influence on C_{PV} , C_{IC} and C_{IF} was due to the variation of the membrane area, which varied from 426 m² to 513 m² and 338 m² when the RR was increased to approximately 100% (not particularly common in practice) and decreased to 66%, respectively, due to the greater membrane area required to recover a higher volume of permeate and vice versa. The extent of the change is a function of their respective calculation formulae (values of the exponent and the constant). The influence on C_m and C_r was also determined by the influence of the membrane area, although the proportion was different and higher in the case of the pressure vessel costs as the number of elements was always overestimated to round up to an integer, the calculation being made based on the number of membrane modules and their individual price. The influence on C_{acc} is directly proportional to the amount of permeate obtained, which depends on the RR selected. No influence was observed on C_p , as it was only a function of the feed flow and working pressure. C_1 and the total CAPEX moved in the same direction as they were directly

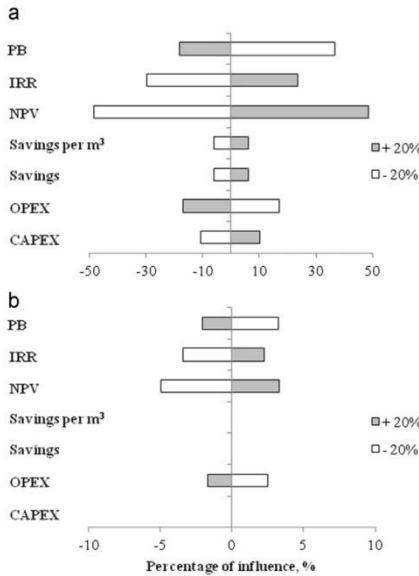


Fig. 4. Percentage of influence of the RR (a) and the membrane lifetime (b) on the economic indicators, taking as reference to the base case study. Abbreviations: CAPEX: capital expenditure or investment, IRR: internal rate of return, NPV: net present value, OPEX: operating and maintenance costs, and PB: payback period.

related to all of the above. With respect to the OPEX, A_c , M_c and AC_c , they changed by the same ratio as the CAPEX, membrane and activated carbon cost evolution, respectively. No changes were observed in E_c as previously explained in the case of pumping costs, nor in C_c , although this was related more to the form of the economic model. At this point, it must be noted that the cleaning protocol was optimized by piloting the conditions of the base case study and no information was available to determine the cleaning frequency when the amount of permeate recovered is increased or decreased. The CRD_c variation was due to the rinsing volume, which depends on the number of membrane elements (higher with the recovery and vice versa). The changes in MA_c and PT_c depend on all the previous variations, so the values obtained encompass a complex combination of the previous percentages, accumulating positive and negative factors, in the same way that the total OPEX behaved.

Finally, the highest influence was observed in CD_c , first of all because, as can be seen in Fig. 3b, this was one of the factors with the highest proportion of the OPEX, and second because the concentrate for treatment changed from 3.4 m³/h in the original case to 0 and 6.8 m³/h, approximately when the recovery varied by 100% and 66%, respectively. Concerning the savings, the E_s and DW_s varied linearly according to the RR. However, no effects on the WD_s factor were observed due to the way in which the economic calculation was proposed with regard to this variable, as it was assumed that the WD_s are always invariant and they are compensated by the concentrate disposal costs of the OPEX.

Regarding the changes in membrane lifetime (Table 4), no differences were observed in the CAPEX or the total savings as there was no parameter which could influence them. However, regarding the OPEX, M_c was clearly modified as the membrane life operated as an exponent in the corresponding equation; with a longer lifetime, the costs of membrane replacement are reduced, and vice versa. With respect to the pre-treatment costs, as they were a summary of all previous ones, they were also affected.

Table 4

Effect of the recovery and the membrane lifetime on the individual components of the CAPEX, OPEX and savings.

	RR, %		Membrane lifetime, year	
	100	66	1.2	0.8
CAPEX				
C_{pv}	8.1	-9.2	0.0	0.0
C_{ic}	13.1	-14.0	0.0	0.0
C_{TF}	10.4	-11.4	0.0	0.0
C_m	20.5	-20.5	0.0	0.0
C_v	23.1	-15.4	0.0	0.0
C_p	0.0	0.0	0.0	0.0
C_{acc}	20.5	-20.5	0.0	0.0
C_I	10.2	-10.9	0.0	0.0
Total	10.2	-10.9	0.0	0.0
OPEX				
A_c	10.2	-10.9	0.0	0.0
M_c	20.5	-20.5	-17.2	25.9
E_c	0.0	0.0	0.0	0.0
C_c	0.0	0.0	0.0	0.0
CD_c	-100.0	100.0	0.0	0.0
CRD_c	15.8	-10.5	0.0	0.0
AC_c	20.5	-20.5	0.0	0.0
MA_c	10.2	-10.9	0.0	0.0
PT_c	-31.9	32.5	-2.6	3.9
Total	-16.9	17.1	-1.7	2.5
Savings				
E_s	20.5	-20.5	0.0	0.0
DW_s	20.5	-20.5	0.0	0.0
WD_s	0.0	0.0	0.0	0.0
Total	6.0	-6.0	0.0	0.0
Savings per m³				
NPV	48.6	-48.5	3.3	-4.9
IRR	23.6	-29.7	2.3	-3.4
PB	-18.1	36.6	-2.0	3.2

Abbreviations: A_c : amortization constituent, AC_c : activated carbon replacement costs, C_{acc} : investment cost of the activated carbon column, C_c : cost of chemicals, C_I : cost of installation, C_{ic} : instruments and controls capital cost, C_m : membranes capital cost, C_p : pumps capital cost, C_{pv} : pipes and valves capital cost, C_{TF} : tanks and frames capital cost, C_v : pressure vessels capital cost, CAPEX: capital expenditure or investment, CD_c : concentrate disposal cost, CRD_c : disposal costs of the cleaning and rinsing solutions, DW_s : demineralized water savings, E_c : total cost of energy, E_s : energy savings, IRR: internal rate of return, M_c : membrane replacement costs, MA_c : maintenance costs, NPV: net present value, OPEX: operating and maintenance costs, PB: payback period, PT_c : pre-treatment costs, RR: recovery rate, and WD_s : water disposal savings.

In Fig. 5, the CAPEX and savings per year (main y axis) and the OPEX, savings per m³ and payback period (secondary y axis) are plotted vs. RR (Fig. 5a) and membrane lifetime (Fig. 5b) to study the behaviour of the economic model in extreme conditions.

With respect to the RR, at values higher than 50% the installation become profitable for the given amortization period when the savings per m³ surpassed the OPEX by a reasonable value able to compensate the initial investment (higher with the size of the installation), thus showing an economy of scale. In the same way, the membrane replacement period within which economic viability could be reasonable was established as approximately 6 months. However, the PB proved to be very competitive when the membrane replacement moved around normal membrane usage times given in the dairy industry, usually situated between 18 months and 3 years, and was highly conditioned by the cleaning cycles [65].

4. Conclusions

The model considered showed good accuracy in predicting the profitability of an RO application. For the case study, the calculated CAPEX differed 13.7% from the commercial offer provided by the membrane manufacturer for a plant with analogous characteristics

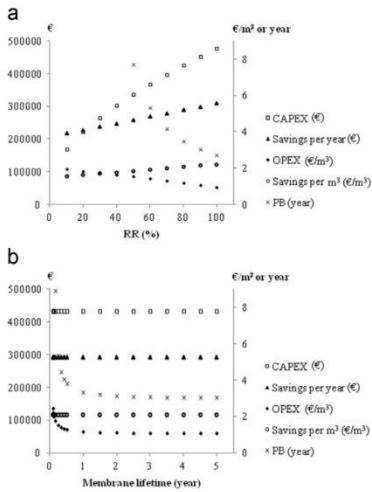


Fig. 5. Evolution of cost and savings indices as a function of RR (a) and membrane lifetime (b). Abbreviations: CAPEX: capital expenditure or investment, OPEX: operating and maintenance costs, PB: payback period, and RR: recovery rate.

and the OPEX values were in good agreement with those reported in the field of food industry wastewater treatment using membrane processes. It was shown that the most important term of the OPEX was the annualized capital cost, representing a percentage of 29.3%, whereas the membrane investment proved not to be relevant to the total capital costs. On the other hand, the application savings showed a strong dependence on particular factory conditions.

Concerning the hypotheses of the case study, the CAPEX, OPEX, savings per m³ and PB were estimated at €432,500, €1.16/m³, €2.09/m³ and 3.3 years, respectively. Thanks to the sensitivity analysis performed, it is possible to determine the influence of some of the parameters studied on the economy of the process. Thus, an increase of 20% in the RR produced an NPV improvement of 48.6%, while a 20% longer membrane lifetime only led to an increment in the NPV of 3.3%, showing significant differences in the percentage of influence. The installation proved to be profitable at RR values above 50%; otherwise, a membrane lifetime of 6 months was reasonable as with this value the PB remained constant.

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Nomenclature: Abbreviations

A_c	amortization constituent
AC_c	activated carbon replacement costs
ACC	activated carbon column
AF	amortization factor
AF_m	amortization factor of the membrane replacement
BOD_5	biological oxygen demand after 5 days
C_{acc}	investment cost of the activated carbon column
C_c	cost of chemicals

C_i	cost of installation
C_C	instruments and controls capital cost
C_m	membranes capital cost
C_{MI}	miscellaneous capital cost
C_P	pumps capital cost
C_{PV}	pipes and valves capital cost
C_{TF}	tanks and frames capital cost
C_V	pressure vessels capital cost
CAPEX	capital expenditure or investment
CD_c	concentrate disposal cost
CEPCI	chemical engineer plant cost index
CIP	cleaning in place
COD	chemical oxygen demand
CRD_c	disposal costs of the cleaning and rinsing solutions
DW_s	demineralized water savings
E_c	total cost of energy
E_s	energy savings
FC	flash cooler
IRR	internal rate of return
M_c	membrane replacement costs
MA_c	maintenance costs
MF	microfiltration
MWCO	molecular weight cut-off
NF	nanofiltration
NPV	net present value
OPEX	operating and maintenance costs
PB	payback period
PT_c	pre-treatment costs
RO	reverse osmosis
RR	recovery rate
TOC	total organic carbon
TSS	total suspended solids
UF	ultrafiltration
UHT	ultra-high temperature
VCR	volume concentration rate
WD_s	water disposal savings

Symbols

A_m	membrane area, m ²
ACL	activated carbon lifetime, year
c_e	energy cost, €/W h
CF	cash flow, €
d_c	factory disposal cost, €/m ³
DL	design life of the plant, year
dw_c	factory demineralized water cost, €/m ³
i	interest rate, decimal %
i_c	interest rate for activated carbon replacement, decimal %
i_m	interest rate for membrane replacement, decimal %
I_o	initial investment, €
J	permeate flow rate, L/m ² h
ML	membrane lifetime, year
n	holding period of investment evaluation, year
η	pump efficiency, decimal %
P	inlet pressure, kPa
P_1	inlet pressure, Pa
P_{ac}	activated carbon price, €/kg
P_m	membrane price per unit area, €/m ²
P_v	pressure vessel price per membrane module, €/membrane module
Q	plant capacity, m ³ /h
Q_1	plant capacity, m ³ /s
r	discount rate of the invested capital, decimal %
R	rejection or reduction, %

sc	factory steam cost, €/t
TMP	Transmembrane pressure, kpa

References

- [1] A. Hafez, M. Khedr, H. Gadallah, Wastewater treatment and water reuse of food processing industries. Part II: techno-economic study of a membrane separation technique, *Desalination* 214 (2007) 261–272.
- [2] Y. Pouliot, Membrane processes in dairy technology—from a simple idea to worldwide panacea, *Int. Dairy J.* 18 (2008) 735–740.
- [3] L.A. Ioannou, C. Michael, N. Vakondios, K. Drosou, N.P. Xekoukoulotakis, E. Diamadopoulos, D. Fatta-Kassinou, Winery wastewater purification by reverse osmosis and oxidation of the concentrate by solar photo-Fenton, *Sep. Purif. Technol.* 118 (2013) 659–669.
- [4] G. Daufin, J.P. Escudier, H. Carrère, S. Bérôt, L. Fillaudeau, M. Decloux, Recent and emerging applications of membrane processes in the food and dairy industry, *Food Bioprod. Process.* 79 (2001) 89–102.
- [5] T. Coskun, E. Debik, N.M. Demir, Treatment of olive mill wastewaters by nanofiltration and reverse osmosis membranes, *Desalination* 259 (2010) 65–70.
- [6] W. Chen, J. Liu, The possibility and applicability of coagulation-MBR hybrid system in reclamation of dairy wastewater, *Desalination* 285 (2012) 226–231.
- [7] J. Schwinge, P.R. Neal, D.E. Wiley, D.F. Fletcher, A.G. Fane, Spiral wound modules and spacers: review and analysis, *J. Membr. Sci.* 242 (2004) 129–153.
- [8] F. Elazhar, M. Tahait, A. Achatei, F. Elmidaoui, M. Taky, F. El Hannouni, L. Laziz, S. Jariri, M. El Amrani, A. Elmidaoui, Economical evaluation of the fluoride removal by nanofiltration, *Desalination* 249 (2009) 154–157.
- [9] A.-S. Jönsson, A.-K. Nordin, O. Wallberg, Concentration and purification of lignin in hardwood kraft pulping liquor by ultrafiltration and nanofiltration, *Chem. Eng. Res. Des.* 86 (2008) 1271–1280.
- [10] L. Malaeb, G.M. Ayoub, Reverse osmosis technology for water treatment: state of the art review, *Desalination* 267 (2011) 1–8.
- [11] S. Loutaidou, B. Chalermthai, P.R. Marpu, H.A. Arafat, Capital cost estimation of RO plants: GCC countries versus southern Europe, *Desalination* 347 (2014) 103–111.
- [12] C. García-Figueroa, B. Montag, A. Bes-Pià, J.A. Mendoza-Roca, E. Soriano-Costa, J. Lora-García, Study of the behaviour of a reverse osmosis membrane for wastewater reclamation – influence of wastewater concentration, *Desalination* 222 (2008) 243–248.
- [13] V.V.L. Ravikumar, S. Kalyani, S.V. Satyanarayana, S. Sridhar, Processing of pharmaceutical effluent condensate by nanofiltration and reverse osmosis membrane techniques, *J. Taiwan Inst. Chem. Eng.* 45 (2014) 50–56.
- [14] S.S. Madaeni, Y. Mansourpanah, COD removal from concentrated wastewater using membranes, *Filtr. Sep.* 40 (2003) 40–46.
- [15] J. Radjenović, M. Petrović, F. Ventura, D. Barceló, Rejection of pharmaceuticals in nanofiltration and reverse osmosis membrane drinking water treatment, *Water Res.* 42 (2008) 3601–3610.
- [16] A. Bódalo-Santoyo, J.L. Gómez-Carrasco, E. Gomez-Gomez, M.F. Maximo-Martin, A.M. Hidalgo-Montesinos, Spiral-wound membrane reverse osmosis and the treatment of industrial effluents, *Desalination* 160 (2004) 151–158.
- [17] B. Durham, M.M. Bourbigot, T. Pankratz, Membranes as pretreatment to desalination in wastewater reuse: operating experience in the municipal and industrial sectors, *Desalination* 138 (2001) 83–90.
- [18] Y. Wibisono, E.R. Cornelissen, A.J.B. Kemperman, W.G.J. van der Meer, K. Nijmeijer, Two-phase flow in membrane processes: a technology with a future, *J. Membr. Sci.* 453 (2014) 566–602.
- [19] B.F. Jirjis, S. Luque, Practical aspects of membrane system design in food and bioprocessing applications, in: Z.F. Cui and H.S. Muralidhara (Eds.), *Membrane Technology*, Butterworth-Heinemann, Oxford, 2010.
- [20] H.T. El-Dessouky, H.M. Ettouney, Chapter 10 – Economic Analysis of Desalination Processes, in: H.T. El-Dessouky, H.M. Ettouney (Eds.), *Fundamentals of Salt Water Desalination*, Elsevier Science B.V., Amsterdam, 2002, pp. 503–524.
- [21] B. Van der Bruggen, K. Everaert, D. Wilms, C. Vandecasteele, Application of nanofiltration for removal of pesticides, nitrate and hardness from ground water: rejection properties and economic evaluation, *J. Membr. Sci.* 193 (2001) 239–248.
- [22] X. Zheng, M. Ernst, M. Jekel, Stabilizing the performance of ultrafiltration in filtering tertiary effluent—technical choices and economic comparisons, *J. Membr. Sci.* 366 (2011) 82–91.
- [23] R. Liikaneen, J. Yli-Kuivila, J. Tenhunen, R. Laukkanen, Cost and environmental impact of nanofiltration in treating chemically pre-treated surface water, *Desalination* 201 (2006) 58–70.
- [24] S. Sethi, M.R. Wiesner, Cost modeling and estimation of crossflow membrane filtration processes, *Environ. Eng. Sci.* 17 (2000) 61–79.
- [25] M.R. Wiesner, J. Hackney, S. Sethi, J.G. Jacangelo, J.-M. Laine, Cost estimates for membrane filtration and conventional treatment, *J. Am. Water Works Assoc.* 86 (1994) 33–41.
- [26] J. Shen, J. Huang, H. Ruan, J. Wang, B. Van der Bruggen, Techno-economic analysis of resource recovery of glycosate liquor by membrane technology, *Desalination* 342 (2014) 118–125.
- [27] M. Nilsson, F. Lipnizki, G. Trägårdh, K. Östergren, Performance, energy and cost evaluation of a nanofiltration plant operated at elevated temperatures, *Sep. Purif. Technol.* 60 (2008) 36–45.
- [28] N. Garcia, J. Moreno, E. Cartmell, I. Rodriguez-Roda, S. Judd, The cost and performance of an MF-RO/NF plant for trace metal removal, *Desalination* 309 (2013) 181–186.
- [29] E. Lapuente, Full cost in desalination. A case study of the Segura River Basin, *Desalination* 300 (2012) 40–45.
- [30] U.K. Kesimee, N. Milne, H. Aral, C.Y. Cheng, M. Duke, Economic analysis of desalination technologies in the context of carbon pricing, and opportunities for membrane distillation, *Desalination* 323 (2013) 66–74.
- [31] A.L. Ahmad, M.F. Chong, S. Bhatia, A comparative study on the membrane based palm oil mill effluent (POME) treatment plant, *J. Hazard. Mater.* 171 (2009) 166–174.
- [32] M.I. Ali, E.K. Summers, H.A. Arafat, J.H. Lienhard V, Effects of membrane properties on water production cost in small scale membrane distillation systems, *Desalination* 306 (2012) 60–71.
- [33] U. Atikol, H.S. Aybar, Estimation of water production cost in the feasibility analysis of RO systems, *Desalination* 184 (2005) 253–258.
- [34] F. Banat, N. Jwaied, Economic evaluation of desalination by small-scale autonomous solar-powered membrane distillation units, *Desalination* 220 (2008) 566–573.
- [35] A.R. Costa, M.N. de Pinho, Performance and cost estimation of nanofiltration for surface water treatment in drinking water production, *Desalination* 196 (2006) 55–65.
- [36] S. Cros, B. Lignot, P. Jaouen, P. Bourseau, Technical and economical evaluation of an integrated membrane process capable both to produce an aroma concentrate and to reject clean water from shrimp cooking juices, *J. Food Eng.* 77 (2006) 697–707.
- [37] A. Gorenflo, D. Velázquez-Padrón, F.H. Frimmel, Nanofiltration of a German groundwater of high hardness and NOM content: performance and costs, *Desalination* 151 (2003) 253–265.
- [38] G. Owen, M. Bandi, J.A. Howell, S.J. Churchouse, Economic assessment of membrane processes for water and waste water treatment, *J. Membr. Sci.* 102 (1995) 77–91.
- [39] R. Pianta, M. Boller, D. Urfer, A. Chappaz, A. Gmünder, Costs of conventional vs. membrane treatment for karstic spring water, *Desalination* 131 (2000) 245–255.
- [40] C. Abels, K. Thimm, H. Wulffhorst, A.C. Spiess, M. Wessling, Membrane-based recovery of glucose from enzymatic hydrolysis of ionic liquid pretreated cellulose, *Bioresour. Technol.* 149 (2013) 58–64.
- [41] C. Aydinler, U. Sen, S. Topcu, D. Ekinci, A.D. Altınay, D.Y. Koseoglu-Imer, B. Keskinler, Techno-economic viability of innovative membrane systems in water and mass recovery from dairy wastewater, *J. Membr. Sci.* 458 (2014) 66–75.
- [42] T. Mezher, H. Fath, Z. Abbas, A. Khaled, Techno-economic assessment and environmental impacts of desalination technologies, *Desalination* 266 (2011) 263–273.
- [43] K. Jevons, M. Awe, Economic benefits of membrane technology vs. evaporator, *Desalination* 250 (2010) 961–963.
- [44] F.A. Riera, A. Suárez, C. Muro, Nanofiltration of UHT flash cooler condensates from a dairy factory: characterisation and water reuse potential, *Desalination* 309 (2013) 52–63.
- [45] A. Suárez, T. Fidalgo, F.A. Riera, Recovery of dairy industry wastewaters by reverse osmosis. Production of boiler water, *Sep. Purif. Technol.* 133 (2014) 204–211.
- [46] A. Suárez, F.A. Riera, Production of high-quality water by reverse osmosis of milk dairy condensates, *J. Ind. Eng. Chem. U* 21 (2015) 1340–1349.
- [47] N.a. Ali, A.W. Mohammad, A.L. Ahmad, Use of nanofiltration predictive model for membrane selection and system cost assessment, *Sep. Purif. Technol.* 41 (2005) 29–37.
- [48] K. Guerra, J. Pellegrino, J.E. Drewes, Impact of operating conditions on permeate flux and process economics for cross flow ceramic membrane ultrafiltration of surface water, *Sep. Purif. Technol.* 87 (2012) 47–53.
- [49] L. Suárez, M.A. Diez, F.A. Riera, Recovery of detergents in food industry: an industrial approach, *Desalin. Water Treat.* (2014) 1–10.
- [50] A.J.P. Verberne, J.W. Wouters, Membranfiltratie voor de drinkwaterbereiding: economische optimalisatie van ontwerpparameters, *H₂O* 26 (1993) 383–387.
- [51] A. Wahab Mohammad, N.a. Ali, A.L. Ahmad, N. Hilal, Optimized nanofiltration membranes: relevance to economic assessment and process performance, *Desalination* 165 (2004) 243–250.
- [52] S. Banvolgyi, I. Kiss, E. Bekassy-Molnar, G. Vatai, Concentration of red wine by nanofiltration, *Desalination* 198 (2006) 8–15.
- [53] J. Lindmark, E. Thorin, J. Kastensson, C.M. Pettersson, Membrane filtration of process water at elevated temperatures—a way to increase the capacity of a biogas plant, *Desalination* 267 (2011) 160–169.
- [54] I. Vincze, G. Vatai, Application of nanofiltration for coffee extract concentration, *Desalination* 162 (2004) 287–294.
- [55] M. Di Luccio, C.P. Borges, T.L.M. Alves, Economic analysis of ethanol and fructose production by selective fermentation coupled to pervaporation: effect of membrane costs on process economics, *Desalination* 147 (2002) 161–166.
- [56] S. Sethi, M.R. Wiesner, Simulated cost comparisons of hollow-fiber and integrated nanofiltration configurations, *Water Res.* 34 (2000) 2589–2597.

- [57] S.S. Adham, J.G. Jacangelo, J.-M. Laine, Characteristics and costs of MF and UF plants, *J. Am. Water Works Assoc.* 88 (1996) 22–31.
- [58] K. Pickering, M.R. Wiesner, Cost model for low-pressure membrane filtration, *J. Environ. Eng.* 119 (1993) 772–797.
- [59] R.H. Perry, C.H. Chilton, *Chemical Engineer's Handbook*, McGraw-Hill, New York, 1991.
- [60] S.P. Max, D.K. Timmerhause, E.R. West, *Plant Design and Economics for Chemical Engineers*, McGraw-Hill, New York, 2003.
- [61] R.A. Bergman, Membrane softening versus lime softening in Florida: a cost comparison update, *Desalination* 102 (1995) 11–24.
- [62] A. Suárez, T. Fidalgo, M.A. Berdasco, F.A. Riera, UHT condensate recovery by reverse osmosis: a pilot-plant study, *Ind. Eng. Chem. Res.* 53 (2014) 15237–15244.
- [63] V. Mavrov, H. Chmiel, E. Bélières, Spent process water desalination and organic removal by membranes for water reuse in the food industry, *Desalination* 138 (2001) 65–74.
- [64] S. Judd, B. Jefferson, *Membranes for Industrial Wastewater Recovery and Re-Use*, Elsevier Science Ltd., Oxford, 2003.
- [65] H. Li, V. Chen, Chapter 10 – Membrane fouling and cleaning in food and bioprocessing, in: Z.F. Cui, H.S. Muralidhara (Eds.), *Membrane Technology*, Butterworth-Heinemann, Oxford, 2010, pp. 213–254.
- [66] E.M. Garcia-Castello, L. Mayor, S. Chorques, A. Argüelles, D. Vidal-Brotóns, M.L. Gras, Reverse osmosis concentration of press liquid from orange juice solid wastes: flux decline mechanisms, *J. Food Eng.* 106 (2011) 199–205.
- [67] L.N. Nguyen, F.I. Hai, J. Kang, W.E. Price, L.D. Nghiem, Removal of trace organic contaminants by a membrane bioreactor–granular activated carbon (MBR–GAC) system, *Bioresour. Technol.* 113 (2012) 169–173.
- [68] H. Chmiel, V. Mavrov, E. Belieres, Reuse of vapour condensate from milk processing using nanofiltration, *Filtr. Sep.* 37 (2000) 24–27.
- [69] C. Blöcher, M. Noronha, L. Fünfroeken, J. Dorda, V. Mavrov, H.D. Janke, H. Chmiel, Recycling of spent process water in the food industry by an integrated process of biological treatment and membrane separation, *Desalination* 144 (2002) 143–150.
- [70] C. Fritzmann, J. Löwenberg, T. Wintgens, T. Melin, State-of-the-art of reverse osmosis desalination, *Desalination* 216 (2007) 1–76.

Conclusiones particulares del apartado 4.5.

La aplicación para la recuperación de condensados de *flash cooler* en forma de agua de alimentación a calderas mediante tratamiento por ósmosis inversa y carbón activo demostró ser económicamente rentable al obtenerse como periodo de recuperación de la inversión un valor de 3,3 años. El modelo económico utilizado, que fue completado para representar una situación más realista, arrojó una inversión muy cercana a la suministrada por el fabricante de membranas para dicha instalación, siendo la desviación del 13,7%. Por otro lado, los costes de operación de la planta, estimados en 1,16 €/m³, demostraron estar en valores habituales para este tipo de aplicaciones (1,36 €/m³ en el caso de Chmiel et al., 2000 y 0,97 €/m³ por parte de Blöcher et al., 2002, por ejemplo).

El análisis de sensibilidad llevado a cabo permitió calcular el impacto de diferentes factores sobre la economía de la aplicación y además controlar la influencia de posibles variaciones paramétricas futuras o cambios en las circunstancias de producción. De todas las variables estudiadas, de interés fue el estudio sobre la durabilidad de las membranas, ya que al no encontrarse evidencias de deterioro durante todas sus horas de uso, fue necesario determinar el tiempo crítico a partir del cual se perdería viabilidad económica en la aplicación. Como resultado, una vida útil por debajo de 6 meses condicionó notablemente la rentabilidad del proceso, aunque se trataría de una circunstancia poco común en el uso de técnicas de membrana en la industria láctea ya que, en este campo, su duración suele establecerse entre 18 meses y 3 años dependiendo de las condiciones de trabajo y la frecuencia e intensidad de las limpiezas.

Capítulo 5: *Conclusiones*

5. Conclusiones

La caracterización de los condensados de *flash cooler* determinó su naturaleza heterogénea, siendo sus propiedades muy variables en función de las circunstancias de producción. Sin embargo, su consideración como aguas de baja carga contaminante ($<700 \text{ mgO}_2/\text{L}$ de demanda química de oxígeno (DQO) y $<2200 \text{ }\mu\text{S}/\text{cm}$ de conductividad) aconsejó su segregación y tratamiento individualizado. De los cuatro esterilizadores en funcionamiento en la factoría, los condensados procedentes de uno de ellos presentaron valores de materia orgánica 25 veces superiores a la media, lo que hizo que fueran descartados para su tratamiento con membranas. En este sentido, esta información ha permitido a los técnicos de la factoría indagar acerca de las razones de esta situación para tratar de resolver el problema.

En base a su temperatura de salida y con el objetivo de un aprovechamiento energético, los condensados fueron procesados alrededor de 50°C , por lo que se requirió de membranas resistentes a temperaturas medias. En estas condiciones de trabajo, la operación de nanofiltración mediante membranas SelRO MPS-34 2540 B2X (Koch Membrane Systems, USA) de 200 Da de tamaño de poro no dio lugar a permeados que cumplieran los requerimientos para su reutilización como aguas de alimentación a calderas (pH 7–10, conductividad (25°C) $<40\mu\text{S}/\text{cm}$, DQO $<10 \text{ mgO}_2/\text{L}$, $\text{Ca}^{2+} <0.4 \text{ mg}/\text{L}$, principalmente).

A través de ensayos en discontinuo a diferentes valores del factor de concentración de volumen (VCR; 1–10), la membrana Duratherm® HWS 4040 HR (GE Water & Process Technologies, USA) de ósmosis inversa dio lugar a los mayores rechazos en cuanto a conductividad y materia orgánica, siendo éstos de hasta el 97.8 y el 98.9%, respectivamente. Lo que hizo que, junto con su coste unitario menor, fuera seleccionada para las siguientes etapas del estudio. Por otro lado, estos ensayos en discontinuo permitieron la predicción de flujos de permeado y rechazos cuando las características de la alimentación se movieron en torno a 174,3 y 1200 $\mu\text{S}/\text{cm}$ de conductividad y la DQO entre 24 y 284 mgO_2/L y las condiciones de trabajo alrededor de $50\text{--}75^\circ\text{C}$ de temperatura y 10–20 bar de presión. Sin embargo se observó que, a valores del grado de recuperación por encima del 90% y presiones de trabajo superiores a 15 bar, las limitaciones objetivo fueron sobrepasadas.

De acuerdo a la información obtenida en discontinuo y a las recomendaciones del fabricante, se trabajó en continuo, en experimentos de larga duración de hasta 100 horas, en las siguientes condiciones: 40 L/hm^2 de flujo de permeado, 1000 L/h de caudal de alimentación (8,2 m^2 de área de membrana), temperaturas alrededor de los 45°C y presión creciente hasta 30 bar, que delimitó las necesidades de limpieza. Además se propuso el uso de un post-tratamiento de carbón activo para asegurar el límite de 10 mgO_2/L de DQO en la experimentación en continuo.

La predicción teórica de rechazos alcanzada en base a modelos de la termodinámica irreversible fue excelente, encontrándose un error de sólo el 1,82% cuando el modelo de *film theory* – *Spiegler* – *Kedem*, que tiene en cuenta fenómenos de polarización por concentración, fue utilizado. A 40 L/hm², las predicciones de rechazos se situaron entre el 84 y el 97% para la conductividad, y alrededor del 98% para la DQO cuando se trabaja a VCRs entre 1 y 10, respectivamente.

El grado máximo de recuperación fue establecido finalmente en un 83,3%. La experimentación en continuo a VCR 6 (que simularía las etapas más restrictivas de una cascada de membranas), donde fenómenos de ensuciamiento hicieron acto de presencia, permitió determinar un valor medio de requerimiento de limpieza de 12 horas, aunque se produjeron incrementos de presión muy importantes cuando se dieron entradas de DQO al sistema en torno a 300 mgO₂/L, por lo que un control y segregación de estos picos de contaminación sería muy aconsejable. El acoplamiento de un post-tratamiento de carbón activo al proceso de ósmosis inversa hizo que se cumplieran los requerimientos de aguas de caldera, encontrándose rechazos a la DQO de hasta el 100%.

En relación al volumen de agua desmineralizada manejado en la actualidad en la factoría y en base al caudal de permeados que se podría generar, se estimó un grado de sustitución de agua desmineralizada del 43%. La dilución generada respetó no sólo los límites de agua de calderas tomados como referencia a lo largo del trabajo, sino también los requisitos establecidos en la norma UNE-EN 12953-10 de calderas pirotubulares.

La aplicación desarrollada, además de técnicamente viable, demostró ser económicamente rentable, obteniéndose un *payback* de 3,3 años. La inversión inicial, los costes de operación y los ahorros fueron establecidos en 432500 €, 1,16 €/m³ y 2,09 €/m³, respectivamente. Durante las horas de uso de la membrana no se encontraron evidencias de deterioro, por ello fue de importancia calcular la durabilidad crítica que representaría una pérdida de viabilidad económica, estableciéndose éste valor en un mínimo de 6 meses.

