Efficiency and sensitivity of the wet oxidation/biological steps in coupled pharmaceutical wastewater treatment

Sergio Collado, David Quero, Adriana Laca, Mario Díaz

Department of Chemical Engineering and Environmental Technology, University of Oviedo, E-33071 Oviedo, Spain

Abstract

In this work, the implementation and competitiveness of a continuous coupled wet oxidation/biological process for the treatment of four different phenolic compounds of a pharmaceutical wastewater are evaluated according to removal efficiency of each compound, sensitivity to feed perturbations and robustness.

Efficiencies of wet oxidation pretreatment for each compound rose to 95%, whereas an important part of the initial COD remained in the medium. In the case of the biotreatment, phenolic compounds were practically eliminated and COD reductions up to 95% were achieved. These values are higher than those obtained by means of the majority of the coupled processes.

The wet oxidation also showed relatively low sensitivities in front of perturbations on the feed composition for compounds with kinetic constants during the wet oxidation process higher than 8.4 h−1. Sensitivity studies indicated that the system is stable to changes in the flow rate for residence times in the bioreactor lower than 25 days. Perturbations of the oxygen flow rate had no effect on the removal of the phenolic compounds, in accordance with the fact of calculated Hatta numbers lower than 0.015, indicating a kinetically controlled regime in the range assayed $(4-10\ kgO_2/m^3_{wastewater})$.

Additionally, during the evaluation of the robustness of the process, "dampening factors" near of 1 were obtained for the removal of phenolic compounds, corroborating the excellent behavior of the coupled wet oxidation/biological system when fast and continuous changes in the pollutant load were assayed.

Keywords

Coupled treatment process; Phenolic compounds; Pharmaceutical wastewater; Robustness; Sensitivity to feed conditions; Wet oxidation

1. Introduction

Wastewaters from pharmaceutical industries contain hazardous and refractory organic pollutants which can cause severe problems for the environment. They must be treated to satisfy the stringent water quality regulations and the demand for recycling of water in the process [1].

A lot of data are available in the literature for the treatment of pharmaceutical wastewaters at laboratory scale by means of different techniques, paying special attention to the effect of the main conditions on the final conversion (see Table 1). The majority of these studies were conducted under discontinuous or steady state conditions and fixing the initial characteristics of the feed (flow rate and composition, mainly), as all other inputs to the system, which remain constant during each experiment.

Table 1. Some relevant studies about the treatment of pharmaceutical wastewaters.

Method	**Wastewater**	**Efficiency**	**Reference**
Biological technologies	Urban-pharmaceutical wastewater (COD = 1616 ppm)	40−95% (COD)	[2]
Ozonation	Formulation of the penicillin Sultamycillin Tosylate Dihidrate (COD = 690 ppm)	34% (COD) 24% (TOC)	[3]
MBR	High-strength traditional Chinese medicine wastewater (COD = 250−12700 ppm)	80−99% (COD)	[4]
MBR-ozonation (placed in the recirculation of MBR)	Production of a antiviral drug (COD = 10900 ppm)	99% (COD)	[5]
Fenton-aerobic biological process	Pharmaceutical phenolic wastewater (COD = 11987 ppm; salicylic acid = 1029 ppm)	67% (COD, Fenton) 93% (COD, biotreatment)	[6]
Fenton-aerobic biological process	Wastewater generated from pyridine manufacturing plants (COD = 65000 ppm)	66% (COD, Fenton) 94% (COD, biotreatment)	[7]
Fenton-aerobic biological process	Wastewater generated from cyanopyridine manufacturing plants (COD = 25600 ppm)	84% (COD, Fenton) 99% (COD, biotreatment)	[7]
Solar photo-Fenton-aerobic biological process	Pharmaceutical wastewater with non-biodegradable nalixidic acid (TOC = 775 ppm)	33% (TOC, photoF.) 62% (TOC, biotreatment)	[8]
Alkaline ozonation	Penicillin formulation effluent (COD = 1395 ppm)	49% (COD) 42% (TOC)	[9]
Photo-Fenton	Penicillin formulation effluent (COD = 1395 ppm)	66% (COD) 52% (TOC)	[9]
CWAO-anaerobic aerobic process	Wastewater from vitamin B6 production (COD = 70000−120000 ppm)	89% (COD, CWO) 99% (COD, biotreatment)	[10]
	High-strength o-cresol wastewater	56% (COD, CWAO)	

Method	Wastewater	Efficiency	Reference
CWAO-aerobic process		91% (COD, biotreatment)	[11]

Fast fluctuations of inflow characteristics, however, are quite common for actual industrial wastewater treatment facilities, mainly due to modifications on the production line associated with stocks or pending order volumes, batch operations, availability of raw materials, failures, work schedule etc. Obviously, a high efficiency industrial wastewater treatment process must be able to reduce the effect of these fluctuations on the final efficiency, in order to avoid peaks of concentration in the discharged effluent. However, there is a high lack of knowledge about the robustness and sensitivity for the different wastewater treatment techniques to changes and perturbations in the feed characteristics, even when they frequently vary during the industrial operation due to fluctuations on the composition and/or the flow rate of the feed or on the oxygen flow rate supplied.

Among wastewater treatment methods, increasing interest is being shown in integrating chemical and biological systems to treat polluting compounds, using a chemical oxidation pretreatment step to convert initially biorecalcitrant organics to more readily biodegradable products [12], [13], [14], [15], [16], [17]. Chemical treatments used to break down toxic and recalcitrant pharmaceutical compounds to molecules suitable for biotreatment include wet air oxidation (WAO), ozonation, photooxidation and Fenton's reaction, which are generally termed advanced oxidation processes (AOP's) [12], [18]. Wet air oxidation uses temperature and pressures over 120 °C and 10 bar and air or oxygen as oxidant, being particularly useful for toxic organic wastewater with a moderate-high COD [19], [20]. Several pharmaceutical wastewaters were successfully treated by means of coupled wet oxidation/biological processes [10], [21], [22].

The aim of this work is to establish the operational capacity of a continuous high efficiency integrated wet oxidation–aerobic biological system for the treatment of the main phenolic compounds of a pharmaceutical wastewater (phenol and salicylic, p-hydroxybenzoic and 5-hydroxyisophthalic acids). Concerning this purpose, removal efficiencies of each phenolic compound, sensitivity to feed perturbations and robustness during the wet oxidation and biotreatment steps were analyzed in order to assess the implementation and competitiveness of the continuous coupled process in front of other strategies of treatment.

2. Materials and methods

Data were obtained from a coupled wet oxidation–biodegradation plant of a pharmaceutical industry. This plant treats an average flow of 130 m3/day of wastewater generated during the process of acetylsalicylic acid production and mainly composed by phenol, salicylic acid, p-hydroxybenzoic acid and 5-hydroxyisophthalic acid.

2.1. Wet oxidation

Oxidation process employs two bubble column reactors in series, using Fe^{2+} as catalyst. Fig. 1 shows a simplified scheme of the coupled industrial operation.

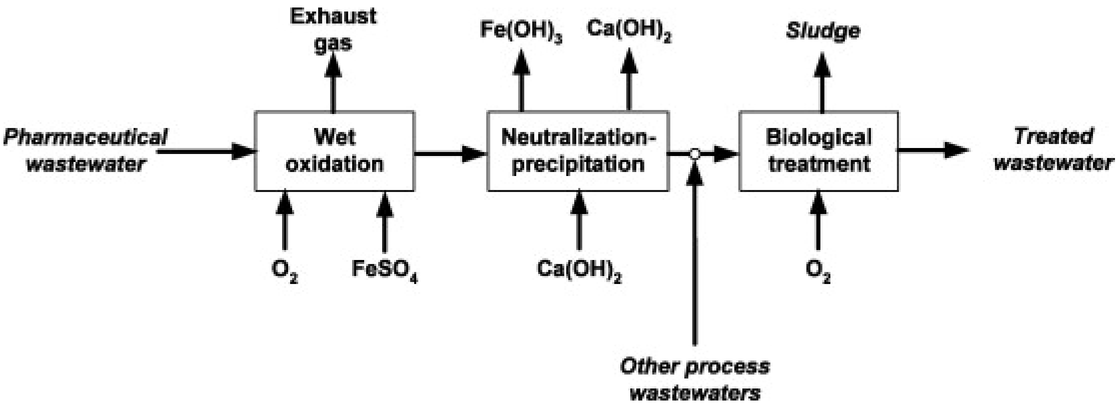

Fig. 1. Industrial flow diagrams for the coupled wet oxidation and biological process.

The pharmaceutical wastewater is initially preheated in heat exchangers and pumped into the first column. A set of special injection nozzles sited at the bottom of the columns allows a good contact between liquid and oxygen during the reaction. The operational conditions are 413 K, 1.01 MPa and a concentration of catalyst (Fe2+) of 14.3 mM (800 ppm). The temperature is controlled by regulating the flow of heat exchangers and injecting water vapor in the bottom of reactor. The control valve of the gas output is used to regulate system pressure. After the first column, the wastewater is leaded to the second column. In contrast to the first reactor, which is completely full, the second reactor contains a 70% of liquid. Oxygen and gases generated during operation are separated from the treated water, which is cooled and stored in a tank. By means of addition of lime to the tank, pH is elevated to suitable values for the biological treatment and sulphate and catalyst are precipitated as calcium sulphate and ferric hydroxide. This homogenization tank, which feed the biological reactor, also receives wastewaters coming from other processes of the plant.

2.2. Biological treatment

After the wet oxidation step, the wastewater treatment is completed by an aerobic biological process (10 gTSS/L, 30 °C). A simplified scheme of the biological treatment process is also shown in Fig. 1. The biological reactor is closed, but an air flown is supplied to ensure aerobic conditions. The concentration of total suspended solids is around 10 g/l and the operation temperature is 30 °C. At the exit of the biological reactor, the sludge and the water are separated by flotation. In order to maintain a constant solids concentration into the bioreactor, sludge was partly returned to the biological. The excess was filtered, stored and sent to landfill.

3. Results and discussion

3.1. Average efficiencies

Table 2 shows the average values of inlet and outlet concentrations and efficiency for the main pollutants of the industrial wastewater during the wet oxidation and the biological treatment.

Table 2. Average values of inlet and outlet concentrations and elimination efficiencies for the main pollutants of the industrial wastewater during the wet oxidation and the biological treatment. (SA: salicylic acid; Ph: phenol; pHBA: p-hydroxybenzoic acid; 5HIA: 5-hydroxyisophthalic acid).

Empty Cell	**Wet oxidation**				**Biological treatment**			**COD**
	SA	**Ph**	**pHBA**	**5HIA**	**SA**	**Ph**	**5HIA**	
Ci,inlet (ppm)	1464	1996	200.0	122.7	497.6	10.0	1.0	9016.0
Ci,outlet (ppm)	2.3	2.6	0.5	0.2	1.5	0.1	0.0	474.6
η (%)	99.84	99.92	99.76	99.79	99.69	99.00	98.95	94.74

It can be corroborated from Table 3 that the selected process is a high-efficiency treatment system. Each one of steps allowed a high removal of the phenolic compounds, being the average efficiencies slightly higher during the wet oxidation. In both steps and for each one of the compound, concentrations lower than 5 ppm were obtained with independence of the concentration of the compound in the feed stream. Thus the use of an advanced oxidation process followed by biological oxidation is generally mentioned as a good option for the treatment of toxic pharmaceutical wastewaters.

Table 3. “Dampening factors” of the studied coupled wet oxidation – biodegradation treatment.

	Wet oxidation				**Biological treatment**			**COD**
	SA	**Ph**	**pHBA**	**5HIA**	**SA**	**Ph**	**5HIA**	
$\text{Load}_{i,inlet}$ (kg/d)	185.9	239.4	25.4	14.6	90.7	1.8	0.17	1616
$\sigma_{i,inlet}$	34.8	61.4	4.4	5.4	35	0.7	0.07	432
$\text{Load}_{i,outlet}$ (kg/d)	0.3	0.19	0.06	0.03	0.3	0.02	0.01	88.7
$\sigma_{i,outlet}$	0.21	0.21	0.03	0.03	0.6	0.02	0.01	64.8
ϕ (%)	99.40	99.66	99.32	99.44	98.29	97.14	85.71	85.00

Efficiencies obtained during the coupled process are higher than the achieved ones by means of the use of an individual technique for the treatment of a pharmaceutical wastewater (see Table 1). Generally, biological treatments are not feasible due to the biotoxic character of this kind of wastewaters, whereas chemical oxidation processes are more expensive, complex and dangerous, particularly if the oxidant dosage is not correct [15].

It can be also seen from Table 1 that the continuous coupled wet oxidation/biological process studied in this work showed efficiencies similar to those obtained in other more complicated integrated processes, as the solar photo-Fenton-aerobic treatment, and higher than other advanced oxidation process/biotreatment.

3.2. Sensitivity to feed composition

Changes on the feed composition refer to the presence of compounds (i) other than the common pollutants of the feed (j, k, l, etc.). From an industrial point of view, these perturbations on the feed are frequently due to modifications in the industrial process, batch production, uncontrolled discharges etc. These perturbations generally provoke new oxidation reactions (ki) and/or inhibition/activation phenomena over the oxidation of the other pollutants (kj > kji; kk < kki etc.). For this reason, the response of the treatment system in front of changes of the kinetic constant must be stationary.

3.2.1. Wet oxidation

Column reactors were modeled as two CSTR in series with residence times of 1.44 and 1.08 h, respectively. Fig. 2a shows the relationship between the kinetic constant of a compound and the achieved efficiency during the wet oxidation.

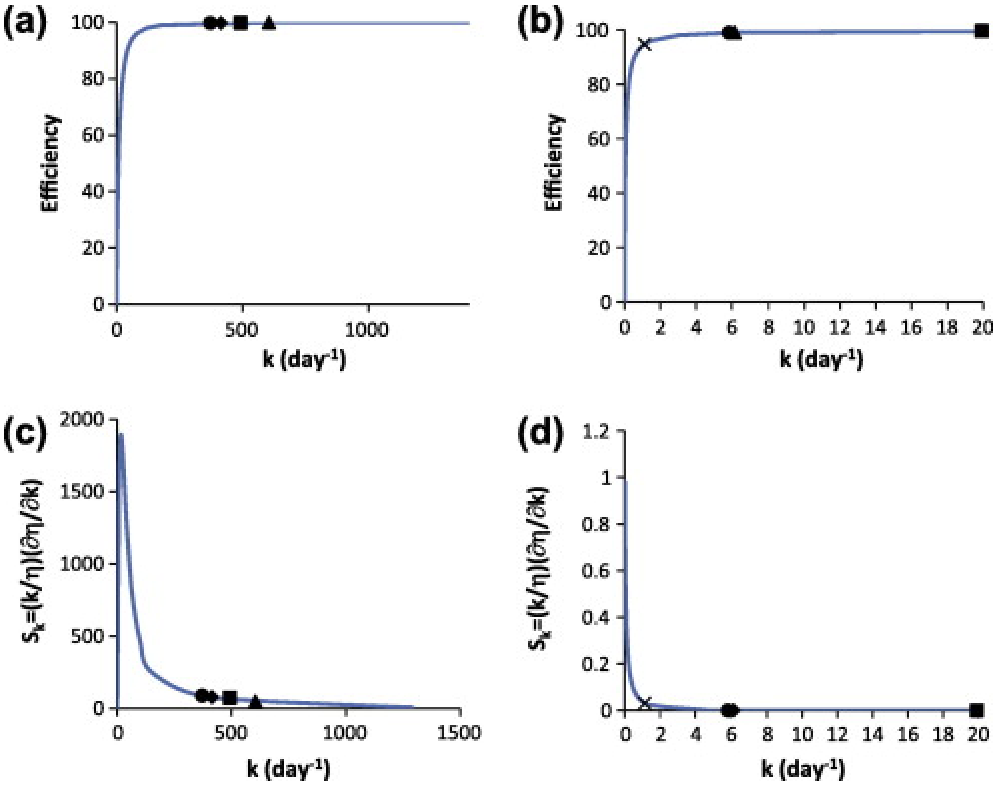

Fig. 2. Theorical relationships between kinetic constants and efficiency for the wet oxidation ((τ_1 = 1.44 h and τ_2 = 1.08 h) (a) and biological treatment (τ = 16 d) (b). Sensitivity to kinetic constant for the wet oxidation (c) and biological treatment (d). In both cases, symbols denote experimental data for salicylic acid (■), phenol (▲), p-hydroxybenzoic acid (♦), 5-hydroxyisophthalic acid (●) and COD (×).

As it can be observed in Fig. 2a, the next reactivity order was obtained: phenol ($k = 6.05 \times 10^2$ d^{-1}) > salicylic acid ($k = 4.92 \times 10^2$ d^{-1}) > p-hydroxybenzoic acid ($k = 4.15 \times 10^2$ d^{-1}) > 5-hydroxyisophtalic acid ($k = 3.72 \times 10^2$ d^{-1}). Fig. 2c shows the sensitivity as function of the kinetic constant of the compound. Sensitivity measures the ratio of efficiency change to kinetic constant

$$S_k = \frac{k}{\eta}\frac{\partial \eta}{\partial k} \qquad (1)$$

Obviously, the higher the kinetic constant, the lower the sensitivity of the system is. Nevertheless, it is also noticeable that the sensitivity showed a maximum for $k = 13$ d^{-1}. In this point, modifications on the kinetic constant can cause drastic changes in the efficiency, with the ratio of efficiency change to kinetic constant change running about 1850:1.

It can be noted that the sensitivities for the four compounds are significant (ratio of efficiency change to kinetic constant change running about 50–90:1), indicating a moderate stability of the wet oxidation system in front of changes on the kinetic constant of these pollutants. According to the previously exposed, it can be concluded that a correct operation of the industrial wet oxidation process requires an intense control of factors that have effect on the kinetic constant, such as changes on the reaction temperature or the presence of inhibitors that acts as radical scavengers.

3.2.2. Biological treatment

Bioreactor was modeled as a CSTR with a residence times of 16 h. Fig. 2b shows the relationship between the kinetic constant of a compound and the achieved efficiency during the biotreatment. In this case, the observed reactivity order was salicylic acid (k = 19.9 d^{-1}) > phenol (k = 6.2 d^{-1}) > 5-hydroxyisophthalic acid (k = 5.8 d^{-1}) > COD (k = 1.1 d^{-1}).

Results showed in Fig. 2b corroborate the high efficiency of the biotreatment during the elimination of the phenolic pollutants, with final conversions higher than 98% in all cases. In order to clarify whether biotreatment can cope with fluctuations, sensitivity of the biodegradation operation was also evaluated (Fig. 2c). The sensitivities of the phenolic compounds during the biotreatment were lower than the obtained ones during the wet oxidation, indicating than the biotreatment was more stable to changes in the kinetic constant, probably due to the high volume of the reactor. So, sensitivity of the biological degradation is around three orders of magnitude lower than the obtained one for the wet oxidation, indicating that variables associated with changes on the kinetic constant are not key factors for the proper functioning of the biotreatment.

3.3. Sensitivity to the flow rate

3.3.1. Wet oxidation

Fig. 3a shows the removal efficiency of the phenolic compounds and the total COD as a function of the flow rate of the wastewater. Wastewater flow rates between 3 and 8 m^3/h were assayed, which correspond to residence times between 4.2 h and 1.6 h, respectively. In all cases, 10 kg of oxygen per cubic meter of wastewater were fed and operating conditions were 423 K and 1.0 MPa. Concentrations of the phenolic compounds on the wastewater were: 1 g/L for phenol, 1.3 g/L for salicylic acid and 0.1 g/L for p-hydroxybenzoic and 5-hydroisophthalic acids.

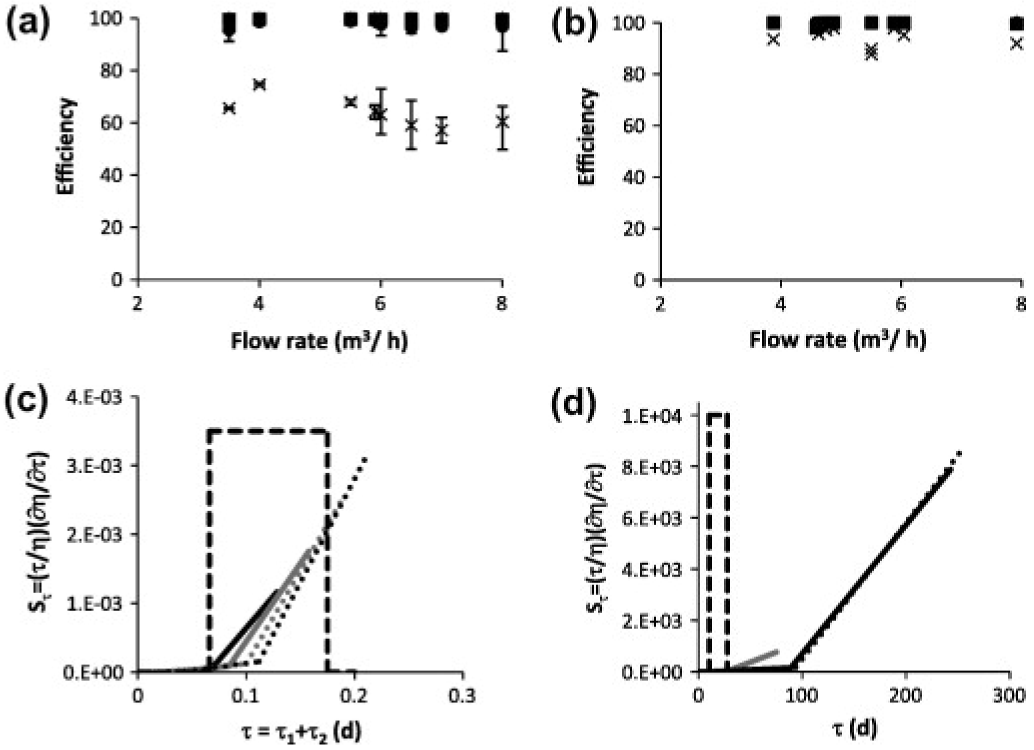

Fig. 3. Effect of wastewater flow rate on the efficiency achieved at the end of the wet oxidation (a) and biological treatment (b). In both cases, symbols denote experimental data for salicylic acid (■), phenol (▲), p-hydroxybenzoic acid (♦), 5-hydroxyisophthalic acid (●) and COD (×). Sensitivity to residence time for the wet oxidation (c) and biological treatment (d) for salicylic acid (grey line), phenol (black line), p-hydroxybenzoic acid (grey dotted line) and 5-hydroxyisophthalic acid (black dotted line). Broken line indicates the assayed range of residence times.

The flow rate (or the residence time) did not have an appreciable effect on the conversion of the four phenolic compounds. Thus, final conversions higher than 97% were achieved for all compounds. A slight increase in the degree of mineralization was observed for low flow rates (residence times higher than 2), probably due to the fact that higher residence times favored the oxidation of intermediates. The complete mineralization of the stream was not achieved in any case, due to the refractory character of the low molecular weight carboxylic acids formed during the degradation of the phenolic compounds [23].

The effect of the flow rate on the efficiency of the wet oxidation process can be explained by means the sensitivity to the residence time, defined as:

$$S_\tau = \frac{\tau}{\eta}\frac{\partial \eta}{\partial \tau} \qquad (2)$$

According to Fig. 3c, residence time had a low effect on the sensitivity of the process, which indicated that the system can respond favorably to perturbations on the flow rate, with the ratio of efficiency change to kinetic constant change running about 0.0015:1 for the assayed residence times. It should be noted that values of Sτ are a lot lower than the corresponding ones to S_k. From this fact, it can be deduced that kinetic constant fluctuations (due to temperature variations, changes of the composition, presence of inhibitors etc.) have a more severe effect on the stability of the system than the residence time fluctuations (due to variations of the flow rate).

3.3.2. Biological treatment

The effect of flow rates on the efficiency of the biological treatment is shown in Fig. 3b. Again, flow rates between 3 and 8 m3/h were selected; however in this case these values are equivalent to residence times between 28 days and 10.5 days, respectively. The concentrations of the phenolic compounds in the feed were: 0.5 g/L for salicylic acid and 0.01 g/L for phenol and 5-hydroxyisophthalic acid. The COD of the wastewater, 850–1500 kg/day, was significantly reduced during the process, even for the highest assayed flow rate, with an average degree of mineralization of 95%. In the same way, the concentrations of the phenolic compounds were considerably reduced in all the cases, with final conversions higher than 97%.

Sensitivity of the biological treatment to the flow rate (or the residence time) is showed in Fig. 3d. According to the obtained values of Sτ, the industrial biological treatment showed a good ability to respond to perturbations on the flow rate, at least in the range of residence time values tested, with an average ratio of efficiency change to kinetic constant change running about 10:1. In this case, the biological treatment is more sensitive to flow rate fluctuations than the wet oxidation process. Comparing S_τ and S_τ, it can be also deduced that the kinetic constant variation (changes of temperature or composition) had a more severe effect on the stability of the biological treatment than variations on the residence time (flow fluctuations).

3.4. Sensitivity to the oxygen flow rate

3.4.1. Wet oxidation

Fig. 4a shows the conversions obtained with different contributions of oxygen per cubic meter of treated water. The flow rate treated was 5 m^3/h and the industrial process of wet oxidation operated at 413 K and 1.01 MPa.

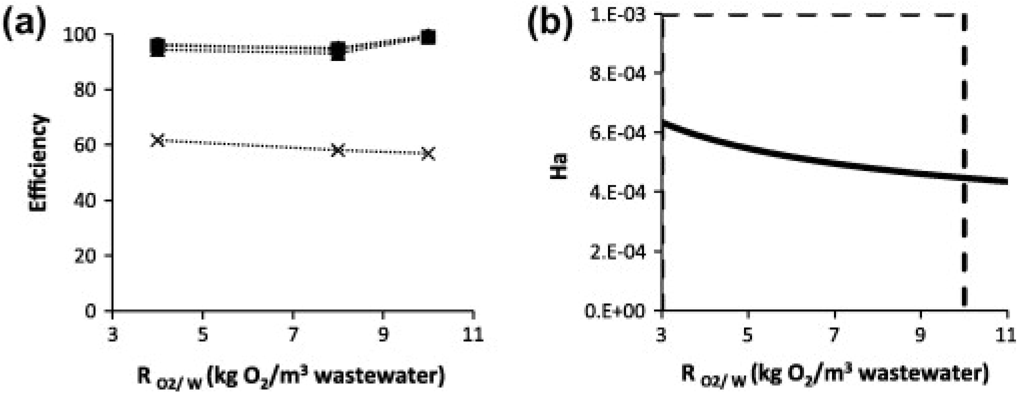

Fig. 4. Effect of the oxygen/wastewater flow rates ratio on the efficiency achieved at the end of the wet oxidation (a). Symbols denote experimental data for salicylic acid (■), phenol (▲), p-hydroxybenzoic acid (♦), 5-hydroxyisophthalic acid (●) and COD (×). Approximated effect of the oxygen/wastewater flow on the Hatta number (b). Broken line indicates the assayed range of oxygen/wastewater flow rates ratios.

The selection of an appropriate oxygen flow rate is essential for optimizing the wet oxidation process so that a kinetically controlled regimen prevails. An increase of the oxygen flow rate only increases the volumetric transfer coefficient, doing higher the oxygen transfer rate from the gas to the bulk liquid As can be seen in the figure, the amount of oxygen fed to the process had a very low effect on the conversion of the compounds in the exit stream. The calculated final conversions indicate that the operation in these operating conditions was kinetically controlled, with negligible mass transfer resistances.

Given that the average COD feed concentration is around 10 g O2/m3 and assuming a 70% COD reduction, an oxygen consumption rate of 2.6 g/m3h can be estimated. The supplied oxygen rate for the minimum oxygen/wastewater flow rates ratio assayed (Fig. 4) is 1498 g/m3h. Therefore, an oxygen transfer efficiency of 0.17% is sufficient to ensure the kinetic control of the reaction. The effectiveness of oxygen transfer is usually around 2–5% [24], so the above calculation corroborates the kinetic control of the reaction (as long as the gas/liquid transfer surface is quite high, i.e., the size of the oxygen bubble is small).

Fig. 4 shows that an increment of the oxygen flow rate also favored the formation of more refractory compounds, reducing the final degree of the mineralization. A similar behavior was also pointed by Chung et al. [25], who observed that the formation of organic acids was increased with the oxidant dose during the wet oxidation of sludge at 250 °C and 50 atm.

In order to quantify the effect of the oxygen flow rate on the efficiency, sensitivity to the oxygen to wastewater flow rates ratio $R_{O_2/W}$ was defined as:

$$S_{(R_{O_2/W})} = \frac{(R_{O_2/W})}{\eta}\frac{\partial\eta}{\partial(R_{R_{O_2/W}})} \qquad (3)$$

Fig. 4b shows the effect of the oxygen to wastewater flow rates ratio on the Hatta number Ha (the calculation of this dimensionless number is provided as [27], [28], [29], [30], [31], [32]). The Hatta number (Eq. (4)) compares the maximum chemical conversion in the mass transfer film to the maximum diffusion flux through this liquid film, showing where the chemical reaction occurs [26]. If the oxygen transfer rate is quite higher than the dissolved oxygen uptake rate ($Ha < 0.02$), no effect on removal rate of the phenolic is observed (dissolved oxygen concentration remains constant). In this case, changes on oxygen flow rate do not have effect on the efficiency (low sensitivities). However, for low transfer rates ($Ha > 0.02$) caused by low oxygen flow rates, the global reaction rate and the efficiency decrease

$$(Ha)_{pollutant} = \frac{1}{k_L}\sqrt{k_r D_L C_{0,pollutant}} \qquad (4)$$

According to Fig. 4b, the Hatta number (Ha) indicated a kinetically controlled regime for $R_{O_2/W} > 1$ ($Ha < 0.015$), indicating that $S_{(R_{O_2/W})} = 0$ for each phenolic compound.

3.5. Robustness of the process

In order to evaluate the ability of the treatment to compensate the fast changes on the conditions of the feed (composition and flow rate), pollutant loads of the main phenolic compounds and COD were measured in the feeds and in the effluents of the wet oxidation and the biological treatments during 3 weeks of normal operation, during which the concentrations of the main phenolic pollutants in the feed and the flow rate changed considerably. With the aim of to obtain a quantitative study of the robustness of the process, a “dampening factor” (ϕ) was defined as:

$$\phi_i = 1 - \frac{\sigma_{i,outlet}}{\sigma_{i,inlet}} \qquad (5)$$

where σ_i is the standard deviation of the measured loads of i (see Fig. 5). The robustness of the coupled treatment can thus be quantitatively estimated by means of the “dampening factor”, which estimates the effect of the oscillations of the feed on the final conversion. A “dampening factor” of 1 indicates that the system is able to compensate the variations of the feed without effect on the final conversion whereas a “dampening factor” of 0 involves that the oscillations in the feed are completely transmitted to the effluent. The results obtained for each pollutant and COD were showed in Table 2.

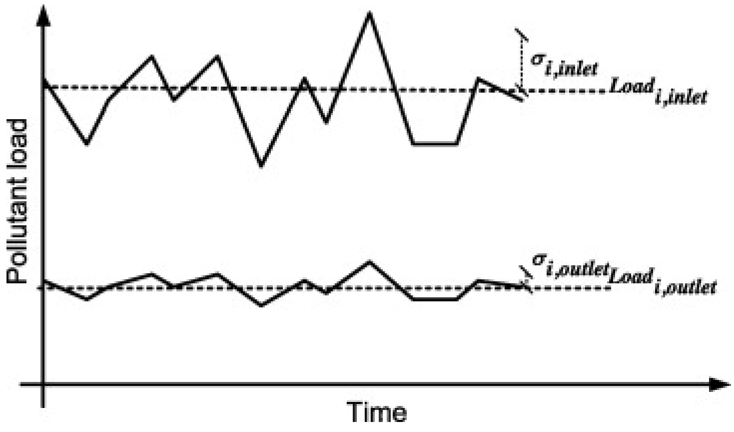

Fig. 5. Schematic representation of the parameters involved in the assessment of the robustness.

According to Table 2, “dampening factors” near of 1 were obtained for each one of the compounds during the two steps of the coupled process, corroborating the excellent behavior of the system in front of changes in the feed. Furthermore, it can be noted that “dampening factors” for wet oxidation were slightly higher than for biological treatment, indicating that biodegradation is more sensitive to changes on the concentrations of the pollutants, probably due to the complex character of the microbial metabolic processes. It must be also taken into account that the toxicity reduction achieved during the wet oxidation pretreatment due to the removal of an important part of the phenolic compounds allowed considerable improvement of the biological process. This fact indicates that the coupling of treatments have a positive effect on the “dampening factors”.

4. Conclusions

A continuous coupled wet oxidation/biological process for the treatment of pharmaceutical wastewaters was evaluated, paying special attention to three factors: removal efficiency of phenolic compounds, sensitivity to feed conditions and robustness during the industrial operation.

Concerning the efficiency, it was corroborated that the selected process is a high-efficiency treatment system. Each one of the steps allowed a high removal of the phenolic compounds (>97%), being the average efficiencies slightly higher during the wet oxidation. These efficiencies are comparable or higher than those obtained in other integrated advanced oxidation process/biotreatment.

Sensitivities to feed conditions studies showed that wet oxidation and biological treatment are able of treating and removing phenolic compounds, responding adequately to modification on the composition and flow of the wastewater. The wet oxidation proved to be more sensitive to changes of the feed composition (inhibition phenomena, new compounds etc.) than the biotreatment, particularly for compounds with kinetic constants lower than 250 d^{-1}. The system also showed its stability in front of flow rate perturbations when the residence time of the biological treatment was lower than 25 d. In addition, the removal efficiency of phenolic compounds during the wet oxidation showed a null sensitivity to changes of the oxygen flow rate in the range assayed (4–10 kgO_2/m^3), whereas high flow rates slightly decreased the mineralization degree. Calculation of the Hatta number corroborated that a kinetically regime prevailed.

The good capacity of adaptation of the coupled process to fast pollutant load perturbations, which are typical in pharmaceutical industries with a discontinuous mode of operation or without a pre-fixed production in the medium to long term, was verified, obtaining “dampening factors” for the phenolic compounds for each step near to one of, being slightly higher for the wet oxidation.

Finally, taking also into account the high efficiency and stability showed by the system in front of perturbations or changes in feed conditions, it can be concluded the high attractive of this option for the design of real facilities.

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Supplementary information for the paper:

Efficiency and sensitivity of the wet oxidation/ biological steps in coupled pharmaceutical wastewater treatment

Estimation of Ha as function of $\left(R_{O_2}/_W\right)$

0.- Estimation of the physical properties

Oxygen solubility (H) [27]

$$A(\log\bar{H})^2 + B\left(1/_{\bar{T}}\right)^2 + C(\log\bar{H})\left(1/_{\bar{T}}\right) + D(\log\bar{H}) + E\left(1/_{\bar{T}}\right) - 1 = 0$$

$\bar{H} = H.10^{-4}$

$1/_{\bar{T}} = 1/_{T}.10^3$

$A = -0.0005943 \quad B = -0.1470 \quad C = -0.05120 \quad D = -0.1076 \quad E = 0.8447$

Vapor pressure of water ($p^0_{H_2O}$) [28]

$$\ln p^0_{H_2O} = C_1 + \frac{C_2}{T} + C_3 \ln T + C_4 T^{C_5}$$

$p^0_{H_2O}[=]Pa \quad T[=]K \quad C_1 = 73.649 \quad C_2 = -7258.2 \quad C_3 = -7.3037 \quad C_4 = 4.1653.10^{-6}$
$C_5 = 2$

Oxygen saturation concentration ($C^*_{O_2}$)

$$C^*_{O_2} = \frac{P - p^0_{H_2O}}{H}$$

Oxygen diffusion coefficient (D_L) [29]

$$D_L = \frac{9.67\ 10^{-8}\ T}{\mu_L}$$

Interfacial tension [28]

$$\sigma = 0.1241 - 0.0002\ T$$

1.- Calculation of the superficial velocity of the gas (u_S)

$$u_S = \frac{R_{O_2/W}\,\breve{L}}{\pi \left({D_c}/{2} \right)^2}$$

2.- Estimation of the gas retention (ϕ_g) [30]

$$\frac{\phi_g}{\left(1-\phi_g\right)^4} = 0.2 \left(\frac{9.8\, D_C\, \rho_L}{\sigma} \right)^{1/8} \left(\frac{g\, D_C^2\, \rho_L^2}{\mu_L^2} \right)^{1/12} \left(\frac{u_g}{\sqrt{D_C\, g}} \right)$$

3.- Estimation of the volumetric mass transfer coefficient ($k_L a$) [30]

$$k_L a = 0.6\, \frac{D_L}{D_C} \left(\frac{\mu_L}{D_L\, \rho_L} \right)^{0.5} \left(\frac{g\, \rho_L}{\sigma} \right)^{0.62} \left(\frac{g}{(\mu_L/\rho_L)^2} \right)^{0.31} \phi_g^{1.1}$$

4.- Calculation of the energy dissipation rate (ε) [31]

$$\varepsilon = \frac{p}{V\, \rho_L} = u_s\, g$$

5.- Estimation of the liquid mass transfer coefficient (k_L) [32]

$$k_L = \frac{2}{\sqrt{\pi}} \sqrt{D_L} \left(\frac{\varepsilon\, \rho_L}{\mu_L} \right)^{1/4}$$

6.- Calculation of the Hatta number (Ha)

$$(Ha)_{pollutant} = \frac{1}{k_L} \sqrt{k_r\, D_L\, C_{pollutant}}$$

$$-\left(r_{pollutant}\right) = k^{\backprime}_r\; C_{pollutant}\, C_{O_2} = k_r\, C_{pollutant}$$

$$Ha = \sum (Ha)_{pollutant}$$