



Study of the aerobic biodegradation of coke wastewater in a two and three-step activated sludge process

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Abstract

A laboratory-scale biological plant composed of two aerobic reactors operating at 35 °C was used to study the biodegradation of coke wastewater. The main pollutants to be removed are organic matter, especially phenols, thiocyanate and ammonium nitrogen. The concentrations of the main pollutants in the wastewater during the study ranged between 922 and 1980 mg COD/L, 133 and 293 mg phenol/L, 176 and 362 mg SCN/L and 123 and 296 mg NH₄⁺-N/L. The biodegradation of these pollutants was studied employing different hydraulic residence times (HRT) and final effluent recycling ratios in order to minimize inhibition phenomena attributable to the high concentrations of pollutants. During the optimisation of the operating conditions, the removal of COD, phenols and thiocyanate was carried out in the first reactor and the nitrification of ammonium took place in the second. The best results were obtained when operating at an HRT of 98 h in the first reactor and 86 h in the second reactor, employing a recycling ratio of 2. The maximum removal efficiencies obtained were 90.7, 98.9, 98.6 and 99.9% for COD, phenols, thiocyanate and NH₄⁺-N, respectively. In order to remove nitrate, an additional reactor was also implemented to carry out the denitrification process, adding methanol as an external carbon source. Very high removal efficiencies (up to 99.2%) were achieved.

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1. Introduction

Coke wastewater is a complex industrial wastewater present in many steel production facilities that originates from the process of destructive distillation of coal at high temperatures (900–100 °C) in the absence of air. The coal breaks down, giving rise to gases, liquid and solid organic compounds of low molecular weight and a non-volatile carbonaceous residue known as coke.

The substances exiting the coke ovens as liquids under ambient conditions undergo further processing so as to obtain by-products such as ammonium sulphate, the resulting wastewater from these processes constituting coke wastewater, which contains considerable amounts of toxic compounds such as CN⁻, SCN⁻ and phenols [1–3].

Phenol is a highly toxic organic compound even at low concentrations and its presence in aqueous media is severely

restricted by current legislation. Coke wastewater also contains high concentrations of ammonium salts, thiocyanates and chlorides, though low concentrations of heavy metals, and very low levels of phosphorus [4,5]. The individual concentrations of each pollutant vary due to the different types of coal and conditions used in the coking process.

In a biological nitrification process, the autotrophic microorganisms that oxidize the NH₄⁺-N are normally sensitive to the presence of certain chemical substances such as phenols [6]. However, this sensitivity can be overcome by decreasing the effective concentration of the inhibiting compounds by means of adsorption, precipitation, quelation and biodegradation. Nitrifying microorganisms may also develop a tolerance to the inhibitors. Other compounds contained in coke wastewater that have a toxic effect on oxidizing bacteria, both autotrophic and heterotrophic, are CN⁻ (at concentrations higher than 50 mg/L), SCN⁻ and NH₄⁺-N itself at high concentrations [7]. Similarly, biological degradation of SCN⁻ is also affected by the presence of compounds such as NH₄⁺-N, phenols, NO₂⁻ and NO₃⁻ [8].

The complexity of coke wastewater resulting from the presence of a great variety of pollutants that may be removed biolog-

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ically but which are also toxic for the microorganisms that carry out their degradation make it necessary to conduct an in-depth study of the biological treatment of these pollutants in order to optimize the process.

This paper presents a study of the biological treatment of coke wastewater that forms part of a European project whose general aim is to study biological processes for treating wastewater from the steel industry. The present study focuses on coke wastewater, since at the time of carrying out the study, no biological treatment plant for this type of wastewater existed in Spain, though a number of industrial plants were in operation in other countries. In Zentralkokerie Saar, Dillingen (Germany), the process has two biological steps: the first includes denitrification and removal of organic matter and is carried out in separate tanks; nitrification takes place in the second step. In other existing plants, such as those in Kaiserstuhl (Germany), Serémage (France) and Sidmar (Belgium), a prior sedimentation step is followed by a biological treatment (combination of aerobic and anoxic tanks) and sludge settling and treatment. The main differences among these plants are the aeration system (pure oxygen or air), the type of coagulant, the concentration of excess sludge and the use or not of dilution water.

The removal of organic matter, phenols, SCN^- and NH_4^+-N in a one-step activated sludge system was previously studied and the results are pending publication. Phenol removal efficiencies were always higher than 90% even for an HRT of 17.6 h and COD removals of up to 75% were obtained. Biodegradation of SCN^- and nitrification varied depending on the addition of bicarbonate to the system (as the alkalinity of the coke wastewater employed in the study was very low). A maximum removal of 90% was achieved for SCN^- working at very high HRT (167 h) and of 71% for NH_4^+-N for an HRT of 54.3 h.

Although it is possible to remove a major part of the pollutants contained in the wastewater using a single-step process, the concentrations obtained in the effluent are not low enough for disposal. In the present paper, a potential solution to obtain higher removal efficiencies involving a two-step process is studied. Organic matter and SCN^- are removed in the first step and nitrification is performed in a second. In order to complete the removal of nitrogen compounds, a series of denitrification experiments were carried out in an additional step.

2. Materials and methods

The wastewater from a coke plant previously underwent a stripping treatment with NaOH to maintain NH_4^+-N concentrations at values of around 200 mg/L. The wastewater was stored in a 200 L tank to which sulphuric acid was added to decrease pH, along with Na_2HPO_4 as a source of phosphorous (130 g/m³), $\text{Al}_2(\text{SO}_4)_3$ to facilitate clarification of the effluent (10 g/m³) and a small amount of antifoaming agent (NALCO 71D5). Start-up of the reactors was carried out using sludge from the leachate treatment plant at the Central Landfill for Municipal Solid Waste of Asturias (COGERSA).

The wastewater was pumped by means of an Ismatec Ecoline pump model ISM 834A into a 17 L volume activated sludge

tank. The mixed liquor from this first reactor passed into a settling tank by gravity, the sludge being recycled to the reactor with a recycling ratio ($R=Q_R/Q$) of 1 by means of an Ismatec Ecoline pump model VC-280. The clarified effluent (effluent 1) from the first settling tank was fed by gravity into a second aerated tank of 15 L volume in which nitrification took place. As the wastewater presents very low alkalinity values, a dosage of sodium bicarbonate that varied between 0.84 and 1.4 kg/m³ depending on the ammonium concentration was added to this reactor as a source of carbon in order to favour the growth of autotrophic microorganisms. The amount added is in accordance with a consumption of 6.5 kgCaCO₃/kgNH₄⁺-N, found to be the optimum in a previous study [9]. The mixed liquor from the second aerated reactor passed by gravity into a second settling tank in which the sludge was separated and recycled to the reactor by means of an Ismatec pump model VC-380 with $R=1$, obtaining a final clarified effluent (effluent 2).

From Day 261 onwards, the final effluent was recycled to the first reactor by an Ismatec pump model ISM 834A with the aim of decreasing the concentration of NH_4^+-N in the reactor and of favouring the biodegradation of SCN^- (as the presence of a higher ammonium concentration was found to decrease SCN^- removal efficiency) [9]. Different recycling ratios ($R=1-3$) were employed to determine the optimum value.

The pH of the first reactor was kept around 6–6.5, found to be the optimum value for the biodegradation of thiocyanates in a previous study [9], in agreement with other researchers [8]. The second reactor was operated at a pH of 8–8.5 to favour nitrification. The temperature of both reactors was kept constant at a value of 35 ± 0.5 °C by means of a heating element. This temperature was chosen due to the fact that the temperature of coke wastewater at the steel works usually varied between 35 and 45 °C. Moreover, as is well known, mesophilic microorganisms operate in the range 10–35 °C, the reaction kinetics increasing with temperature.

The volatile suspended solids in the mixed liquors represented an average percentage value of 75% of total suspended solids and ranged between 2.0 and 3.0 g/L. The sludge generally presented good settling conditions throughout the entire operation (Sludge Volume Index, SVI, lower than 100 mL/g). The oxygen concentration in the reactors was always kept above 3 mg/L.

Different volumetric flow rates were employed and thus different hydraulic retention times (HRT). Table 1 shows the different HRT employed and the average concentrations of pollutants during the different steps of the study. Due to variations in the composition of the coke wastewater, it was very difficult to maintain a fixed value for the organic loading rate (OLR) and for the nitrogen loading rate (NLR), and so the chosen operating parameter was the HRT. Table 2 shows the values of OLR, NLR and food to microorganisms ratios (F/M) for the different working conditions.

The study of the final denitrification stage commenced once the two-step process was operating steadily, with HRT of 96 and 86 h in the first and the second reactor, respectively, and an effluent recycling ratio of 2. The final effluent from the two-step

Table 1
Average composition of coke wastewater under different working conditions

HRT ₁ (h)	HRT ₂ (h)	R	pH ^a	COD (mg O ₂ /L)	SCN ⁻ (mg/L)	NH ₄ ⁺ -N (mg/L)	Phenols (mg/L)
27.8	20.3	0	6.9	1539	316	193	264
42.4	31	0	6.7	1454	298	204	255
61	44.6	0	5.8	1197	234	186	194
98	86	0	5.3	1175	266	233	237
98	86	1	2.6	1187	215	194	187
98	86	2	2.2	1361	277	206	221
98	86	3	2.2	1609	326	180	193

^a These values are obtained after the addition of 98% H₂SO₄ (initial pH values: 8.1–8.8).

process was fed into a 10L volume reactor. The study lasted 156 days, employing different HRT (86.4, 61.7 and 43.2 h), SRT (71, 52 and 37 days) and F/M ratios (0.17, 0.30 and 0.44 kgNO₃⁻/kgSSV/day). The oxygen concentration in the denitrification reactor was kept around 0.16 mg/L to maintain the anoxic conditions required for the denitrification process [10].

The pH inside the denitrification tank was kept between 8.3 and 8.5 [11]. The average concentration of total suspended solids (TSS) in the denitrification reactor was 3.0 g/L, 78% being volatile suspended solids (VSS).

With the aim of monitoring the biodegradation process taking place inside the reactors, the influent and the effluents were analysed using standard methods [12]. In the case of not being able to carry out immediate analyses, the samples were always kept under refrigeration at 4 °C. Phenols, COD and nitrates were analysed by colorimetric methods using a HACH DR/2010 Spectrophotometer. NH₄⁺-N concentration was measured by potentiometry using an Orion 95–12 BN ion selective electrode. SCN⁻ was analysed by means of a colorimetric method based on the formation at an acid pH of an intense red complex between Fe⁺³ and SCN⁻.

3. Results and discussion

3.1. Removal of thiocyanate

Fig. 1 shows the concentration of SCN⁻ in the influent and effluents from both reactors, as well as the total removal efficiency obtained throughout the study. Removal efficiencies higher than 90% were obtained for a recycling ratio of 2, the maximum being 98.7%. Very low SCN⁻ concentrations in the effluent were likewise achieved (minimum value: 4 mg/L). An important decrease in removal was observed when the recycling ratio was increased to 3. This ratio gave rise to hydrodynamic problems in the reactors and system instability, resulting in final SCN⁻ concentrations of up to 81 mg/L.

Note should be taken that SCN⁻ removal occurred in both reactors, since its biodegradation may take place via different mechanisms [8,13]. According to Kim and Katayama [14], *Thiobacillus thioparus* oxidizes thiocyanate as an energy and nitrogen source to CO₂, NH₃ and SO₄⁻² during autotrophic growth. Likewise, several heterotrophic bacteria degrade thiocyanate during their growth and use the released ammonia as a source of nitrogen [15,16].

Table 2
Average COD and NH₄⁺-N removals under different working conditions

SRT	HRT	R	kgCOD/m ³ d	VSS (g/L)	kgCOD/kgVSS/day	COD removal (%)
Reactor 1						
38	27.8	0	1.33	3.0	0.41	45.5
42	42.4	0	0.82	2.6	0.31	68.6
47	61	0	0.48	2.0	0.26	77.6
76	98	0	0.29	2.1	0.13	65.9
76	98	1	0.35	2.5	0.13	79.6
93	98	2	0.42	2.8	0.13	86.2
100	98	3	0.78	2.6	0.15	74.9
SRT	HRT	R	kgNH ₄ ⁺ -N/m ³ d	VSS (g/L)	kgNH ₄ ⁺ -N/kgVSS/day	NH ₄ ⁺ -N removal(%)
Reactor 2						
32	20.3	0	0.14	3.0	0.04	65.6
32	31	0	0.08	2.2	0.03	67.1
32	44.6	0	0.10	1.5	0.05	34.7
52	86	0	0.09	1.9	0.03	99.0
64	86	1	0.04	2.1	0.02	97.6
73	86	2	0.02	1.9	0.01	99.3
54	86	3	0.05	2.2	0.01	32.4

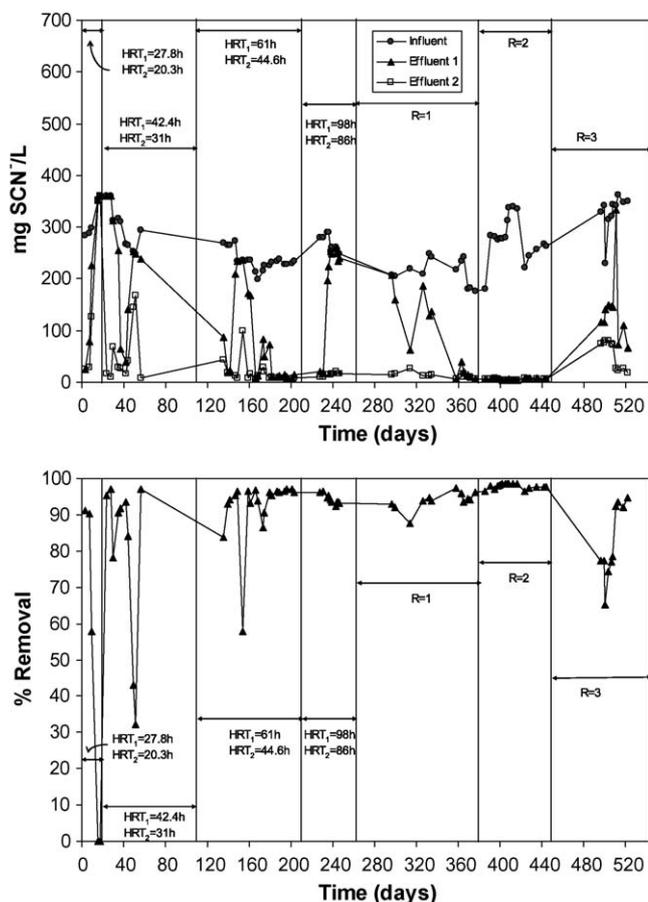


Fig. 1. SCN^- evolution in the influent and effluents and total removal efficiencies obtained in the biological treatment of coke wastewater.

Recycling of the effluent favoured the biodegradation of SCN^- in the first reactor, as it leads to a decrease in NH_4^+-N concentration. The biodegradation of SCN^- may be influenced by the presence of other compounds such as NH_4^+-N , phenols, nitrates or nitrites [7,8]. To evaluate this influence, the effect of NH_4^+-N concentration on SCN^- removal was studied for an HRT of 98 h and different recycling ratios. The ammonia concentration in the first reactor is plotted against removed SCN^- in Fig. 2. The experimental data can be fitted ($r=0.994$) to a theoretical curve according to the following equation:

$$\% \text{SCN}^- = 100 + 15.1 \times (1 - e^{0.0056 \times [\text{N}-\text{NH}_4^+]})$$

According to this curve, employing an HRT of 98 h, removal efficiencies of SCN^- higher than 98% are obtained when NH_4^+-N concentrations are lower than 23 mg/L. If the NH_4^+-N concentration increases above 260 mg/L, however, the efficiency will fall below 50%. Other authors [8] found that ammonium nitrogen presents a slightly inhibitory effect on thiocyanate degradation for concentrations higher than 3 g/L. However, these authors employed synthetic wastewaters in their studies. Industrial coke wastewater may present a greater complexity owing to the presence of different types of toxic pollutants.

The removal of SCN^- in the first reactor by heterotrophic bacteria is a relevant factor for the subsequent correct function-

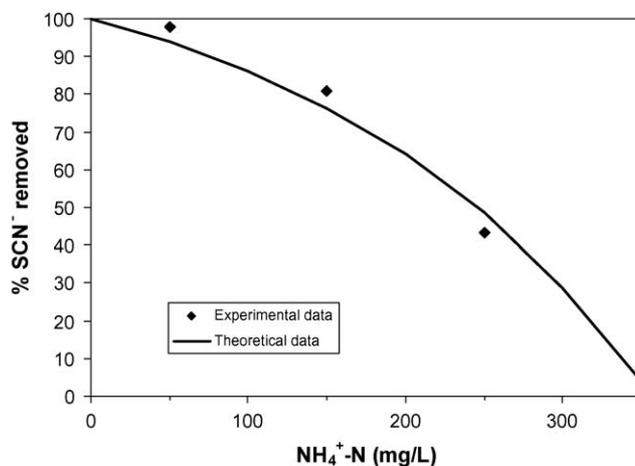


Fig. 2. NH_4^+-N influence on SCN^- biodegradation for an HRT of 98 h.

ing of the nitrification process in order to avoid inhibitory effects in the nitrifying bacteria [9].

3.2. Removal of COD

Fig. 3 shows the COD concentration in the process influent and effluents as well as total removal efficiencies. COD removals

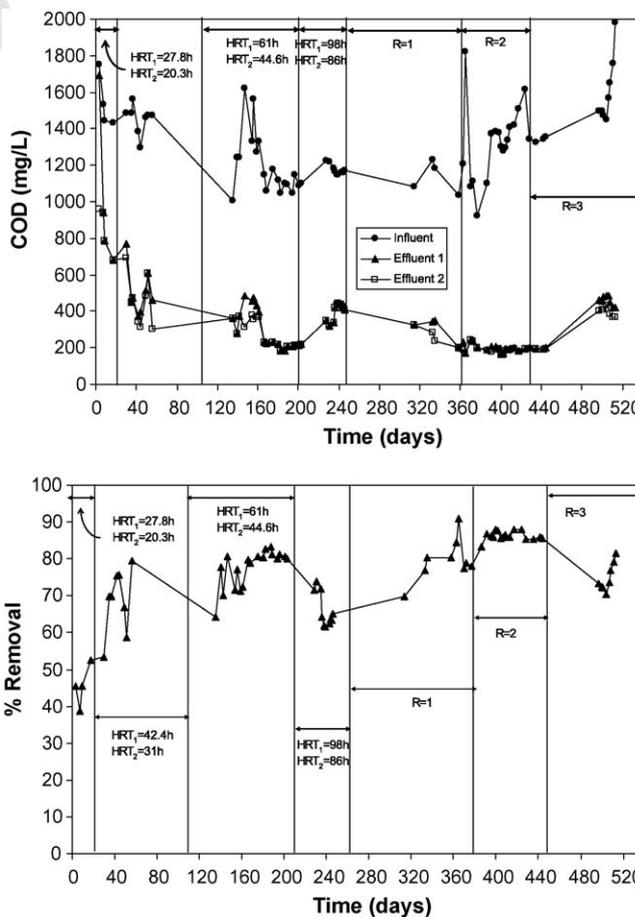


Fig. 3. COD evolution in the influent and effluents and total removal efficiencies obtained in the biological treatment of coke wastewater.

of around 80% were obtained for an HRT₁ of 61 h, increasing to around 90% when the effluent was recycled, except for a recycling ratio of 3, for the aforementioned reason.

Apart for the first few days of operation, in which the system was not steady, the concentration in the effluent from Reactor 1 was very similar to that from Reactor 2, which means that the COD is almost totally removed in the first step. The lower COD concentration obtained in the final effluent was 159 mg/L for an HRT₁ = 96 h and R = 2.

As can be seen in Table 2, except for the lowest HRT employed (OLR = 1.3 kgCOD/m³ d), the average COD removals were always ≥70% under the different working conditions (OLR from 0.3 to 0.8 kgCOD/m³ d. and F/M ratios from 0.13 to 0.31 kgCD/kgVSS/day).

3.3. Removal of phenols

The concentration of phenols in the final effluent varied between 2.3 mg/L for R = 2 and 16 mg/L for R = 3, being very similar to that obtained in effluent 1. This means that phenols are also mainly removed in the first reactor (Fig. 4). Very high total removal efficiencies (≥95%) were obtained under all the conditions employed, values higher than 98% being obtained for a recycling ratio of 2. Removal decreased slightly when operating at R = 3, due to the aforementioned problems of instability.

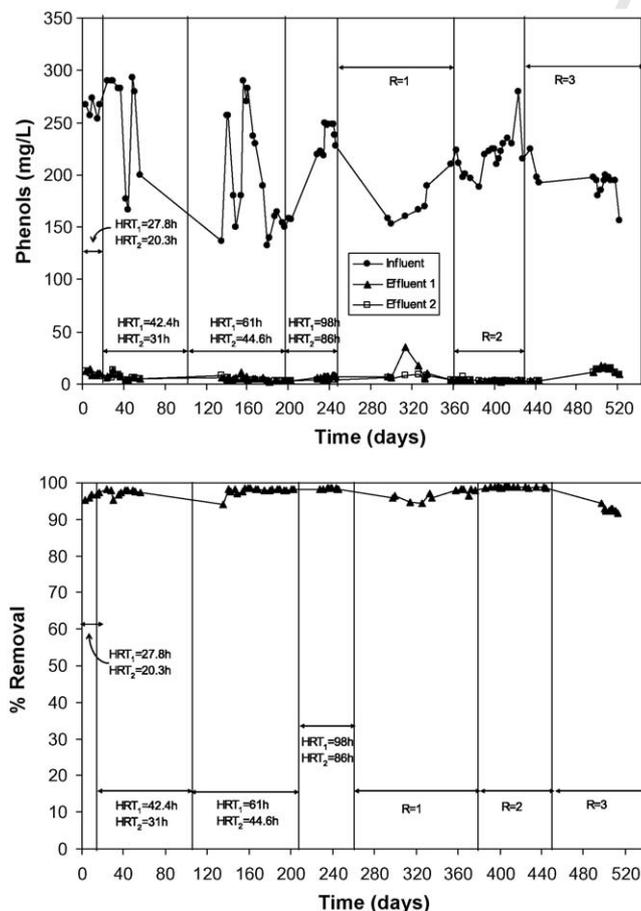


Fig. 4. Phenols evolution in the influent and effluents and total removal efficiencies obtained in the biological treatment of coke wastewater.

3.4. Removal of NH₄⁺-N

One of the aims of the two-step process was to remove NH₄⁺-N in a second reactor once the major part of COD, phenols and SCN⁻ had been removed in the first step. Autotrophic nitrifying microorganisms need to have a certain available alkalinity. With an average alkalinity value in the wastewater of 0.25 gCaCO₃/L and for an initial NH₄⁺-N concentration of around 200 mg/L, the ratio kgCaCO₃/kgNH₄⁺-N is 1.25, a clearly low value [10,17]. In a previous study, a value of 6.5 kgCaCO₃/kgNH₄⁺-N was found to be the optimum for NH₄⁺-N removal in this coke wastewater [9]. Therefore, alkalinity was added throughout the entire study to the nitrification reactor in the form of sodium bicarbonate.

Fig. 5 shows the variation in NH₄⁺-N concentration in the influent and effluents as well as the total removal obtained via nitrification. The ammonia concentration in the influent ranged between 123 and 296 mg/L. Throughout the first part of the experiment (from Day 1 to 140), effluent 1 presented lower NH₄⁺-N concentrations than the influent, which means that nitrification was partially taking place in the first reactor. This could be the result of poor control of pH during that period (average pH 8.5 in the first reactor), since pH values of between 7.8 and 8.9 favour the nitrification process [18,19]. From Day 150 to 240, operating at higher HRT but without recycling of the final

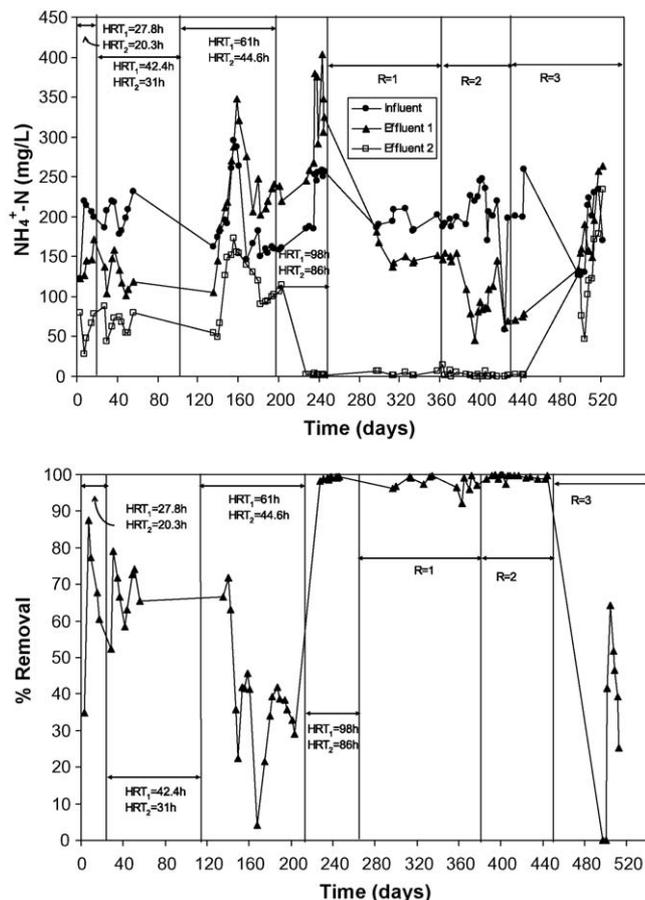


Fig. 5. NH₄⁺-N evolution in the influent and effluents and total removal efficiencies obtained in the biological treatment of coke wastewater.

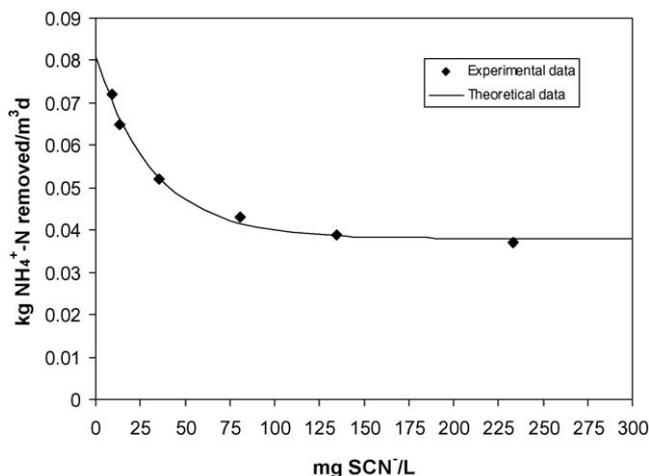


Fig. 6. Influence of SCN^- on removed NH_4^+ -N loading rate in the nitrification reactor for an HRT of 44.6 h.

effluent, the ammonia concentration increased in the first reactor. This may be due to both the transformation of organic nitrogen into NH_4^+ -N and the biodegradation of SCN^- into NH_4^+ , CO_2 and SO_4^{2-} [7,8,13].

The highest ammonium removal (99%) was obtained when operating at an HRT_2 of 86 h and a recycling ratio of 2 (minimum effluent concentration of 0.12 mg NH_4^+ -N/L), although very high removals were also obtained for the same HRT without recycling of the final effluent. As occurs with the other pollutants, a recycling ratio of 3 gave rise to a decrease in removal efficiency. Table 2 shows the average removals obtained under the different working conditions. For an SRT of 32 days, an increase in the nitrification efficiency was not observed when increasing the HRT. With respect to the specific loading rate, values higher than 0.04 kg NH_4^+ -N/kg VSS/day led to a decrease in nitrification. A marked increase in nitrification was observed for an SRT of 52 days and an HRT of 98 h. Under these working conditions, the presence of thiocyanate does not seem to have a notable influence on nitrification. When the recirculation ratio was increased from 2 to 3, removal decreased from 99 to 32% due to hydrodynamic problems.

To study the influence of SCN^- on nitrification when operating at low HRT, experiments were carried out with coke wastewater containing different concentrations of SCN^- for an HRT of 44.6 h. The experimental results, shown in Fig. 6, were fitted to an exponential curve ($r=0.997$) according to the following equation:

$$N = 0.081 - \{0.043 \times (1 - e^{-0.031[\text{SCN}^-]})\}$$

where N is the volumetric nitrification rate (kg NH_4^+ -N removed/m³/day).

According to the theoretical curve, in the absence of SCN^- , 0.081 kg NH_4^+ -N/m³/day could be removed, whereas for SCN^- concentrations higher than 150 mg/L, the denitrification rate decreases to 0.037 kg NH_4^+ -N/m³/day.

To evaluate whether the nitrification process functions correctly, measurement of the NH_4^+ -N concentration alone would be insufficient, since this does not confirm that the final product obtained is NO_3^- . In some cases, the final transformation of NO_2^- to NO_3^- in the final nitrification step may be inhibited, especially when the concentration of dissolved oxygen in the mixed liquor is lower than 2 mg/L or when SRT lower than 15 days are employed [20,21].

Throughout this study, the concentration of both compounds was measured regularly, no NO_2^- being detected, the NO_3^- concentration ranging between 282 and 428 mg NO_3^- -N/L.

In order to remove the nitrate formed in the nitrification process, the effluent from the two-step process was treated in a third reactor of 10 L volume. Table 3 shows the average concentrations of the different pollutants in the effluent entering the denitrification reactor for the different HRT employed. The concentrations of COD, phenols and SCN^- fed into the denitrification reactor were very low, since these pollutants had already been removed in the previous steps. COD values ranged between 165 and 220 mg/L and therefore, as denitrifying microorganisms are heterotrophic, methanol was added in this study as an external organic carbon source.

The methanol dosage employed was varied throughout the study so as to determine the optimum value that would give rise to maximum nitrate removal and would not increase the COD of the effluent. During the first 16 days, a ratio of 6.7 mg COD/mg NO_3^- -N was used to favour heterotrophic growth. A high removal of nitrates was observed, although an important increase of the effluent COD also occurred (Figs. 7 and 8). Different ratios were subsequently assayed, ranging between 3 and 4 mg COD/mg NO_3^- -N. The optimum value was 3.5, corresponding to a dosage of 1.2 L methanol/m³. This value was subsequently used in the experiments from Day 48 onwards.

The nitrate loading rate varied between 0.09 kg NO_3^- -N/m³/day for HRT of 86.4 h and 0.23 kg NO_3^- -N/m³/day for 43.2 h. Fig. 7 shows the evolution of the nitrate concentration in the influent and effluent of the denitrification process as well as the removal obtained for the different conditions employed. Influent concentrations ranged between 282 and 428 mg NO_3^- -N/L and effluent concentrations were lower than 0.12 mg NO_3^- -N/L. Removal

Table 3
Average characteristics of coke wastewater and the influent to the denitrification reactor during the three-step study

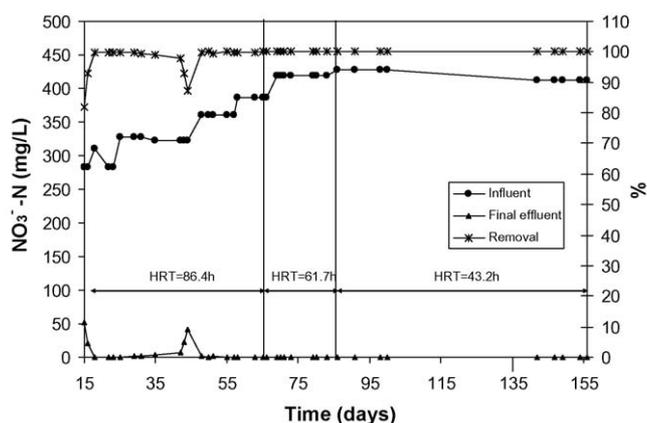
HRT ₃ (h)	COD (mg/L)		Phenols (mg/L)		SCN ⁻ (mg/L)		NH ₄ ⁺ -N (mg/L)		NO ₃ ⁻ -N (mg/L)	
	WW	DN	WW	DN	WW	DN	WW	DN	WW	DN
86.4	1312	220	210	4.4	234	10.9	196	5.6	n.d.	331
61.7	1337	165	220	2.6	297	4.8	218	1.6	n.d.	412
43.2	1400	175	221	2.7	272	6.0	197	1.3	n.d.	420

n.d., not detected.

Table 4

Average characteristics of the final effluent and removal obtained in the three-step biological treatment of coke wastewater under different working conditions

HRT ₃ (h)	SRT (day)	kgNO ₃ ⁻ -N/m ³ /day	kgNO ₃ ⁻ -N/kgSSV/day	COD (mg/L)		Phenols (mg/L)		SCN (mg/L)		NH ₄ ⁺ -N (mg/L)		Total-N (mg/L)	
				Effluent	%	Effluent	%	Effluent	%	Effluent	%	Effluent	%
86.4	71	0.07	0.04	306	75.4	4.4	97.8	10.9	95.3	5.6	97.1	16.4	95.3
61.7	52	0.16	0.07	261	80.5	2.6	98.8	4.8	98.3	1.6	99.3	2.8	99.3
43.2	37	0.24	0.10	251	82.0	2.7	98.7	6.0	97.7	1.3	99.2	2.9	99.2

Fig. 7. NO₃⁻-N evolution in influent and effluent and removal efficiency of the denitrification process.

efficiencies were very high (ranging between 81.9 and 99.9%), even for the lowest HRT tested (or highest loading rates: 0.23 kgNO₃⁻-N/m³/day and 0.44 kgNO₃⁻-N/kgVSS/day).

The COD of the influent to the denitrification reactor varied between 148 and 269 mg/L, as can be seen in Fig. 8. When a ratio of 6.7 mg COD/mg NO₃⁻-N was used (Day 1–16), although high removal efficiencies of nitrates were obtained, the excess of methanol employed increased the effluent COD to 704 mg/L. When a ratio of 3 mg COD/mg N was used (Day 17–44), the influent COD decreased to 143 mg/L, although nitrate removal efficiency also decreased (Fig. 7). Using the optimum value of 3.5 mg COD/mg N, the effluent COD increased slightly to 245 mg/L.

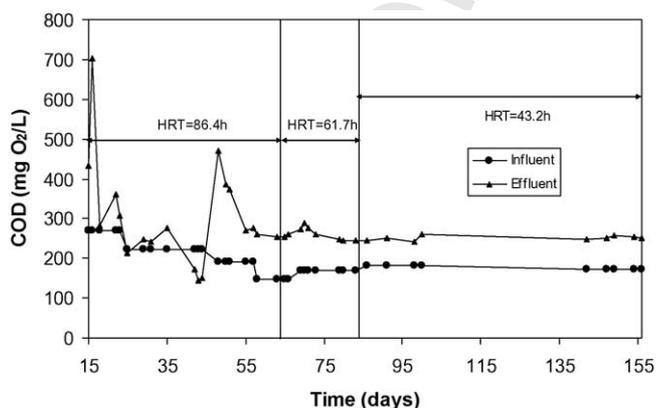


Fig. 8. COD evolution in the influent and effluent of the denitrification process.

The concentration of the rest of the pollutants did not experiment any change during this final step. Table 4 shows the average concentrations of the different pollutants in the final effluent as well as the average removal efficiencies obtained under the different working conditions employed in the three-step process. The lowest concentrations of pollutants obtained were 251 mg COD/L, 2.6 mg phenols/L, 4.8 mg SCN⁻/L, 1.3 mg NH₄⁺-N/L and 2.8 mg Total-N/L.

4. Conclusions

The presence of NH₄⁺-N influences the biodegradation of SCN⁻. Employing an HRT of 98 h, no removals would be obtained for an ammonia concentration higher than 360 mg/L. Likewise, the presence of SCN⁻ influences the nitrification process, decreasing the nitrification rate from values of 0.08 kgNH₄⁺-N/m³/day in the absence of SCN⁻ to 0.04 kgNH₄⁺-N/m³/day for SCN⁻ concentrations between 125 and 230 mg/L.

The biological treatment of coke wastewater in a two-step activated sludge system is favoured when an effluent recycling ratio of 2 is employed, obtaining average removal efficiencies of 86.2, 98.8, 97.9 and 99.3% for COD, phenols, SCN⁻ and NH₄⁺-N, respectively, for a total HRT of 184 h (98 h in the first step and 86 h in the second). Under these conditions, the removal of COD, phenols and SCN⁻ takes place mainly in the first reactor, whereas nitrification occurs in the second. Recycling of the effluent leads to lower concentrations in the reactors and less inhibition phenomena between the microorganisms responsible for SCN⁻ and NH₄⁺ biodegradation.

If denitrification is carried out as a third step, a methanol dosage of 1.2 L/m³ (which represents a consumption of 3.5 mg COD/mg NO₃⁻-N) must be added in order to achieve very high removal efficiencies (>99%). A slight increase in the final effluent COD takes place (from 176 to 251 mg O₂/L) as a result of this addition of methanol.

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