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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Keywords: Coke wastewater; Phenol; Ammonium; Thiocyanate; Activated sludge; Nitrification; Denitrification

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 (900–1000°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-
The wastewater was pumped 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 NH4+-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 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 feed 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
process was fed into a 10 L 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 Fe³⁺ and SCN⁻.

### Table 1

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<thead>
<tr>
<th>HRT₁ (h)</th>
<th>HRT₂ (h)</th>
<th>R</th>
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<th>COD (mg O₂/L)</th>
<th>SCN⁻ (mg/L)</th>
<th>NH₄⁺–N (mg/L)</th>
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* These values are obtained after the addition of 98% H₂SO₄ (initial pH values: 8.1–8.8).

### 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

<table>
<thead>
<tr>
<th>SRT</th>
<th>HRT</th>
<th>R</th>
<th>kgCOD/m³/d</th>
<th>VSS (g/L)</th>
<th>kgCOD/kgVSS/day</th>
<th>COD removal (%)</th>
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### Table 2

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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:

\[
\% \text{SCN}^- = 100 \times \left(1 - e^{0.0056 \times [N-HG]}\right)
\]

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 200 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 functioning 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 in the first reactor are shown in Fig. 3.
of around 80% were obtained for an HRT 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 1.59 mg/L for an HRT = 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 kgCOD/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, removal rates 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.

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
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 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 nitrification was observed for an HRT of 86 h 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 recycle 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 ($r^2$ = 0.997) according to the following equation:

$$N = 0.081 - [0.043 x (1 - e^{-0.05[SCN^-]})]$$

where $N$ is the volumetric nitrification rate (kg NH$_4^+$–N removed/m$^3$/day).

According to the theoretical curve, in the absence of SCN$^-$, 0.081 kg NH$_4^+$–N/m$^3$/day could be removed, whereas for SCN$^-$ concentrations higher than 150 mg/L, the nitrification rate decreases to 0.037 kg NH$_4^+$–N/m$^3$/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$_3^-$–N. In some cases, the final transformation of NO$_3^-$ to NO$_2^-$ 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 0.165 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/m$^3$. This value was subsequently used in the experiments from Day 48 onwards.

The nitrate loading rate varied between 0.09 kg NO$_3^-$–N/m$^3$/day for HRT of 86.4 h and 0.23 kg NO$_3^-$–N/m$^3$/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 efficiencies. Table 2 shows the average removals obtained under the different working conditions. For an SRT of 32 days, an increase in nitrification was observed for an HRT of 86 h 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 recycle ratio was increased from 2 to 3, removal decreased from 99 to 32% due to hydrodynamic problems.

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Table 3

<table>
<thead>
<tr>
<th>HRT (h)</th>
<th>COD (mg/L)</th>
<th>Phenols (mg/L)</th>
<th>SCN$^-$ (mg/L)</th>
<th>NH$_4^+$–N (mg/L)</th>
<th>NO$_3^-$–N (mg/L)</th>
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A.d., not detected.


### Table 4

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<th>kpNO3− N/kgVSS/day</th>
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<td>86.4</td>
<td>71</td>
<td>0.07</td>
<td>0.04</td>
<td>306</td>
<td>75.4</td>
<td>4.4</td>
<td>97.8</td>
<td>10.9</td>
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<tr>
<td>61.7</td>
<td>52</td>
<td>0.16</td>
<td>0.07</td>
<td>261</td>
<td>80.5</td>
<td>2.6</td>
<td>98.8</td>
<td>4.8</td>
</tr>
<tr>
<td>43.2</td>
<td>37</td>
<td>0.24</td>
<td>0.10</td>
<td>251</td>
<td>82.8</td>
<td>2.7</td>
<td>98.7</td>
<td>6.0</td>
</tr>
</tbody>
</table>

The concentration of the rest of the pollutants did not experience 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+-N 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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