

Simultaneous removal of phenol, ammonium and thiocyanate from coke wastewater by aerobic biodegradation

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Abstract

A laboratory-scale activated sludge plant composed of a 20 L volume aerobic reactor followed by a 12 L volume settling tank and operating at 35 °C was used to study the biodegradation of coke wastewater. The concentrations of ammonium nitrogen ($\text{NH}_4^{+}\text{-N}$), phenols, chemical oxygen demand (COD) and thiocyanate (SCN^-) in the wastewater ranged between 504 and 2340, 110 and 350, 807 and 3275 and 185 and 370 mg/L, respectively. The study was undertaken with and without the addition of bicarbonate. The addition of this inorganic carbon source was necessary to favour nitrification, as the alkalinity of the wastewater was very low. Maximum removal efficiencies of 75%, 98% and 90% were obtained for COD, phenols and thiocyanates, respectively, without the addition of bicarbonate. The concentration of ammonia increased in the effluent due to both the formation of NH_4^+ as a result of SCN^- biodegradation and to organic nitrogen oxidation. A maximum nitrification efficiency of 71% was achieved when bicarbonate was added, the removals of COD and phenols being almost similar to those obtained in the absence of nitrification. Batch experiments were performed to study the influence of pH and alkalinity on the biodegradation of phenols and thiocyanate.

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1. Introduction

Coke wastewater is a complex industrial wastewater present in many steel production facilities. The carbon and calorific power required for iron smelting is obtained from the destructive distillation of coking coals at temperatures of between 900 and 1100 °C. When coal is heated in the absence of air, complex organic molecules within the coal break down to yield gases, liquid and solid organic compounds of lower 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 and the resulting wastewater from these processes constitutes coke wastewater, which contains considerable amounts of toxic compounds such as CN^- , SCN^- and phenols [1–4]. 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 ammo-

nium salts and chlorides, though low concentrations of heavy metals, and very low levels of phosphorus [5,6]. Hence, if the aim is to treat this wastewater biologically, the aforementioned nutrient will have to be added in the form of phosphate or phosphoric acid. The individual concentrations of each pollutant vary due to the different types of coal and conditions employed in the coking process.

This paper presents a study of the biological treatment of coke wastewater. It is 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 organic matter removal and is carried out in separated tanks; nitrification takes place in the second step. In other existing plants, such as 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

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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 possibility of performing the treatment by means of a one-step activated sludge process, was researched to verify whether most of the pollutants contained in the wastewater (N-NH_4^+ , COD, phenols and SCN^-) could be efficiently removed. However, this might prove somewhat difficult due to possible inhibition phenomena among the pollutants. Some authors found that phenol concentrations of 5.6 mg/L inhibit nitrification 75% [7,8]. However, the sensitivity of ammonium oxidizers to various chemicals does not necessarily mean that nitrifiers are absent in an activated sludge reactor treating substances that are inhibitory to nitrification in the long term. The effective concentration of the inhibitor may be lowered by adsorption, precipitation, chelation and biodegradation, and/or nitrifying organisms may develop tolerance to the inhibitor. In fact, nitrification activity has been found in laboratory activated sludges supplied with phenolic compounds [9].

According to Staib [7], as a result of nitrification inhibition, simultaneous biological oxidation of both organic and nitrogenous compounds with a single sludge system requires not only a high hydraulic residence time for the nitrification process to start once the organic matter has been completely removed but also an excess solid retention time of 30 days to maintain a nitrifying population. A single sludge system also requires inhibition of the nitrifying microorganism by the compounds that they are exposed to, so that nitrification may occur once these compounds have been removed.

2. Materials and methods

The laboratory plant employed consisted of a 20 L volume aerobic reactor made of transparent PVC with several outlets at different heights, followed by a 12 L volume and 24.5 cm diameter settling tank. Oxygen was introduced into the reactor through 12 orifices of 1 mm diameter located at the bottom. A mechanical stirrer was employed to keep the liquor completely mixed.

The temperature was kept constant at a value of $35 \pm 0.5^\circ\text{C}$ by means of a heating element. Ismatec Ecoline, model VC-280 pumps were used to feed the reactor and to recycle the sludge.

The reactor influents and the effluents were analysed using standard methods [10], in order to monitor the biodegradation process taking place inside the reactor. In the case of not being able to carry out immediate analyses, samples were always kept under refrigeration at 4°C . Phenol and COD were analysed by colorimetric methods using a HACH DR/2010 spectrophotometer. N-NH_4^+ concentration was measured by potentiometry using an ORION 95-12 BN ion selective electrode. Although SCN^- was initially analysed by potentiometry, the colorimetric method was preferred on account of problems of interference.

The influent fed into the reactor was coke wastewater from a steelworks that had previously been subject to a stripping treatment. Its composition was variable, as can be seen in Table 1. It contained phenols (110–350 mg/L), N-NH_4^+ (504–2340 mg/L), thiocyanate (185–370 mg/L) and COD (807–3275 mg/L) as its main components. Other components present were cyanide (28–32 mg/L), organic nitrogen (70–200 mg/L), sulphate (90–110 mg/L), phosphate (0.4–0.6 mg/L), chloride (1200–1390 mg/L), and very low sulfide concentrations (0.1–0.2 mg/L). Metals (mainly iron, calcium, magnesium and zinc) were also present in low concentrations, though high enough for the needs of the biological process. The experimental work was carried out in three steps: (1) start-up, (2) study of biodegradation adding bicarbonate to favour nitrification and (3) study of biodegradation without the addition of bicarbonate. Additionally, different batch experiments were performed to study the influence of pH, ammonium concentration and alkalinity on the biodegradation processes.

Different volumetric flow rates were employed and consequently different hydraulic retention times (HRT), as shown in Table 1. 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); therefore, the HRT was the chosen operating parameter. The solid retention time (SRT) increases with the

Table 1
HRT, SRT and average concentration of the different pollutants in the feed coke wastewater for the different experimental conditions

Stage	HRT (h)	SRT (days)	COD (mg/L)	SCN^- (mg/L)	Phenols (mg/L)	$\text{NH}_4^+\text{-N}$ (mg/L)
Start-up	10	3.6	1827	–	–	–
	15	4.0	984	272	–	–
	18	6.4	774	277	–	–
Organic matter removal with nitrification	18.4	7	1012	–	–	520
	23	9	912	334	215	591
	40.3	11	1544	375	292	948
	54.3	14	1596	–	200	1048
	96.1	23	1851	–	280	1095
	17.6	10.4	1273	202	187	671
	31.2	21	1852	365	232	2228
Organic matter removal without nitrification	48.1	33	2293	256	265	928
	96.1	69	1928	–	267	1061
	125	72	1192	213	173	699
	167	82	1274	202	168	694
	236	154	992	210	177	629

HRT (Table 1) and was kept high enough for it not to be the limiting factor in the biodegradation of pollutants.

The influent was neutralised with hydrochloric acid before entering the reactor. In accordance with the data found in the bibliography [11], phosphate was added at a dosage of 130 g $\text{Na}_2\text{HPO}_4/\text{m}^3$, since coke wastewater does not contain sufficient phosphorus for the growth of microorganisms. A small amount of antifoaming agent also had to be added. From day 198 on, a coagulant was added (0.3 mL $\text{Al}_2(\text{SO}_4)_3/\text{L}$ wastewater or 10 g/ m^3) to facilitate clarification of the effluent.

3. Results and discussion

3.1. Start-up of the reactor

In a first step lasting 48 days, an attempt was made to start up the reactor with active sludge from a nearby sewage plant that treats wastewater from a population of 259 125 equivalent inhabitants, 172 875 being urban and the rest industrial. The average wastewater flowrate in the plant is 1012 L/s. The plant presents an initial modified U.C.T. type configuration, which may be varied depending on the characteristics of the “raw” water to be treated (the Foslex system). This sludge had a concentration of TSS of between 30 and 35 g/L, 90% being VSS, and its SVI was 70 mL/g.

The reactor was filled with this sludge up to 1/3 of its volume and was fed with a synthetic water using glucose as carbon source and adding the necessary nutrients for bacterial development. Once the functioning of the reactor had been stabilised, coke wastewater mixed with the synthetic water was introduced, giving rise to the appearance of bulking which in turn resulted in complete flotation of the sludge. This led to the need to modify the start-up of the reactor.

After emptying the reactor, sludge from a plant that treats the leachate from a municipal waste landfill was introduced into the reactor. This plant, which treats 500 m^3 leachate/day, consists of a pressurised (2 bar) nitrification–denitrification process followed by an ultrafiltration system to separate the sludge. The reactor was initially fed with a mixture of leachates from the aforementioned landfill and water from the coke process in different proportions, progressively increasing the percentage of coke wastewater from 25 to 100%. This stage lasted from days 49 to 71.

As good results were not obtained using the mixture of leachate and coke wastewater, the reactor was fed from day 72 onwards with coke wastewater diluted with distilled water at a ratio of 2:1 until a good adaptation of the microorganisms was observed (high COD removal of up to 70% for an HRT of 18 h).

3.2. Study of the biodegradation of coke wastewater with the addition of bicarbonate

Although most coke wastewater contains enough alkalinity to carry out the nitrification process, the wastewater employed in this study had an average concentration of 0.25 g CaCO_3/L . Bearing in mind the high $\text{NH}_4^+\text{-N}$ concentration of the wastewater employed in this study, the ratio kg $\text{CaCO}_3/\text{kg NH}_4^+\text{-N}$ would

be around 0.28, which is clearly inadequate to carry out the nitrification process. Data found in the bibliography show that values of between 2.86 and 5.07 kg $\text{CaCO}_3/\text{kg N-NH}_4^+$ should be used [12,13]. During the present study, bicarbonate was added to the feed wastewater (2.8 kg $\text{NaHCO}_3/\text{m}^3$) to be used as a source of carbon by autotrophic microorganisms [14], thus favouring the nitrification process. The pH in the reactor ranged between 8.0 and 8.5. The removal of organic matter, thiocyanate and ammonium was studied for the different HRT employed.

The sludge presented good settling conditions throughout the entire operation (sludge volume index values lower than 100 mL/g). As regards the oxygen concentration in the reactor, this always remained at values of around 5 mg O_2/L . The average value of the volatile suspended solids in the mixed liquor ranged between 0.8 and 1.7 g/L, representing a percentage of between 58.5 and 77.5% of total suspended solids.

Monitoring of the COD allows the biodegradation of the organic matter taking place in the reactor to be evaluated. Fig. 1 shows the evolution of the COD of the coke wastewater for the different HRT employed and the removal obtained. COD removal ranged between values of 65.6% for an HRT of 23 h ($\text{COD}_{\text{effluent}} = 279 \text{ mg O}_2/\text{L}$) and 38.4% for an HRT of 40.3 h ($\text{COD}_{\text{effluent}} = 982 \text{ mg O}_2/\text{L}$). Table 2 shows the average removal values expressed as percentage removal and as specific removal rate. No clear effect of HRT or SRT on COD removal was observed, the specific removal rate ranging between 335 and 470 mg COD removed/g VSS.day. The OLR did not remain constant for each value of the HRT due to the variation in the composition of the coke wastewater and this may influence removal.

The concentration of phenols in the influent varied between 110 and 350 mg/L, and between 6 and 14 mg/L in the effluent (Fig. 2). The phenol removal obtained was always very high, above 93.5%, no increase in removal being appreciated with increasing HRT or SRT, as can be also seen in Table 2 [15].

Fig. 3 shows the ammonium concentration in the reactor influent and effluent and the nitrification efficiency as a function of HRT. The minimum concentration achieved in the effluent was 318 mg/L, the maximum removal obtained being 71% for HRT of 54.3 and 96.1 h and the minimum, 7.7% for 23 h. As can

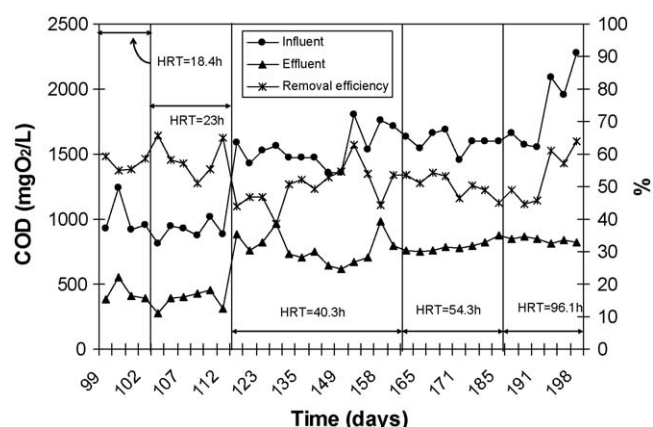


Fig. 1. COD evolution in the influent and effluent and removal obtained with addition of bicarbonate.

Table 2
Average removals of pollutants under the different experimental conditions

HRT (h)	SRT (days)	TSS (g/L)	VSS (g/L)	mg COD _{removed} /g VSS day	COD removal (%)	Phenol removal (%)	NH ₄ ⁺ removal (%)	SCN removal (%)
Organic matter removal with nitrification								
18.4	7	2.23	1.67	449.9	58	95	12	n.d.
23	9	2.38	1.53	363.5	60	96	20	45
40.3	11	1.60	0.99	470.4	51	99	38	37.
54.3	14	1.46	0.79	454.3	52	97	65	n.d.
96.1	23	1.36	0.88	334.9	56	98	67	n.d.
Organic matter removal without nitrification								
17.6	10.4	2.02	1.65	454.5	31	92	–	0
31.2	21	2.34	1.98	341.9	50	96	–	0
48.1	33	2.44	2.03	396.2	66	98	–	49
96.1	69	2.74	2.19	70.3	32	96	–	n.d.
125	72	2.19	1.78	71.1	50	97	–	65
167	82	1.93	1.55	50.0	42	96	–	85
236	154	2.98	2.44	25.3	38	96	–	90

n.d.: not determined.

be observed, nitrification increased with increasing HRT and SRT up to a value of 54.3 h, no higher removal values being obtained at higher HRT, as can be also observed in Table 2. In addition, Fig. 3 shows the removal of total nitrogen by oxidation, considering organic nitrogen, ammonium nitrogen and thiocyanate. As can be observed, taking these other forms of nitrogen into account, the trend of the curve would be the same, though with slightly higher removal efficiencies. The transformation of organic nitrogen into ammonium nitrogen was very high, around 96%.

The experimental data were fitted to an exponential curve ($r=0.982$) which suggests that from 75 h on no higher removal than 65.6% would be achieved, even by increasing the HRT. Nitrification does not take place using HRT below 12.6 h. The equation obtained was

$$\% \text{NH}_4^+\text{-N removed} = 65.6\{1 - \exp[-0.05(\text{HRT} - 12.6)]\}$$

The biodegradation of thiocyanate was quite low; values of 45% and 37% being found for HRT of 23 and 40.3 h, respectively (Table 2). The presence of certain compounds such as phenols, NH₄⁺-N, NO₃⁻ and NO₂⁻ may have a high inhibitory effect

over SCN⁻ biodegradation, resulting in low removal efficiency [16–18]. In this case, the concentration of NH₄⁺-N in the influent was both very high and variable (ranging from 506 to 1108 mg/L) due to certain problems in the prior stripping treatment carried out at the steelworks. Under these conditions, competition between nitrifying bacteria and thiocyanate-degrading bacteria is very likely to occur at these low HRT. It was not possible to

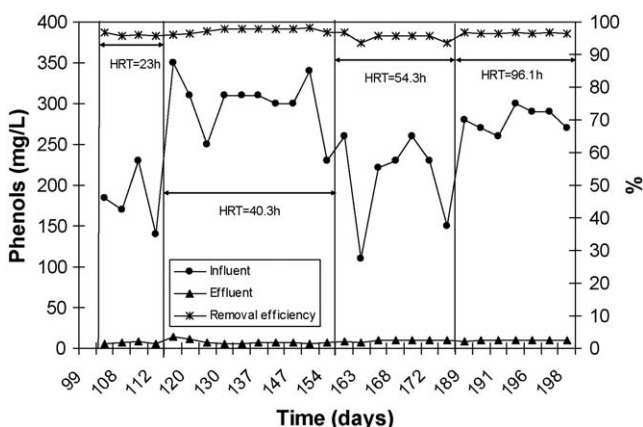
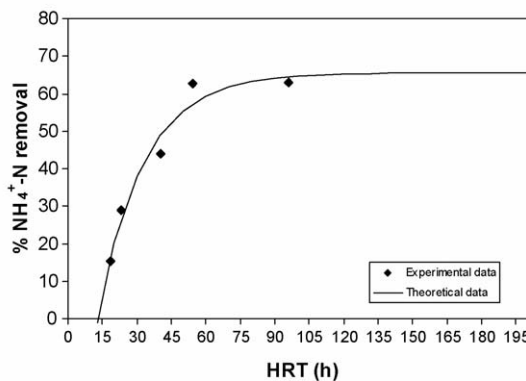
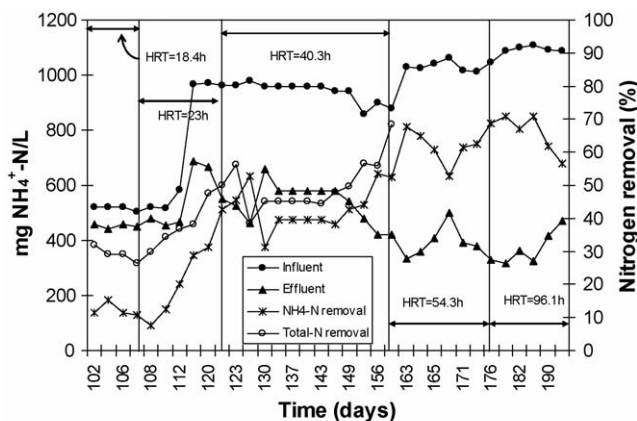


Fig. 2. Phenols evolution in the influent and effluent and removal obtained with addition of bicarbonate.

Fig. 3. NH₄⁺-N evolution in the influent and effluent, nitrogen removal efficiencies and relationship between NH₄⁺-N average removal and HRT with addition of bicarbonate.

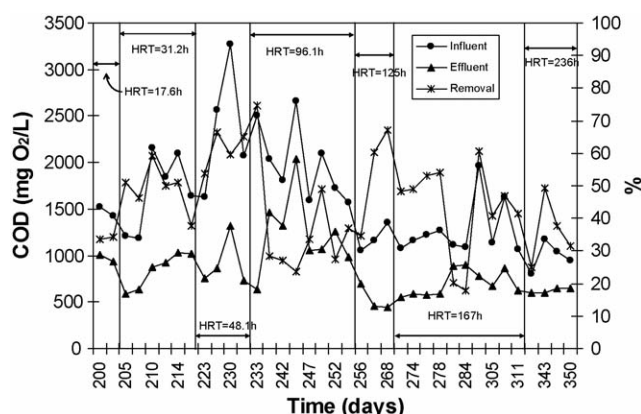


Fig. 4. COD evolution in the influent and effluent and removal obtained without addition of bicarbonate.

monitor biodegradation for higher HRT due to certain problems of interferences in the analytical method applied.

This process, which sought to remove organic matter, NH_4^+ -N and SCN^- in a single step was not successful enough to obtain adequate concentration values of the different pollutants in the effluent. This result is in keeping with some of the data reported in the bibliography [18]. A possible way to obtain lower pollutant values in the effluent would be to employ a two-step configuration. Organic matter and SCN^- would be removed in the first step and the nitrification process would take place in the second step.

As a prior stage to the two-step process, the removal of organic matter and SCN^- was studied without the addition of bicarbonate.

3.3. Study of the biodegradation of coke wastewater without the addition of bicarbonate

To prevent the growth of autotrophic nitrifying microorganisms, bicarbonate was no longer added as a source of inorganic carbon. The reactor was fed with coke wastewater and the influence of HRT on the removal of pollutants was studied. The pH in the reactor during this study ranged between 6.0 and 7.5. The organic loading rate at which the reactor was fed generally decreased with increasing HRT, except when operating at an HRT of 125 h, for which the OLR was lower than expected, as the feed for this HRT presented lower levels of COD. The average concentration of volatile suspended solids in the mixed liquor remained between 1.6 and 3.1 g/L, representing 80–86% of total suspended solids. The concentration of dissolved O_2 remained around 5 mg/L throughout the process and the sludge presented good settling properties (SVI lower than 100 mL/g).

Fig. 4 shows the variation in COD in the reactor influent and effluent as well as the removal obtained for the different HRT and SRT employed during the experiments. The COD of the influent ranged between 3275 and 807 mg O_2/L , and that of the effluent between 2036 and 447 mg O_2/L . The specific removal rate was similar to that of the previous experiments for HRT up to 48.1 h (Table 2), decreasing for higher HRT. This behaviour may be the result of the different composition of the industrial coke

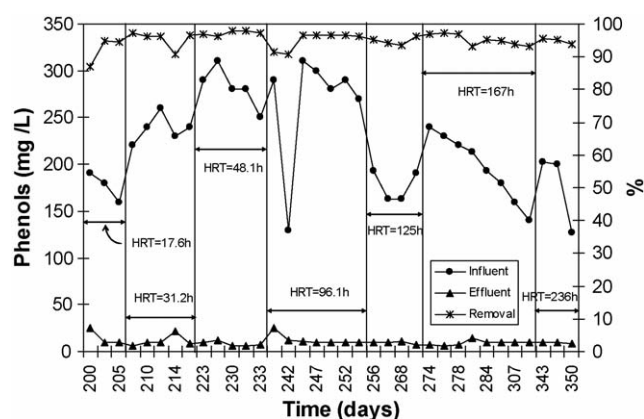


Fig. 5. Phenols evolution in the influent and the effluent and removal obtained without addition of bicarbonate.

wastewater, which presented lower COD values, as well as the very high HRT reached in this stage. Thus, the specific removal rate decreased from values of around 400 to values lower than 71 mg COD removed/g VSS day for HRT higher than 96 h.

The evolution of the biodegradation of phenols is shown in Fig. 5. The concentration of phenols in the influent ranged between 310 and 127 mg/L, whereas that of the effluent ranged between 25 mg/L for HRT of 96.1, 17.6 h and 6 mg/L for HRT of 17.6, 48.1 and 167 h. Removal ranged between 87% and 98% and was independent of HRT for the values employed, as in the experiments with nitrification. It can thus be concluded that biodegradation of phenols always takes place to a very high degree even at short HRT. Some authors report that HRT between 8 and 10 h are long enough for phenolic wastewater treatment by means of the activated sludge process [19].

As can be observed in Fig. 6, the concentration of NH_4^+ -N in the effluent is usually greater than that of the influent. This is due to the presence of organic nitrogen and thiocyanate in the influent, since the former is transformed into NH_4^+ during the process of biodegradation and the latter into NH_4^+ , CO_2 and SO_4^{2-} [16,17,20]. This behaviour was confirmed by means of respirometric assays employing synthetic water containing SCN^- and not NH_4^+ ; it being observed that the biodegradation of the thiocyanate gave rise to the generation of ammonia. It should be

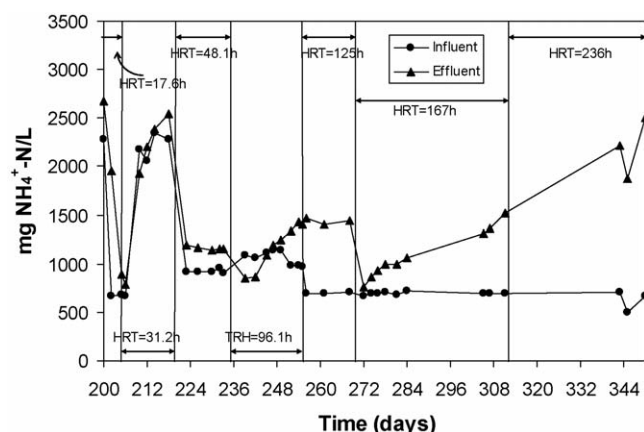


Fig. 6. NH_4^+ -N evolution in the influent and effluent without addition of bicarbonate.

pointed out that during this operation period the organic nitrogen concentrations were very variable, ranging between 114 and 1215 mg/L, an abnormally high value. The increase in the concentration of $\text{NH}_4^+\text{-N}$ due to thiocyanate biodegradation accounted for 4.1%, 99.5%, 20.2%, 5.3%, 9.3% and 2.5% of this increase for HRT of 17.6, 31.2, 48.1, 125, 167 and 236 h, respectively. For HRT of 31.2 h, the concentration of organic nitrogen in the influent was only 114 mg/L. Thus, the increase in the $\text{NH}_4^+\text{-N}$ in the effluent was mainly due to thiocyanate biodegradation. However, for HRT of 236 h, the concentration of organic nitrogen was 1215 mg/L and the contribution to the increase in $\text{NH}_4^+\text{-N}$ in the effluent represented only 2.5%. The removal of nitrogen is not represented in Fig. 6 since nitrification only took place on very few occasions, in which a maximum removal of 5% was obtained. The transformation of organic nitrogen into $\text{NH}_4^+\text{-N}$ reached very high performances, ranging between 91 and 98%.

Fig. 7 presents the variation in the concentration of SCN^- for the different HRT employed as well as the influence of HRT on the average removal efficiency. The concentrations in the influent ranged between 370 and 185 mg/L. As can be seen, biodegradation of SCN^- took place in the reactor except for the lower HRT (17.6 and 31.2 h), in which no biological degradation of SCN^- could be appreciated. It may therefore be deduced that for removal of SCN^- under the conditions employed in the activated sludge reactor, it is necessary to work with HRT higher

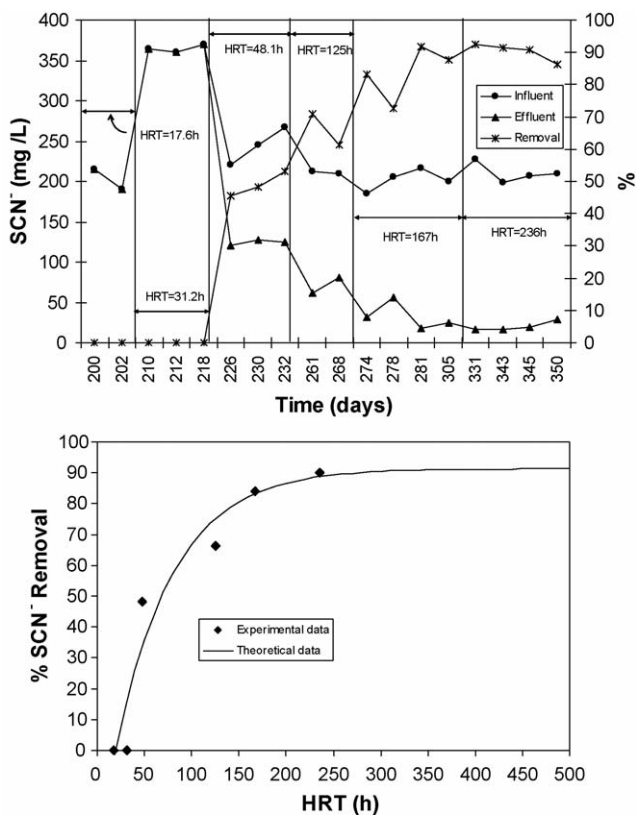


Fig. 7. SCN^- evolution in the influent and effluent, removal efficiencies and relationship between SCN^- average removal and HRT without addition of bicarbonate.

than 31.2 h. According to Kwon et al. [17] complete biodegradation of thiocyanate would be possible in 23 h in the absence of inhibitory compounds such as $\text{NH}_4^+\text{-N}$, NO_2^- , NO_3^- or phenols. The presence of these compounds produces a delay in the biodegradation process that may last 60 h in the presence of phenol or even 82 h when nitrite is present at a concentration of 50 mg/L in the wastewater.

The minimum concentration of SCN^- obtained in the effluent was 17 mg/L for an HRT of 236 h. Biodegradation increased with HRT, the highest removal ranging between values around 90% for an HRT of 236 h, and the minimum being 45.4% for an HRT of 48.1 h.

In the previous step, in which simultaneous removal of organic matter and ammonium took place, SCN^- biodegradation was observed at a lower HRT (23 h). This may be due to the lower concentrations of $\text{NH}_4^+\text{-N}$ found in the wastewater used in the previous step (Figs. 3 and 6) and to the different mechanism of biodegradation [17,20]. Thiocyanate may be a carbon source as well as an energy source in the growth of autotrophic microorganisms, although some heterotrophs are also able to biodegrade SCN^- using the NH_4^+ produced during biodegradation as a nitrogen source. Both types of thiocyanate degradation mechanisms have been reported [21–24].

The experimental data obtained for the average removal efficiency as a function of HRT can be fitted to an exponential curve ($r=0.96$), according to the equation

$$\% \text{SCN}^- \text{ removal} = 90\{1 - \exp[-0.016(\text{TRH} - 19.8)]\}$$

As the theoretical curve suggests, a maximum removal of 90% could possibly be achieved by means of this process using an HRT of 300 h, and no removals would be obtained with an HRT below 19.8 h.

3.4. Batch experiments

Batch experiments were performed to study the influence of several factors such as pH or $\text{NH}_4^+\text{-N}$ concentration on biodegradation. To study the influence of pH, experiments were carried out in a stirred reactor seeded with biomass (2.5 g VSS/L) at different pH (6.0, 6.5, 7.0, 7.5 and 8.0). The average concentrations of pollutants in the coke wastewater were: 195 mg phenols/L, 236 g $\text{N-NH}_4^+\text{/L}$ and 257 mg SCN^- /L. Samples were taken and the phenol concentration was measured after 15 h and the SCN^- concentration after 63 h, obtaining the results shown in Fig. 8. As can be seen, phenol biodegradation improves with increasing pH, ranging from 64% at pH 6 to a maximum of 95.7% in 15 h. With respect to SCN^- biodegradation, at pH >6.5 the biodegradation is very poor. At pH 6, a removal efficiency of 96.9% was obtained in 63 h, decreasing to 10% at pH 7. Since SCN^- takes much longer to biodegrade and the required HRT for the treatment of coke wastewater are always long enough to reach high phenol removal efficiencies, the pH in the reactor will be kept at values between 6 and 6.5 in future studies.

The kinetics of SCN^- biodegradation was affected by the presence of ammonium. The experiments were carried out in a reactor under the same conditions of stirring and biomass concentration and at a pH 6.5, but with variable ammonium

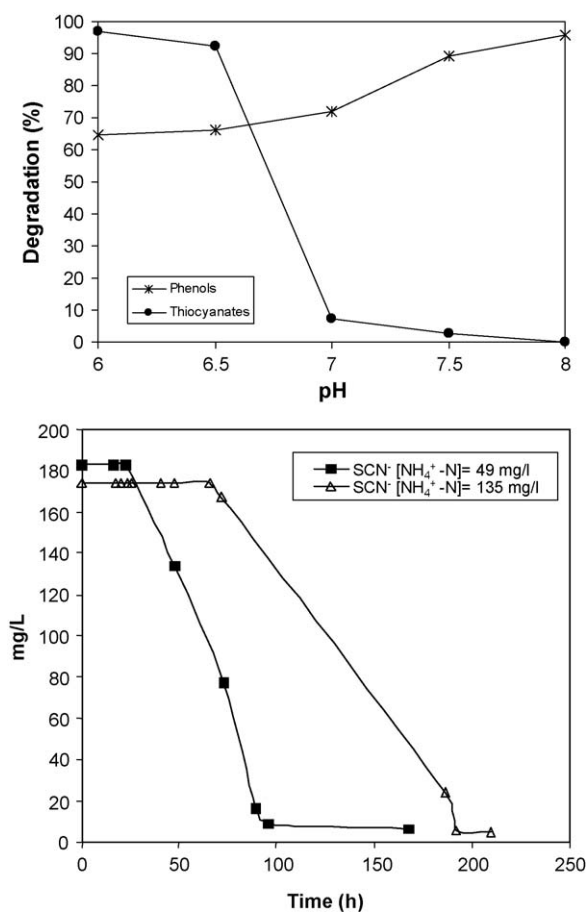


Fig. 8. Effect of pH and N-NH₄⁺ concentration on biodegradation.

concentration in the wastewater (obtained by modifying conditions in the pre-stripping treatment). As can be observed in Fig. 8, the time needed to obtain 90% biodegradation doubled when the concentration of NH₄⁺-N increased from 49 mg/L to 135 mg NH₄⁺-N/L. This effect is also observed in the biomass acclimatization time needed to start biodegradation (plateaus in Fig. 8).

Although coke wastewater is often sufficiently alkaline to achieve nitrification, addition of bicarbonate is required in some cases [25]. Different batch experiments were performed at pH 8.3 once the sludge was acclimatized (2.5 g VSS/L) in order to ascertain the optimum alkalinity for the nitrification process to take place in the coke wastewater under study. The initial concentration of NH₄⁺-N in the coke wastewater was 300 mg/L. After 100 h without removal, nitrification commenced immediately when bicarbonate was added as a source of alkalinity, a final concentration of approximately 50 mg/L being obtained in 50 h (Fig. 9).

This experiment was repeated using different alkalinity concentrations, measuring the efficiency of NH₄⁺-N removal in each experiment. The obtained results were fitted to a theoretical curve, achieving efficiencies of 98% for an alkalinity of 3.5 g CaCO₃/L. This dose implies a consumption of 6.5 kg CaCO₃/kg N-NH₄⁺ and this ratio will be used to calculate the bicarbonate dosage in the future study of the two-step process.

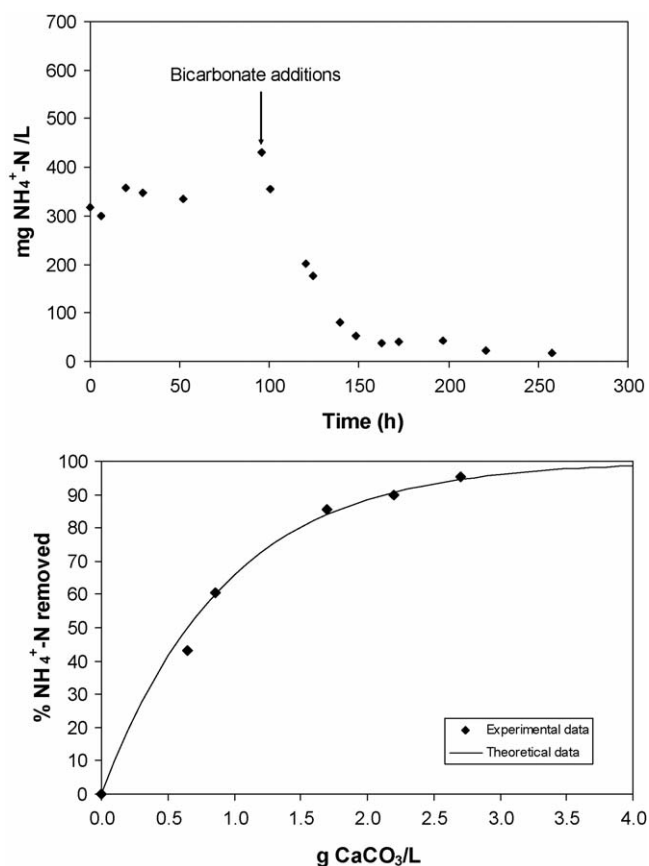


Fig. 9. Effect of alkalinity addition on the nitrification process.

4. Conclusions

Activated sludge from a municipal sewage treatment plant could not be used for the start-up of the reactor since the different characteristics of the coke wastewater caused bulking of the biomass. However, when sludge from a landfill treatment plant was used, the acclimatization took place in a short period of time.

In the simultaneous removal of NH₄⁺-N, organic matter and SCN⁻ in a single step, adding bicarbonate to stimulate the growth of autotrophic microorganisms, NH₄⁺-N removals of 71% were obtained for an HRT of 54.3 h. The maximum removals achieved for COD and phenols were 65.6% and 97%, respectively.

When bicarbonate was not added, the concentration of NH₄⁺-N in the effluent increased due to both biodegradation of SCN⁻ and organic nitrogen transformation. Very high removals of phenols were achieved, which were similar to those obtained when bicarbonate was added, an HRT of 17.6 h being found to be sufficient for a removal efficiency of 95%. The maximum average removal of COD was 74.8% for an HRT of 96.1 h.

The biodegradation of SCN⁻ took place under both conditions (with or without the addition of bicarbonate), although very high HRT (167 h) were needed to obtain removal percentages of around 90%.

The biodegradation of phenol improves with increasing pH, achieving 96% at pH 8 in 15 h. In contrast, the biodegradation of SCN⁻ increases with decreasing pH, achieving 97% at pH 6

in 63 h. High concentrations of ammonium were found to affect the kinetics of thiocyanate biodegradation.

Addition of alkalinity was needed for nitrification to take place in the reactor. An alkalinity consumption of at least 6.5 kg CaCO₃/kg NH₄⁺-N was required to achieve 90% removal efficiencies.

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