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Electrochemical oxidation of saline industrial wastewaters using boron-doped diamond anodes

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Similarly to other catalytic advanced oxidation processes electro-oxidation by means of boron-doped diamond (BDD) anodes generates a very efficient oxidant media containing, among others, hydroxyl radicals. In this work BDD electro-oxidation is demonstrated to be an efficient alternative to treat a wide variety of saline industrial effluents, which main properties were as follows: TOC = 266–4479 mg/L; [N-NH_3] = 61–1150 mg/L; [Cl^-] = 1996–37,645 mg/L; conductivity = 5.6–64 mS/cm. Experiments were conducted at laboratory and pilot scale. Treatment efficiency was evaluated in terms of TOC and N-NH_3 removal, and of formation of undesired by-products such as nitrate ions and trihalomethanes. The results showed that the high concentration of chloride ions in the wastewaters resulted in chloride oxidation taking place primarily, favouring ammonia oxidation in detriment of TOC elimination. Consequently, complete elimination of ammonia could be achieved for all the wastewaters studied while TOC removals reached values as high as 90%. Additionally, biodegradability of the effluent prior to and after treatment was also evaluated by means of the respirometry technique and the energy consumption of the process was estimated. The analysis of the energy consumption recommends the application of process integration approaches for the treatment of heavily polluted industrial effluents.

1. Introduction

Increased public concern about water quality coupled with regulatory pressure is forcing municipalities and industrial users to examine their wastewater treatment practices. Effluents originated from industrial activities usually contain pollutants that are inhibitory, toxic or resistant to biological treatment. In this respect, advanced technologies based on chemical oxidation may be the only viable option for decontaminating biologically recalcitrant effluents [1]. Among these processes electro-oxidation by means of boron-doped diamond (BDD) anodes has proved to be an efficient technology that is able to eliminate non-biodegradable and/or toxic organic pollutants and ammonia nitrogen [2–5]. Most studies have been performed on a laboratory scale and only recently has it been implemented successfully on a pilot scale [6,7]. Nevertheless, further research at pilot scale is still needed in order to validate the results obtained at laboratory scale and confirm the versatility and robustness of the process.

In this study, the versatility of BDD electro-oxidation was evaluated by treating five different real saline industrial effluents. In a first step, the wastewaters were treated at laboratory scale. Effect of applied current density on conversion of TOC and ammonia, as well as on the formation of undesired by-products such as nitrate ions and trihalomethanes was assessed. Biodegradability of the effluent prior to and after treatment was also evaluated by means of the respirometry technique and the energy consumption of the process was estimated. Finally, the results obtained in the laboratory were validated at pilot scale.

2. Materials and methods

2.1. Industrial wastewaters

The five wastewaters treated in this study had different origins and were taken from various treatment processes of two industrial waste management facilities. Their physicochemical characteristics are given in Table 1. During the study, the initial characteristics of the wastewaters were re-determined before each electro-oxidation run. At lab scale, the same sample was usually used to carry out all the experiments whereas in the pilot plant a fresh sample was employed. As the characteristics of the wastewaters object of this study vary constantly in terms of origin and concentration, considerable fluctuations in the initial concentrations of chloride, TOC and NH_3 occurred in the course of pilot testing. Table 1 shows that apart from *SIII*, all the effluents had very high conductivity values due mainly to the high concentration of chloride ions. The effluents' pH was either close to neutrality or highly alkaline (7.4–10.3). The concentration of total organic

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Table 1
Physicochemical characteristics of wastewaters treated in this work in the course of laboratory (Lab) and pilot plant (PP) testing.

Effluent	Scale	TOC (mg/L)	IC (mg/L)	N-NH_3 (mg/L)	N-NO_3 (mg/L)	N-NO_2 (mg/L)	[Cl^-] (mg/L)	Conductivity (mS/cm)	pH
SI	Lab	266 (261–275)	469 (460–470)	668 (644–700)	n.d.	n.d.	6768 (6470–7216)	20.6 (19.2–21.6)	7.6 (7.5–7.7)
	PP	546 (539–560)	443 (420–465)	574 (535–630)	n.d.	n.d.	5917 (4550–7021)	16.6 (19.5–24.7)	8.2 (7.9–8.4)
SII	Lab	721 (681–747)	15.4 (14–16)	210	1072 (1000–1166)	n.d.	36,283 (34,870–37,645)	64 (63–68)	9.0 (8.7–9.1)
	PP	754 (430–936)	77 (53–101)	260 (154–441)	1370 (1307–1482)	187 (179–201)	14,333 (10,107–17,052)	49 (26.3–65.6)	7.4 (6.3–8.3)
SIII	Lab	392 (389–395)	26.1 (25.5–26.5)	61 (28–84)	n.d.	n.d.	2427 (1996–2793)	5.6 (4.0–7.2)	8.8 (8.7–9.0)
	PP	430 (376–510)	200	104 (22–255)	8.7 (n.d.–26)	n.d.	4025 (3244–4495)	16.8 (14–20)	10.3 (8.6–12.2)
SIV	Lab	4479	98	539	5	n.d.	17,992	34	10.0
SV	Lab	2425 (2362–2488)	625 (556–695)	1150 (1120–1187)	n.d.	n.d.	6200 (5898–6414)	23 (21.4–24)	7.7 (7.5–7.9)

carbon (TOC) and NH_3 varied in a wide range. On the one hand, *SI*, *SII* and *SIII* with lower but still considerable TOC and NH_3 concentrations. On the other hand, *SIV* and *SV* with a much higher contaminant load, reaching the concentration of TOC values as high as 4479 mg/L. Inorganic carbon (IC) represented a low percentage of the total carbon (TC) in *SII*, *SIII* and *SIV* while its concentration in *SI* and *SV* amounted to 64% and 20% of the TC concentration, respectively. Finally, NO_2^- and NO_3^- ions were either not detected or present in low concentrations. The exception was *SII* which had a high concentration of NO_3^- ions.

2.2. Electrolytic systems

The electrochemical cell used in the laboratory was comprised of a circular BDD on silicon anode and a stainless steel cathode with a surface area of 70 cm^2 each and an inter-electrode gap of 5 mm. Other experimental details can be found in a previous work [4].

The pilot plant consists of a tank of 750 L and three pumps that feed the electrolyte to be treated into three parallel fluid lines. Each line consists of five sets, containing each set ten anode–cathode pairs (electrode gap 1 mm). The electrode materials are the same as those used in the laboratory but in this case the total anode surface is 1.05 m^2. A more detailed description was given by Anglada et al. [6] in a previous study.

The electro-oxidation units were run in batch mode and at a constant current density. At lab scale, 1–2 L of wastewater was electrochemically oxidized in each experiment whereas at pilot scale 250 L were treated in each run.

2.3. Analytical methods

Samples were withdrawn at regular time intervals and preserved at 4 °C. Total organic carbon (TOC) analysis was performed using a TOC-V CPH Shimadzu. Ammonium nitrogen concentration was obtained by distillation and titration according to the Standard Method 4500 [8]. Ion chromatography was used to determine the concentrations of chloride, sulphate, nitrate and nitrite ions. A BM3-LAB respirometer was used to determine the oxygen consumption from the electro-oxidation samples. The concentration of trihalomethanes was determined by headspace injection followed by GC-ECD (Agilent HP 6890 Series).

3. Theory: mechanisms of electrochemical oxidation

Three oxidation mechanisms can be responsible for the elimination of pollutants in electro-oxidation processes: direct anodic oxidation [9], hydroxyl radical mediated oxidation [4] and oxidation in the bulk solution by oxidants formed in situ from salts contained in the waste [9]. In particular, electro-oxidation of organic matter by means of BDD anodes is thought to take place through the first two mechanisms. Among the models that have been developed to describe BDD electro-oxidation of wastewaters containing organic pollutants, the model developed by Comninellis' group [10] has received much attention. In this model, two types of operating regimes are defined depending on the value of the applied current density: (i) if $j_{appl} < j_{lim}$, the reaction is charge-controlled and COD decreases linearly with time; (ii) if $j_{appl} > j_{lim}$ the process is mass-transfer-controlled and COD evolution follows an exponential trend.

On the other hand, ammonia oxidation has been observed to occur through indirect oxidation by active chlorine formed during the electrochemical process [6,11]. During indirect oxidation of ammonia, chlorine evolution occurs at the anode (Eq. (1)). At pH >3.3, chlorine diffusion away from the anode is coupled to its disproportionation reaction to form chloric (I) acid at pH <7.5 (Eq. (2)) and chloric (I) ions at pH >7.5 (Eq. (3)). Then, HOCl reacts with

NH_3 through breakpoint chlorination reactions to regenerate chloride ions. Consequently, theoretically chloride concentration should remain constant. Nevertheless, chloride concentration can decrease for different reasons: accumulation of active chlorine in the bulk solution, AOX formation, stripping of chlorine and chlorate formation at alkaline pH.

$$Cl^- \rightarrow \tfrac{1}{2}Cl_2 + e^- \qquad (1)$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \qquad (2)$$

$$HOCl \rightarrow OCl^- + H^+ \qquad (3)$$

4. Results and discussion

4.1. Laboratory scale electro-oxidation results

4.1.1. Electro-oxidation of SI, SII and SIII; effect of current density

The effect of current density on treatment efficiency was assessed as it is a determining factor in electrochemical reactions. Instead of subjecting all the effluents to the same current densities, the range within which the current density was varied for each type of wastewater was independently chosen based on their physico-chemical characteristics. The criteria used was the following: the limiting current density for the initial COD concentration (estimated by considering a COD/TOC ratio of 2.7) was calculated for each effluent and then the influence of the current density was evaluated by modifying this variable within close range (Table 2). The exception was *SI*; in this case current densities higher than the sum of $j_{\text{lim,COD}} + j_{\text{lim,Cl}}$ were applied. The rationale behind this decision was that indirect oxidation mechanisms such as ammonia oxidation are favoured at high current densities and *SI* was characterized by much higher ammonia than TOC concentration.

Table 2
Limiting current density, calculated for the initial COD (estimated for a COD/TOC ratio of 2.7) and chloride concentration of each wastewater as follows; $j_{\text{lim,COD}} = 4Fk_m\text{COD}_o$; $j_{\text{lim,Cl}} = 1Fk_m[\text{Cl}^-]_o$. Current densities applied in this work at laboratory scale as well as the percentage of N-NH_3 eliminated as N-NO_3^- during electro-oxidation of the wastewaters object of this study, is also shown.

Wastewater	$j_{\text{lim,COD}}$ (A/m^2)	$j_{\text{lim,Cl}}$ (A/m^2)	j_{appl} (A/m^2)	%N-NH_3 eliminated as N-NO_3^-
SI	106	224	300	3.3
			500	6.1
			700	10.7
SII	286	1203	100	–
			200	–
			300	–
			400	–
SIII	156	82	150	13
			300	11
			400	50
SIV	1779	596	1140	16
SV	963	206	800	17

Figs. 1–3 show the effect of current density on the normalized TOC, ammonia and chloride concentration profiles during electrochemical treatment of *SI*, *SII* and *SIII*, respectively. At this point it should be mentioned that as these data have been plotted against the specific electrical charge, these figures give a measurement of the efficiency of the electro-oxidation process [2]. Complete elimination of ammonia and TOC removals of up to 90% were obtained. Overall, the use of higher current densities resulted in lower TOC removal efficiencies while the efficiency of ammonia oxidation was practically independent of the applied current density.

In the case of *SI*, an initial delay in the removal of TOC was observed when working at 500 and 700 A/m^2 (Fig. 1a). The

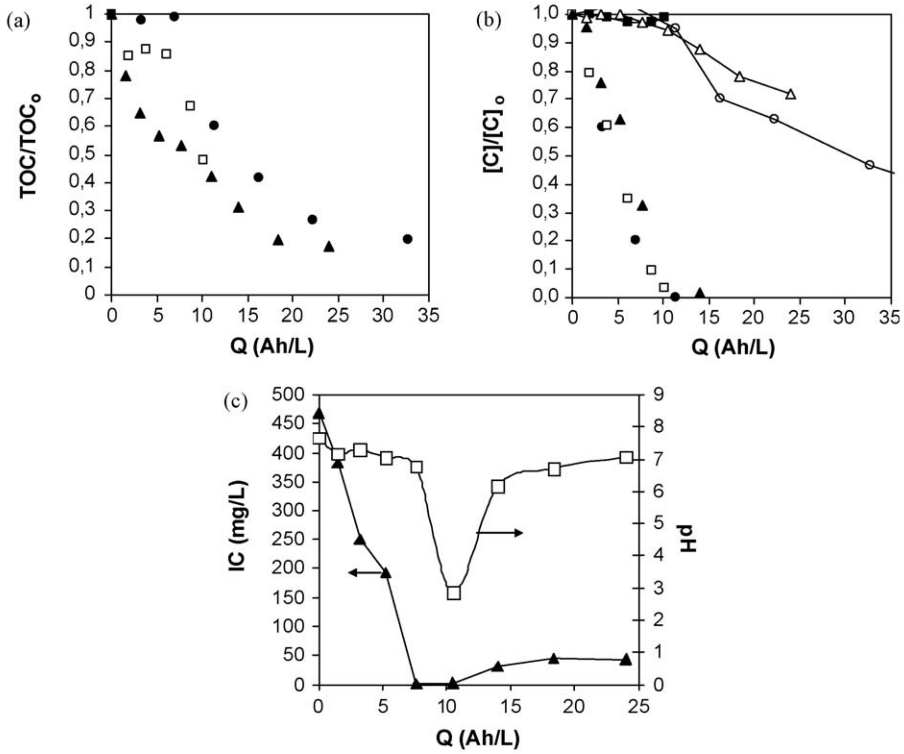

Fig. 1. Effect of current density (▲, j = 300 A/m^2; □, j = 500 A/m^2; ●, j = 700 A/m^2) on the evolution of (a) TOC/TOC$_o$ and (b) $[NH_3]/[NH_3]_o$ and $[Cl^-]/[Cl^-]_o$ during electrochemical oxidation of *SI* in the laboratory. In (b) "△, j = 300 A/m^2; ■, j = 500 A/m^2; ○, j = 700 A/m^2" represent $[Cl^-]/[Cl^-]_o$ profiles. (c) pH and IC concentration profiles during electro-oxidation of *SI* at 300 A/m^2 are represented.

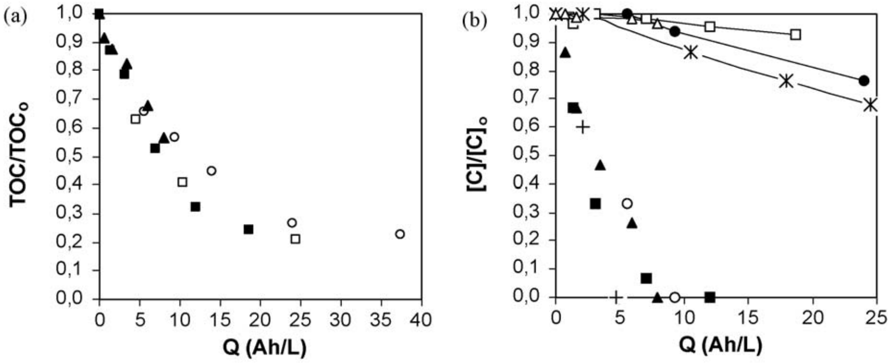

Fig. 2. Effect of current density (▲, j = 100 A/m^2; ■, j = 200 A/m^2; +, j = 300 A/m^2; ○, j = 400 A/m^2) on the evolution of (a) TOC/TOC$_o$ and (b) [NH$_3$]/[NH$_3$]$_o$ and [Cl$^-$]/[Cl$^-$]$_o$ during electrochemical oxidation of *SII* in the laboratory. In (b), [Cl$^-$]/[Cl$^-$]$_o$ profiles are represented by: △, j = 100 A/m^2; □, j = 200 A/m^2; ✱, j = 300 A/m^2; ●, j = 400 A/m^2.

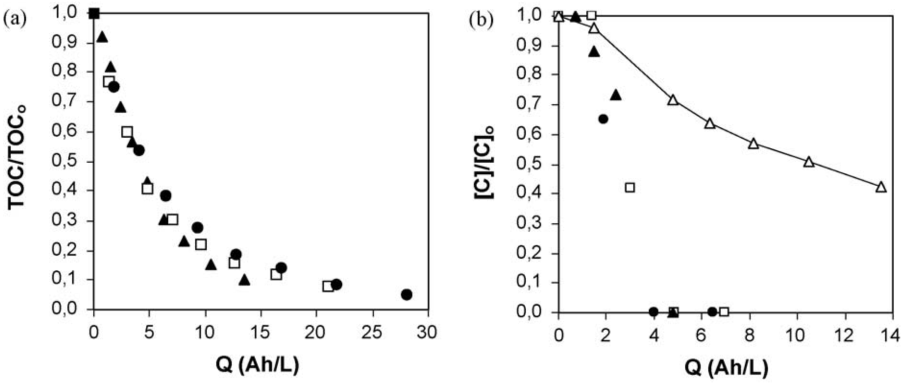

Fig. 3. Effect of current density (▲ j = 150 A/m^2; □, j = 300 A/m^2; ●, j = 400 A/m^2) on the evolution of (a) TOC/TOC$_o$ and (b) [NH$_3$]/[NH$_3$]$_o$ and [Cl$^-$]/[Cl$^-$]$_o$ during electrochemical oxidation of *SIII* in the laboratory. In (b) Chloride depletion at j = 150 A/m^2 is represented by △.

existence of the time lag in the removal of TOC was more pronounced as the current density increased. This could be due to the side reaction of chlorine evolution at the anode. As it can be observed in Fig. 1b, chloride concentration remained practically constant while ammonia was being oxidized. However, once ammonia had been completely eliminated the concentration of chloride ions decreased as it is theoretically expected if no other pollutants compete for chlorine [6,12]. Moreover, chloride depletion increased at higher current densities. Consequently, the use of higher current densities seems to have enhanced chlorine evolution at the anode but not TOC removal.

In contrast to *SI*, no time lag in the elimination of TOC was observed during the electro-oxidation of *SII* and *SIII*. The differences observed could be due to the range of current densities employed. Whereas $j_{\mathrm{appl}}/j_{\mathrm{lim,COD}}$ ratios ranging from 3 to 7 were employed to treat *SI*, ratios ranging from 0.35 to 1.4 and from 1 to 2.7 were used when *SII* and *SIII* were subjected to electro-oxidation, respectively. This would also explain why the oxidation efficiency of TOC was observed to decrease for the whole range of current densities studied for *SI* (Fig. 1a) and *SIII* (Fig. 3a) while different behaviours were found for *SII* (Fig. 2a). In the latter case, an increase from 100 to 300 A/m^2 led to higher TOC oxidation rates while a further increase to 400 A/m^2 hardly affected the oxidation rate of TOC. This behaviour can be explained on the basis of the different operating regimes defined by Panizza et al. [10] and that have been explained in the *Theory* section of this article. Consequently, in accordance to previous observations [4], organic matter oxidation at BDD anodes takes place through direct anodic or hydroxyl radical mediated oxidation but not by indirect oxidation by means of electro-generated active chlorine.

On the contrary to TOC oxidation, the elimination of ammonia was enhanced at higher current densities for all the wastewaters studied; no significant differences were found between the ammonia profiles against the specific electrical charge at the different current densities assessed (Figs. 1b, 2b and 3b). Furthermore, the evolution of the concentration of chloride ions during electro-oxidation of *SII* followed a similar behaviour to that reported for *SI* (Fig. 2b). However, chloride depletion occurred almost from the beginning of the experiments performed with *SIII* as it is exemplified in Fig. 3b for 150 A/m^2. The much lower concentration of ammonia in this effluent could be responsible for this behaviour; 61 mgN-NH$_3$/L in *SIII* in contrast to 668 mg N-NH$_3$/L and 210 mg N-NH$_3$/L in *SI* and *SII*.

Moreover, comparison between the TOC and ammonia profiles reveals that the oxidation of TOC occurred at a slower rate than that of ammonia. This is in disagreement with the results obtained by our group in previous studies in which landfill leachate was electrochemically oxidized by means of BDD anode [4,6]. In those studies, oxidation of organic matter occurred preferentially and an initial delay in the oxidation of ammonia was observed when working near or below the limiting current density calculated for the initial COD concentration. The differences observed in the relative oxidation of TOC and ammonia during electro-oxidation of *SI*, *SII*, *SIII* and landfill leachate could be due to the lower salinity of the latter ([Cl$^-$] = 1600–3000 mg/L). In fact, *SIII*, which had an average concentration of Cl$^-$ of 2427 mg/L, showed similar behaviour to landfill leachate in that the concentration of N-NH$_3$ remained constant at the beginning of the process (0.7–1.4 Ah/L), though TOC was being oxidized. Obviously, mass-transport of chloride towards the anode surface is enhanced when high

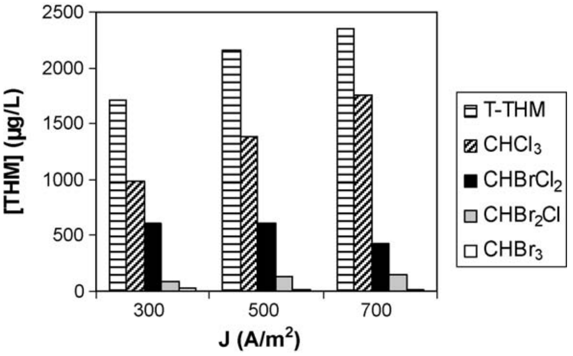

Fig. 4. Effect of current density on trihalomethane formation during electrochemical oxidation of *SI* after 10.5 Ah/L, in the laboratory.

concentrations of chloride ions are present in the effluent. As a result, chlorine evolution increases in detriment of anodic oxidation of TOC.

Formation of undesired by-products such as nitrate ions and organo-chlorinated compounds should also be monitored. In Table 2 the percentage of N-NH_3 eliminated in the form of N-NO_3^- during electro-oxidation of *SI* and *SIII* is shown. The results obtained for *SII* are not presented since this effluent initially contained a very high concentration of nitrate ions (1072 mg N-NO_3^-/L) which remained practically constant throughout the electro-oxidation process. In Table 2, it can be observed that the use of higher current densities usually favoured the formation of nitrate ions. Interestingly, electro-oxidation of *SI* yielded lower "N-NO_3^- formed/N-NH_3 removed" ratios than *SIII*. This could be due to the lower chloride content of *SIII*. Cabeza et al. [11] observed that the ratio "N-NO_3^- formed/N-NH_3 removed" decreased by increasing the initial chloride concentration during electro-oxidation of landfill leachate.

Relatively high concentrations of chlorinated by-products were also detected. In all cases, chloroform was the main by-product, e.g. the concentration of chloroform constituted between 86% and 100% of the total trihalomethane concentration formed during electro-oxidation of *SII*. Similar results were reported by Comninellis and Nerini [13]. Regarding the effect of current density, an increase in current density generally yielded higher THM concentrations (Fig. 4).

Concerning other aspects of the operation, the effluents' pH decreased substantially during the initial stages of the treatment reaching values as low as 3. However, further treatment brought about an increase of the pH value which was finally stabilized at the effluent's initial pH (*SI*) or at values close to neutrality (*SII*, *SIII*). In all cases, pH profiles followed a similar trend to that of the concentration of IC. This behaviour is exemplified in Fig. 1c for *SI* where the pH and IC concentration profiles obtained during the electro-oxidation process at 300 A/m^2 are shown. A similar behaviour was observed by Anglada et al. [6] during electro-oxidation of biologically pre-treated leachate.

From the above-mentioned data, it can be concluded that current density plays a key role on selectivity and on oxidation kinetics. On the basis of the pollutant whose elimination is chosen as priority, the electro-oxidation system can be operated at different current densities to maximize the depletion rate of the target species. On one hand, if only TOC is to be oxidized then operation near the limiting current density for the initial COD concentration is recommended. On the other hand, if ammonia is the target pollutant then operation at current densities that exceed the $j_{\text{lim,COD}}$ is advised. However, these suggestions should be viewed with care since by-product formation is also affected by current density. Nitrate formation is enhanced at higher current densities although the presence of high chloride concentrations in the wastewater may limit its formation. Taking these considerations into account and that the aim of this work was to eliminate first and foremost ammonia and as much TOC as possible, 300 A/m^2 was chosen as the best current density among those studied in this work. This current density was chosen to safeguard efficient ammonia removal at acceptable "N-NO_3^- formed/N-NH_3 removed" ratios and without compromising safety issues (due to "active chlorine" formation).

Finally, energy consumption is directly related to the specific electrical charge and to the cell potential: W (kWh/m^3) = $Q\cdot v$. At 300 A/m^2, the energy consumption necessary to eliminate ammonia from *SI*, *SII* and *SIII* completely was 60 kWh/m^3 (92 kWh/kg N-NH_3), 30.5 kWh/m^3 (145 kWh/kg N-NH_3) and 36 kWh/m^3 (433 kWh/kg N-NH_3), respectively. At this point 58% (389 kWh/kg TOC), 47% (70 kWh/kg TOC) and 41% (157 kWh/kg TOC) TOC reductions were obtained, respectively.

4.1.2. Electro-oxidation of SIV and SV

Electro-oxidation of *SIV* and *SV* was carried out at 1140 and 800 A/m^2, respectively (Table 2). It should be mentioned that although 1140 A/m^2 is much lower than the $j_{\text{lim,COD}}$ calculated for the initial COD concentration of *SIV* (Table 2), higher current densities could not be applied due to limitations of the available power supply.

The results obtained are displayed in Fig. 5 as the variation of TOC and ammonia concentration with the specific electrical charge. It can be observed that electro-oxidation was able to eliminate TOC from such polluted effluents to a high extent (Fig. 5a). However, the charge required was high. In particular, electro-oxidation of *SIV* yielded higher TOC removal efficiencies than *SV*. This is because the lower concentration of TOC in *SV* results in lower mass transfer rates of organic compounds to the BDD surface [5,7].

Regarding ammonia oxidation, ammonia was completely eliminated with around 17% of N-NH_3 eliminated as N-NO_3^- in both cases. Fig. 5b shows that specific electrical charges of up to 19 Ah/L resulted in low ammonia removals from *SIV*; from this point onwards, ammonia removal accelerated. In comparison to *SIV*, oxidation of ammonia calls for lower electrical charges when *SV* is being electro-oxidized. On the basis that ammonia was the pollutant whose elimination was chosen as priority in this work, electro-oxidation may pose an interesting treatment alternative for *SV*. However, its deployment as a single treatment step is constrained due to economical limitations; 420 kWh/m^3 were consumed to achieve 93% of NH_3 oxidation for *SV*. For this reason, the feasibility of applying electro-oxidation as pre-treatment to activated sludge was also assessed in this case by performing respirometry tests.

Respirometry assays provide a good indicator of biodegradability, where the solutions to be analysed are added to endogenously respiring activated sludge [14]. It is based on the measurement of the oxygen uptake rate and it has also been used to assess if a sample is toxic or if it contains any inhibitors. The biomass used in this work was taken from the activated sludge treatment of the waste-management facility. The raw effluent and samples withdrawn from the electrochemical treatment at 16 Ah/L (140 kWh/m^3), 37 Ah/L (340 kWh/m^3) and 87 Ah/L (790 kWh/m^3) were tested. Different behaviours were observed along the electro-oxidation process. At the beginning of the treatment (0–16 Ah/L), an increase in biodegradability was observed. Nevertheless, oxidation between 16 and 37 Ah/L seemed to impart resistance towards biodegradability and for specific electrical charges greater than 37 Ah/L, the wastewater exerted a toxic effect on the biomass. The formation

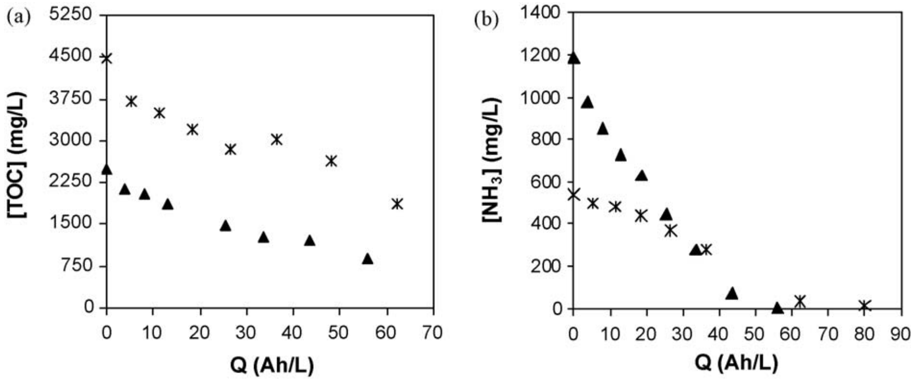

Fig. 5. (a) TOC and (b) NH_3 concentration versus the specific electrical charge during electrochemical oxidation of (✱) *SIV* and (▲) *SV* at lab scale.

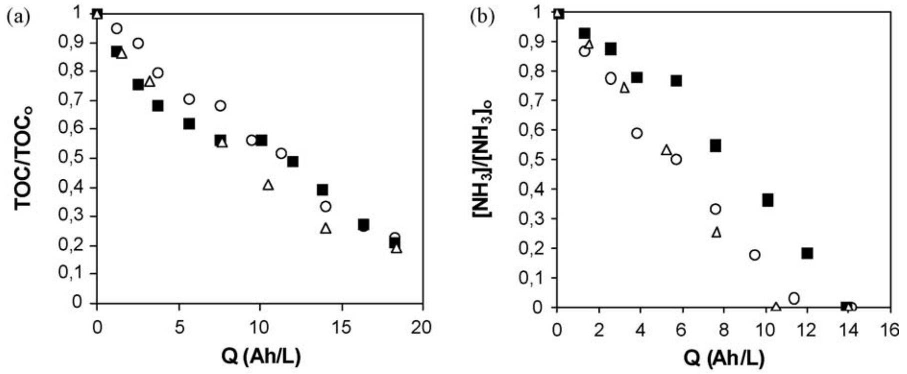

Fig. 6. Evolution of the dimensionless concentration of (a) TOC and (b) NH_3 with specific electrical charge passed during pilot-scale electro-oxidation of *SI* at different influent chloride concentrations ((■) 4550 mg/L, (○) 6400 mg/L). Comparison with data obtained at lab scale (△).

of organo-chlorinated compounds does not seem to be the cause of the appearance of toxicity; the evolution of the concentration of total THMs suggests that these compounds were present in lower concentrations at 87 Ah/L ([T-THM] = 3358 μg/L), when the sample was toxic, than at 37 Ah/L ([T-THM] = 4649 μg/L), when no toxicity was detected. Cañizares et al. [15] and Chatzisymeon et al. [5] also reported a decrease in biodegradability after prolonged electrolysis with BDD anodes of effluents of door manufacturing and olive mill wastewaters, respectively.

4.2. Pilot scale electrolysis test results

From the five wastewaters tested in the laboratory only streams *SI*, *SII* and *SIII* were treated at pilot scale. The rationale behind this decision was that ammonia could be eliminated from these effluents with reasonable energy consumptions (in terms of kWh/m^3). The pilot-scale electro-oxidation unit was operated at 300 A/m^2. As it was pointed out in Section 2, considerable fluctuations in the influent characteristics occurred during pilot testing.

Regarding the treatment of *SI* and *SIII*, the oxidation efficiency of TOC was not affected by fluctuations in the initial characteristics of the effluents. On the contrary, ammonia oxidation was enhanced at higher chloride concentrations and/or lower ammonia loads. This behaviour is exemplified in Fig. 6 in which the variation of treatment efficiency caused by changes in the characteristics of the influent is shown for *SI*. It should be pointed out that although ammonia oxidation was affected by fluctuations in the initial contaminant load, it could be eliminated completely in all cases. In this context, electro-oxidation poses an advantage over biological processes which require excessively long periods of time to restart-up the process in case of an accidental lost of microorganisms caused for example by abrupt changes in the characteristics of the influents [15]. In Fig. 6, the results obtained at pilot scale are also compared with those obtained in the laboratory. In this respect, only slight discrepancies were found for similar initial characteristics of the effluents. This remark is further corroborated by comparison of the specific energy consumption at both scales; e.g. 68 kWh/m^3 (111 kWh/kg N-NH_3) and 60 kWh/m^3 (92 kWh/kg N-NH_3) to achieve complete elimination of ammonia from *SI* at pilot and laboratory scale, respectively.

5. Conclusions

BDD electro-oxidation of five different kinds of bio-refractory saline industrial wastewaters was carried out at laboratory and pilot scale. The initial concentration of pollutants varied in the following ranges: TOC = 266–4479 mg/L; [N-NH_3] = 61–1150 mg/L; [Cl^-] = 1996–37,645 mg/L; conductivity = 5.6–64 mS/cm. The aim of this work was to eliminate first and foremost ammonia and as much TOC as possible. The high concentration of Cl^- in the wastewaters favoured ammonia elimination, enabling the fulfilment of this objective. Consequently, complete elimination of ammonia could be achieved in all cases. The efficiency of ammonia elimination was not significantly affected by changes in current density but it increased at higher concentrations of Cl^-. Moreover, ammonia was mainly converted to nitrogen gas as low conversions of ammonia to nitrate ions were usually obtained. In most cases, the conversion of $N\text{-}NH_3$ to $N\text{-}NO_3$ was in the range 3.3–20%. On the other hand, TOC removals as high as 90% were also achieved although in this case the highest efficiencies were generally obtained at the lowest current density applied for each type of wastewater.

Similar oxidation efficiencies were found at laboratory and pilot scale with specific energy consumptions, to achieve complete elimination of ammonia, ranging from 36 to 106 kWh/m^3 for initial concentrations of pollutants of: TOC = 260–560 mg/L; $[N\text{-}NH_3]$ = 20–700 mg N/L; $[Cl^-]$ = 1996–7216 mg/L. Removal of higher contaminant loads required high energy consumption (in kWh/m^3). In these cases the use of electro-oxidation as a pre-treatment step to activated sludge may pose an interesting alternative as was demonstrated by the increase in biodegradability in the initial stages of BDD electro-oxidation.

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Appendix A

j_{appl}: applied current density (A/m^2)
$j_{lim,COD}$: limiting current density for COD
$j_{lim,Cl}$: limiting current density for Cl^-
F: faraday constant (C/mol)
Q: specific electrical charge (Ah/L)
v: cell potential (V)
W: specific energy consumption (kWh/m^3)

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