



Electrochemical degradation of nitroaromatic wastes in sulfuric acid solutions: Part I

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Abstract

This paper describes the development of electrochemical processes for the oxidative degradation of nitroaromatic compounds, including 2-nitrotoluene, 2-nitroaniline and 4-nitroaniline, in acid wastewaters. The electrolysis process results in the formation of a dark solution in which the concentration of nitroaromatics had been reduced to much lower levels and COD removal efficiencies reached 50%. It was found that the best electrolysis conditions were 96% acid strength, 1000 A m⁻² current density and ambient temperature. In addition, electrochemical degradations were always more effective when substituents are in the *para*-position and lead to significant electrophilic character. A black powdery product was isolated from the dark solution; this resulted from the anodic oxidation of amines initially produced at the cathode. The black product was further destroyed by anodic oxidation during prolonged electrolysis.

1. Introduction

Nitroaromatic compounds are used in numerous industrial processes including the manufacture of explosives, dyes, cosmetics and pharmaceutical products; some of these processes generate acid wastewaters. Moreover, nitroaromatic compounds are obtained by combustion and they have the ability to autogenerate atmospheric photochemical reactions.

According to the literature [1–3], 2-nitroaniline causes chromosomic degeneration and 2-nitrotoluene has a very toxic character. Molecules derived from these systems are also very toxic [4, 5]. In addition, all these kinds of chemical molecule are biorefractory pollutants and cannot be effectively removed from industrial effluents by biological treatment [6–10], a situation that causes high COD strength and colour in wastewater. Therefore, to enhance the efficacy of biological processes, an effective pretreatment process is required in order to destroy the nitroaromatic pollutants.

In recent years, electrochemical oxidation has been shown to be a promising technique for wastewater treatment due to its effectiveness and ease of operation. Electrolysis can be used for partial or total degradation of toxic and refractory organic substances. Many organic compounds in aqueous solution can be anodically

oxidized by direct electron action or by oxygen atom transfer. The oxidation process can lead ultimately to carbon dioxide and water through successive reactions, each of which has several steps, mass transport and direct or indirect adsorption at the electrode surface [11–16].

The work described in this paper involves the use of an electrochemical oxidation process to destroy nitrated organic pollutants namely 4-nitroaniline, 2-nitroaniline and 2-nitrotoluene. The effects of operating factors, such as current density, temperature and concentration of sulfuric acid have been studied. COD tests and UV-visible spectrophotometry profiles have also been obtained in order to evaluate the feasibility of the process for the pretreatment of industrial acid wastewater.

2. Experimental details

2.1. Experimental design

The acid wastewaters investigated in this study were prepared in the laboratory using pure chemicals: 2-nitrotoluene, 2-nitroaniline and 4-nitroaniline (Fluka, Spain) and concentrated sulfuric acid (Panreac, Spain).

Table 1. Experimental design. Levels of the parameters

Parameter	Lower level	Upper level
$T/^\circ\text{C}$	25	40
Current density/ A m^{-2}	500	1000
H_2SO_4 concentration/wt %	50	96

The experimental design employed to study the influence of the main variables was a two level factorial design. Parameters temperature, current density and acid concentration were studied for two levels (Table 1). Therefore, 2^3 experimental combinations were considered for every pollutant compound [17].

2.2. Electrolyses

2.2.1. Electrolytic cell

The experiments were carried out in a 150 ml isothermal batch reactor. The electrolytes to be treated initially contained nitrocompounds at a concentration of 0.015 M. The cell was equipped with a mechanical stirrer (Schott Ibérica, Ika labortechnik, Eurostar) in order to maintain the homogeneous nature of the medium during the electrolyses. The anode consisted of a three-dimensional carbon felt (RVC-4002, Le Carbone Lorraine, France) covered with a protective polyethylene window cover and this unit was connected to an iridium dioxide coated titanium plate as a current conductor, since this material shows a very good resistance to corrosion [18, 19]. The cathode was made up in a similar way, but the aforementioned current conductor was replaced by a graphite plate. Both electrodes had a working surface area of 12 cm^2 and were positioned vertically and parallelly to each other. A Promax model FAC-522B power supply with current-voltage monitor was used.

2.2.2. Electrolytic procedures

COD tests were carried out using standard methods UNE-77-004-89 [20]. The UV-visible spectroscopy profiles were recorded using a Hewlett Packard 8452A spectrophotometer. The UV-visible samples were made up by taking $50\ \mu\text{l}$ of electrolyte at different times during electrolysis experiments. The samples were subsequently diluted to 5 ml.

The solutions for experimental conditions of 1000 A m^{-2} , $25\ ^\circ\text{C}$ and H_2SO_4 , were diluted with water ($\sim 500\text{ ml}$) and treated with NH_3 to increase the pH to 7.5. The resultant precipitate was filtered off and the filtrate extracted with ether. The extracts were dried using MgSO_4 and the ether evaporated. The residue was analysed by GC-MS and thin layer chromatography. The dark precipitate was washed with water, methanol and ether and dried in an oven at $90\ ^\circ\text{C}$. The precipitate was characterized by IR spectroscopy and microanalyses studies.

2.3. Analyses

Both qualitative and quantitative identification of the oxidation products of the electrolytic solutions were performed using a Hewlett Packard GC-MS analyser with a 5890 gas chromatograph and a 5988A mass spectrometer. The products were separated on a polyethyleneglycol column. The isothermal conditions were $3\ ^\circ\text{C min}^{-1}$ to $180\ ^\circ\text{C}$ and $30\ ^\circ\text{C min}^{-1}$ to $230\ ^\circ\text{C}$, initial temperature of $45\ ^\circ\text{C}$ and initial time of 2 min. The injector temperature was $220\ ^\circ\text{C}$ and the oven and diode array detector temperatures were both 245. The extracts were also separated by thin layer chromatography on $1.5\text{ cm} \times 4.5\text{ cm}$ silica gel plates (Macherey-Nagel, Spain) using acetone-hexane mixtures (1:1, 1:2 and 2:1 (v/v)) as mobile phases.

The IR spectra were recorded on an FTIR model Spectrum 2000 (Perkin Elmer, Spain) using a KBr discs. The UV-visible spectra were recorder on a Hewlett Packard 8452A spectrophotometer. Microanalyses were performed by the Microanalysis Department at the Organic Chemistry Institute, CSIC, Madrid, Spain.

3. Results and discussion

3.1. COD removal

Each experiment was denoted a code based on the name of the appropriate organic molecules (2-nitrotoluene-ONT-, 2-nitroaniline-ONA-, and 4-nitroaniline-PNA-) plus an arbitrary number between 1 and 8 as illustrated below in Table 2. To optimize the electrolysis conditions, studies were carried out on solutions of ONT, ONA and PNA in 96% and 50% sulfuric acid. The concentrations of the solutions were 0.015 M, which is close to the usual values in acid wastewaters.

To investigate the effects of temperature, current density and acid strength, the COD removal efficiencies of refractory pollutants in electrolysis were compared. Figures 1 and 2 show the results for 2-nitroaniline and 4-nitroaniline at current densities of 500 A m^{-2} and 1000 A m^{-2} , respectively. Acid strength and current density did not have a significant effect on the destruction of nitroanilines, although better results were found

Table 2. Typical experimental conditions for 4-nitrotoluene

Experiment	Temperature $^\circ\text{C}$	Acid concentration /%	Current density A m^{-2}
ONT1	40	50	500
ONT2	25	50	500
ONT3	40	96	500
ONT4	25	96	500
ONT5	40	50	1000
ONT6	25	50	1000
ONT7	40	96	1000
ONT8	25	96	1000

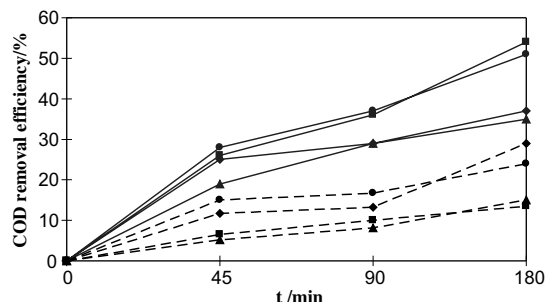


Fig. 1. Electrolysis results for 2-nitroaniline (broken line) and 4-nitroaniline (continuous line) with $i = 500 \text{ A m}^{-2}$: PNA1 and ONA1 (40 °C, 50% acid concentration, \blacklozenge); PNA2 and ONA2 (25 °C, 50% acid concentration, \blacksquare); PNA3 and ONA3 (40 °C, 96% acid concentration, \blacktriangle) and PNA4 and ONA4 (25 °C, 96% acid concentration, \bullet).

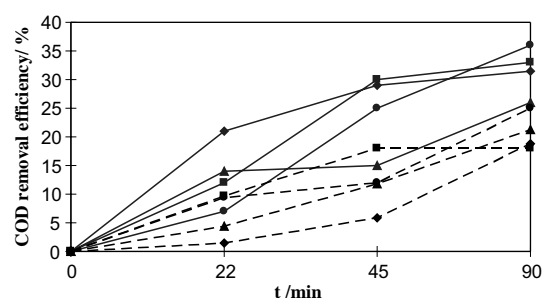


Fig. 2. Electrolysis results for 2-nitroaniline (broken line) and 4-nitroaniline (continuous line) with $i = 1000 \text{ A m}^{-2}$: PNA5 and ONA5 (40 °C, 50% acid concentration, \blacklozenge); PNA6 and ONA6 (25 °C, 50% acid concentration, \blacksquare); PNA7 and ONA7 (40 °C, 96% acid concentration, \blacktriangle) and PNA8 and ONA8 (25 °C, 96% acid concentration, \bullet).

at ambient temperature than at 40 °C, as compared to the results reported by Gedye et al. [12]. Moreover, the best COD removal efficiencies were obtained in the PNA4 nitroaniline electrolysis experiment (with 96% acid strength and 25 °C, as well as PNA2 experiment with 50% acid strength and at 40 °C, Figure 1) and experiment PNA8 (with 96% acid strength, 25 °C and $i = 1000 \text{ A m}^{-2}$, Figure 2). Overall, we found that electrolytic degradation was always more effective when the amine group was in the *para*-position.

Similar results were obtained in studies involving 2-nitrotoluene. Again, electrolytic reactions at 25 °C and with 96% concentrated sulfuric acid showed good efficiency (Figures 3–6). Figures 3 and 4 show that the worst experimental condition were 25 °C and 50% sulfuric acid when the amine and methyl group are situated in the *ortho*-position of the aromatic ring with respect to the nitro group. On the other hand, COD removal efficiency increased to the highest values in the presence of a methyl group. As a consequence, substituents that give rise to electron donor character are beneficial to the electrochemical degradation of nitroaromatic compounds. On comparing the results for 2-nitrotoluene and 4-nitroaniline (Figures 5 and 6), we observed similar COD removal efficiencies for both compounds, except in the cases of experiments PNA2

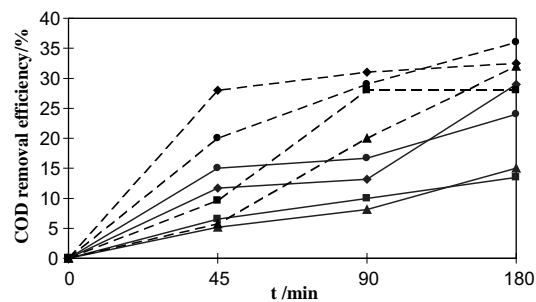


Fig. 3. Electrolysis results for 2-nitroaniline (continuous line) and 2-nitrotoluene (broken line) with $i = 500 \text{ A m}^{-2}$: ONT1 and ONA1 (40 °C, 50% acid concentration, \blacklozenge); ONT2 and ONA2 (25 °C, 50% acid concentration, \blacksquare); ONT3 and ONA3 (40 °C, 96% acid concentration, \blacktriangle) and ONT4 and ONA4 (25 °C, 96% acid concentration, \bullet).

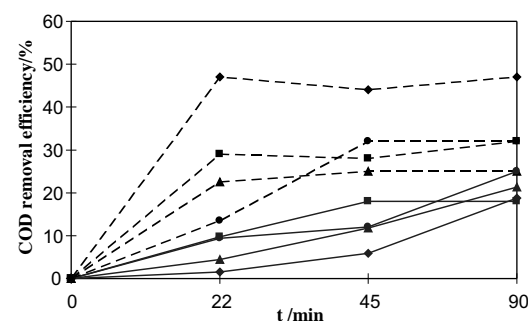


Fig. 4. Electrolysis results for 2-nitroaniline (continuous line) and 2-nitrotoluene (broken line) with $i = 1000 \text{ A m}^{-2}$: ONT5 and ONA5 (40 °C, 50% acid concentration, \blacklozenge); ONT6 and ONA6 (25 °C, 50% acid concentration, \blacksquare); ONT7 and ONA7 (40 °C, 96% acid concentration, \blacktriangle) and ONT8 and ONA8 (25 °C, 96% acid concentration, \bullet).

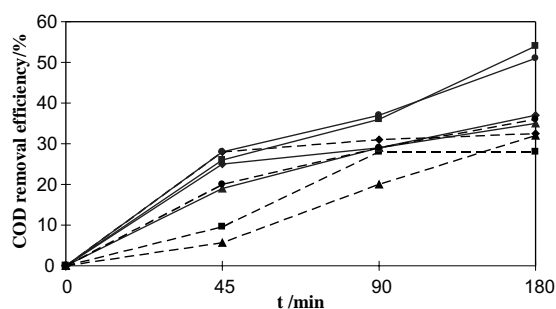


Fig. 5. Electrolysis results for 2-nitrotoluene (broken line) and 4-nitroaniline (continuous line) with $i = 500 \text{ A m}^{-2}$: PNA1 and ONT1 (40 °C, 50% acid concentration, \blacklozenge); PNA2 and ONT2 (25 °C, 50% acid concentration, \blacksquare); PNA3 and ONT3 (40 °C, 96% acid concentration, \blacktriangle) and PNA4 and ONT4 (25 °C, 96% acid concentration, \bullet).

and PNA4 (Figure 5) and experiment ONA5 (Figure 6), where the results were better.

Figure 7 illustrates the variation in the COD removal from experiments PNA4 and PNA2, a comparison that represents a doubling of the electrolysis time. These two reactions, which led to the best efficiencies of the 4-nitroaniline electrolyses in the first study, reached a COD removal efficiency around 50%, although they did

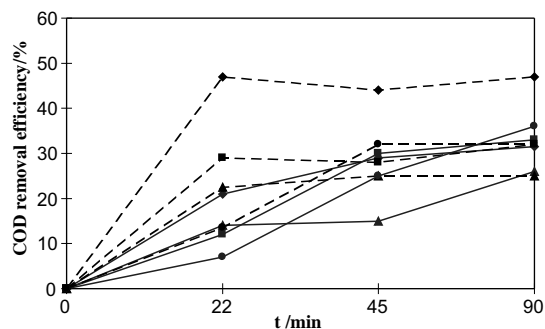


Fig. 6. Electrolysis results for 2-nitroaniline (broken line) and 4-nitroaniline (continuous line) with $i = 1000 \text{ A m}^{-2}$: PNA5 and ONT5 (40 °C, 50% acid concentration, \blacklozenge); PNA6 and ONT6 (25 °C, 50% acid concentration, \blacksquare); PNA7 and ONT7 (40 °C, 96% acid concentration, \blacktriangle) and PNA8 and ONT8 (25 °C, 96% acid concentration, \bullet).

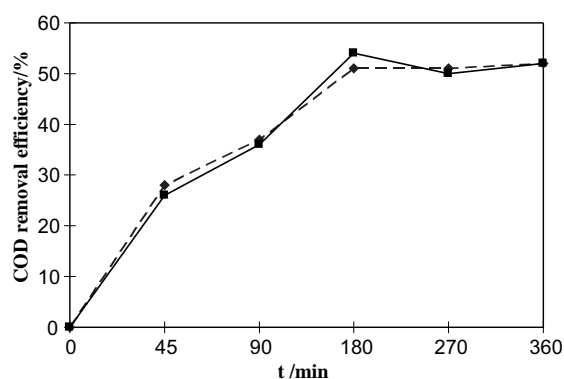


Fig. 7. Double time electrolysis results for PNA4 (broken line, \blacklozenge) and PNA2 (continuous line, \blacksquare). Experiment PNA4 with $i = 500 \text{ A m}^{-2}$, 96% acid concentration and 25 °C. Experiment PNA2 with $i = 500 \text{ A m}^{-2}$, 50% acid concentration and 25 °C.

not continue to give a progressive increase in efficiency after this point. In contrast, doubling the electrolysis time for 2-nitrotoluene gave rise to a constant increase in COD removal (Figure 8). Experiment ONT5 did not lead to a smooth increase in efficiency due degradation

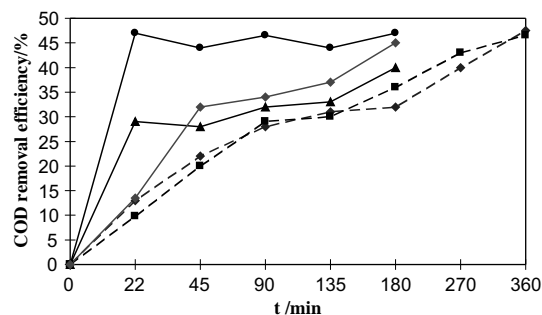


Fig. 8. Double time electrolysis results for ONT1 (broken line, \blacklozenge), ONT4 (broken line, \blacksquare), ONT5 (continuous line, \bullet), ONT6 (continuous line, \blacktriangle) and ONT8 (continuous line, \blacklozenge) experiments. Experiment ONT1 with $i = 500 \text{ A m}^{-2}$, 50% acid concentration and 40 °C. Experiment ONT4 with $i = 500 \text{ A m}^{-2}$, 96% acid concentration and 25 °C. Experiment ONT5 with $i = 1000 \text{ A m}^{-2}$, 50% acid concentration and 40 °C. Experiment ONT8 with $i = 1000 \text{ A m}^{-2}$, 96% acid concentration and 25 °C.

evolution oxygen in 50% acid. It was also found that the rate of the electrolysis increased with increasing current density. In the case of 2-nitrotoluene, it was decided not to carry out double time electrolysis because the COD removal efficiency was the worst found in the initial study.

3.2. Nitroaromatic degradation pathway

Electrolysis of solutions of nitroaromatic compounds in concentrated sulfuric acid resulted in the formation of dark brown or black solutions. In all experiments it was possible to isolate a black powdery product from the dark electrolysed solution by neutralization with NH_3 followed by filtration. These products were found to have similar characteristics to a compound previously isolated by Gedye et al. [12] in the electrolysis of 2,4-dinitrotoluene in concentrated sulfuric acid. The compounds showed good thermal stability and did not melt below 300 °C. They were insoluble in organic solvents at ambient temperature, but sparingly soluble in concentrated H_2SO_4 and HCl . Microanalyses confirmed the presence of C, N, H, O and S.

The chemical structure of the black material has yet to be confirmed by organic synthesis experiments, although IR spectra show a similar profile to that found for the copolymer formed between aniline and metanilic acid [21]. Given this fact, along with the characteristics of the black products discussed above, it was initially supposed that a kind of black amorphous polyaniline might be formed during the electrolysis *via* cathodic reduction to an amine, followed by anodic oxidation. The GC-MS analyses confirmed this degradation pathway. We detected the presence of 2-methylquinoxaline (retention time 41.98 min and abundance 430 000), 2,3-dimethylquinoxaline (retention time 45.5 min and abundance 200 000) and quinoxaline (retention time 39.79 min and abundance 250 000) products of polyaniline degradation [22] and, we believe that the polymerization of 4-aminoaromatic molecules is significant. Initial nitroaromatic compounds were not detected except in the case of 2-nitroaniline which gave the worst COD removal efficiency.

The data for the UV-visible spectra in concentrated sulfuric acid are shown in Table 3. The data were obtained for experiments ONT8, ONA8 and PNA5 as representative examples. The UV-visible spectra of 4-nitroaniline were only obtained from samples in 50% sulfuric acid as the absorbance values obtained at 96% concentration were not representative. It is thought that the high auxochromic effect of sulfonate is responsible for this phenomenon [23].

The 2-nitrotoluene degradation spectra are dominated by two broad absorption bands at 344 nm (peak 1) and 655 nm (peak 2). According to the general practice of peak assignment, peak 1 was attributed to the π - π^* transition of the $\text{C}_{\text{arom}}\text{-NO}_2$ bond in a planar molecule [24]. Peak 2 was assigned to a benzenoid-quinoid transition in the emeraldine form (middle oxidation

Table 3. UV-visible spectra data of representative electrolytic reactions

ONT8*			ONA8*		PNA5†	
<i>t</i> /min	λ /nm	A	λ /nm	A	λ /nm	A
0	344	0.450	219	0.750	258	0.107
	656	0.060	281	1.000	328	0.080
22	344	0.530	218	0.430	256	0.162
	656	0.240	272	0.560	338	0.299
45	344	0.270	218	0.320	256	0.155
	656	0.140	272	0.400	338	0.316
90	344	0.230	216	0.370	256	0.149
	656	0.180	252	0.340	336	0.286
180	344	0.180				
	656	0.240				

Samples were taken at different times (*t*) during electrolyses; wavelength (λ); absorbance (*A*).

* 96% H₂SO₄ as sample solvent.

† 50% H₂SO₄ as sample solvent.

state) of 2-aminotoluene [23, 25, 26]. A decrease in the absorbance of peak 1 from 0.450 to 0.180 and simultaneous increase in the absorbance of peak 2 from 0.060 to 0.240 was observed, thus confirming the initial reduction of the nitro group to an amine followed by oxidation of this amine.

The 2-nitroaniline and 4-nitroaniline degradation spectra followed a similar trend. An absorption band at 281–252 nm, attributed to C_{arom}-NH₂, was detected. However, this band increased its absorbance when 4-nitroaniline was degraded, a fact related to the auxochromic effect of sulfuric acid on the amine group, but decreased during electrolysis to 0.340 and 0.286 for 2-nitroaniline and 4-nitroaniline, respectively. A peak at 338 nm was found in the spectra for the degradation of 4-nitroaniline while for 2-nitroaniline a band was observed at 219–216 nm, due to torsion in the molecule.

4. Conclusion

Electrochemical oxidation gave good efficiency values for the destruction of nitroaromatic pollutants. The COD of 2-nitrotoluene, 2-nitroaniline and 4-nitroaniline can be decreased significantly by an electrochemical oxidation process. It was found that increases in the current density and acid concentration decreased the COD. On the other hand, molecules with an amino group in the *ortho*-position gave rise to poorer electrochemical behaviour. 2-Nitrotoluene showed the best COD removal efficiency in the series studied.

The UV-visible spectroscopy studies and GC-MS analysis demonstrated that electrolyses of nitroaromatic compounds in concentrated H₂SO₄ led to reduction of the three initial compounds to give the corresponding amine, which was then oxidized at the anode to give a high molecular weight, black product containing C, N, O and S. Thus, electrochemical oxidation is a promising process for the pretreatment of refractory pollutants such as nitroaromatic compounds.

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