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Electrochemical degradation of C. I. Acid Orange 7

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Abstract

The electrochemical oxidation of C. I. Acid Orange 7 (AO7) was performed on a boron doped diamond electrode (BDD). Bulk electrolysis was studied using two different supporting electrolytes—KCl and Na_2SO_4. The influence of electrolyte concentration, initial dye concentration and current density on the degradation rates was investigated. Samples were collected at pre-selected intervals and absorbance measurements and chemical oxygen demand (*COD*) tests were performed, to compare the rates of colour and *COD* removal in each case. From the *COD* measurements over the time of electrolysis mass transfer coefficients were determined, and the current efficiency was estimated using a theoretical model. Results have shown an almost complete colour removal and *COD* removal, higher than 90%. A preliminary electro degradation study of an effluent from an UASB reactor, used on the biodegradation of a textile wastewater containing AO7, was also performed with colour and *COD* removals of 98% and 77%, respectively.

Keywords: Acid Orange 7; Electrochemical degradation; Diamond electrodes; Wastewater treatment; Dyeing house effluent

1. Introduction

Azo dyes form the largest group among the synthetic colorants (60–70%) [1]. Their chromophoric system consists of azo groups (–N=N–) in association with aromatic systems and auxochromes (–OH, $-SO_3$, etc.). It was estimated that about 50,000 tons of dye are discharged from dyeing and colouration industries every year [2]. Currently, the textile dyeing industry is under considerable pressure to reduce the colour in effluents discharged to municipal wastewater treatment plants or, in case of on-site treatment plants, directly to water courses.

Although the biological degradation for organic pollutants is the most economic process, the response of the various types of dyes towards biodegradation is not consistent. Depending on its solubility and bio elimination characteristics, dyes may be precipitated in the clarifier (coagulation/flocculation tank), biodegraded, retained in the biomass or overcome to all these processes, giving an unwanted colour to the final effluent. In such cases, colour has to be removed by tertiary treatments. Furthermore, even when decolourisation occurs by azo dye reduction in anaerobic environments, the resulting aromatic amines, that could be mutagenic and carcinogenic, should be mineralised in a post-treatment unit [3,4]. Several wastewater treatment technologies have been applied to colour removal, including physical,

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chemical and biological. All of them have advantages and drawbacks and a combination of different technologies is generally required.

The application of electrochemical techniques as a tertiary treatment to eliminate colour has received great attention in the last years [5–8]. These techniques use the electron as the main reagent, but also require the presence of supporting electrolytes. In general, the latter exist in the wastewaters to be treated, but not always in sufficient concentrations. These processes can operate at ambient temperature, without the need of temperature control.

Decolourisation can be achieved either by electro-oxidation with non-soluble anodes or by electrocoagulation using consumable materials. The degradation products in the oxidation of azo dyes are typically carbon dioxide, nitrate and sulphate, with the possible formation of aromatic esters, phenols, aromatic carboxilic acids, cyclic and aliphatic hydrocarbons, etc., as intermediates. Usually, the oxidation of the azo group occurs, followed by the oxidation of the decomposition products [7].

The oxidation rate depends, among other variables, on the material of the anode. Different anodes have been successfully used in the electrodegradation of hazardous compounds [9–15]. For industrial applications, materials like noble metals or dimensionally stable anodes are required to obtain suitable oxidation rates. Diamond is another choice, specially since it is possible to prepare anodes with a relatively large area [16]. Boron doped diamond (BDD) electrodes have demonstrated very good chemical, mechanical and thermal resistance, wide electrochemical potential window in aqueous solutions, very low voltammetric background current, high resistance to deactivation via fouling, extreme electrochemical stability and no significant corrosion even under high current densities. These properties of the BDD electrodes meet the requirements for their use as anodes in the electrochemical degradation of organic pollutants [16].

The aim of this work is the study of the electrochemical degradation as a polishing technology of a monoazo dye (AO7), using a commercially available boron doped diamond electrode (BDD-DiaChem®) as the anode. AO7 was chosen because, being a simple molecule, it is very useful as test and it is widely used in paperboard industries, for coloration, and in wool textile dyeing. The effect of the operating conditions, namely the time of electrolysis, the current density and especially the type of supporting electrolyte used were investigated, to maximize the rates of colour and *COD* (chemical oxygen demand) removal.

The electrochemical oxidation of an effluent arisen from an Upflow Anaerobic Sludge Blanket (UASB) reactor feeding with a basal medium, in which glucose was used as carbon source, and supplemented with AO7 (60 mg/L) was also performed in order to investigate if the resulting anaerobic dye metabolites could eventually be degraded in a sequential electrochemical pos-treatment.

A theoretical model developed by Panizza et al. [17], and already tested with several organic pollutants, was used to estimate the current efficiency during the time of electrolysis, using a BDD anode. Efficiency is a very important issue in this kind of treatment, due to the relatively high costs of the electric power. In BDD electrodes the current efficiency is mainly determined by the occurrence of mass transport limitations of the components from the bulk of the solution to the electrode surface; these are expected to be present in the case of large molecules being processed (due to their low diffusivities) or chemical species in low concentrations. The latter is usually the case of dyes, that are generally found in very low concentrations in industrial effluents (i.e., concentrations of ppm). According to the previously cited model, under mass transport control, organic compounds are completely mineralised, but secondary reactions (oxygen evolution, electrolyte decomposition, etc.) can take place, resulting in a loss of current efficiency and leading to a decreasing of the removal yield. In this case, the rate of oxidation of the organic species can be followed by the decrease of the *COD*, that can be given by the following equation:

$$\frac{\partial COD}{\partial t} = -\frac{A\, k_{\mathrm{m}} COD}{V} \tag{1}$$

where *COD* is the chemical oxygen demand ($\mathrm{mg_{O_2}/L}$), t is the time (s), A is the electrode area (m^2), V is the volume of the solution (m^3) and k_m is the mass transfer coefficient (m s^{-1}). Integration of this equation from $t = 0$ and initial *COD* (COD_i) to t and *COD* leads to the following equation:

$$COD = COD_i \exp\left(-\frac{A\,k_m}{V}t\right) \tag{2}$$

If the applied current density is higher than a certain limit current density, j_{lim}, defined as [17]:

$$j_{\mathrm{lim}} = (1/8)\,F\,k_m\,COD \tag{3}$$

the electrochemical process is controlled by mass transport, F being the Faraday constant. In this case, the Instantaneous Current Efficiency (*ICE*) will be given by [17]:

$$ICE = \frac{j_{\mathrm{lim}}}{j_{\mathrm{exp}}} \tag{4}$$

where j_{exp} is the applied current density. Otherwise, i.e., if the applied current density is lower than the limit one, *ICE* will be 1.

2. Experimental

Electrochemical experiments were conducted at 25 °C in a conventional three-electrode cell, with a working volume of 0.25 L, equipped with an external water-jacket to keep constant temperature. The bulk electrolysis were performed in galvanostatic mode, using a computer controlled Potentiostat-Galvanostat Tacussel, model PJT 35-2.

A boron doped diamond electrode (BDD-DiaChem®), with an immersed area of 10 cm^2, was used as anode and a copper foil (40 cm^2) as cathode.

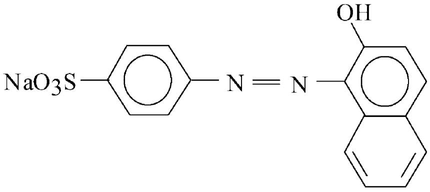
Fig. 1. C. I. Acid Orange 7 structure.

The reagent C. I. Acid Orange 7 (Fig. 1), P.A., +85%, from Aldrich, was used without further purification. A stock aqueous solution of 800 mg AO7/L was prepared, being all the other solutions obtained by an appropriate dilution with the electrolyte solution. Two different electrolytes were tested: sodium sulphate (Merck, PA, +99.5%), and potassium chloride (Merck, PA, +99.5%). The former was selected to be studied because it is usually present in the dyeing baths, and the later due to its ability of producing chlorine and hypochlorite during electrolysis.

The electro-oxidation of AO7 was investigated for each electrolyte type and concentration (Na_2SO_4 with concentrations ranging from 0.01 to 0.035 M and KCl in concentrations of 0.07 and 0.1 M), for several initial dye concentrations (20–360 mg L^{-1}) and for different current densities (1.25–10 mA cm^{-2}). Because the electrochemical degradation should also be considered as an alternative treatment of partial residual dyebath streams, all the essays were conducted in duplicate in the pH range of 3.5–5, analogous to the pH of dyeing baths. Furthermore, preliminary tests had shown little influence of the pH on the electrochemical degradation rate.

During the degradation tests, dye concentration was determined by spectrophotometry at 482 nm, according to Lambert–Beer law, using a Perkin-Elmer Lambda 6 UV/VIS spectrophotometer. A dye free cell was used as control.

Chemical Oxygen Demand tests were also made, according to Standard Methods [18].

3. Results and discussion

3.1. Study of the possible degradation of the supporting electrolytes

The possibility of electrolyte degradation was first investigated, performing the electrolysis of solutions of KCl without the addition of the dye. The expected KCl degradation during electrolysis was confirmed following the OCl^- presence by UV-Visible spectrophotometry as shown in Fig. 2. As it can be seen, there is a maximum, at 292 nm,

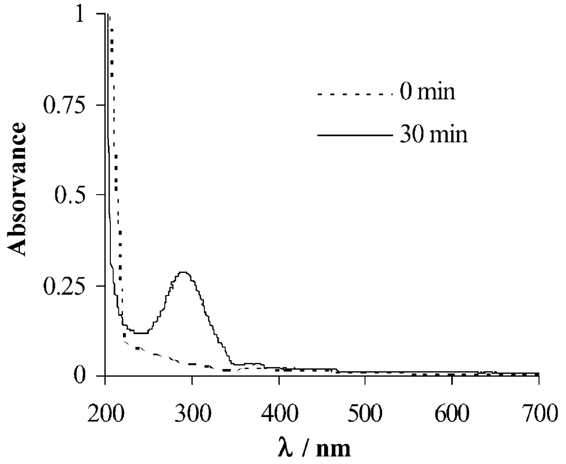

Fig. 2. UV–visible spectra of a 0.1 M KCl solution submitted to a current density of 5 mA cm^{-2} at $t=0$ and $t=30$ min.

that corresponds to OCl^{-} [17]. According to these authors the electrolysis mechanism is as follows:

Anode: $2\ Cl^{-} \rightarrow Cl_2 + 2\ e^{-}$
Cathode: $2\ e^{-} + 2\ H_2O \rightarrow 2\ HO^{-} + H_2$
Overall: $2\ HO^{-} + Cl_2 \rightarrow Cl^{-} + OCl^{-} + 2\ H_2O$

Accordingly, when the electrolyte was KCl, all the UV–visible measurements were made against a KCl degraded solution, instead of deionised water. The same procedure was followed for Na_2SO_4 solutions, but no degradation was observed.

3.2. Effect of the electrolyte type and concentration

The influence of sodium sulphate concentration on the AO7 degradation rate was tested for three different solutions (0.01, 0.02 and 0.035 M), with an initial dye concentration of 60 mg L^{-1} and a current density of 5 mA cm^{-2} (see Fig. 3). Using Na_2SO_4 as electrolyte, it seems that for concentrations higher than 0.02 M, there is no influence of the electrolyte concentration on the rate of colour removal. For lower concentrations, there is a decrease of that rate, probably because there are not enough ions to conduct the current. Thus it may be concluded that the increasing of the electric resistance of the solution affects negatively the efficiency of the process.

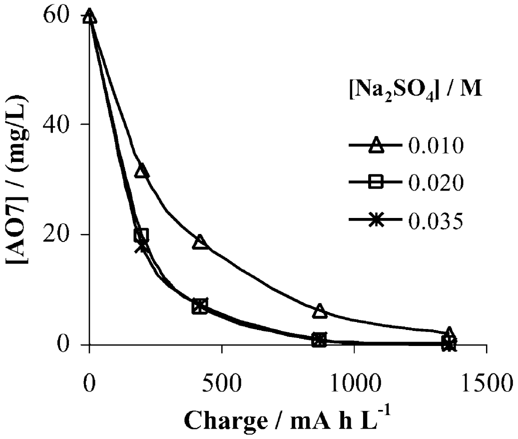

Fig. 3. Influence of the electrolyte concentration on the rate of degradation of AO7 at a current density of 5 mA cm^{-2}, using Na_2SO_4 as electrolyte and an initial dye concentration of 60 mg L^{-1}.

In the case of KCl, two different concentrations were also used (0.07 and 0.1 M), for an initial dye concentration of 20 mg L^{-1} and a current density of 5 mA cm^{-2}. The results obtained are presented in Fig. 4. When KCl was used, the electrolyte concentration seems not to alter the rate of dye degradation, in the range of concentration tested. So it may be concluded that, for KCl, the concentrations to be used in practice can probably be decreased.

In Fig. 5, results obtained with both electrolytes, at an initial dye concentration of 20 mg L^{-1} and a current density of 5 mA cm^{-2}, are presented. It may be concluded that, in general, the AO7 degradation is faster when KCl is used as electrolyte. However, the use of KCl involves the possibility of the formation of organochloride compounds, mainly due to the OCl^{-} presence, as a possible side reaction. In that case, the formation of those unwanted compounds can only be prevented if the complete mineralization of the organic compounds is assured, i.e., for high enough times of electrolysis. UV–visible spectra from samples gathered throughout the reaction time seem to indicate an almost complete degradation of dye molecule (Fig. 6), for an initial dye concentration of 40 mg L^{-1}.

The KCl concentrations were higher than those of Na_2SO_4 for two main reasons: first, KCl is a 1:1

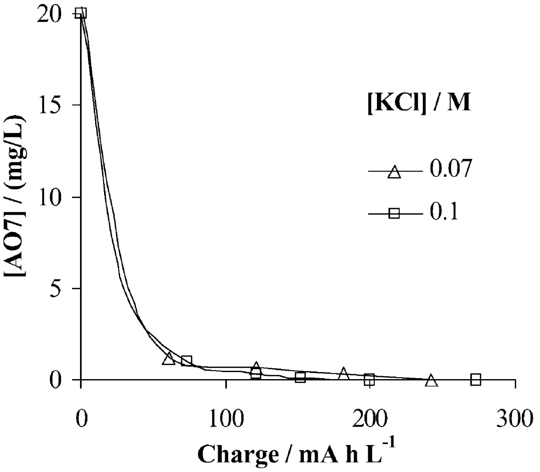

Fig. 4. Influence of the electrolyte concentration on the rate of degradation of AO7 at a current density of 5 mA cm^{-2}, using KCl as electrolyte and an initial dye concentration of 20 mg L^{-1}.

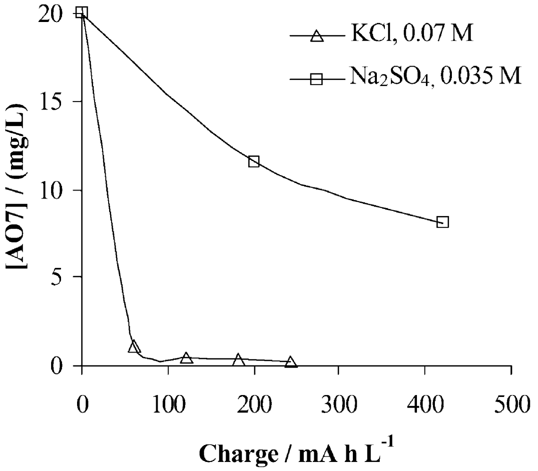

Fig. 5. Influence of the electrolyte, Na_2SO_4 and KCl, on the rate of degradation of AO7: initial dye concentration 20 mg L^{-1}, current density 5 mA cm^{-2}.

electrolyte and needs higher concentration for same number of charges in solution; and second, the purpose of testing KCl was a different one, because the main idea was to use it as electrolyte and, simultaneously, verify the ability of hypochlorite to oxidize the organic compounds, helping the electrochemical degradation, even at very low dye concentrations.

3.3. Effect of AO7 initial concentration

The influence of the initial dye concentration was studied, for concentrations ranging from 20 to 100 mg L^{-1}, in solutions containing as electrolyte Na_2SO_4 (0.035 M) or KCl (0.1 M). These electrolyte concentrations were chosen because it was made clear in previous discussion that they were high enough to guarantee no influence on the degradation rate. Results are presented in Fig. 7 and it may be concluded that the colour removal yield increases with initial dye concentration. This fact strongly suggests that, under these conditions, the rate of degradation of the dye is controlled by mass transfer limitations; in that situation, the AO7 concentration at the interface becomes zero because the electrochemical reaction rate is higher than the diffusion rate, thus making the degradation rate proportional to the bulk concentration. Once again, the charge needed for the electrochemical degradation of a certain amount of dye is lower when KCl is the electrolyte.

The electrochemical degradation of AO7, in Na_2SO_4 0.035 M, was also studied for initial dye concentrations in the range from 150 to 360 mg L^{-1} and a current density of 10 mA cm^{-2}. The results obtained are presented in Fig. 8 and conclusions are similar to those obtained for a lower dye concentration, although, for 360 mg L^{-1}, the beginning of the electrochemical reaction is under kinetic control, since the applied current density is lower than the limit density current for the initial *COD* ($j_{\mathrm{lim}} \cong 13$ mA cm^{-2}).

3.4. Effect of current density

The effect of current density for an AO7 initial concentration of 20 mg L^{-1} was studied using Na_2SO_4 (0.035 M) as electrolyte (Fig. 9). For the studied current densities, it can be seen that the charge needed for an equivalent decrease in concentration increases with current density and the rate of colour removal is almost independent of the current density. This is probably because the oxidation rate is being controlled by the diffusion of AO7 molecules from the bulk to the interface anode/solution and not by the electrons flow rate.

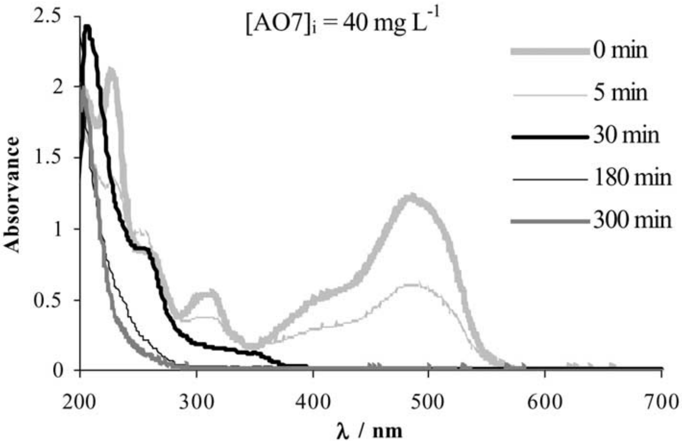

Fig. 6. UV–visible spectra of a 40 mg AO7/L solution in Na_2SO_4 0.035 M, submitted to a current density of 5 mA cm^{-2}, at different times.

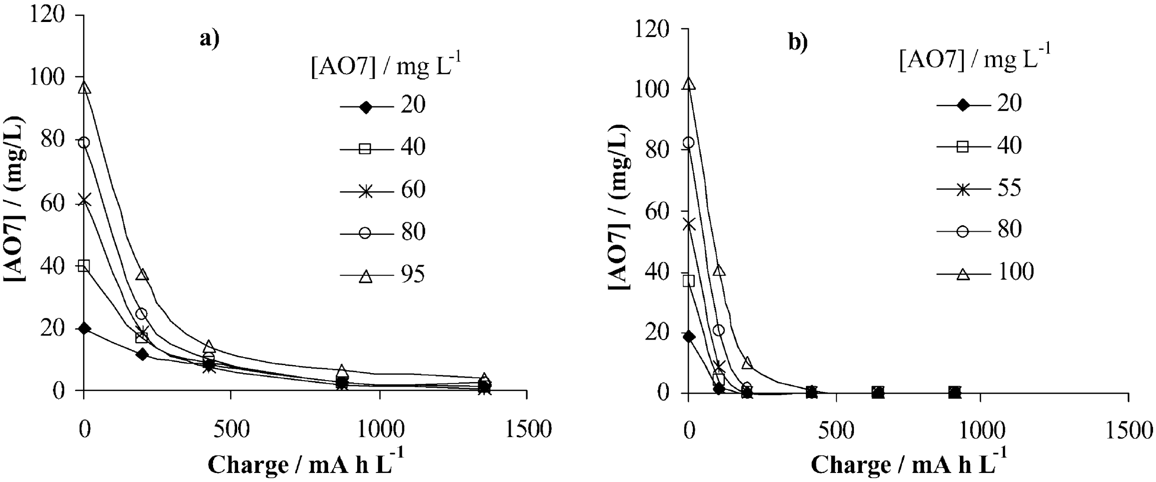

Fig. 7. Influence of the initial dye concentration on the degradation rate of AO7, at a current density of 5 mA cm^{-2} with two different electrolytes: (a) 0.035 M Na_2SO_4; (b) 0.1 M KCl.

3.5. Rate of COD removal and mass transfer coefficients

For initial dye concentrations ranging from 150 to 360 mg L^{-1} degradation tests were conducted at 10 mA cm^{-2} current density and using a 0.035 M Na_2SO_4 solution as supporting electrolyte. The rate of the electrochemical degradation of AO7, besides being followed by Ultraviolet-Visible Spectrophotometry, was also analyzed by COD tests.

Adjusting Eq. (2) to the experimental values of *COD* versus time, for the various essays, an average mass transfer coefficient of 1.46×10^{-5} m s^{-1}, with a standard error of $\pm3\times10^{-7}$ m s^{-1}, was obtained. Experimental results, as well as the fitting curves, are presented in Fig. 10a. In Fig. 10b, the Instantaneous Current Efficiency (*ICE*), calculated as the ratio $j_{\mathrm{lim}}/j_{\mathrm{exp}}$ [Eq. (4)], is presented as a function of time. Except for the beginning of the test with 360 mg L^{-1} initial dye concentration, all the experiments were run under diffusion control conditions. For that particular essay, and during a certain initial period of time, the electrochemical degradation is under kinetic control, thus allowing efficiency to be maximum.

If a comparison between percentage of *COD* removal and percentage of colour removal is made, as in Fig. 11, it can be clearly seen that the rate of *COD* removal is lower than that of colour, suggesting that the cleavage of the azo bond is the first step of the electrochemical degradation mechanism. Only after that, the aromatic rings are prone to be degraded, thus contributing to the continuation of the *COD* removal. A similar degradation mechanism is known that occurs in the biological anaerobic treatment of this type of dye, although, in this case, the cleavage of the azo bond is obtained by a reduction reaction, giving sulphonated aromatic amines, which are very resistant to the biological treatments [3,19].

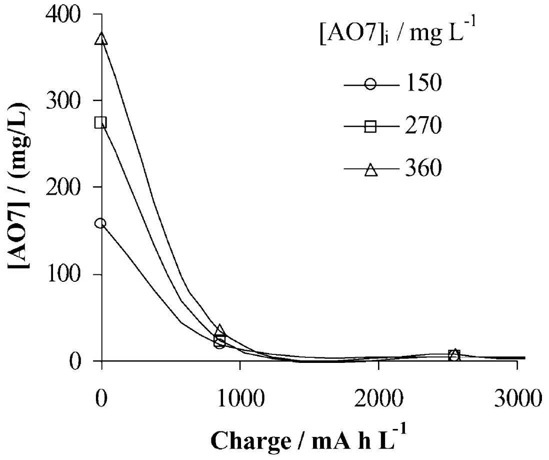

Fig. 8. Influence of the initial dye concentration on the rate of degradation of AO7: 0.035 M Na_2SO_4 as electrolyte; current density 10 mA cm^{-2}.

3.6. *COD and colour removal of an effluent from an UASB reactor*

Preliminary tests on the electrochemical degradation of an effluent arisen from an Upflow Anaerobic Sludge Blanket (UASB) reactor feeding with a basal medium in which glucose was used as carbon source and supplemented with AO7 (60 mg/L) were also carried out. A BDD anode with an immersed area of 15 cm^2 was used in the electrochemical degradation of 275 mL of this effluent, with an applied current density of 6.7 mA cm^{-2} for 10 h. The effluent was previously filtered in glass micro filters (GF/C) for suspended solids removal and no electrolyte was added. Results

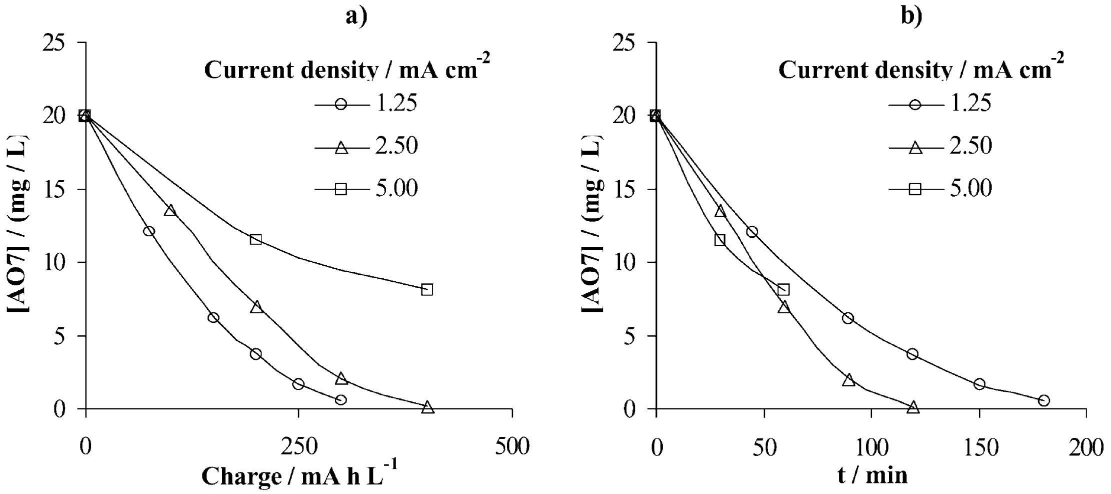

Fig. 9. Variation of AO7 concentration with the charge passed (a) and time of electrolysis (b) during the degradation essay, using 0.035 M Na_2SO_4 as electrolyte and initial dye concentration of 20 mg L^{-1}.

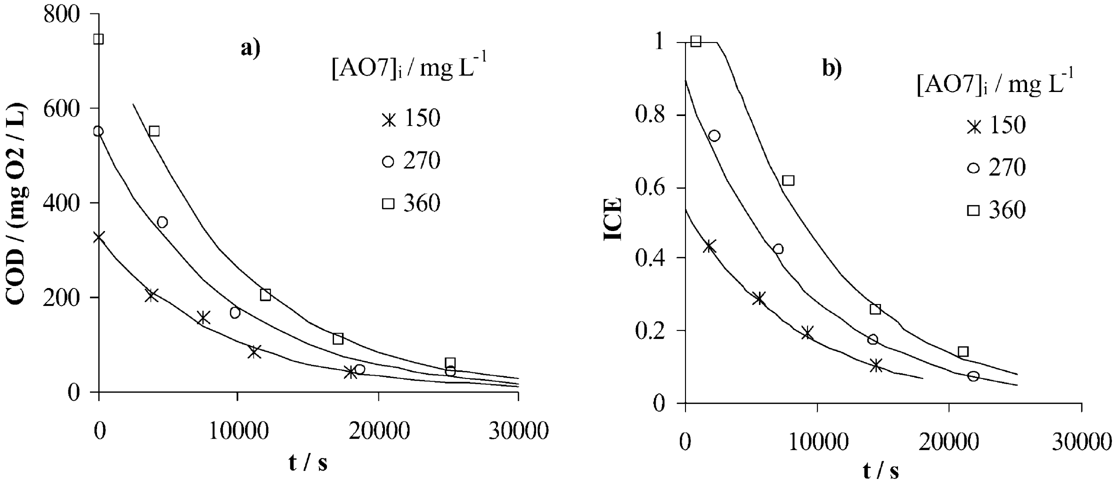

Fig. 10. Variation of *COD* (a) and *ICE* (b) with time for three different initial concentration of AO7, using as electrolyte 0.035 M Na_2SO_4 and 10 mA cm^{-2} current density: (a) symbols: experimental; lines: fitting assuming diffusion control.

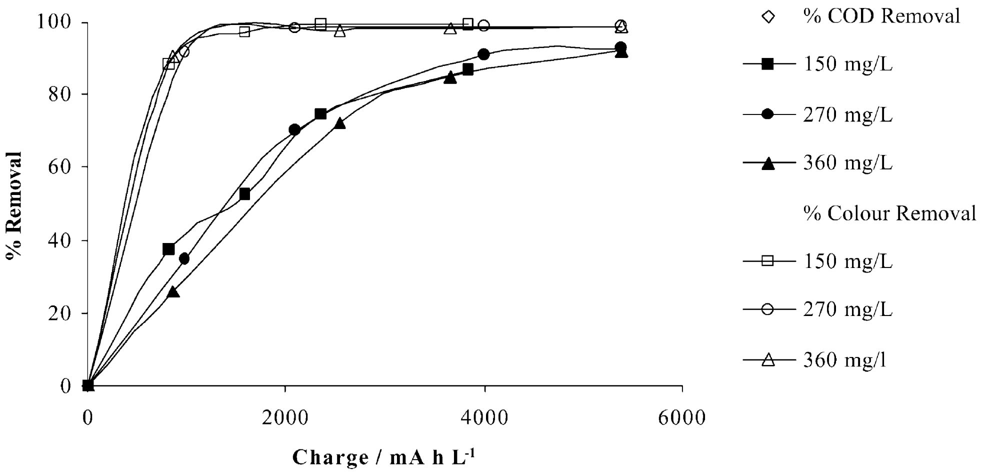

Fig. 11. Comparison between percentage of colour and *COD* removal for the degradation essays performed with different initial dye concentration, at 10 mA cm^{-2} in a 0.035 M Na_2SO_4 electrolyte solution.

indicate (Fig. 12) significant alterations on UV–visible spectra, suggesting that aromatic amines resulting from dye reduction in anaerobic conditions were almost mineralised, along with degradation of residual glucose and biomolecules (cell metabolic compounds) that also contribute to the total *COD*. A *COD* and a color removal rates of 77% and 98% were achieved, respectively. In these essays a dye free run was also studied and used as blank to the spectrophotometry analysis.

4. Conclusions

The electrochemical method, using a BDD anode, has been employed in the present study to mineralize a monoazo dye, AO7. Degradation of the dye was followed by UV–visible spectrophotometry and *COD* determinations. An almost complete colour removal and very high *COD* removal are obtained using this technique. Several aspects, such as type and concentration of the

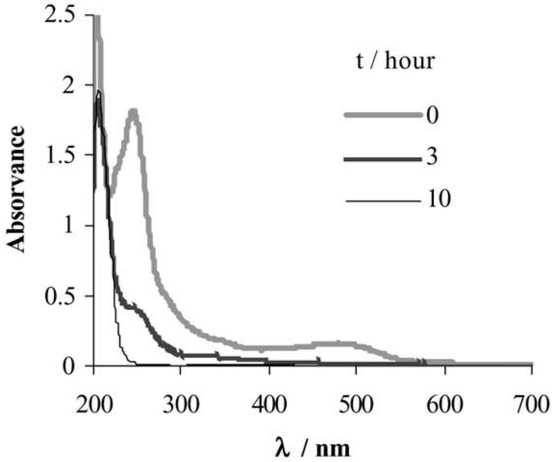

Fig. 12. UV–visible spectra of an effluent from an UASB reactor submitted to electrochemical degradation at 5 mA cm^{-2} current density at different times.

supporting electrolyte, initial dye concentration and current density, were explored.

Tests using KCl as electrolyte gave higher rates of colour removal than those obtained with Na_2SO_4. However, Na_2SO_4 has the advantage of being present usually in the dyeing bath and, on the other hand, it doesn't involve the possibility of formation of organ-chlorinated compounds. It was also identified that mass transfer limitations play a central role on determining the rates of degradation of the dye, but the degradation rates are not independent of the type of electrolyte used.

The electrochemical treatment of an effluent from an UASB reactor, containing AO7, seems to be feasible on aromatic amines degradation, even when present in very low concentrations and using only the electrolyte already present in the effluent. Although some more research is required on this subject, the application of electrochemical oxidation (electrolysis) as polishing treatment could be considered as an alternative process.

Acknowledgements

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