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Electrochemical treatment of the pollutants generated in an ink-manufacturing process

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Abstract

The effluents of ink-manufacturing processes contain a large variety of pollutants such as dyes, surfactants, biocides, water soluble solvents, etc. In this work, the electrochemical oxidation of several dyes (methylene blue and rhodamine B), solvents (monoethylene glycol, diethylene glycol and glycerol) and surfactants (sodium dodecylbenzenesulfonate) has been studied. To carry out the electrolyses, a bench-scale plant with a single-compartment electrochemical flow-cell was used. Boron doped diamond (BDD) was used as anode and stainless steel (AISI 304) as cathode. For all the compounds tested, the conductive diamond electrooxidation allows achieving the almost complete removal of COD of the waste with a very high current efficiency. The efficiencies of the electrochemical processes seem to depend on the current density and on the nature of the anions contained in the waste (chlorine, sulphate, phosphate). Thus, it has been observed that the use of chloride media favours the treatment of dyes. On the contrary, the use of sulphate- or phosphate-containing solutions improves the removal of the aliphatic compounds studied (solvents). These results suggest an important role of the mediated electrochemical processes on the overall performance of the reaction system.

Keywords: Electrochemical oxidation; Conductive diamond; Inks; Surfactant

1. Introduction

Industrial effluents of the ink-manufacturing and paper recycling processes contain a great variety of pollutants (such as dyes, surfactants, biocides, water soluble solvents, etc.), which are highly toxic and persistent [1–5]. This kind of wastewater is generated in large amount [6,7] and, therefore, this involves a serious environmental pollution problem.

In literature, the treatment of these flow streams by conventional technologies, such as adsorption, coagulation, or biological processes, has been studied. However, all these methods present important drawbacks. The mixture of compounds dissatisfies the recovery of the organics, the low calorific power of the waste frustrates the use of incineration, and the non-biodegradability disappoints the biological treatment. Likewise, coagulation generates large amounts of sludge and, in same cases, the removal efficiencies are not enough to achieve the discharge limits (due to the high content in hydro soluble compounds), and hence, other final treatments are also required [3,8]. Under these circumstances the use of advanced oxidation processes (AOP) appears as a very promising answer to solve the environmental problem generated by the discharge of these effluents [9,10]. Recently, it has been demonstrated that hydroxyl radicals are formed during the conductive diamond electrochemical oxidation (CDEO) of aqueous wastes [11], and this has allowed classifying this technology as an AOP. This radical is a very powerful oxidant (E^0 2.80 V versus SHE) which leads to a very effective oxidation process. In addition to this mechanism, the global electrochemical oxidation process with conductive-diamond anodes is known to be complemented by direct electrooxidation on the surface and also mediated oxidation by other oxidants electrogenerated on the surface from the electrolyte salts [12–21]. The combination of these oxidation mechanisms has been shown to increase the current efficiency

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of this technique [22], as compared with other oxidation technologies (such as the ozonation or the Fenton process).

The goal of this work has been to study the electrochemical oxidation with conductive diamond electrodes of typical pollutants contained in the effluents of ink industries. Three kinds of compounds were tested: dyes, solvents and surfactants. In every case it was tried to determine the influence of the current density and the electrolyte support and to clarify the differences observed as a function of the nature of the pollutants.

2. Experimental/materials and methods

2.1. Analytical procedure

The carbon concentration was monitored using a Shimadzu TOC-5050 analyzer. The chemical oxygen demand (COD) was determined using a HACH DR200 analyzer. Measurements of pH and conductivity were carried out with an InoLab WTW pH-meter and a GLP 31 Crison conductimeter, respectively.

The COD method was used for the determination of the current efficiency. In this method, the COD was measured during electrolysis and the instantaneous current efficiency (ICE) was calculated using the relations:

$$\mathrm{ICE} = \frac{[\mathrm{COD}_{t+\Delta t} - \mathrm{COD}_t]FV}{8I\Delta t} \qquad (1)$$

where COD_t and $\mathrm{COD}_{t+\Delta t}$ are the COD (in g O_2 dm^{-3}) at times t and $t + \Delta t$ (in seconds), respectively, I is the current intensity (A), F is the Faraday constant (96487 C mol^{-1}), V is the volume of the electrolyte (dm^3) and 8 is a dimensional factor for unit consistence (32 g O_2 mol^{-1} O_2/4 mol e^{-1} mol^{-1} O_2).

2.2. Conductive diamond electrochemical oxidation

In this work, the CDEO assays were carried out in a single-compartment electrochemical flow-cell working under a batch operation mode. The experimental setup has been described elsewhere [15]. Diamond-based material was used as anode and stainless steel (AISI 304) as cathode. Both electrodes were circular (100 mm diameter) with a geometric area of 78 cm^2 and an electrode gap of 9 mm. The wastewater (0.5 dm^3) was stored in a glass tank and circulated through the electrolytic cell by means of a centrifugal pump (flow rate 2.5 dm^3 min^{-1}). Electrolyses were carried out in galvanostatic mode. During the electrolyses no control of pH was carried out. Boron-doped diamond films were provided by CSEM (Switzerland) and synthesized by the hot filament chemical vapor deposition technique (HF CVD) on single-crystal p-type Si (100) wafers (0.1 Ω cm, Siltronix).

3. Results and discussion

Figs. 1–3 show the changes in the COD and TOC removal during the CDEO of synthetic aqueous wastes polluted with dyes (rhodamine B, methylene blue), solvents (ethylene glycol, glycerol, diethylene glycol) and surfactants (sodium dodecylbenzenesulfonate), respectively. The initial concentrations of pollutants are about the typical values in which these organic

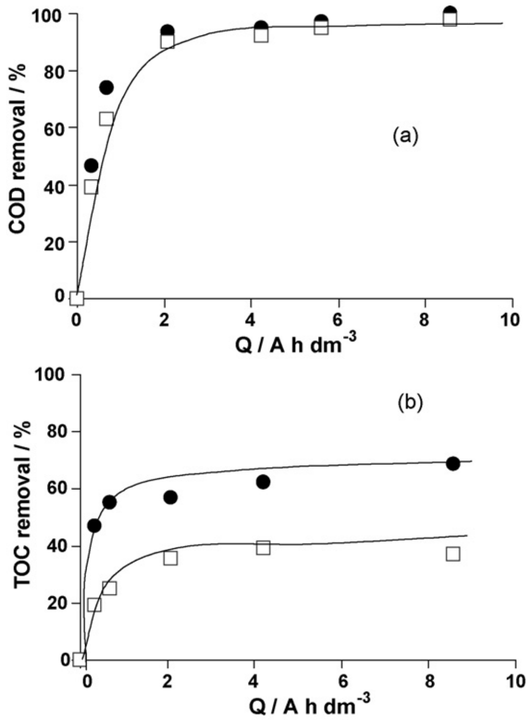

Fig. 1. Percentage of COD and TOC removal as a function of the specific electrical charge passed in the CDEO of dyes. (●) Methylene blue (TOC_0: 33 mg dm^{-3}) and (☐) rhodamine B (TOC_0: 36 mg dm^{-3}). Experimental conditions: COD_0: 100 mg dm^{-3}; T: 25 °C; j: 30 mA cm^{-2}; neutral pH; electrolyte support: 0.1 M NaCl.

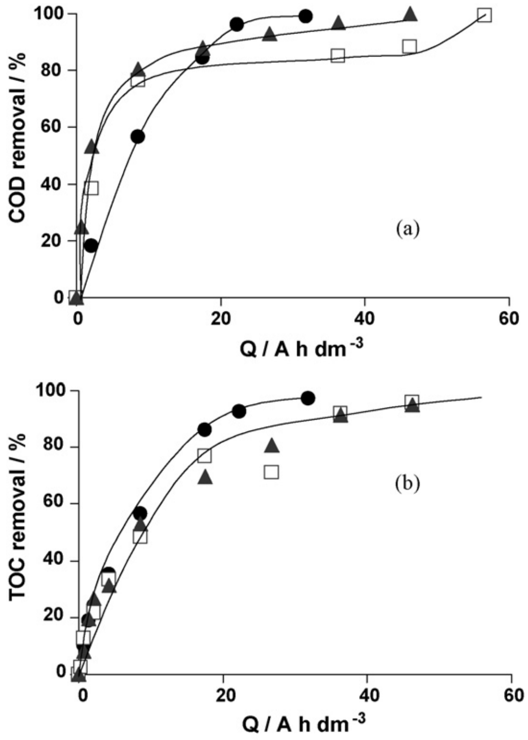

Fig. 2. Percentage of COD and TOC removal as a function of the specific electrical charge passed in the CDEO of solvents. (●) Ethylene glycol (TOC_0: 250 mg dm^{-3}), (▲) glycerol (TOC_0: 240 mg dm^{-3}) and (☐) diethylene glycol (TOC_0: 220 mg dm^{-3}). Experimental conditions: COD_0: 1000 mg dm^{-3}; T: 25 °C; j: 30 mA cm^{-2}; neutral pH; electrolyte support: 0.1 M NaCl.

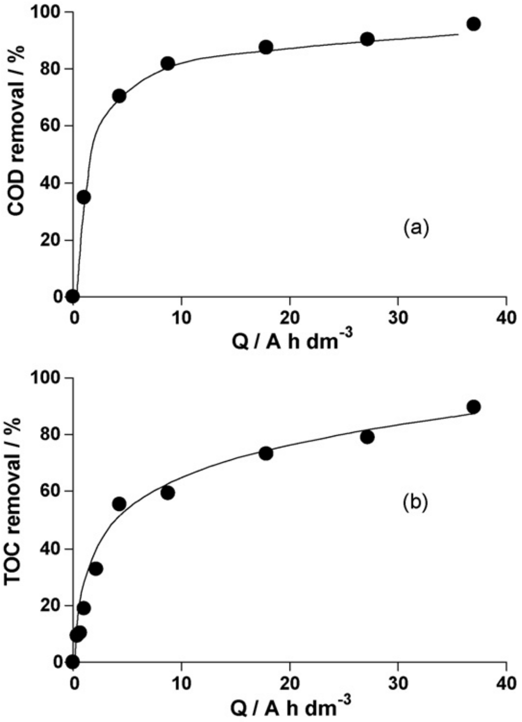

Fig. 3. Percentage of COD and TOC removal as a function of the specific electrical charge passed in the CDEO of surfactants. (●) Sodium dodecylbenzenesulfonate (TOC$_0$: 225 mg dm^{-3}). Experimental conditions: COD$_0$: 1000 mg dm^{-3}; T: 25 °C; j: 30 mA cm^{-2}; neutral pH; electrolyte support: 0.1 M NaCl.

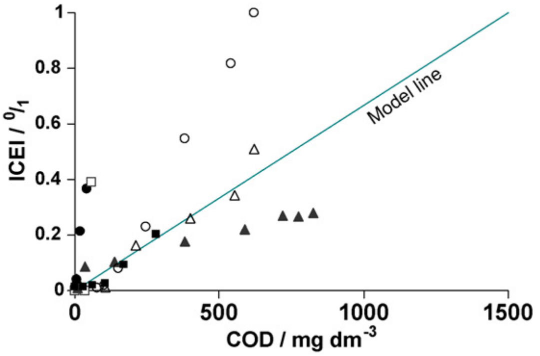

Fig. 4. Variation of the instantaneous current efficiency (ICE) with the COD in the electrochemical oxidation of wastes containing methylene blue (●), rhodamine B (□), ethylene glycol (▲), glycerol (■), diethylene glycol (△) and sodium dodecylbenzenesulfonate (○).

compounds are present in the industrial effluents of the ink-manufacturing process (around 10^2 mg dm^{-3} for dyes and 10^3 mg dm^{-3} for solvents and surfactants).

As it can be observed, the almost complete removal of COD is obtained for all the compounds tested. Current charges passed smaller than 20 kAh m^{-3} are required to complete the treatment (according to the COD measurements). In every case, the mineralization rate (TOC removal) seems to be smaller than that of COD removal. This change is especially important in the CDEO of dyes. This could be related to the structure of the pollutants studied, and also to the nature of the intermediates generated in the process. In the treatment of solvents and surfactants, changes in COD and TOC occur almost simultaneously. This means that no net accumulation of intermediates is obtained, indicating that the generation of intermediates (from the partial oxidation of the initial pollutant) and their destruction is very rapid and thus, that the carbon dioxide is formed almost directly from the pollutants. On the other hand, during the initial stages of the CDEO of dyes the changes in the COD are more abrupt than those in the TOC. Likewise, there is a wide range of current charges (2–10 Ah dm^{-3}) in which TOC does not change in spite of the great changes observed for the COD. In this case, the large molecular weight of dyes and the existence of many functional groups should favour the formation of a great variety of intermediates (changes in the COD) without carbon dioxide formation (changes in the TOC). In addition, in the oxidation of these compounds, the maximum TOC removal percentages obtained are around 40–80% (in contrast with the almost 100% COD removal) whereas the electrochemical treatment of solvents and surfactants leads to the complete mineralization of the waste. According to literature [23,24], the CDEO of complex pollutant can lead to the accumulation of some intermediates (short-chain carboxylic acids, mainly) with low oxidizability and low COD/TOC ratio as final products. These intermediates may explain the experimental behaviour obtained in the treatment of the two colorants studied in this work.

Fig. 4 shows the instantaneous current efficiencies obtained during the CDEO of the synthetic wastewater studied in this work. Likewise, and with purpose of comparison, it also represents the results predicted by a model proposed in literature [13,25] that assumes direct electrochemical reaction and hydroxyl-radical mediated oxidation in the anode surface with efficiencies only limited by mass transport. This model has been validated [13–16,25] with the results obtained in the treatment of many compounds such as phenol, chlorophenols, nitrophenols, naphtol, and it has been observed that it reproduces successfully the experimental behaviour of the CDEO except for systems in which the influence of the chemical mediated processes is very important such as the treatment of wastes containing large amounts of inorganic ions (such as chlorine, sulphate and phosphate). In these systems, the electrogeneration of high concentration of oxidants (from the oxidation of the electrolyte support) takes place and their effects in the overall oxidation process are not considered in the former model, although they should be very significant.

Taking this into account, it seems clear that in the system studied the mediated electrochemical oxidation processes have a strong influence. The model proposed in literature reproduces satisfactorily the oxidation of solvents but the efficiencies of the oxidation of dyes and surfactants are over the expected value. This suggests that the oxidation of solvents should be carried out mainly by direct electrooxidation or hydroxyl-radical mediated oxidation (taking into account the low average lifetime of hydroxyl radicals, the oxidation carried out by these species can be considered as a direct process from the mass-transport point of view). On the contrary, the oxidation of surfactants and dyes (with a complex structure) is influenced by the electrochemically-formed reagents. In literature, it is pro-

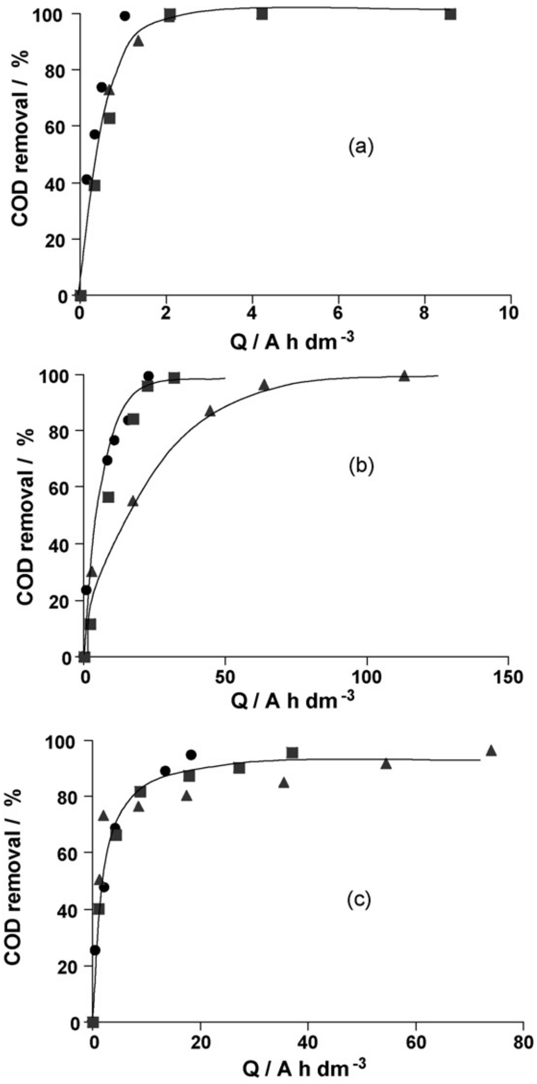

Fig. 5. Percentage of COD removal as a function of the current density applied during the galvanostatic electrolyses of rhodamine B (a), ethylene glycol (b) and sodium dodecylbenzenesulfonate (c). Experimental conditions: *T*: 25 °C; neutral pH; electrolyte support: 0.1 mol NaCl dm^{-3}. Current density: (●) 15 mA cm^{-2}, (■) 30 mA cm^{-2}, (▲) 60 mA cm^{-2}.

posed that the CDEO of wastes containing chloride ions leads to the formation of hypochlorite [25,26] (or hypochlorous acid as a function of the pH). The stability of the chlorinated oxidants and their high oxidation capacity extend the oxidation reaction through the complete reaction volume. Thus, the results obtained suggest that chlorine oxidants can play an important role in the oxidation of dyes and surfactants and, that both direct and mediated electrooxidation coexist.

Fig. 5 shows electrolyses of the pollutants studied in this work at different current densities. As it can be seen, in the CDEO of the dyes and surfactant studied in this work an increase in the current density does not lead to an increase in the efficiency of the oxidation process, and similar electrical charges are required in all cases to remove the same amount of organic matter (the COD removal profiles obtained at different current densities are overlapped). This means that the current density does not have influence on the efficiency in the range studied (150–600 A m^{-2}) and, it also suggests that, in accordance with that previously commented, chemical oxidation by stable electrogenerated oxidants (hypochlorite) plays an important role in the overall electrochemical oxidation process of rhodamine B and sodium dodecylbenzenesulfonate. In this case, mediated oxidation mechanism can be much more significant than the direct oxidation of pollutants on the electrode surface. Conversely, in the CDEO of a synthetic wastewater polluted with ethylene glycol an increase in the current density leads to lower process efficiencies. This behaviour is characteristic of mass-transfer-controlled processes [13,14,25] in which an increase in the current density cannot raise the rate of oxidation of the organics at the electrode and favours anodic side reactions (formation of O_2, O_3, etc.). This suggests that the oxidation of glycols with chlorinated oxidants is not very efficient and hence that the direct oxidation (or the oxidation by hydroxyl radicals) controls the overall oxidation rate. This fact is in agreement with the behaviour observed in Fig. 4.

To confirm the role of oxidants electrochemically-formed in the CDEO of aqueous wastes, the oxidation of solutions of pollutants with three different electrolyte supports have been studied: NaCl, Na_2SO_4 and Na_3PO_4. Fig. 6 shows the results obtained (COD removal percentage versus electrical charge passed) in the CDEO of rhodamine B, ethylene glycol and sodium dodecylbenzenesulfonate. As can be observed, the complete removal of organic load (expressed as COD) is obtained, independently of the supporting media. However, the oxidation rates and the efficiencies seem to depend on the electrolyte (and thus on the electrochemically-formed oxidant) and on the pollutant. Hence, it can be observed that the electrochemical treatment of ethylene glycol in Na_2SO_4 or Na_3PO_4 medium is more effective that in NaCl media. On the contrary, the oxidation rate of rhodamine B using NaCl as electrolyte support is higher than using Na_2SO_4 and Na_3PO_4. The influence of the three studied electrolytes in the CDEO of the surfactants is less important but it can be clearly discerned that the phosphate media obtained the worse efficiencies. To explain this, it has to be taken into account that the CDEO of aqueous solutions containing chloride, sulphate and phosphate anions promotes the formation of hypochlorite [25,26], peroxodisulphates [27,28] and peroxodiphosphates [29,30], respectively, and that these three chemical species are very powerful oxidant with high standard reduction potentials.

According to literature [31–34], the oxidation of an organic compound by any of these reagents does not only depend on the oxidation potential, and thus the results obtained are indicative of:

- the low oxidizability of ethylene glycol by hypochlorite (hence, and according to the results previously discussed, the oxidation of solvents is mainly caused by direct or hydroxyl-radicals mediated oxidation). Conversely, the oxidation of these aliphatic compounds by persulphate and perphosphate is very favoured, especially by perphosphate.
- the high oxidizability of dyes by hypochorite, in comparison with perphosphate and with persulphate. In this case, the oxidation characteristics of both oxidants are similar.

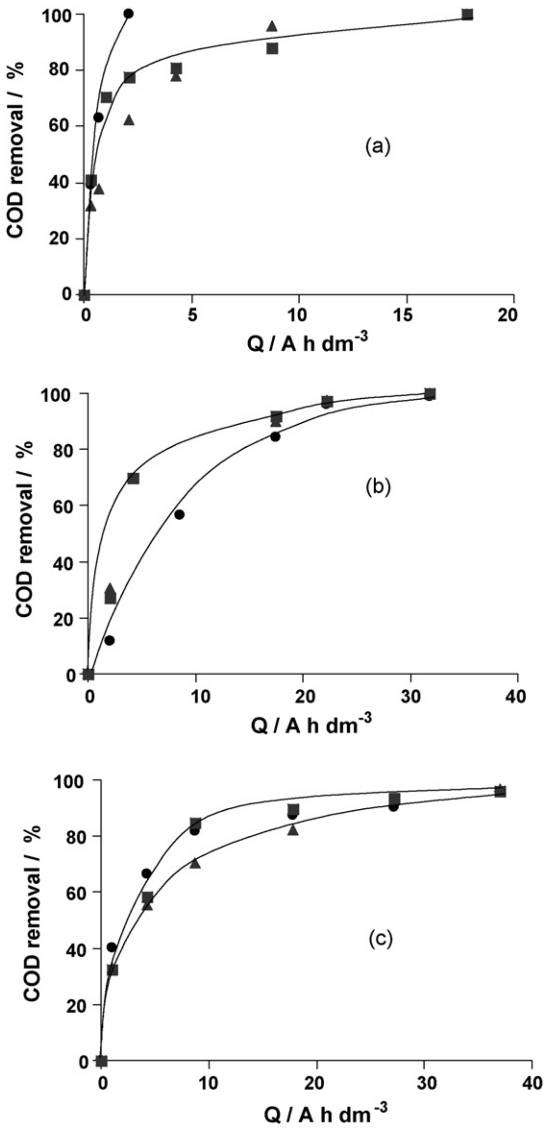

Fig. 6. Percentage of COD removal as a function of the current density applied during the galvanostatic electrolyses of rhodamine B (a), ethylene glycol (b) and sodium dodecylbenzenesulfonate (c). Experimental conditions: T: 25 °C; j: 30 mA cm^{-2}; neutral pH. Electrolyte support: (●) 0.1 mol NaCl dm^{-3}, (■) 0.1 mol Na_2SO_4 dm^{-3}, (▲) 0.1 mol Na_3PO_4 dm^{-3}.

- the similar oxidizability of the surfactants by the three oxidants, that can be explained taking into account the complex structure of the compound with both aliphatic and aromatic groups, which results in very different possibilities for the oxidation reaction.

4. Conclusions

The conductive diamond electrochemical oxidation allows achieving the almost complete COD removal and high mineralization percentages of synthetic aqueous wastes polluted with dyes (thiazine dye methylene blue, xanthene dye rhodamine B), solvents (ethylene glycol, glycerol, diethylene glycol) and surfactants (sodium dodecylbenzenesulfonate). Independently of the nature of the pollutant, the percentages of removal COD obtained are higher than those of mineralization, indicating the accumulation in the system of intermediate compounds with very low COD and with low oxidizability. The current efficiencies of the processes seem to depend on the nature of the pollutant studied. An increase in the current density does not lead to an increase in the efficiency of the oxidation process, and similar electrical charges are required in all cases to remove the same amount of organic matter, indicating that chemical oxidation by stable electrogenerated oxidants plays an important role in the overall electrochemical oxidation process. Chlorine media favours the oxidation process of dyes and aromatic surfactant, whereas its effect is less significant in the treatment of aliphatic compounds (glycolic compounds). This indicates that the oxidation of an organic compound by any of the electrochemically-formed reagents does not only depend on its oxidation potential, but also on the structure of the compounds.

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