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Research article

Degradation of C. I. Direct Red 80 by the Electro-Fenton Process

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Abstract.
Electro-Fenton process was applied in the degradation of the textile dye C. I. Direct Red 80 (DR80), using a boron-doped diamond anode and a carbon-felt cathode. The influence of the applied current density and of the type of iron source was evaluated. The iron sources studied were iron sulfate, ferric chloride, iron oxide and chalcopyrite, a natural iron-containing mineral. The obtained results showed that the electro-Fenton process is effective in the DR80 degradation and in the pollutant load elimination. Higher treatment efficiencies were attained when using iron sulfate as iron source. Still, the results obtained with the natural mineral chalcopyrite were quite promising. Although DR80 removal was more efficient at lower applied current densities, the same was not observed for the chemical oxygen demand removal, indicating that, at lower applied current densities, the dye is not completely mineralized, but rather transformed into other by-products.

Keywords: C. I. Direct Red 80; Advanced oxidation processes; Electro-Fenton, Boron-doped diamond anode, Carbon-felt cathode.

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1. Introduction

Freshwater contamination by synthetic dyes is a global environmental concern. According to the literature, there are more than 100,000 commercially available dyes, with an estimated annual production of more than 7×10^5 tonnes, which are used by different types of industry, such as textile, papermill, cosmetic, pharmaceutical, food industry, among others [1]. As a result, large volumes of wastewater, containing high concentrations of dyes, are daily produced, being aesthetic and with potential toxicity and carcinogenicity [2].

The degradation of synthetic dyes by conventional wastewater treatment processes is often ineffective, and thus, the development of new treatment technologies, capable of degrading these contaminants into non-toxic and biodegradable products, is required [2]. The application of electrochemical processes to degrade synthetic dyes has

received great attention in the last years, due to the high potential of these processes to eliminate different types of organic compounds, including compounds with recalcitrant properties [1]. Among them, the electro-Fenton (EF) process, an electrochemical process based on Fenton's reaction (Eq. (1)), has stood out due to the promising results achieved [3,4].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + HO^{-} \quad (1)$$
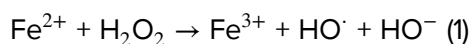
In the EF process, the organic compounds are oxidised by the hydroxyl radicals produced in the Fenton reaction, being the H_2O_2 continuously electrogenerated *in situ* through the reduction of oxygen gas injected into a carbon cathode, generally carbon-felt (Eq. (2)). The H_2O_2 formed is decomposed to $HO^{\cdot}$ by the Fenton reaction (Eq. (1)). In this electrochemical process, Fe^{3+} is reduced at the cathode, generating Fe^{2+}, which results in a higher degradation rate of organic pollutants than the traditional Fenton process [5]. Iron sulfate or chloride are the most common iron sources for EF process, but, in the recent years, the use of heterogeneous iron sources, such as pyrite (FeS_2) and chalcopyrite ($CuFeS_2$), have gained significant attention [6].

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (2)$$
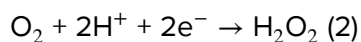
According to the literature, the efficiency of the EF process can be further enhanced by utilizing a high O_2-overpotential anode, such as boron-doped diamond (BDD) anode, being the organic compounds additionally oxidised through adsorbed hydroxyl radicals ($BDD(HO^{\cdot})$), formed as an intermediate of the anodic water discharge (Eq. (3)) [5,6].

$$BDD + H_2O \rightarrow BDD(HO^{\cdot}) + H^+ + e^- \quad (3)$$
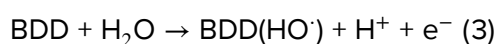
The aim of the present work was to evaluate the feasibility of EF process, using a BDD anode, to degrade the azo dye C. I. Direct Red 80 (DR80), and to study the influence of different operational parameters, namely the applied current density (j) and the iron source, on the effectiveness of the treatment.

2. Material and methods

The DR80 aqueous solutions were prepared with ultrapure water, using Direct Red 80, dye content 25% (CAS Number 2610-10-8), purchased from Sigma-Aldrich. Iron(III) sulfate pentahydrate, 97% (CAS Number 10028-22-5), ferric chloride hexahydrate, 97% (CAS Number 10025-77-1), and iron(III) oxide, 96% (CAS Number 1309-37-1), were also purchased from Sigma-Aldrich. Chalcopyrite was mined from Jendouba (Tunisia) and presented an iron content of 30.6%. Its preparation and characterization are described elsewhere [6]. The DR80 solutions studied in this work were prepared to contain an

initial concentration of 50 mg L^{-1} of DR80 and 10 mg L^{-1} of iron. The composition of the different solutions is presented in Table 1.

TABLE 1: Composition of the DR80 aqueous solutions used in the experiments.

Reagent	DR80 + Iron sulfate	DR80 + Ferric chloride	DR80 + Iron oxide	DR80 + Chalcopyrite
Direct Red 80 (mg L^{-1})	201 ± 2	202 ± 3	201 ± 1	200 ± 2
Fe$_2$(SO$_4$)$_3$.5H$_2$O (mg L^{-1})	45.1 ± 0.4	–	–	–
FeCl$_3$.6H$_2$O (mg L^{-1})	–	49.0 ± 0.3	–	–
Fe$_2$O$_3$ (mg L^{-1})	–	–	29.0 ± 0.4	–
Chalcopyrite (mg L^{-1})	–	–	–	789 ± 1

The EF experiments were conducted in batch mode, using an undivided and cylindrical glass cell, with a useful volume of 200 mL. During the experiments, the solution was continuously stirred, with a magnetic bar, to enhance the mass transport of reactants/products toward/from the electrodes. A carbon-felt piece (Carbone Loraine) with a thickness of 0.5 cm and an immersed area of 136 cm^2 was used as cathode, and a BDD electrode (Neocoat), with an immersed area of 20 cm^2, was used as anode. The anode was centered in the cell and surrounded by the cathode, which covered the inner wall of the cell. Continuous O$_2$ saturation at atmospheric pressure was ensured by bubbling compressed air through a fritted glass diffuser at 1 L min^{-1}, starting 10 min before the assay, to reach a steady O$_2$ concentration that allowed H$_2$O$_2$ electrogeneration (Eq. (2)).

The experimental setup utilized a DC power supply GW, Lab DC, model GPS-3030D (0–30 V, 0–3 A), being the anodic current densities studied 12.5, 25, and 50 A m^{-2}. At 12.5 A m^{-2}, experiments were performed with 2, 4, and 8 h duration (180, 360, and 720 C, respectively). To apply the same electric charge (180, 360, and 720 C) to the experiments run at 25 A m^{-2}, these assays had 1, 2, and 4 h duration, respectively, and at 50 A m^{-2} had 0.5, 1, and 2 h duration. The initial and final solutions from each experiment were utilized for DR80, chemical oxygen demand (COD), total carbon (TC), inorganic carbon (IC), total organic carbon (TOC), total dissolved iron (TDI), dissolved Fe^{2+}, H$_2$O$_2$, pH, and conductivity determinations.

COD determinations were performed according to the standard methods [7]. TC, IC, and TOC were measured in a Shimadzu TOC-V CPH analyser. DR80 concentration was spectrophotometrically determined at 526.5 nm. TDI and dissolved Fe^{2+} determinations followed the 1,10-phenanthroline method [8]. H$_2$O$_2$ concentration was determined by the colorimetric metavanadate method [9].

3. Results and discussion

The characterization of the DR80 aqueous solutions used in this study is presented in Table 2. It can be seen that, although the solutions were prepared to have 10 mg L^{-1} of iron, the initial dissolved Fe^{3+} concentration, in the solutions prepared with the iron salts, was much lower, indicating that the iron salts were not completely solubilized during the initial stage of the solutions preparation. In fact, for the solutions prepared with iron oxide, a solid residue was observed along all the EF experiments duration, corresponding to non-dissolved iron oxide. For the solutions prepared with the heterogeneous iron source, chalcopyrite, a residual Fe^{3+} concentration was detected during the samples characterization, since, in this case, iron is slowly released from the mineral source during the experiments.

The initial pH of the solutions prepared with iron sulfate and ferric chloride was around 3-4, which is the optimum pH for the EF process, due to its influence on iron speciation and on H_2O_2 decomposition [5,6]. However, the solutions prepared with iron oxide and chalcopyrite presented a higher initial pH, especially the solution prepared with iron oxide.

TABLE 2: Characterization of the DR80 aqueous solutions used in the experiments.

Parameter	DR80 + Iron sulfate	DR80 + Ferric chloride	DR80 + Iron oxide	DR80 + Chalcopyrite
DR 80 (mg L^{-1})	52 ± 3	54 ± 2	52 ± 1	55 ± 3
Fe^{3+} (mg L^{-1})	3.4 ± 0.1	3.3 ± 0.5	0.7 ± 0.1	0.6 ± 0.2
COD (mg L^{-1})	74 ± 1	76 ± 2	75 ± 3	76 ± 2
TC (mg L^{-1})	23.0 ± 0.9	25.9 ± 0.7	25.8 ± 0.4	24.6 ± 0.5
IC (mg L^{-1})	0.4 ± 0.1	0.5 ± 0.1	1.3 ± 0.1	0.6 ± 0.2
TOC (mg L^{-1})	22.6 ± 0.9	25.4 ± 0.6	24.5 ± 0.4	24.0 ± 0.6
pH	3.67 ± 0.04	3.54 ± 0.05	6.74 ± 0.09	4.85 ± 0.05
Conductivity (µS cm^{-1})	372 ± 6	362 ± 9	256 ± 5	297 ± 8

Fig. 1 presents the DR80 relative concentration decay with applied electric charge for the EF experiments performed with different iron sources, at different applied current densities. At the lowest j studied, 12.5 A m^{-2}, the experiments performed with iron sulfate and ferric chloride presented the highest DR80 removal rates, being the results of these two iron sources similar. After 2 h of assay (180 C), the DR80 removal was 91% for the solutions prepared with iron sulfate and ferric chloride, being 79% and 54%, respectively, for the solutions prepared with chalcopyrite and iron oxide. After 4 h of assay (360 C), for all the solutions studied, the DR80 concentration was inferior to 1 mg L^{-1}.
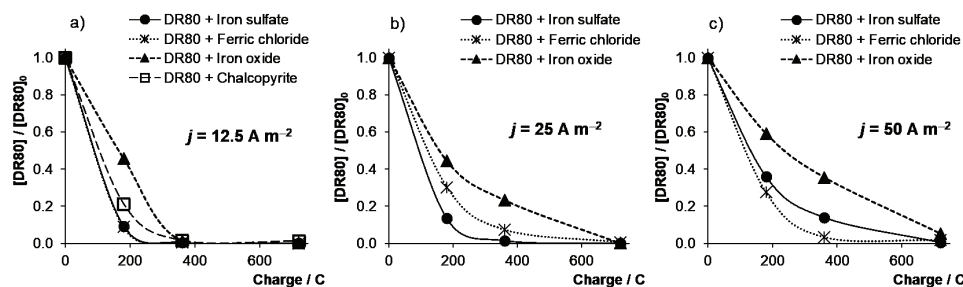
Figure 1: DR80 relative concentration decay with applied electric charge, for the EF experiments performed with different iron sources at: (a) 12.5 A m^{-2}, (b) 25 A m^{-2}, and (c) 50 A m^{-2}.

With the increase in j to 25 A m^{-2}, the DR80 removal rate decreased for all the iron sources studied, being this decrease more pronounced in the experiments with ferric chloride than in the experiments with iron sulfate. However, when j was further increased to 50 A m^{-2}, an increase in the DR80 removal rate was observed for the experiments performed with ferric chloride, compared to 25 A m^{-2}, although a decrease in the DR80 removal was observed for experiments performed with iron sulfate and iron oxide. These DR80 removal results can be explained by the Fe^{2+} concentration evolution in solution along the experiments (Fig. 2).
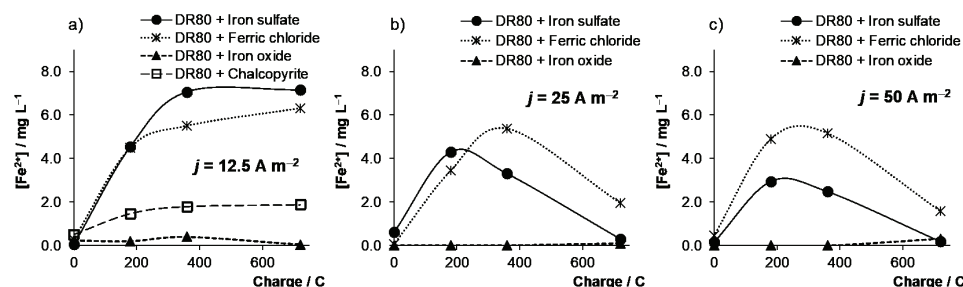

Figure 2: Dissolved Fe^{2+} concentration evolution with applied electric charge, for the EF experiments performed with different iron sources at: (a) 12.5 A m^{-2}, (b) 25 A m^{-2}, and (c) 50 A m^{-2}.

In fact, solutions prepared with iron sulfate and ferric chloride are those with higher concentrations in dissolved Fe^{2+} and, the higher the Fe^{2+} concentration, the larger the extension of the Fenton reaction and, consequently, the higher the concentration of hydroxyl radicals available for oxidation. Focusing on the applied charge of 180 C, where the highest DR80 removal occurs for all the experimental conditions studied, it can be seen that, at 12.5 A m^{-2}, solutions prepared with iron sulphate and ferric chloride present similar Fe^{2+} concentration; at 25 A m^{-2}, Fe^{2+} concentration is higher for the solution with iron sulfate; but at 50 A m^{-2}, the highest Fe^{2+} concentration is presented by the solution with ferric chloride. The Fe^{2+} concentration also explains the lower DR80 removals obtained with iron oxide, since, in these solutions, Fe^{2+} concentration was practically zero.

At 25 and 50 A m^{-2}, a decrease in Fe^{2+} concentration is observed after a certain point of the experiments performed with iron sulfate and ferric chloride. This can be due to parallel sulfate and chloride oxidation reactions that inhibit the Fe^{2+} regeneration reaction. In fact, analysing the TDI evolution (Fig. 3), no decrease in the TDI concentration is found for these experiments, indicating that the iron in solution is in the form of Fe^{3+}.
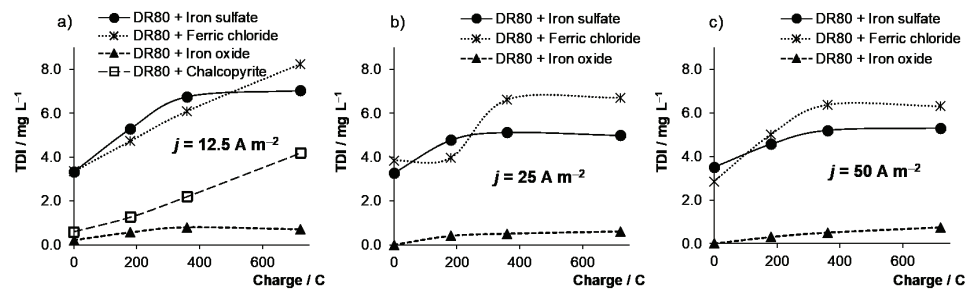

Figure 3: TDI concentration evolution with applied electric charge, for the EF experiments performed with different iron sources at: (a) 12.5 A m^{-2}, (b) 25 A m^{-2}, and (c) 50 A m^{-2}.

In Fig. 3, it can also be seen that TDI concentration was higher in the experiments performed at 12.5 A m^{-2}, which can be explained by the fact that, at this j, the experiments had longer duration and therefore the release of iron in solution was enhanced.

Regarding the COD decay (Fig. 4), although the experiments performed with iron sulfate attained the highest COD removals for all the j studied, at 50 A m^{-2}, and until an applied electric charge of, approximately, 400 C, the COD removal rate of the experiments performed with ferric chloride was significantly higher than that of the experiments with iron sulfate.
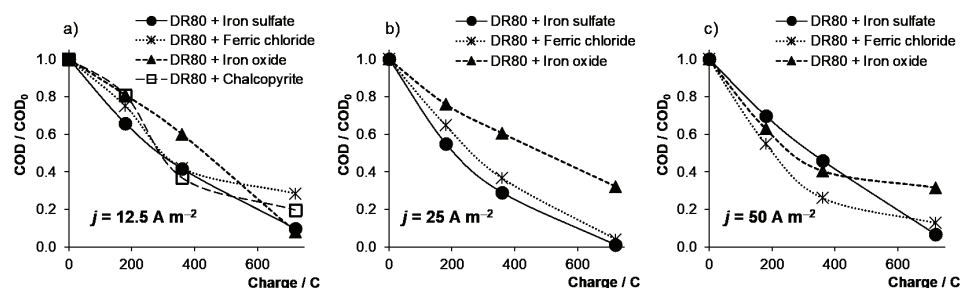

Figure 4: COD relative decay with applied electric charge, for the EF experiments performed with different iron sources at: (a) 12.5 A m^{-2}, (b) 25 A m^{-2}, and (c) 50 A m^{-2}.

This enhanced performance of the experiments run with ferric chloride at 50 A m^{-2}, also observed for the DR80 removal, probably results from the higher Fe^{2+} concentration found in the ferric chloride solution, as described above. Also, the additional indirect oxidation of the pollutant load by oxidizing species, such as sulfate radical and

hypochlorite, resulting from the oxidation of sulfate and chloride, may explain the COD removal in the last period of the experiments run at 25 and 50 A m^{-2}.

Iron oxide was the iron source that led to the lowest COD removals, except for the experiments performed at 12.5 A m^{-2}, where, despite initially presenting the lowest removal rate, it reached a final removal like that obtained with iron sulfate. Given the low dissolved Fe^{2+} concentration in the solutions prepared with iron oxide (Fig. 2), this high COD removal at 12.5 A m^{-2} is probably due to the organics oxidation by hydroxyl radicals formed from water electrolysis. In fact, the solutions prepared with iron oxide and chalcopyrite presented the highest pH values during the first period of assay (Fig. 5) and, according to the literature [1], hydroxyl radical generation from water electrolysis is favoured at higher pH values.
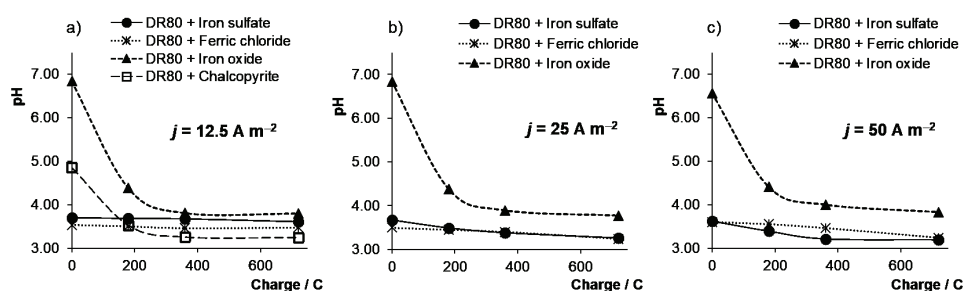

Figure 5: pH evolution with applied electric charge, for the EF experiments performed with different iron sources at: (a) 12.5 A m^{-2}, (b) 25 A m^{-2}, and (c) 50 A m^{-2}.

Fig. 6 presents the TOC relative concentration decay with applied electric charge for the EF experiments performed with different iron sources, at different applied current densities. At 12.5 A m^{-2}, the solution prepared with iron oxide is the one that presents the highest TOC removal, and consequently the one that attained the highest mineralization degree, followed by the solution prepared with chalcopyrite. These results agree with the organics oxidation by hydroxyl radicals produced from water electrolysis, since, according to the literature [1], the organics degradation through hydroxyl radicals, formed on the surface of the BDD anode by water oxidation, leads to higher mineralization degrees. For the highest applied current densities, 25 and 50 A m^{-2}, the iron source that led to the highest DOC removals was iron sulfate.

4. Conclusions

EF process, using a BDD anode and a carbon-felt cathode, is effective in DR80 degradation and in the pollutant load elimination. From the different iron sources studied, at the experimental conditions assayed, iron sulfate led to the best DR80 degradation
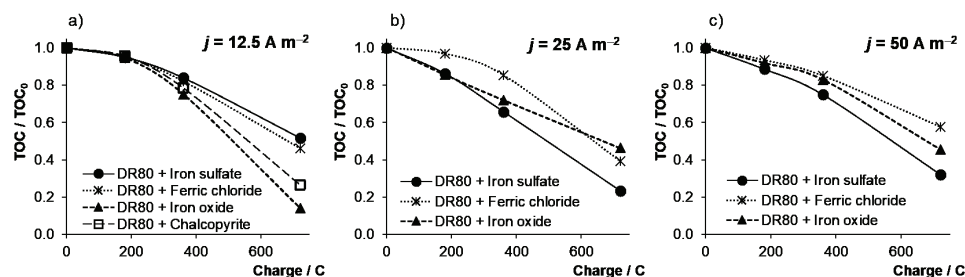
Figure 6: TOC relative decay with applied electric charge, for the EF experiments performed with different iron sources at: (a) 12.5 A m^{-2}, (b) 25 A m^{-2}, and (c) 50 A m^{-2}.

results, followed by ferric chloride. Although DR80 removal was more efficient at the lowest applied current density, 12.5 A m^{-2}, attaining DR80 removals of 91% at 180 C, the same was not observed for COD and TOC removals, indicating that, at 12.5 A m^{-2}, the dye is not completely mineralized, but rather transformed into other by-products. Thus, to significantly reduce the solutions organic load it is necessary to increase the applied current density. The highest COD removals, 99% and 96%, were obtained, respectively, with iron sulfate and ferric chloride, at the applied current density of 25 A m^{-2}. Solutions prepared with iron oxide also led to high COD (92%) and TOC (86%) removals, mainly due to the anodic oxidation of the dye and its degradation products, and not to the electro-Fenton process. For this iron source, the solutions initial pH adjustment to pH 3 should increase the effectiveness of the electro-Fenton process. As for chalcopyrite, despite not showing the best results in any of the parameters evaluated, the results obtained with this natural mineral are quite promising. At 12.5 A m^{-2}, complete DR80 removal was attained after 4 h assay, and COD and TOC removals of 80% and 74%, respectively, were achieved after 8 h treatment. Given the observed pH values, these results might be improved if the initial pH of the solution is adjusted to values close to 3, the optimum pH value for the electro-Fenton process.

Acknowledgements

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