

Heterogeneous photo-electro-Fenton process using different iron supporting materials

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Abstract In this work, the application of heterogeneous photo-electro-Fenton processes using iron supported on Nafion membranes and ion exchange amberlite and purolite resins is studied. Spectroscopic and TOC results using as a model pollutant an aqueous Orange II dye solution indicate that the process can be carried out with any of the iron supporting materials under study. While the resins can incorporate between 59 and 65 mg Fe/g of substrate, a Nafion membrane can fix 45 mg Fe/g of supporting material. Iron desorption analysis after a photo-electro-Fenton degradation test on the other hand, indicates that the ion exchange resins and the Nafion membrane hold more than 90% of iron. An alkaline rinse after the activation exchange process for the amberlite resin and the Nafion membrane, results in a larger stability of the fixed iron species.

Keywords Photo-electro-Fenton · Iron support resins · Nafion membranes · Azo Orange II

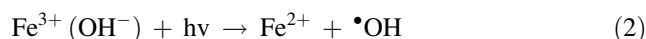
1 Introduction

Fenton's reagent consists of a mixture of H_2O_2 and Fe^{2+} that, according to reaction (1), results on the generation of hydroxyl free radicals; a species that is well known for its high oxidation power.

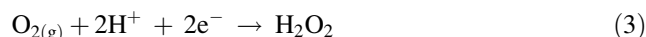


Although reaction (1) has been known for over a century, its potential as an alternative for wastewater treatment was not widely considered until the early 1990s [1–3]. In this context Fenton based systems have been intensively studied in recent years, achieving good degradation efficiencies in aqueous effluents contaminated with persistent organic compounds such as pesticides and dyes [4, 5].

Fenton's reaction is typically carried out in homogeneous aqueous phase (consisting on a solution of H_2O_2 and Fe^{2+} or Fe^{3+} [6]) and its performance can be improved using UV light in an arrangement known as photo-Fenton. As shown by reaction (2), the increased efficiency of the photo-Fenton process is due to the light promoted re-generation of the Fe^{2+} species [7].



In order to develop electrically controlled Fenton based oxidation technologies for water treatment [7], the electrochemical generation of H_2O_2 from reduction of dissolved O_2 has been employed.



The combination of the electrochemical production of H_2O_2 and UV light is called photo-electro-Fenton process and constitutes a very powerful system for the degradation of a wide variety of pollutants. This process for instance has been used to eliminate phenol [8] and reactive black 5 dye [9] from water, and studied in our group for the destruction of the azo dye Orange II using carbon felt electrodes [7] and on an optical fiber anode [10].

Due to its homogeneous nature however, Fenton based processes produce a high concentration of iron ions in the final effluent [11]. The required elimination of iron from the

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resulting aqueous solutions produces waste sludge whose disposal is expensive and difficult [12]. This disadvantage can be eliminated by utilizing solid materials to support the iron species, maintaining at the same time, a reasonable efficiency of the process. Using this approach, different materials have been studied in *photochemical* reactors and among these, zeolitic materials [13–16], pillared clays [11, 17–19], alumina [20], Nafion membranes [21–23], ion-exchange resins [6, 24–26], silice [27], silica [28, 29] alginate [30] and ashes [31] stand out. On the other hand, there are some studies that evaluate the effects of supported iron species in Fenton processes [32–39]. The work of Kiwi et al. [21] for example, have demonstrated that iron compounds supported on a Nafion membrane can give good results in a photo-Fenton water treatment process.

To investigate lower cost alternatives for iron supporting materials than Nafion, in this work we evaluate and compare Nafion membranes and ion exchange resins as iron support systems for the treatment of a model pollutant in aqueous phase (the azo dye Orange II) using a photo-electro-Fenton process. The use of this approach is attractive in a photo-Fenton process and also in a photo-electrochemical reactor because the iron used for the Fenton reaction can be held by the supporting material and not lost in the solution.

2 Experimental

2.1 Preparation of Nafion membranes and ion exchange resins

To remove all the species that could interfere with the anchoring of ferric ions and activate the material, the Nafion membrane was immersed in a 3% H₂O₂ solution (JT Baker) and heated on a hot plate (Barnstead) at 95 °C for 60 min. After washing, the membrane was rinsed with distilled water, immersed in 0.5 M H₂SO₄ (JT Baker) for 60 min at 95 °C and rinsed again. In order to evaluate the maximum amount of Fe that can be fixed in the Nafion membrane, FeCl₃ (ferric chloride hexahydrate JT Baker) solutions were prepared at 6 different concentrations in the 725–14,500 mg L⁻¹ range and set in contact with the membrane. Later the membrane was rinsed with distilled water and analyzed using SEM and EDS. For these experiments, a JEOL-5400LV microscope with an accelerating voltage of 25 kV was employed. The content of iron in the samples was determined using a Perkin Elmer Induced Coupled Plasma (ICP) model Optima 3000 XL and employed to define the saturation concentration of iron in all the supporting materials studied. To evaluate the effect of the alkaline rinse on the stability of iron, some membranes were rinsed with a NaOH 1 M (Karal) solution.

These membranes were characterized in the same way that those not treated with the alkaline solution.

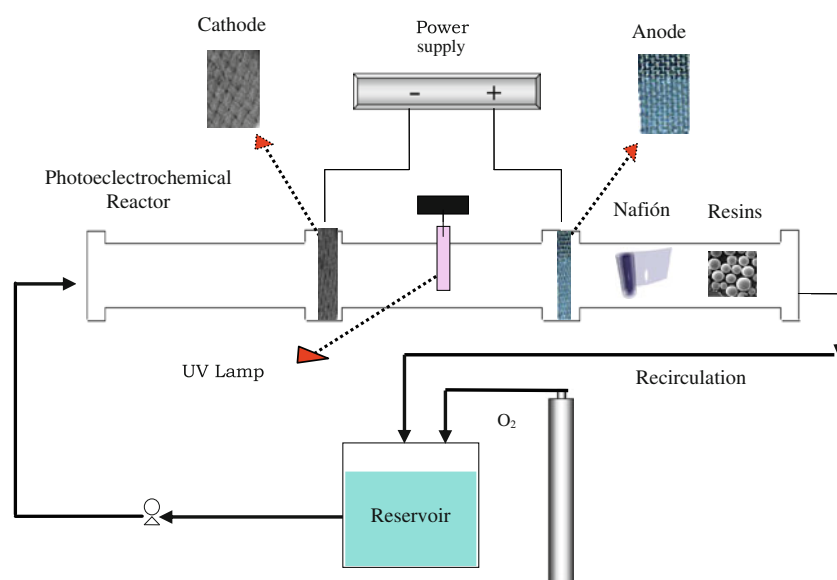
Purolite and amberlite resins on the other hand, were activated by mixing the materials with 5% H₂SO₄ for 1 h. Later, the resin was placed in contact with FeCl₃ solutions in different concentrations between 270 and 54,000 mg L⁻¹, rinsed with distilled water until the washing water reached a pH between 6 and 7 and dried for 24 h at 60 °C in a stove (Fisher). As in the case of the Nafion membranes, some resins were rinsed with a solution of 1 M NaOH (Karal) after cationic exchange and dried for 24 h at 60 °C. Characterization studies were similar to those performed on the membranes.

2.2 Iron desorption tests

To evaluate the desorption of iron from the supports in a photo-electro-Fenton process, 0.5 g of the iron saturated membrane were immersed in 400 mL of a pH 3 sulfate buffer solution placed in a beaker. To generate H₂O₂ in the system, two carbon cloth electrodes (Carbone Lorraine Inc.) of 10 cm² were located inside the oxygen saturated solution and used as anode and cathode. A UV mercury lamp (P = 75 mW cm⁻², λ = 365 nm, UVP Inc.) was also located at one side of the beaker and a current of 100 mA was applied to the system for 60 min. The collected samples at the end of the process were analyzed using ICP to determine the concentration of ionic Fe in solution; the whole process was carried out under high turbulence conditions using magnetic stirring. In the case of the resins, the procedure was the same.

2.3 Degradation of Orange II

Degradation of the model dye was evaluated using a three compartment photo-electrochemical reactor arranged as shown in Fig. 1. In this reactor, the dye containing aqueous solution is pumped across the porous electrode materials from the first to the third compartment. In this way, while a carbon cloth electrode (A = 10 cm²) was used as a cathode fixed between the first and second compartments, a carbon cloth coated with sintered nanostructured titanium dioxide (prepared as described in previous work [40]) (A = 10 cm²) was used as the anode positioned between the second and third compartments. As can be seen in Fig. 1, while the resin or the Nafion membrane particles are suspended in the third compartment, the central part of the reactor is modified with a glass-made cylindrical chamber in which a UV lamp (P = 75 mW cm⁻², λ = 365 nm, UVP Inc.) is located and used to illuminate the reaction medium. It is important to note that the amount of UV light reaching the third compartment was not evaluated and

Fig. 1 Experimental system

corresponds to the fraction of radiation capable of going through the anode porous material.

A 15 L of a sulfate buffer (Karat anhydrous sodium sulfate) solution was prepared and adjusted to pH 3. The buffer was saturated using oxygen (UAP Infra) bubbling for 45 min; later, the solution was fed to the photoelectrochemical reactor using a diaphragm pump (Shurflo) maintaining the recirculation. A current of 100 mA was applied for 150 min to the electrochemical cell using a power supply (Instek GPR-6060D) for the cathodic generation of hydrogen peroxide. At that point, 300 mg of Orange II (Orange II sodium salt Sigma) was added to the system in order to contaminate the water at a concentration of 20 mg L^{-1} and 4 g of the membrane (cut into pieces), or 10 g of the resins, were located in a side chamber of the reactor (see Fig. 1). Then the UV lamp was turned on and the solution was recirculated for 1 h. The removal of color was followed using a spectrophotometer (Spectronic 20D+ Milton Roy) and total organic carbon (TOC) levels of the test solution were determined using a TOC-VCSN analyzer (Shimadzu Co.).

3 Results

3.1 Iron supporting materials characterization

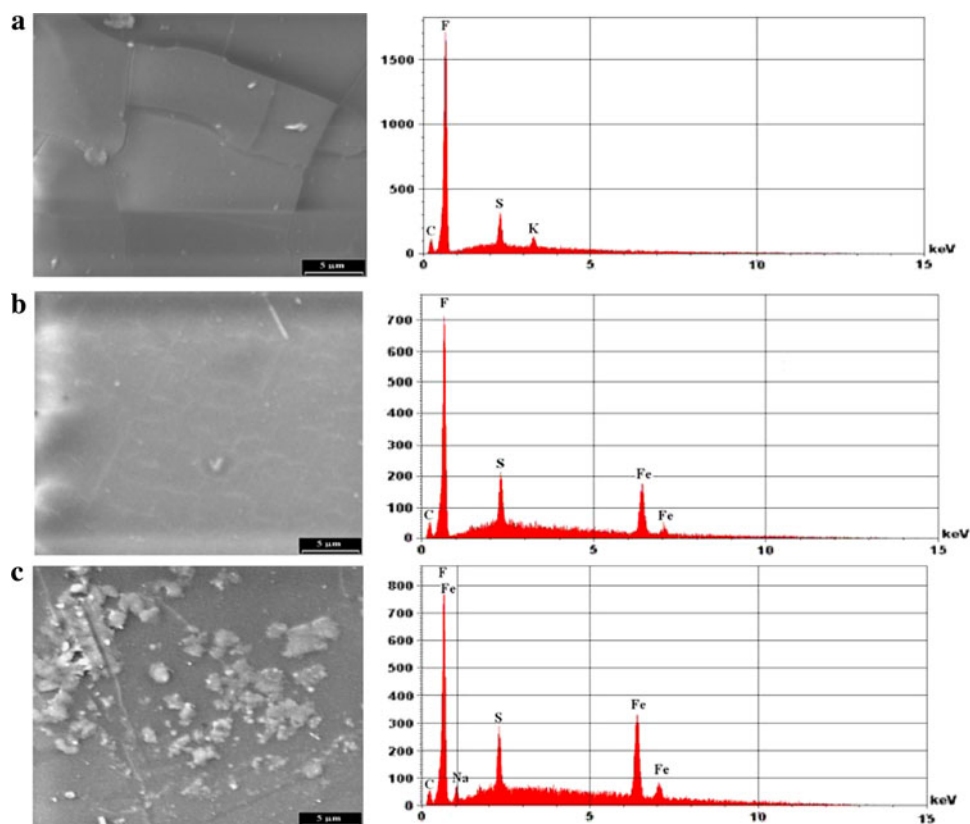
SEM images of the Nafion membrane before and after ion exchange (see Figs. 2a, b), indicate similar appearance; however, elemental analysis shows the presence of iron on the exchanged membrane. After the alkaline rinse (Fig. 2c), deposit formation was observed revealing clusters distributed over the surface of the polymer and EDS

analysis confirmed the presence of Fe in the membrane. In the case of the amberlite and purolite resins, SEM images are similar to those obtained for the Nafion membranes so that there is no difference in the superficial appearance before (Figs. 3a, d) and after (Fig. 3b, e) ion-exchange. Resins with alkaline treatment (Fig. 3c, f) also show the formation of a precipitate that corresponds to an iron containing compound as revealed by EDS analysis (results not shown).

3.2 Iron loading

In order to determine the amount of iron loaded on the different supporting materials, the supports were digested (after loading) and the quantity of iron measured by ICP. In the case of Nafion membranes, the iron loading increase exponentially between 0 and $2,175 \text{ mg L}^{-1}$ of FeCl_3 where a maximum value is reached (45 mg of iron/kg of membrane). On the other hand, the iron loading curves in the case of the resins indicate that the quantity of supported iron increases exponentially between 0 and $33,000 \text{ mg L}^{-1}$ for FeCl_3 and later shows a tendency to reach a constant value (65 mg of iron/kg of resin). The obtained results at the iron saturation conditions (see experimental part and Fig. 4) show that all the studied supporting materials are capable of fixing significant amounts of iron in the range of 46 and 65 mg Fe/g of substrate. The best results were obtained for the two resins under study for which 65 mg/g of substrate can be anchored. In the case of the Nafion membrane on the other hand, the iron loaded corresponds to 46 mg/g substrate. In this way, we observed that the resins can fix more than 30% of iron than the Nafion membranes at significant lower cost, so the possibility of

Fig. 2 SEM micrographs and EDS analysis for **a** the Nafion membrane, **b** membrane exchanged with a 0.075 mm solution of FeCl_3 , **c** membrane exchanged with a 0.075 mm solution of FeCl_3 and rinsed with NaOH 1 N



using these materials in heterogeneous Fenton process is promising. When the alkaline rinse is applied to the supports on the other hand, the values of loaded iron in the material do not vary significantly; in the case of the amberlite resin however there is a decrease in the iron content after the rinsing that may be due to Na substitution of iron.

According to the obtained results, the iron concentration used for the preparation of the membrane for the degradation test was $2,175 \text{ mg L}^{-1}$ in the case of the Nafion membrane and $47,250 \text{ mg L}^{-1}$ in the case of the resins. In this context, it is important to point out that Kiwi et al. [21] conducted a study on Nafion membranes and found that the iron supported corresponds to 1.78% by mass. In the case of this study, we obtained 4.6% by mass, i.e., 2.6 times the value reported in the above mentioned work. The difference is probably due to the use of more concentrated iron ion solutions.

3.3 Iron desorption tests

The results presented in Fig. 5 indicate that more stable iron adsorption conditions are achieved when purolite resin is employed in comparison with the other two supports under study. In this way, the iron concentration in the desorption solution is 1.1 mg L^{-1} for purolite resin, compared to 4.8

for amberlite and 4.7 mg L^{-1} for the Nafion membrane. Considering the initial iron loading values, the purolite resin retains 98% of the iron, while the amberlite and the Nafion membrane preserve 93 and 90%, respectively. On the other hand, and following previous reports by Kiwi et al. [21] we carried an alkaline preparation treatment of the supporting material as described in Sect. 2. In this way, and consistently with the reported observations, we found that alkaline rinsing reduces the release of iron from the support to the solution, particularly in the case of the amberlite resin where the concentration decreases to 2 mg L^{-1} and for the Nafion membrane where the corresponding value reaches 1.92 mg L^{-1} . In the case of the purolite resin there was no significant change. The obtained results clearly indicate that alkaline rinsing improves the iron retention properties, so the degradation of the dye was evaluated using iron supported on materials previously treated with the alkali. Although the mechanism by which the alkaline treatment results in a stronger retained Fe species is unclear, it is possible to speculate that basic salts of iron have smaller solubility constants that stabilize the Fe attached to the supporting surface. In any case, the mechanism as well as detailed studies of the nature and stability of the iron based active species are currently under study in our laboratory and will be the subject of a further coming communication.

Fig. 3 SEM micrographs and EDS analysis for **a** amberlite IR-120 resin, **b** exchanged with 15 mM of FeCl₃ solution, **c** exchanged with 15 mM of FeCl₃ solution and rinsed with NaOH 1 N, **d** purolite C-100 resin, **e** exchanged with a 15 mM solution of FeCl₃, **f** exchanged with 15 mM of FeCl₃ solution and rinsed with NaOH

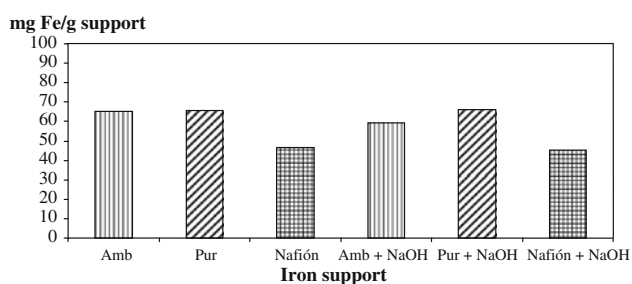
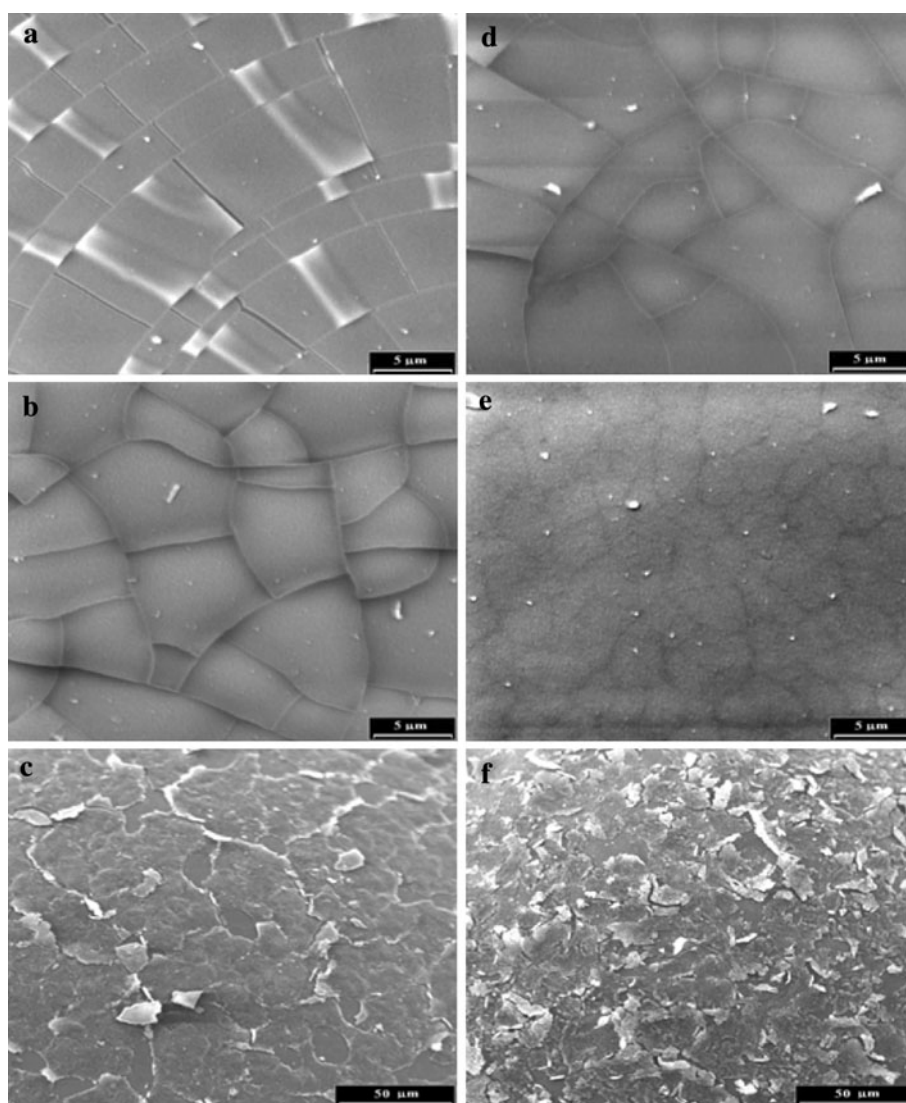


Fig. 4 Quantity of iron exchanged on Nafion membrane and resins. Contact time 30 min

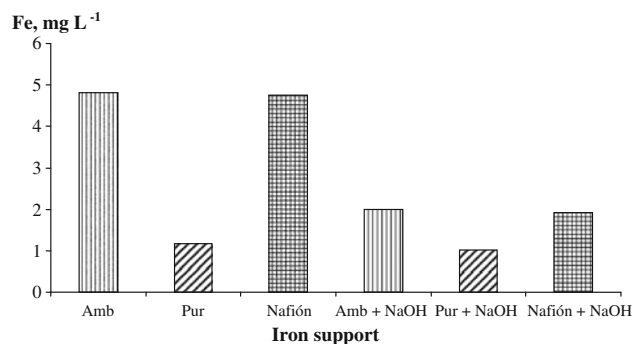


Fig. 5 Desorption iron tests using the Nafion membrane and resins with and without alkaline rinsing. V = 400 mL, pH 3, sulfate buffer, t = 60 min

3.4 Degradation of Orange II

Orange II degradation experiments were carried out in order to test if the supported iron could efficiently work in a Fenton based system for water treatment. These

experiments were therefore performed in the absence of iron ions in solution using the experimental system shown in Fig. 1. Figure 6 shows the spectra of 20 mg L⁻¹ Orange

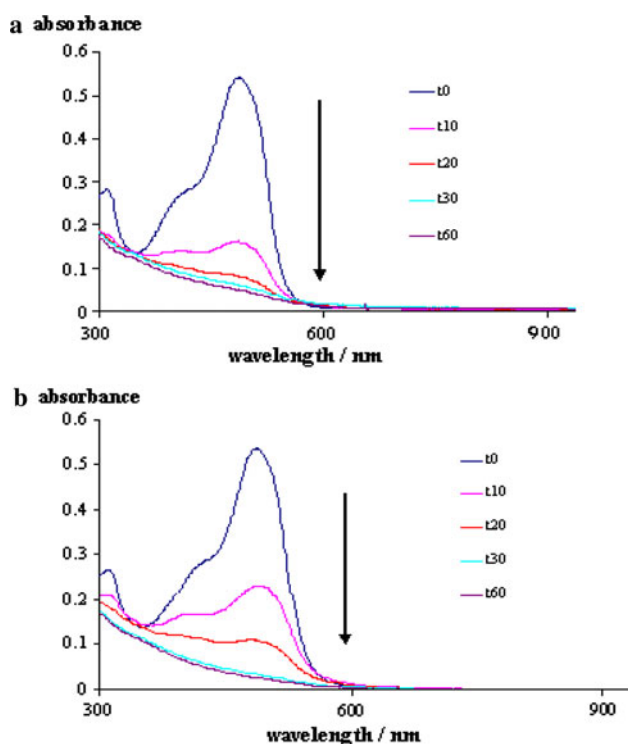
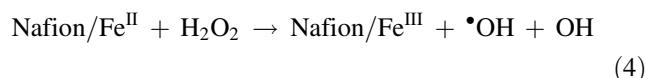


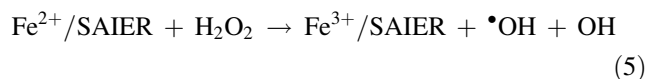
Fig. 6 Spectra of 20 mg L⁻¹ Orange II solution as a function of time applying photo-electro-Fenton process using iron supports. **a** Purolite resin, **b** Nafion membrane. Sulfate buffer pH 3, 150 min of polarization, 60 min of degradation and applied current of 100 mA ($t_0 = 0$ min, $t_{10} = 10$ min, $t_{20} = 20$ min, $t_{30} = 30$ min, $t_{60} = 60$ min)

II solutions at different reaction times applying the photo-electro-Fenton process in the presence of (a) purolite resin treated with NaOH and (b) Nafion membrane also rinsed with NaOH. In the case of the resin, the absorption peak associated to the azo bond at 487 nm decreases rapidly during the first 10 and at 20 min, it virtually disappears. When the Nafion membrane is used, while the loss of color is a bit slower compared to that obtained with the resin, at 30 min the absorption peak has disappeared. In both cases, the photo-electro-Fenton process is efficient for the removal of color indicating that the iron on the supports is available for the reaction with hydrogen peroxide to generate free radicals according to reaction (1). It is important to note that the quantities of Fe in both systems were not equivalent (there are 3.6 times more iron in the resin than in the membrane) and therefore, these experiments only show that the anchored iron is active for the photo-electro-Fenton process in Nafion as well as in the resins studied.

As we assume for the materials considered in this study, Kiwi et al. [21] proposed a mechanism for the photo-Fenton process using Nafion membranes as iron support. According to this mechanism, the process can be described by reaction (4),



In the same way, Feng et al. [6] suggested a similar mechanism for resin support materials in a photo-assisted Fenton system (reaction (5)),



where SAIER = Strongly acid ion exchange resin.

In both cases, membrane and resins, the iron supported in the supporting surface reacts with the hydrogen peroxide in the solution to generate hydroxyl radicals that eventually oxidize the dye in solution.

Comparing the results obtained in this work with those of previous studies carried out in our group using homogeneous Photo-electro-Fenton processes [41] it is possible to observe similar results with equivalent quantities of iron (in these experiments we obtained decolorization of a 50 mg L⁻¹ solution of Orange using 0.2 and 0.5 mM concentration of iron, equivalent to 13.7 and 27.5 mg L⁻¹). When the membrane and purolite resins are used, the equivalent concentrations of iron, if dissolved in the liquid, are 12 and 43 mg L⁻¹). This suggests that activity, as far as the photo-electro-Fenton reaction of the iron supported on the membrane and the resins, is of the same order of magnitude than that of iron ions in solution as previously tested in our group [41].

To verify the mineralization of the dye, Total Organic Carbon was determined for the same samples studied by UV-vis spectroscopy (Fig. 7). The best results were obtained when the amberlite resin is used in the reactor, since TOC values decreased to levels close to 60%. In the case of the purolite resin and Nafion membranes, TOC removal achieved 45 and 25% respectively. According to these results, the photo-electro-Fenton process can be carried out using iron supported on resins and membrane removing the color completely and obtaining a partial mineralization of the dye.

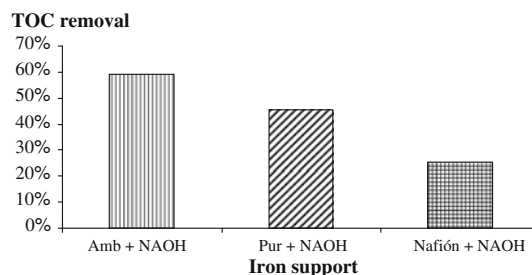


Fig. 7 Removal of TOC using photo-electro-Fenton processes and different iron supports after 60 min. 20 mg L⁻¹ Orange II solution sulfate buffer pH 3, 150 min of polarization, 60 min of degradation and applied current of 100 mA

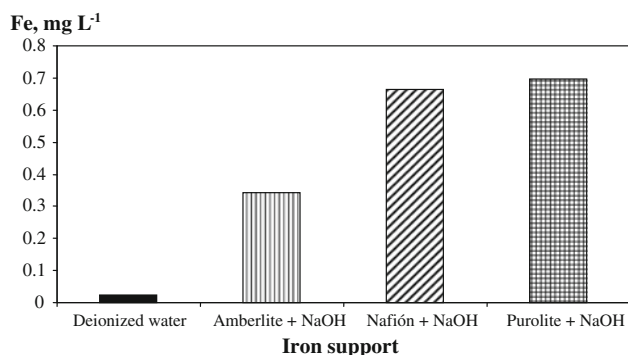


Fig. 8 Iron concentration in the solution after the photoelectrochemical treatment

3.5 Determination of iron concentration in the solution

After assessing the capability of the catalysts for the removal of Orange II, samples were taken from the reactor after 60 min of treatment and analyzed using ICP to determine the concentration of Fe in the effluent. Figure 8 shows the results of iron concentrations in the solution indicating that in all cases iron concentration is less than 0.7 mg L^{-1} . The amberlite rinsed with NaOH is the best support due to the fact that the iron concentration in the solution (0.3 mg L^{-1}) is the smallest of all. Calculation of the iron retained in the supports, showed that while in the case of both resins 98% of the iron loaded was maintained after the photo-electrochemical treatment was carried out, in the membrane the percentage achieved was 94%; a value that is similar to those obtained in the previously discussed desorption tests. In the context of these results it is interesting to note that Feng et al. studied the photo-Fenton degradation of salicylic acid using ion exchange resins; detecting approximately 1.2 mg L^{-1} in the treated solution [2]. Comparing these results with those obtained in this investigation, it is possible to suggest that the treatment applied to the resin causes a smaller desorption of Fe towards the aqueous solution.

On the basis of all the experiments performed, the best support to fix iron is the purolite resin since this species retains most of the iron loaded, providing at the same time a larger efficiency for the decolorization and TOC removal processes of a model Orange II dye solution. Considering the price of the support materials and the quantity used in these experiments, the difference is noteworthy. While the cost of the Nafion membrane is US\$29, the corresponding costs of the amberlite and purolite resins are US\$ 0.55 and US\$ 0.02, respectively.

4 Conclusions

It is possible to fix Fe on Nafion membranes, amberlite and purolite ion exchange resins. The rinsing with NaOH

causes the precipitation of an iron compound on the surface, providing more stability towards desorption. The photo-electro-Fenton experiments indicate that supported iron undertakes Fenton reaction so that the color can be completely removed from an Orange II solution. In the case of TOC measurements, the removal is only 60% under the experimental conditions employed. According to these results, the best support is the purolite resin due to the combined efficiency of the degradation process and low cost.

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