Research Article

Catalytic Activity of Porous Phosphate Heterostructures-Fe towards Reactive Black 5 Degradation

Marco S. Lucas, 1 Manuel Algarra, 2 José Jiménez-Jiménez, 3 Enrique Rodríguez-Castellón, 3 and José A. Peres 1

1 Centro de Química de Vila Real, Universidade de Trás-os-Montes e Alto Douro, Apartado 1013, 5001-801 Vila Real, Portugal
2 Centro de Geologia do Porto, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre 687, 4169-007 Porto, Portugal
3 Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Málaga, 29071 Málaga, Spain

Correspondence should be addressed to Marco S. Lucas; mlucas@utad.pt

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Fenton’s reaction is often used to decompose stable substances in wastewater. In this study, experiments based on the effect of porous phosphate heterostructures as catalyst sorbent of Fe$^{2+}$ synthesised by different procedures were planned. The examined PPH-Fe/H$_2$O$_2$ as oxidant in a heterogeneous process under mild conditions at pH 5 was found to be very efficient for decolorization of a simulated wastewater containing 50 mg L$^{-1}$ of a commercial azo dye ( Reactive Black 5) reaching 95% of decolorization. Under the described conditions total visual decolourization was achieved after 360 min. This study can provide a simple, effective, and economic system ideal for the treatment of toxic and nonbiodegradable azo dyes.

1. Introduction

Synthetic dyes are extensively used for textile dyeing, paper printing, color photography, and as additives in petroleum products [1]. In the textile manufacturing industry, up to 10–25% of the dyes are lost after the dyeing process and about 2–20% of them are directly discharged to the aqueous effluents in different environmental components [2]. Azo and triphenylmethane dyes are primarily produced and used in the textile industry and cause pollution if not properly treated before discharge to the environment [3, 4]. In this context, the textile industry is concerned with these xenobiotics compounds to improve the existing technologies to treat the dye containing wastewater, because they pose lethal, mutagenicity, genotoxicity, and carcinogenicity effects [5].

Conventional treatment processes have long been established such as chemical precipitation, coagulation, adsorption, and flocculation [6], but they have their own disadvantages, mainly used for insoluble dyestuff wastewater. Bioremediation techniques are considered unsatisfactorily because they need further processes. The chemical methods are based in the oxidation of the organic materials by oxidizing agents, such as O$_3$ [7–9], H$_2$O$_2$ [10, 11], UV light [12], or combination of such oxidants [13, 14], known as advanced oxidation processes (AOPs).

Among these, the Fenton reaction, iron-based photocatalytic systems via hydroxyl radicals produced by H$_2$O$_2$ under UV, has attracted much attention for wastewater treatments because of their efficient, low cost, and benignity to environment [15, 16]. This catalytic system decolourizes completely and partially mineralized textile dyes in short reaction time [17]. Common Fenton processes involve the application of ferrous or ferric salts and hydrogen peroxide in order to produce hydroxyl radicals (HO$^\cdot$). However, despite the high efficiency, the process generates a high amount of sludge in the coagulation step for the elimination of the iron added. For this reason, in the last years, an important effort has been done in the field of heterogeneous catalysis to facilitate the elimination and reuse of iron [18, 19].

Advanced oxidation processes (AOPs) have been developed in the last decades to environmental applications, mainly focused on the removing by mineralization of refractory organic compounds. For this, Fenton reaction catalysed by Fe$^{2+}$ is used with hydrogen peroxide as oxidizing agent and
for photo-Fenton process with the UV irradiation. Normally, Fenton and photo-Fenton are homogeneous processes where Fe$^{2+}$ cations are in solution; however some limitations related with the eventually precipitation of insoluble ferric hydroxides, which require an acidification of solution and by their use the materials of reactor must be resistant to corrosion. Furthermore, in homogeneous processes, an additional step of separation must be made for recovering the catalyst. Because of these limitations heterogeneous catalyst can be an alternative, and several solid catalysts which incorporate Fe$^{2+}$ are tested in Fenton or photo-Fenton reactions. Thus, has been tested as heterogeneous catalyst iron-containing zeolites [20], clay pillared by Fe hydroxos complexes or by Fe$^{2+}$ cationic exchange, or wet impregnation with a Fe$^{2+}$ solution of an adequate support.

On the other hand, porous phosphate heterostructures (PPH) are a new kind of versatile porous materials, which are application as catalyst and sorbent. The synthesis of this material combines the methodologies of pillared layered structures (PLS) and silica mesostructured with surfactant as MCM-41 type. Thus, into interlayer space of zirconium phosphate, silica galleries are formed using surfactant molecules as templates. After surfactant removing a mesoporous material is obtained with high specific area (600 m$^2$ g$^{-1}$) and a cationic exchange capacity (CEC) of surface 1.7 meq g$^{-1}$ due to the presence of PO-H and SiO-H surface groups [21]. Because of these properties, this material has been tested as solid acid catalyst and as support of metallic species as Ru or Cu in the synthesis of catalysts [22, 23]. Also, hybrid PPH are also synthesized adding an organosilane derivate together with tetraethyl orthosilicate (TEOS) as silica precursor. Thus, propionitrile, aminopropyl, or mercaptopropyl groups are incorporated on the surface of silica galleries, and surface chemical and physics properties can be modified for specific applications [24–31]. In this line, mercaptopropyl groups can be oxidized to sulfonic acid increasing the acidity and CEC [27].

High specific surface area and CEC are two parameters interesting for the synthesis of Fe$^{2+}$ exchanged PPH or Fe$^{2+}$ supported PPH as well PPH pure silica or a hybrid sulfonic-PPH obtained by oxidation of the respective mercaptopropyl-PPH precursor, obtaining new materials with potential use as heterogeneous catalyst for Fenton and photo-Fenton reactions.

In the present work, Fe$^{2+}$-PPH materials were synthesized by different procedures, and the decolorization of Reactive Black 5, a textile azo dye, was achieved by means of heterogeneous Fenton reagent process. Colour and iron leaching were followed along experiments.

2. Experimental

2.1. Materials. Azo dye Reactive Black 5 (RB5, CI 20505) was obtained from Dystar Anilinas Texteis Lda (Portugal) and used without any further purification. H$_2$O$_2$ (Perhydrol, 30% w/w) and FeSO$_4$·7H$_2$O were purchased from Merck (Darmstadt, Germany) and Sigma-Aldrich Spain, respectively, and other chemicals were at least analytical grade reagents. Solutions were prepared by dissolving the dye in deionized Millipore water accordingly to desired final concentrations (w/v). The pH was monitored in initial and treated samples (Denver Instrument Company).

2.2. Preparation of the Catalyst. Porous phosphate heterostructures (PPH) were synthesized according to previously reported procedures [21]. Thus, to a solution of CTMA-Br in 1-propanol and H$_3$PO$_4$ (85%), zirconium(IV) propoxide (70%) is added with a respective molar ratio CTMA-Br:H$_3$PO$_4$:Zr-Pr 1.5:1:0.5. After 3 days under stirring, the obtained cetyltrimethylammonium-ZrP (CTMAZrP) was centrifuged and washed three times with 1-propanol and suspended in water (10 L$^{-1}$). Next, a solution of hexadecylamine in 1-propanol (35 g L$^{-1}$) was added as a cosurfactant. After one day of stirring, a solution (50%, v/v in 1-propanol) of tetraethylorthosilicate (TEOS) is added. After three days under stirring the solid is recovered by filtration, washed three times with deionised water, and dried 1 day at 60°C in air. The solid was calcined at 550°C for 5 hours (1.5 K min$^{-1}$ heating rate) and PPH is obtained.

Hybrid S-PPH was obtained by a similar process [25], but mercaptopropyltrimethoxysilane (MPTMS) was added together with TEOS at 5:1 TEOS:MPTMS molar ratio. In this case, it is not possible to remove surfactant molecules by calcination, and an acid extraction was carried out with an HCl: ethanol solution (1:10 v/v). To oxidize thiol group to sulfonate, S-PPH (1 g) was suspended in methanol (10 mL), and H$_2$O$_2$ (33%, 1 mL) was added. After 1 day under stirring, the solid is filtered and washed with water, ether and acidified with a solution of H$_2$SO$_4$ 0.2 M [27]. The solid is dried in air at 60°C, and SO$_3$-PPH is obtained. Thus, with the incorporation of sulfonic acid on the surface of silica galleries, the CEC is increased from 1.7 to 3.10 meq g$^{-1}$ for PPH. Fe exchanged materials were obtained by adding PPH and SO$_3$-PPH to an adequate volume of solution, which contains 10 times the respective CEC. The solid was washed three times with deionised water and dried in air at 60°C. These solids were named Fe-PPH (exc) and FeSO$_3$-PPH (exc), respectively. Fe impregnated PPH material, PPH-Fe (imp), was prepared by wet incipient impregnation of the PPH support using an aqueous solution FeCl$_2$ (0.2 M) which contains 2 times the CEC. After impregnation the sample was dried at 60°C in air.

2.3. Fenton's Reagent Experiments. Batch experiments for Fenton oxidation were performed in a cylindrical borosilicate glass reactor of 800 mL of capacity, with sampling ports at the top. The reaction temperature was kept at the desired value within ±5°C using a thermostatically controlled outer water jacket. For every experiment performed, the reactor was initially loaded with PPH (1g L$^{-1}$) and 500 mL of RB5 (50 mg L$^{-1}$) aqueous solution, and continuous mixing was maintained by means of a magnetic stirrer. In all experiments necessary quantities of freshly RB5 and H$_2$O$_2$ (2 × 10$^{-3}$ M) were prepared from stock solutions. Experiments were carried out, at an initial pH 5 because the nonbuffered solutions used in the reaction of Fenton suffer a pH decrease during the reaction time to a pH range around 3–4 [23]. Absorbance readings at visible maximum peak (λ$_{max}$ = 595 nm) were
Figure 1: N\textsubscript{2} adsorption-desorption isotherms at 77 K: (a) Fe-PPH (exc), (b) FeSO\textsubscript{3}-PPH (exc), and (c) PPH-Fe (imp).
and due to the small size or amorphous structure, no sharp diffraction peaks are produced (see Supplementary Information in Supplementary Material available online at http://dx.doi.org/10.1155/2013/658231).

Table 1: Textural parameters of the different substrate used in RB5 decolourization.

<table>
<thead>
<tr>
<th>Material</th>
<th>$d_{001}$ (Å)</th>
<th>$S_{BET}$ (m$^2$ g$^{-1}$)</th>
<th>$V_p$ * (cm$^3$ g$^{-1}$)</th>
<th>$d_p$ * (Å)</th>
<th>mmol Fe g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeSO$_3$-PPH (exc)</td>
<td>42</td>
<td>372</td>
<td>0.448</td>
<td>28.9</td>
<td>1.39</td>
</tr>
<tr>
<td>Fe-PPH (exc)</td>
<td>40</td>
<td>490</td>
<td>0.610</td>
<td>37.3</td>
<td>0.8</td>
</tr>
<tr>
<td>PPH-Fe (imp)</td>
<td>40</td>
<td>462</td>
<td>0.677</td>
<td>114</td>
<td>1.17</td>
</tr>
</tbody>
</table>

*Porous volume and porous diameter using Cranston and Inkleym method.

3.2. The Fenton Process in the Decolourization of RB5. Figure 2 presents the results obtained with the Fenton's reaction in the experiments using as source of iron three PPH catalysts. FeSO$_3$-PPH (exc) and Fe-PPH (exc) revealed to be ineffective in promoting the Fenton process. The decolourization achieved with these two PPH catalysts was small, 15.3 and 20.8%, respectively. This can be explained by the low iron available to catalyse the generation of hydroxyl radicals and consequently decolourize the RB5 solution. For other side, PPH-Fe (imp) showed an excellent capacity to catalyse the production of hydroxyl radicals. This PPH catalyst allowed reaching an RB5 decolourization of 95%, for the same reaction time, 360 minutes.

The mechanism of reaction can be described as presented in Figure 3. The iron present in the PPH-Fe (imp) structure (Fe$^{2+}$) reacts with the H$_2$O$_2$ to generate HO$^\cdot$ radicals, which will break the azo bonds (–N=N–) and promote the RB5 decolourization.

Figure 4 presents the UV-Vis spectra and the RB5 colour evolution along the Fenton experiment with the PPH-Fe (imp) catalyst. The RB5 UV-Vis spectra ($t = 0$) consist in two main characteristic absorption bands: one in the UV region (at 310 nm) and other in the visible region, at 595 nm.

The UV band is characteristic of two adjacent rings, whereas the visible band is owing to long conjugated $\pi$ system linked by two azo groups [32]. The RB5 decolourization spectra show that the intensity of the visible band (at 595 nm) starts to decrease faster. The UV band (at 310 nm) also vanishes but at a lower rate than the visible band. Thus, the spectra suggest that HO$^\cdot$ radicals generated first attacks azo groups, through transfer of one electron, and open the –N=N– bonds, destructing the long conjugated $\pi$ systems and degrading it efficiently.

Afterwards, the aromatic rings elimination also took place but needs a relative longer period of time [33]. From Figures 4(a) and 4(b) it is also possible to observe a fast color disappearance in the first minutes. This behavior reveals that iron is available to react with hydrogen peroxide as long as the experiment started, taking into account that any adsorption step was performed before Fenton's experiment, H$_2$O$_2$ and Fe$^{2+}$ generating hydroxyl radicals immediately, when Fe$^{3+}$ belongs to the PPH structure. Thus, it is possible to assume that Fenton's process starts without any iron leaching from PPH catalyst. Nonetheless, the concentration of Fe in solution was monitored at the end of each Fenton's process.

The experiment performed with FeSO$_3$-PPH (exc) revealed an iron concentration of 0.81 mg Fe L$^{-1}$, the Fe-PPH (exc) 1.58 mg Fe L$^{-1}$ and the PPH-Fe (imp) 4.92 mg Fe L$^{-1}$, after a reaction time of 360 minutes. Therefore, although apparently at the beginning of each experiment iron is linked to the PPH, throughout the Fenton's experiment its leaching occurs and influences the RB5 color removal. Moreover, the highest RB5 decolourization occurs precisely with the PPH catalyst that releases more iron to the solution, PPH-Fe (imp).
Figure 3: Mechanistic representation of reactions possible involved in heterogeneous Fenton-like catalysed by Fe-PPH.

presented the best results regarding RB5 decolourization, although its application as iron source did not avoid the presence of iron on the final treated solution.

4. Conclusions

In summary, PPH revealed to be useful as Fe$^{2+}$ support in the Reactive Black 5 decolourization through Fenton reagent, although PPH ability to promote a heterogeneous Fenton reaction without iron leachate, under the experimental conditions used, seems to be inefficient. In order to overcome the drawback of the fixation of Fe$^{3+}$ onto PPH supports avoiding the iron leaks, subsequent studies are planned to improve the system proposed to be applicable to water treatment.

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