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Immobilization of active and stable goethite coated-films by a dip-coating process and its application for photo-Fenton systems

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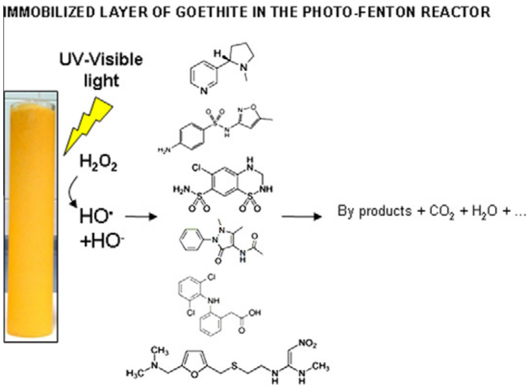
HIGHLIGHTS

- Immobilization of a goethite catalyst by a dip-coating procedure.
- Resistant and stable catalyst layers for photo-Fenton processes.
- Activity comparable with that of powder goethite in slurry photo-reactors.
- Degradation and partial mineralization of pharmaceuticals in complex aqueous mixtures.

GRAPHICAL ABSTRACT



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ABSTRACT

The immobilization of active photo-Fenton heterogeneous catalysts over different materials, mainly polymers, has been studied in the literature to avoid their separation from the reaction solution. However, those materials exhibited a high preparation cost and low stability in the process, being difficult their application in an industrial wastewater treatment plant. In this work, a dip-coating method for the immobilization of goethite film on the wall of a photo-Fenton reactor was studied. The influence of the concentration of the initial goethite suspension as well as the withdrawal speed on the coating process, were evaluated. Both variables have shown to be critical in the homogeneity and the optical properties of the layer and therefore in its activity in the photo-assisted reaction.

The immobilized photo-Fenton system was tested in the degradation of a mixture of six selected pharmaceutical compounds (nicotine, 4-acetamidoantipyrine, hydrochlorothiazide, ranitidine, diclofenac sodium and sulfamethoxazole) in aqueous solution. The influence of the goethite layer thickness in the photo-activity of the system was established and the results were compared with those obtained using goethite powder in a slurry photo-reactor. One coating cycle, corresponding to 0.05 g/L of catalyst was enough to obtain 100% degradation of the selected pharmaceutical compounds after 6 h of reaction using a low oxidant concentration, except for the nicotine, that seems to be refractory to the tested photo-Fenton system. The use of a commercial goethite as catalyst and the simplicity of the dip-coating procedure make this process an attractive alternative for the design of wastewater treatments based on the heterogeneous photo-Fenton reaction.

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1. Introduction

The immobilization of photo-Fenton active species over heterogeneous matrices has been extensively studied in order to overcome the recovery of the homogeneous iron ions that involves precipitation and re-dissolution techniques with the additional operational costs. On the one hand, the deposition of iron species supported over different materials (zeolites, clays, silicas, carbon nanotubes, etc.) has been widely reported in the literature as photo-Fenton like heterogeneous catalysts for the degradation of a variety of pollutants in aqueous solutions [1–5]. Nevertheless, those catalysts are usually employed as powders, being necessary an appropriate catalyst recovering process after the treatment, such as sedimentation or filtration units, for an industrial application.

On the other hand, a different approach is the preparation of active photo-Fenton catalysts immobilized over different materials such as glass or polymers, from which stable coating films can be made. The benefit of this alternative is that the separation of the catalyst from the reaction solution is not needed after the treatment. Fe exchange Nafion polymers were one of the first immobilized photo-Fenton catalysts used as films or polymer beads packed in a fixed bed reactor in the degradation of different azo dyes [6,7]. However, those materials exhibited a relatively low activity and a high preparation cost, which made difficult their application in an industrial wastewater treatment plant. Parra et al. reported a novel Fe/Nafion film with superior performance in terms of activity and stability for the photo-Fenton degradation of 4-chlorophenol, than those obtained using the commercial Dupont 117 Nafion/Fe film. However, the high cost of these catalysts seems to be the remaining problem. [8,9].

In order to overcome the high cost of immobilized catalysts originally employed, another alternative has been recently proposed in the literature regarding to the preparation of Fe supported over low cost polymers which can act similar to Nafion films for the photo-Fenton reactions. Thus, Dhananjeyan et al. anchored Fe_2O_3 and Fe^{3+} ions over a polyethylene block copolymer, obtaining a photo-Fenton catalyst with remarkable activity and stability for the degradation of 4-chlorophenol and azo-dye Orange II. In this case, the initial degradation rate was slightly lower than that obtained when using Fe_2O_3 powder [10]. More recently, functionalization of poly(acrylic acid)-poly(vinilydene fluoride) films with Fe^{2+} and nanoparticles of iron oxide was studied as photo-Fenton catalyst for the degradation of pentachlorophenol. The conversion of the organic pollutant hardly reached 27%, although it is higher than that obtained with a homogeneous Fe^{3+}/H_2O_2 system carried out under similar reaction conditions [11]. In all those cases however, the stability of the immobilized catalyst is a controversial issue due to the partial degradation of the polymeric film with dissolution of the iron species. In fact, the high catalytic activity of several Fe doped polypropylene and polyethylene films for the degradation of resorcinol has been recently attributed to the leaching of iron species due to the capacity of these films to release iron into the reaction medium [12].

Therefore, the preparation of inorganic coating films can be a better alternative in photo-Fenton systems. The inorganic films could be characterized by a higher stability than that reported for the polymeric catalysts under appropriate oxidant and acidic conditions for the photo-Fenton reaction. Additionally, they can be prepared following different techniques. Thus, Feng et al. developed a Fe-bentonite nanocomposite coated on the inner wall surface of a photo-reactor by a thermal sprayer technique, for the photo-Fenton treatment of azo-dyes [13]. In this case, the catalyst was cheaper than the Nafion films. Moreover, the Fe-bentonite coated film exhibited a remarkable activity and stability in the degradation of Orange II in aqueous solutions. In a similar approach, several authors prepared synthetic allophane-like materials coated with iron oxides, using a wet impregnating technique [14]. The stability of these materials as heterogeneous catalysts in Fenton-like reactions however, has not been yet investigated [15]. Another method widely studied in literature for the preparation of inorganic films for photocatalytic applications is the sol–gel dip coating technique using different precursors [16–19]. The dipping of an appropriate substrate (polymer, quartz, slime soda, silica, etc.) into the sol and its subsequent pulling up at an appropriate rate allows the deposition of the film onto the substrate surface. This process is optimal for producing highly uniform coatings, by a simple control of the thickness with the withdrawal speed from the coating solution. Moreover, there are several advantages as compared to other film-formation technologies, such as low process cost, high uniformity of the films and the possibility of varying the film properties by changing the composition of the solution. Van Grieken and co-workers proposed recently an alternative using a simple dip coating method for the immobilization of TiO_2 particles on a borosilicate glass wall of an annular photo-catalytic reactor for the disinfection of *Escherichia coli* from wastewater streams. In that case, a dispersion of Degussa P-25 was used as dipping solution instead of the preparation of a sol by partial hydrolysis and condensation of a titanium alkoxide as a precursor [20].

The aim of this work is focused on the optimization of the dip-coating method for the immobilization of goethite. This material is an interesting catalyst for a photo-Fenton system with major possibilities in the field of solar photo-Fenton reactions [21]. The use of a commercial goethite as an active phase for the photo-Fenton reaction is an economical alternative for those processes, whereas its immobilization over the wall of an annular reactor eliminates a further recovering step of the catalyst particles. Additionally, this method allows the preparation of a coating film made of 100% iron oxide, in contrast with those found in literature based on different polymeric films reported in literature, with iron loadings of i.e. 1.1–3.1% [9]. The activity and stability of the immobilized photo-Fenton system was evaluated for the degradation of a mixture of pharmaceutical compounds in aqueous solution as a test reaction. This kind of reaction was selected according to different criteria. First of all, pharmaceutical compounds are pollutants of growing interest due to their potential effect on the environment, leading to the inclusion of these chemicals among the so-called emerging pollutants [22]. Additionally, photo-Fenton systems, mainly with homogeneous catalysts, have been reported as effective methods for the elimination of these kind of compounds [23,24]. Finally, the influence of critical variables such as the mass of the goethite immobilized and the hydrogen peroxide concentration in the overall catalytic properties of this novel photo-Fenton system was studied.

2. Experimental

2.1. Chemicals

The goethite powder (α-FeOOH) was supplied by Chemical Products Manuel Riesgo S.A. with no further purification. Hydrogen peroxide (30% w/w) was supplied by Scharlab. Sulfamethoxazole, diclofenac sodium, hydrochlorothiazide, 4-acetamidoantipyrine (4-AAA), nicotine and ranitidine hydrochloride were Sigma reagents used as received.

2.2. Experimental photo-Fenton set-up

The experimental set-up for the photo-Fenton reactor was a batch-type annular reactor consisted of a vessel of 12 cm of