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Full Length Article

Magnetically-extractable hybrid of magnetite, mesoporous silica and titania for the photo-degradation of organic compounds in water

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ABSTRACT

This work addresses the development of a magnetically extractable magnetite-silica-titania photocatalyst to be applied in the degradation of organic compounds in water. MCM-41 silica was successfully deposited on magnetite, providing large surface area for anchoring of TiO_x species, and preventing thermally induced conversion of magnetite to hematite. A good correlation between the calculated values and amount of titania deposited on the silica-covered magnetite particles was obtained for a synthesis route involving the treatment of magnetite-silica in boiling ethanolic Ti-precursor solution. Photocatalytic activity in conversion of 4-chlorophenol could only be observed for compositions containing larger than ~50 wt% titania, whereas increasing the titania content did not significantly improve performance. Experiments carried out at pH ~ 3.0 and ~7.2 demonstrated the performance is relatively pH-independent. The structure activity-correlation of the materials is briefly discussed.

1. Introduction

The increasing diversity and concentration of toxic components in water resources requires efficient technology for purification. Several organic pollutants are persistent and not easily degraded through conventional bio-based methods [1–3]. Heterogeneous photocatalysis, utilizing slurries of titanium dioxide and UV radiation in aqueous media, has been demonstrated a very effective alternative technology [4]. Reactive oxygen species (*ros*) are formed by reaction of the photo-activated TiO_2-based photocatalyst with oxygen (reductively, yielding super-oxide anions), and water (oxidatively, yielding hydroxyl radicals), respectively. Once formed, *ros* convert organic substances to CO_2 and H_2O [3–5].

Until recently, difficulties in the separation of particulate photocatalysts through conventional methods (e.g. filtration and centrifugation) still have posed serious limitations on their application in large-scale chemical processes. Consequently, the full potential of their active surface area has not been fully exploited at industrial scales. In an attempt to solve such issue, magnetic titania-based particulate photocatalysts have been developed in the last decades, aiming the incorporation of magnetic properties to these photocatalysts to enable a practical and cost-effective strategy for particle retrieval and separation from slurries [6–11]. Core-shell structure materials proved to enable efficient particle separation, and different types of ferrites have been commonly used to constitute their cores because of their simple syntheses, low cost, low toxicity and controllable magnetic properties

Abbreviations: M, magnetite; *M(c)*, calcined magnetite; *S(c)*, calcined MCM-41 silica; *MS(c)*, calcined silica-coated magnetite; *MST-#*, magnetite-silica-titania composite containing # wt.% titania; *ST-60*, titania-coated silica containing 60 wt% titania; *MT-60*, titania-coated magnetite containing 60 wt% titania; *4-CP*, 4-chlorophenol; ros, reactive oxygen species; *ATR-FTIR*, attenuated total reflectance Fourier transform infrared spectroscopy; *XRD*, X-ray diffractometry; *XRF*, X-ray fluorescence; *SEM*, scanning electron microscopy; *EDX*, energy-dispersive X-ray spectroscopy; *CTAB*, cetyltrimethylammonium bromide; *TEM*, transmission electron microscopy; *TEOS*, tetraethylorthosilicate; *TIP*, titanium isopropoxide

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through doping with other elements [10,11].

Photocatalysts with titania deposited directly on ferrites present drawbacks related to photodissolution of the cores of such materials and the alteration of the electronic properties of titania, however these effects were effectively circumvented by the incorporation of an intermediary silica layer between the magnetic core and the titania layer in such materials [6,8–13]. Silica intermediary layer was also found to play a crucial role on the phase preservation of ferrite cores of the hybrid materials by not allowing them to convert to less magnetic iron oxides phases [6,10]. Despite the deposition of continuous silica has been commonly described, not much is reported on the use of mesoporous silica for magnetically-extractable photocatalysts, being the main interest in the application of mesoporous silica to increment significantly the surface area of the photocatalysts and therefore its photocatalytic efficiency.

This paper addresses the issue of separation/immobilization of the catalyst by the synthesis of a magnetite-silica-titania composite, allowing magnetic extraction of the particles from the liquid media. A mesoporous silica-based interface between titania and magnetite was deposited to prevent conversion of magnetite to hematite upon thermal treatment as well as the leaching of $Fe^{2+/3+}$ in solution, and at the same time to provide a high surface area (which for TiO_2 is typically less than 100 $m^2 g^{-1}$ [5]), potentially contributing to efficient generation of *ros* and pollutant conversion. MCM-41-type porous silica was employed to attain mesopores and surface areas higher than 1000 $m^2 g^{-1}$ [14]. A titania coating step, involving the treatment of magnetite-silica in boiling ethanolic precursor solution was developed, and the obtained materials were characterized through techniques such as ATR-FTIR, XRD, XRF, Raman spectroscopy, SEM, EDX, TEM and surface area measurements. 4-chlorophenol was used as a target substrate to evaluate the photocatalytic performance of the developed materials for the decomposition of recalcitrant organics. The effect of various process parameters was evaluated, such as pH, substrate concentration, and catalyst concentration.

2. Experimental

2.1. Synthesis of the mesoporous silica-covered magnetite

6.0 g of $FeCl_3$ (Sigma-Aldrich, 97%) was dissolved in 75.0 mL of dionized water. In another vessel, 6.0 g of $FeCl_2{\cdot}4H_2O$ (Sigma-Aldrich, > 99%) was dissolved in 35.0 mL of de-ionized water. Under nitrogen atmosphere, both solutions were mixed together into a 250 mL Erlenmeyer flask, and the final mixture was heated to 80 °C. Afterwards, 50.0 mL of NH_4OH (Dinâmica, 29%) was added and the mixture was kept agitated for 30 min using a magnetic stirrer. By applying a magnetic field (with the aid of a rare-earth magnet) at the bottom of the vessel for some minutes (from outside the flask), the magnetite could be easily decanted and retained inside the reaction vessel, while the supernatant was removed (the magnet should be as large as the bottom of the Erlenmeyer for an effective decantation). Approximately 100 mL of deionized water were added to the flask with magnetite, which was again stirred to remove residual reactants and then the magnetic decantation and retention of the magnetite were repeated. The washing step with deionized water was repeated two more times, and then the magnetite was stored in water, whose colloidal concentration was determined to 34.0 mg of magnetite per milliliter of solution. (Every time magnetite had to be synthesized, the colloidal concentration of the final mixture could be easily adjusted to the desired concentration by magnetically decanting the magnetite and removing or adding water to the flask). Part of the synthesized magnetite was calcined at 600 °C for 4 h. The bare magnetite and the calcined magnetite are named throughout the text as *M* and *M(c)*, respectively. The silica-covered magnetite particles were prepared in a mixture containing 200.0 mL of NH_4OH (29% w/w) and 250.0 mL of deionized water, to which 2.0 g of cetyltrimethylammonium bromide (*CTAB*) was added. The mixture was kept under agitation at 30 °C until complete dissolution of the surfactant. Afterwards, 20.0 mL of the magnetite colloidal solution were added to the reaction mixture, followed by 10.0 mL of tetraethylorthosilicate (*TEOS*) (Sigma-Aldrich, > 99%). The mixture underwent agitation for 2 h, and then was filtered through a Büchner funnel. The reaction produced a grey powder, which was stored in a heated chamber at 45 °C overnight to remove the solvent. The dry material was softly minced and then was also calcined at 600 °C for 4 h. Bare silica was synthesized and calcined following the same steps, except that 270 mL of deionized water were used, and the addition of the magnetite solution was omitted. As the calcination step may cause the condensation of surface silanol groups, hydration was carried out by agitating 5 g of the silica-based materials in 100 mL of deionized water under reflux at ~100 °C (boiling water) for 4 h. Afterwards the materials were dried at 70 °C overnight to remove excess of water. The materials produced in this step are called *S(c)* and *MS(c)* for the calcined silica and the magnetite-silica hybrid, respectively.

2.2. Titania coating through ethanol boiling

The material *MS(c)* had its surface activated at 105 °C in a drying oven for one hour at room pressure. Then 1.20 g was transferred to a beaker containing 80 mL of absolute ethanol (AA Chemie B.V., 99.8%). The mixture was heated up to mild boiling (~80 °C) under magnetic agitation, and as soon as the solvent started to boil, a certain volume of titanium isopropoxide (*TIP*) (Sigma-Aldrich, 97%) was added. Heating was provided up to complete dryness of the mixture and a slurry was formed nearly at the end of the drying process, which required it to be manually revolved with the aid of a glass stick. Much care had to be taken at this point, once the mixture started 'popping', with evolution of a white gas. The obtained dry materials were softly milled and then taken to a calcination oven, in which they were calcined at 500 °C for 4 h. The volumes of *TIP* evaluated in this study were 0.70, 3.50, 5.26, 7.00 and 14.0 mL, which stoichiometrically should provide approximately 13, 43, 53, 60 and 75% in mass (considering that all the *IPT* was converted to titania, and that all the titania was deposited as a layer over the *MS(c)* particles). These values will be used to refer to the materials along this work as follows *MST-13*, *MST-43*, *MST-53*, *MST-60* and *MST-75*. Finally, a selection of the most efficiently magnetically-extractable particles was carried out prior to the degradation experiments, which consisted of stirring the materials in a NaOH solution at pH 10 for 5 h (1.7 g in 100 mL) and collecting the particles with the aid of a large rare-earth magnet wrapped in solution-impermeable plastic (the magnet was kept in the mixture for 10 min without stirring), and discarding the non-retained particles that remained in the mixture. After the stirring step with NaOH solution just mentioned, the material was also dispersed in deionized water and recollected with the magnet during 10 min in the same way as just described. This step was carried out a couple of times, and the particles not attached to the magnet within the established extraction time were discarded as well. Such process was carried out until there were virtually no particles dispersed in the aqueous medium after a treatment-time of 10 min. The reason for stirring the material with NaOH solution at pH 10 was to promote the disaggregation of clusters by charging their surfaces negatively. Alternatively, in order assess the contribution of each constituent of the composites in the degradation process, the route to obtain the material *MST-60* was also directly applied to bare magnetite (*M*) and to the bare mesoporous silica [*S(c)*] as precursor materials [in contrast to *MS(c)*] to obtain, respectively, the materials *MT-60* and *ST-60*, which also had their performances evaluated in terms of their initial degradation rates, for comparison.

2.3. Characterization of the materials

Infrared spectra of the samples were collected through ATR mode in a *Perkin Elmer Spectrum 100 series spectrometer* at a resolution of 4 cm^{-1}.

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