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Magnetic diatomite(Kieselguhr)/Fe_2O_3/TiO_2 composite as an efficient photo-Fenton system for dye degradation

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ABSTRACT

We explored the potential use of diatomite/Fe_2O_3/TiO_2 composites as catalysts for heterogeneous photo-Fenton degradation of methylene blue under neutral pH. Such system consists in magnetic solids synthesized by co-precipitation with Fe^{2+}/Fe^{3+} in the presence of diatomite, followed by impregnation of TiO_2. The results showed that the optimal amount of the catalyst was 2.0 g L^{-1}, since aggregation phenomena become significant above this concentration, which decreases the photodegradation activity. The catalyst is highly efficient in the degradation of methylene blue and shows an easy recovery by an external magnetic field. This allows for an effective catalyst reuse without significant loss of activity in catalytic cycles, which is a highly interesting prospect for recyclable dye degradation systems.

1. Introduction

Ever-growing dye emissions from textile, cosmetics and food industries have become a major source of water pollution worldwide. In order to avoid any possible environmental impacts several methods to remove persistent organic compounds released into aquatic systems, such as adsorption, or chemical oxidation have been employed [1–5]. Heterogeneous catalysts for photo-Fenton degradation attract increasing attention among oxidation methods due capability in the catalyst reuse [6,7]. In this sense, diatomite, also known as Kieselguhr, is a cheap, widely available and stable material. Diatomite is a siliceous biological sedimentary rock material with a porous structure, with high oil and water absorption capacity and low density, thus showing ideal advantages for catalysis applications [8,9].

In spite of these suitable properties, only few reports investigate the application of diatomite as a catalyst support, as for instance in combination with magnetic materials [10]. Hence, the study of magnetic composites such as diatomite/Fe_2O_3/TiO_2 as catalysts is relevant because magnetic particles provide a convenient method to remove the catalyst from the reaction medium via an appropriate magnetic field [11,12]. In addition, this system is a highly convenient approach to bypass complex synthesis steps, due to the use of naturally occurring materials as inorganic supports, which reduces costs of catalyst preparation. Therefore, we report a novel magnetic diatomite-based composite obtained by co-precipitation of Fe^{2+}/Fe^{3+} and impregnation with TiO_2 by a sol-gel process. We evaluated the potential use of this material in the photo-Fenton degradation of methylene blue (MB), as well as recovery and reuse of this composite in order to verify its catalytic potential.

2. Experimental

Diatomite was supplied by Nova Refratil (Brazil). Analytic grade $FeCl_3 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$, $Ti(OC_4H_{10})_4$, $NH_{3(conc.)}$, methylene blue (MB, $[C_{16}H_{18}N_3S]Cl$) were used as reactants. Fe_3O_4 particles were obtained according to Philipse et al. [13]. Typically, diatomite (300 g L^{-1}) was dispersed in 20 mL (1.0 mol L^{-1}) aqueous $FeCl_3$ followed by addition of 5 mL (2 mol L^{-1}) $FeCl_2$ dissolved in 2 mol L^{-1} aqueous HCl, under stirring for 30 min, with a Fe^{2+}/Fe^{3+} = 1/2 M ratio. The resulting solution was added to 250 mL of

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0.7 mol L^{-1} aqueous ammonia ($Fe^{3+}/NH_3 = 1/8.75$) under mechanical stirring. After 30 min, the material was separated using a magnet, washed with deionized water and ethanol and dried at 70 °C. The final solid was dispersed in 0.4 mol L^{-1} $Ti(OC_4H_{10})_4$ in ethanol and kept for 24 h at 25 °C. The material was finally washed with ethanol and calcined leading to the diatomite/Fe_2O_3/TiO_2 catalyst. As temperatures higher than 650–700 °C leaded to the complete conversion of magnetite into maghemite and hematite (γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$) (thermal analysis, Supporting Information), calcinations were performed at 600 °C for 8 h. Characterization details and photocatalysis procedures are presented in the Supplementary Information (SI).

3. Results and discussion

SEM images (Fig. 1 and SI) indicate that both unmodified and final diatomite have highly porous structures and can potentially consist in efficient solid catalysts, confirming that the proposed modifications do not affect the porous nature of the substrate. Energy dispersive X-ray spectroscopy (EDS) results (SI) confirm an effective modification with Fe_2O_3 and TiO_2, leading to improved amounts of Fe and Ti [O/Al/Si/Fe/Ti/Cu (mol%) composition: natural diatomite-57.60/4.59/36.92/0.27/0.18/0.42; diatomite/Fe_2O_3/TiO_2 catalyst: 26.92/1.38/16.44/14.53/2.77/0.22]. Transmission electron microscopy (TEM) images (Fig. 1b/SI) also indicate the partial filling of the diatomite pores after the post-synthesis procedures, attesting for the effective modification with the additional inorganic phases.

X-ray diffraction (XRD) patterns (Fig. 1c) indicate the inclusion magnetite particles in the diatomite support, since characteristic peaks of the reverse-spinel Fe_3O_4 structure (JCPDS-10-0319) are observed. After the thermal treatment, the final diatomite/Fe_2O_3/TiO_2 catalyst still display the characteristic peaks related to the $Fd3m$ (O_h^7) structure with peaks slightly displaced to higher 2θ values. This is in agreement with the production of a γ-Fe_2O_3 (maghemite) phase after oxidation of Fe^{2+} ions, which is crucial for keeping magnetic properties after the thermal treatment process. Small amounts of α-Fe_2O_3 (hematite, $R3c$ space group) can be formed by the partial collapse of the maghemite structure in the diatomite/Fe_2O_3/TiO_2 systems, as indicated by small signals at 33.3° ([104]), 37.2° ([110]), and 39.2° ([113]). Addition of TiO_2 in the final solid led to the appearance of a diffraction halo, indicating that titanium dioxide occurs as an amorphous solid in the final catalyst. Small amounts of crystallized TiO_2 may also be present, since main peaks of anatase or rutile phases can be superposed to the diffraction halo or maghemite signals.

Despite the partial conversion of γ-Fe_2O_3 into non-magnetic α-Fe_2O_3, final catalysts still display characteristic paramagnetic properties (Fig. 1c). The magnetization saturation (Ms) of the diatomite/Fe_2O_3/TiO_2 catalyst (4 emu g^{-1}) is dramatically reduced in comparison to pure magnetite (27.5 emu g^{-1}) both due to the hematite formation and to the effect of the diamagnetic diatomite support. Such value is close to those observed for similar compositions [14,15]. Both curves showed negligible hysteresis, with remnant magnetization around 0.005 emu g^{-1}. Although low Ms values are observed, the magnetic response is sufficiently high to provide separation from a dispersing solution with a common magnet, which is highly advantageous for catalyst recuperation and reuse.

N_2 adsorption/desorption isotherms of the diatomite/Fe_2O_3 and diatomite/Fe_2O_3/TiO_2 composites (Fig. 2) show hysteresis in relative pressures between 0.65 and 0.95, which is typical of materials with mesoporous domains [16]. Results yielded surface areas of 45.1 m^2 g^{-1} for diatomite/Fe_2O_3 and 36.7 m^2 g^{-1} after incorporation of Fe_2O_3/TiO_2 and calcination, whereas specific pore volumes (0.19 and 0.15 cm^3 g^{-1}, respectively) and pore diameters (9.6 and 9.5 nm,

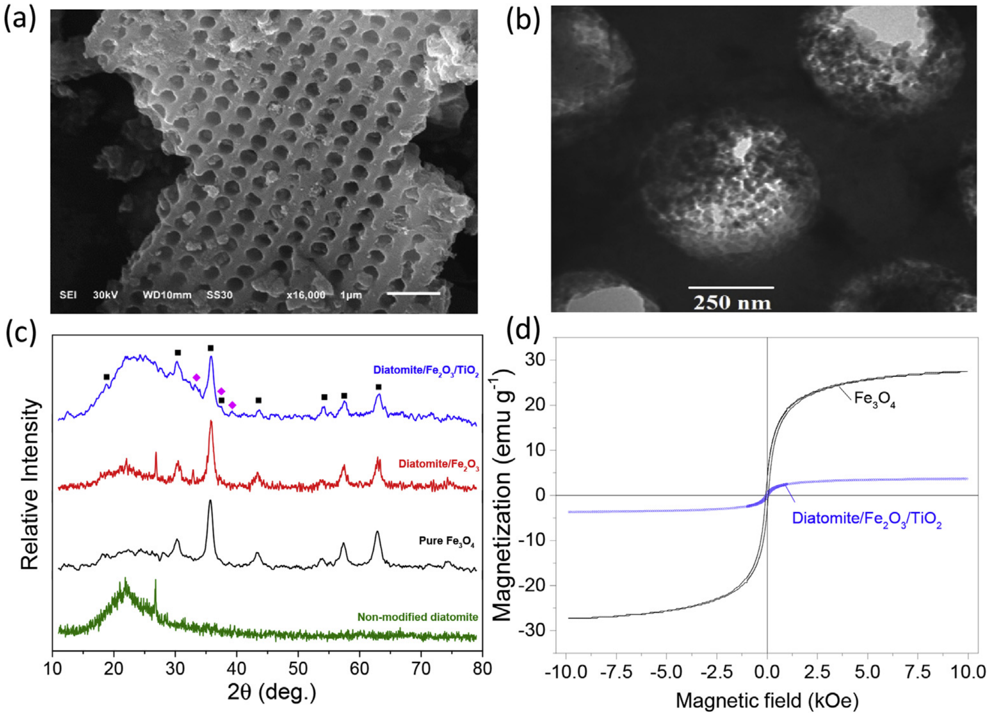

Fig. 1. (a) SEM and (b) TEM images of the final diatomite/Fe_2O_3/TiO_2 composite. (c) Powder XRD of non-modified diatomite (green), pure Fe_3O_4 particles (black), diatomite modified with Fe_2O_3 (red), and final diatomite/Fe_2O_3/TiO_2 composite (blue) [■ JCPDS-10-0319, magnetite/maghemite; ◆ JCPDS-13-534 hematite]. (d) Magnetization curves of pure Fe_3O_4 particles (black) and final diatomite/Fe_2O_3/TiO_2 composite (blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)