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A novel magnetic reusable nanocomposite with enhanced photocatalytic activities for dye degradation

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ABSTRACT

In this research, a magnetically separable Fe_3O_4 loaded TiO_2 nanocomposite with enhanced photocatalytic activity was synthesized through a novel simple strategy. The proposed method benefits from simplicity and involves no multi steps or high temperature. Scanning electron microscopy, X-ray diffraction, transmittance electron microscopy, energy dispersive X-ray spectroscopy, nitrogen adsorption–desorption isotherms, vibrating sample magnetometry and Mossbauer spectroscopy were performed to investigate the properties of the prepared magnetic photocatalyst. Moreover, the photocatalytic efficiency of the prepared nanocatalyst was evaluated with decomposition of Methylene Blue under UV light illumination. One factor response surface methodology was applied to study the influence of Fe^{2+}/TiO_2 molar ratio in the prepared nanocomposite. The results suggested the potential of the proposed facile method in producing a nanocatalyst with high dye photodegradability and no adverse effects on the aquatic environment. The prepared nanocomposite indicated excellent photodegradation of Methylene Blue, 1.6 times superior to nano TiO_2 Degussa P25. Due to the existence of magnetite particles on the surface of TiO_2, the transferred charge carriers are accessible to the oxidants or reductants and initiate the redox reactions. Fe_3O_4 nanoparticles may retard the electron–hole recombination rate evidenced by photoluminescence spectroscopy. Moreover, repeated usage of the photocatalyst proved its liability to be collected and reused.

1. Introduction

With the advent of nanomaterials and their various applications, there have been many efforts overcoming their associated drawbacks [1]. Nanocomposites with different functionalities are attractive candidates for high performance nanomaterials [2].

It is important to avoid the propagation of nanoparticulate contamination into the aquatic environment and effective methods are required to remediate nanoparticles environmental problems [3]. TiO_2 nanoparticles have fascinated researchers for their great efficiency in photocatalytic processes [4–14], however, recollecting such nanomaterials from wastewater involves difficulties restricted their performance [15,16]. The existence of nano TiO_2 in suspension after photocatalytic reaction threatens the environment and poses risk to human health [17]. Filtration, centrifuge and immobilization of nanoparticles on supported materials are some of the suggested solutions that require additional separation step and further expenses [18].

The idea of using magnetic force, as a long-range attraction, for nanoparticles separation has been widely investigated [19–23]. Magnetic separation is a convenient approach capable of purifying a large amount of wastewater within a short time [24]. Attempts have been made to impart magnetic property into nanomaterials removing them by use of external magnetic field, preventing effluent contamination and damage to the environment [25–29].

Iron oxides, such as maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4), are the most useful materials with ferromagnetism [30,31]. Superiority of nanostructured iron oxides to their bulk is due to the higher surface area, better distribution and higher rate of reactivity [32]. Different methods have been proposed for preparing iron oxides and magnetic nanomaterials with iron oxides incorporation [33,34], among which co-precipitation is the most convenient and low-cost method [35–39].

Coating of magnetite by titania has been investigated, aiming at modifying different properties of the applied materials obtaining some required specifications [16,40]. TiO_2/Fe_3O_4 nanocomposite with photocatalytic activity and magnetic property has been synthesized in previous studies [25,26,28,29]. Preparing the composite

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particles with photocatalytic efficiency comparable to the manufactured TiO_2 along with magnetism at a high level is dependent on many factors such as molar ratio of TiO_2 to Fe_3O_4 and the preparation technique [28,41]. A SiO_2 membrane was effectively added between Fe_3O_4 core and TiO_2 shell to reduce the adverse effects of Fe_3O_4 on the photocatalytic activity of TiO_2 [16,25]. Loading silver on $TiO_2/SiO_2/Fe_3O_4$ composite was also efficient in enhancing the photocatalytic activity [16]. A new sonochemical method for the synthesis of Fe_3O_4/TiO_2 photocatalyst as an effective and conveniently recyclable nanomaterial has been recently reported [42]. Mesoporous Fe_2O_3-doped TiO_2 fibers with high photocatalytic activity toward decomposition of Methylene Blue have been prepared [43]. A novel magnetic $TiO_2/SiO_2/Fe_3O_4$ was immobilized on a graphite electrode surface with high photo electrochemical activity [17]. A novel process for the self-assembly of Fe_3O_4 nanoparticles onto titania nanotubes to synthesize magnetic titanate nanocomposites has been reported recently [44].

In most of the reported core–shell Fe_3O_4:TiO_2 nanocomposites, the magnetic property was imparted into TiO_2 along with reducing its photocatalytic activity [28,29]. However, in the current study for the first time a reusable Fe_3O_4 loaded TiO_2 nanocomposite with high photocatalytic activity superior to nano TiO_2 Degussa P25 was successfully prepared by a novel facile chemical method. In contrast to the common preparation techniques, in which pre-synthesized iron oxide nanoparticles were used to prepare magnetic nanoparticles, our proposed method was free from the complicated multi steps and resulted in magnetic/TiO_2 nanocomposites with high photocatalytic activity. In comparison to almost all the previous studies preparing TiO_2:Fe_3O_4 nanocomposite with shell-core structure [45–47], in this study magnetite was synthesized on TiO_2 surface. Moreover, one factor response surface methodology (RSM) was used to investigate the efficiency of the prepared nanophotocatalyst and the optimum Fe^{2+}/TiO_2 molar ratio for high photocatalytic activity.

2. Materials and methods

2.1. Materials and catalyst preparation

Nanosize TiO_2 (Degussa P25) was employed as a photocatalyst. NaOH, $FeCl_3$ (98%), and $FeSO_4$, $7H_2O$ (pure) were purchased from Merck and used as received. Methylene Blue (C.I. basic blue 9) was used as a model compound for dye photodegradation.

In the preparation procedure of Fe_3O_4 loaded TiO_2 nanocomposite at room temperature in ambient atmosphere (Fig. 1), pre-calculated amount of $FeCl_3$ and $FeSO_4$, $7H_2O$ (Fe^{2+}/Fe^{3+} molar ratio = 2) were added to the nano TiO_2 dispersion. This mixture was vigorously stirred for 10 min to allow the adsorption of Fe^{2+}/Fe^{3+} on TiO_2 nanoparticles. NaOH was added dropwise into the obtained dispersion to maintain pH = 11. The resultant mixture was mechanically stirred for another 3 h. The suspension was then cleaned by cycles of centrifugation/washing/redispersion in water. Finally, the as-prepared product was separated by external magnetic field and dried at 60 °C. Pure Fe_3O_4 nanoparticles were also synthesized in a manner identical to the procedure described above in the absence of TiO_2.

According to reactions (1) and (2), Fe^{2+} and Fe^{3+} are changed into hydroxide compounds after dropwise addition of NaOH [20].

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \qquad \text{(reaction 1)}$$

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \qquad \text{(reaction 2)}$$

Ferric hydroxide ($Fe(OH)_3$) can be further transformed into FeOOH, resulting in FeOOH–$Fe(OH)_2$ intermediate compounds formation [48]. Magnetic nanoparticles (Fe_3O_4) can be made by conversion of FeOOH–$Fe(OH)_2$ compounds based on reaction (3) [20].

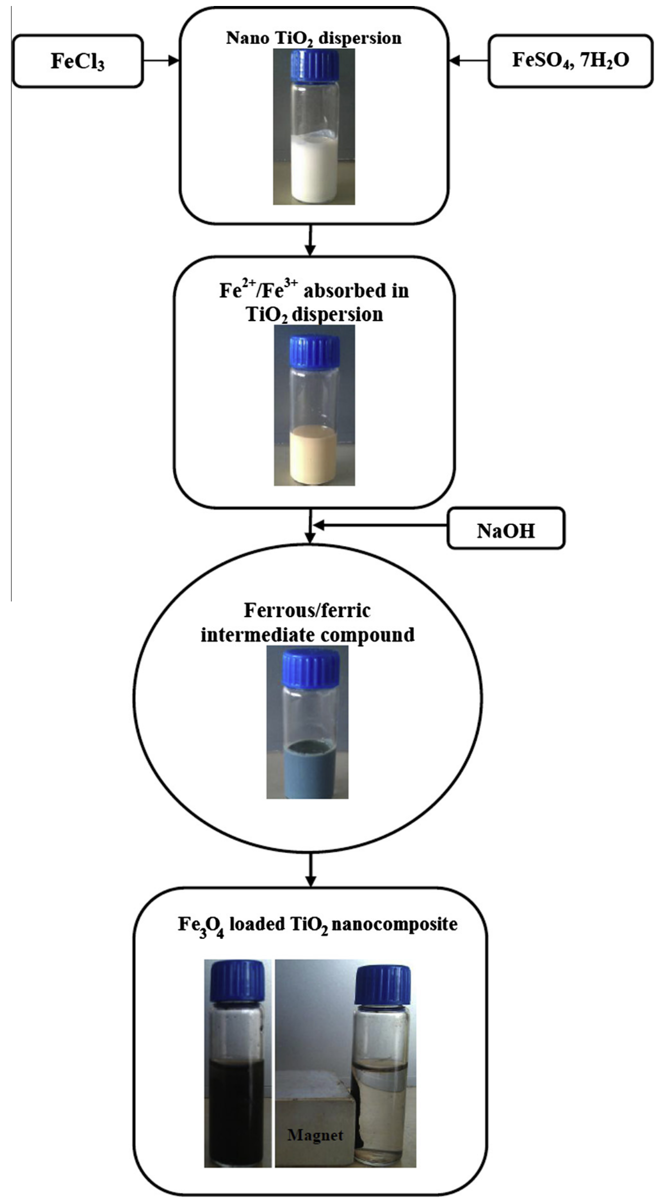

Fig. 1. Fe_3O_4 loaded TiO_2 nanocomposite preparation procedure.

$$Fe(OH)_2 + 2FeOOH \rightarrow Fe_3O_4 + 2H_2O \qquad \text{(reaction 3)}$$

In the previous studies [42,49,50], the Fe^{2+}/Fe^{3+} molar ratio for the formation of Fe_3O_4 was kept 0.5 based on reaction (3). However, creation of Fe_3O_4 with the aforementioned Fe^{2+}/Fe^{3+} ratio is very slow and requires high temperature. In the proposed method Fe^{2+}/Fe^{3+} ratio was 2, which led to more consumption of FeOOH in an excess of $Fe(OH)_2$ [48]. Therefore, Fe_3O_4 preparation can be effectively carried out at room temperature.

In contrast to the previous reports on Fe_3O_4 preparation by co-precipitation method [50], in the proposed preparation technique, a black precipitation of Fe_3O_4 nanoparticles was not formed immediately after mixing the iron salts with NaOH solution (Fig. 1). A dark green precipitate was formed during the synthesis confirming the formation of intermediates prior to the gradual production of Fe_3O_4. As the molar ratio of ferrous ions is higher than ferric ions, dehydration reaction of ferrous hydroxide and ferric oxyhydroxide