γ-Fe₂O₃ nanoparticles: An easily recoverable effective photo-catalyst for the degradation of rose bengal and methylene blue dyes in the waste-water treatment plant

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A B S T R A C T

γ-Fe₂O₃ nanoparticles (NPs) were synthesized from a single-source precursor complex [Fe₃O(C₆H₅-COO)₆(H₂O)₃]NO₃ by a simple thermal decomposition process and have been characterized by X-ray diffraction analysis (XRD), transmission electron microscopy (TEM) and UV–vis spectroscopic techniques. The NPs were highly pure and well crystallized having hexagonal morphology with an average particle size of 35 nm. The prepared γ-Fe₂O₃ (maghemite) NPs show effective photo-catalytic activity toward the degradation of rose bengal (RB) and methylene blue (MB) dyes under visible light irradiation and can easily be recoverable in the presence of magnetic field for successive re-uses. The possible photo-catalytic decomposition mechanism is discussed through the detection of hydroxyl radical (OH•) by terephthalic acid photo-luminescence probing technique.

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1. Introduction

The textile dyes with high aromaticity and low biodegradability have emerged as major environmental pollutants [1,2] and nearly 10–15% of the dye is lost in the dyeing process and is released in the waste-water which is an important source of environmental contamination. Considerable amount of water is used for dyeing and finishing of fabrics in the textile industries. The waste-water, from textile mills, causes serious impact on natural water bodies and in the surrounding lands. As dyes are designed to be chemically and photolytically stable, they are highly persistent in natural environments. The improper handling of hazardous chemicals in textile water also has some serious impact on the health and safety of workers putting them into the high-risk bracket for contracting skin diseases like chemical burns, irritation, ulcers, etc. and respiratory problems [3]. Various physical, chemical and biological pre-treatment and post-treatment techniques have been developed over the last two decades for the treatment of textile waste water, although most of them were found to be ineffective and expensive [4,5]. Thus, decomposition of organic pollutants using various nanomaterials in the presence of sun light has been a topic of contemporary interest. Semiconducting nanomaterials are especially important for this purpose, as they functions effectively at mild condition and even at very low

concentrations. During the past 20 years, many photo-excitable inorganic semiconductors have been used as photo-catalysts to decompose or destroy the organic pollutants [6–11]. The development of facile, cheap and green methods for treatment of organic pollutants has been a focal subject in the field of environmental science and technology. Among many strategies including physical, chemical, biological and photo-catalytic methods, the photo-catalytic method is a promising technology for the treatment of contaminants due to its potential use of sunlight as the energy source to degrade organic pollutants [12–14]. Organic dyes have the attractive advantages of possessing high molar absorptivity in the visible region, which matches the light source emission spectrum with solar light [15]. TiO₂ is a well-known catalyst for photo-degradation of toxic organic compounds [16–19], however, it is catalytically active only under UV irradiation (λ < 387 nm) because of its wide band gap energy (Eg ≈ 3.2 eV) [20]. Of late, a few non-titania-based several metal oxides (e.g. CuO, ZnO, MnO₂, Fe₂O₃, Fe₃O₄, Co₃O₄, Al₂O₃) and metal sulfides (e.g. CdS, CuS, ZnS, MnS, Sb₂S₃, In₂S₃, Bi₂S₃, etc.) [21–25] have been found to exhibit visible-light-driven catalytic activity. Obviously, there remains great demand for exploration of inexpensive and environmental friendly materials that might be used for photo-degradation of organic dyes in sun light, especially for effluents of textile waste-water. In this regard, the use of iron oxide nanoparticles, which is commonly known as super paramagnetic nanoparticles (MNPs), as catalyst carriers is very promising due to their large surface area resulting in high catalyst loading capacity, high dispersion, outstanding stability, low-cost

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preparation and environmental-friendly materials [26–28]. Another major advantage for the use of iron oxide nanoparticles is that, owing to the presence of their interesting magnetic properties, the separation at the end of the reaction is facilitated by their attraction to a magnetic field [29–31] which is much easier than by cross-flow filtration and centrifugation. In addition, the magnetic properties of the particles are stable enough to tolerate most chemical environments, with the exception of those that are extremely acidic or corrosive. For this reason, recently, some iron oxide-based nanomaterials have been investigated for photo-degradation of organic pollutants like 4-chlorophenol, congo red, phenol, etc. [32–34]. To the best of our knowledge, no one has developed to decompose rose bengal (RB) and methylene blue (MB) dyes, which are also extensively used in dying and printing industries, using γ-Fe_2O_3 NPs through photo-catalytic degradation process. Moreover the removal technique of these dyes from waste-water has not received sufficient attention recently. This was our encouragement for doing this work.

Keeping this in mind, in this article, we have synthesize γ-Fe_2O_3 NPs through a very simple thermal decomposition process from a trinuclear iron(III) single-source precursor complex. Then it was tested as photo-catalyst for the degradation of organic dyes and exhibits enhanced photo-catalytic efficiency toward decomposition of rose bengal and methylene blue compared to that of commonly used visible-light photo-catalyst WO_3.

2. Experimental

2.1. Chemicals and materials

All chemicals were of reagent grade and used without further purification. $Fe(NO_3)_3 \cdot 9H_2O$, sodium benzoate (C_6H_5COONa) and terephthalic acid (TA) were purchased from commercial sources. Rose bengal (RB), methylene blue (MB), tungsten (VI) oxide (WO_3) and 2-hydroxyterephthalic acid (HTA) were purchased from Sigma–Aldrich. Solvents were used as received.

2.2. Preparation of γ-Fe_2O_3 NPs

0.50 g precursor complex $[Fe_3O(C_6H_5COO)_6(H_2O)_3]NO_3$ (see supplementary materials) was taken in a quartz boat, placed inside a quartz tube and was put in a horizontal tubular furnace. The complex was heated under flow of nitrogen at 670 °C and kept at that temperature for 1 h. After that the furnace was turned off and the product was cooled to room temperature under the steady stream of nitrogen.

2.3. Physical measurements

Powder XRD pattern was obtained on a Philips PW 1140 parallel beam X-ray diffractometer with Bragg–Bretano focusing geometry and monochromatic CuKα radiation (λ = 1.540598 Å). Field emission scanning electron microscopy (FESEM) was carried out with a Gemini Zeiss Supra™ 35VP model; Carl Zeiss Microimaging GmbH, Berlin, Germany, using an accelerating voltage of 4.9 kV. TEM measurement was made on a JEOL JEM-2100 microscope using an accelerating voltage of 200 kV. UV–vis absorption spectra and photo-catalytic activities were studied on a JASCO V-530 UV–vis spectrophotometer. N_2-sorption isotherms were obtained using a Quantachrome Instruments analyzer at 77 K.

2.4. Photo-catalytic activity measurements

The as-prepared γ-Fe_2O_3 NPs was tested as photo-catalysts by the degradation of rose bengal (RB) and methylene blue (MB) dyes in aqueous solution under neutral pH. The experiments were

carried out in a round bottom flask kept in a thermostated bath at 22 °C and a visible-light source was used for the degradation process. The solution of RB and MB were prepared by dissolving it in Milli-Q Millipore water to obtain solutions of 6×10^{-5} M (RB) and 2.25×10^{-6} M (MB). The catalytic experiments were carried out with 40 mL aqueous solution using 25 mg of the catalyst (γ-Fe_2O_3). Before irradiation, the suspensions were magnetically stirred in the dark for 30 min to reach the adsorption–desorption equilibrium of RB/MB with the catalyst. After a given interval of illumination, 3 mL of the aliquot was withdrawn from the solution mixture and NPs were separated using magnetic field. The clear solutions of the dyes were measured on a UV–vis spectrophotometer at 540 nm for RB and 650 nm for MB, respectively. Commercial visible light photo-catalyst WO_3 was also used as the reference to compare the photo-catalytic activity under the same experimental conditions.

In order to investigate the mechanism of the photo-degradation process where hydroxyl radical may be photo-degenerated, the commonly used terephthalic acid (TA) photoluminescence probing technique [35] was adopted. In this experiment, 40 mL aqueous solution of sodium terephthalate (2×10^{-3} M) containing 30 mg of γ-Fe_2O_3 NPs was irradiated under visible light for 1 h. After a given interval of time, 3 mL of the aliquot was withdrawn from the solution mixture and similarly NPs were magnetically separated. Then the luminescence spectrum was recorded with clear solution between 330 and 540 nm using 315 nm as the excitation wavelength.

3. Results and discussion

3.1. Synthesis and characterization of the precursor complex $[Fe_3O(C_6H_5COO)_6(H_2O)_3]NO_3$

The single source precursor complex $[Fe_3O(C_6H_5COO)_6(H_2O)_3]NO_3$ was synthesized by reacting $Fe(NO_3)_3 \cdot 9H_2O$ with two equivalents of sodium benzoate in aqueous medium (Scheme 1). The result of elemental analyses for the complex is in good agreement with the theoretical requirements of the composition. The FT-IR spectrum for $[Fe_3O(C_6H_5COO)_6(H_2O)_3]NO_3$ (Fig. S1) shows the most important features of these types of carboxylate-bridged compounds, i.e. the presence of the symmetric and asymmetric stretching of coordinated carboxyl groups which are appeared at 1563 (for $\nu_{asym}(CO_2)$) and 1407 cm^{-1} (for $\nu_{sym}(CO_2)$), respectively. The positions and intensities are similar to those reported for the other metal coordinated carboxylates [36–39] and their separation (Δ values) falls in the range 150–160 cm^{-1} (i.e. 156 cm^{-1}) which supports the bridging mode of binding [40,41]. In addition, the strong bands at 674 and 627 cm^{-1} are assigned to the angle of deformation, δ(OCO), and out-of-plane deformation $\pi(CO_2)$ which are compared with the values to the corresponding acetate complex [42]. In comparison with Wu et al. [43], who have assigned a weak band appearing at 520 cm^{-1} in the acetate complex to the asymmetric vibration of the Fe_3O moiety, we have assigned the band at 486 cm^{-1} for vibrational modes of the central Fe_3O core i.e. asymmetric in-plane-stretch $\nu_{as}(Fe_3O)$. Finally the

$[Fe_3O(C_6H_5COO)_6(H_2O)_3]NO_3$
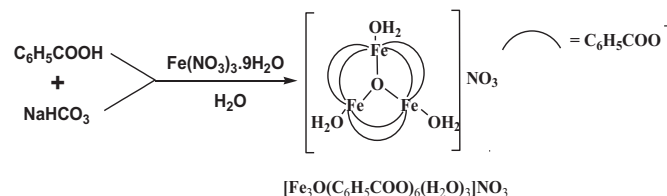
Scheme 1. Schematic representation of preparation of single source precursor complex $[Fe_3O(C_6H_5COO)_6(H_2O)_3]NO_3$.