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ORIGINAL RESEARCH PAPER

Synthesis, Characterization and Photocatalytic Activity of Fe_2O_3-TiO_2 Nanoparticles and Nanocomposites

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ABSTRACT

In this pepper Fe_2O_3 nanoparticles were synthesized via a fast microwave method. Then Fe_2O_3-TiO_2 nanocomposites were synthesized by a sonochemical-assisted method. The prepared products were characterized by X-ray diffraction pattern, scanning electron microscopy and Fourier transform infrared spectroscopy. The photocatalytic behaviour of Fe_2O_3-TiO_2 nanocomposites was evaluated using the degradation of Rhodamine B under ultra violet irradiation. The results show that nanocomposites have applicable magnetic and photocatalytic performance.

INTRODUCTION

Fe_2O_3, as an n-type band gap semiconductor (band gap=2.1 eV), has attracted much research attention because of its applications in waste water treatment, pigments, drug carriers electrochemistry, and gas sensors [1, 2]. Magnetic metal oxides have many important applications such as solar energy transformation, catalysts, storage media, biotechnology to produce polymer-matrix composites for cell separation, electronics devices, implantable drug-delivery and protein-purification systems [3, 4]. Fe_2O_3 was synthesised via chemical reactions such as microwave, vapor-phase pyrolysis, sonochemical, oxidation of pre-synthesized Fe_3O_4 and mechano-chemical processing of Fe metal in water reactions in emulsions [5-7] Property of metal–metal oxide nanocomposites can be adjustable through control of core/shell structure, shell thickness, oxide composition and metal/oxide interface quality. Elimination of pollutants from water for providing safe water is a major challenge for scientists [8-12]. Among various methods the advanced oxidation processes like photo-degradation reactions have great importance. In these processes, organic molecules destroy by interacting with a photo-catalyst material and UV or visible light and finally CO_2 and H_2O are achieved [13-16]. TiO_2 nanoparticle is the best known photocatalytic material for the decomposition of organic contaminants. However separation of TiO_2 from clean water is a difficulty and health-threat is disadvantages of using of nanoparticles. By preparation of magnetic nanocomposite can collect all TiO_2 nanoparticles and this safety problem can be solved. The specific properties of magnetic nanoparticles including suitable mechanical hardness, excellent chemical stability, cost-effectiveness and possibility for precise control on the composition along with its ability to be separated by a magnet, has made them very attractive candidate to be used in nanocomposite photocatalysts [17,18]. Microwave approach is a fast way for production of powders with different morphologies and fine nanoparticles. Obtaining ultrafine materials with

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desirable properties in a short period of time is the most significant advantages of microwave method [19, 20].

Microwave irradiation as a heating method has found a number of applications in chemistry. Compared with the other method, microwave synthesis has the advantages inclusive of: very short time, small particle size, narrow particle size distribution, and high purity. The main advantage of microwaves compared to other techniques is the extremely rapid kinetics for synthesis. Microwave can be used along with the hydrothermal synthesis and this has been found to increase the kinetics of crystallization [21, 22].

In the present work at the first step Fe_2O_3 nanoparticles were synthesized via a fast microwave method a short time and at second step Fe_2O_3-TiO_2 nanocomposites were synthesized by a sonochemical procedure. The effect of time and surfactants on the morphology of the product was investigated in order to optimize the reaction condition for obtaining an efficient photocatalyst.

MATERIALS AND METHODS

$Fe(NO_3)_2$ $9H_2O$, poly ethylene glycol (MW:4000), propylene glycol, NaOH, sodium dodecyl benzene sulphate (SDBS), distilled water and ethanol were purchased from Merck Company. All the chemicals were used as received without further purifications. SEM images were obtained using a LEO instrument model 1455VP. Prior to taking images, the samples were coated by a very thin layer of Pt (using a BAL-TEC SCD 005 sputter coater) to make the sample surface conductor and prevent charge accumulation, and obtaining a better contrast. X-ray diffraction patterns were recorded by a Philips, X-ray diffractometer using Ni-filtered $CuK_{\acute{a}}$ radiation. A multiwave ultrasonic generator (Bandeline MS 73), equipped with a converter/transducer and titanium oscillator, operating at 20 kHz with a maximum power output of 150 W was used for the ultrasonic irradiation.

Synthesis of Fe_2O_3 *nanoparticles*

First 1 g of $Fe(NO_3)_3$. $9H_2O$ was dissolved in 50 mL of propylene glycol. Then SDBS was slowly added to the solution, was mixed on magnetic stirring for 60 min. The solution put in the microwave under 750W power for 10-15 min at 600-900 W with pulses (30s On, 30s Off). NaOH (1M) was slowly added to reaching pH of solution to 10-11. The obtained brown precipitate was

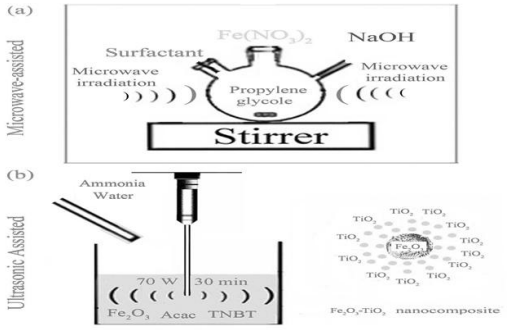

Fig. 1. Schematic of (a) microwave (b) ultrasonic

washed with distilled water and ethanol and was calcinated at 550æ%C for 3h (Fig 1a).

Synthesis of Fe_2O_3-TiO_2 nano*compositess*

Firstly 50 mg of synthesized iron oxide was dispersed in 50 ml of ethanol under ultrasound waves (70W) for 60min. Then under magnetic stirring 1 ml acetyl acetone and 0.5 ml of tetra n-butyl titanate were added to the solution. Slowly 15 ml of distilled water and 3 ml of 30% ammonia were added and the solution was stirred for 3h. After 24 hours, the precipitate was washed and was calcinated at 550æ%C for 2h (Fig 1b).

Photo-catalytic degradation process

40 ml of the dye solution (10 ppm) was used as a model pollutant to determine the photocatalytic activity. 0.04 g catalyst was applied for degradation of 40 ml solution. The solution was mixed by a magnet stirrer for 40 min in darkness to determine the adsorption of the dye by catalyst and better availability of the surface. The solution was irradiated by a 400 W UV lamp which was placed in a quartz pipe in the middle of reactor. It was turned on after 40 min stirring the solution and sampling (about 10 ml) was done every 15 min. The samples were filtered, centrifuged and their concentration was determined by UV-Visible spectrometry.

RESULTS AND DISCUSSION

Fig. 2 illustrates XRD pattern of Fe_2O_3 product. It can be observed that Rhombohedral phase of (JCPDS No. 13-0534) is present in the pattern. The composition of the Fe_2O_3-TiO_2 nanocomposite was investigated by XRD pattern and it is depicted in Fig. 3. It confirms presence of both Rhombohedral phase of Fe_2O_3 (JCPDS

No.13-0534, space group: R-3) and Anatase phase of TiO_2 (JCPDS No 04-0477, space group, I41/amd) in the pattern. The peak intensities related to each counterpart is relatively similar which is representative of rather equal portion of the shared compounds in the composite. The calculated crystalline sizes from Scherrer equation, $D_c=K\lambda/\beta Cos\theta$, where β is the width of the observed diffraction peak at its half maximum intensity (FWHM), K is the shape factor, which takes a value of about 0.9, and λ is the X-ray wavelength (CuK_α radiation, equals to 0.154 nm) were about 5and 32 nm for Fe_2O_3 and Fe_2O_3-TiO_2 nanoparticles, respectively.

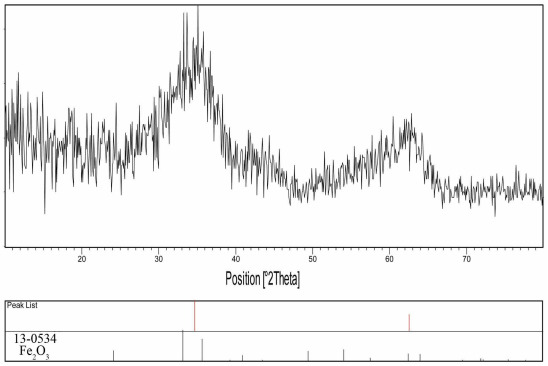

Fig. 2. XRD pattern of Fe_2O_3 nanoparticles

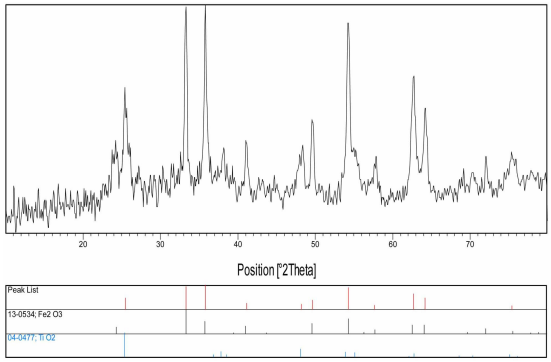

Fig. 3. XRD pattern of Fe_2O_3-TiO_2 nanocomposite

Reaction time and power effect on the morphology and particle size was investigated Fig. 4a exhibit SEM image of the as-synthesized Fe_2O_3 nanoparticles obtained at 10 min and 600W which demonstrate nanoparticles with average diameter size less than 50 nm were prepared. Fig. 4b illustrate SEM image of the as-synthesized Fe_2O_3 nanoparticles obtained at 15 min and 900W which show nanoparticles with mediocre

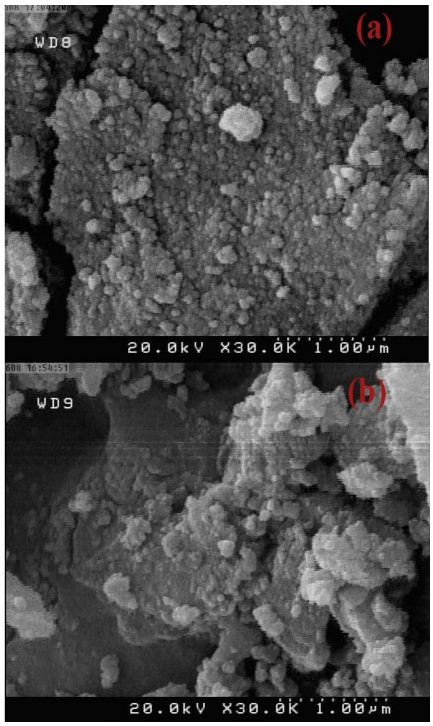

Fig 4. SEM images of nanoparticles obtained at (a) 10min (b) 15min

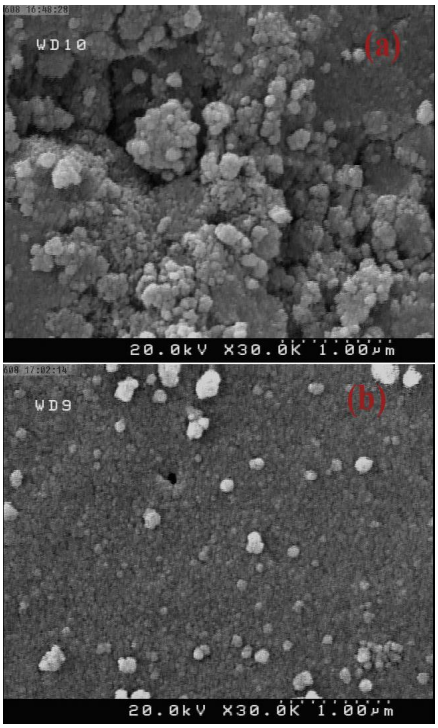

Fig 5. SEM images of Fe_2O_3 at presence of (a) PEG (b) SDBS

diameter size about 80-90 nm. In both reactions the nucleation was preferential compare to crystal growth. The influence of capping agent and surfactants on the morphologies were examined.

Fig. 5a illustrate SEM image of the product obtained by poly ethylene glycol (as polymeric capping agent) which confirm formation of nanoparticles with mediocre size between 20-30 nm. Fig. 5b exhibit SEM image of Fe_2O_3 that achieved by sodium dodecyl benzene solfate (as an anionic surfactant) which approve the size of mono-disperse particles is about 10 nm.

SEM image of Fe_2O_3-TiO_2 nanocomposite is shown in Fig. 6. Image approve formation of mono-disperse nanostructures with average particle size around 50 nm.

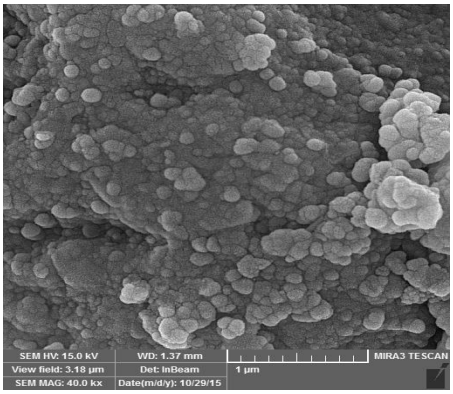

Fig. 6. SEM image of Fe_2O_3-TiO_2 nanocomposite

Fig. 7 shows the FT-IR spectrum of the as-prepared products at 15 min. The absorption bands at 445 and 580 cm^{-1} are assigned to the Fe-O (metal-oxygen) stretching mode. The spectrum exhibits broad absorption peaks at 3418 cm^{-1}, corresponding to the stretching mode of O-H group of adsorbed hydroxyl group and the weak band near 1646 cm^{-1} is assigned to H–O–H bending vibration mode due to the adsorption of moisture on the surface of nanoparticles.

Fig. 8 shows the FT-IR spectrum of the as-prepared Fe_2O_3-TiO_2 nanocomposite at 15 min and 900W. It can be observed that the strong absorption band at 440 and 580cm^{-1} which is ascribed to phonon absorptions of the Fe_2O_3-TiO_2 lattice and broad absorption peaks at 3390 cm^{-1} are assigned to adsorbed O-H groups on the surface of nanoparticles. There are no other significant peaks related to precursors and other impurities.

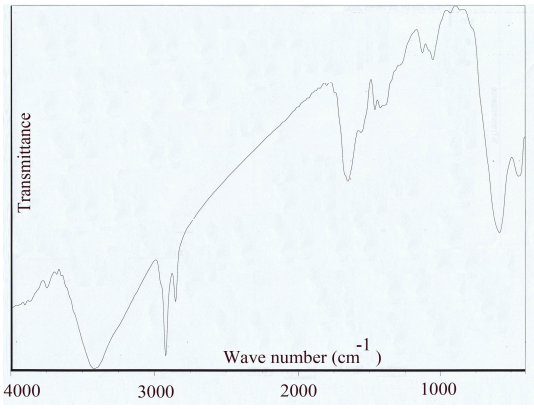

Fig. 7. FT-IR spectrum of Fe_2O_3 nanoparticles

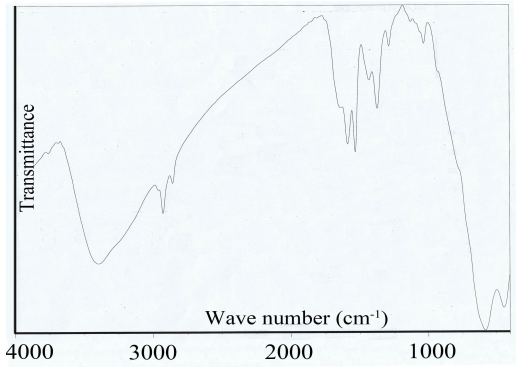

Fig. 8. FT-IR spectrum of Fe_2O_3-TiO_2 nanocomposite

The absorption spectrum of the titanium dioxide under UV-visible was investigated, diffuse reflectance spectroscopy (DRS) is depicted in Fig. 9. Band-gap of TiO_2 nanoparticles was estimated by Tauc's equation using the absorption data $\alpha=\alpha_0 (h\upsilon-Eg)^n /h\upsilon$ where α is absorption coefficient, α_0 and h are the constants, $h\upsilon$ is the photon energy, Eg is the optical band gap of the material, and n depends on the type of electronic transition and can have any value between 0.5 to 3. The energy gap of the sample (Eg) has been distinguished by extrapolating the linear portion of the plots of $(\alpha h\upsilon)^2$ against $h\upsilon$ to the energy axis. The approximation of band gap for TiO_2 nanoparticles is 3.3 eV which has agreement with literatures [23-26].

The photo-catalytic activity of the Fe_2O_3-TiO_2 nanocomposite was evaluated by monitoring the degradation of Rhodamine B in an aqueous solution, under irradiation with UV light. The changes in the concentration of dye are illustrated in Fig. 10.

Rhodamine B was degraded about 80% in 100 min. Organic dyes decompose to carbon dioxide, water and other less toxic or nontoxic residuals. Fig. 11 shows degradation of the Rhodamine B dyes after 100 min exposure to the Fe_2O_3-TiO_2 nanocomposite.

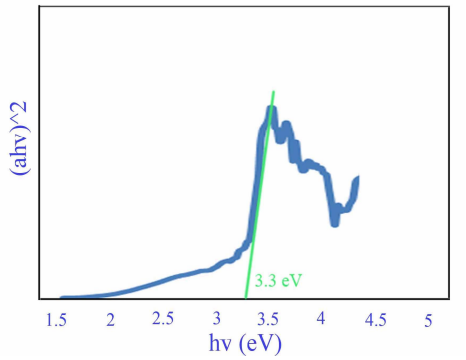

Fig. 9. Diffuse reflectance spectroscopy analysis of Fe_2O_3-TiO_2 nanoparticles

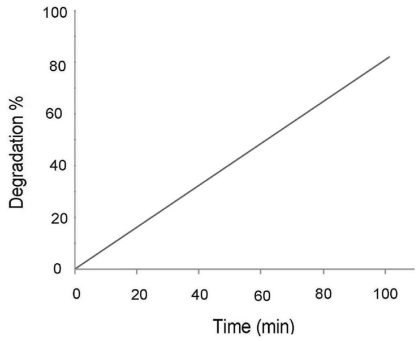

Fig. 10. Photodegradation of Rhodamine B by Fe_2O_3-TiO_2 nanoparticle

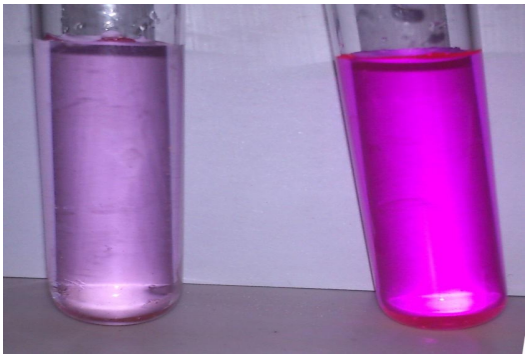

Fig 11. Rhodamine B after 100 minutes photodegradation in the presence of Fe_2O_3-TiO_2 nanoparticle

CONCLUSION

Firstly hematite nanoparticles were synthesized at a short period of time at 10 to 15 min, then Fe_2O_3-TiO_2 nanocomposites were prepared via a simple ultrasonic-assisted method. Effect of power, reaction time and various surfactants were investigated on the morphology and particle size of the products. The photocatalytic behaviour of Fe_2O_3-TiO_2 nanocomposite was evaluated using the degradation of Rhodamine B under UV light irradiation. The results show that microwave and ultrasonic method are suitable method for preparation of Fe_2O_3-TiO_2 nanocomposites as a candidate for photocatalytic applications.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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