Highly monodispersed hematite cubes for removal of ionic dyes

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Abstract

This study demonstrates fast and efficient removal of ionic dyes using highly monodispersed single crystalline hematite. Highly monodispersed single crystalline hematite with similar cube-shape but different sizes were successfully fabricated via a series of facile template-free microwave (MW)/ultrasound (US) assisted hydrothermal (HT) techniques. The products were characterized by seven techniques including powder X-ray diffraction, fourier transform infrared and ultraviolet – visible spectroscopies, field emission scanning electron microscopy, transmission electron microscopy, X-ray photoelectron microscopy, Brunauer–Emmett–Teller analysis, and dynamic light scattering analysis. Hematite microcubes with an average edge size of 1535 nm were prepared during a 12 h hydrothermal process at 180 °C. Decreasing the time or temperature led to a goethite/hematite mixture. Nevertheless, applying 1 h of MW refluxing or US waves before 2 h of hydrothermal treatment, resulted in submicro hematite cubes with the average sizes of 640 or 236 nm in edge, respectively. The removal of three dyes using prepared hematite cubes was systematically investigated. The sample prepared by US+HT technique showed the best visible light photocatalytic activity towards reactive black 5 (RB5), an azo-dye, where almost all of the dye molecules were degraded in less than 40 min under a white LED-3W irradiation. In order to compare the photocatalytic activity of this sample with that of hematite structures in the literature, the removal of Methylene blue (MB) and Rhodamine B (RhB) was investigated. Our catalyst represented an enhanced photocatalytic activity against the photodegradation of 10 ppm MB (~100% in 12.5 min) and 10 ppm RhB (~96% in 25 min) with reaction rates constants of 0.641 and 0.127 min⁻¹.

Keywords: Hematite; Cube structure; Visible light photodegradation; Organic dye; Ultrasound.

1. Introduction

Dyes are an important class of chemicals which are widely used in several industrial processes such as leather, textile, and printing industries. The release of the dyes in the effluents of these industries may cause major environmental problems. Most of these dyes are major environmental concern because they may cause cancer or other effects [1]. Various chemical and physical treatment techniques and processes have been used to remove the dye pollutants from contaminated water. The adsorption [2-4] and catalytic oxidation processes, especially heterogeneous photocatalysis [5, 6], are the most successful methods for removal of dye pollutants from water. The development of new materials with higher pollutant removal capacity and reuse ability has contributed significantly to the treatment of contaminated effluents. In photocatalysis, as one of the best removal methods, light of energy greater than the band gap of a semiconductor (SC), excites an electron (e^-) from the valence band (VB) to the conduction band (CB) generating a positive hole (h^+) in the VB [7]. The electron and hole can degrade the pollutants by producing some active radicals such as $O_2^{\bullet -}$ and $OH^{\bullet}$ (Scheme 1).

Hematite ($\alpha\text{-Fe}_2\text{O}_3$), an n-type semiconductor ($E_g = 1.8\text{-}2.2$ eV) and the most thermodynamically stable species of iron oxides, has been widely studied in recent years [8, 9]. It has been used extensively in catalysts [10], pigments [11], gas sensors [12, 13], water splitting [14, 15], water treatment [16], and lithium ion batteries [17] owing to its nontoxicity, low processing cost, and high resistance to corrosion [18]. Hematite structures have been studied as the photocatalysts in several work [19-21]. They possess a small band gap energy falling in the solar light region. However, they suffer from slow charge transfer, a short hole diffusion length, and more importantly, a high probability of electron-hole recombination which hinder their promising applications in photocatalysis [7]. Of course, their size and shape affect on the performance [22]. Some efforts, therefore, have been performed for the fabrication of surface active hematite structures with high-index facets [20, 23] or hollow structures with a high light harvesting efficiency [19, 22], which show enhanced photocatalytic activities. However, despite of their ability to degrade the organic pollutants, these structures are usually fabricated by organic-phase methods using toxic precursors which are difficult to handle under normal conditions and usually

consume too much time. Furthermore, these routes are not applicable, from the scaling up point of view, because of their high cost and generation of large volume of chemical wastes [24]. Also, the conduction band edge of hematite lies in a position unfavorable for single-electron reduction of O₂. Therefore, it is a weak photocatalyst for degradation of organic molecules under O₂. Overcoming this limitation, some work manipulated the band positions by making composites with high band gap semiconductors like TiO₂ [25] or CdS [26]. Nevertheless, the photodegradation efficiency is not high in these cases and usually the rates are slow. A more efficient and simple way is adding a very small amount of hydrogen peroxide, H₂O₂, to the aqueous suspension of iron oxide as an electron scavenger with a possible mechanism presented in Scheme 1 (Photo-Fenton reaction) [27].

In this work, we present fast and facile routes for the fabrication of highly monodispersed hematite cubes with great photocatalytic activities. In all these methods, the safe and cheap precursors of ferric chloride and sodium acetate were used. For the first time, a series of hydrothermal (HT) or combined (microwave (MW) and/or ultrasound (US) assisted HT) techniques were employed to prepare hematite structures with similar cubic shape but in different sizes. Synthesized hematite particles were used for the photodegradation of three organic dyes, Reactive black 5 (RB5) as a new pollutant model, Methylene Blue (MB), and Rhodamine B (RhB) (details are listed in Table S1), from aqueous solutions under visible light irradiation by LED and krypton lamps. Seven characterization techniques including X-ray diffraction (XRD), FTIR spectroscopy, UV-Vis spectroscopy, field emission-scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Brunauer–Emmett–Teller analysis (BET), and dynamic light scattering (DLS) analysis were used to obtain information on structure, purity, morphology, size, surface area, and chemical composition of the particles.

2. Materials and methods

2.1. Materials

Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), sodium acetate (CH_3COONa), and hydrochloric acid (37%), all from Merck, Germany, were of analytical grade and used without further purification. The water used in this work was purified (electrical conductivity = $0.42 \mu\text{S}/\text{cm}$).

2.2. Fabrication of hematite nanoparticles

2.2.1. Pure hydrothermal route

In this synthesis, an aqueous solution of sodium acetate and ferric chloride hexahydrate was prepared in a 3:1 molar ratio [28] (Solution A). The resultant homogenous solution was transferred to a 100 mL Teflon-lined autoclave, which was kept in an oven at 160°C (H1) or 180°C for 8 h (H2), or 180°C for 12 h (H3). H4 sample was prepared by doubling the concentration of precursors following by those conditions for H3. Then, the precipitate was collected by centrifugation and washed more than three times with water and dried in a vacuum oven at 80°C for 4 h.

2.2.2. Combined Routes

The details of combined techniques are summarized in Table 1. MH1 sample was fabricated by a MW-reflux assisted hydrothermal method. Before 4 h of conventional heating in the autoclave at 180°C , the solution A was refluxed in a modified household microwave system (Panasonic NN-ST342W, Japan), equipped by a condenser, for 30 min and high output power. In comparison with MH1, RH sample was prepared by a 30 min conventional reflux followed by 4 h heating in the autoclave at 180°C . MH2 sample was synthesized by 1 h MW- refluxing and 2 h of hydrothermal heating. In the case of MUH (1h MW-reflux pretreated) and UH samples, ultrasonic irradiation (with a total power of 50 W for 1 h at 70°C) was accomplished with probe immersed directly in the medium reaction (solution A) to form the initial colloidal hematite cores. Afterward, the suspension was transferred to the autoclave and heated at 180°C for 2 h. The resulted particulates were washed and dried like above (H3).

2.3. Characterization

The crystalline structure of the samples was obtained using X-ray powder diffraction. The XRD patterns were recorded with a Bruker/D8 ADVANCED diffractometer, using Cu-K α radiation ($\lambda = 0.15406$ nm) in the 2θ range of $20\text{--}70^\circ$ by the step of 0.05° . The FTIR spectra of hematite particles were recorded at room temperature with a KBr pellet using a Shimadzu 4300 spectrophotometer in the region of $400\text{--}4000\text{ cm}^{-1}$. Diffuse reflectance spectroscopy (DRS) was performed using AvaSpec-2048TEC spectrometer. The DLS analysis was measured by the VASCO-3 Particle Size Analyzer (Cordouan Technologies). The surface morphology and structure of the as-prepared samples were examined with a TESCAN-XMU field-emission scanning electron microscopy (FESEM) system, using an acceleration voltage of 15 kV. Energy dispersive X-ray spectroscopy (EDX) analysis and elemental map of the samples were obtained with an EDAX detector installed on the same FE-SEM. Transmission electron microscopy (TEM) experiments were performed using a Philips-CM120 instrument and the electron beam accelerating voltage was 120 kV. The TEM samples were prepared by dispersing the particles in ethanol and depositing them onto a 200 mesh carbon coated Cu grid. Specific surface area was measured by the Brunauer–Emmett–Teller analysis (BET) method from the N₂ isotherms collected with a Belsorp mini II BEL system on degassed samples. Surface composition was analyzed by X-Ray photoelectron spectroscopy (XPS) equipped with an Al K α x-ray source at energy of 1486.6 eV in an ultrahigh vacuum system with a base pressure lower than 2×10^{-9} Torr. The peaks were referenced to the C 1s peak (binding energy = 284.0 eV).

2.4. Photocatalytic activity

Photocatalytic activities of the hematite samples were evaluated by degradation of three model dyes of RB5, MB, and RhB dissolved in water. The photodegradation was carried out by the visible light sources of 3W white-color high power LED lamp (for RB5) or 400 W krypton lamp (for MB and RhB). The Pyrex glass vessel containing 50 mL dye solution and appropriate quantity of photocatalyst was magnetically stirred. A water jacket connected to a circulating cooling water bath was wrapped around the photoreactor to maintain its temperature throughout the experiment. The optimum conditions for removal of RB5 were obtained experimentally at different pHs and several concentrations of hydrogen peroxide. The initial pH values were adjusted by adding HCl solution. To investigate the kinetics of

removal of RB5, the experiments were performed at several temperatures in the optimum conditions. For the MB and RhB dyes, the experiments were performed at the pH of solution (not adjusted) in the presence of 0.255 ml of H₂O₂, having the conditions similar to previous reported data in the literature [29]. Prior to irradiation, the suspension was magnetically stirred in the dark for 15 min to establish an adsorption-desorption equilibrium (see Fig. S1). At designated time intervals, an aliquot of 3 mL was sampled and centrifuged. The filtrates were analyzed using UNICO 2100 spectrophotometer by monitoring the maximum absorption wavelength of the dye. All experiments were repeated twice.

3. Results and discussion

3.1. Morphology and structure

The crystal structure, purity, and morphology of fabricated samples was evaluated using different characterization methods.

3.1.1. XRD analysis

The crystallinity of as-prepared hematite were examined by using powder XRD measurements, as shown in Fig. 1a. The resolved diffraction peaks match the standard hexagonal α -Fe₂O₃ sample perfectly (JCPDS 33-0664) with lattice constants of $a=b= 5.0356 \text{ \AA}$ and $c = 13.7489 \text{ \AA}$, and no characteristic peaks of impurities were observed indicating the thorough phase transformation from α -FeOOH to α -Fe₂O₃ (except for H1 and H2). As Fig. 1a shows, in the pure HT technique with increasing the temperature and process time, the peak at $2\theta=21^\circ$ attributed to α -FeOOH is removed. However, in the combined methods there is no peak at $2\theta=21^\circ$. The possible mechanism for the fabrication of hematite in the presence of sodium acetate may be as follows: Fe³⁺ reacts with the OH⁻ produced by the hydrolysis of CH₃COO⁻ to form the FeOOH suspension. The formation of solid-phase α -FeOOH nuclei was confirmed by the XRD measurements for H1 and H2 samples (Fig. 1a) during the HT process. Then, α -FeOOH can be easily dehydrated during further hydrothermal treatment; consequently, α -Fe₂O₃ particles could be obtained. However, the enhanced peak intensity in Fig. 1a indicates the well crystallization of hematite particles via HT or more significantly MW treatments. The lowest peak intensities belong for the samples prepared by US pre-treatment. The peak attenuation may

originate from US action on crystallization process. In other word, a huge number of nuclei could form at much lower supersaturation levels in the nucleation stage by applying US waves [30]. Subsequently, HT treatment allows the nuclei to grow and obtain weaker crystalline samples than those prepared by pure-HT or MW-assisted HT techniques with lower number of nuclei in the primary stage.

The average crystallite size, D_{hkl} , can be calculated using the well-known Scherrer's formula [31]. Table 1 gives the experimental conditions for the fabrication of samples, crystallite size, particle size, and specific surface area. According to the number of nuclei produced in the primary stage, the crystallite size can be arranged in the order of $US < MW < HT$, i.e. the dominant step in HT and MW-assisted techniques is growth while it is the nucleation for the US-assisted technique.

3.1.2. Optical spectroscopy

Fig. 1b shows the FTIR spectra of prepared hematite in the middle infrared region. The spectra show two prominent peaks approximately at 480 and 560 cm^{-1} assigned to the E_u and $A_{2u}+E_u$ phonon modes (Fe—O vibrational mode in $\alpha\text{-Fe}_2\text{O}_3$ [32]), respectively. The FTIR spectra of H2 represents a peak attributed to Fe — OH at ~ 770 confirming the presence of $\alpha\text{-FeOOH}$ impurities in H2 and two peaks at ~ 1600 and ~ 3420 cm^{-1} assigned to bending and stretching vibrational modes of O — H.

The reflectance spectra of cubic-hematites are measured by UV–Vis diffuse reflectance spectrometer (Fig. S2). The band gap, E_g , was predicted using the Tauc-equation [33]:

$$\alpha h\nu = A (h\nu - E_g)^n \quad (1)$$

where α is absorption coefficient, h is Planck's constant, ν is the frequency of light, A is a constant, and n is equal to 2 for an allowed indirect transition or 1/2 for an allowed direct transition. For $\alpha\text{-Fe}_2\text{O}_3$, the transition is direct and corresponds to the $\text{O}^{2-} 2p \rightarrow \text{Fe}^{3+} 3d$ charge transfer [34]. A plot of $(\alpha h\nu)^2$ versus $h\nu$ would have a linear region with slope A and whose extrapolation to zero absorption ($\alpha h\nu = 0$) would obtain the E_g value. The band gap values obtained for the MH1, MUH, and UH samples are 1.86, 1.94, and 1.98, respectively, which are in accord to the values reported in the literature [35].

3.1.3. Electron microscopy

Comprehensive morphology studies of the samples prepared by HT method (H3 and H4 samples) are shown in Fig. 2. Fig. 2a displays the FE-SEM image of H3 which is composed of uniform monodispersed microcubes. A higher magnification of this image (shown in the inset) indicates that the surfaces of the cubes with an average edge size of 1535 nm are relatively rough. It is further confirmed by the corresponding low and high magnifications TEM images as shown in Fig. 2b and its inset, respectively. The close-up inset shows that the nanorods with a diameter about 30 nm grow up on the crust of microcubes which constructs a “virus-like” structure. Also, the particles with a diameter about 30 nm are visible between nanorods. Fig. 2c and d represent the FE-SEM and corresponding TEM images of H4 with an average size of 1835 nm in edge. In this case, the concentration of precursors was two times of H3. The surface smoothness and bigger size of H4 compared with that of H3 may be due to the higher concentration of precursors which leads to the faster growth of hematite particles during the process.

The morphology of the hematite submicro-cubes prepared by the reflux pre-treated HT method was visualized by FE-SEM. High and low magnification FE-SEM images of the MH1 are shown in Figs. 3a and 3b, respectively. The corresponding images for the RH sample are displayed in 3c and 3d panels, respectively. Fig. 3 clearly shows that the MH1 sample is not only smaller in size, but also more uniform than that of prepared by RH process. This difference may originate from the heating mode. The microwave technique provides a rapid volumetric heating while in the conventional reflux, the thermal energy is transferred through the reactor wall and the core of the sample takes much longer to achieve the boiling temperature of solvent [36]. Also, because the cool solvent droplets fall into the center of reactor in a reflux system, the core is always cooler than the regions near the walls in the conventional reflux, leading a temperature gradient throughout the bulk media. In the MW system, the primary seeds in the process of iron oxide formation feel a more uniform medium compared to the conventional reflux system; and final MH product will be more uniform than that of prepared by RH. Another difference goes back the morphology of particle surfaces. As shown in the high magnification FE-SEM images, in contrast of RH particles, MH1 particles possess a highly porous structure with a specific surface area of 30.5 m²/g (from BET analysis). It is probably due to the hydrolysis of FeCl₃

into H^+ and Cl^- which play an etching role in shaping the morphology of the hematite crystals. The higher the energy input of MW irradiated, the higher the etching degree in MH1 sample will gain [37].

Representative FE-SEM images in Fig. 4a shows that the as-synthesized MH2 sample consists of highly uniform hematite cube particles with an average edge length of 640 nm. A close observation shows that these submicro-cubes may assembled from rod-like subunits (the inset of Fig. 4a). TEM characterization was applied to further investigate the morphology and structure of the products. Fig. 4b reveals that two opposite corners MH2 particles are more elongated and form a walnut-like shape. A further pre-treatment by ultrasonic waves before heating the sample in the autoclave, will decrease the size of hematite cubes dramatically (MUH). The results show that cube-like hematite particles with uniform size of 238 nm can be obtained (Fig. 4c). The inset of the same figure displays a high magnification FE-SEM of MUH sample which represents a porous structure. TEM image shown in Fig. 4d, shows a shape similar to MH2 for the MUH sample but in much lower size.

The morphology of the sample obtained in the last set of experiments, 1 h ultrasound irradiation followed by 2 h hydrothermal treatment (UH), is shown in Fig. 5. FE-SEM (Fig. 5a and b) and TEM (Fig. 5c) images reveal that highly monodispersed hematite cubes with an edge of 236 nm and a pleasant dispersity percent of 2.47 were formed by the help of ultrasonic waves. The local elemental composition of the hematite cubes was studied by EDX microanalysis, as shown in Fig. 5d. It confirms the presence of Fe and O; and no impurities are visible. Also, the color chemical map of Fe and O on a representative area of the sample is presented in Fig. 5e and show the distribution of the components on the surface.

3.1.4. BET analysis

Nitrogen gas adsorption measurements were conducted to determine the BET specific surface area of UH cubes. Fig. 5f shows a typical type IV adsorption isotherm with a hysteresis loop in the relative pressure range of 0.4–0.9, which suggests that the prepared UH hematite cubes are mesoporous materials. The $\alpha\text{-Fe}_2\text{O}_3$ sub-micro cubes show a surface area of $10.8 \text{ m}^2 \text{ g}^{-1}$ which is not as high as those for the MUH and MH1 samples in spite of its smaller size (see Table 1). The Barrett-Joyner-

Halenda (BJH) pore size distribution show that most of the pores range from 2 to 20 nm (i.e. radius of 1 to 10 nm) as shown in the inset of Fig. 5f, which can be observed more clearly in high magnification FE-SEM image in Fig. 5a.

3.1.5. XPS analysis

XPS was used to study the surface properties including iron oxidation state and chemical composition of the UH sample. The wide survey spectrum presented in Fig. 6a identified the presence of carbon (C 1s), oxygen (O 1s), and iron (Fe 1s and Fe 2p). Carbon could originate from the XPS instrument itself. Higher resolution spectrum of Fe was shown in Fig. 6b. The Fe 2p_{3/2} and 2p_{1/2} are located at ~710.8 eV and ~724 eV (with a spin energy separation of 13.2 eV due to the spin-orbit coupling), respectively, agree well with the literature values for Fe (III) [20, 37-42]. Also, a characteristic shakeup satellite peak located approximately 8 eV higher than the main peak of Fe 2p_{3/2} is clearly distinguishable and does not overlap Fe 2p peaks and confirms the presence of hematite [40, 42, 43]. In the O 1s region (Fig. 6c), the peak at 529.5 eV can be assigned to lattice O²⁻ (Fe-O). Another peak located at 531.5 eV is attributed to adsorbed hydroxyl (Fe-OH_{ad}) or chemisorbed oxygen [20, 38, 43]. Two extra peaks at 527 and 525 eV appear too, after deconvolution of the main spectrum which have not been reported in the literature for Fe(III) oxides/hydroxides yet. However, some papers expressed that in Fe₃O₄ (magnetite) exposed to H₂O, the peaks may be ascribed to chemisorbed oxygen and hydroxyl groups at non-equivalent sites [44, 45]. They indicated at pressures as low as 10⁻⁴ Torr, hydroxyl groups can form due to the dissociation of moisture and strongly adjoin on the magnetite surface.

3.1.6. DLS analysis

The size distribution of the UH sample was measured by a DLS analyzer (Fig. S3). The DLS histogram of UH sample suggests that the sample mostly consists of particles of about 250 nm. Clearly, the particle size by DLS analysis is larger than of TEM analysis since the hydrodynamic radius is probed with DLS.

3.2 Photocatalytic degradation

After characterizing the hematite cubes, their photocatalytic properties under visible light irradiation were evaluated for three organic dyes as the model contaminants. The photodegradation of RB5 has not been investigated by hematite yet. Of course, its photocatalytic degradation has been investigated by a red mud residue (an important waste of the aluminum industry rich in iron oxide) where the iron phases were reduced by a chemical vapor deposition of ethanol [46], as well as ZnS nanoparticles [5], and WO₃/graphitic carbon nitride nanocomposites [47]. The photocatalytic decolorization of two other well-known dyes, MB and RhB, was studied to compare the performance of our photocatalysts with those in the literature.

3.2.1. RB5 photodegradation

The characteristic absorption of RB5 at 598 nm was used to monitor the concentration of RB5 during the degradation process. The optimum conditions for removal of dye pollutant were investigated at different initial pHs, several initial H₂O₂ concentrations (denoted as [H₂O₂]), and various temperatures. In this study, the change in dye concentration was monitored over the time and expressed in terms of removal efficiency (*R.E.*), defined as:

$$R.E. = 100 \times \left(\frac{C_i - C_t}{C_i} \right) \quad (2)$$

where C_i is the initial concentration of dye at $t = 0$ and C_t denotes the concentration of dye at time t .

The pH of solution changes the charges at the surface of a photocatalyst and shifts the potential of some redox reactions. Thus, it affects the adsorption of organic solutes. To determine the optimum initial pH, the photocatalytic experiments were carried out at the pH values of 1, 2, 3, and 4 with fixed H₂O₂ concentration. Fig. 7a demonstrates that the photocatalytic degradation of 50 ppm RB5 by 1 g/L of UH and H3 samples was more favorable in acidic conditions. After 30 min of irradiation by LED 3W at pH = 1, more than 66% and 97% of RB5 degrade by H3 and UH samples, respectively while the corresponding removal was only 3 and 20 percent for pH = 4. Pham et al. have analyzed adsorption of an anionic azo dye, new coccine, onto α -alumina micro – beads in aqueous media [48]. They showed that the adsorption amounts of dye decrease with increasing pH of solutions due to less positive

charges of α - Al_2O_3 surface at high pH. The influence of pH can be explained on the basis of zero-point charge of hematite. The pH of zero point charge (zpc), pH_{zpc} , of various types of synthetic hematite are in the range of 7-8.8 [49]. Therefore, hematite surface is positively charged in acidic media whereas it is negatively charged under alkaline conditions. On the other hand, RB5 is a tetra-anionic dye in aqueous solutions. Therefore, at low pH values electrostatic interactions between the positive catalyst surface and dye anions lead to strong adsorption of the dye.

Fig. S4 shows the influence of the initial H_2O_2 concentration on R.E. of RB5 by H3 (1 g/L) sample after 45 min irradiation under visible light. In the absence of H_2O_2 , 20% RB5 can be decomposed after 45 min. It means the number of hydroxyl radicals produced by light excitation of H3 is very low. Upon excitation of H3 by visible light irradiation, electron-hole pairs are produced. The produced holes could accept electrons from water to generate hydroxyl radicals. However, the electron-hole recombination rate is very high in hematite [7]. As $[\text{H}_2\text{O}_2]$ increases, the value of R.E. increases. Hydrogen peroxide generates Fe^{3+} species and hydroxyl radicals which are capable of degrading dye. Hence, both light and H_2O_2 are needed for the degradation of RB5 to follow heterogeneous photo Fenton reaction. Hydrogen peroxide can also react with hydroxyl radicals. When its concentration is low, its reaction with hydroxyl radicals is negligible. The hydroxyl radicals produced by H_2O_2 degrade the dye and hence R.E. increases. When hydrogen peroxide is too much, its extra amount reacts with $\text{OH}^\bullet$ and hence the R.E. decreases. In this study, $[\text{H}_2\text{O}_2] = 25 \text{ mM}$ is considered as the optimum concentration.

The RB5 decolorization in the presence of different hematite samples at optimum conditions ($\text{pH} = 1$ and $[\text{H}_2\text{O}_2] = 25 \text{ mM}$) and fixed initial RB5 concentration (50 ppm) is summarized in Fig. 7b. For comparison, three sets of experiments were conducted in the absence of the catalyst but in the presence of H_2O_2 (blank), in the presence of bulk hematite, and in the presence of P25 (TiO_2) as the best UV-active photocatalyst. The dye degradation in the presence of P25 similar to the blank experiment (the dye is degraded during the photolysis process) was only $\sim 5\%$. The UH sample shows the best visible-light photocatalytic degradation of RB5. As table 1 shows UH sample has the smallest size. Hence, the decrease in the size of cubes leads to increase the performance of the photocatalyst. In a similar work,

RB5 was degraded during a photo-Fenton reaction by iron (0) under illumination of a 300 W sunlight simulator [46]. The removal efficiency was the same as UH in pH=3 (~ 50%) while our light source was a 3 W LED lamp. After 40 min, the efficiency of RH (~59%) is about two third of that for UH (~ 97%) while it is more efficient than those of bulk Fe₂O₃ (~ 34%). The values show the impact of the size which is directly proportional to the total active sites on the surface of catalyst. Of course, the MH1 sample with the highest surface area (30.5 m²/g) among all of the synthesized samples shows a lower efficiency than MUH and UH cubes with 11.2 and 10.8 m²/g specific surface area, respectively. This demonstrates that other factors besides surface area may affect the performance of a photocatalyst. Recently, our group fabricated ZnS nanopaticles by ultrasound technique and showed an advanced visible ligh photocatalytic activity compared with the ZnS nanoparticles prepared classically. This was attributed to to the production of defect energy states in the ZnS band gap which can act as intermediate distinations of exited electron [5]. Ding et al. reported the enhanced photocatalytic activity towards MB and RhB by low surface hematite cubes but with high-index facets [37]. As well as their experiments, their simulation results also revealed that a special facet of the photocatalyst is more positively charge and has a lower LUMO energy compared with that of other facets.

The influence of the UH catalyst, the most efficient sample, dosage (0.50, 0.75,1.00 g/L) on RB5 decomposition under optimum condition, was investigated. As shown in Fig. S5, the concentration of photocatalyst has little impact on the removal process so that after 30 min., 95% or greater of the dye was degraded by hematite cubes for all dosages.

The photocatalytic experiments of RB5 removal at optimum conditions were carried out at temperatures of 20, 30, 40, and 50 °C by 1 g/L of H3, MUH, and UH samples. The inset of Fig. 7c demonstrates that increasing temperature leads to increase in R.E . For example, the R.E. increases from 91 to 98 % when temperature raises from 20 to 50 °C . Several studies applied pseudo(P)-first order kinetics for the analysis of heterogeneous photocatalytic reactions [7, 22, 23]:

$$\text{rate} = -\frac{dC}{dt} = k_{ap} C \xrightarrow{\text{integration}} \ln\left(\frac{C_t}{C_i}\right) = -k_{ap} t \quad (3)$$

where C_o is the initial concentration of dye, C is the concentration of dye after time t of photocatalytic degradation, and k_{ap} is apparent rate constant. In principle, the photocatalytic degradation of RB5 by the hematite photocatalyst is an interface process which might follow the Langmuir–Hinshelwood model:

$$\text{rate} = -\frac{dC}{dt} = \frac{K_{L-H}k_{sur} C}{1 + k_{sur} C} \quad (4)$$

where k_{sur} is the surface reaction rate constant and K_{L-H} is the Langmuir–Hinshelwood adsorption equilibrium constant. When C is very small, Eq. 4 can be written in form of Eq. 3. The plot $\ln(C_t/C_i)$ vs. irradiation time (the first 20-30 minutes) for the removal of RB5 by H3 and MUH at mentioned temperatures is linear and this suggests that the initial reaction rates follow P-first order reaction kinetics (Fig. S6). However, the kinetics for UH is more complicated. The results showed that experimental data could be fitted by a P-1.5th order kinetics:

$$\frac{1}{\sqrt{C_t}} = \frac{1}{\sqrt{C_i}} + k_{ap} t \quad (5)$$

where the plot of $C^{0.5}$ vs. time would be linear. This model is justifiable because of the nature of reactions (radical path) for degradation of dye molecules. The coefficient of determination, R^2 , as a measure of linearity, and k_{ap} for the reactions kinetics at mentioned temperatures are listed in Table 2. As this table shows (and Figs. 7c and S4) Eq. (3) well fits the experimental points of RB5 degradation by H3 ($R^2 > 0.959$) and MUH ($R^2 > 0.975$) samples and data for the UH sample were successfully fitted by Eq. (5) ($R^2 > 0.986$). The activation energy for each set of experiments was calculated by the Arrhenius relationship:

$$\ln k_{ap} = \ln A - \frac{E_a}{RT} \quad (6)$$

where E_a is the activation energy (J mol^{-1}), R ($\text{J mol}^{-1} \text{K}^{-1}$) is gas constant, T (K) is temperature, k_{ap} is the rate constant of degradation, and A is the Arrhenius factor. The parameter E_a/R was calculated as 3926, 3020, 2435 K for the reaction catalyzed by H3, MUH, and UH, respectively. The lowest activation energy belongs for the UH sample which is due to the highest number of its active sites and

provides an excellent platform for the radical reactions. Furthermore, the highest value of band gap for the UH sample among other synthesized catalysts, prevents the recombination of electron-hole successfully which leads to the faster formation of active radicals ($\text{OH}^\bullet$ and $\text{O}_2^{\bullet-}$) compared with other prepared photocatalysts.

The stability of a photocatalyst is an important factor for its practical application. The recyclability of UH and MH1 samples was investigated to determine their stability for five cycles with the same catalyst dosage (1 g/L) and 50 ppm dye concentration (Fig. 7d). After each run, the photocatalyst powders were rinsed carefully and used for the new test. The photocatalytic activity of UH sample did not change after five cycles under 3W-LED irradiation for 30 min (R.E. was greater than 98% indicating excellent photostability). On the other hand, the activity of MH1 sample decreased slightly after each run. The MH1 sample degraded the RB5 dye within 60 min and its R.E. was 88% and 84% after the first and fifth cycles, respectively. Even though the specific surface area of the MH1 sample is approximately 3 times that of UH sample, its activity is much less than the later. As mentioned above, this may be due to the special active facets in the UH cubes [37, 43].

3.2.2. Photodegradation of MB and RhB

In order to compare the performance of our best catalyst, UH sample, with the hematite structures reported in the literature, the removal of MB and RhB dyes from aqueous solutions was investigated. A krypton arc lamp (400 W, Osram) equipped with a filter to remove the UV region of the light, was used in these tests. The *R.E.* of UH sample was evaluated by the change in the absorption of MB and RhB solutions in their characteristic absorption peaks of 664 and 550 nm, respectively and shown in Fig. 8a. As it can be seen, both dyes degraded quickly when exposed to the lamp. Near 100% of MB and 96% of RhB were degraded by UH sample within 12.5 and 25 min, respectively. The calculated apparent reaction rate constants based on a P- first order kinetics were 0.6416 and 0.127 min^{-1} for MB and RhB, respectively. Figs. 8b and c display a comprehensive comparisons of rate constants between this work and recent published studies based on the removal of MB and RhB, respectively by hematite photocatalysts [7, 19, 20, 29, 37, 38, 40, 50-61]. It can be clearly seen that the performance of UH

photocatalyst is much better than those facet-controlled or hollow hematite nano/microstructures reported in the literature. A complete data for the comparison of UH catalytic activity and those references mentioned in Fig. 8, are given in Table S2.

4. Conclusions

In summary, single crystal hematite cubes with different sizes, from 238 to 1825 nm, were fabricated via facile HT or MW/US assisted techniques using only the precursors of FeCl_3 and CH_3COONa . No surfactant or organic compound was used to control the shape or the size of $\alpha\text{-Fe}_2\text{O}_3$ samples.

The visible light photocatalytic performance of as-prepared hematite cubes was evaluated against the removal of RB5 from aqueous solutions where the sample prepared by US assisted HT (UH) technique showed the best activity. The results showed that the photodegradation of RB5, MB, and RhB dyes using hematite samples follows heterogeneous photo Fenton process under visible light irradiation. Both light and H_2O_2 besides hematite are needed for the degradation of the dyes. The photocatalytic degradation of RB5 by the UH sample obeys the a P-1.5th- order kinetics with activation energy of 20.24 kJ/mol. The recyclability tests for UH sample revealed that it can be regenerated and utilized several times without loss in its activity.

The removal efficiency of UH toward MB and RhB was investigated for comparison with that of hematite structures in the literature where it exhibited a superior activity to others. Finally, this work may suggests a promising strategy for the fabrication of high performance hematite catalyst which are not only suitable for water treatment but also could be beneficial in solar cell, water splitting, sensing, biomedical applications, etc.

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Appendix A. Supplementary data

Supplementary Information available: Details of the used dyes, DRS spectra for some of fabricated samples, DLS histogram of UH sample, the influence of $[\text{H}_2\text{O}_2]$ and catalyst (UH) dosage on R.E., kinetics

study of RB5 photodegradation, and a comprehensive comparison of the conditions for removal of MB and RhB by UH and the using different hematite structures reported in the literature.

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Table 1 Experimental conditions for the fabrication of samples, crystallite size, particle size, and specific surface area.

Sample	Heating mode		Average crystallite size (nm) ^a	Average particle size (nm) ^b	BET SA (m ² /g)
	Pre-treatment (Duration time in hour)	Conventional			
		Temperature (°C)	Time (h)		
H1		160	8	-	-
H2		180	8	-	-
H3		180	12	31.30	1535
H4		180	12	33.50	1825
MH1	MW (0.5)	180	4	29.80	677
RH	Reflux (0.5)	180	4	27.80	797
MH2	MW (1)	180	2	29.53	640
MUH	MW (1) – US (1)	180	2	24.12	238 (2.27) ^c
UH	US (1)	180	2	24.31	236 (2.47) ^c

^a from XRD

^b from FE-SEM or TEM

^c Dispersity % = $\sigma_x/\bar{x}$; σ_x : standard deviation in the edge size of x

Table 2 The coefficients of determination and apparent reaction rates for the photodegradation of RB5 at different temperature.

Temperature	H3 (P- 1 st order)		MUH (P- 2 nd order)		UH (P-1.5 th order)	
(°C)	R^2	k_{ap}^a	R^2	k_{ap}^a	R^2	k_{ap2}^b
20	0.9594	0.0157	0.9753	0.0371	0.9862	0.1133
30	0.9962	0.0203	0.9985	0.0743	0.9942	0.1444
40	0.9988	0.0372	0.9897	0.0780	0.9997	0.1763
50	0.9973	0.0512	0.9950	0.0977	0.9971	0.2506
E_a/R (K)	3926		3020		2435	

^a min⁻¹

^b (L/mol)^{0.5} min⁻¹

Figures

Scheme 1. Photocatalysis mechanism by hematite in the presence of hydrogen peroxide.

Fig. 1. (a) XRD patterns (b) FTIR spectra of hematite samples fabricated by different methods. (c) Tauc plot of optical band gap for direct transition of some prepared hematite samples.

Fig. 2. FE-SEM and TEM images of the samples obtained by pure HT method at 180 °C for 12 h: (a) low-magnification and high-magnification (the inset) FE-SEM; and (b) Corresponding low-magnification and high-magnification (the inset) TEM images of H3; FE-SEM (c) and TEM (d) images of smooth H4. Scale bare=1 μm (inset scale bars=100 nm).

Fig. 3. FE-SEM images of the samples prepared by reflux-assisted HT method: (a) high (scale bare=100 nm) and (b) low (scale bare=1 μ m) magnification FE-SEM of MH1. (c) High and (d) low magnification FE-SEM of RH.

Fig. 4. (a) FE-SEM and (b) TEM images of MH2 sample. (c) FE-SEM and (d) TEM images of MUH sample. Scale bars: 1 μm (inset scale bars 200 nm).

Fig. 5. High-magnification (scale bar: 200 nm) (a), low-magnification (scale bar: 1 μm) (b) FE-SEM, and (c) TEM images of UH cubes. EDX elemental analysis (d) and chemical color map (e) of UH sample. (f) Nitrogen adsorption-desorption isotherms and pore size distribution curve (inset) of UH.

Fig. 6. Survey XPS spectrum (a) and high resolution XPS in the Fe2p (b) and O1s (b) regions for UH sample.

Fig. 7. (a) pH dependence of the removal efficiency for 1 g/L of the samples UH and H3 for 50 ppm RB5 (b) Photocatalytic activity of fabricated hematite against RB5 (lines are guide to eye). (c) Kinetic curves of the degradation of RB5 by UH sample at different temperatures. The inset shows the temperature dependence of R.E.. (d) Recyclability of UH and MH1 samples in degrading of 50 ppm RB5.

Fig. 8. (a) Photodegradation of 10 ppm MB and RhB in the presence of 0.2 g/L UH sample. Comparison of apparent rate constants of MB (b) and RhB (c) degradation by different hematite structures in the literature.