

Synthesis and characterisation of TiO₂ nanoparticles/Fe₂O₃ waste chips composite

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Water contamination along with the environmental issues resulted by industrial wastewaters have caused a trend in applying semiconducting photocatalysts, among which TiO₂ composites have been particularly focused on to overcome the drawbacks of titanium(IV) oxide also known as titania. In the current investigation, waste chips of a structural steel bar with the chemical composition of Fe₂O₃ were utilised to obtain the TiO₂-Fe₂O₃ composite. X-ray diffraction (XRD), field-emission scanning electron microscopy, energy dispersive spectroscopy, diffusive reflectance spectra, and Brunauer-Emmett-Teller analyses were made to evaluate the composition and structure of the samples. Furthermore, the photocatalytic performance of the samples was studied by methyl orange (MeO) degradation. XRD spectra proved the presence of anatase and Fe₂O₃ phases in the sample of 10%wt. Fe₂O₃. The results indicate that as the Fe₂O₃ content rises, the bandgap narrows. However, the specific surface area enlarges as this amount goes up to a certain limit (10%wt.), from which any further increase leads to a reduction in the specific surface area. The obtained results of MeO decolourisation presented the Fe₂O₃ of 10%wt. and bandgap of 2.72 eV, and the specific surface area of 63 m²/g to be of the highest efficiency (96%).

1. Introduction: Nowadays semiconductor nanoparticles are increasingly employed in photocatalytic applications of treating industrial wastewaters [1, 2]. The most commonly used semiconductor is TiO₂ (titania). While possessing incomparable properties, titania suffers from its drawbacks. However, various solutions have been introduced to overcome them [2, 3]. The downside of titania is partly caused by the high rate of electron-hole recombination which happens in a nanosecond after exciting titania [4–6]. Moreover, owing to its relatively high bandgap (3.02–3.2 eV), TiO₂ is excited by UV light, yet UV light constitutes roughly 5% of sunlight. Doping TiO₂, and compositing it with various materials are two typical and effective means of tackling these problems [2, 7–10].

Thus, to date, a variety of TiO₂-based composites have been made and used to treat water and air, among which are TiO₂ composites with other metal oxides, various metals, non-metals, and organic compounds [3, 11]. When TiO₂-based composites are excited by a light which has sufficient energy, electrons or the holes between them are replaced. Therefore, the electron-hole recombination stops and they can actively participate in redox reactions [5–7]. Additionally, compositing TiO₂ with compounds of lower bandgaps will decrease the composite's energy. Hence, lights of higher wavelengths will be able to excite [8, 12].

Amongst TiO₂-based composites, compositing it with metals and their oxides has been of much interest to scholars. Thus far composites of TiO₂ with metals such as Ni, Ag, Au, Cu, and Cr have been synthesised and studied through different means. Metals trap electrons and hence the suppression of electron-hole recombination [12–14].

Fe₂O₃ is one of the stable forms of iron oxide in ambient conditions. On account of its stability, magnetic properties, lower band-gap, simple synthesis, and low cost, Fe₂O₃ is an important material in catalysts, and is used as gas sensors, and pollution removal [5, 12, 14]. The combination of TiO₂ with Fe₂O₃ can improve photocatalytic properties and TiO₂'s response to visible light by reducing the rate of electron-hole recombination [12, 15]. Several investigations have been conducted to examine the potential of TiO₂ doped with Fe₂O₃ for photocatalytic applications [11, 16, 17]. It has been proved that adding a proper amount of Fe₂O₃ to TiO₂ leads to a desired condition of light and physico-chemical properties of TiO₂ [3, 14].

In the current study, the TiO₂-Fe₂O₃ composite was obtained and closely examined. The waste chips of a structural steel bar with the chemical composition of Fe₂O₃ were utilised. In fact, the practical and advantageous reusing waste iron oxide was targeted as a new study. Therefore, TiO₂ nanoparticles were precipitated on Fe₂O₃ and then their physical and photocatalytic properties were analysed.

2. Experimental

2.1. Materials: Titanium tetraisopropoxide, hydrochloric acid (HCl), 2-propanol, and methyl orange (MeO) were purchased from MERCK manufacturer. Chips of a structural steel bar were utilised to make the composite.

2.2. Synthesis of TiO₂-based composites: To produce the composites, TiO₂ nanoparticles were synthesised by using chemical method as described in our previous work [4, 10]. In brief, distilled water (85 cc), HCl (6 cc), and 2-propanol (6 cc) were mixed and stirred together at room temperature. After thorough mixing, titanium isopropoxide (5.2 cc) was gradually added to the solution. After 30 min and clearing the solution, its temperature was slowly increased to 60°C by immersing it into a water bath of controlled temperature. Iron oxide waste chips in the form of Fe₂O₃ particles were then added to the solution. The solution was left overnight to allow precipitation of rigid gel. The composites were then washed with deionised water and dried. The samples were then calcined at 450°C for 2 h.

2.3. Characterisations: The crystalline phases of the synthesised samples were obtained by using an X-ray diffractometer (Bruker D8, Germany) with monochromated Cu-K α radiation ($\lambda = 1.54056$ Å). The morphology of the composite was characterised by a field-emission scanning electron microscope (MIRA3 TESCAN, Czech Republic).

The diffusive reflectance spectra (DRS) of the samples were recorded by a UV-Vis spectrophotometer (Avaspec-2048-TEC, Netherlands) using BaSO₄ as a reference in the region from 200 to 900 nm. The Brunauer-Emmett-Teller (BET)-specific surface area was determined using a Belsorp mini II (Japan) system.

2.4. Photocatalytic performance: Adsorption studies were performed by adding 150 mg/l of composite to 50 ml solutions with 5 mg/l initial concentration of MeO. The pH was maintained

constant, equal to the initial pH of the MeO solution (i.e. 6.5). Each solution was stirred for 60 min in full darkness to achieve adsorption-desorption equilibrium. UV irradiation from two 6 W lamp (Philips, China) was then applied to the catalyst containing solution. The distance between the surface of the solution and the light source was 10 cm. Samples were then taken out for analysis at the intervals of 30 min.

The concentration of dye in the solution was measured spectrophotometrically at the wavelength of the maximum absorbance (λ_{max} : 612 nm). The adsorption percentage for each dye, that is the dye removal efficiency, was determined using the following expression [12, 18]:

$$\%R_e = \left[\frac{(C_0 - C_e)}{C_0} \right] \times 100 \quad (1)$$

where C_0 and C_e represent the initial and equilibrium (after adsorption) concentrations of MeO in mg/l, respectively.

The total organic carbon (TOC) value was measured by using a TOC-VCPH analyser (Shimadzu Co., Japan) to evaluate the photo-degradation efficiency of MeO.

For investigation of reusability of $\text{TiO}_2\text{-Fe}_2\text{O}_3$ photocatalyst, after each time of adsorbing the pollutants, so as to reuse the composite, it was washed for 10 h in water and dried at 80°C for 10 h.

3. Results and discussion: The crystalline structure of $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite was examined applying X-ray diffraction (XRD) analysis. Fig. 1 illustrates the XRD pattern of the sample with 10%wt. of Fe_2O_3 particles. In this figure, the identified peaks at the angle of $2\theta = 25.56, 37.87, 48.09, 54.16,$ and 62.47 are related to anatase phase (JCPDS Card No. 21-1272). The peaks of Fe_2O_3 phase appeared at the angles of $32.88, 35.78,$ and 41.08 . Abbas *et al.* [14] studied the phase structure of $\text{TiO}_2\text{-Fe}_2\text{O}_3$ composites. According to their study, at high amounts of Fe_2O_3 (beyond 15%wt.), the intensity of anatase phase lowers and rutile phase forms gradually. This phenomenon has also been reported by others [14, 19, 20]. This well explains why pure anatase phase was present in the sample with 10%wt. of Fe_2O_3 . According to the pattern and by using Debye-Scherrer equation ($d = (kl/\beta \cos\theta)$) [21], the crystallite size of anatase phase was determined to be of the order of 23 nm.

Anatase TiO_2 generally performs better in photocatalytic experiments compared to rutile TiO_2 systems [19, 22]. The superior performance of anatase over rutile in photocatalysis can be attributed to a number of factors, such as better charge-carrier mobility, lengthier exciton diffusion, bigger size of rutile particles, and higher bandgaps [22].

Fig. 2 indicates field-emission scanning electron microscopy (FESEM) images and energy dispersive spectroscopy (EDS) analysis of the 10% Fe_2O_3 sample. Fig. 2a shows how TiO_2

particles precipitated on Fe_2O_3 particles. At a greater magnification of the precipitated particles, in Fig. 2b, the morphology of the particles is recognisable. The particles formed are pseudo-spherical and the dimensions are larger than 50 nm. The EDS analysis in Fig. 2c confirms the presence of the two phases of TiO_2 and Fe_2O_3 .

The specific surface area is of vital importance in nanoparticles activities. Accordingly, BET analyses of different samples were conducted. The results can be seen in Table 1. The specific

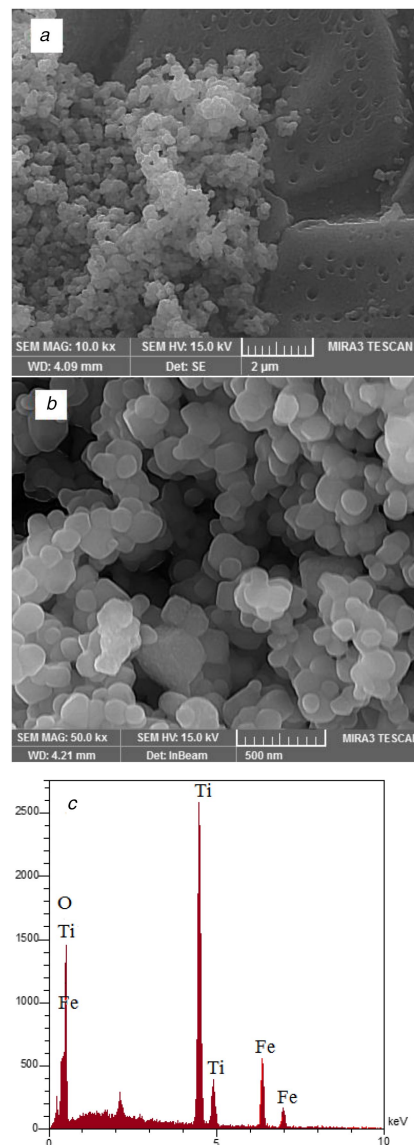


Fig. 2 $\text{TiO}_2\text{-10}\%\text{Fe}_2\text{O}_3$ composite

a, b FESEM images

c EDX pattern

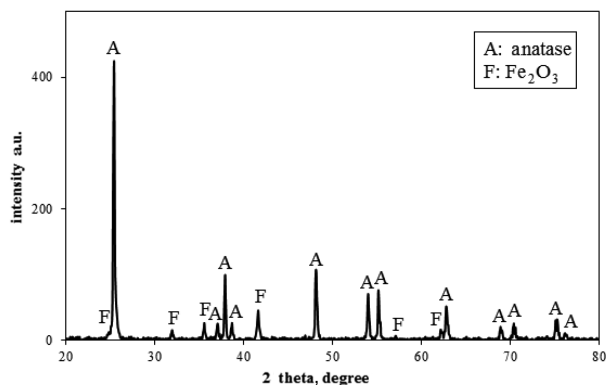


Fig. 1 XRD pattern of $\text{TiO}_2\text{-10}\%\text{Fe}_2\text{O}_3$

Table 1 Physical parameters of $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composites

Samples	S_{BET} , m^2/g	Bandgap energy, E_g , eV	Absorption onset (λ_g , nm)
TiO_2	38	3.12	397
$\text{TiO}_2\text{-5}\%\text{Fe}_2\text{O}_3$	47	2.91	425
$\text{TiO}_2\text{-10}\%$	63	2.72	455
Fe_2O_3			
$\text{TiO}_2\text{-15}\%$	61	2.53	490
Fe_2O_3			
$\text{TiO}_2\text{-20}\%$	54	2.34	532
Fe_2O_3			

surface area for the compound of TiO_2 –10% Fe_2O_3 was measured to be $63 \text{ m}^2/\text{g}$, which is wider than those of pure TiO_2 and other compounds. When Fe_2O_3 is present in larger amounts, since they own less porosity and are of bigger dimensions, there exist a decline in the specific surface area. The large specific surface area in the sample of 10% Fe_2O_3 can remarkably aid the photocatalytic applications and help to provide the proper contact between the reactors and catalyst's surface.

Light properties of the obtained composites were examined by UV–Vis diffuse reflectance spectroscopy. Under such conditions it would be beneficial to determine the bandgap, which was consequently calculated through Kubelka-Munk as follows [7]:

$$(\alpha h\nu) = \beta(h\nu - E_g)^n \quad (2)$$

where E_g is energy bandgap of semiconductors (eV), ν is the frequency of light (s^{-1}), h is Planck's constant (J.s), β is the absorption constant, and α is the absorption coefficient defined by the Beer–Lambert law as $\alpha = (2.303 \times \text{Abs})/d$, where d and Abs are the sample thickness and sample absorbance, respectively; whereas, the value of index n for allowed direct transition, forbidden direct transition, or indirect transition is $1/2$, $3/2$, and 2 , respectively [4, 7]. The bandgap can be determined by extrapolating the linear portion of the $(\alpha h\nu)^n - h\nu$ curve. $n = 1/2$ value better defines our material. The graphs in Fig. 3 were produced thereupon.

Fig. 3a displays the UV–Vis DRS spectra of the pure titania and $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composites with different Fe_2O_3 content. In general, the presence of Fe_2O_3 has resulted in the increase in the absorption intensity in the UV and visible light area. The red-shifting was attributed to the additional energy levels created by the composition of TiO_2 with Fe_2O_3 [12, 14].

Optical bandgaps (E_g) estimated from extrapolation of Tauc's plot on x intercepts are shown in the legend of Fig. 3b. Table 1 displays the determined bandgaps for different composites. It can be observed that as the Fe_2O_3 content grows, the bandgap lowers in a way that for 20% of Fe_2O_3 , the TiO_2 bandgap falls from 3.12 to 2.34 eV.

The photocatalytic activities of $\text{Fe}_2\text{O}_3/\text{TiO}_2$ composites were investigated by the degradation of MeO. MeO ($\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$ – a heterocyclic aromatic compound) survives in wastewater as a hazardous organic dye [1, 23]. MeO is hazardous for aquatic life and is accepted as a model pollutant for photocatalytic degradation reactions [24].

Fig. 4a represents the degradation behaviour of MeO dye during irradiation as a function of time in the presence of TiO_2 and $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composites. The presence of TiO_2 has ameliorated the photocatalytic performance since in a time span of 180 min, pure TiO_2 solely degraded 74% of MeO while Fe_2O_3 has promoted the efficiency. Maximum degradation efficiency was obtained for

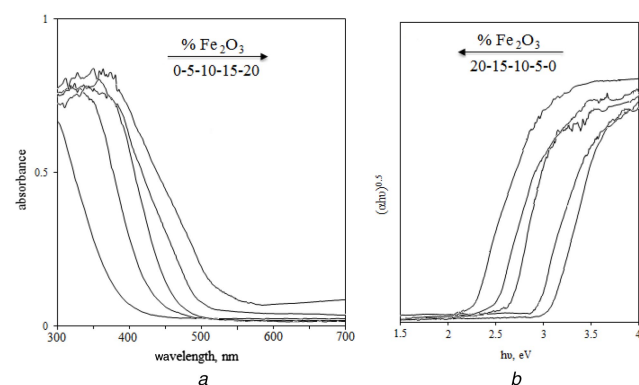


Fig. 3 TiO_2 – Fe_2O_3 nanocomposites
a UV–Vis diffuse reflectance spectra
b Tauc plot obtained from UV–Vis DRS spectra

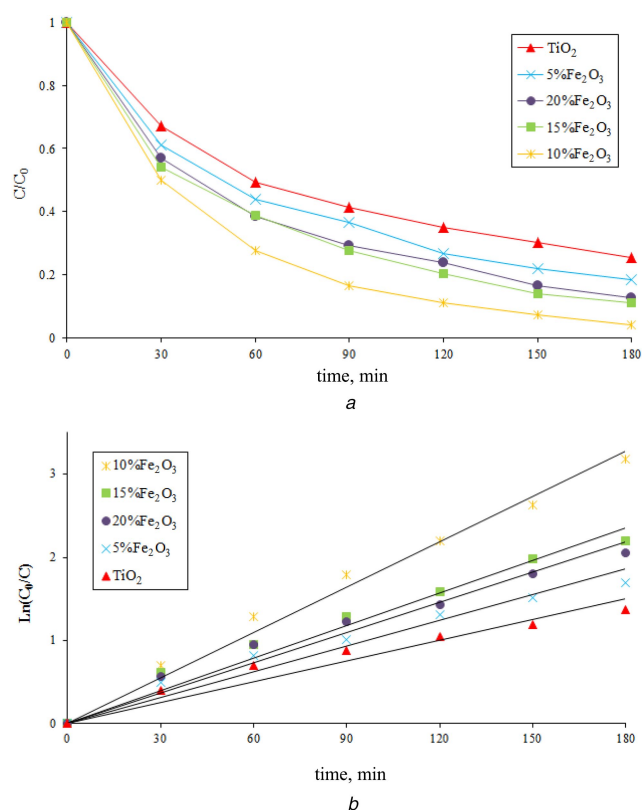


Fig. 4 Photocatalytic performance of samples
a Degradation of methylene orange
b Linear correlation between reaction time and logarithm of relative concentration of methylene orange ($\ln C_0/C$)

the reaction carried out in the presence of TiO_2 –10% Fe_2O_3 , after which the efficiency reduced with a further increase of Fe_2O_3 percentage. This finding is similar to Ahmed *et al.* study, which indicated the maximum performance for the sample containing 7 wt.% of Fe_2O_3 in TiO_2 – Fe_2O_3 composite.

The schematic bandgaps of TiO_2 and Fe_2O_3 have been depicted in Fig. 5. Regarding the bandgaps of these two, under the radiation of visible light, TiO_2 cannot be excited to generate electron–holes. On the contrary, its bandgap being small (2.2 eV), Fe_2O_3 can easily be stimulated, and it is capable of creating charge carriers [16, 25]. It is self-evident that photocatalytic performance does not only depend on generating electron–hole pairs, and preventing the recombination of electron–holes is equally important for the reaction [26, 27].

Adding Fe_2O_3 to TiO_2 not only facilitates the generation of electrons in the conduction band, but also slows down the electron–hole

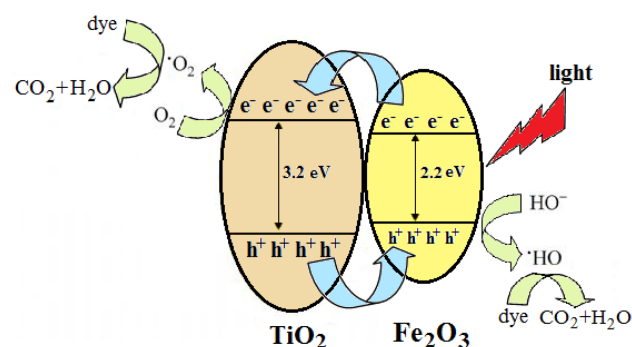


Fig. 5 Schematic representation of interfacial charge carrier generation, transfer and separation between TiO_2 and Fe_2O_3

Table 2 Comparison of removal rates obtained by UV–Vis and TOC after the reaction time for 180 min

Samples	UV–Vis, %	TOC, %	Kinetic parameters	
			Rate constant, min ^{−1}	R ²
TiO ₂	74	38.6	0.0084	0.949
TiO ₂ –5%Fe ₂ O ₃	82	47.8	0.0103	0.954
TiO ₂ –10%Fe ₂ O ₃	96	65.1	0.0182	0.986
TiO ₂ –15%Fe ₂ O ₃	89	56.2	0.0131	0.969
TiO ₂ –20%Fe ₂ O ₃	87	54.3	0.0121	0.962

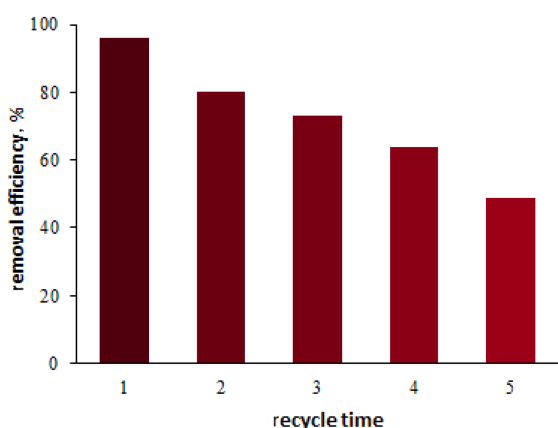
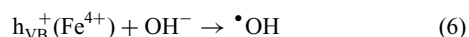
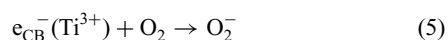
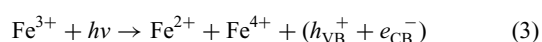


Fig. 6 Reusability of the TiO₂–10%Fe₂O₃ for MeO degradation

recombination rate due to the lower position of the conduction band as a capture for electron–holes [15, 25, 26, 28]. By radiating light and generating electron–holes, the electrons migrate from the conduction band of Fe₂O₃ to that of TiO₂, whereas the holes accumulate in the valance band of Fe₂O₃ [3]. The negative electrons in the conduction band of TiO₂ react with the dissolved molecules in the dye solution and superoxide anion and hydrogen peroxide are resulted in [28, 29]. On the other hand, the accumulated holes in the valance band of Fe₂O₃ react with the OH[−] species on the surface of the catalyst and form hydroxyl radicals. These reactions can be stated as follows [2, 30]:



Fe³⁺ ion acts as a good electron capture agent, and the substitution of Fe³⁺ for Ti⁴⁺ boosts electron flow capture, promotes the half-life of electron–hole pair, and betters the photocatalytic activity. Furthermore, the captured electron by Fe³⁺ can transfer to Ti⁴⁺ with ease. Hence, the interaction between Fe₂O₃ and TiO₂ enhances charge separation, and develops the response of TiO₂ to the visible area [3, 14, 29].

Fig. 4b represents the plots of ln(C₀/C) versus time for the different samples. The constant of rate (k) shifts for different samples which illustrate the heavy dependence of photocatalytic activity upon structural properties and chemical composition of the samples. Values of the constant of rate and R² for each sample can be seen in Table 2. Due to the results, the 10%Fe₂O₃ sample had a higher constant rate (0.0182 min^{−1}). The differences in photocatalytic activities based on the Fe₂O₃ contents confirms that the performance of the obtained composites is influenced by the

amount of Fe₂O₃ existing in the composite which impacts crystallinity, size of the particles, porosities, and light performance of TiO₂–Fe₂O₃ composites [14]. Maximum degradation of MeO, which was of the value of 96%, was caused by TiO₂–10%Fe₂O₃.

Table 2 lists the removal results obtained by UV–Vis and TOC measurements after the reaction time of 180 min. Under the same condition, TiO₂–10%Fe₂O₃ has the best efficiency for MeO degradation.

Reusability of TiO₂–10%Fe₂O₃ composite in degradation of MeO was also investigated. Fig. 6 shows the photocatalytic performance of the composite having been reused for five times. As it can be seen, the efficiency of the composite in degradation of the dye gradually lowers, dropping from 96 to 49% after five times' reuse. This reduction of efficiency can be due to dissolution and separation of TiO₂ particles after each time being used.

4. Conclusion: In the current investigation, TiO₂ composites were successfully obtained using waste chips of a structural steel bar with the chemical composition of Fe₂O₃. The synthesised samples were examined by XRD, FESEM, DRS, and BET analyses. Moreover, the photocatalytic performance of the samples was evaluated by MeO degradation. XRD analysis affirms the presence of the two phases of anatase and Fe₂O₃ in the structure. Examining the effect of the content of Fe₂O₃ illustrated that the content of 10% of Fe₂O₃ maximised the rate of decolourisation by realising a specific surface area of 63 m²/g and bandgap of 2.72 eV.

5 References

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