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PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE USING Fe_2O_3-TiO_2/KAOLINITE UNDER VISIBLE LIGHT ILLUMINATION

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ABSTRACT

Combining TiO_2 and a semiconductor with a smaller band gap, such as Fe_2O_3, to form a heterojunction composite can increase its photocatalytic activity. In this work, the Fe_2O_3-TiO_2/kaolinite composites were successfully synthesized by ultrasonic-assisted coprecipitation using titanium-tetraisopropoxide (TTIP) dan Fe $(NO_3)_3.9H_2O$ as precursors. Using kaolinite as a matrix also increases the photocatalyst's surface area. The obtained Fe_2O_3-TiO_2/kaolinite composites were characterized. The crystal phase was characterized using X-Ray Diffraction and resulted in anatase with a crystallite size average of 9,7 nm. Fourier Transform Infrared Spectrophotometer (FTIR) shows the peak at a wavenumber 574-1210 cm^{-1} ascribed TiO_2 and Fe_2O_3 incorporated into kaolinite. The Optical properties show the absorption edge of Fe_2O_3-TiO_2/kaolinite is redshift toward the visible light region. The result showed that the photocatalytic activity of Fe_2O_3-TiO_2/kaolinite composites with heterostructure was more active than the corresponding Fe_2O_3 or pure TiO_2 in the degradation of methylene blue under visible light illumination, which can degrade 83% for 180 minutes. Fe_2O_3 and kaolinite cause its synergistic effect as supporting materials. Furthermore, it indicates that the recombination of photo hole and photoelectron charge pair can be minimized. The Fe_2O_3-TiO_2/kaolinite composite is a promising photocatalyst to degrade organic pollutants for wastewater treatment.

Keywords: *Fe_2O_3-TiO_2, kaolinite, composites, sol-gel, ultrasonic assisted coprecipitation*

INTRODUCTION

The world's population is overgrowing, causing the need for clean water to be very high. However, the availability of clean water resources on the earth's surface is increasingly worrying due to pollution from industrial and household waste [1]. Several compounds that can pollute the aquatic environment include coloured organic compounds, pesticides, heavy metals and pathogenic bacteria [2].

Methylene blue, an organic compound derived from phenothiazines, is generally used in the printing, textile, laboratory, and manufacturing industries. Unfortunately, methylene blue solution wasted in aquatic environments is difficult to decompose by microorganisms. Therefore, it can interfere with the aquatic photosynthetic process, ultimately negatively impacting human health [3]. Several techniques have been used to eliminate these compounds, including adsorption, ozonation and using microorganisms. However, it can only transfer from the solution medium to the surface of the adsorbent used [4].

Semiconductor such as TiO_2 has been widely used as a photocatalyst to degrade organic pollutants because they can convert contaminants into harmless substances, working at the ambient condition with high efficiency and low cost [5]. However, the application of TiO_2 photocatalyst is limited because it has a wide band gap (3.0-3.2 eV) which can only be activated by UV light. When the TiO_2 surface is exposed to light with an energy corresponding to the band gap energy, a photo hole (H^+) and photoelectron (e-) charge pair will form and then form a hydroxy radical (•OH). These charge pairs tend to recombine so that the quantity of •OH formed on the surface is small, resulting in low photocatalytic activity [6]. In addition, the adsorption ability of organic substrates is relatively small because the surface area of TiO_2 particles is relatively small, causing the photodegradation efficiency to be low. Therefore, development needs to be done to obtain photocatalysts that are responsive to visible light and easy to recycle. TiO_2 coupling with other semiconductors with a smaller band gap energy can minimize photoelectron and photo-hole charge recombination, thereby increasing photocatalytic activity [5,7]. The Fe_2O_3 with small band gap energy (2.2 eV) is very suiTable for coupling with TiO_2 to produce a composite. Mixing hematite, Fe_2O_3, with TiO_2 forms a composite heterojunction Fe_2O_3-TiO_2 with unique properties. When the surface of TiO_2 is irradiated with photon energy, it will form a photoelectron in the conduction band. Species (e-) are injected onto the surface of Fe_2O_3 so that the quantity charge (H^+) increases on the surface, causing the efficiency of photocatalysis to increase [8]. Sharma et al. reported the results of the TiO_2-Fe_2O_3 nanocomposite using the mechanochemical ball milling method [9]. Banisarif et al. have succeeded in synthesizing Fe_2O_3-TiO_2 composites by ultrasonic coprecipitation method, which provides photocatalytic degradation activity of trichloroethylene under visible light illumination [10]. composite of Fe_2O_3-TiO_2/activated carbon was prepared by coprecipitation and ultrasonication methods, showing the degradation activity of trichloroethylene under visible light illumination [11].

In recent years, many publications have reported the advantages of Fe_2O_3-TiO_2 composites for degrading coloured aromatic compounds and phenols working in ambient conditions, low cost and high efficiency [4,12]. The synthesis of Fe_2O_3 using the solvothermal method. The different nanostructures of Fe_2O_3 synthesized by the solvothermal method showed excellent photocatalytic activity for deleting methylene blue by adding H_2O_2 under visible light illumination [7,13]. TiO_2 /α-Fe_2O_3 composite from iron sand by mechanical ball milling method and reported high photodegradation activity (100%) against indigo carmine dye under UV light irradiation [14]. The composite dispersion system in solution is less effective because it is difficult to separate from the solution when the reaction has been completed [13].

The impregnation of TiO_2 on kaolinite as supporting materials can increase the effectiveness of the catalyst. Kaolinite has several -OH groups on its surface and is estimated to interact easily with TiO_2 to form a sTable composite [15]. In addition, kaolinite has a reasonably large pore which can increase the adsorption capacity of organic substrates [8]. The pillared kaolinite using Fe_2O_3 increases the surface area and enhances the organic substrates' adsorption capacity [16]. However, no detailed discussion has been found regarding the optimal ratio (% w/w) Fe_2O_3: TiO_2: kaolinite.

In this work, Fe_2O_3-TiO_2/kaolin was synthesized using a combined sol-gel method and ultrasonication-assisted coprecipitation, using titanium-tetraisopropoxide (TTIP), Fe $(NO_3)_3.9H_2O$ and kaolinite. Kaolinite was obtained from the village of Capkala Sungai Raya West Kalimantan. Based on our previous research, the composition of kaolinite Capkala is an alumina-silicate type of clay mineral with the molecular formula $Si_4Al_4O_{10}(OH)_8$. The ratio of Al_2O_3: SiO_2: H_2O are 1:2:2 per unit cell, which has a 1:1 layered structure with an average particle size of 2 m and a specific surface area of 7-20 m^2/g [17]. The composites obtained were characterized by the crystal structure, functional groups, optical properties and pore distribution. Photocatalytic activity will be evaluated on the degradation of methylene blue solution under visible light illumination.

METHODS

The materials used in this study were acetic acid with purity 98% (Merck), acetylacetone 97% (Merck), hydrochloric acid (96% sigma Aldrich), iron oxide Fe_2O_3 (96% sigma aldrich), acetate buffer (CH_3COOH) Merck, absolute ethanol (C_2H_5OH) 98% Merck, kaolinite from capkala regency, methylene blue (Merck), titanium-tetra-isopropoxide (TTIP) 97% Sigma Aldrich and distilled water.

The apparatus and instruments used in this research are 170 mesh sieve, ultrasonicator (Branson 3510, 42 kh), Fourier Transform Infrared (Shimadzu), X-Ray Diffraction (Philips, X-Ray 40 kv), Ultra Violet-Visible Diffuse Reflectance Spectrophotometry (Agilent Technologies Cary 60), and UV-Vis Spectrophotometer Shimadzu UV-128.

Composites preparation

Preparation of the TiO_2 powder

The TiO_2 was prepared by the sol-gel method [6]. Preparation begins by making solutions of 2 mL of acetic acid and 2 mL of aquabides into 26.5 mL of ethanol. The TTIP 7.5 mL was dissolved in 26.5 mL of ethanol. The mixture of solution B was put into a reflux flask set at 55ºC for ± 2 hours and stirred using a magnetic stirrer. A total of 1 mL of acetylacetone was added to the solution mixture. During the reflux process, solution A is dripped slowly into solution B. After the reflux process is complete, the mix of solutions is allowed to stand for 10 minutes until a sol of Ti(OH)n is obtained. Next, the Ti(OH)n sol was air-dried to form a gel. The gel was dried at 80ºC for ± 1 hour, followed by calcined of 450ºC, until later, the TiO_2 was obtained in the form of a white powder.

Synthesis of Fe_2O_3-TiO_2 composites.

Synthesis of Fe_2O_3-TiO_2 composite by sonication method referring to modified [17]. 50 mL of a solution of Fe $(NO_3)_3.9H_2O$ in ethanol (0.5 M) added 1.5 g of TiO_2 powder, stirring with a magnetic stirrer for 30 minutes at room temperature, then sonicated for 30 minutes. The mixture was dried in an oven at 65°C, then calcined at 450°C for 1 hour. The samples were then rinsed with ethanol and sonicated for 30 minutes, then dried in an oven and calcined at 450°C for 3 hours.

Preparation of the kaolinite capkala composites

Kaolinite was prepared from kaolin capkala according to the method of Aritonang et al. [18]. First, kaolin was washed in distilled water to form colloids and precipitates from impurities and silica. This washing was carried out repeatedly until pure kaolin was obtained at a pH of 7.0 and then dried at 100°C. Then, uniform the size using 170 mesh sieves.

Synthesis of Fe_2O_3-TiO_2/kaolinite

The Fe_2O_3- TiO_2/kaolinite composites were synthesized using the ultrasonic-assisted coprecipitation method [19]. Briefly, 1.5 g of kaolinite was mixed with 1.5 g of Fe_2O_3-TiO_2. Next, the mixture was dissolved in 50 mL of water while stirring using a magnetic stirrer for 1 hour, followed by sonication for 1 hour. Next, the samples were dried in an oven at 105°C for 3 hours to produce the powder. Finally, powders were calcined at 450°C for 3 hours to obtain Fe_2O_3-TiO_2/kaolinite composites.

The structure phases were identified at 293 K on X-Ray Diffraction (Philips, X-Ray 40 kv), using Cu Kα radiation (λ = 0.15419 nm). Crystallite sizes of the composites were estimated using Debye Scherrer's formula: [10]

$$D = \frac{0.9\,\lambda}{\beta\, Cos\ \theta} \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where D is the diameter of the nanoparticles, λ (CuKα) = 0.15406 nm and is the full-width at half-maximum of the diffraction lines. Functional groups in the obtained composites were recorded with a Fourier Transform Infrared (Shimadzu),) over a wavenumber range of 400-4000 cm^{-1}. The specific surface area and pore size distribution were measured by Brunauer-Emmet-Teller, using Quantachrome Instruments. The optical properties of composites were recorded by a diffuse reflectance spectrophotometer (Agilent Technologies Cary 60). The samples were recorded by a spectrophotometer with the software UV Probe (DRS-8000 Shimadzu), and UV-Vis Spectrophotometer Shimadzu UV-128 recorded the concentration of the methylene blue.

Photocatalytic Activity for Methylene Blue Degradation

The photocatalytic activity was evaluated for degradation of methylene blue (MB, 10 ppm). The Photocatalytic evaluation was conducted under dark and visible light with (λ ≥ 400 nm) irradiation using a lamp Light Emitting Diode (100 watts), which was placed 20 cm beside the reactor tube to induce photocatalytic reaction for 180 minutes. After the exposure, MB concentration was measured by measuring absorbance at 600 nm wavelength using a UV-visible spectrophotometer Shimadzu UV-128.

RESULTS AND DISCUSSION

Characterization of Fe_2O_3-TiO_2/kaolinite Composites

The X-ray measurement of the TiO_2, Fe_2O_3, and Fe_2O_3-TiO_2/kaolinite is carried out to investigate the crystal phase of these samples, as shown in Figure 1.

Diffractions peaks at 25.32°, 37.68°, 46.38°, 54.86°, 61.70°and 68.00° 2theta can be attributed to (101), (100), (200), (105), (211), (213), (116) and (107) crystal planes of anatase phase of the TiO_2 respectively, were matched with JCPDS card no. 01-075-8897. Figure 1(b) showed absorption peaks at about 2θ 26°, 34° and 48°, which can be attributed to (101), (110) and (113) from crystal plane Fe_2O_3.

We can be seen in Figure 1(d), the diffraction peaks at (2θ) 26.55° and 59.81° are observed, which are characteristic of TiO_2 and Fe_2O_3, respectively, an indication that a Fe_2O_3-TiO_2/Kaolinite composite heterojunction has been formed which agrees with the reported [20]. Based on calculations using Debye Scherrer's equation, the crystallite size estimate is shown in Table 1.

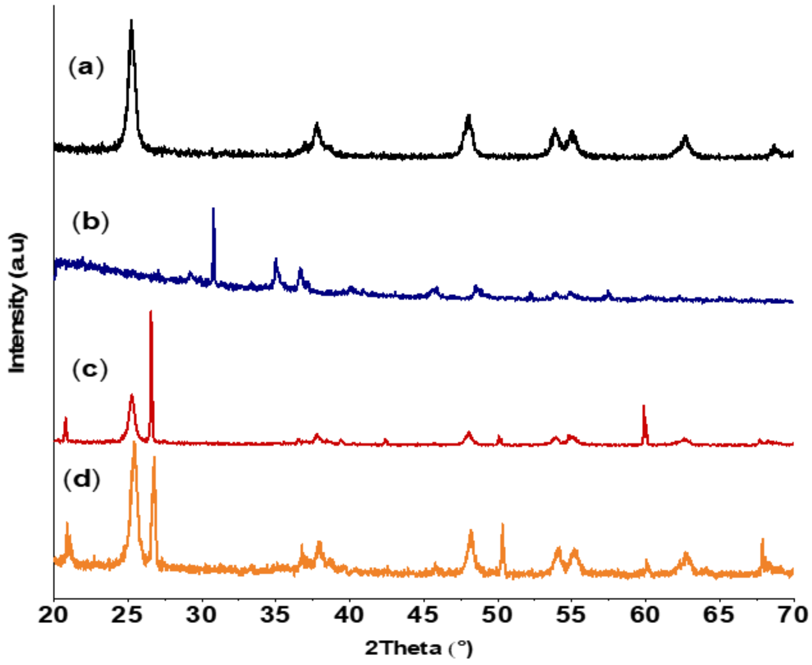

Figure 1. XRD pattern of: (a) TiO_2, (b) Fe_2O_3, (c) Fe_2O_3-TiO_2 and (d) Fe_2O_3-TiO_2/kaolinite

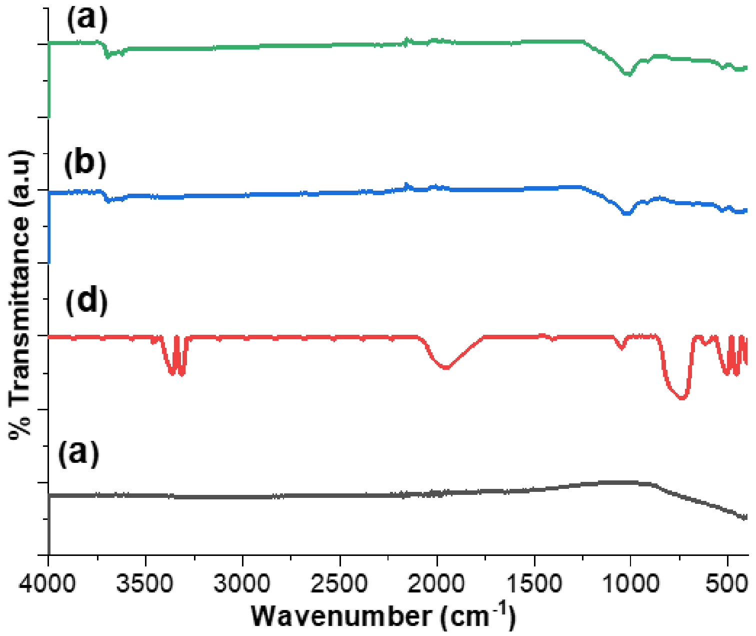

Figure 2. FTIR Spectra pattern for (a) TiO_2, (b) Fe_2O_3, (c) Fe_2O_3-TiO_2, and d) Fe_2O_3-TiO_2/kaolinite composites

The impregnation of the Fe_2O_3-TiO_2 composite on the kaolinite surface causes a decrease in the crystallinity from 16.12 nm to 9.70 nm. The calcination process at 450°C causes the transformation of kaolinite into an amorphous phase of metakaolinite [15]. In Table 1, it can be seen that the crystallite size of the Fe_2O_3-TiO_2 composite is decreased (16.12 nm) to 9.70 nm. Fe_2O_3-TiO_2 has been impregnated on the Kaolinite surface by [5,9,18].

Table 1. Size of photocatalyst crystalline

Sampel	Angle 2θ (°)	Crystallite size (nm)
TiO_2	25,26	12,46
Fe_2O_3	33,22	17,94
Fe_2O_3-TiO_2	26,55	16,12
Fe_2O_3-TiO_2/Kaolinite	25,41	9,70

The FTIR spectra were carried out to determine the vibration bands present in the prepared Fe_2O_3-TiO_2/kaolinite composites are shown in Figure 2. The absorption peak of TiO_2 at wavenumber 512 cm^{-1} is a characteristic of Ti-O-Ti stretching vibrations [18,19]. The vibration band can be scanned in 500-4000 cm−1 wavenumber range. This intense peak occurs at a wavenumber between 3510 and 1632 cm^{-1} due to the which is the stretching and bending

We can be seen in Figure 2(d) absorption peak occurs at a wavenumber 574-1210 cm^{-1} ascribed TiO_2 and Fe_2O_3 incorporated into kaolinite. The absorption peaks at 994 cm^{-1} and 602 cm^{-1} were characteristic of Al-O vibrations [15]. However, the absorption peak of the Fe-O bond was not visible because covered by kaolinite [10,15]. The vibration of Si−O−Si was shown the absorption peak at 698 cm−1 and 785 cm−1. The absorption peak at 1012 cm−1 was the Si−O strain. FTIR spectra of TiO_2/kaolinite and Fe-TiO_2/kaolinite showed vibrations of Si−O−Ti at a wavenumber of 918 cm^{-1} [21]. This absorption peak is an indication that TiO_2 forms bonds with kaolinite. In the Fe_2O_3-TiO_2/kaolinite samples, it was observed that the absorption peak of the Ti-O-Ti stretching vibrations did not shift due to the coalescence of the particles only on the surface of the TiO_2 and Fe_2O_3 particles supported by the XRD data.

The optical properties of prepared composites were investigated using DRS UV-Visible and recorded at room temperature, as shown in Figure 3. The anatase TiO_2 exhibits absorption in a wavelength region below 380 nm (band gap 3,2 eV) due to the intrinsic inter-band transition absorption of anatase TiO_2 (Figure 3(a)). Based on the characterization of the optical properties, it is known that the Fe_2O_3-TiO_2/kaolinite composite gives an absorption peak that extends to the wavelength region of 550 nm.

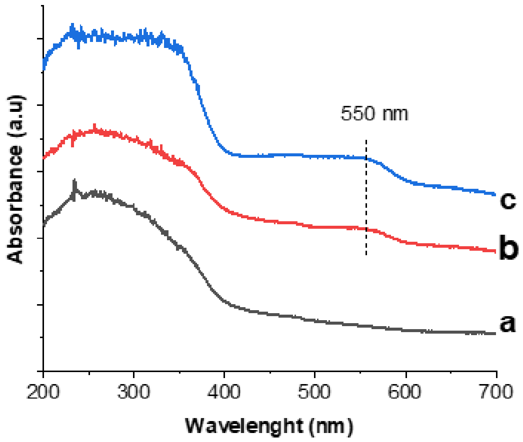

Figure 3. DRS Spectra pattern of (a) TiO_2, (b) Fe_2O_3, (c) Fe_2O_3-TiO_2, and (d) Fe_2O_3-TiO_2/kaolinite Composite

The red shift in the absorption band is the contribution of Fe_2O_3, which has a band gap (2.2 eV). The band gap of the TiO_2 decrease after mixing with Fe_2O_3 to form the Fe_2O_3/TiO_2 composite to become 2.6 eV. The electronic structure of TiO_2 is disturbed after being combined with Fe_2O_3. Meanwhile, the *d-d* orbital transition of Fe^{3+} or charge transition between Fe^{3+} and Fe^{3+} can also cause a redshift of the absorption band [22]. Charge transfer on the surface of the composite causes charges (e-) and (h+) to be separated, so the recombination of these charge pairs can be minimized, thereby increasing the efficiency of photocatalysis [22,23].

2. Studies Photocatalytic Activity of Fe_2O_3-TiO_2/kaolinite Composites

The activity test of the evaluated composites was used for the degradation of MB in aqueous solutions TiO_2, Fe_2O_3-TiO_2 and Fe_2O_3-TiO_2/kaolinite as photocatalysts. Figure 4 shows the correlation curve % degradation of MB by photocatalysis under visible light illumination for 180 minutes.

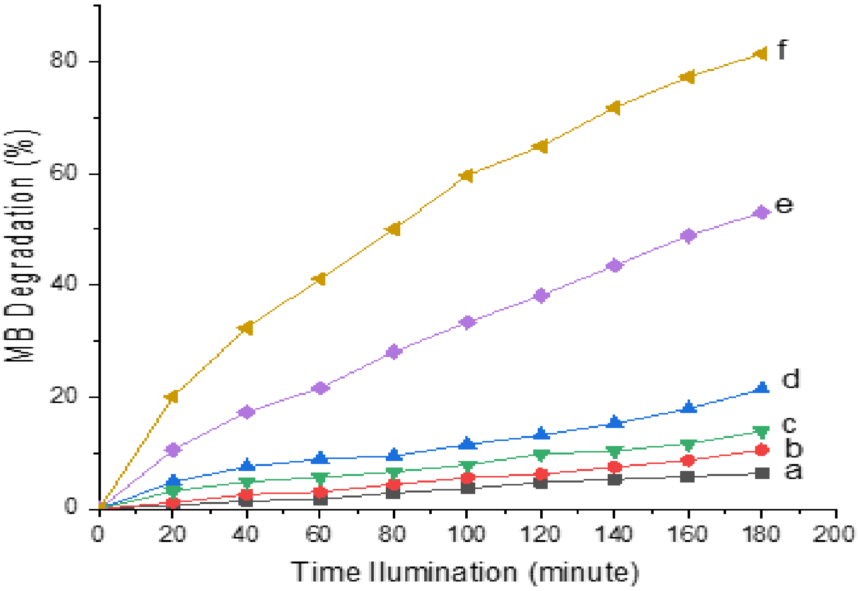

Figure 4. % Degradation of Methylene Blue (10 ppm) by: (a) Photolysis; (b) Adsorption; Photocatalysis using: (c) TiO_2; (d) Fe_2O_3; (e) Fe_2O_3-TiO_2, and (f) Fe_2O_3-TiO_2/Kaolinite.

TiO_2 was able to degrade MB as much as 16.5% higher than the adsorption and photolysis processes of only 4% and 7%, respectively, as a control. Generally, TiO_2 is not active as a photocatalyst under visible light illumination. LED lamp used as a light source emits UV light. It combines TiO_2 with Fe_2O_3 and forms a Fe_2O_3-TiO_2 composite, causing TiO2 to absorb visible light up to the 550 nm wavelength region (Figure 4(b)). The Fe_2O_3-TiO_2 composite could degrade MB (51%) higher than 21% Fe_2O_3.

The Fe_2O_3-TiO_2/kaolinite as photocatalyst after 180 min visible light illumination shows higher photocatalytic activity than all photocatalysts and can degrade MB over 83%. Kaolinite has a large surface area that can increase the adsorption of MB on the composite surface. The amount of MB to be degraded enhances photocatalytic efficiency [15]. The mixing of Fe_2O_3 with TiO_2 has a significant effect on the photocatalytic properties of TiO_2. According to bandgap (2,6 eV), Fe_2O_3 has a lower band gap energy than TiO_2 and can act as a sensitizer because it can transfer electrons to the large band gap of TiO_2. The low charge pair recombination contributes to the high photocatalytic activity of the Fe_2O_3-TiO_2/kaolinite composite [24]. Therefore, the simultaneous integration of Fe_2O_3 and kaolinite can synergistically improve the photocatalytic performance of the Fe_2O_3-TiO_2/kaolinite composite.

CONCLUSION

In summary, the Fe_2O_3-TiO_2/Kaolinite composites were prepared. The photocatalytic activity test results revealed that the Fe_2O_3-TiO_2/kaolinite composites with heterostructure were more active than the corresponding Fe_2O_3 pure TiO_2 in the photocatalysis degradation of methylene blue under visible light illumination for 180 min. The enhanced photocatalytic activities of Fe_2O_3-TiO_2/kaolinite composites were synergistic effects of Fe_2O_3 and kaolinite as supporting materials. Furthermore, the degradation of MB is contributed by photogenerated electron-hole separation efficiency due to electron transfer from the TiO_2 surface into the Fe_2O_3 lattice.

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