



# Enhanced photocatalytic reduction of Cr(VI) under visible light a magnetically separable TiO<sub>2</sub>-Fe/Fe<sub>3</sub>O<sub>4</sub> photocatalyst prepared from iron rusty waste

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## Abstract

This research deals with enhancing the visible activity and generating the magnetic property of TiO<sub>2</sub> by Fe doping and Fe<sub>3</sub>O<sub>4</sub> impregnation respectively, using rusty iron waste as Fe source. The prepared TiO<sub>2</sub>-Fe/Fe<sub>3</sub>O<sub>4</sub> photocatalysts were characterized by SR-UV/Visible, FTIR, XRD, and SEM-EDX instruments. The resulting photocatalysts are responsive to visible light and can be separated magnetically and used for photoreduction of Cr(VI) ions. In the photoreduction of Cr(VI) over TiO<sub>2</sub>-Fe/Fe<sub>3</sub>O<sub>4</sub> photo-catalysts with various amounts of Fe dopant and alteration of Fe<sub>3</sub>O<sub>4</sub> fraction, the photocatalyst mass, irradiation time, and solution pH were optimized. The research results assign that doping Fe to TiO<sub>2</sub> photo-catalysts can decrease the band gap energy (E<sub>g</sub>) consequently improving its activity under visible irradiation. Furthermore, the magnetization of TiO<sub>2</sub>-Fe allows it to be separated practically and effectively. The best detachable and the most active photocatalyst is shown by TiO<sub>2</sub>-Fe/Fe<sub>3</sub>O<sub>4</sub> having a Ti/Fe mole ratio of 1:0.05 and Fe<sub>3</sub>O<sub>4</sub> fraction of 50.00%. The highest photoreduction of Cr(VI) 10 mg·L<sup>-1</sup> in 100 mL solution, 92.5%, can be achieved by applying 0.2 g of the photocatalyst mass, solution pH 3, in 90 min of reaction time under visible light.

## 1. Introduction

Chromium (Cr) in aqueous media exists in two stable oxidation states: Cr(III) and Cr(VI) ions. The cationic Cr(III) ions, Cr<sup>3+</sup>, are less toxic and are even beneficial for mammals to increase milk production, can settle to alkaline pH, and play an essential role in glucose metabolism for humans [1]. Conversely, Cr(VI) ions form anions, CrO<sub>4</sub><sup>2-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, dissolve in the pH range of 1 to 14, are toxic even at low concentrations, potentially carcinogenic and mutagenic, and cause various adverse health effects such as allergic reactions, weakening of the immune system, kidney and liver damage, and even death [2]. Environmental pollution by Cr(VI) occurs due to wastewater disposal from industries such as metallurgy, textile, wood, paint, paper, and electroplating without proper treatment [3]. The World Health Organization (WHO) sets the maximum concentration limit for Cr(VI) in the environment at 0.05 mg·L<sup>-1</sup> [4]. Given the negative consequences caused by Cr(VI) ions, wastewater treatment must be carried out to remove or decrease the concentration of Cr(VI) anions in wastewater.

Reported effective methods of handling Cr(VI) anions include photocatalytic reduction, which converts toxic Cr(VI) anions into safer Cr(III) cations. This process involves using light-induced reduction accelerated by a photocatalyst such as TiO<sub>2</sub> [5,6]. When TiO<sub>2</sub> is exposed to sunlight, it releases electrons (e<sup>-</sup>) and forms positive radicals (h<sup>+</sup>). Positive radicals can oxidize and degrade various organic solid compounds [7]. At the same time, the released electrons can act as a reducing agent and react with Cr(VI) ions to facilitate the reduction

[8]. TiO<sub>2</sub> accelerates oxidation/degradation and reduction reactions and possesses qualities such as good stability, affordability, and non-toxic properties [9]. However, TiO<sub>2</sub> has a wide bandgap (E<sub>g</sub>) energy of 3.2 eV (for TiO<sub>2</sub> anatase), which can only be activated by UV light. UV light only contains about 5% of the spectrum of sunlight, about 40% to 50% of visible light, and the rest is infrared radiation [10,11]. This limits the application of TiO<sub>2</sub> under sunlight.

Attempts to enhance TiO<sub>2</sub> activity under visible light exposure have often been made by doping transition metals, such as Fe [12,13]. Doping TiO<sub>2</sub> with dopant metal can generally form new bands between gaps in the TiO<sub>2</sub> structure so that the gaps become narrowed. Doping TiO<sub>2</sub> with Fe effectively decreases the E<sub>g</sub> value corresponding to visible light energy, thereby increasing TiO<sub>2</sub> activity under visible light [14]. The source of the Fe dopant that has been used is in the form of expensive commercial salts such as FeCl<sub>3</sub> [15], FeSO<sub>4</sub> [16], and K<sub>3</sub>Fe(CN)<sub>6</sub> [17]. The use of cheap dopant sources, iron rust waste, has also been reported [18]. However, an application for a reduction in Cr(VI) has never been reported.

At the end of the photocatalysis process, it is essential to separate the photocatalyst powder from the wastewater medium, often done by filtration. This separation method is considered less efficient as it is time-consuming and costly. Fast and practical separation was achieved by contacting magnetic rods on magnetic TiO<sub>2</sub> powder. The magnetization of TiO<sub>2</sub> was done by coating magnetite (Fe<sub>3</sub>O<sub>4</sub>), a strong magnetic material [19]. Fe<sub>3</sub>O<sub>4</sub> coatings are commonly made by depositing Fe<sup>2+</sup> and Fe<sup>3+</sup> ions from expensive commercial salts [20].

An alternative approach involves obtaining the  $\text{Fe}^{3+}$  solution from the dissolution process of iron rust waste, making iron rust a more cost effective source of  $\text{Fe}^{3+}$  and a substitute for commercial salts.

In this research,  $\text{TiO}_2$ -Fe preparation was carried out to increase  $\text{TiO}_2$  activity in the visible light region, with the addition of  $\text{Fe}_3\text{O}_4$  to improve the material's magnetic properties and utilization of rust waste as a source of iron (Fe). The resulting  $\text{TiO}_2$ -Fe/ $\text{Fe}_3\text{O}_4$  photocatalyst will be characterized with various instruments to ensure that doping has been successful. Furthermore,  $\text{TiO}_2$ -Fe/ $\text{Fe}_3\text{O}_4$  were tested for photoreduction of Cr(VI) ions under visible light exposure. To obtain the best photoreduction conditions, optimization of solution pH, photocatalyst weight, reaction time, and initial concentration of Cr(VI) will be carried out.

## 2. Materials and methods

### 2.1 Materials

The materials used in this study were analytical grade without further purification. P25 Titanium dioxide (Degussa AG Company), ammonia solution ( $\text{NH}_3$ , 25% purity), iron(II) sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), hydrochloric acid (HCl, 35% purity), nitric acid ( $\text{HNO}_3$ , 68% purity), potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ), 1,5-diphenylcarbazid ( $\text{C}_{13}\text{H}_{14}\text{N}_4\text{O}$ ) were purchased from Merck. Distilled water was used in this work. Iron rust waste was obtained from the area around UGM Yogyakarta.

### 2.2 Preparation of $\text{Fe}^{3+}$ solution from iron rust waste

The iron rust waste was mashed by mortar and pestle until it formed a powder. 0.8 g of iron rust powder was dissolved into aqua regia (HCl:  $\text{HNO}_3$  with volume ratio 3:1) and heated at  $70^\circ\text{C}$  for 30 min. The brownish-yellow solution indicates the presence of  $\text{Fe}^{3+}$  ions, then diluted with distilled water.

### 2.3 Preparation of $\text{TiO}_2$ doped Fe using hydrothermal method

$\text{TiO}_2$ -Fe photocatalyst was synthesized using the hydrothermal method. Initially, 1.303 g  $\text{TiO}_2$  was dissolved in 50 mL  $\text{Fe}^{3+}$  solution from iron rust waste (mole ratio  $\text{TiO}_2$ :Fe = 1: 0.25). The solution was stirred with a magnetic stirrer for 3 h and sonicated for 30 min. Then, the hydrothermal process was carried out in an autoclave at  $140^\circ\text{C}$  for 14 h. After hydrothermal, the material was washed at neutral pH and dried at  $80^\circ\text{C}$ . The procedure was repeated by varying the mass of  $\text{TiO}_2$  to obtain a variation in the  $\text{TiO}_2$ -Fe mole ratio of 1:0.25, 1:0.5, 1:0.75, and 1:1.

### 2.4 Preparation of $\text{TiO}_2$ -Fe/ $\text{Fe}_3\text{O}_4$

The magnetization process was carried out by adding 2.828 g of  $\text{TiO}_2$ -Fe material into 40 mL of 10 M  $\text{NH}_4\text{OH}$ . Then, it was stirred until homogeneous and heated to a constant temperature of  $70^\circ\text{C}$ . The solution was added Fe(II) and Fe(III) in a ratio of 1:2 with

a  $\text{Fe}_3\text{O}_4$  fraction of 25%, then a black precipitate was formed. The black precipitate was washed with distilled water until the pH was neutral and then dried in an oven at  $80^\circ\text{C}$ . The procedure was repeated by varying the mass of  $\text{TiO}_2$ -Fe to obtain a variation of the  $\text{Fe}_3\text{O}_4$  fraction of 33.3%, 50%, 66.67%, and 75%.

## 2.5 Characterization of $\text{TiO}_2$ -Fe/ $\text{Fe}_3\text{O}_4$ photocatalyst

The photocatalyst powders were characterized by SR-UV/Visible, FTIR, XRD, and SEM-EDX. Spectrophotometer Reflectance Specular UV-Visible (SR-UV-Vis, 1700 Phamrmaspec) was used in the wavelength 200 nm to 800 nm, Fourier Transform Infrared Spectrophotometer (FTIR, Shimazu Prestige 21) was used in the wavenumber  $4000\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$ , X-ray diffractometer (XRD, Shimadzu 6000) was used in Cu K $\alpha$  radiation  $\lambda = 0.15406\text{ nm}$  as the source of X-rays, operated at 40 kV, 25 mA, the angular range of  $2\theta = 10^\circ$  to  $80^\circ$  and nickel as the filter), and Scanning Elektron Microscope with Energy Dispersive X-Ray Spectrometer (SEM-EDX, JEOL JSM-6510LA) with images taken from the microscope with  $\times 3000$  magnification.

## 2.6 Photocatalytic activity

The photocatalytic process was carried out using a closed reactor and a visible lamp (Philips TLD 18 W/54-765) as a light source (Figure 1).  $\text{TiO}_2$ -Fe and  $\text{TiO}_2$ -Fe/ $\text{Fe}_3\text{O}_4$  photocatalytic tests were conducted to determine the optimum variations for Fe dopant and  $\text{Fe}_3\text{O}_4$  magnetization for Cr(VI) reduction. The parameter variables tested were pH, catalyst dosage, Cr(VI) concentration, irradiation time, type of photocatalyst, and light source. Each process began with stirring in the dark for 30 min to obtain adsorption-desorption equilibrium. Then, the photocatalytic reaction was carried out by stirring under visible light. The process of separating the  $\text{TiO}_2$ -Fe/ $\text{Fe}_3\text{O}_4$  photocatalyst from the Cr(VI) solution was attracted using an external magnet. The separated solution was complexed with 1,5-diphenylcarbazide, and the Cr(VI) concentration was measured using a wavelength of 542 nm. The reduction in Cr(VI) concentration in percentage was calculated by the following Equation:

$$\text{Photocatalytic of Cr(VI)}(\%) = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

where  $C_0$  was the initial concentration of Cr(VI) ( $\text{mg}\cdot\text{L}^{-1}$ ) and  $C_t$  was the final concentration of Cr(VI) ( $\text{mg}\cdot\text{L}^{-1}$ ).

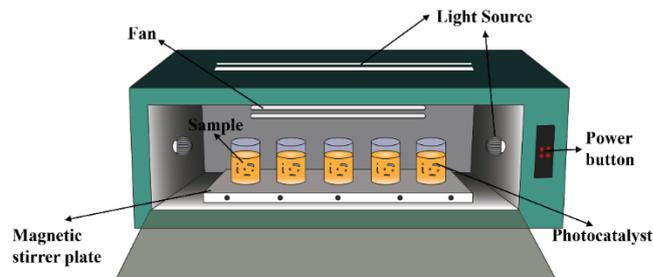


Figure 1. Schematic diagram of photocatalytic reactor.

### 3. Results and discussion

#### 3.1 Analysis of iron rust waste

The XRD characterization results confirmed the type of iron oxide, as shown in the diffraction pattern in Figure 2(a). Iron rust has a semicrystalline pattern and forms diffraction peaks at 2θ: 24.17°; 49.50°; 54.23°; 62.26°; and 75.37° which shows the material characteristics of hematite (Fe<sub>2</sub>O<sub>3</sub>) [21]. Diffraction peaks are also formed at 2θ: 34.20°; 35.30°; 36.34°; 38.38°; and 39.38° which is a FeOOH material characteristic [22]. It indicates that rust waste has iron (Fe) content of Fe<sub>2</sub>O<sub>3</sub> and FeOOH.

Figure 2(b) shows the FTIR spectra of rusty waste, confirming the presence of iron oxide. Peak absorption at wavenumber 555 cm<sup>-1</sup> from the hematite compound (α-Fe<sub>2</sub>O<sub>3</sub>) [23]. Several peaks at wavenumbers 1635 cm<sup>-1</sup>, 1126 cm<sup>-1</sup>, and 447 cm<sup>-1</sup> are absorption from Fe-O bonds in the compounds of β-FeOOH, γ-FeOOH, and δ-FeOOH [24,25]. The absorption peak at wavenumber 3448 cm<sup>-1</sup> and 1404 cm<sup>-1</sup> is the extended vibration of the O-H bond and the carbonate bond

from FeCO<sub>3</sub>, this compound is formed from CO<sub>2</sub> dissolves in water and interacts with iron oxide, the formation of this compound in iron rust can influenced by environmental [26]. Based on analysis with AAS, the percentage of Fe<sub>2</sub>O<sub>3</sub> in rust waste is 81.42%.

#### 3.2 Variation of Fe dopant (TiO<sub>2</sub>-Fe)

TiO<sub>2</sub>-Fe was characterized to determine changes in photocatalyst material before and after Fe doping. Based on XRD results shown in Figure 3(a), the undoped TiO<sub>2</sub> has a crystalline pattern with JCPDS TiO<sub>2</sub> anatase (00-021-1272) with several peaks appearing at 2θ: 25.28°; 36.98°; 37.93°; 48.34°; 53.99°; 54.93°; 62.69°; 70.09°; and 75.03° [27]. Diffraction patterns of TiO<sub>2</sub>-Fe with varying levels of Fe dopants have the same peaks as TiO<sub>2</sub> anatase. The addition of Fe dopants decreases the peak intensity with increased Fe dopant levels indicating the successful TiO<sub>2</sub>-Fe formed. The presence of Fe dopants interferes with the layout of the TiO<sub>2</sub> crystal structure and decreases the crystallinity of TiO<sub>2</sub>.

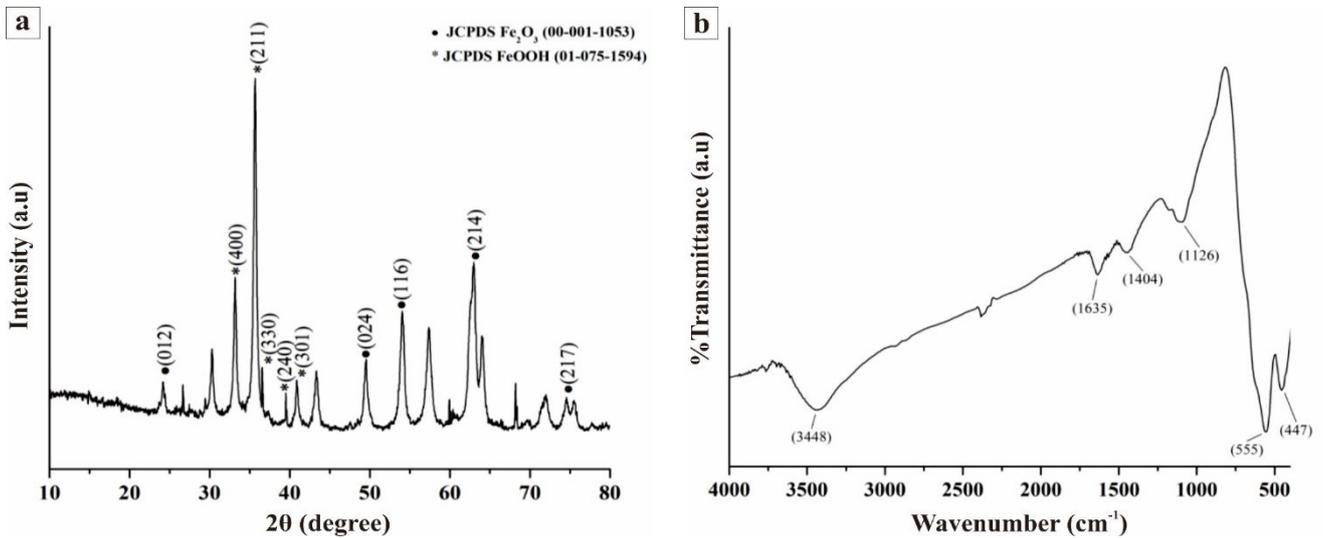


Figure 2. (a) XRD pattern and (b) FTIR spectra of waste rust.

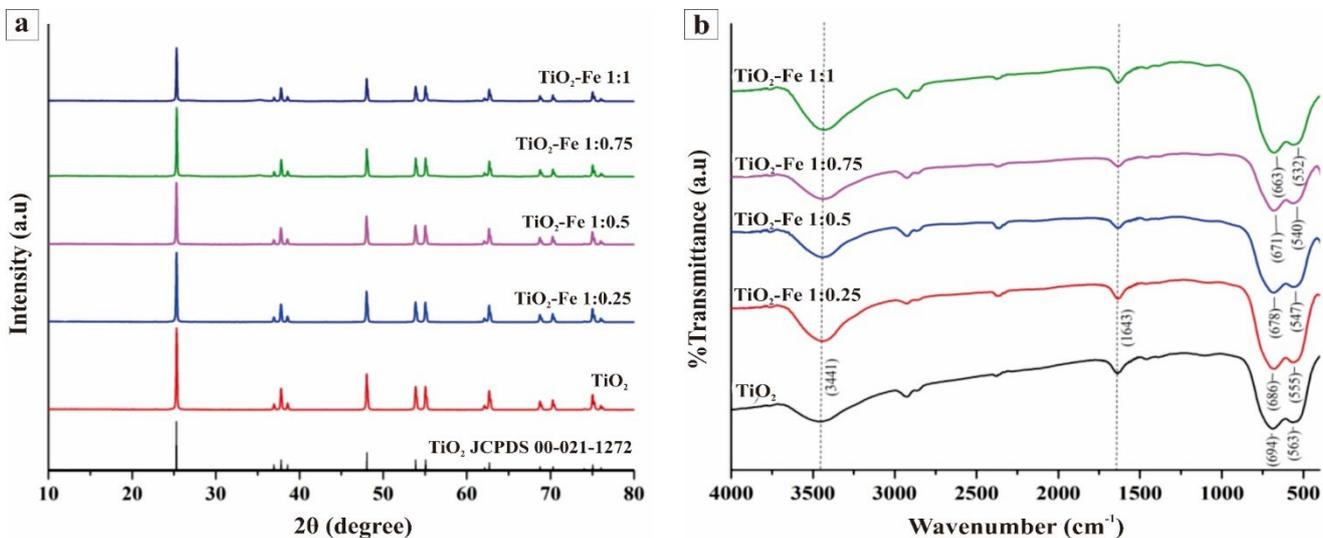
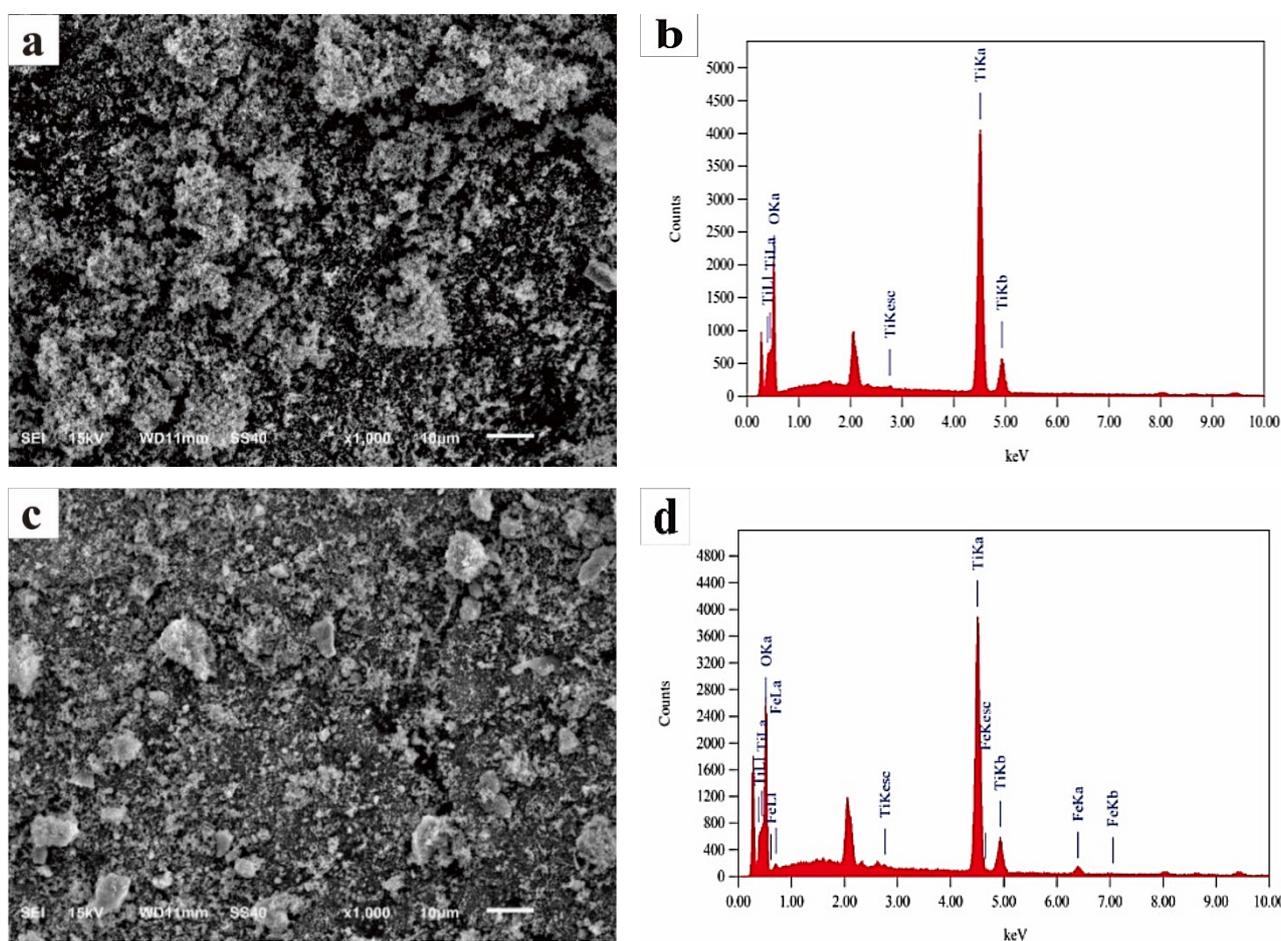


Figure 3. (a) XRD patterns and (b) FTIR spectra of TiO<sub>2</sub> and TiO<sub>2</sub>-Fe.

Figure 3(b) displays the FTIR spectra, there is peak at  $3441\text{ cm}^{-1}$  and  $1643\text{ cm}^{-1}$  are associated with the absorption of surface O-H bonds and O-H bending vibrations from adsorbed water molecules [28]. The undoped  $\text{TiO}_2$  has absorption at  $694\text{ cm}^{-1}$  and  $563\text{ cm}^{-1}$ , which is characteristic of Ti-O bonds [29]. After adding Fe, no new peaks were formed, indicating that the doping of Fe into the  $\text{TiO}_2$  site occurred by interstitial mechanism.  $\text{Fe}^{3+}$  ions which has a partial positive charge, interacts with the oxygen atom, which has a negative charge in the  $\text{TiO}_2$  bond. There is a shift in the absorption peak in the Ti-O-Ti bond in the wavenumber region of  $500\text{ cm}^{-1}$  to  $600\text{ cm}^{-1}$ ; the more Fe content is added, the absorption peak shifts towards a lower wavenumber and the Ti-O-Ti bond weakens due to the interaction between the O atom and the Fe atom [30].

Fe dopant also affects the crystal size, as shown in Table 1. The  $\text{TiO}_2$  crystal size tends to decrease as the Fe content increases to the

$\text{TiO}_2$ -Fe ratio (1:0.5). Fe doping can inhibit crystal growth, which causes the crystal size to shrink compared to undoped  $\text{TiO}_2$ . However, the  $\text{TiO}_2$ -Fe (1:0.75) has a larger crystal size, the excess dopant added causes the dopant not to dissolve properly and form excess iron aggregates in the  $\text{TiO}_2$  matrix [30]. The decrease in crystal size confirmed by the increasing shift of the inner lattice distance also indicates that  $\text{Fe}^{3+}$  ions can enter the interstitial cavity of the  $\text{TiO}_2$  lattice [31]. The surface morphology and element content on the material surface were analyzed for  $\text{TiO}_2$  and  $\text{TiO}_2$ -Fe (1:0.5), the most optimal mole ratio. Figure 4(a,c) displays SEM images of  $\text{TiO}_2$  and  $\text{TiO}_2$ -Fe (1:0.5).  $\text{TiO}_2$ -Fe has a non-uniform surface compared to  $\text{TiO}_2$  photocatalyst due to the accumulation of Fe occurs on the surface of the photocatalyst shows by clumping at several points in surface structure analyzed.



**Figure 4.** SEM images of (a)  $\text{TiO}_2$ , (c)  $\text{TiO}_2$ -Fe 1:0.5; EDX spectrum of (b)  $\text{TiO}_2$ , (d)  $\text{TiO}_2$ -Fe 1:0.5.

**Table 1.** The crystallite size of  $\text{TiO}_2$  and  $\text{TiO}_2$ -Fe.

Material	$2\theta$ (101) ( $^\circ$ )	$d$ (101) ( $\text{\AA}$ )	D (nm)
$\text{TiO}_2$	25.313	3.516	85.083
$\text{TiO}_2$ -Fe 1:0.25	25.298	3.518	85.080
$\text{TiO}_2$ -Fe 1:0.5	25.284	3.520	85.078
$\text{TiO}_2$ -Fe 1:0.75	25.322	3.514	85.084
$\text{TiO}_2$ -Fe 1:1	25.306	3.517	85.082

The EDX spectrum is also shown in Figure 4(b,d) where Ti and O element peaks were observed in the TiO<sub>2</sub> photocatalyst. After Fe doping, a new peak appeared: the Fe element peak that indicates the Fe doping process on the TiO<sub>2</sub> photocatalyst has been successful. Adding Fe can also reduce the percentage of the Ti element because the interaction between Fe atoms doped in the TiO<sub>2</sub> structure causes a redistribution of atoms in the crystal matrix and changes the proportion of Ti atoms in the material. The levels of each element are presented in Table 2.

The SR-UV spectrum shows that the higher the amount of dopant added, the more significant the shift towards visible light wavelengths (Figure 5(a)). Absorption edges correspond to the transfer of electrons from the valence band to the conduction band. In the Fe<sup>3+</sup> ion, the 3d orbital is half-filled, when doped with TiO<sub>2</sub>, the empty state is at the bottom of the conduction band while the filled t<sub>2g</sub> is at the top of the valence band. The TiO<sub>2</sub>-Fe absorption band shows a wider band than the TiO<sub>2</sub> absorption band which confirms that Fe<sup>3+</sup> doping on TiO<sub>2</sub> induces electronic states (Fe<sup>4+</sup> and Fe<sup>2+</sup>) in the TiO<sub>2</sub> band gap.

Band gap energy (E<sub>g</sub>) was calculated using the Tauc plot method and displayed in Figure 5(b). It shows that the addition of Fe<sup>3+</sup> dopant to the TiO<sub>2</sub> crystal lattice results in a decrease in the E<sub>g</sub> value to the TiO<sub>2</sub>-Fe variation (1:0.5). The reduction in the E<sub>g</sub> value occurs due to the formation of a new band by inserting a new energy level from the Fe<sup>3+</sup> dopant into the TiO<sub>2</sub> band gap. The higher the Fe<sup>3+</sup> concentration, the narrower the valence and conduction band gaps in TiO<sub>2</sub> and the smaller the band gap energy formed. However, when the dopant level increases (1:0.75 and 1:1), the energy in the bandgap increases due to the Fe<sup>3+</sup> dopant concentration that exceeds the optimal dopant concentration will form large deposits covering the photocatalyst's surface, thereby reducing the effective surface area for absorbing light [32]. Cr(VI) photoreduction results in Figure 5(c) show that the Fe-doped TiO<sub>2</sub> photocatalyst material provides higher photoreduction activity than undoped TiO<sub>2</sub>. The doping process with Fe reduces the E<sub>g</sub> of TiO<sub>2</sub> and shifts its absorption band to the visible light wavelength region so that the Cr(VI) photoreduction process works effectively in visible light and the TiO<sub>2</sub>:Fe variation (1:0.5) has the highest photoreduction percentage. The high concentrations of Fe dopant lead to the saturated TiO<sub>2</sub> crystal lattice with Fe<sup>3+</sup> ions and competition occurs with the redox reactions on the photocatalyst surface [33].

### 3.3 Variation magnetization of Fe<sub>3</sub>O<sub>4</sub> (TiO<sub>2</sub>-Fe/Fe<sub>3</sub>O<sub>4</sub>)

Characterization was carried out after adding various variations of Fe<sub>3</sub>O<sub>4</sub> to the TiO<sub>2</sub>-Fe photocatalyst. The diffraction pattern of Fe<sub>3</sub>O<sub>4</sub> material is shown in Figure 6(a), which has peak at 2θ: 30.09°, 35.42°, 43.05°, 53.40°, 56.94°, and 62.52°. This diffraction pattern

corresponds to the cubic plane crystal structure of Fe<sub>3</sub>O<sub>4</sub> with JCPDS 00-019-0629 [34]. After adding Fe<sub>3</sub>O<sub>4</sub>, a diffraction pattern of Fe<sub>3</sub>O<sub>4</sub> appears; the higher the Fe<sub>3</sub>O<sub>4</sub> content, the higher the peak intensity [35]. Figure 6(a) shows an anatase peak, such as TiO<sub>2</sub>-Fe, before adding Fe<sub>3</sub>O<sub>4</sub>. The intensity of the anatase peak decreased with increasing Fe<sub>3</sub>O<sub>4</sub> levels due to structural changes as evidenced by FTIR data in the form of overlapping peaks forming Ti-O-Fe bonds and a decrease in the amount of TiO<sub>2</sub>-Fe in the sample in Table 3. Adding Fe<sub>3</sub>O<sub>4</sub> tends to reduce the crystal size because the presence of Fe<sub>3</sub>O<sub>4</sub> can inhibit crystal growth in the TiO<sub>2</sub>-Fe mixture. Increasing the levels of Fe<sub>3</sub>O<sub>4</sub> added did not change the crystal size significantly. When the Fe<sub>3</sub>O<sub>4</sub> particles interact with TiO<sub>2</sub>-Fe, it causes deformation or changes in the TiO<sub>2</sub>-Fe lattice structure [49]. This deformation can cause a reduction in the distance between planes and shrinkage or compaction of the TiO<sub>2</sub>-Fe crystal structure [36].

The FTIR results graph in Figure 6(b) shows the absorption characteristics of Fe<sub>3</sub>O<sub>4</sub> material. Absorption peaks at wavenumbers 3441 cm<sup>-1</sup> and 1643 cm<sup>-1</sup> indicate the O-H stretching and bending vibrations of H<sub>2</sub>O molecules, and vibrational extension of Fe-O bonds appears at wavenumber 601 cm<sup>-1</sup> [37]. The FTIR spectra of the TiO<sub>2</sub>-Fe/Fe<sub>3</sub>O<sub>4</sub> material with various magnetization concentrations show peaks at wavenumbers 676 cm<sup>-1</sup> and 686 cm<sup>-1</sup>, indicating the increased vibration of the Ti-O bond. With higher TiO<sub>2</sub>-Fe content, the vibration frequency shifts to a higher wavenumber, means the stronger the Ti-O bond. Increasing the percentage of Fe<sub>3</sub>O<sub>4</sub> addition results in a widening of the Ti-O peak in the frequency region of 500 cm<sup>-1</sup> to 700 cm<sup>-1</sup> due to the overlap of the peaks of the Ti-O bond and the Fe-O bond, which confirms the success of the magnetization process of Fe<sub>3</sub>O<sub>4</sub> with TiO<sub>2</sub>-Fe [38].

Based on the SEM image in Figure 7(a), the morphology of the Fe<sub>3</sub>O<sub>4</sub> material is in the form of large aggregates. This aggregation occurs due to the magnetic properties of Fe<sub>3</sub>O<sub>4</sub>, which causes the particle's tendency to group and interact with the charged Fe<sub>3</sub>O<sub>4</sub> particles [39]. Figure 7(b-f) shows the morphology of the TiO<sub>2</sub>-Fe/Fe<sub>3</sub>O<sub>4</sub> material. The higher the Fe<sub>3</sub>O<sub>4</sub> content added, the surface morphology of the material forms large lumps similar to the surface of Fe<sub>3</sub>O<sub>4</sub>. The addition of Fe<sub>3</sub>O<sub>4</sub> causes agglomeration by van der Waals forces and magnetic dipoles in iron magnetic particles, as well as a higher band gap in TiO<sub>2</sub> particles [40].

The EDX spectra are shown in Figure 7; the Fe<sub>3</sub>O<sub>4</sub> material has characteristic peaks for the elements Fe and O. In the TiO<sub>2</sub>-Fe/Fe<sub>3</sub>O<sub>4</sub> material, peaks indicate the presence of the elements Ti, Fe, and O. The EDX spectrum shows the absence of other elements; confirms the absence of other impurities in the structure of the synthesized TiO<sub>2</sub>-Fe/Fe<sub>3</sub>O<sub>4</sub>. Table 4 confirmed the success of the synthesis process of adding Fe<sub>3</sub>O<sub>4</sub> to the TiO<sub>2</sub>-Fe material.

**Table 2.** The elements composition of TiO<sub>2</sub> and TiO<sub>2</sub>-Fe from EDX analysis.

Element	Mass percentage (%)	
	TiO <sub>2</sub>	TiO <sub>2</sub> -Fe
Ti	26.19	22.39
O	73.81	76.36
Fe	-	1.25



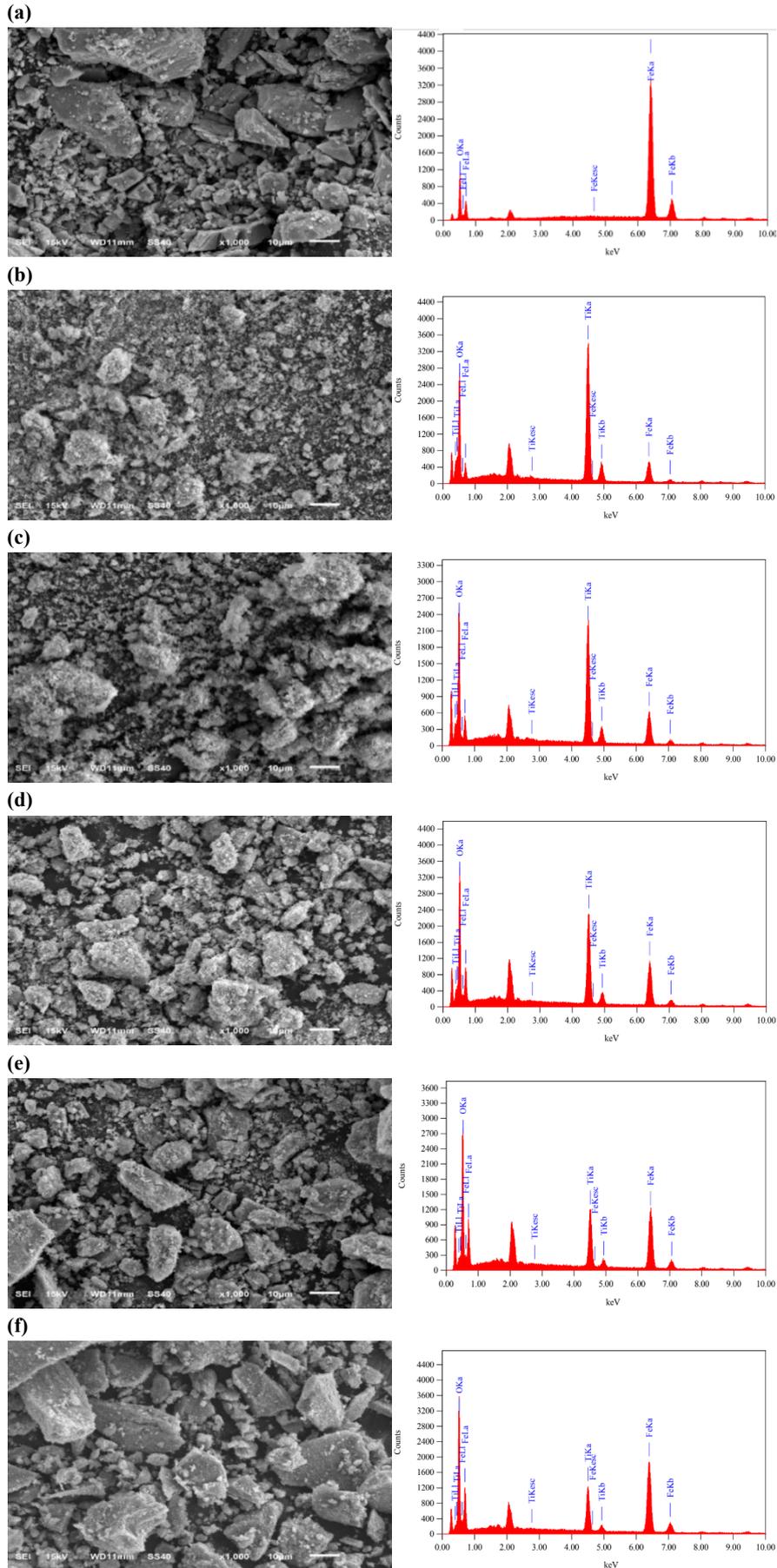
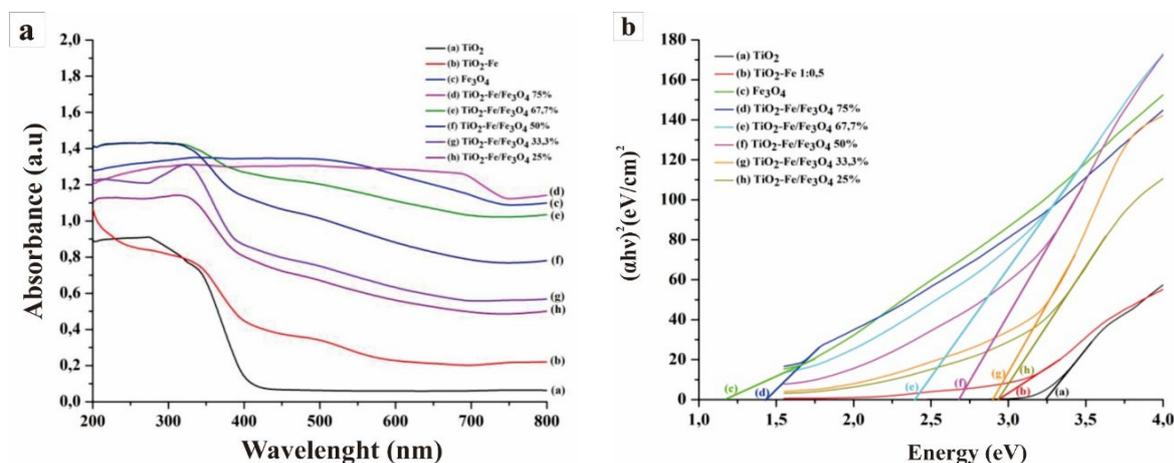


Figure 7. SEM images and EDX spectrum of (a) Fe<sub>3</sub>O<sub>4</sub> and TiO<sub>2</sub>-Fe/Fe<sub>3</sub>O<sub>4</sub> (b) 25%, (c) 33.3%, (d) 50%, (e) 67.7%, (f) 75%.

**Table 4.** The elements composition of Fe<sub>3</sub>O<sub>4</sub> and TiO<sub>2</sub>-Fe/Fe<sub>3</sub>O<sub>4</sub> from EDX analysis.

Element	Mass percentage (%)					
	Fe <sub>3</sub> O <sub>4</sub>	TiO <sub>2</sub> -Fe/Fe <sub>3</sub> O <sub>4</sub> (1:0.3)	TiO <sub>2</sub> -Fe/Fe <sub>3</sub> O <sub>4</sub> (1:0.5)	TiO <sub>2</sub> -Fe/Fe <sub>3</sub> O <sub>4</sub> (1:1)	TiO <sub>2</sub> -Fe/Fe <sub>3</sub> O <sub>4</sub> (1:2)	TiO <sub>2</sub> -Fe/Fe <sub>3</sub> O <sub>4</sub> (1:3)
Ti	-	20.98	16.67	13.98	9.94	8.28
O	22.09	72.50	74.15	71.93	68.57	63.57
Fe	77.91	6.52	9.18	14.09	21.49	28.15

**Figure 8.** (a) SRUV-Vis spectrum, and (b) Tauc's plot of TiO<sub>2</sub>, TiO<sub>2</sub>-Fe, and TiO<sub>2</sub>-Fe/Fe<sub>3</sub>O<sub>4</sub>.

The SR-UV spectra of TiO<sub>2</sub>, TiO<sub>2</sub>-Fe, and TiO<sub>2</sub>-Fe/Fe<sub>3</sub>O<sub>4</sub> materials are shown in Figure 8(a). Fe<sub>3</sub>O<sub>4</sub> has strong absorption in the visible light region. The spectrum tends to be straight due to the transfer of electrons from the valence to the conduction band at a very short distance. The energy required is small, so the absorption distribution becomes relatively low, even in certain spectral areas. The magnetization process expands the light absorption range of TiO<sub>2</sub>-Fe in visible light; the higher the Fe<sub>3</sub>O<sub>4</sub> content, the more the additional wavelength reaches the visible light area. The increase in absorption is caused by a charge transfer transition between the iron oxide nanoparticle electrons and the conduction band (or valence band) of TiO<sub>2</sub>. The Tauc plot equation measures the E<sub>g</sub> of the TiO<sub>2</sub>-Fe/Fe<sub>3</sub>O<sub>4</sub> photocatalyst and the result is displayed in Figure 8(b). Increasing the added levels of Fe<sub>3</sub>O<sub>4</sub> causes the band gap energy value to become smaller due to the inclusion of iron oxide (Fe<sub>3</sub>O<sub>4</sub>) into the TiO<sub>2</sub> structure [37,41].

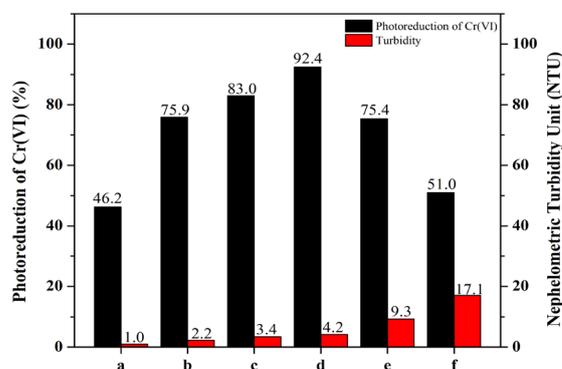
### 3.4 Photocatalytic reduction of Cr(VI) using TiO<sub>2</sub>-Fe/Fe<sub>3</sub>O<sub>4</sub> photocatalyst

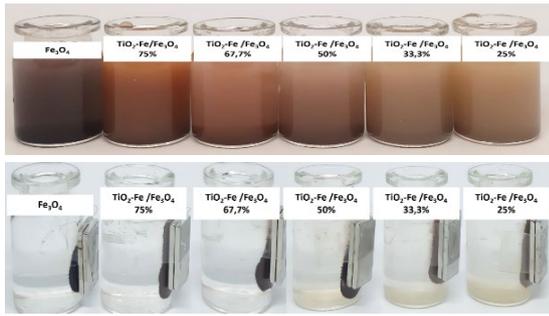
#### 3.4.1 Photocatalytic activity

Testing the effect of the Fe<sub>3</sub>O<sub>4</sub> content added to the TiO<sub>2</sub>-Fe/Fe<sub>3</sub>O<sub>4</sub> photocatalyst aims to determine the optimum Fe<sub>3</sub>O<sub>4</sub> that can produce maximum effectiveness in the Cr(VI) photoreduction process and the magnetization separation process. Based on Figure 9, there was a significant increase in the effectiveness of Cr(VI) photoreduction. The addition of Fe<sub>3</sub>O<sub>4</sub> content increases the effectiveness of Cr(VI) photoreduction due to its support in the adsorption process. Moreover, higher Fe<sub>3</sub>O<sub>4</sub> content decreases the E<sub>g</sub> value of TiO<sub>2</sub>-Fe/Fe<sub>3</sub>O<sub>4</sub> and enhancing the absorption of visible light. However, excessive Fe<sub>3</sub>O<sub>4</sub> levels reduce Cr(VI) photoreduction activity by covering the TiO<sub>2</sub>-Fe

photocatalyst surface, hindering light absorption and suboptimal electron production. Subsequently, the photocatalyst process, aided by sunlight, facilitates the reduction of Cr(VI) to Cr(III).

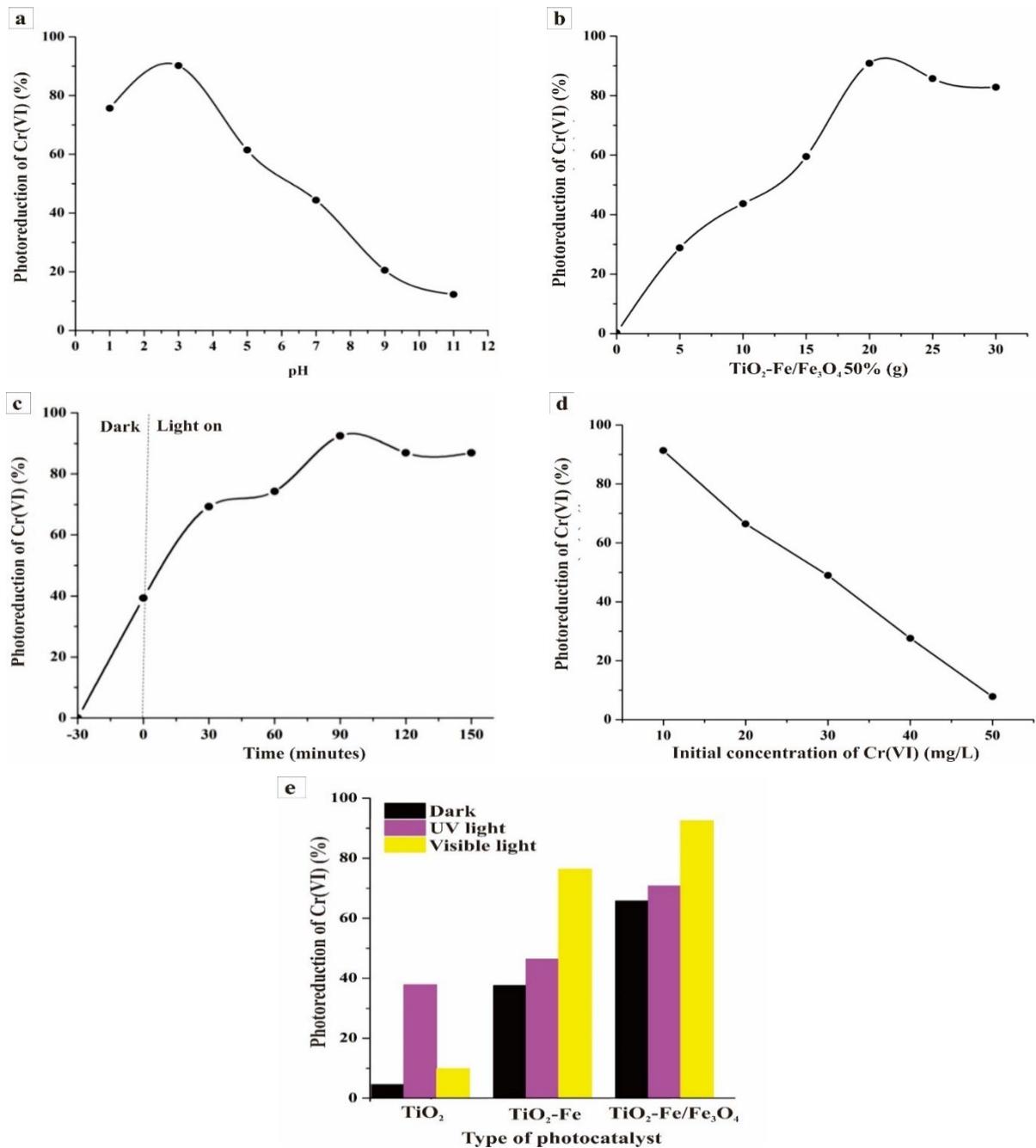
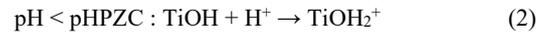
The ability to separate the photocatalyst from the Cr(VI) photoreduction solution was tested using a magnetic bar, as shown in Figure 10. Qualitatively, the results of separating filtrate with higher Fe<sub>3</sub>O<sub>4</sub> content tend to be clearer because its magnetic properties are stronger. On the other hand, a lower Fe<sub>3</sub>O<sub>4</sub> content results in weaker the magnetic properties and increase the turbidity. Quantitative testing using a turbidimeter confirmed these findings. Figure 10 illustrates that as the Fe<sub>3</sub>O<sub>4</sub> content increases, the turbidity value decreases, leading to a clearer filtrate. The optimal photocatalyst content was found to TiO<sub>2</sub>-Fe/Fe<sub>3</sub>O<sub>4</sub> variation of 50%, as it demonstrated good Cr(VI) photoreduction activity and effective filtrate separation. As a result, the TiO<sub>2</sub>-Fe/Fe<sub>3</sub>O<sub>4</sub> photocatalyst at 50% is used in this research for further optimization.

**Figure 9.** Cr(VI) photoreduction ability and turbidity of the separation filtrate with magnets for (a) Fe<sub>3</sub>O<sub>4</sub> and TiO<sub>2</sub>-Fe/Fe<sub>3</sub>O<sub>4</sub> (b) 25%, (c) 33.3%, (d) 50%, (e) 67.7%, and (f) 75%.



**Figure 10.** Magnetic separation of Fe<sub>3</sub>O<sub>4</sub> and TiO<sub>2</sub>-Fe/Fe<sub>3</sub>O<sub>4</sub> after photoreduction Cr(VI).

Figure 11(a) shows the maximum photoreduction Cr(VI) effectiveness at pH 3. The TiO<sub>2</sub>-Fe/Fe<sub>3</sub>O<sub>4</sub> photocatalyst has a PZC value of 6.8, indicating that the pH of the surface charge of the photocatalyst is neutral. When the pH is 3, the photocatalyst becomes positively charged, leading to adsorption processes and electrostatic interactions between the photocatalyst surface and Cr(VI) ions. The surface charge of the photocatalyst can be either positive or negative depending on the pH of the solution, as determined by the Equation:



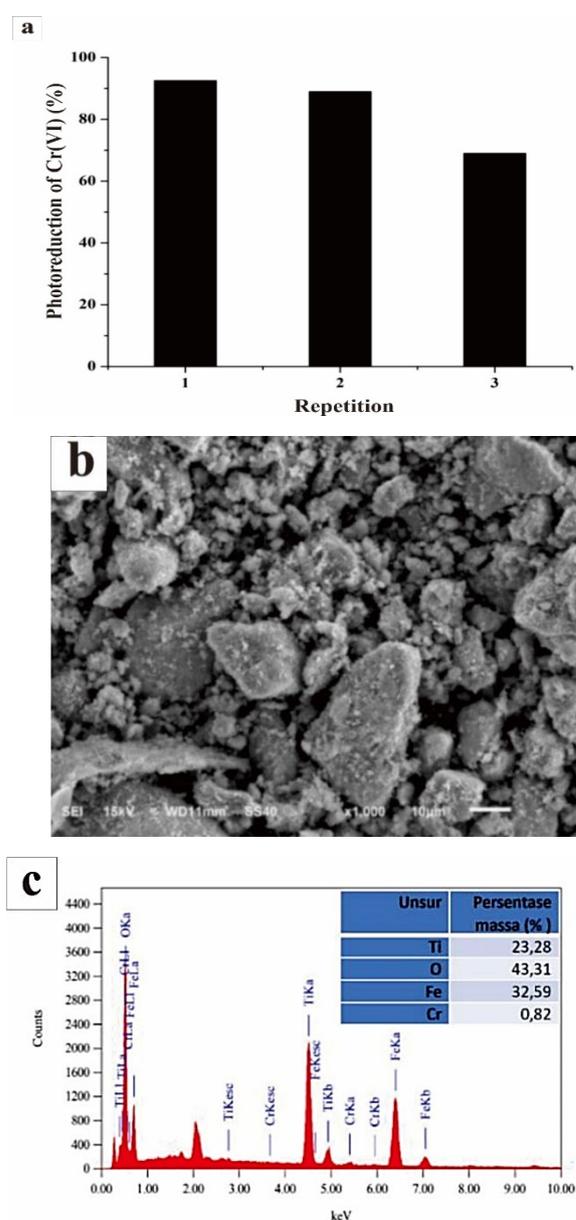
**Figure 11.** Influence of (a) pH, (b) dosage photocatalyst, (c) irradiation time, (d) initial concentration of Cr(VI), (f) light source on photoreduction Cr(VI) using TiO<sub>2</sub>-Fe/Fe<sub>3</sub>O<sub>4</sub> 50%.

At pH 1, a highly acidic environment hinders photoreduction due to increased production of hydrogen ions ( $H^+$ ), which can interact with the surface of  $TiOH$  (hydrated  $TiO_2$ ) to form  $TiOH_2^+$  (Equation (1)) and inhibits the release of electrons on the photocatalyst [7]. As the pH increases within the acidic range, electron release improves. However, at pH 5 and 7, the percentage of photoreduction  $Cr(VI)$  decreases due to fewer electronic interactions. Under alkaline solution conditions (pH 9 and pH 11), the surface of the photocatalyst is negatively charged, and there is a repulsive force between the surface charge of the photocatalyst and  $Cr(VI)$  ions, where  $Cr(VI)$  in alkaline solution exists in the form of  $CrO_4^{2-}$ , which reduces its ability to reduce  $Cr(VI)$ . High pH conditions can create a negative surface on  $TiO_2$  and form  $TiO^-$  which can inhibit electron release (Equation (2)) [7], leading to the formation of  $Cr(OH)_3$  solids which cover the active surface of the photocatalyst, and reducing absorption of chromate ions [42].

The impact of photocatalyst dosage on the effectiveness of  $Cr(VI)$  photoreduction is illustrated in Figure 11(b). As the photocatalyst dosage increases from 2 mg to 20 mg, the efficiency of  $Cr(VI)$  photoreduction also increases. It attributed to the larger surface area for the photocatalytic reaction and enhanced light absorption as a result of the greater dosage [43]. Meanwhile, when the dosage exceeds 20 mg, the effectiveness of  $Cr(VI)$  photoreduction decreases. The excess dosage of the photocatalyst causes turbidity and light reflection in the solution. Consequently, the interaction between light and the photocatalyst is reduced. Resulting in lowered photoreduction of  $Cr(VI)$  [44].

The impact of photocatalyst dosage on the effectiveness of  $Cr(VI)$  photoreduction is illustrated in Figure 11(b). As the photocatalyst dosage increases from 2 mg to 20 mg, the efficiency of  $Cr(VI)$  photoreduction also increases. It attributed to the larger surface area for the photocatalytic reaction and enhanced light absorption as a result of the greater dosage [43]. Meanwhile, when the dosage exceeds 20 mg, the effectiveness of  $Cr(VI)$  photoreduction decreases. The excess dosage of the photocatalyst causes turbidity and light reflection in the solution. Consequently, the interaction between light and the photocatalyst is reduced. Resulting in lowered photoreduction of  $Cr(VI)$  [44]. The effect of irradiation time is presented in Figure 11(c). The initial irradiation stage is carried out in dark conditions for 30 min to assess adsorption capability and ability to maintain the adsorption-desorption balance of the photocatalyst [45]. The longer the irradiation time, the higher the percentage of photoreduction  $Cr(VI)$ . The longer irradiation time increases the contact between light and the photocatalyst, resulting in a greater number of electrons [46]. Longer irradiation time enhances the interaction between electrons and  $Cr(VI)$  ions, increasing the effectiveness of  $Cr(VI)$  photoreduction. The photo-reduction time of  $Cr(VI)$  reaches its maximum level at 90 min of light. When the irradiation time is more than 90 min, there is a decrease in the percentage of photoreduction  $Cr(VI)$  because the active side of the photocatalyst has been saturated to absorb photon energy. Hence, the electrons produced are not optimal. Irradiation times longer than the optimum time can also produce vast quantities of product that prevent contact between reacting substances. As a result, the performance of the photocatalyst is inhibited to release more electrons so that it cannot increase the photoreduction of  $Cr(VI)$  [7].

The influence of photocatalyst type was investigated to assess the effect of  $TiO_2$  photocatalyst without and with Fe doping, and the inclusion of  $Fe_3O_4$  magnetic material on  $Cr(VI)$  photoreduction under varied light circumstances. Figure 11(e) shows the photocatalyst efficiency of  $TiO_2$ ,  $TiO_2-Fe$ , and  $TiO_2-Fe/Fe_3O_4$  respond similarly to dark conditions, UV light, and visible light. The photocatalyst effectiveness in dark conditions rises with the addition of Fe dopant and  $Fe_3O_4$  due to Fe dopant increasing surface porosity and adsorption capacity, also  $Fe_3O_4$  is an adsorbent with high adsorption efficiency [19]. Under UV light irradiation, adding Fe and  $Fe_3O_4$  improves the photocatalyst effectiveness since these two substances can reduce the recombination rate [37]. When exposed to visible light, the effectiveness of the photocatalyst increases due to the inclusion of Fe and  $Fe_3O_4$  shifting the wavelength from UV to visible light, allowing the photocatalyst to absorb light optimally [37].



**Figure 12.** (a) Reusability tests of  $Cr(VI)$ , (b) SEM image, and (c) EDX spectrum of  $TiO_2-Fe/Fe_3O_4$  after 3 runs.

### 3.4.2 Reusability test

The photocatalyst reuse test aims to evaluate the stability of the photocatalytic activity of TiO<sub>2</sub>-Fe/Fe<sub>3</sub>O<sub>4</sub> photocatalysts. Figure 12(a) displays that the first and second uses of TiO<sub>2</sub>-Fe/Fe<sub>3</sub>O<sub>4</sub> photocatalysts demonstrate effective and stable Cr(VI) photoreduction. However, during the third use, photocatalysts experienced a significant decrease in Cr(VI) photoreduction due to the disruption of the photocatalyst's performance caused by the presence of Cr(III) ions from the absorbed photoreduction process. These ions lead to the formation of Cr(OH)<sub>3</sub> deposits on the surface of the photocatalyst, blocking photon light absorption and limiting the performance of its active sites. Additionally, it can also promote the recombination of electron charge (e<sup>-</sup>) and hole (h<sup>+</sup>) [47]. The results of SEM in Figure 12(b) show that the particle size of the TiO<sub>2</sub>-Fe/Fe<sub>3</sub>O<sub>4</sub> photocatalyst appears larger due to the accumulation of Cr(OH)<sub>3</sub> on its surface after the Cr(VI) photoreduction process. This is further supported by the EDX results in Figure 12(c), indicating 0.82% mass percentage of Cr, confirming the presence of Cr solids on the surface of the photocatalyst.

## 4. Conclusions

Doping Fe from iron rusty waste and impregnation of Fe<sub>3</sub>O<sub>4</sub> to TiO<sub>2</sub> photocatalyst was successfully synthesized, adding Fe dopant (1:0.5) can shift the photocatalyst absorption to the visible light area and 50% Fe<sub>3</sub>O<sub>4</sub> makes the photocatalyst separation process easier. The highest Cr(VI) photoreduction, 92.5%, is achieved by applying 10 mg·L<sup>-1</sup> Cr(VI) at pH 3 with 0.2 g TiO<sub>2</sub>-Fe/Fe<sub>3</sub>O<sub>4</sub> in 90 min under visible light. After three uses, the photocatalyst still exhibited good results, showing potential for addressing the environmental issue of Cr(VI) waste.

### Credit author statement

Khoirunisa: Methodology, Writing-Original draft, N. D. Lestari: Software, Writing-Review and Editing, E. T. Wahyuni: Conceptualization, Supervision, T.A. Natsir : Supervision, Writing-Review and Editing.

### Conflict of Interest Statement

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest

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