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Ferrate(VI) Synthesis Using Fe(OH)₃ from Waste Iron Electrolysis and Its Application for the Removal of Metal Ions and Anions in Water

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Abstract: *Ferrate(VI) salt is an effective oxidant and coagulant for water treatment and removal of metal ions. This study demonstrates a new approach to processing metal ions and anions in water by Fe(VI) through Fe(III) obtained from the electrolysis of waste iron transformer. The electrolysis was successfully carried out in the Na_2SO_4 electrolyte using waste iron and zinc plates as anode and cathode, respectively. Fe(III) electrolysis results through the characterization of FTIR and XRD indicate compliance with $Fe(OH)_3$ standards. Synthesis of ferrate was carried out by adding Fe(III) from electrolysis with NaOCl in alkaline conditions. The formed ferrate solution shows a purple color with a typical maximum wavelength of 505 nm. Furthermore, the ferrate obtained is used to remove metal ions (Fe(III), Cu(II), Zn(II), Mg(II), Pb(II)) and anions (sulfate, nitrate, and carbonate) in water with pH variations. Ferrate treatment filtrate was analyzed using AAS for metal ions, while sulfate, nitrate, and carbonate anions used UV-Vis spectrophotometry, turbidimetry, and titration methods. The results showed that ferrate effectively eliminates metal ions and anions in water with optimum pH 6. The heavy metal removal by ferrate(VI) occurred through ionic bonding and adsorption mechanisms.*

Keywords: *ferrate; electrolysis; water treatment; metal ion; anion*

■ INTRODUCTION

Wastewater is one of the most severe challenges facing our world today, as various pollutants such as metal ions (lead, zinc, magnesium, iron, copper, and cadmium) and anions (sulfate, nitrate, and carbonate) continue to enter the aquatic environment from various industrial and household sectors [1]. Therefore, it is essential to study the treatment of polluted water into clean water free of contaminants. One of the methods used for the treatment of polluted water is to use oxidizers. Ferrate (FeO_4^{2-}) is a powerful and environmentally friendly oxidation agent in the aqueous media [2]. Ferrate(VI) has various functions, such as oxidation, disinfectant, coagulation, sterilization, adsorption, and deodorization [3-6]. Fe(VI) as a coagulant is very effective in removing metals and non-metals in water, dyes [7-9], and greywater [10]. The main iron species that act as coagulants is nanocrystal Fe(III) oxide/hydroxide, produced through

Fe(VI) reduction. The use of ferrate as a coagulant in water treatment and polluted water containing inorganic chemicals, such as thorium, cyanide, and thiocyanate [11-14].

Iron is one of the metals widely used in almost all areas of life, but after it is unused, iron will become a waste because it is difficult to degrade. Meanwhile, according to Barisci et al. [15], iron is an oxidizing agent with a positive standard reduction potential. Iron metal is electrolyzed to form gelatin $Fe(OH)_3$ to be used as a source of Fe(III) ions for ferrate synthesis. Reusing waste transformer iron as an anode is also able to reduce environmental pollution. Wet ferrate synthesis is mainly carried out by reacting iron(III) ions with sodium hypochlorite under very alkaline conditions [7]. In general, the iron(III) used comes from commercial iron(III) such as $FeCl_3$, $Fe(NO_3)_3$, and $FeSO_4$. Meanwhile, research on the use of transformer waste as

an iron(III) ion source by electrolysis based on our view has never been carried out.

This paper studied the ferrate synthesis through electrolysis process from iron(III) waste by reacting iron(III) and NaOCl in an alkaline solution. The ferrate was used as a coagulant for the removal of Pb(II), Zn(II), Mg(II), Fe(III), Cu(II), Cd(II), sulfate, nitrate, and carbonate ions at various pH ranges.

■ EXPERIMENTAL SECTION

Materials

The solutions containing Pb(II), Zn(II), Mg(II), Fe(III), Cu(II), Cd(II), sulfate, nitrate, and carbonate ions were prepared from their salts, $Pb(NO_3)_2$, $ZnCl_2$, $MgCl_2$, $FeCl_3$, $CuSO_4$, $CdSO_4$, Na_2SO_4, $NaNO_3$, and Na_2CO_3, respectively. All these salts were obtained from Merck with analytical grade. NaOH, $KMnO_4$, H_2SO_4, and KCNS were also supplied from Merck while NaOCl was supplied from Sigma Aldrich (analytical grade). Iron plate (i-shaped) was got from the transformer waste as the anode and zinc plate was used as cathode electrode.

Instrumentation

The instruments used were magnetic stirrer with a magnetic bar, multimeter (DT-830B), the analytical balance of Ohaus (Pioneer), power supply with regulator (Aditeg APS 3005), FTIR (Fourier Transform Infrared Spectrophotometer, Spotlight 200), SEM (Scanning Electron Microscopy), EDX (Energy Dispersive X-Ray, JEOL JSM-6510LA), and XRD (X-Ray Diffraction Shimadzu XRD-7000), XRF (X-ray Fluorescence Spectrometer, Rigaku Supermini 200). UV-Vis Spectrophotometer (UH 5300 Spectrophotometer), and AAS (Atomic Absorption Spectroscopy, Analyse-400 Perkin Elmer).

Procedure

Synthesis of Fe(III) hydroxide by electrolysis of waste iron plate as anode

Iron and zinc plates were assembled in an electrolysis chamber. Before use, iron and zinc plates were cleaned with soap, distilled water, and alcohol to remove impurities that stick to the surface of the plate. Next, iron and zinc plates were positioned as anode and cathode electrodes, respectively. Then, the electrodes were connected to a DC power supply, and they were immersed in 100 mL Na_2SO_4 1 M solution and electrolyzed with a potential of 3 V for 60 min. The iron area immersed was 3.0 cm × 1.2 cm. The electrolysis solution was filtered, and a blackish-brown precipitate of $Fe(OH)_3$ was obtained. The precipitate formed was dried at 110 °C, then characterized using FTIR, XRD, SEM, and EDX. In addition, the waste iron plate after and before use was characterized using SEM, and to know the contents of the initial iron plate was investigated using XRF.

Effect of electrolysis time. The effect of time on the concentration of iron(III) hydroxide produced was determined by varying the electrolysis times with the interval time of 15 min (15, 30, 45, and 60 min). After the electrolysis process, the solution was added using concentrated H_2SO_4 to dissolve the $Fe(OH)_3$ formed until the solution turned clear. After that, all solutions resulting from the variation of electrolysis time were added with 1 M KSCN as a complexing agent to prove the formation of Fe(III) ions in the electrolysis results. KSCN only reacts with Fe(III) ions to form a brick-red $Fe(SCN)^{2+}$ complex. After stirring, a red brick solution was obtained. The solution was measured using a UV-Vis spectrophotometer at 200–800 nm. Absorbance data were converted to Fe(III) concentration using calculations based on Fe(III) standard calibration.

Synthesis of Ferrate using Fe(OH)₃ and NaOCl in alkaline condition

The synthesis of ferrate(VI) was carried out by the wet oxidation method. A precipitate of $Fe(OH)_3$ (5 g) obtained from transformer iron waste electrolysis was added with NaOH 14 M and 50 mL NaOCl in beakers accompanied by stirring for 1 h. The solution was stored for one night in a dark bottle. The color of the solution was changed to purple, and the remaining $Fe(OH)_3$ deposits were removed by filtering using glass wool. Ferrate was the result of the filtrate from filtering the precipitate. The wavelength and concentration of Fe(VI) were determined using the spectrophotometer UV-Vis. (Ferrate concentration = 535.7 mg/L).

Characterization of electrolysis product, iron plate, and analysis of metal ions and anions

The surface morphology of the electrolysis product was characterized using SEM. The chemical element composition was determined by EDX analysis. Characterization using FTIR was used to determine the presence of functional groups and bonds in the sample. The crystal phase of the sample was checked by X-ray diffraction (XRD) with Cu Kα radiation (1.5406 A) at an angle of 10–80°. The composition of the initial iron plate was investigated using XRF. UV-Vis spectrophotometer was used to measure the electrolysis solution's absorption spectra and determine synthesized ferrate. Absorption measurements were performed at 200–800 nm. The filtrates of ferrate-treated solutions were analyzed using AAS to determine the decreased values of metal ions. In contrast, for anions of nitrate (NO_3^-), sulfate (SO_4^{2-}), and carbonate (CO_3^{2-}) ions were tested using UV-Vis spectrophotometry (APHA Method 4500-NO_3), turbidimetry (SNI 06-6989.20-2004), and titration methods (SNI 06-6989 12-2004), respectively.

Application of ferrate for removal of metal ions and anions in water

Treatment of metal ions (cations) with ferrate. Metal ion solutions of Cu(II), Pb(II), Zn(II), Mg(II), Cd(II), and Fe(III) were prepared from the stock solution. As much as 25 mL of 20 mg/L metal ion solution was prepared from a stock solution of 1000 mg/L. The metal ion solution then adjusted pH from 6–12 to determine the effect of pH on the degradation of metal ions by ferrate. As much as 25 mL of 20 mg/L ferrate solution was prepared from a ferrate solution from electrolysis with a concentration of 535.7 mg/L. The pH of the ferrate solution was also adjusted from 6–12. The final concentration of metal ion and ferrate was set at 10 mg/L in 50 mL. The mixture solution was stirred for 10 min and then filtered. After stirring, a brownish floating precipitate was obtained. The filtrate was analyzed by the AAS method to determine the concentration of metal ions (reduced metal ion concentrations after being treated by ferrate).

Treatment of anion with ferrate. The procedure was similar to the metal ion treatments, using sulfate, carbonate, nitrate ions with concentrations of 100 mg/L.

The results were filtered, and the solution was analyzed using a UV-Vis spectrophotometer, turbidimeter, and titration, respectively.

■ RESULTS AND DISCUSSION

Initial Characterization of Transformer Waste Iron Plate

Using XRF spectrometer, measurement of used iron transformers as an iron source provides results in the form of a spectrum of elements contained in used iron transformers. The component of these elements is shown in Table 1. From the table, it was found that the dominant element contained in the iron transformer is iron. However, the XRF results showed that the transformer scrap iron used as an anode is not 100% pure, but other elements are contained in it.

Synthesis of Fe(III) Hydroxide by Electrolysis of Waste Iron Plate as Anode

Fe(III) formation was done by electrolysis with iron as anode and zinc as the cathode. Electrolysis was carried out on Na_2SO_4 electrolyte because it was in a neutral pH. In the electrolysis system, an oxidation-reduction reaction occurs. At the anode, an oxidation process occurs, namely the iron plate is oxidized to produce iron cations (Fe^{2+}), while at the cathode, there is a water reduction reaction to produce hydrogen gas and hydroxide anions (OH^-). The electrolysis process obtained decomposition voltage or potential c.a. 2.03 V as shown in Fig. 1, so for the following process, the potential used was 3 V to produce iron(III) ions.

Table 1. XRF analysis of iron from transformer waste

Component	Result (%)
Fe	96.40
Mg	1.35
Si	0.83
Cr	0.79
Mn	0.37
P	0.08
S	0.07
Ca	0.05
K	0.04
Cl	0.02

The iron plate, after oxidation in the electrolysis system, will produce $Fe(OH)_3$. The following mechanisms occur when the formation of $Fe(OH)_3$ [16]:

Anode:

$$3\ Fe(s) \rightarrow 3\ Fe^{2+}(aq) + 6e^- \tag{1}$$

Cathode:

$$6\ H_2O(l) + 6e^- \rightarrow 3\ H_2(g) + 6\ OH^-(aq) \tag{2}$$

$$\underline{3\ Fe^{2+}(aq) + 6\ OH^-(aq) \rightarrow 3\ Fe(OH)_2(s)} \tag{3}$$

Overall:

$$3\ Fe(s) + 6\ H_2O(l) \rightarrow 3\ Fe(OH)_2(s) + 3\ H_2(g)$$
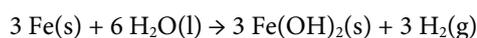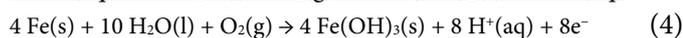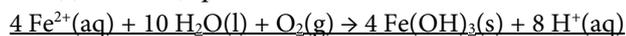
The presence of dissolved oxygen and oxygen from electrolysis causes ferrous hydroxide to be oxidized to ferric hydroxide.

Anode:

$$4\ Fe(s) \rightarrow 4\ Fe^{2+}(aq) + 8e^-$$

$$\underline{4\ Fe^{2+}(aq) + 10\ H_2O(l) + O_2(g) \rightarrow 4\ Fe(OH)_3(s) + 8\ H^+(aq)}$$

$$4\ Fe(s) + 10\ H_2O(l) + O_2(g) \rightarrow 4\ Fe(OH)_3(s) + 8\ H^+(aq) + 8e^- \tag{4}$$

Cathode:

$$\underline{8\ H^+(aq) + 8e^- \rightarrow 4\ H_2(g)} \tag{5}$$

Overall:

$$4\ Fe(s) + 10\ H_2O(l) + O_2(g) \rightarrow 4\ Fe(OH)_3(s) + 4\ H_2(g)$$
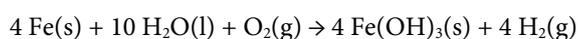
Electrolysis products are blackish-brown deposits and then characterized using UV-Vis spectrophotometers, FTIR, SEM, and EDX to prove the formation of $Fe(OH)_3$.

Variation of electrolysis time

The electrolysis product is iron(III) ions which could be proved by reacting the electrolyzed solution with KSCN. However, KSCN only reacts with Fe(III) ions to form a brick-red complex. The complex ions formed may vary, such as $[Fe(SCN)_2]^{2+}$, $[Fe(SCN)_2]^+$, $[Fe(SCN)_4]^-$, $[Fe(SCN)_5]^{2-}$, and $[Fe(SCN)_6]^{3-}$. The complex depends on the relative amounts of iron and thiocyanate present in the solution.

Fig. 2(a) shows the spectra of Fe(III) complexed with thiocyanate with different iron(III) standard concentrations, and Fig. 2(b) is the standard curve for iron(III)-thiocyanate measured using UV-Vis spectrophotometer at a maximum wavelength of 465 nm. The solution resulting from the variation of electrolysis time after being added using KSCN produced a reddish-orange color, indicating that the electrolysis solution contains Fe^{3+} ions. Furthermore, the wavelength scanning showed that the longer the electrolysis time, the greater the absorbance of the electrolysis, the longer the electrolysis process, the greater the concentration of Fe^{3+}, as shown in Fig. 2(c). From these results, the concentration of Fe^{3+} from the variation of electrolysis time at 15, 30, 45, and 60 min was 0.000509, 0.000925, 0.001394, and 0.001904 mol/L. Table 2 showed that the average efficiency of the formation of $Fe(OH)_3$ through electrolysis using iron waste as an anode is 29.6%, with the reaction rate following reaction order 1 [17-18].

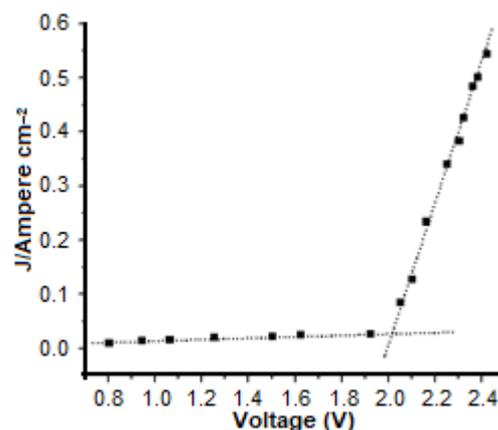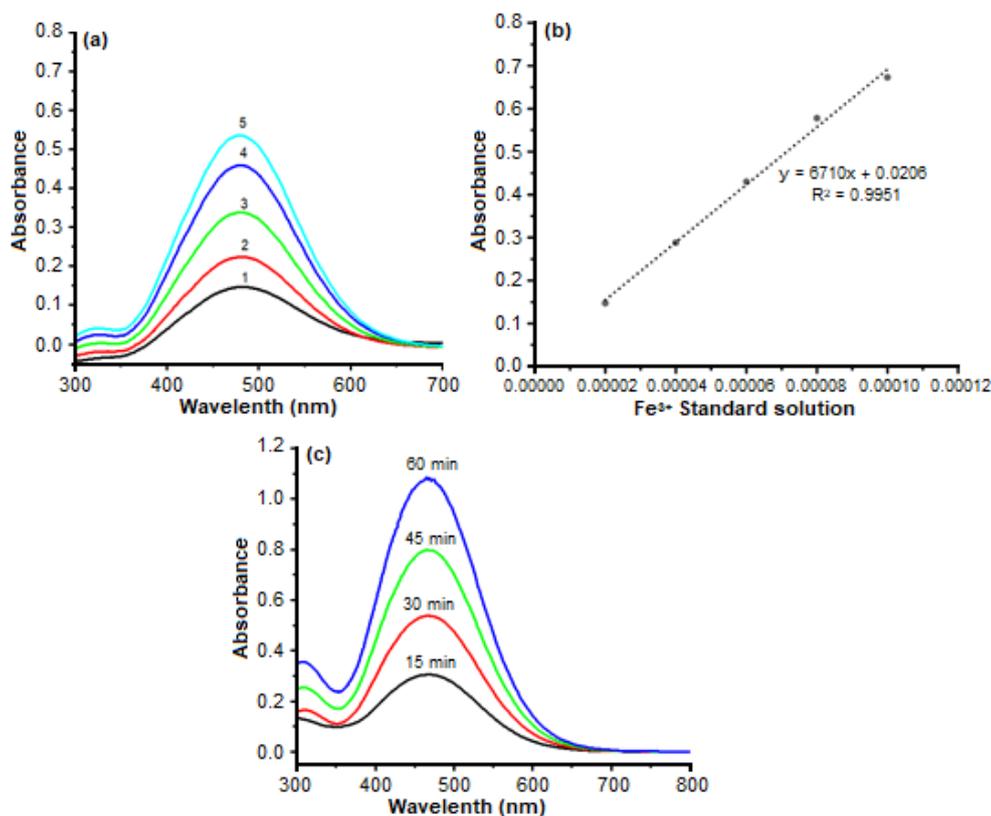**Fig 1.** The current-voltage curve for electrolysis using iron waste anode

Table 2. Results of variation in electrolysis time

T (second)	Mass of $Fe(OH)_3$ (mg)	$[Fe(OH)_3]$ (mol/L)	% Efficiency
900	5.44	0.000509	31.5
1800	9.90	0.000925	28.6
2700	14.91	0.001394	28.8
3600	20.37	0.001904	29.5

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Fig 2. (a) Relation of absorbance and wavelength with variations in the concentration of iron(III) standard complexed with thiocyanate, (b) standard curve of iron(III)-thiocyanate and (c) curve of the effect of electrolysis time on iron(III) ions formed in solution (measured by the thiocyanate method)

Characterization

FTIR and XRD spectra of $Fe(OH)_3$ are shown in Fig. 3. The absorption at 620 and 874 cm^{-1} was associated with the Fe-O stretching vibration indicating the formation of $Fe(OH)_3$. Absorption at 1640 cm^{-1} showed the OH bending vibration of H_2O [19-20]. The peaks that appear at 2θ = 35.00, 43.01, 52.61, 57.69, and 62.57° indicate a good agreement with $Fe(OH)_3$ (JCPDS no 22-0346) [21]. In addition, the peaks at 2θ = 36.87, 47.13, 59.44, and 71.67° indicated a congruence with α-FeO(OH) (goethite) (JCPDS no 29-0713). The peaks at 2θ = 23.53, 33.88, and 48.80° indicate a correspondence with β-FeO(OH) (akaganeite) (JCPDS no 34-1266). XRD and FTIR results show that the resulting electrolysis product is Iron hydroxide $Fe(OH)_3$. The crystal size (D) was calculated using the following Scherrer formula [22]:

$$D = k\lambda/(\beta\cos\theta) \qquad (6)$$

Using the Scherrer formula, the average crystal size of $Fe(OH)_3$ was 81.23 nm.

Surface analysis of the sample using SEM is shown in Fig. 4. It can be seen that the iron plate that has been used for electrolysis has been changed. Before being used for electrolysis, the waste iron plate shows a uniform and homogeneous surface. Meanwhile, after being used, the iron plate dissolves into iron ions, thus, the surface becoming porous and heterogeneous. In the iron(III) precipitate, it can be seen that the surface forms aggregates.

The elemental composition of $Fe(OH)_3$ is shown in Table 3. The presence of the Fe and O components in EDX confirms the formation of the desired material, namely iron hydroxide. The carbon peaks in the EDX spectrum are due to the carbon bands used during SEM and EDX measurements. Some of the other elements present in the sample may come from waste iron which is not pure iron.

Fig 3. FTIR spectra (left) and XRD diffractogram (right) of $Fe(OH)_3$

Fig 4. SEM images on (a) iron plate before electrolysis, (b) after 4× electrolysis, (c) $Fe(OH)_3$ precipitate at 5000× magnification

Table 3. EDX of $Fe(OH)_3$

Element	Percentage (%)
O	51.57
Fe	17.98
N	11.41
C	9.96
Na	7.90
S	0.69
Si	0.49

Synthesis of Ferrate

The synthesis of ferrate solution in this study was done by wet chemical method, using $Fe(OH)_3$ as a source of Fe(III) added with NaOCl as the oxidation agent in a strong alkaline condition (NaOH) and produced a purple ferrate solution. The ferrate formation reaction is presented below:

$$\underset{\text{brown}}{2Fe^{3+}} + 3ClO^- + 10OH^- \rightarrow \underset{\text{purple}}{2FeO_4^{2-}} + 3Cl^- + 5H_2O \qquad (7)$$

The formed ferrate solution (sodium ferrate) was then determined its wavelength and concentration using a UV-Vis spectrophotometer. The measurement result showed the maximum wavelength at 505 nm with an absorbance of 0.944 (Fig. 5). The absorption spectrum of ferrate at 505 nm had been confirmed by other studies [23-24]. Furthermore, from the literature, it can be seen that the molar extinction coefficient of ferrate at this wavelength is 1170 M^{-1} cm^{-1} so that in the synthesis, ferrate can be seen that the resulting ferrate concentration is 535.74 mg/L (with a dilution factor of 4x) [25].

Furthermore, ferrate stability was performed by measuring wavelengths using UV-Vis from day to day. The results showed a decrease in absorbance from the first day of 0.563 to 0.327; 0,281; 0.254, and 0.196, respectively, on days 2, 3, 4, and 8. The decrease in the ferrate absorbance value indicates that the ferrate

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solution has undergone reduction and decreased concentration, as shown in Fig. 6(a). Ferrate has low stability, so if left too long in unsuitable conditions will be reduced from Fe(VI) purple to Fe(III) brown. The decrease of ferrate for a longer time follows reaction order 2 (Fig. 6(b)) with a k value of 1.8×10^{-10} s^{-1}. Reduction of ferrate from Fe(VI) to Fe(III) according to Bartzatt and Carr [26] shown in the following reaction:

$$2FeO_4^{2-} + 5H_2O \rightarrow 2Fe(OH)_3 + 3/2O_2 + 4OH^- \tag{8}$$
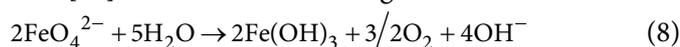
Application of Ferrate for Removal of Cations and Anions in Water

Treatment of metal ions (cation) with ferrate

Ferrate is a coagulant substance that effectively removes metals and non-metals in water [26-27]. Fig. 7 and 8 show that ferrate is proven effective for eliminating metal ions and anions. At pH 6, Cd ion concentration after treatment experienced a significant decrease than before treatment from 8.62 to 0.54 mg/L. Thus, even Mg metal could be entirely eliminated. Ferrate is also effective for eliminating nitrate anions at pH 6 by 65% [28].

The mechanism of heavy metal removal by ferrate(VI) can be explained by ionic bonding and adsorption [29]. Ferrate(VI) is present in the form of species $H_3FeO_4^+$, H_2FeO_4, $HFeO_4^-$, dan FeO_4^{2-} depending on the pH of the solution. In neutral solution (approximately pH 6–7), ferrate(VI) exists as the $HFeO_4^-$ species. Under these experimental conditions, heavy metals present as divalent cations (Cu^{2+}, Mg^{2+}, Pb^{2+}, Cd^{2+}, Fe^{2+}, and Zn^{2+}) can precipitate through ionic bonds with

$HFeO_4^-$, ferrate(VI) anion species. At pH 7 or less, Fe(VI) species readily self-decompose and thus result in rapid oxidation of metal ions. With increasing pH (> 7), the main species Fe(VI) becomes FeO_4^{2-}, which is more stable but has a weak oxidation capacity [30], thus explaining the decrease in metal ion degradation. In this study, the highest removal efficiency by ferrate is observed in neutral conditions (pH = 6). Similar effects have also been reported for the ferrate reaction with 2,4,6-trichlorophenol (TCP), which shows the highest degradation at pH 5.8 [31]. Filip et al. [32] found that various metal ions (e.g., Cu^{2+} and Zn^{2+}) can combine into the crystalline structure of iron(III) oxide or hydroxide nanoparticles, which are formed from the decomposition of Fe(VI), and with thus yielding a metallic ferrite spinel
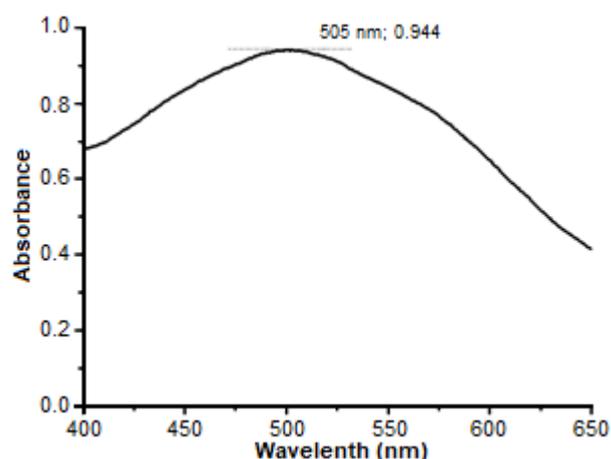
Fig 5. Ferrate solution spectrum measured using UV-Vis spectrophotometer
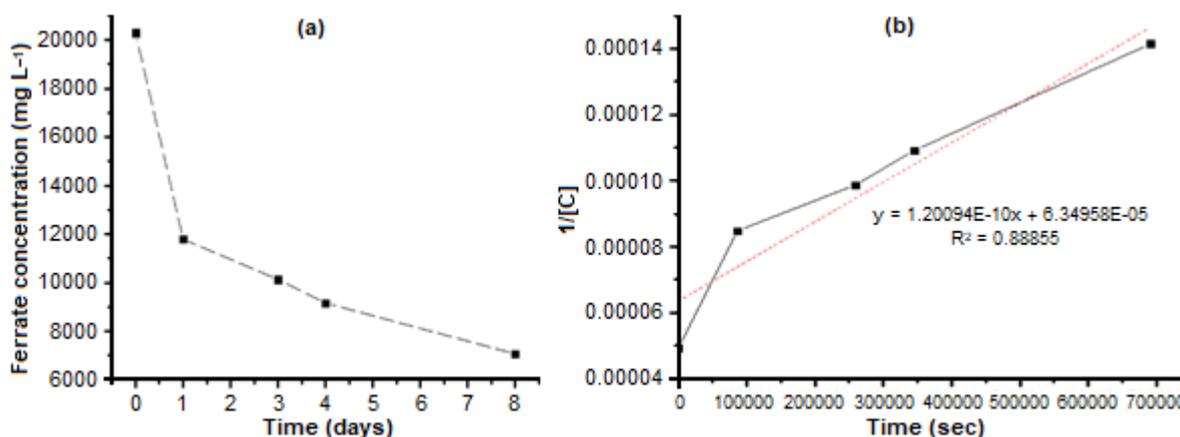
Fig 6. Ferrate concentration as a function of time (a) and the decrease of ferrate as a function of time follows reaction order 2 (b)
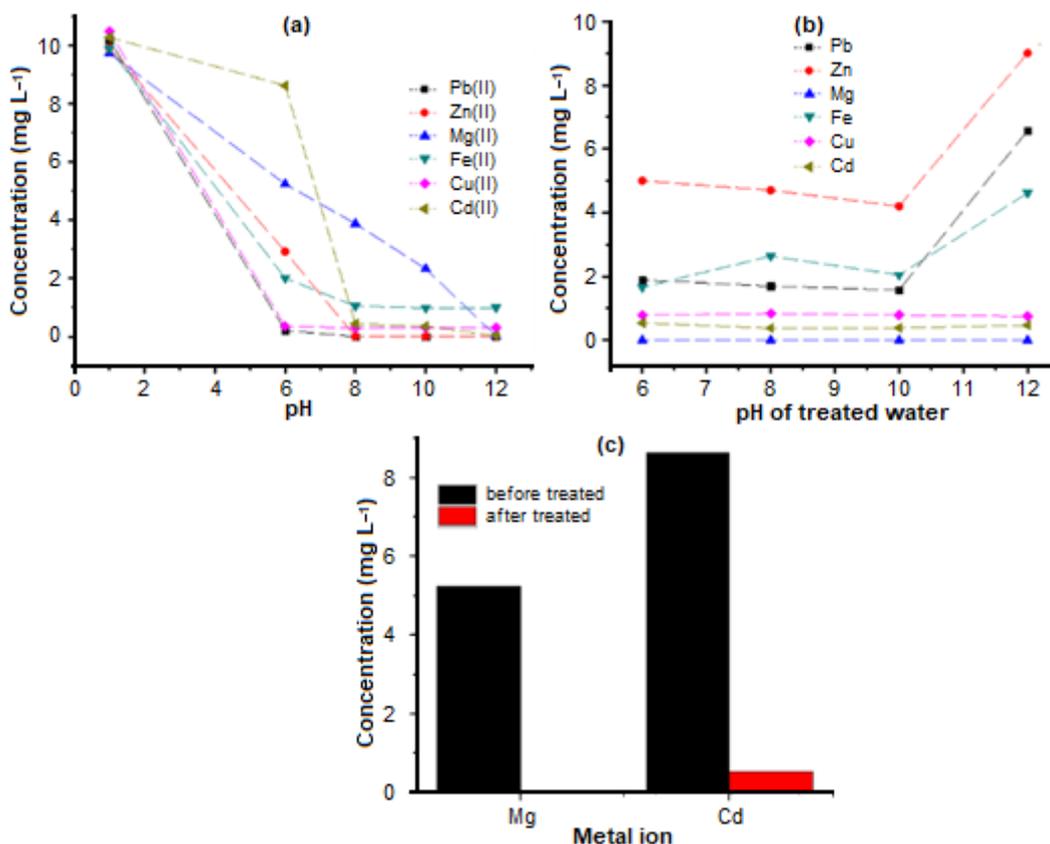
Fig 7. (a) The effect of pH on the initial metal ion concentrations, (b) Metal ion concentrations after treatment with ferrate, and (c) Results of Mg and Cd metal treatments with ferrate at pH 6
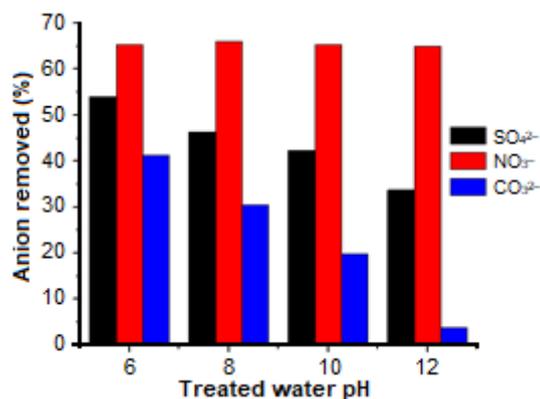

Fig 8. Anion treatment results with ferrate at pH 6, 8, 10 and 12

phase (e.g., $CuFe_2O_4$ and $ZnFe_2O_4$). In contrast, the Cd(II) ion does not form a ferrite spinel structure or is not incorporated into the iron(III) oxide phase lattice but through absorption on the y-Fe_2O_3/y-FeOOH core/shell nanoparticles [14]. The iron(VI) removal mechanism for various metals may depend on each metal ion's ionic

radius, valence, and electronic structure. The overall reaction of metal ions with Ferrate [33]:

$$Fe(VI) + M(II) \rightarrow Fe(III) + \text{ Product} \qquad (9)$$

The interaction between CO_3^{2-} (or HCO_3^-) and Fe hydroxide will occur and form an inner spherical monodentate complex through a ligand exchange reaction (Eq. (9)) [30].

$$Fe-OH + CO_3^{2-} \rightarrow Fe-O-CO_2^- + OH^- \qquad (10)$$
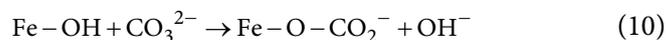
Hydrolysis of CO_3^{2-} ions can increase the pH of the solution, thereby reducing the oxidation potential of Fe(VI) and reducing the efficiency of anion reduction [34].

■ **CONCLUSION**

Synthesis of ferrate using iron ions from the electrolysis of the used transformer iron has been successfully obtained. Electrolysis occurs with E_d = 2.03 V. The iron ion was then reacted with sodium hypochlorite in alkaline conditions to produce ferrate

with a purple solution color. The resulted ferrate synthesis was applied as metal ion and anion treatments with pH variations of 6, 8, 10, and 12. The characterization of the electrolyzed iron plate showed that there was the dissolution of iron into iron(III) ions with a different surface from the previous plate. The results showed that ferrate is effective for eliminating metal ions and anions in water with the optimum condition at pH 6

■ ACKNOWLEDGMENTS

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