

SYNTHESIS OF FERRATE (VI) BY ELECTROCHEMICAL METHOD

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TÓM TẮT

NGHIÊN CỨU TỔNG HỢP DUNG DỊCH FERAT (VI) BẰNG PHƯƠNG PHÁP ĐIỆN HÓA

Mục đích của nghiên cứu này là tổng hợp ferat (FeO_4^{2-}) bằng phương pháp điện hóa. Một loạt các điều kiện điện hóa bao gồm nồng độ natri hydroxit, mật độ dòng điện áp dụng và thời gian điện phân để chỉ ra mối quan hệ giữa các yếu tố này và nồng độ của ferat được tạo thành. Các mẫu sau khi tạo ra được đo phổ hấp thụ IR và UV-vis để xác định liên kết đặc trưng và nồng độ của ferat. Kết quả cho thấy nồng độ ferat đạt cao nhất khi sử dụng dung dịch $NaOH$ 15 M để tổng hợp. Nồng độ ferat tăng tuyến tính theo thời gian điện phân theo phương trình tuyến tính $y = 0,0098x + 0,0861$.

Từ khóa: Chất oxy hóa mạnh, dung dịch Ferat (VI) điện hóa, phương pháp dòng tĩnh.

1. INTRODUCTION

Ferrate (FeO_4^{2-}), a very strong oxidant, has received the attention of many researchers around the world because of its wide range of applications in treating toxic organic substances and inactivating some viruses and bacteria [1-3]. Besides, the product formed after the ferrate reduction process is iron (III) hydroxide which is an environmentally friendly flocculant removing inorganic pollutants such as arsenite (III), cadmium (II), and copper (II) [4-6]. Thanks to these benefits, ferrate (VI) is considered a “green” chemical. However, ferrate, an unstable substance, easily converts to ferric hydroxide [7,8]. This is the main disadvantage of ferrate, lack of stability for long-term storage, so more studies are needed to improve its stability.

There are three main methods to generate ferrate including wet chemical, thermal process, and electrochemical method [9,10]. The wet chemical method, which is the most common way to prepare ferrate, needs oxidants for ferrate synthesis such as Cl_2 , ozone,

hypochlorite. This is a disadvantage of this method because the residual oxidant is mixed with the product. The thermal synthesis of ferrate is rarely used to synthesis ferrate because of the high risk of explosion and low efficiency.

The electrochemical method (with the constant current), a simple way without harmful chemicals as ClO^- , BrO^- , etc. [11], was used to synthesize ferrate. It needs a shorter synthesis time and reduces the cost. Otherwise, it can control the concentration of ferrate easily by adjusting the current density, electrolytic time, and concentration of electrolyte [12,13].

There have been many previous studies [14,15] discussing the effect of electrolyte type and concentration on the efficiency of the electrochemically formed ferrate (EFF) process in highly alkaline environments. According to the report of Karel Bouzek and et al., the current yield of the ferrate generation in $NaOH$ solution increased dramatically that in the KOH solution [15]. Besides, the result of comparing the ferrate stability in the different

electrolytes (NaOH, KOH, mix NaOH, and KOH) indicated that ferrate is the most stable in the NaOH media [8]. Therefore, NaOH media was chosen as the alkaline electrolyte to generate ferrate in our research. This paper will report some of the ferrate synthesis results discussed in detail below.

2. EXPERIMENT

2.1. Chemical and material

Sodium hydroxide is provided by Merck (purity of $\geq 98\%$). The material for anode electrode is the CT3 steel with chemical composition shown in Table 1.

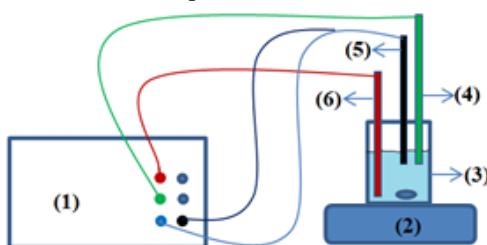
Table 1. The chemical composition of CT3 steel for anode

Elements	(%)
C	0.14-0.22
Mn	0.40-0.60
Si	0.12-0.30
S	< 0.05
P	< 0.04
Fe	> 98.80

2.2. Synthesis process and research methods

The synthesis of ferrate by the electrochemical method used a three-electrode cell including reference electrode (calomel), cathode electrode (stainless steel), and anode electrode (CT3 steel). The experiments were carried out on the electrochemical system using an IM6 equipment (Germany) as describing in Figure 1.

The amount of formed ferrate in electrolyte solution was determined by Perkin Elmer UV/Vis spectrometer Lambda 35. The characteristic bond of ferrate was analyzed by Perkin Elmer IR spectrometer.



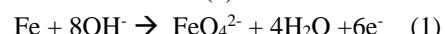
1. The electrochemical equipment IM6
2. The magnetic stirrer
3. The electrolyte solution (NaOH)
4. The reference electrode (calomel)
5. The anode electrode (CT3 steel)
6. The cathode electrode (stainless steel)

Figure 1. The electrochemical system

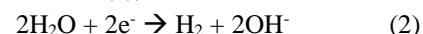
3. RESULT AND DISCUSSION

3.1. The characteristics of electrochemically formed ferrate

The redox reactions can occur on the electrodes during synthesis of EFF in alkaline media. At the iron anodic electrode, iron is directly oxidized to the ferrate as reaction (1) below.



In the cathode electrode side, there is only the reduction reaction in hydrogen (see reaction (2)).



The total reaction of ferrate generation in the electrolytic cell can be written following reaction (3).

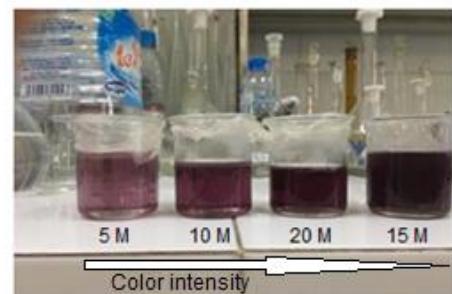
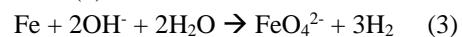


Figure 2. The color of obtained samples from different NaOH concentration

The color of solutions after synthesis (see Figure 2) is purple which is one of the characteristics of ferrate. Figure 3 presents the IR spectrum of one among them. There is a peak at 885.51 cm^{-1} indicating that ferrate is formed thanks to the vibration of Fe - O bond in the FeO_4^{2-} anion [16].

The UV-vis spectra of above solutions show only one peak at the wavelength of around 510 nm (see Figure 4, 5 and 7 below). This peak reflects the main ferrate features that are similar to previous work [17].

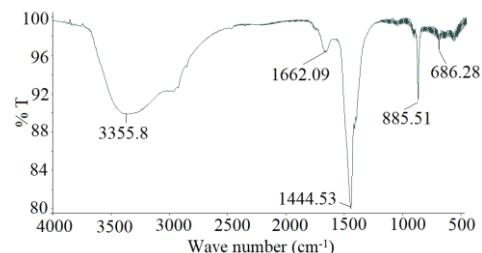


Figure 3. The IR spectrum of ferrate solution

3.2. Effect of sodium hydroxide concentration on the electrochemically formed ferrate concentration

The UV-vis spectra shown in Figure 4 and the data given in Table 2 belong to the EFF solutions prepared from different NaOH concentrations (5-20 M).

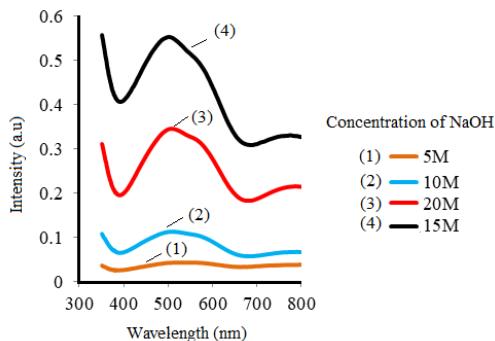


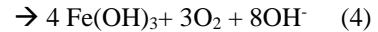
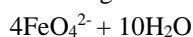
Figure 4. The UV-vis spectra of ferrate solutions prepared from different NaOH concentrations

Table 2. Effect of NaOH concentrations on the peak intensity of UV-vis spectra

i (mA/cm ²)	Intensity (a.u)	Wavelength (nm)
15	0.6353	506
20	0.5435	506
30	0.4030	506
45	0.2948	506

There is one peak on the UV-vis spectra belonging to ferrate at around 510 nm. Its intensity increases from 0.0417 to 0.5539 (a.u) with increasing NaOH concentration from 5 to 15 M, respectively. The reason is that the higher the alkaline environment (until 15 M), the more stable ferrate will be produced, resulting in a more concentrated ferrate concentration. However, it then decreased to 0.3449 (a.u) at the NaOH concentration of 20 M. It can be explained that the viscosity of NaOH solution increases with increasing NaOH concentration. This decreases the ability of ferrate diffusion from the surface of anode electrode into the electrolyte.

The result is that the electrochemical dissolution of the CT3 steel electrode is lower [13]. Besides, ferrate easily decomposed following the reaction (4).



3.3. Effect of the current density on the electrochemically formed ferrate concentration

The results from Figures 5 & 6 and Table 3 show the obtained ferrate content decreasing linearly with the current density. The dependence of peak strength on the current density follows the linear equation (5).

$$y = -0.011x + 0.7783 \quad (5)$$

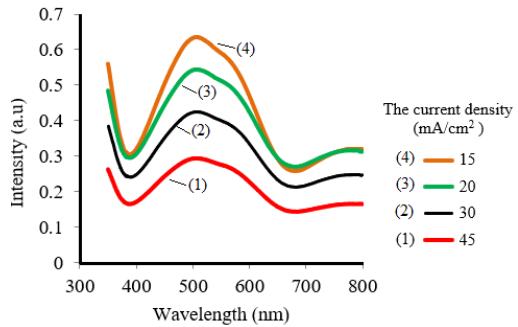
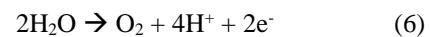


Figure 5. The UV-vis spectra of EFFs prepared at different current densities

Table 3. Effect of current densities on the peak intensity of UV-vis spectra

C _{NaOH} (M)	Intensity (a.u)	Wavelength (nm)
5	0.0417	515
10	0.1119	510
15	0.5539	506
20	0.3449	506

First, the passive layer (oxide-hydroxide layer) is formed on the surface of the anode, which is then dissolved to form ferrate [8]. At the same time, the higher the current density is, the more the amount of charge on the electrode surface will have. This made that the dissolution process of the layer has not yet happened so that some of electrical energy will be consumed by the electrolysis of the water releasing oxygen (see reaction (6)) at the anode.



3.4. Effect of the electrolysis time on the EFF concentration

Studying the effect of electrolysis time on the ferrate formation with constant current density

and electrolyte amount is similar to studying the effect of charge density because the relationship between the electrolysis time and density follows the Faraday equation (7).

$$Q = q \cdot V = I \cdot t \quad (7)$$

where I is current (in A), t is time (in s), Q is quantity of electricity (in C), q is charge (in C/L), and V is volume of electrolyte in (L).

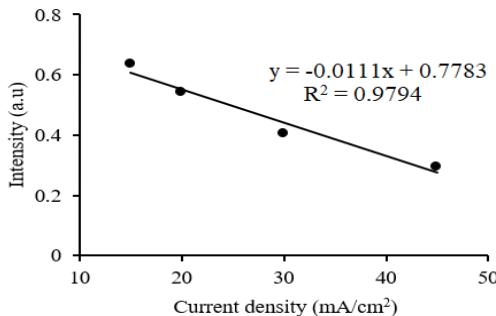


Figure 6. Effect of current densities on the peak intensity of UV-vis spectra

From the observed results in Figures 7 & 8 and Table 4 it shows that the obtained ferrate concentration increases linearly with electrolysis time. The dependence of peak strength on the electrolysis time follows the linear equation (8).

$$y = 0.0098x + 0.0861 \quad (8)$$

The dependence of peak strength on the charge density follows the linear equation (9).

$$y = 0.0004x + 0.0861 \quad (9)$$

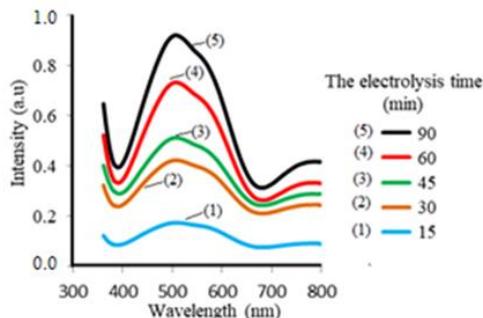


Figure 7. The UV-vis spectra of EFF solutions prepared with the different electrolysis times

4. CONCLUSIONS

Ferrate (VI) solution was synthesized successfully by the electrochemical way at constant current. The highest efficiency of EFF production was found in the alkaline medium of 15 M NaOH. The EFF concentration increased linearly with electrolysis times (in

the range from 15 to 90 min). By contrast, the EFF decreased linearly with increasing current density in the investigated range from 15 to 45 mA/cm².

Table 4. Effect of electrolysis times (t) on the peak intensity of UV-vis spectra

T (min)	q (C/L)	Intensity (a.u.)	λ (nm)
15	337.5	0.1697	506
30	675.0	0.4153	506
45	1012.5	0.5011	506
60	1350.0	0.7163	505
90	2025.0	0.9020	506

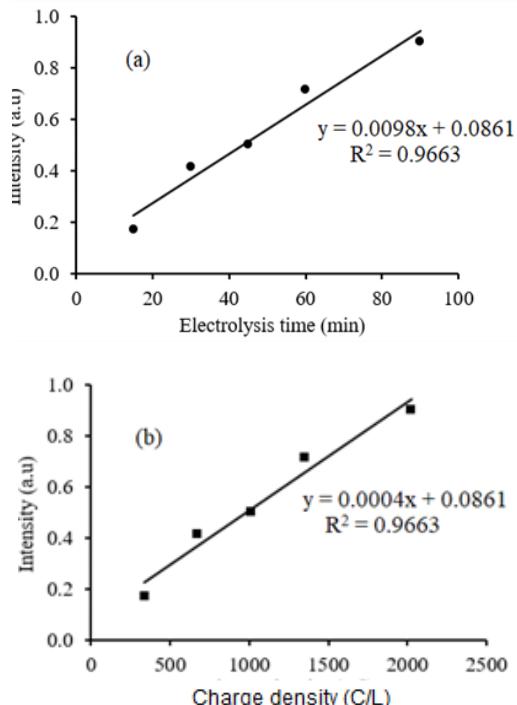


Figure 8. Effect of electrolysis times (a) and charge densities (b) on the peak intensity of UV-vis spectra

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