



Investigation of different reactor configurations for electrochemical ferrate (VI) synthesis

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Received: 09 August 2018, Revised: 22 September 2018; Accepted: 24 September 2018

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Citation: Barisci, S. *Int. J. Chem. Technol.* 2018, 2 (2), 89-94.

ABSTRACT

There are numerous methods used for wastewaters treatment. The agents to be used in those methods should be harmless and degraded to non-hazardous byproducts. Ferrate (VI) has high oxidation capability and is reduced to a non-toxic byproduct, Fe (III), during the degradation of pollutants. Thus, ferrate (VI) is one of the most influential and eco-friendly chemical for water and wastewater treatment. This study aimed to investigate electrochemical ferrate (VI) synthesis, using two different reactor configurations using pure iron plates (R1) and cast-iron flakes (R2) as electrode. In this study, the optimum conditions have been determined experimentally for electrochemical synthesis of ferrate (VI). Ferrate (VI) yield and current efficiency are leading parameters for this purpose. The most appropriate electrolyte concentration is found as 16 M, and the applied current of 1 A is the optimum value with the highest determined current efficiency for both reactor configurations. In comparison with reactor configurations, R2 with iron flakes provided higher ferrate (VI) yield and current efficiency providing higher surface area and higher dissolution rates.

Keywords: Ferrate (VI), reactor design, electrochemical synthesis method, optimum conditions.

Elektrokimyasal ferrat (VI) sentezi için farklı reaktör konfigürasyonlarının araştırılması

ÖZ

Atık suların arıtılmasında kullanılan çok sayıda yöntem bulunmaktadır. Bu proseslerde kullanılan kimyasalların zararsız olması ve tehlikesiz ürünlere parçalanması gerekmektedir. Ferrat (VI), yüksek yükseltgeyici yeteneğe sahiptir ve kirleticilerin parçalanması sırasında toksik olmayan bir yan ürüne, Fe (III)' e indirgenir. Bu sebeple, ferrat (VI) su ve atık su arıtım için en etkili ve çevre dostu kimyasallarından biridir. Bu çalışma elektrot olarak saf demir plaka (R1) ve sert 2) demir pullar (R2) kullanarak elektrokimyasal ferrat (VI) sentezini incelemeyi amaçlamıştır. Bu çalışmada, ferrat (VI)'ın elektrokimyasal sentezi için optimum şartlar deneysel olarak belirlenmiştir. Ferrat (VI) verimi ve akım verimliliği bu amaç için önde gelen parametrelerdir. En uygun elektrolit konsantrasyonu 16 M olarak bulunmuştur ve uygulanan 1 A akım, her iki reaktör konfigürasyonu için en yüksek belirlenen akım verimliliğine sahip optimum değerdir. Reaktör konfigürasyonlarına kıyasla, demir pullu R2 daha yüksek ferrat (VI) verimi ve daha yüksek yüzey alanı ve çözünme oranları sağlayan akım verimliliği sağlamıştır.

Anahtar Kelimeler: Ferrat (VI), reaktör tasarımı, elektrokimyasal sentez metodu, optimum şartlar.

1. INTRODUCTION

Iron has wide variety of valence states ranging from 2- to 8+. All those valence states have different electron structures, co-ordination numbers and geometries. However, apart from metallic iron, only two ions of iron are stable in aqueous medium, namely, iron (II) and iron (III). However, 6+ valence state of iron which is known as ferrate (VI), is also stable at alkaline pH values.

Ferrate (VI) with characteristic purple color is powerful oxidant. At acidic conditions, its redox potential is more than that of ozone (2.2 V). For this reason, the synthesis of ferrate (VI) has been considered by many researchers and ferrate has been used for water and wastewater treatment agent for years.

Commonly, there are three ferrate (VI) synthesis methods, i.e., (1) wet oxidation, by oxidizing a Fe (III) salt at an extremely alkaline medium by hypochlorite or

chlorine, (2) dry oxidation, by heating or melting several iron-oxide-containing minerals at the conditions of robust alkaline and oxygen flow, and (3) an electrochemical method, by anodic oxidation of iron or its alloys in strong alkaline media using NaOH or KOH as electrolyte. Among those methods, electrochemical method has numerous advantages for instance safety, simplicity and cost-effectiveness.¹ The electrochemical ferrate (VI) synthesis is noticeably affected by many factors, mainly, the electrolyte type²⁻³ and its concentration, current density⁴⁻⁵, temperature⁶, anode type⁷ and anode structure.⁸

This study focuses on the determination of optimum operating conditions for the electrochemical ferrate (VI) synthesis using two different reactor configurations. High purity iron plates and iron flakes as anode were used for the first (R1) and second (R2) reactor configuration, respectively. NaOH concentration and applied current were considered as key parameters that impact ferrate (VI) synthesis in each electrochemical reactor. Current efficiency and ferrate (VI) yield were considered for the determination of optimum conditions for each reactor, and the comparison of reactor configurations was presented in this paper.

2. MATERIALS AND METHODS

2.1. Materials

Potassium ferrate (K_2FeO_4 , purity of 97%) and sodium hydroxide (pellets, anhydrous, purity of $\geq 98\%$) were supplied from Sigma Aldrich. All solutions were prepared with high quality pure water using Millipore Water Purification System. High purity iron plate electrodes with iron content of 99.195% and cast-iron flakes were provided by Artı Makina, Turkey. The electrodes were appropriate for the EN 10025-2 standards.

2.2. Experimental set-up

2.2.1. Reactor configuration using pure iron plates (R1)

The electrochemical synthesis of ferrate (VI) was conducted in an electrochemical cell made of plexiglass material. The dimensions of the cell are 15.5 x 14 x 16 cm, and the wall thickness is 1 cm. Two anodes and two cathodes (iron plates) were used and they were connected by way of monopolar mode for each experiment. Electrolyte solution was mixed using magnetic stirrer. The experimental set-up for R1 can be seen in Figure 1.

2.2.2. Reactor configuration using iron flakes (R2)

The electrosynthesis was conducted in a plexiglass electrochemical cell with the dimensions of 22 x 14 x 10 cm,

and the wall thickness is 0.4 cm. As seen in Figure 2, plexiglass material with 20 holes which have 1 cm in diameter was placed to the bottom of the reactor over 1 cm above. These holes provided input of the electrolyte to the reactor. Then iron flakes as anode were located on this perforated material. Pure iron plate as cathode with the same shape and dimensions of plexiglass material was situated to top part of the reactor, and insulant plastic with the same dimensions was placed between the cathode and iron flakes to prevent short circuit. To allow stirring the electrolyte, air from air compressor was provided with silicon pipe. The R2 set-up can be seen in Figure 2.

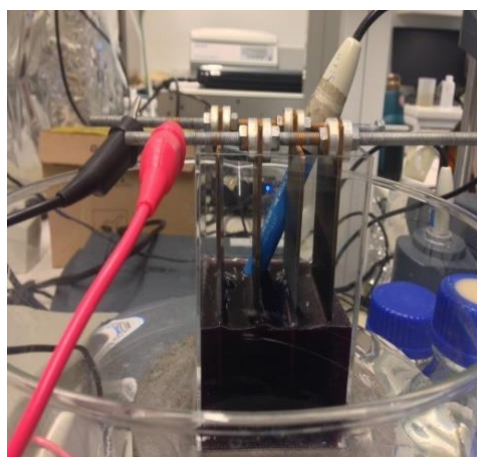


Figure 1. First reactor configuration with pure iron plates (R1).

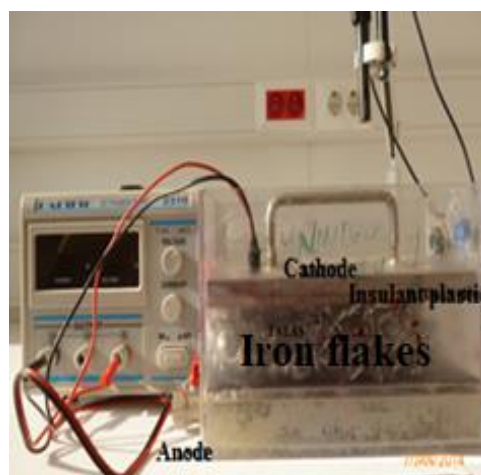


Figure 2. Second reactor configuration with iron flakes (R2).

2.3. Methods

The concentration of ferrate (VI) was measured by HACH DR-5000 UV/VIS Spectrophotometer at 505 nm of wavelength. Calibration curves were prepared for each NaOH concentration according to the experiments. For this purpose, NaOH solutions at various concentrations

(15 M, 16 M, 18 M and 20 M) were prepared, and various amounts of potassium ferrate were added to each solution. After that 0.10; 0.20; 0.25; 0.5; 1.0; 1.5; 2; 2.5 mM potassium ferrate solutions in NaOH were obtained. The absorbance values were measured at $\lambda = 505$ nm. R^2 values of calibration curves were found more than 0.99. The calibration curve and UV spectrum of ferrate (VI) can be found in Figure 3.

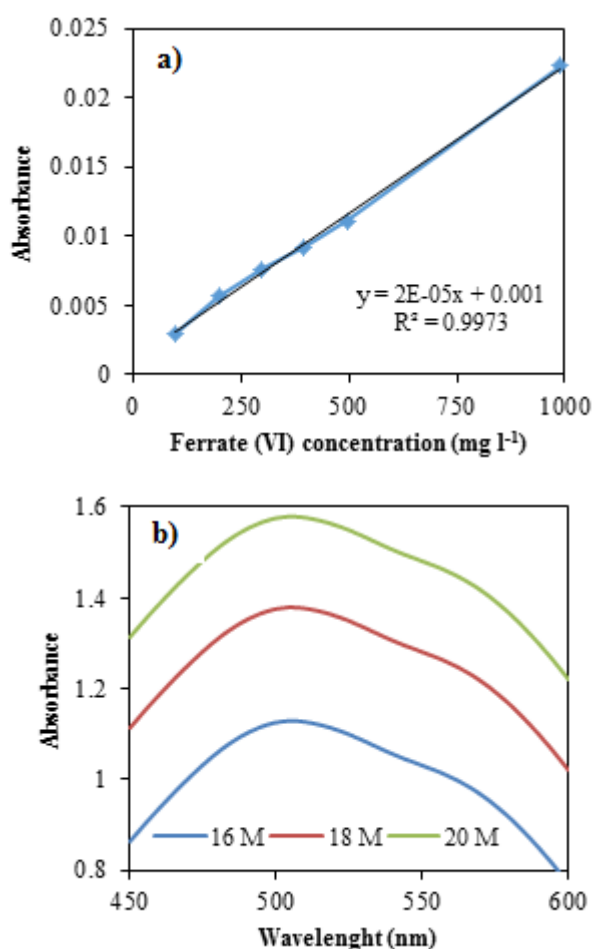


Figure 3. (a) Calibration curve for ferrate (VI) analysis and (b) the wavelength scan of ferrate (VI) at different NaOH concentrations.

After reactor set-up, the procedure was followed: before electrochemical synthesis, electrodes were washed with 0.5 N H_2SO_4 solution for 5 minutes and rinsed with deionized water, then they were dehydrated in the oven and located in a desiccator to turn cold. The same process was applied after each experiment. At that point the electrodes were weighed before and after the experiments to notice total amount of dissolved iron experimentally. As it is seen in Eq. (1), current efficiency (CE) was determined considering the ratio of the experimental ferrate (VI) concentration, $[Fe(VI)]_e$ to the amount of ferrate(VI) which was calculated theoretically, $[Fe(VI)]_t$,

according to the Faraday's Law in Eq. (2).

$$\text{Current Efficiency (CE) (\%)} = \frac{[Fe(VI)]_e}{[Fe(VI)]_t} \times 100 \quad (1)$$

$$[Fe(VI)]_t = M_w \times i \times t / z \times F \quad (2)$$

Where M_w is the molecular weight of ferrate (VI) (120 g mol^{-1}), i is applied current (A), t is electrolysis time (sec); z is electron number in the reaction, F is a constant of Faraday's Law ($96485 \text{ Coulomb/mol}$).

All experiments were conducted at room temperature. Continual current (DC) was provided by GW Instek PSP-405 Programmable power source. The electrolytic voltage was noted through the electrolysis. Different alkaline concentrations were used to evaluate the effect of NaOH concentration on the ferrate (VI) synthesis yield. Besides, different applied current values (1, 3 and 5 A) were applied to see the effect. Electrolysis period was 3 hours for all applied current values. Samples were analysed using UV-Vis spectrophotometer. Measurements were repeated, and the average value was presented. The optimum conditions were determined considering ferrate (VI) yield and CE.

3. RESULTS AND DISCUSSION

3.1. Effect of parameters for reactor configuration-R1 (pure iron plates)

One of the key factors that affects the electrochemical ferrate (VI) synthesis is the type of electrolyte and its concentration.⁹ The electrolyte type determines the dissolution rate of iron anode and the formation of oxo-hydroxide layers occurring on the anode surface.¹⁰ NaOH is the principal electrolyte for electrochemical synthesis of ferrate (VI).¹¹ Figure 4 presents the ferrate (VI) yield at different electrolyte concentrations and applied current values.

As seen from Figure 4, the maximum ferrate (VI) yield was obtained with 16 M NaOH media at applied current of 5 A (1.28 g l^{-1}). 20 M NaOH media also provided high ferrate (VI) yield (1.278 g l^{-1}). It can be said that increasing electrolyte concentration provided higher ferrate (VI) yield. Increasing electrolyte concentration provides higher dissolution rates of iron electrode and prevents formation of oxo-hydroxide layer on the anode surface. Furthermore, increasing alkalinity enhances produced ferrate (VI) stability. In other words, ferrate (VI) stability decreases with decreasing NaOH concentration. While ferrate (VI) formation takes place in a reactor, it simultaneously reduces to Fe (III). In this case, only 18 M NaOH media provided less ferrate (VI) yield.

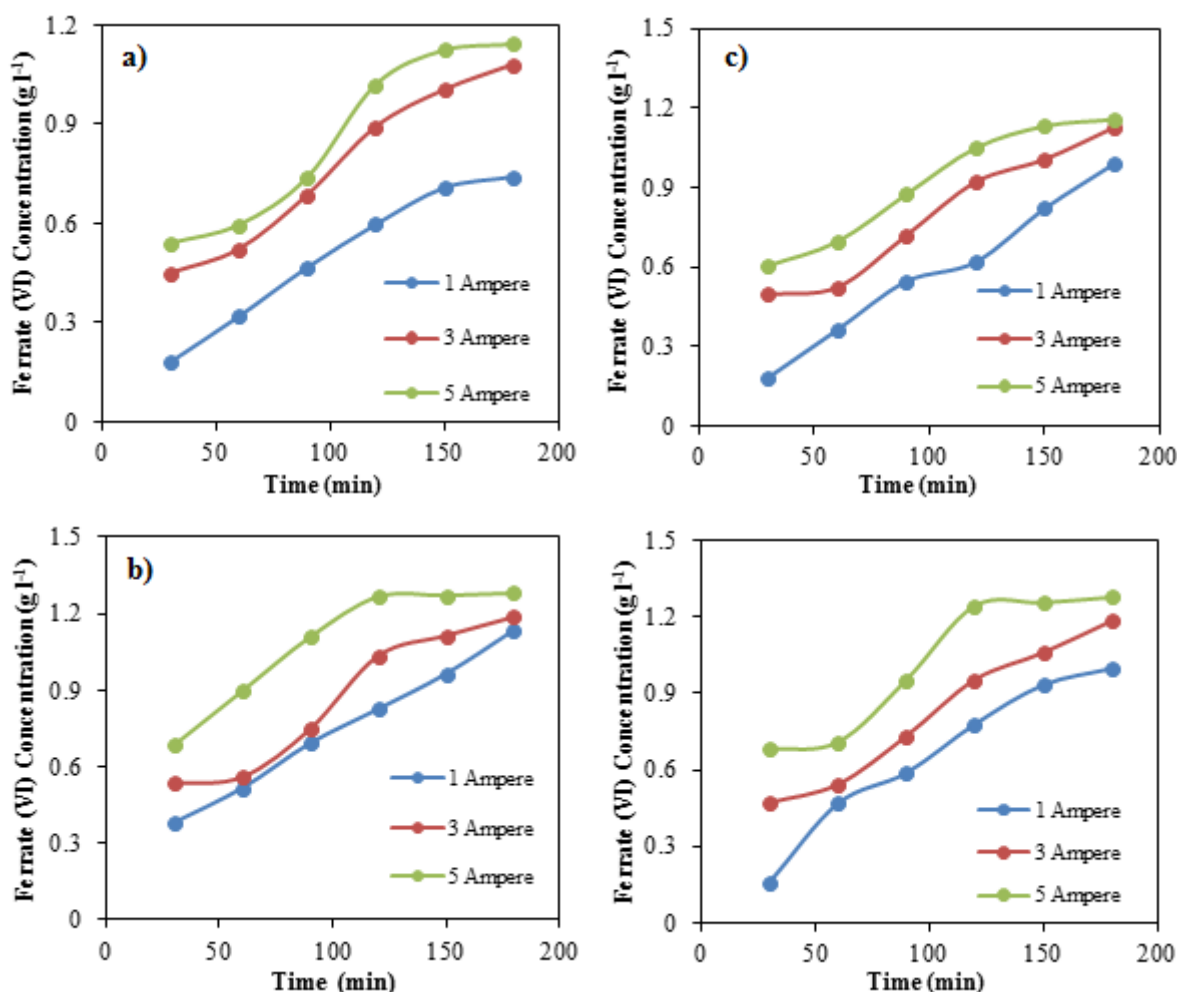


Figure 4. Ferrate (VI) yield in terms of different applied current values and NaOH concentrations: a) 15 M, b) 16 M, c) 18 M and d) 20 M for reactor design, R1.

Applied current is another important parameter which affects ferrate (VI) formation yield. As seen from Figure 4, increasing applied current provided higher ferrate (VI) concentration independent from NaOH concentration. Figure 5 shows current efficiency values in terms of applied current and NaOH concentrations. As seen, current efficiencies were found as 71.5%, 55.9% and 68.3% for applied current values of 1, 3 and 5 A at 16 M NaOH media, respectively. Similar trends were observed at other mentioned NaOH concentrations. It can be said that the lowest applied current value provided the highest current efficiency. This may be due to the competition between produced ferrate (VI) and oxygen evolution on the anode surface. Increasing current and potential causes more participation of this adverse reaction to the mechanism and this lowers current efficiency.¹² Besides, the formation of H₂ gas on the cathode side increases with increasing current and this may lower electron transfer area due to hydrogen bubbles.¹³ Consequently, in the case of reactor design-R1, applied current of 1 A can be chosen for optimal

point providing the highest current efficiency and reasonable ferrate (VI) yield (1.14 g l⁻¹).

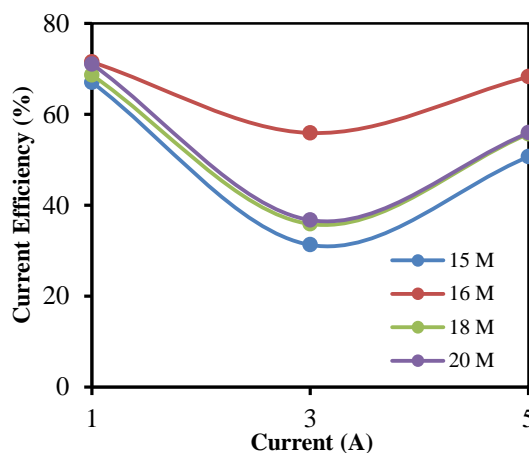


Figure 5. Current efficiencies and in terms of applied current and NaOH concentration for reactor design, R1.

3.2. Effect of parameters for the second reactor configuration-R2 (iron flakes)

To determine the effect of anode type and reactor configuration on the electrochemical ferrate (VI) synthesis, the experiments were conducted at the same electrolyte concentrations and applied current values and Figure 6 represents ferrate (VI) yields at those conditions. As seen from Figure 6, the highest ferrate (VI) yield was gained under the applied current of 5 A with 16 M NaOH media (2.28 g l^{-1}) after 3 h. This is

similar with the results for R1. While ferrate (VI) yield increased with increasing NaOH concentration from 15 M to 16 M, further increase in NaOH concentration did not provide higher ferrate (VI) yield. Also, increasing applied current provided higher efficiency for all NaOH concentration except 20 M NaOH media. Beyond applied current of 3 A, ferrate (VI) yield significantly reduced in 20 M NaOH media.

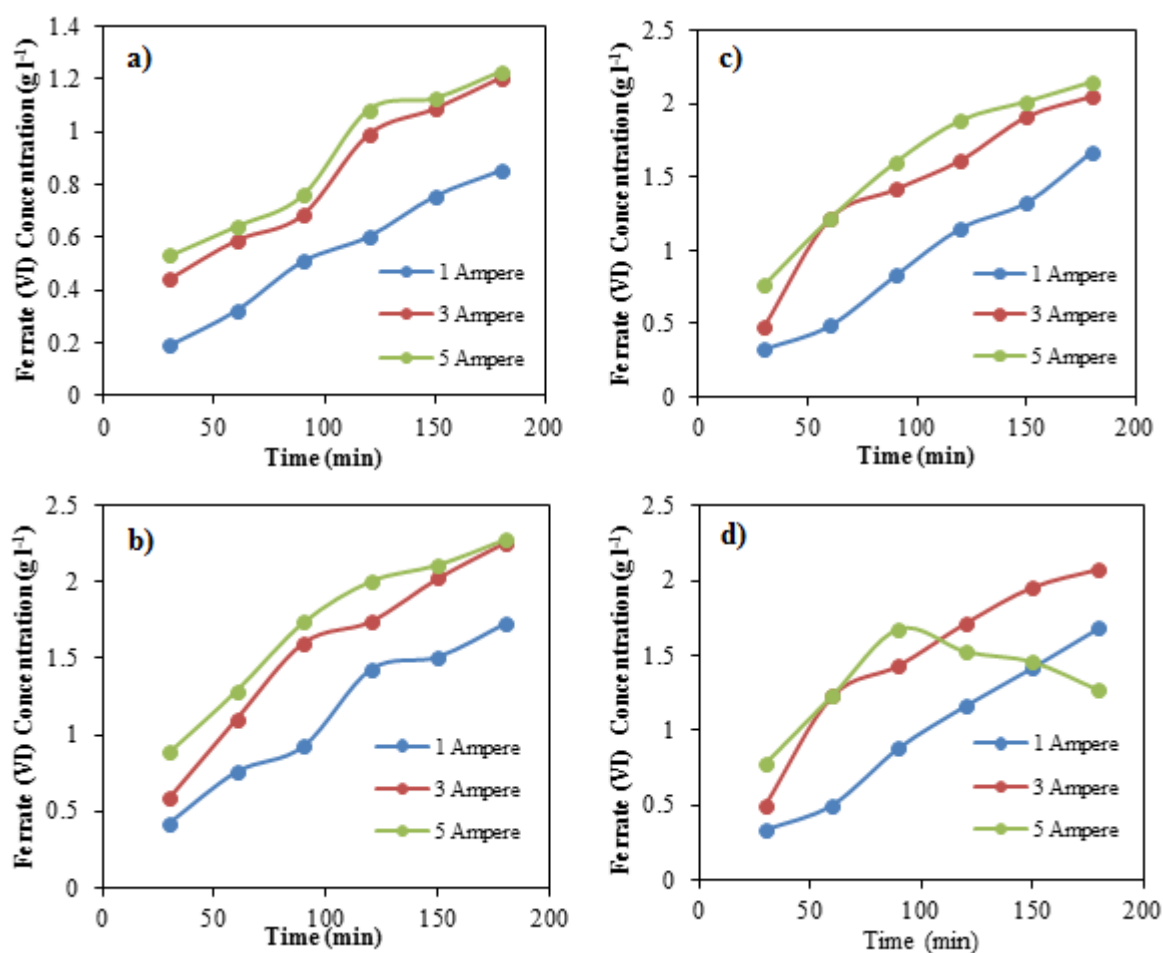


Figure 6. Ferrate (VI) yield in terms of different applied current values and NaOH concentrations: a) 15 M, b) 16 M, c) 18 M and d) 20 M for reactor design, R2.

When current efficiencies are considered (see Figure 7), the highest efficiency was observed with applied current of 1 A, and the efficiency reduced with increasing applied current values for all NaOH concentrations. Increasing applied current provides higher dissolution of iron anode. However, oxygen evolution also increases with increasing applied current which may affect ferrate (VI) yield negatively. When ferrate (VI) starts to form in the anode surface with dissolving iron anode, oxygen evolution also participates to the mechanism as

mentioned above. Besides, electrical energy affects the electrochemical reactions by the generation of H₂ gas. The domination of these situations determines ferrate (VI) yield. In this case, applied current of 5 A provided the highest yield. However, current efficiency was the lowest. Consequently, in this case, applied current of 1 A can be chosen for optimal condition with 1.73 g l^{-1} ferrate (VI) yield and 169.9% current efficiency in 16 M NaOH media. In the overall assessment, where the most suitable electrolyte concentration was 16 M, applied current of 1

A was the optimum value with the highest provided current efficiency for both reactor configurations.

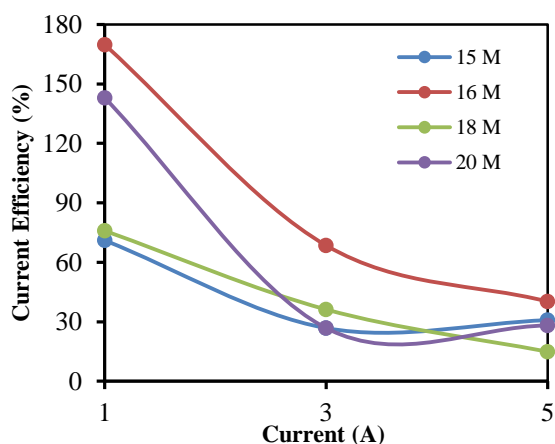


Figure 7. Current efficiencies in terms of applied current and NaOH concentration for reactor design, R2.

When reactor configurations were compared, R2 with iron flakes provided higher ferrate (VI) yield and current efficiency. This may be due to higher surface area of iron flakes and high dissolution rates.

4. CONCLUSIONS

Ferrate (VI) was produced using different reactor configurations with iron plates and cast-iron flakes in this study. Optimum conditions such as electrolyte concentration and applied current were determined for both reactor configurations considering the ferrate (VI) yield and the highest current efficiency. Using cast-iron flakes with high surface area provided higher ferrate (VI) yields with the highest current efficiency.

ACKNOWLEDGEMENTS

The authors are grateful to The Scientific and Technological Research Council of Turkey (TUBITAK) for their financial support (Project number: 112Y258).

Conflict of interest

I declare that there is no a conflict of interest with any person, institute, company, etc.

REFERENCES

1. Alsheyab, M.; Jiang, J.Q.; Stanford, C. *Journal of Environmental Management*, **2009**, 90, 1350-1356.

2. Bouzek, K.; Roušar, I. *Journal of Applied Electrochemistry*, **1993**, 23, 1317-1322.

3. Bouzek, K.; Roušar, I. *Journal of Applied Electrochemistry*, **1997**, 27, 679-684.

4. Yu, X.; Licht, S. *Journal of Applied Electrochemistry*, **2008**, 38, 731-742.

5. He, W.; Wang, J.; Yang, C.; Zhang, J. *Electrochimica Acta*, **2006**, 51, 1967-1973.

6. Barisci, S.; Ulu, F.; Sarkka, H.; Dimoglo, A.; Sillanpaa, M. *International Journal of Electrochemical Science*, **2014**, 9, 3099-3117.

7. Sun, X.; Zu, K.; Liang, H.; Sun, L.; Zhang, L.; Wang, C.; Sharma, V. K. *Journal of Hazardous Materials*, **2018**, 344, 1155-1164.

8. Liu, C.; Zhou, Z.; Yuan, B.; Liu, S. *Journal of Environmental Engineering*, **2018**, 144, 1-7.

9. Macova, Z.; Bouzek, K.; Sharma, V.K. *Journal of Applied Electrochemistry*, **2010**, 40, 1019-1028.


10. Macova, Z.; Bouzek, K. *Journal of Applied Electrochemistry*, **2012**, 42, 615-626.

11. Sun, X.; Zhang, Q.; Liang, H.; Ying, L.; Xiangxu, M.; Sharma, V.K. *Journal of Hazardous Materials*, **2016**, 130-136.

12. Hives, J.; Gal, M.; Kerekes, K.; Kubinakova, E.; Mackulak, T. *ACS Symposium Series: Ferrites and Ferrates: Chemistry and Applications in Sustainable Energy and Environmental Remediation*, **2016**, 1238, Chapter 8, 221-240.

13. Vogt, H.; Aras, O.; Balzer, J. *International Journal of Heat and Mass Transfer*, **2004**, 47, 787-795.

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