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Fast and Efficient Removal of Iron from Industrial Wastewater Using Electrochemical Deposition

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Among the proposed methodologies for heavy metal removal from industrial wastewaters, electrochemical treatment has drawn attention due to its simplicity and high performance. In this study, experiments were carried out using a bench-scale electrochemical cell incorporating a flow-by porous graphite electrode for iron removal. The influence of the initial iron concentration, feed flow rate, and current density on the removal efficiency and current efficiency were studied. The maximum removal efficiency (99.7%) was obtained after 10 min of operation at a flow rate of 0.278 ml/s, a current density of 0.98 mA/cm^2 and a pH of 4, and a maximum current efficiency of 95.5% was obtained at a flow rate of 0.833 ml/s for an initial iron concentration of 200 ppm.

Keywords: iron removal; electrochemical cell; flow-by electrode

1. INTRODUCTION

Heavy metal ions are not biodegradable and have a tendency to accumulate in living beings, and many such ions are known to be toxic [1]. Therefore, heavy metals must be removed from wastewater to protect humans and the environment [2]. Discharging large amounts of heavy metal-polluted wastewater is the main problem facing many industries. Copper, cadmium, lead, iron, mercury, zinc, chromium and silver are the heavy metals of greatest concern in wastewater treatment [3]. Several techniques have been used to remove heavy metal ions, including chemical precipitation [4]; ion exchange [5]; adsorption onto different adsorbates (e.g., activated carbon [6, 7], carbon nanotubes [8, 9], and wood sawdust [10]); membrane filtration, including ultrafiltration and reverse osmosis [11-13]; coagulation and flocculation [14]; electrochemical treatment [2]; photocatalysis; and nanotechnological approaches [15].

Among the proposed heavy metal removal processes, electrochemical remediation has attracted the greatest attention because it is an economic and safe approach for the long-term clean-up of metal-bearing aqueous wastes [16-19]. Moreover, electrochemical-based operations provide a means of continuous, selective removal of metal contaminants and offer end-of-pipe processes for the recovery of metals. Furthermore, operation at room temperature and atmospheric pressure, which is possible in electrochemical processes, reduces the possibility of volatilization and discharge of unreacted wastes [20]. Essentially, electrochemical treatment is concerned with the transfer of electrons at the solution–electrode interface by applying an external current to drive the process [21].

In electrochemical techniques, metal ions are precipitated on a cathode surface and can be recovered in their elemental state. These techniques are considered to be rapid and well-controlled, require fewer chemicals, give good reduction yields and produce less sludge. In addition, in the direct reduction of heavy metal ions, which mainly depends on the activity of the target ions, the active ions can be indirectly precipitated by adequate electrochemical oxidation of the active ions to form water-insoluble salts. Furthermore, the removal of undesirable components from the aqueous phase depends on the choice of an appropriate electrode material and potential or the use of membrane systems to selectively drive the electrode processes [22]. There are several such electrochemical operations, including electrocoagulation (EC) [23, 24], electroflotation (EF) [25] and electrodeposition [26].

Iron ions are the most widespread pollutants in industrial wastewaters due to the corrosion of equipment and pipelines in industrial plants. Therefore, special attention should be paid to the removal of iron ions from industrial wastewaters to satisfy environmental restrictions. Due to their excellent chemical stability, very good electrical conductivity and low cost, carbonaceous materials are the best candidates for use as electrodes in electrochemical cells. Additionally, the ease of fabricating porous carbon materials strongly encourages the fabrication of high-surface-area and efficient electrodes. Various electrolysis cells use porous materials such as carbon and graphite felt as electrodes [27].

Conventional electrodes operate with non-uniform reaction rates, resulting in lower extents of utilization of the bed [28]. A flow-by porous electrode works like a flow-through porous electrode, but the difference is that in flow-by electrodes, the electric current flows perpendicular to the flow of the electrolyte. The flow-by configuration is superior because the system yields a greater return on investment, as well as operational flexibility in terms of variable flow rate and conversion [29]. Electrochemical reactors incorporating flow-by porous electrodes can give rise to a powerful technique in metal recycling where metal ions are reduced and deposited on the porous electrode (cathode) [30]. The current density and flow rate are the most important parameters for metal ion removal from wastewater.

In this study, a bench-scale electrochemical cell incorporating flow-by porous graphite electrodes was utilized as a proposed unit to remove iron from simulated industrial wastewater. The influence of the initial iron concentration, flow rate, current density and pH on the removal efficiency was studied.

2. MATERIALS AND EXPERIMENTAL

Ferrous sulfate heptahydrate ($FeSO_4.7H_2O$), pure sodium chloride (NaCl), and sulfuric acid with 99% purity were purchased from El-Nasr Pharmaceutical Chemicals Co., Egypt, and were utilized without any prior treatment. Distilled water was utilized as the solvent.

Fig. 1 displays a schematic diagram of the used cell. Briefly, the cell consisted of two co-axial cylinders, one of Plexiglas with an internal diameter of 15 cm and height of 18 cm fixed to end flanges made from PVC. The second cylinder was made of a highly corrosion-resistant stainless steel screen (mesh 5) with an inner diameter of 10 cm enclosed in a polyamide membrane and was used as the anode compartment. The cathode was the annular space between the two cylinders. Graphite granules passing sieve no. 10 and retained on sieve no. 30 were used to fill the cathode and anode compartments to a height of 13 cm. A graphite rod with a diameter of 10 mm and two stainless steel rods with a diameter of 8 mm and length of 250 mm were used as current collectors. The feed solution entered through an opening at the bottom of the cell using a dosing pump (Kompact AMC, SEKO group, Via Salaria Km, Rieti, Italy) to control the feed flow rate, while the outlet flow and the gas vents were located at the upper flange of the cell. A DC power supply (BK PRECISION VICIOR VC830L) was used with a digital multi-meter to measure the potential and current. pH was measured using a pH meter (model OAKTON pH/˚C), and the iron concentration was measured by using a T80 UV/VIS spectrometer after adding HI93721-0 iron HR reagent, which was purchased from Hanna Instruments Co., Egypt. Simulated iron-polluted solutions with different iron concentrations were prepared by dissolving $FeSO_4.7H_2O$ in distilled water. Sulfuric acid was added to adjust the pH. Certain amounts of NaCl were added to improve the conductivity and ionic mobility through the electrolyte.

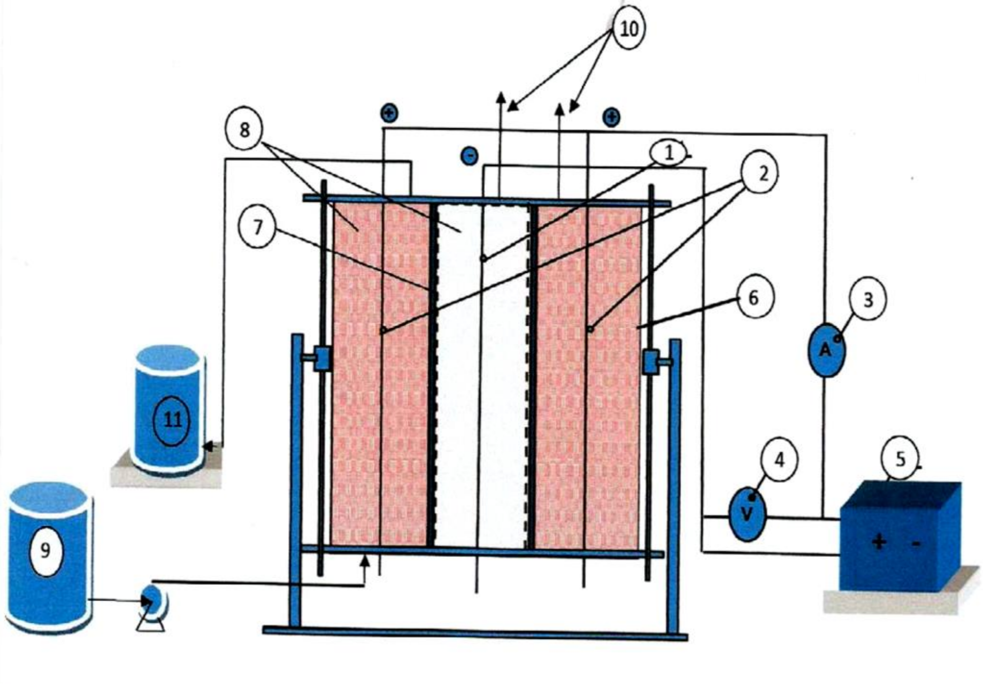

Figure 1. Schematic of the experimental setup: 1) anode current collector; 2) cathode current collector; 3) ammeter; 4) voltmeter; 5) DC power supply; 6) Plexiglas cylinder; 7) stainless steel cylinder; 8) graphite; 9) iron solution tank; 10) gas vents; 11) treated water tank; 12) dosing pump.

3. RESULTS AND DISCUSSION

3.1. Effect of initial concentration on removal efficiency and removal rate

The amount of removed metal ions was measured in terms of % removal efficiency by the following equation:

$$\% \text{ Removal} = ((C_i - C_o)/ C_i) \times 100 \qquad (1)$$

where C_i and C_o are the inlet and outlet iron concentrations in the solution, respectively. Fig. 2 displays the effect of the initial concentration of iron ions in the feed on the removal efficiency at a current density of 0.98 mA/cm^2, pH = 4 and different feed flow rates. As shown, at all rates, increasing the initial concentration of iron from 50 to 200 ppm caused an increase in the removal efficiency since dissolved salts increase the electrical conductivity and ionic mobility of ions through the solution, whether toward or away from the electrodes [31]. However, as the initial concentration increased to 300 ppm, the removal efficiency decreased at all flow rates. This result may be due to the limited capacity of the electrode for iron removal, which is determined by the bed height and diameter [32, 33]. This trend is in agreement with the results of Taleb [33], Esmaeil [34] and Salehzadeh [35].

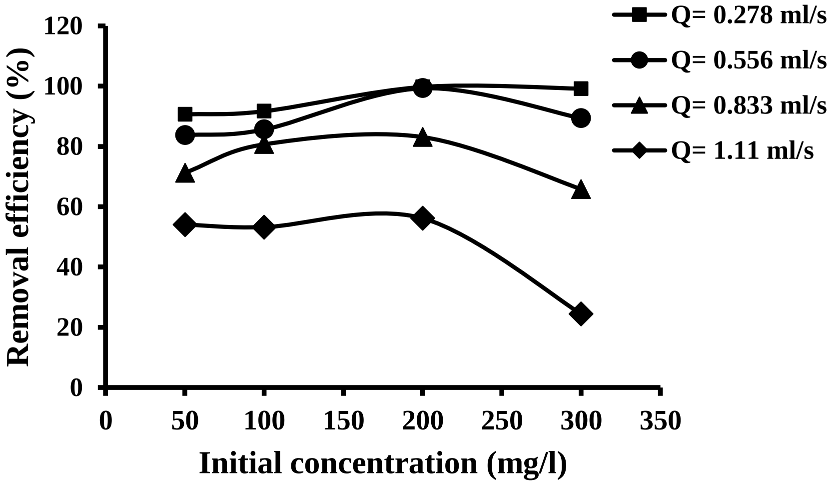

Figure 2. Effect of initial concentration on removal efficiency at different flow rates, a current density of 0.98 mA/cm^2 and pH 4.

The removal rate (R (mol/sec)) can be defined as the rate of iron ion depletion per second and can be calculated from the following equation:

$$R = Q \times (C_i - C_o) \qquad (2)$$

where Q is the flow rate in ml/s. The effect of the inlet concentration on the removal rate of iron at a cell current density of 0.98 mA/cm^2 is shown in Fig. 3. The removal rate increases with increasing initial concentration because the removal rate process is mass-transfer controlled [36]; this result is consistent with previous studies [27, 33].

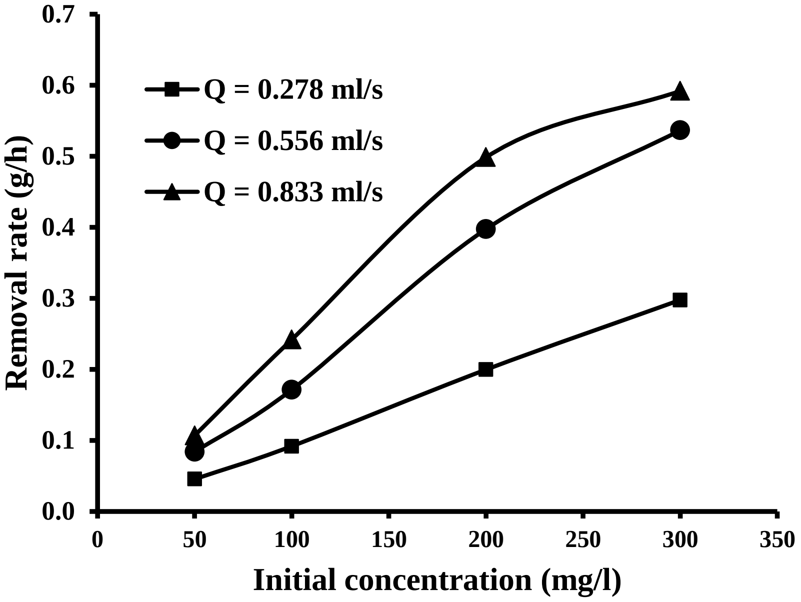

Figure 3. Effect of initial concentration on removal rate at different flow rates, a current density of 0.98 mA/cm^2 and pH 4.

3.2. Effect of feed flow rate on removal efficiency and removal rate

Fig. 4 demonstrates the influence of the feed flow rate on the removal efficiency at an applied current density of 0.98 mA/cm^2, pH = 4 and different initial iron concentrations. As shown in the figure, the influence of the feed flow rate on the removal efficiency depends on the utilized flow rate. In other words, the influence of the flow at a low feed rate is almost negligible, while the impact is considerable at high flow rates. Typically, an increase in flow rate from 0.278 to 0.556 ml/s was not significant as the decrease in the removal efficiency was trivial, while increasing the flow rate from 0.556 to 1.1 ml/s caused a distinct decrease in removal efficiency. This finding can be explained by the fact that high flow rates result in a low retention time, so the contact time between the solution and electrode decreases, which in turn decreases the amount of iron deposited on the surface of the electrode. Maltosz and Newman [37] obtained the same results when they studied the removal of mercury using carbon flow-through electrodes. Cerisola [38] also made a similar observation and reported that the removal efficiency was determined by residence time rather than mass transport. The maximum removal efficiency was 99.7% for an initial iron concentration of 200 ppm at a flow rate of 0.278 ml/s.

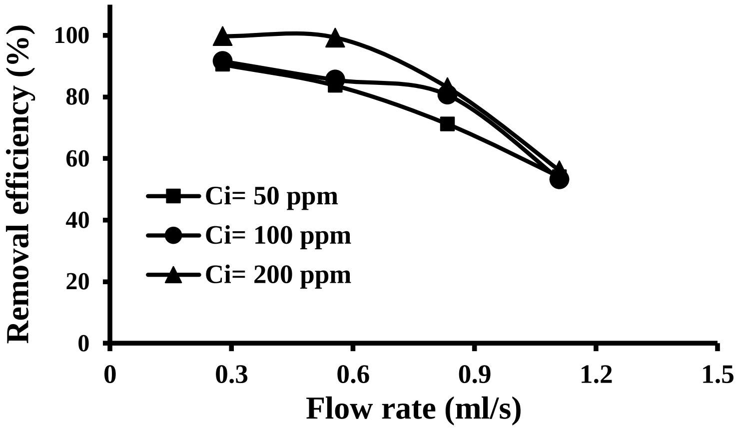

Figure 4. Effect of feed flow rate on removal efficiency at different initial concentrations, a current density of 0.98 mA/cm^2 and pH 4.

Similarly, the influence of the flow rate on the iron removal rate was studied (Fig. 5). As expected, the removal rate increased with increasing feed flow rate. These results are in agreement with Newman [39], who observed that the removal process was mass-transfer controlled. The results are also supported by other authors [33, 34] who used flow-through porous electrodes for the recovery of iron, copper and chromium from industrial wastewater. Scientifically, the results can be explained by the fact that the removal process is mass-transfer controlled, as mentioned before. As the flow rate increases, the mass transfer will increase, and consequently, the removal rate will increase.

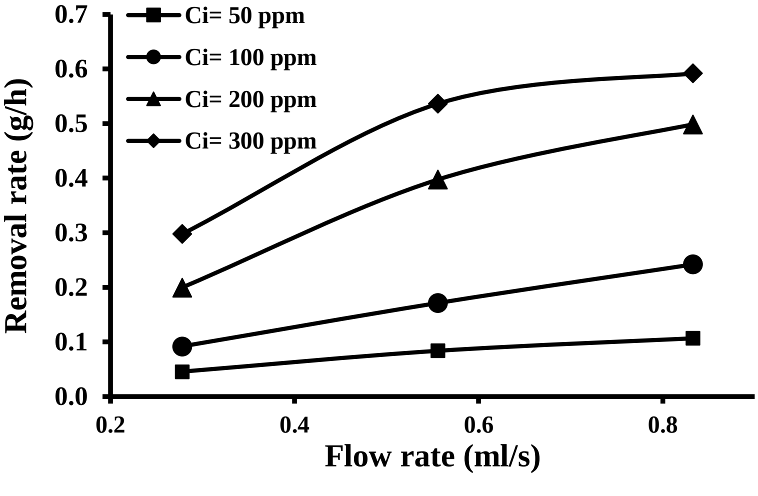

Figure 5. Effect of feed flow rate on removal rate at a constant current density of 0.98 mA/cm^2 and pH 4.

3.3. Effect of feed flow rate on current efficiency

During the process, one of the most competitive reactions at the cathode is the reduction of H^+ into hydrogen gas [15].

$2H^+ + 2e^- \rightarrow H_2$ (3)

From Fig. 6, as the flow rate increased, the current efficiency increased. With the same total charge consumption, the charge used to form the product will increase as the flow rate increases due to low hydrogen evolution and high electrode capacity [34]. Consequently, the current efficiency will increase. The maximum current efficiency was 95.5% at 200 ppm. This value was obtained at a flow rate of 0.833 ml/s and current density of 0.98 mA/cm^2.

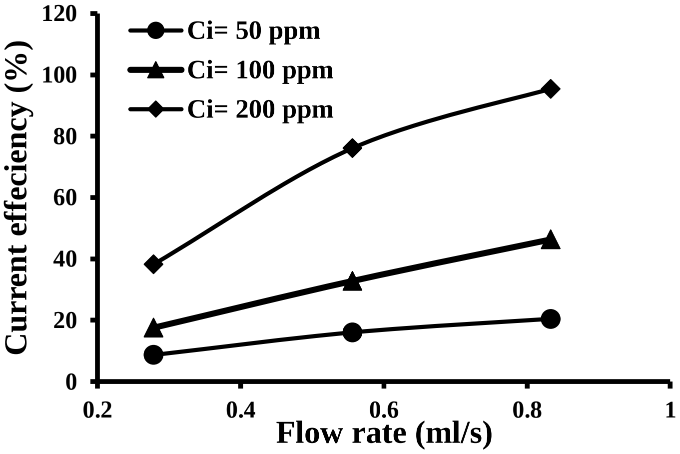

Figure 6. Effect of flow rate on current efficiency at a current density of 0.98 mA/cm^2 and pH= 4.

3.4. Effect of applied current density on removal efficiency

As shown in Fig. 7, increases in current density above 0.98 mA/cm^2 were ineffective, as the increase in removal efficiency was very low; the removal efficiency increases with increasing current density until the evolution of hydrogen from the main reaction occurs and steady state is reached [34]. This trend is similar to that reported by Pascu [21]. The maximum efficiency was obtained at a current density of 0.98 mA/cm^2 for different initial iron concentrations.

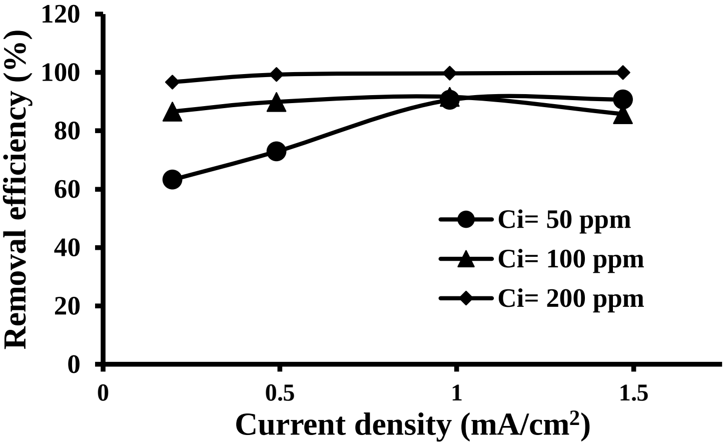

Figure 7. Effect of current density on removal efficiency at a flow rate of 0.278 ml/s and pH 4.

3.5. Effect of pH on removal rate and removal efficiency

Notably, iron is widely present in acidic wastewaters because it precipitates in alkaline media in the form of iron hydroxide. Therefore, in this study, we focused on the acidic range. As illustrated in Figs. 8 and 9, the removal rate and removal efficiency of iron were not greatly affected by solution pH in the range of 3 to 5. These findings indicate that increasing the hydrogen ion concentration does not have a distinct influence on iron removal. Considering that hydrogen evolution is a competing reaction at the cathode surface, the results highlight that the removal of iron was achieved by precipitation in the form of insoluble salts rather than direct reduction to iron metal at the cathode surface. It is known that iron can be precipitate in the alkaline media due to formation of the insoluble iron hydroxide. On the other hand, in the acid media iron ions have a high stability in solution. Accordingly, the pH influence has been investigated in the acidic media. As shown in the figures, the pH has trivial influence on the removal efficiency which indicates that the removal of iron depends mainly on the electrochemical parameters.

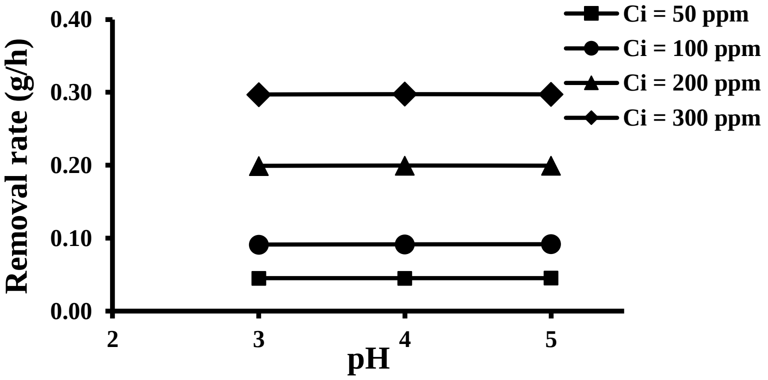

Figure 8. Effect of pH on removal rate at different initial concentrations, a current density of 0.98 mA/cm^2 and a flow rate of 0.278 ml/s.

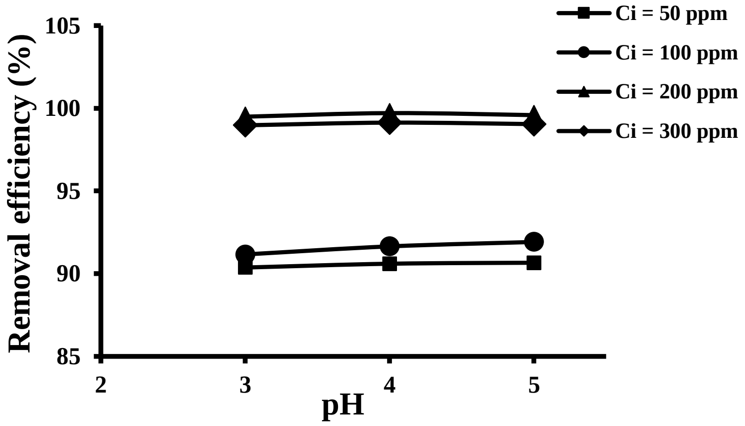

Figure 9. Effect of pH on removal efficiency at different initial concentrations, a current density of 0.98 mA/cm^2 and a flow rate of 0.278 ml/s.

3.6. Proposed mechanism

In addition to our study, many reports have concluded that the addition of sodium chloride distinctly enhances the removal of heavy metals. Moreover, evolved gases, as well as a brownish (and sometimes green) precipitate, were obtained. Therefore, NaCl has a crucial role in the removal mechanism [40]. The following general reactions are expected in the proposed system.

Bulk $H_2O \Leftrightarrow H^+ + OH^-$ (4)

$NaCl \Leftrightarrow Na^+ + Cl^-$ (5)

$FeSO_4 \Leftrightarrow Fe^{++} + SO_4^-$ (6)

Accordingly, based on the ions present in the medium, the anodic and cathodic reactions are as follows:

Anodic reactions

$2Cl^- \Leftrightarrow Cl_2\uparrow + 2e^-$ $E_o = -1.36$ V (7)

$Fe^{+2} \Leftrightarrow Fe^{+3} + e^-$ $E_o = +0.771$ V (8)

$4OH^- \Leftrightarrow H_2O + O_2 + 4e^-$ $E_o = -0.4$ V (9)

Due to working in an acidic medium, the third reaction is not favoured. Thermodynamically, the second reaction is highly predicted. However, due to the overpotential and high current density, the first reaction also occurs. Experimentally, the evolution of chlorine gas was observed at the anode.

Cathodic reactions

$2H^+ + 2e^- \Leftrightarrow H_2\uparrow$ $E_o = 0.0$ V (10)

$Fe^{+2} + 2e^- \Leftrightarrow Fe$ $E_o = -0.44$ V (11)

Thermodynamically, hydrogen evolution is highly favoured rather than the deposition of iron metal, especially in treatment processes carried out in acidic media.

In addition to the thermodynamics, the reaction kinetics also strongly affect the reaction pathway. Based on the aforementioned equations, ferric ions are strongly predicted. From a kinetic point of view, the formation of ferric hydroxide is strongly predicted because of its extremely low solubility in water. According to the solubility constants of ferric and ferrous hydroxides (6.3×10^{-38} and 1.59×10^{-5} mol/L, respectively), $Fe(OH)_3$ is not soluble in water (at room or high temperature). Therefore, the formation of ferric hydroxide is strongly favourable in the forward direction because the product is removed from the reaction medium.

Overall, from the thermodynamics and kinetics of the expected chemical reaction, iron ions are removed from the proposed cell in the form of ferric hydroxide (the main product) and some metallic iron due to Fe^{+2} reduction (with very low content). Moreover, by oxidation of chloride ions, hypochlorite and chlorate anions (strong oxidizing agents) can be formed in the solution according to the following reactions [31]:

$Cl_2 + H_2O \rightarrow HOCl + Cl^- + H^+$ (12)

$HOCl \rightarrow + OCl^- + H^+$ (13)

$2HClO + OCl^- \rightarrow ClO^- + 2HCl$ (14)

Regardless of the reaction mechanism, the removal efficiency obtained in the present study is very satisfactory compared to previous reports. Table (1) gives a comparison of iron removal efficiencies from wastewater using various treatment methods. As shown in the table, the proposed strategy has a distinct priority which can be assigned to the high electrode surface area and the good design of the cell. Moreover, based on the environmental restrictions, the achieved removal efficiency is highly accepted. Furthermore, from the industrial point of view, the required time adds an additional advantage for the proposed strategy as it is small compared to the other procedures. Overall, the obtained results strongly recommended exploiting the proposed cell in treatment of the heavy metals-contaminated industrial wastewaters.

Table 1. Removal efficiency of iron from industrial wastewater using various treatment methods.

Treatment method	Initial iron concentration (mg/l)	pH	Time (min)	Removal efficiency (%)	Ref.
Combined photoelectrochemical method	12	3	15	46	[21]
Electrocoagulation	25	7.5	35	99.2	[40]
Electroflotation	50	7.8	15	98	[15]
Adsorption	10	4	90	97.9	[35]
Flow-through porous electrode	485	4	60	79.3	[34]
Flow-by porous electrode	200	4	10	99.7	Our study

4. CONCLUSIONS

The electrochemical remediation of iron-containing acidic industrial wastewaters was investigated to decrease the iron content to environmentally acceptable levels. However, both the removal efficiency and removal rate depend mainly on the feed flow rate, iron concentration, current density and pH of the solution. Typically, increasing the feed flow rate causes a significant decrease in removal efficiency. An increase in current density above 0.98 mA/cm^2 was ineffective, as the increase in efficiency was very low. Additionally, an increase in feed flow rate improved the current efficiency. Overall, based on the abovementioned results, electrochemical cells incorporating flow-by porous graphite electrodes are an effective method for the treatment of wastewater containing iron ions.

References

1. D. Hong-gui, G. Teng-Feng, L. Ming-hui, D. Xu, *Int J Electrochem Sci*, 7 (2012) 5286.
2. F. Fu, Q. Wang, *J. Environ. Manage.*, 92 (2011) 407.
3. C.-V. Gherasim, P. Mikulášek, *Desalination*, 343 (2014) 67.
4. Y. Ku, I.-L. Jung, *Water Res.*, 35 (2001) 135.
5. S.-Y. Kang, J.-U. Lee, S.-H. Moon, K.-W. Kim, *Chemosphere*, 56 (2004) 141.

6. A. Jusoh, L.S. Shiung, M. Noor, *Desalination*, 206 (2007) 9.
7. K.C. Kang, S.S. Kim, J.W. Choi, S.H. Kwon, *J. Ind. Eng. Chem.*, 14 (2008) 131.
8. N.A. Kabbashi, M.A. Atieh, A. Al-Mamun, M.E. Mirghami, M. Alam, N. Yahya, *J. Enviro. Sci.*, 21 (2009) 539.
9. C.-Y. Kuo, H.-Y. Lin, *Desalination*, 249 (2009) 792.
10. M. Šćiban, B. Radetić, Ž. Kevrešan, M. Klašnja, *Bioresour. Technol.*, 98 (2007) 402.
11. M. Mohsen-Nia, P. Montazeri, H. Modarress, *Desalination*, 217 (2007) 276.
12. A. Fane, C. Tang, R. Wang, *Treatise on water science*, (2011).
13. J. Landaburu-Aguirre, V. García, E. Pongrácz, R.L. Keiski, *Desalination*, 240 (2009) 262.
14. A. El Samrani, B. Lartiges, F. Villiéras, *Water Res.*, 42 (2008) 951.
15. A. Azimi, A. Azari, M. Rezakazemi, M. Ansarpour, *ChemBioEng Reviews*, 4 (2017) 37.
16. N. Barakat, M. Alajami, Z.K. Ghouri, S. Al-Meer, *Int. J. Hydrogen Energy*, 43 (2018) 5561.
17. A. Yousef, R.M. Brooks, M. El-Halwany, M.A. Abdelkareem, J.A. Khamaj, M.H. EL-Newehy, N. Barakat, H.Y. Kim, *Int. J. Electrochem. Sci*, 10 (2015) 7025.
18. G.M. Tolba, M. Motlak, A. Bastaweesy, E. Ashour, W. Abdelmoez, M. El-Newehy, N.A. Barakat, *Int. J. Electrochem. Sci.*,10 (2015) 3117.
19. Z.K. Ghouri, N.A. Barakat, A.-M. Alam, M. Park, T.H. Han, H.Y. Kim, *Int. J. Electrochem. Sci,*, 10 (2015) 2064.
20. M.H. Mahmoud, N.M. Abdel-Monem, O.E. Abdel-Salam, A.F. Nassar, *J. Life Sci.*, 10 (2013).
21. D.-E. Pascu, G. Alina Traistaru, A.C. Nechifor, A. Raluca Miron, *J. Electrochem. Sci. Eng.*, 6 (2016) 47.
22. N. Mohan, N. Balasubramanian, C.A. Basha, *J. Hazard. Mater.*, 147 (2007) 644.
23. G. Chen, *Sep. Purif. Technol.*, 38 (2004) 11.
24. M. Al-Shannag, Z. Al-Qodah, K. Bani-Melhem, M.R. Qtaishat, M. Alkasrawi, *Chem. Eng. J.*, 260 (2015) 749.
25. M. Belkacem, M. Khodir, S. Abdelkrim, *Desalination*, 228 (2008) 245.
26. G. Issabayeva, M.K. Aroua, N.M. Sulaiman, *Desalination*, 194 (2006) 192.
27. O.E. Abdel-Salam, I.M. Ismail, A. Soliman, A.A. Afify, H.M. Aly, *Port. Electrochimica Acta*, 32 (2014) 65.
28. M.M. Saleh, *J. Chem. Phys. B.*, 108 (2004) 13419.
29. B. Joseph, S. Authur, Water and Waste Control for the Plating Shop, Gradner Publication, 1994.
30. D.C. Daewon P, Jeh BJ. , *Water Res.*, 35 (2011) 57.
31. E.M. Kamel, *Int. J. Chem.*, (2012) 2306.
32. R. Sioda, *Electrochimica Acta*, 16 (1971) 1569.
33. E.M.A.A. Taleb, electrochemical recovery of copper (II) and chromium (VI) from industrial wastewater, chemistry, Cairo, faculty of science, 2004.
34. Z.A. Esmaeil, Recovery of iron powder from machine turnings, Chemical engineering, Cairo, Faculty of engineering, 2008.
35. J. SALEHZADEH, *Leonardo J. Sci.*, (2013) 97.
36. R. Alkire, P.K. Ng, *J. Electrochem. Soc.*, 124 (1977) 1220.
37. M. Matlosz, J. Newman, *J. Electrochem. Soc.*, 133 (1986) 1850.
38. C. Solisio, M. Panizza, P. Paganelli, G. Cerisola, *Resour Conserv Recy*, 26 (1999) 115.
39. J. Newman, W. Tiedemann, *AlChE J.*, 21 (1975) 25.
40. D. Ghosh, H. Solanki, M. Purkait, *J. Hazard. Mater.*, 155 (2008) 135.