

## REDUCTION OF IRON IN INDUSTRIAL WASTEWATER USING FLOW-BY POROUS ELECTRODES

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### Abstract:

Many industries produce and discharge large quantities of dilute metal ion solutions from the acid treatment of alloys, electroplating rinses, and leaches and effluents from the manufacture of chemicals. This discharge is considered to be a serious environmental threat. Electrochemical treatment is used as a sustainable effective technology for removal of heavy metals. In this study, experiments were carried out using a bench-scale electrochemical cell incorporating flow-by porous graphite electrodes for deposition of iron. The effect of current density, feed flow rate, and initial iron concentration on removal efficiency and current efficiency were studied. Experimental results showed that the maximum removal efficiencies (99.7%) and (99.9%) were obtained at flow rate of 0.278 ml/s, for initial iron concentration of 100 ppm and 200 ppm respectively. For concentration of 50 ppm it was 99.48% at flow rate of 1.11 ml/s, current density of 0.98 mA/cm<sup>2</sup> and pH of 4. and maximum current efficiencies were 53% at 100 ppm, 99.9% at 200 ppm, at flow rate of 0.833 ml/s, and 38.05% at 50 ppm at flow rate of 1.11 ml/s all obtained at current density of 0.98 mA/cm<sup>2</sup>. Solution pH in the range of 3 to 5 has a little effect on the deposition of iron.

**Keywords:** *Iron removal, heavy metals, electrochemical cell, flow-by electrode, wastewater.*

### 1. Introduction:

One of the most important environmental impacts is the presence of heavy metals in water resources. Increase and expansion of industrial activity has a great contribution in the significant rise of heavy metal pollution in water resources which threatens on life of living beings[1]. Heavy metals are not biodegradable and tend to accumulate in living organisms and many heavy metal ions are known to be toxic. So they should be removed from the wastewater to protect the people and the environment[2]. Many techniques have been used to remove heavy metal ions including chemical precipitation[3], ion-exchange[4], adsorption onto activated carbon[5, 6], membrane filtration including ultrafiltration[7] and reverse osmosis[8], coagulation and flocculation[9] electrochemical treatment technologies[2].

Electrochemical remediation is an economic and safe approach for long-term clean-up of metal bearing aqueous wastes because it provides a means of continuous, selective removal of metal contaminants, and offers end-of pipe processes for recovery of the metals.

The process runs at very high electrochemical efficiency and operates essentially under the same conditions for a wide variety of wastes. Operation at room temperature and atmospheric pressure

reduces the possibility of volatilization and discharge of unreacted waste[10]. The removal of undesirable components from aqueous phases is based on the choice of the appropriate electrode material and potential, or by assisting membrane systems to drive the electrode processes selectively[11].

Electrochemical methods involve the plating-out of metal ions on a cathode surface and can recover it in the elemental state. Electrochemical treatment techniques of heavy metal wastewater are regarded as rapid and well-controlled that require fewer chemicals, provide good reduction yields and produce less sludge[2]. The established technologies are electrocoagulation(EC)[12],electro flotation (EF)[13]and electrode position[14].Iron ions in aqueous solution were effectively removed by electrode position on the carbon electrode.

There are increasing in use of electrochemical technologies because of using porous electrodes in the design of electrochemical reactors. Porous materials such as carbon and graphite felt have been used as electrodes in various electrolysis cells, because of their high specific surface area, high mass transfer rate and high In this study, experiments were carried out using a bench-scale electrochemical cell incorporating flow-by porous graphite electrodes for deposition of iron.

### 1. Materials and Experimental:

Ferrous sulphate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), pure sodium chloride ( $\text{NaCl}$ ),sulphuric acid with 99%purity and distilled water were used.

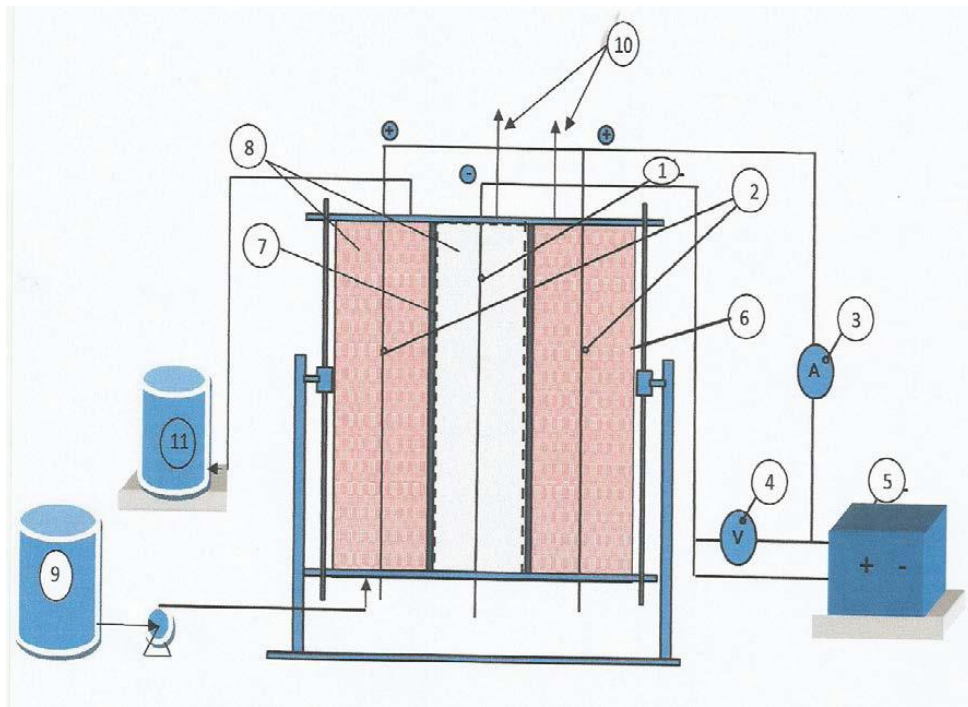
A schematic of the laboratory cell used for batch experiments is shown in Fig.1.It is consisted of two co-axial cylinders, one of Plexiglas material with internal diameter of 15 cm, and height of 18 cm fixed to end flanges made from PVC. The second was of stainless steel screen (mesh 5) with internal diameter of 10 cm that enclosed in a polyamide membrane and used as anode compartment. The cathode was contained in

conductivity[15]. However, porous electrodes frequently operate with non-uniform reaction rates, resulting in lower extents of utilization of the bed[16].

Flow-by porous electrode works as flow-through porous electrode but in case of flow-by the electric current flows perpendicular to that of the electrolyte and the system yields a greater return on investment, also offers the operational flexibility of variable flow rate and conversion[17].Electrochemical reactors incorporating flow-by porous electrodes can provide a powerful method in metal recycling. Where metal ions are reduced and deposited on the porous electrode (cathode)[18].

The current density and flow rate are the main parameters for the removal of metal ions from wastewater.

the annular space between the two cylinders. Graphite granules passing sieve no. 10 and retained on sieve no. 30 were used to fill cathode and anode compartments to a height of 13 cm. Three stainless steel rods (one of  $D = 10$  mm and two of  $D = 8$  mm,  $L = 250$ mm) were used as current collectors. The feed entered through an opening at the bottom of the cell using a Kompact dosing pump to control the feed flow rate, while the outlet flow and the gas vents were located at the upper flange of the cell. The cell current was supplied by a laboratory DC power supply type BK PRECISION. VICIOR VC830L digital multi-meters used to measure the potential and current.pH was measured using pH meter, model OAKTON pH/ $^{\circ}\text{C}$  and Iron concentration measured by using Spectrometer T80 UV/VIS.



**Fig. 1 Schematic of experimental setup** (1- anode current collector, 2- cathode current collector, 3- ammeter, 4- voltmeter, 5- D.C. 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)

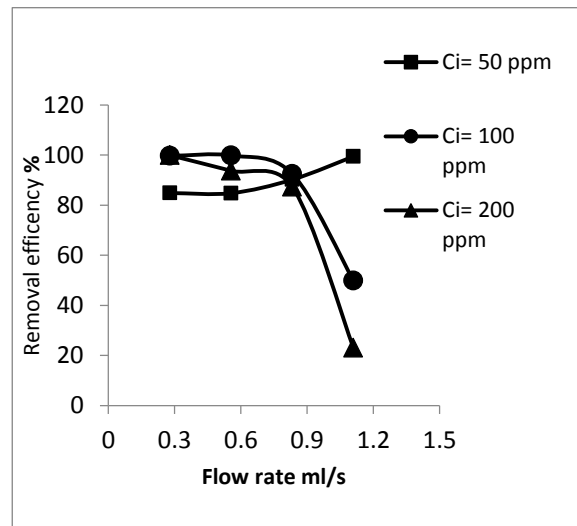
The investigated solutions of different iron concentrations were prepared by dissolving  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  into distilled water. Sulphuric acid was added to obtain the desired pH. Definite amounts of NaCl were added to improve the conductivity and ionic mobility through the electrolyte

### 3. Results and Discussion:

#### 3.1 Effect of Feed Flow Rate on Removal Efficiency

Figure 2 shows that for initial iron concentration of 50 ppm when flow rate increased the removal efficiency increased. However, for 100 and 200 ppm, the increase in flow rate from 0.278 to 0.556 ml/s was not significant as the increase in removal efficiency was very low, while increase in flow rate from 0.556 to 1.1 ml/s caused significantly decreases in removal efficiency. The maximum removal efficiencies were (99.48%), (99.7%) and (99.9%) for initial iron concentration of 50 ppm, 100 ppm and 200 ppm respectively. These values were obtained at minimum flow rate of 0.278 ml/s for 100 and 200 ppm,

and maximum flow rate of 1.11 ml/s for 50 ppm.



**Fig. 2 Effect of feed flow rate on removal efficiency at current density  $0.98 \text{ mA/cm}^2$  and pH 4**

#### 3.2 Effect of Feed Flow Rate on Removal Rate

Removal rate (R) is the rate of iron ion deposition on the surface of cathode

persecond, and it is calculated from the equation:

$$R = Q \times (C_i - C_o), \text{ in (gm-mol/sec)} \quad (1)$$

where Q is the flow rate,  $C_i$  and  $C_o$  are the iron concentration of influent and effluent respectively[15].Figure3 shows that the removal rate increased as the feed flow rate increased. This result explained by the fact that removal process is mass transfer controlled.

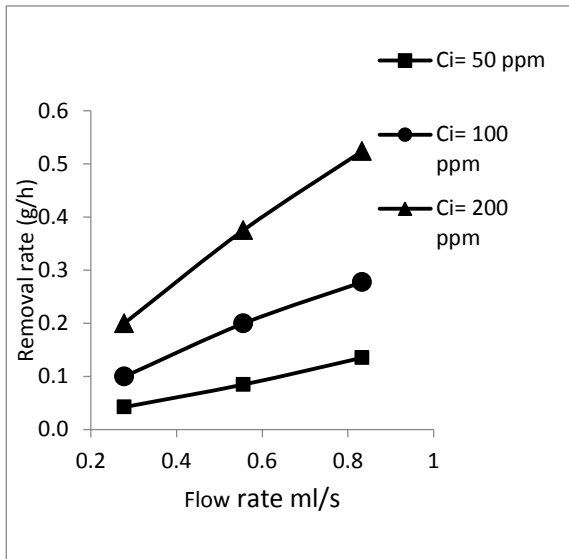


Fig.3 Effect of feed flow rate on removal rate at current density 0.98 mA/cm<sup>2</sup> and pH 4

### 3.3 Effect of Feed Flow Rate on Current Efficiency

From figure 4 it is clear that as the flow rate increased, the current efficiency increased. This is due to the fact that, at the same total charge consumed, the charge used in forming product will increase as the flow rate increases, and consequently the current efficiency will increase. The maximum current efficiencies were 99.9% at 200 ppm, 53% at 100 ppm and. These values were obtained at flow rate of 0.833 ml/s and current density of 0.98 mA/cm<sup>2</sup>.

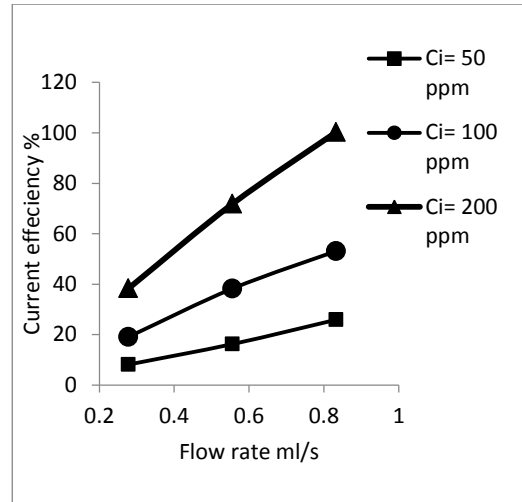


Fig.4 Effect of flow rate on current efficiency at current density= 0.98mA/cm<sup>2</sup>and pH= 4

### 3.4 Effect of Initial Concentration on Removal Efficiency

As shown in figure 5 an increase in initial concentration of iron from 50 to 100 ppm causes increase in the removal efficiency then as the initial concentration increases up to 300 ppm the removal efficiency decreases at all current densities. This may be due to the limited capacity of the electrode for iron removal; which is determined by the bed height and diameter.

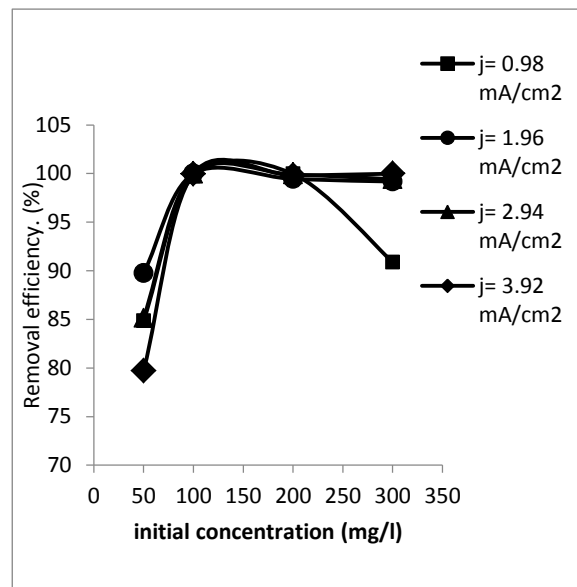


Fig. 5 Effect of initial concentration on removal efficiency at flow rate 0.277 ml/s and pH 4

### 3.5 Effect of Initial Concentration on Removal Rate

The effect of the inlet concentration on the removal rate of iron at cell current density of 0.98 mA/cm<sup>2</sup> is shown in Fig. 6. It is observed that the removal rate increases with increasing the initial concentration, as the removal rate process is mass-transfer controlled as mentioned before[19].

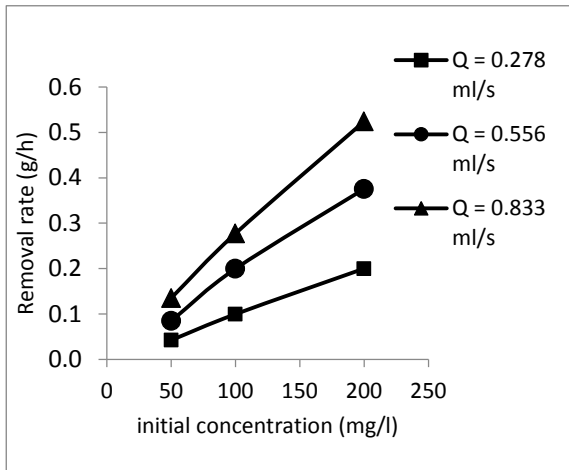


Fig. 6 Effect of initial concentration on removal rate at flow rate 0.277 ml/s and pH 4

### 3.6 Effect of Applied Current Density on Removal Efficiency

As shown in Figure 7 for initial iron concentration of (100 and 200 ppm), and in figure 8 for 50 ppm, their crease in current density above 0.98 mA/cm<sup>2</sup> was ineffective where the increase in removal efficiency was very low. The maximum efficiency was obtained at current density of 0.98 mA/cm<sup>2</sup>.

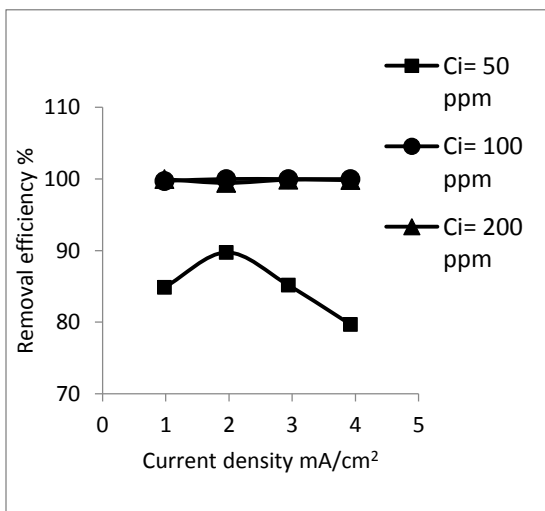


Fig. 7 Effect of current density on removal efficiency at flow rate 0.278 ml/s and pH 4

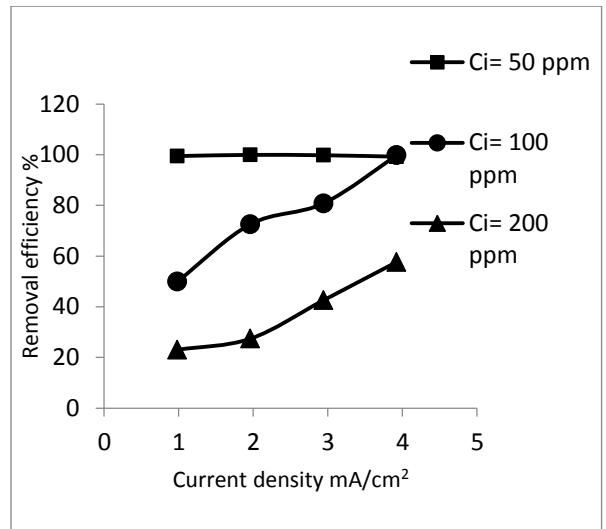


Fig. 8 Effect of current density on removal efficiency at flow rate 1.11 ml/s and pH 4

### 3.7 Effect of Applied Current Density on Current Efficiency

The deposition of iron on the cathode surface may be accompanied by a hydrogen evolution. The individual contribution of each reaction is given by its current efficiency and may be calculated by Faraday's law. The current efficiency was calculated from the following equation:

$$\% \text{ Current efficiency} = (I / I_{\text{total}}) \times 100 \quad (2)$$

Where, I is the current equivalent to the deposition rate of iron and I total is the total cell current. I was calculated from following equation:

$$I = n \cdot F \cdot R \cdot (C_i - C_o) \quad (3)$$

Where I is the electric current, n is the number of electrons in the electrode reaction, F is Faraday's constant = 96500 coulombs/g equivalent, R is the flow rate (mL/sec) and Ci, Co are influent and effluent concentration of iron in (gmol/mL)[15].

Figures 9 to 11 show that as applied current density increases the current efficiency decreases. This may be due to increase in hydrogen evolution on the surface of the cathode. Sarfarazi and Ghoroghchian, [1994], observed the same trend was for copper precipitation on flow-by porous electrode[15]. At current density of 0.98 mA/cm<sup>2</sup> the current efficiency reached a maximum value of 99.9% for feed flow rate

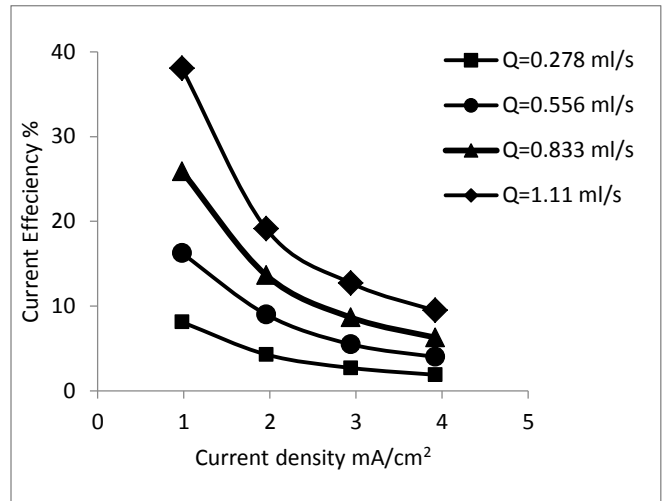
of 0.833 mL/s and concentration of 200 mg/l and 38.05% for feed flow rate of 1.11 ml/s and concentration of 500 mg/l.

This can be explained by the fact that as the applied current density increased, iron ions are reduced so fast that they are limited on the surface of the cathode, then parallel reaction of the hydrogen gas formation increases and therefore, the cathodic current efficiency decreases [15].

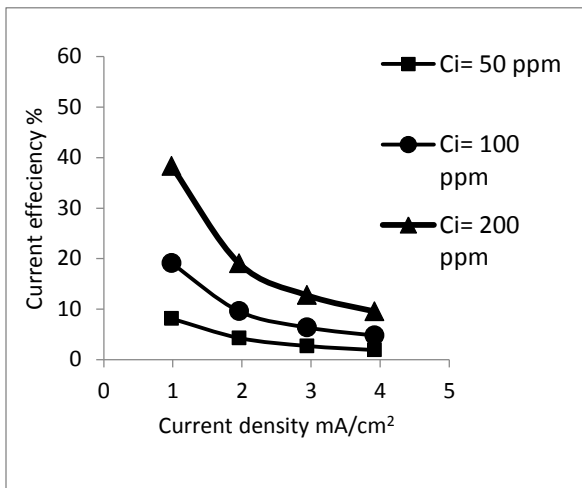
### 3.8 Effect of pH on Removal Rate and Removal Efficiency

As illustrated in figures 12 to 14, the removal rate and removal efficiency of iron were not greatly affected by solution pH in the range of 3 to 5.

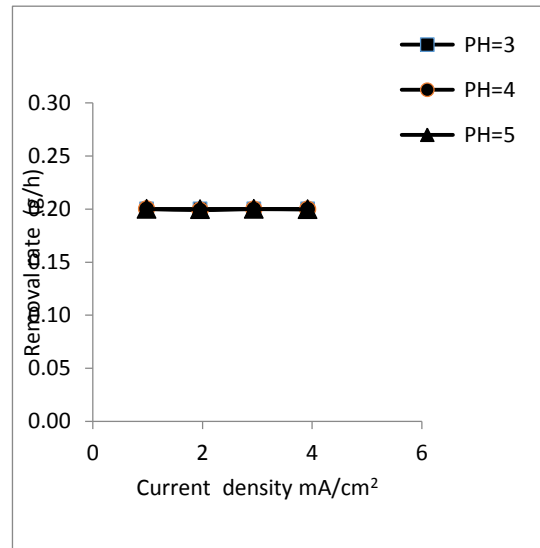
**Fig.10** Effect of current density on current efficiency at initial concentration 200 mg/l and pH 4



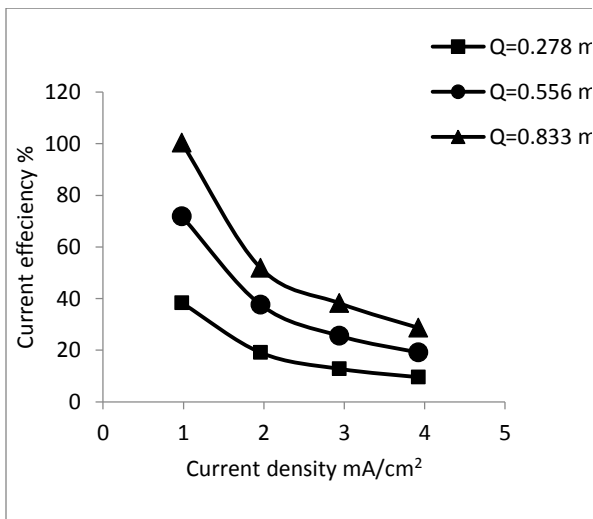
**Fig. 11** Effect of current density on current efficiency at initial concentration 50 mg/l and pH 4

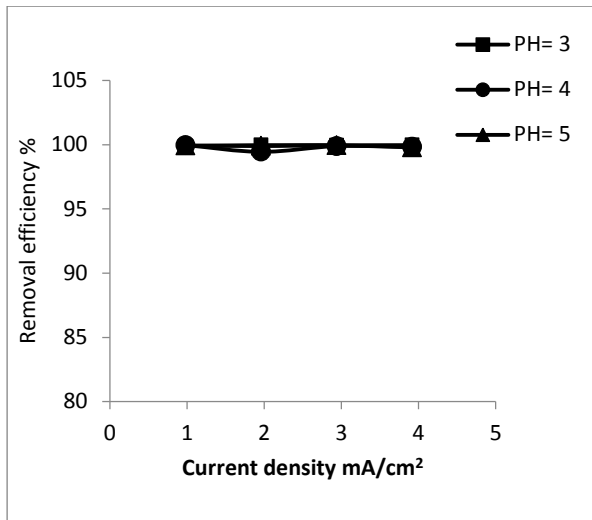


**Fig.9** Effect of current density on current efficiency at flow rate 0.278 ml/s and pH 4

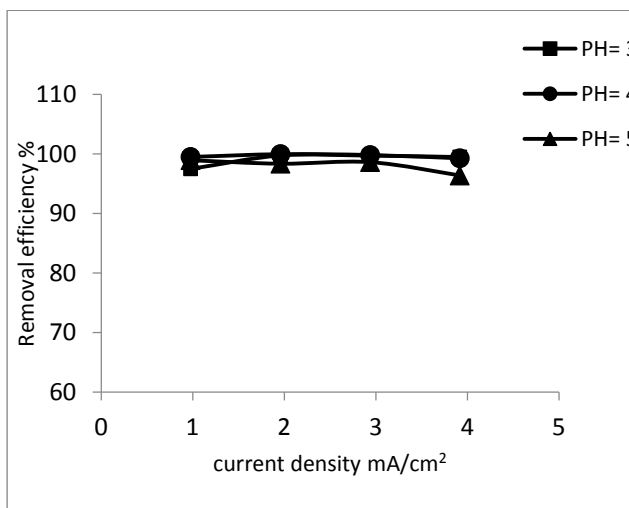


**Fig. 12** Effect of pH on removal rate at initial concentration 100 mg/l and flow rate 0.278 ml/s





**Fig. 13** Effect of pH on removal efficiency at initial concentration 200 mg/l and flow rate 0.278 ml/s



**Fig. 14** Effect of pH on removal efficiency at initial concentration 50 mg/l and flow rate 1.11 ml/s

#### 4. Conclusions

In this study experimental results showed that The maximum removal efficiency of 99.7% and 99.96% were obtained at feed flow rate of 0.278 ml/s, current density of 0.98 mA/cm<sup>2</sup> and pH 4, for iron initial concentrations of 100 and 200ppm, respectively. For iron initial concentrations of 50 ppm it was 99.48% at feed flow rate of 1.11 ml/s, current density of 0.98 mA/cm<sup>2</sup> and pH 4.

For 100 and 200 ppm iron initial concentration, increase in feed flow rate

caused significantly decreases in removal efficiency but for 50 ppm, it caused increases in removal efficiency. However, increase in current density above 0.98 mA/cm<sup>2</sup> was ineffective as increase in efficiency is very low. Removal efficiency was not greatly affected by solution pH in the range of 3 to 5.

Also increases in feed flow rate improved the current efficiency while increases of current density resulted in significant decrease in the current efficiency. The maximum current efficiencies were 53% at 100 ppm, 99.9% at 200 ppm, at flow rate of 0.833 ml/s, and 38.05% at 50 ppm at flow rate of 1.11 ml/s all obtained at current density of 0.98 mA/cm<sup>2</sup>.

From these results it could be concluded that electrochemical cell incorporating flow-by porous graphite electrodes is an effective method for the treatment of wastewater containing iron.

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## اختزال الحديد من مياه الصرف الصناعي باستخدام الأقطاب المسامية

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### الملخص باللغة العربية

تقوم العديد من الصناعات بإنتاج وتصريف كميات كبيرة من محاليل أيونات المعادن المخففة مثل عملية المعالجة الحمضية للسبائك ، وشطف الطلاء الكهربائي ، والنفايات السائلة الناتجة عن تصنيع المواد الكيميائية، والتي تعتبر بمثابة تهديدا خطيرا للبيئة. تستخدم المعالجة الكهروكيميائية تكنولوجيا فعالة ومستدامة لإزالة المعادن الثقيلة. في هذه الدراسة ، أجريت التجارب العملية باستخدام خلية كهروكيميائية تشتمل على أقطاب مسامية من الجرافيت لترسيب الحديد عليها. وفيها تمت دراسة تأثير كثافة التيار ، معدل تدفق محلول تغذية الخلية وكذلك تركيز الحديد الأولي على كل من كفاءة الإزالة وكفاءة التيار. وقد أظهرت النتائج أن أقصى كفاءة إزالة (99.7%) و (99.9%) تم الحصول عليها بمعدل تدفق يبلغ 0.278 مل / ثانية ، لتركيز الحديد الأولي البالغ 100 جزء في المليون و 200 جزء في المليون على الترتيب. بالنسبة لتركيز 50 جزء في المليون كان 99.48% بمعدل تدفق 1.11 مل / ثانية ، وكثافة تيار 0.98 مللي أمبير / سم 2 وأس هيدروجيني 4 ، وكانت كفاءة التيار القصوى 53% عند 100 جزء في المليون ، 99.9% عند 200 جزء في المليون ، بمعدل تدفق 0.833 مل / ثانية ، و 38.05% عند 50 جزء في المليون وبمعدل تدفق 1.11 مل / ثانية، تم الحصول عليها جميعا عند كثافة تيار 0.98 مللي أمبير / سم 2. كما تم ملاحظة ان الأس الهيدروجيني لمحلول التغذية في نطاق 3 إلى 5 له تأثير بسيط على ترسب الحديد.