

## REMOVAL OF HEAVY METALS FROM INDUSTRIAL WATER USING ELECTRO-COAGULATION TECHNIQUE

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### ABSTRACT

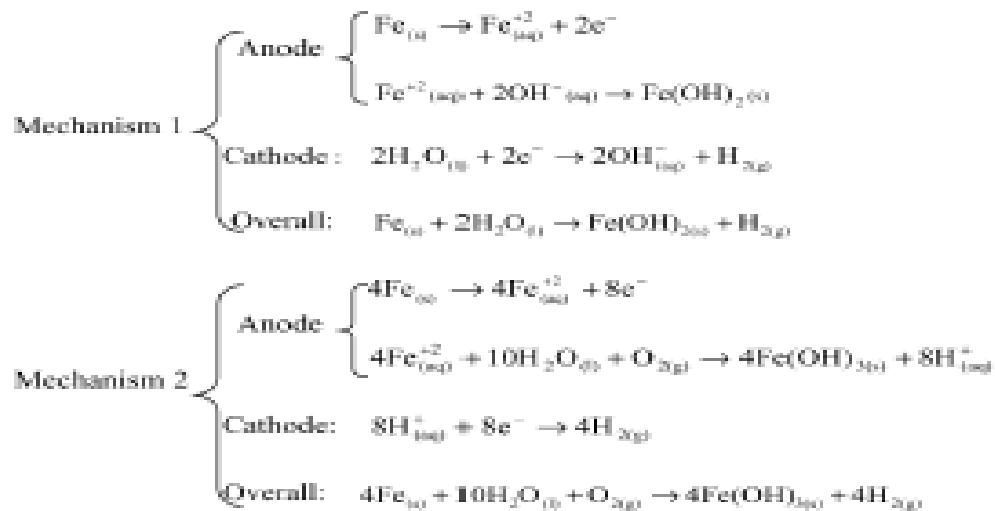
Heavy metal removal by electrocoagulation using iron electrodes material was investigated in this paper. Several working parameters, such as pH, current density and heavy metal ions concentration were studied in an attempt to achieve a higher removal capacity. A simple and efficient treatment process for removal of heavy metals is essentially necessary. The continuous flow electrocoagulation system, with reactor consists of a ladder series of twelve electrolytic cells, each cell containing stainless steel cathode and iron anode. The treatment of synthetic solutions containing Zn<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Cr<sup>3+</sup>, Cd<sup>2+</sup> and Co<sup>2+</sup> has been investigated.

Results obtained with synthetic wastewater revealed the following:

- The most effective removal capacities of studied metals could be achieved when the pH was kept at ~7.
- Charge loading was found to be the only variable that affected the removal efficiency significantly.
- An increase of charge loading is observed for all metals ions, when current density was varied in the range 0.27-1.35 mA/cm<sup>2</sup>.
- The removal efficiencies of all studied ions increased with charge loading (Qe).
- The removal rate has decreased upon increasing initial concentration.
- The amount of iron delivered per unit of pollutant removed is not affected by the initial concentration.
- Longer electrolysis times are necessary for chromium, cadmium and cobalt removal.
- Lower efficient removal of chromium compared to zinc, copper and nickel and the less efficient removal of cadmium and cobalt.
- Result show that iron is very effective as sacrificial electrode material for heavy metals removal efficiency and cost points.

## 1. INTRODUCTION

Heavy metals are strictly regulated and must be treated before being discharged in the environment. One of the most techniques has been employed for the treatment of heavy metals, is electrocoagulation. Electrocoagulation is an emerging water treatment technology that has been applied successfully to treat various wastewaters. It has been applied for treatment of potable water (Vik et al., 1984; Holt et al., 2002), urban wastewater (Pouet and Grasmick, 1995), heavy metal laden wastewater (Mills, 2000), restaurant wastewater (Chen et al., 2000), and colored water (Jiang et al., 2002). Further, electrocoagulation offers possibility of anodic oxidation and in situ generation of adsorbents (such as hydrous ferric oxides, hydroxides of aluminum). One of the most widely used electrode materials in electrocoagulation process is iron. When iron is used as anodes, upon oxidation in an electrolytic system, it produces iron hydroxide,  $\text{Fe(OH)}_n$  where  $n = 2$  or 3. Two mechanisms for the production of the metal hydroxide have been proposed (Daneshvar, 2003).



The aims of this paper were to investigate the effect of initial pH, initial metal ion concentrations, current density, and treatment time on the removal efficiency of zinc, copper, nickel, chromium, cadmium and cobalt using iron anodes. The Kinetic models for heavy metals removal were studied also.

## 2. EXPERIMENTAL WORK

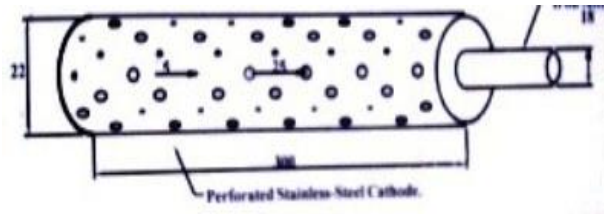
Synthetic solutions were prepared from reagent grade chemical without any further purification. All glassware were cleaned with water and 1 N  $\text{H}_2\text{SO}_4$  and then rinsed with distilled water, while, the working solutions containing heavy metals were prepared by dissolving appropriate amount of each heavy metal in tap water. Moreover, tap water was tested for the pH and alkalinity. The pH of the tap water varied from 7.8-8.2, bicarbonate alkalinity was approximately 75-80 mg/l as  $\text{CaCO}_3$ .

A continuous flow electrocoagulation process was built in lab having a device containing twelve electrolytic cells. The device consists of a ladder series of electrolytic cells containing (carbon steel) anodes and stainless-steel cathodes.



**Fig. (1) Photo of the experimental apparatus.**

Electrolytic cells iron anodes (low carbon steel, LCS) (99.5%), each of them is constructed to achieve a narrow concentric gap of about 2 mm between the central anode and the surrounding cathode as shown in figure (2). The volume of the electrolytic cells basin alone was approximately (4.5 liters). The active surface for each (27.3 cm) anode surface area is approximately (154 cm<sup>2</sup>).



**Fig. (2) Electrolytic cell**

Each (27.30 cm) carries a DC current of (1.0 – 5.50) amp and a current densities of (6.5 – 35.7) mA/cm<sup>2</sup>. The over all electrolytic cell pack has dimension of (30 cm) width, (43.50 cm) height and (3.5 cm) in its thickness. All the terminals of electrodes are attached to a power source by using copper strip which acts as a single anode of electrolytic cell assembly, while the outer stainless steel strip which connects the stainless-steel perforated pipe assembly acts as a cathode . The electrolytic cell assembly was operated with flow rates up to 1.9 m<sup>3</sup>/hr.

By the end of each run, the power supply was switched off and the electrolytic solution was transferred to the settling container. Without polymer addition, about (12 hours) retention time is desirable. The clarified effluent was filtered and analyzed for the

improvement of its quality to specify the electrocoagulation process efficiency for each heavy metal effluents treatment.

### **3. RESULT AND DISCUSSION**

Electrode assembly is the heart of the present treatment facility. Therefore the appropriate selection of its materials is very important. The most common electrode materials for electrocoagulation are iron and aluminum. However it is usually to use iron for wastewater treatment and aluminum for water treatment because iron is relatively cheaper (Chen, 2004).

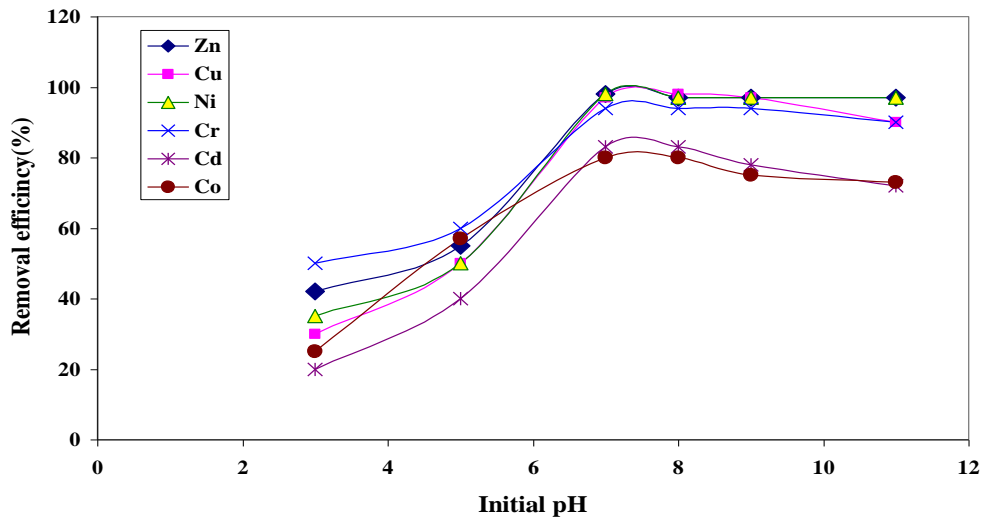
#### **3.1 Effect of pH**

It has been established that the initial pH (Chen et al., 2000 and Do et al., 1994) is an important factor and has a considerable influence on the performance of electrocoagulation process. Generally, the pH of the medium changes during the process, as observed by other investigator (Vic et al., 1984).this change depends on the type of electrode and on initial pH.

To evaluate the pH effect, a series of experiments were performed, using solutions containing each of the six heavy metals ( $Zn^{2+}$ ,  $Cu^{2+}$ , Cr (VI),  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Cd^{2+}$ ) of 50 mg/l each with initial pH varying in the range (2-10). The solutions of these metals were adjusted to the desired pH for each experiment using sodium hydroxide or hydrochloric acid.

As illustrated in Figure (3), the removal efficiency of zinc, copper, Cr (VI) and nickel, reached value as high as 99%, when pH is 7 and seem to be not affected by pH for zinc, copper and nickel, as long as this kept in the range between 7 and 12, in contrast a slightly decrease of the removal efficiency of chromium is observed, when the initial pH is increased above 7.

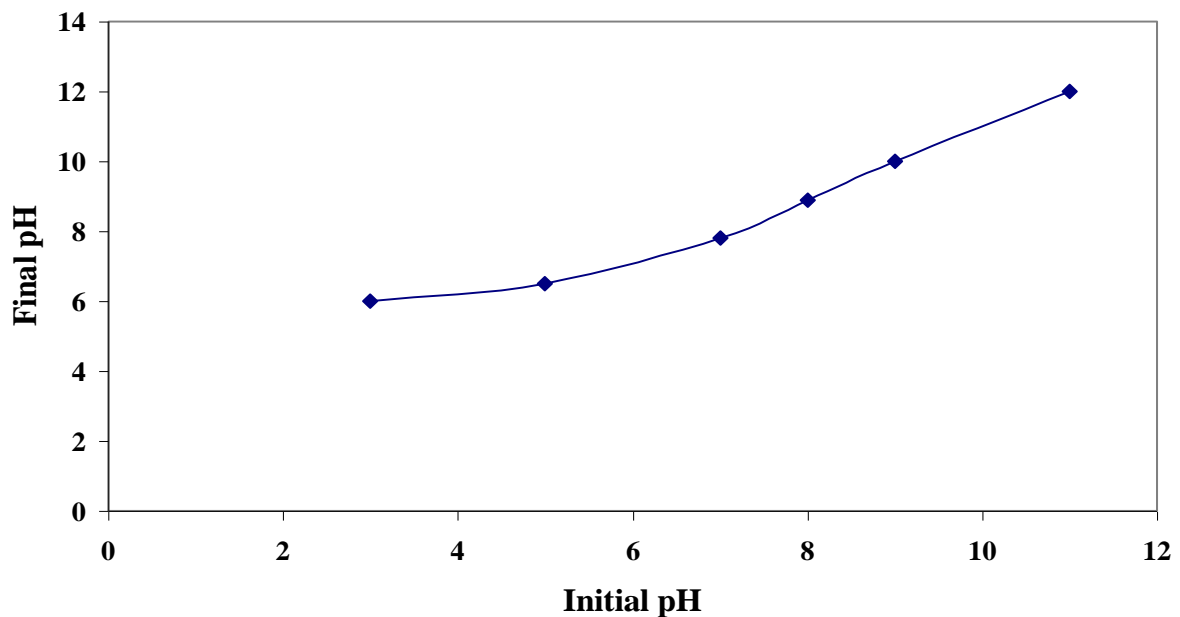
The removal efficiency of cadmium and cobalt reaches a maximum of about 83% and 80% respectively when initial pH is 7 as it seems from the same figure. However as the same as chromium, when the initial pH is increased above 7, a slightly decrease of the removal efficiency of cadmium and cobalt is observed. Furthermore, it can be seen that the removal efficiency of all studied ions decreased significantly upon decreasing initial pH and there is maximum removal efficiency at the pH of 7, which is almost neutral. Therefore, it can be concluded that when pH is 7, the majority of iron complexes (coagulants) are formed and it's the optimum pH for carrying out the electrocoagulation. From the Pourbaix diagram (Pourbaix, 1974), it can be deduced that the major complexes formed at this pH are  $Fe(OH)_2^+$  and  $Fe(OH)^{2+}$ .



**Fig. (3) Effect of initial pH on metal ions removal by using iron anodes material. Initial concentration of Zn, Cu, Ni, Cr, Cd, Co = 50mg/l each, current density 1.35 mA/cm<sup>2</sup>, anode surface = 1848 cm<sup>2</sup>, time of electrolysis = 22.2 min.**

Using solutions of containing mixture of the six heavy metals of 50 mg /l each, Figure (4) shows that the final pH is always higher than initial pH. This may be explained by the excess of hydroxyl ions produced at the cathode in sufficiently acidic conditions (Chen et al., 2000) .The difference between initial and final pH values diminishes for initial pH > 7.

As a result of previous discussion of the effect of pH on the removal efficiency, the initial pH was adjusted to 7 for all subsequent studies.



**Fig. (4) pH variation after electrocoagulation. Initial concentrations of Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cr<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup> = 50 mg/l each, current density = 1.35 mA/cm<sup>2</sup>, anode surface = 1848 cm<sup>2</sup>, time of electrolysis = 22.2 min.**

### 3.2 Effect of current density

The current density not only determines the coagulant dosage rate, but also the bubble production rate and size (Kobia et al., 2003 and Holt et al., 2002). Thus, this parameter should have a significant impact on pollutants removal efficiencies. A large current means a small electrocoagulation unit. However, when too large current is used, there is a high chance of wasting electrical energy in heating up water.

To investigate the effect of current density on the removal efficiency, a series of experiments were carried out on solutions containing a constant pollutants loading with current density being varied from 0.27 mA/cm<sup>2</sup> to 1.35 mA/cm<sup>2</sup>.

Figures (5) to (10) show the concentrations profiles of the studied metal ions for typical electrocoagulation runs, where the initial pH was fixed at 7. The removal rate of all studied metal ions increased upon increasing current density. The highest current (1.35 mA/cm<sup>2</sup>) produced the quickest removal rate, with a 99% concentrations reduction occurring just after 6.4 min for zinc, copper and chromium and after 9 min for nickel. While the removal rate with 87% and 80% concentration reduction occurring just after 30 min for cadmium and cobalt respectively. This is ascribed to the fact that at high current, the amount of iron oxidized increased, resulting in a greater amount of precipitate for the removal of pollutants. In addition, it was demonstrated that bubbles density increases with increasing current density (Holt et al., 2002), resulting in more efficient and faster removal. Moreover, it was previously shown (Khosla et al., 1991) that the bubble size decreases with increasing current density, which is beneficial to the separation process.

Indeed, the amounts of iron and hydroxide ions generated at a given time, within the electrocoagulation cell are related to the current flow, using Faraday's law:

$$m = I t M / z F \quad (1)$$

where I is the current intensity, t is the time, M is the molecular weight of iron or hydroxide ion (g/mol), z is the number of electrons transferred in the reaction and F is the Faraday's constant (96486 C/mol).

As the current decreased, the time needed to achieve similar efficiencies increased. This expected behavior is explained by the fact that the treatment efficiency was mainly affected by charge loading ( $Q = I * t$ ), as reported by Chen et al. (2000). As the time progresses, the amount of oxidized iron and the required charge loading increase. However, these parameters should be kept at low level to achieve a low-cost treatment.

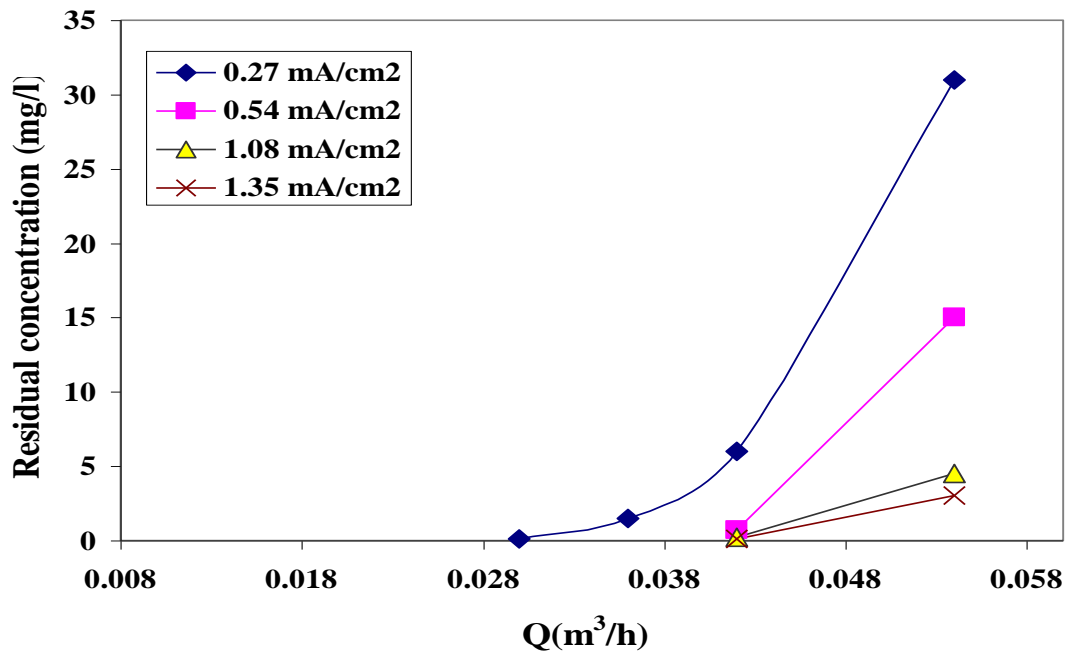


Fig. (5) Effect of current density on the removal rate of Zn<sup>2+</sup> ions. Initial concentrations of ions = 50 mg/l, anode surface = 1848 cm<sup>2</sup>.

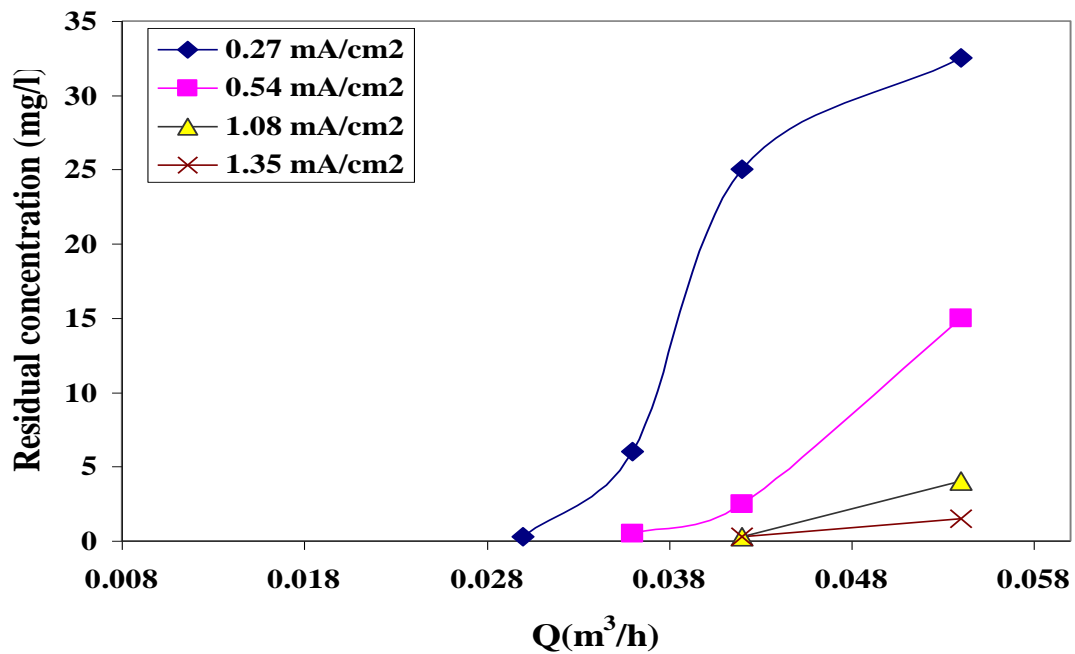


Fig. (6) Effect of current density on the removal rate of Cu<sup>2+</sup> ions. Initial concentrations of ions = 50 mg/l, anode surface = 1848 cm<sup>2</sup>.

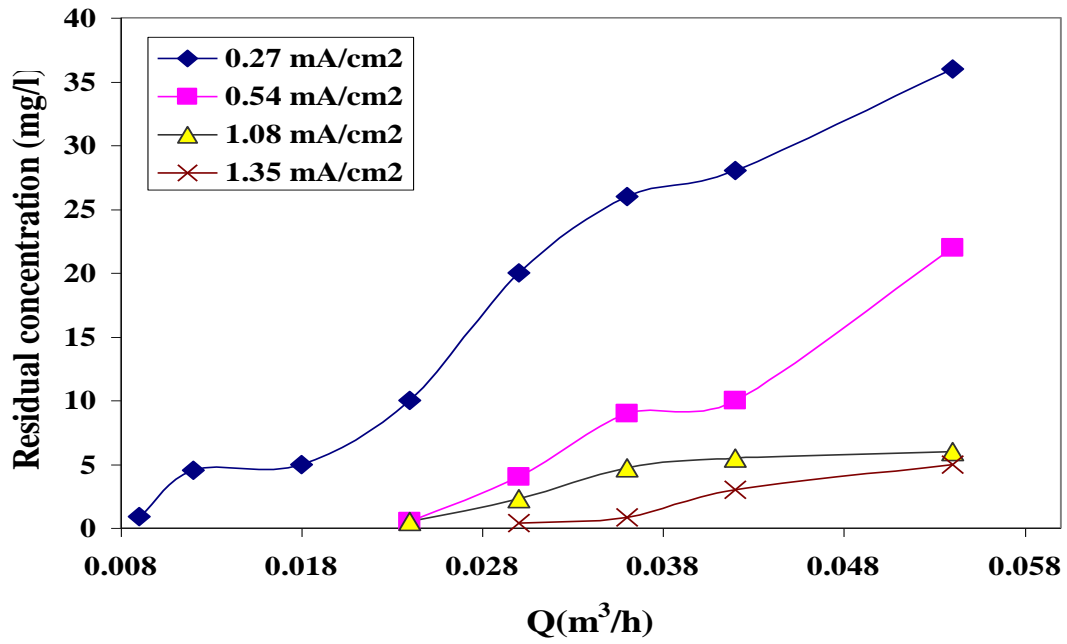


Fig. (7) Effect of current density on the removal rate of Cr<sup>3+</sup> ions. Initial concentrations of ions = 50 mg/l, anode surface = 1848 cm<sup>2</sup>.

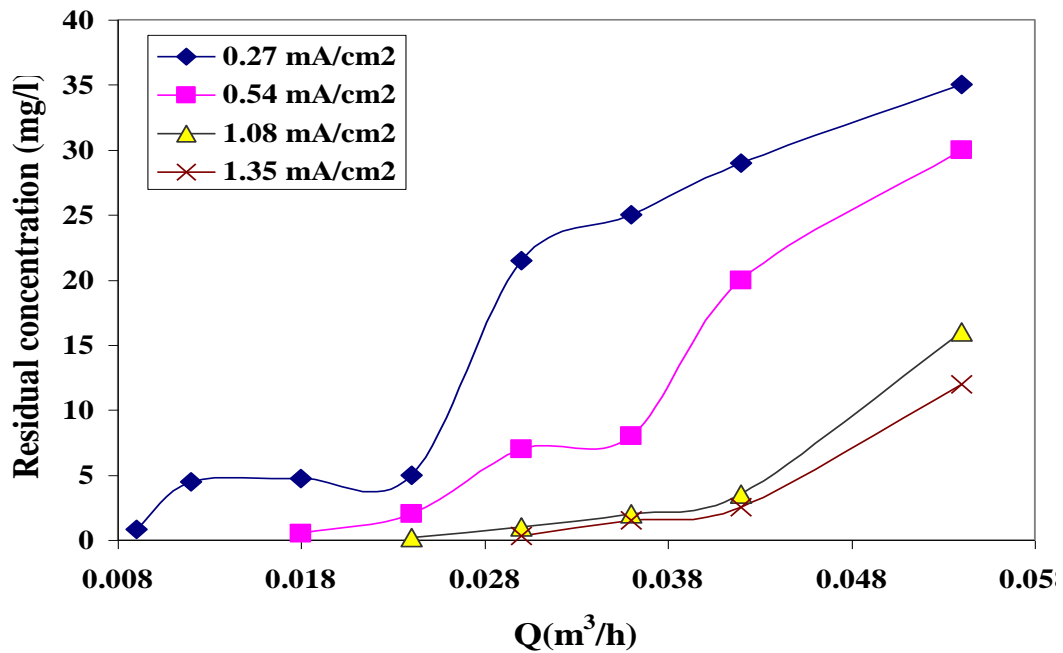


Fig. (8) Effect of current density on the removal rate of Ni<sup>3+</sup> ions. Initial concentrations of ions = 50 mg/l, anode surface = 1848 cm<sup>2</sup>.



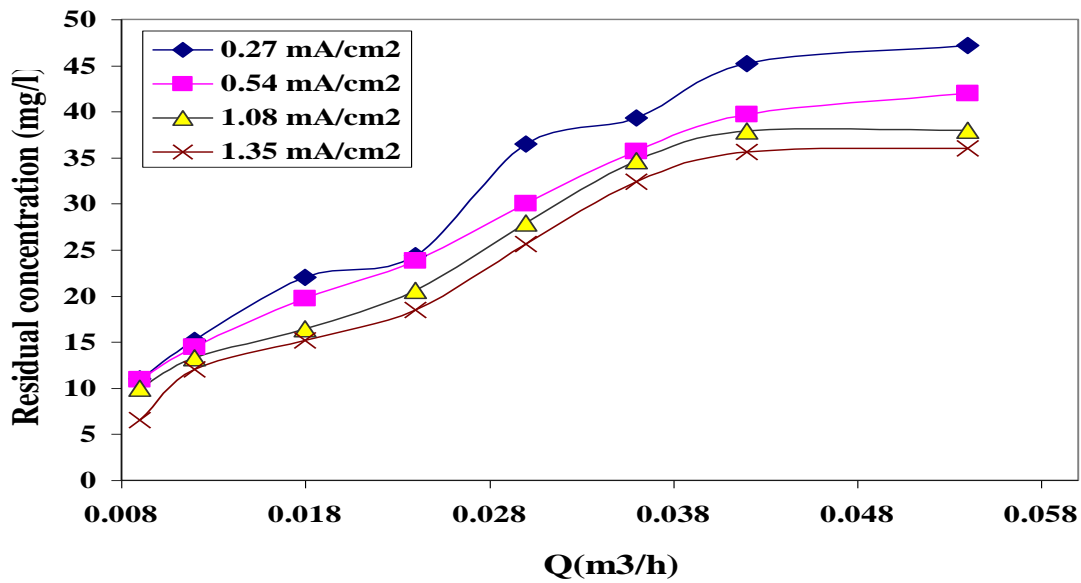


Fig. (9) Effect of current density on the removal rate of  $\text{Cd}^{2+}$  ions. Initial concentrations of ions = 50 mg/l, anode surface = 1848  $\text{cm}^2$ .

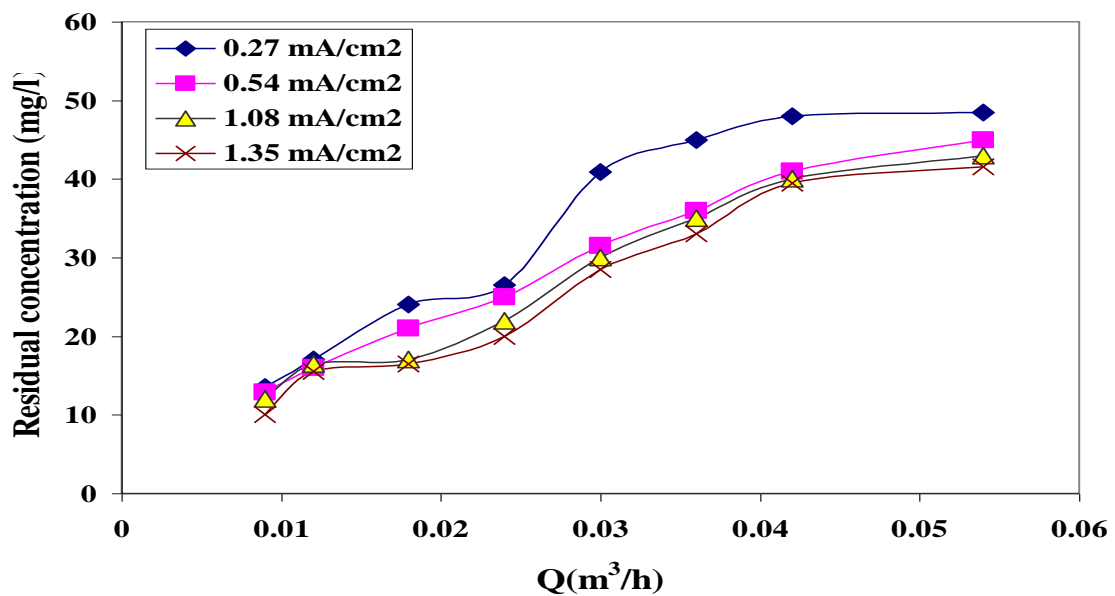


Fig. (10) Effect of current density on the removal rate of  $\text{Co}^{2+}$  ions. Initial concentrations of ions = 50 mg/l, anode surface = 1848  $\text{cm}^2$ .

To optimize the treatment efficiency, optimum charge loading required to achieve high removal yields (residual concentration under 2 mg/l for each metal ions except cadmium and cobalt) for each metals ion, were calculated at different current densities. The results shown in Figure (11), point out that the removal rate of zinc and copper is almost three times faster than that of chromium and nickel. Indeed, the volumetric

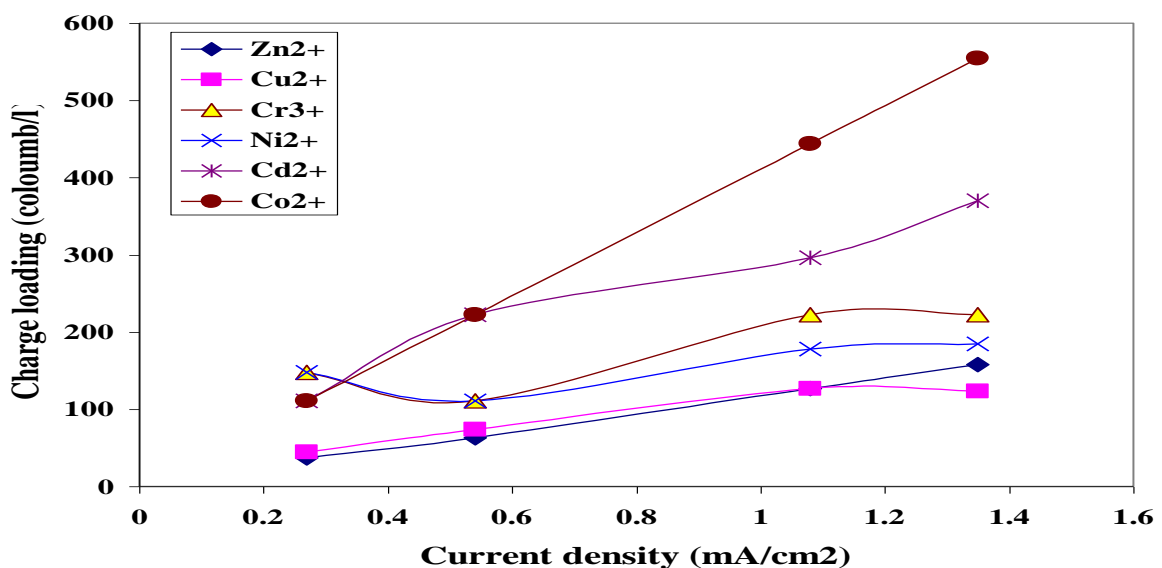
electrical charges ensuring 96% removal of zinc and copper were 44.42 coulomb/l, while that needed to achieve the same removal efficiency of chromium and nickel was 148.1 coulomb/l. For cadmium and cobalt, the optimum charge loading required to achieve 70% removal yields were calculated at different current densities. Furthermore, as observed by other investigators (Adhoum et al., 2004 and Holt et al., 2002), an increase of charge loading is observed for all metals ions, when current density was varied in the range 0.27-1.35 mA/cm<sup>2</sup>.

At high current density, the bubble density and upwards flux increased and resulted in a faster removal of the coagulant by floatation. Hence, there is a reduction in the probability of collision between the coagulant and pollutants. The lowest current should be selected to obtain the best removal rate without increasing of cost.

The removal efficiencies of all studied ions increased with charge loading (Qe). According to Faradays law, the concentration of Fe<sup>2+</sup> ions released from anodes can be calculated by:

$$[\text{Fe}^{2+}] = Q_e / ZF, \quad Z = 2 \text{ for Fe}^{2+} \quad (2)$$

The Fe<sup>2+</sup> ions form iron hydroxide flocs to remove heavy metal ions. However, there is a critical charge loading required. Once the charge loading reaches the critical value, the effluent quality does not show significant improvement for further current increase (Chen et al., 2000). Figure (12) illustrates the effect of the charge loading on removal efficiency when the current density is the lowest (0.27 mA/cm<sup>2</sup>). Sharp increase of removal efficiencies are clearly shown initially. The optimum charge loading should be at the end of the sharp increase stage. In this case, they are 31.6, 37 and 44.4 coulomb/l for zinc, copper and nickel respectively and it is 55.5 coulomb/l for each of chromium, cadmium and cobalt.



**Fig. (11) Effect of current density on charge loading. Initial concentration of metals ions = 50mg/l each, anode surface = 1848 cm<sup>2</sup>.**

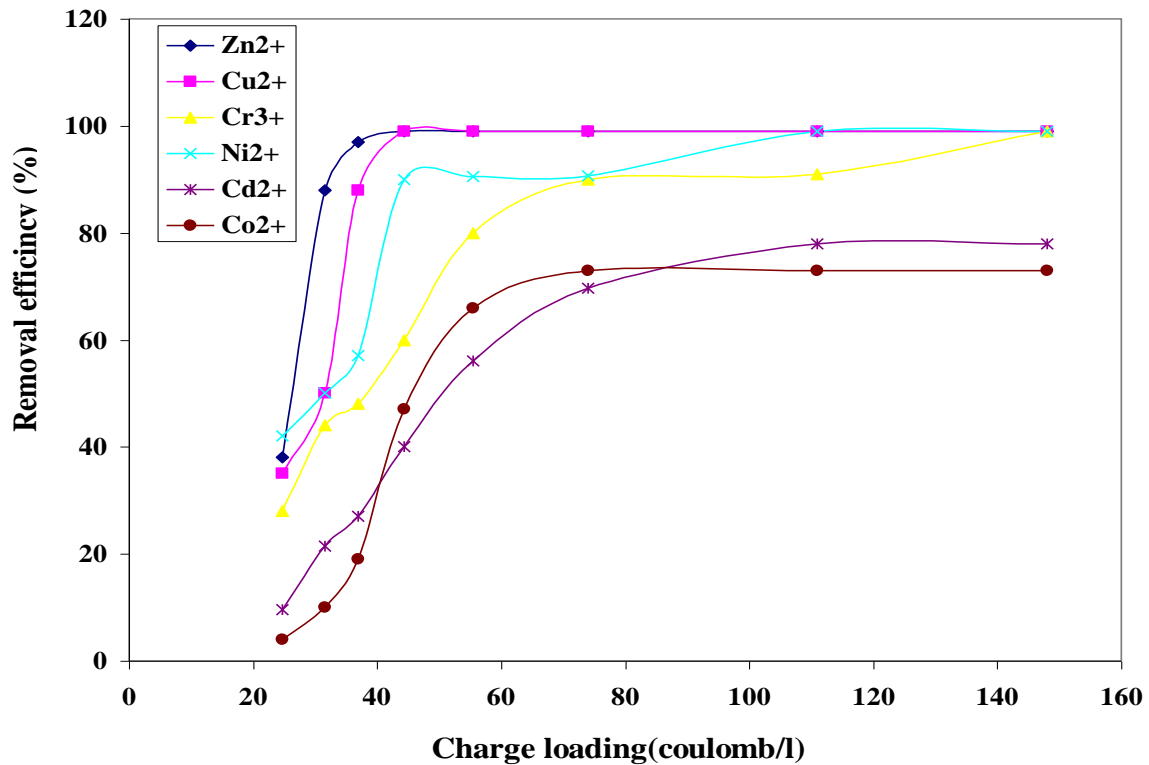


Fig. (12) Effect of charge loading on removal efficiency. Current density = 0.27 mA/cm<sup>2</sup>.

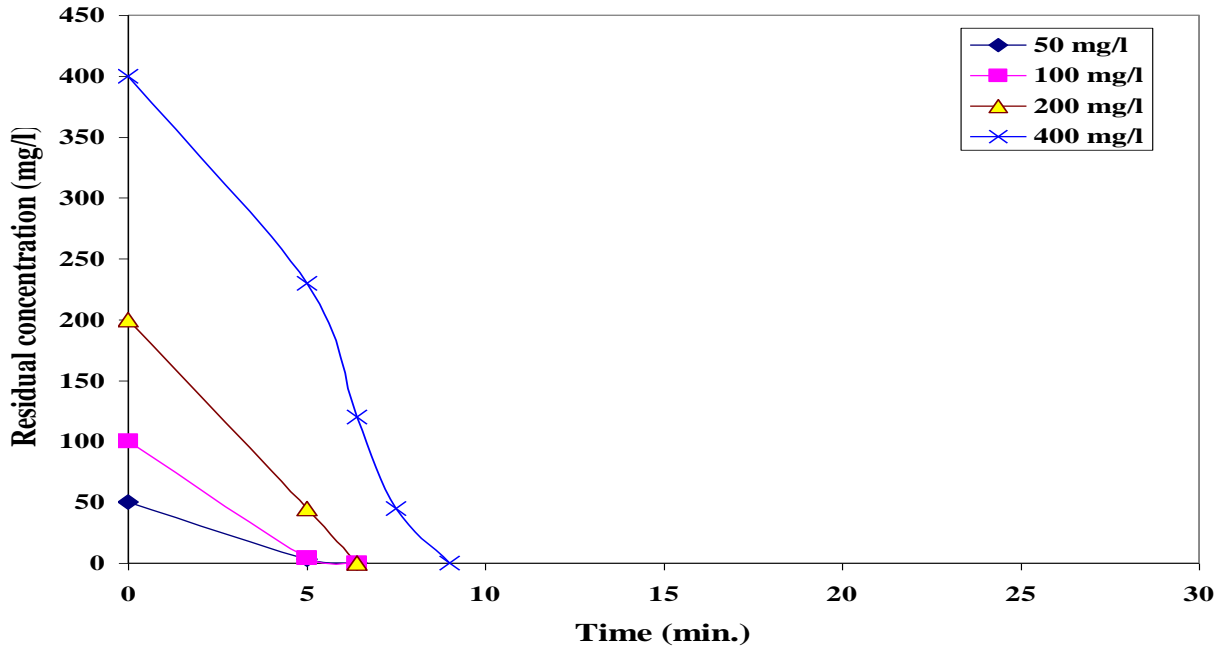
### 3.3 Effect of metal ion concentration

In order to examine the effect of metal ion concentration on the removal rate, several solutions containing increased concentrations (50-400 mg/l) of all six heavy metals were prepared and treated. The residual concentrations of ions were measured at different times.

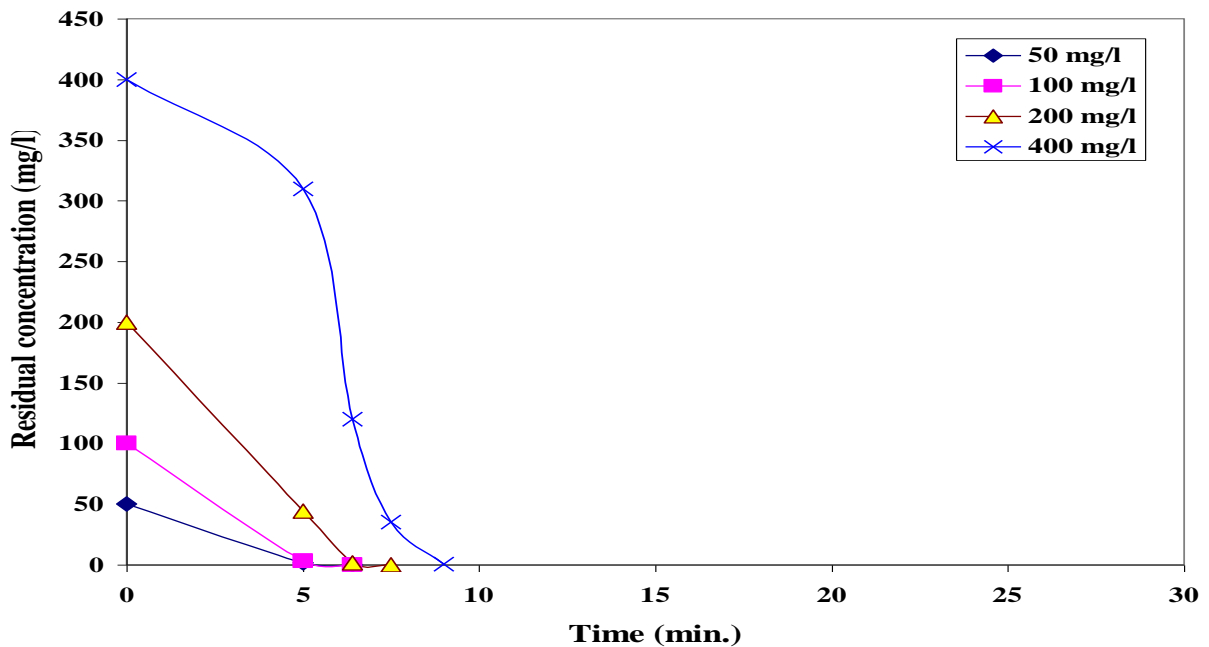
Figures (13) to (18) show the change in the removal rate of zinc, copper, chromium, Nickel, cadmium and cobalt with initial concentration. They all showed the same trends. As expected, it appears that the removal rate has decreased upon increasing initial concentration. This induced a significant increase of charge loading required to reach residual metal concentrations below the levels admissible for effluents discharge into the sewage system (2 mg/l) for zinc, copper, chromium and nickel and which is required to reach residual concentration of (30 mg/l) for cadmium and cobalt as shown in Fig. (19).

It can be observed that charge loading undergo an increase with initial concentration. This result proves that the amount of iron delivered per unit of pollutant removed is not affected by the initial concentration. In addition, the charge loading required to remove chromium to the admissible level, is higher than that required for zinc, copper and nickel. Moreover the charge loading required to reach residual concentration of (30 mg/l) of cadmium and cobalt is much more than the other. This confirmed lower efficient removal of chromium compared to zinc, copper and nickel and the less

efficient removal of cadmium and cobalt which indicated that longer electrolysis times are necessary for chromium, cadmium and cobalt removal.



**Fig. (13) Effect of initial concentration on the removal efficiency of Zn<sup>2+</sup> ions.**  
 Current density = 1.35 mA/cm<sup>2</sup>, anode surface = 1848 cm<sup>2</sup>.



**Fig. (14) Effect of initial concentration on the removal efficiency of Cu<sup>2+</sup> ions.**  
 Current density = 1.35 mA/cm<sup>2</sup>, anode surface = 1848 cm<sup>2</sup>.

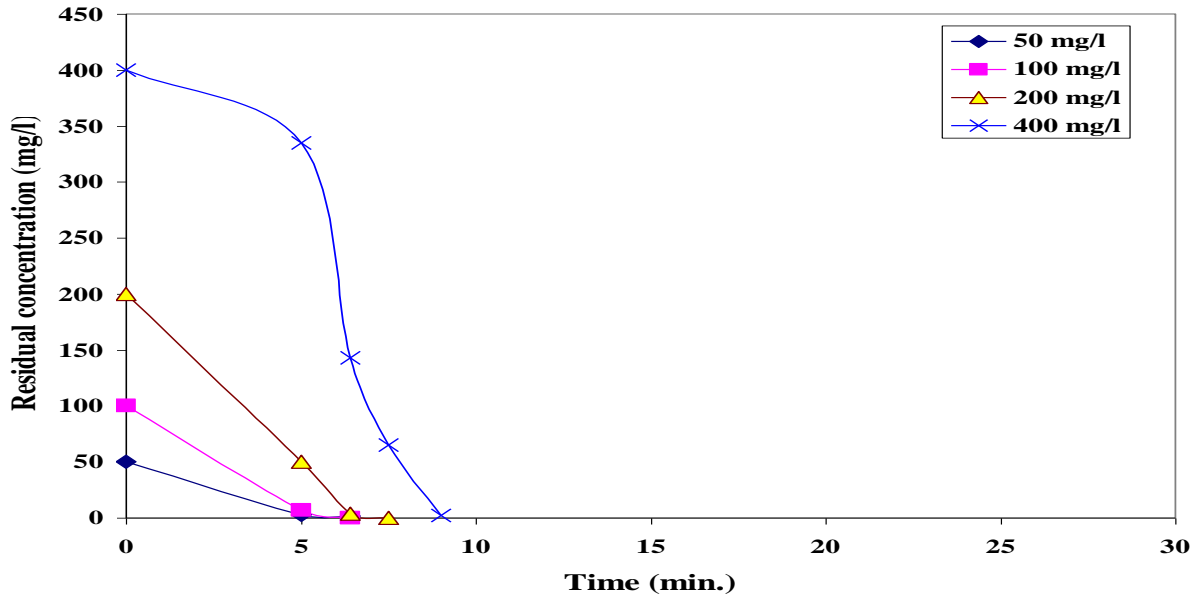


Fig. (15) Effect of initial concentration on the removal efficiency of Ni<sup>2+</sup> ions.  
Current density = 1.35 mA/cm<sup>2</sup>, anode surface = 1848 cm<sup>2</sup>.

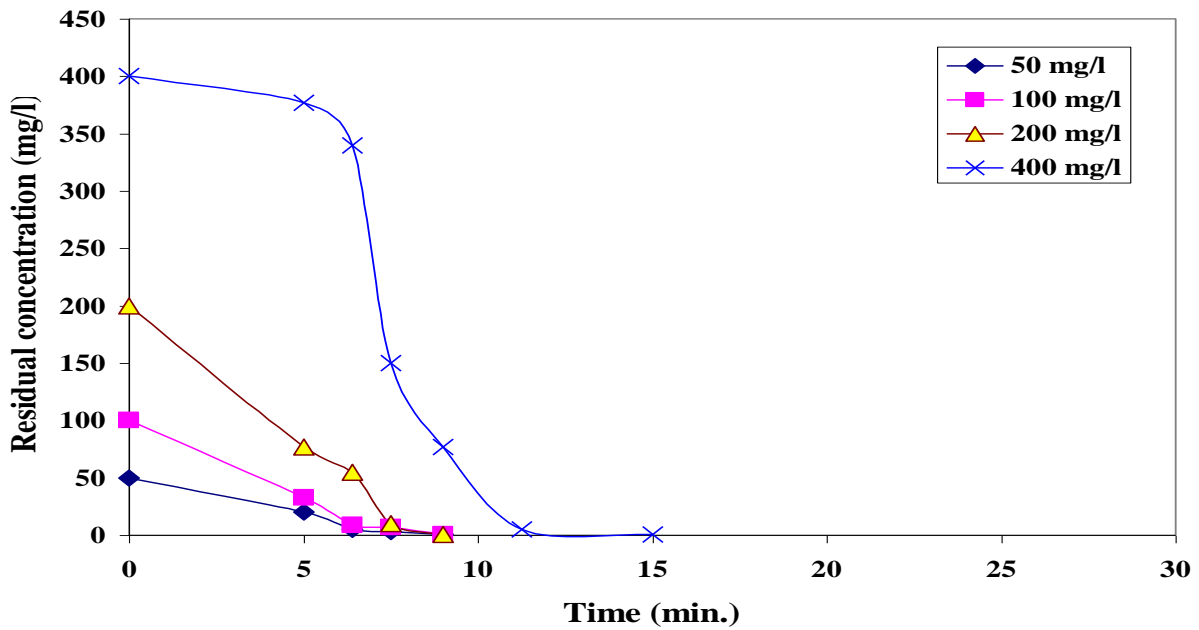
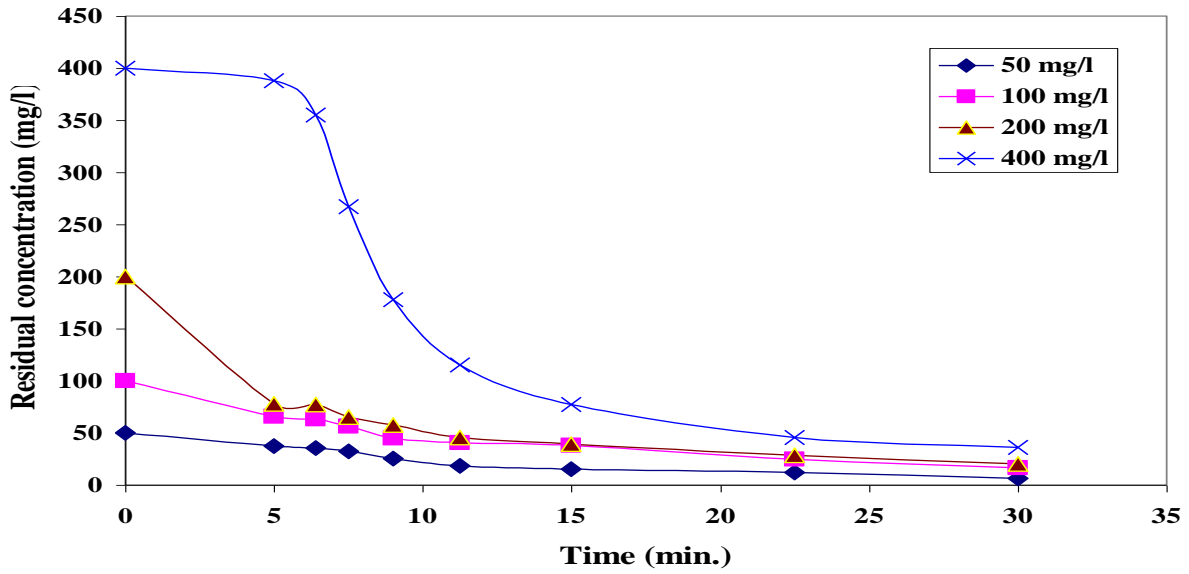
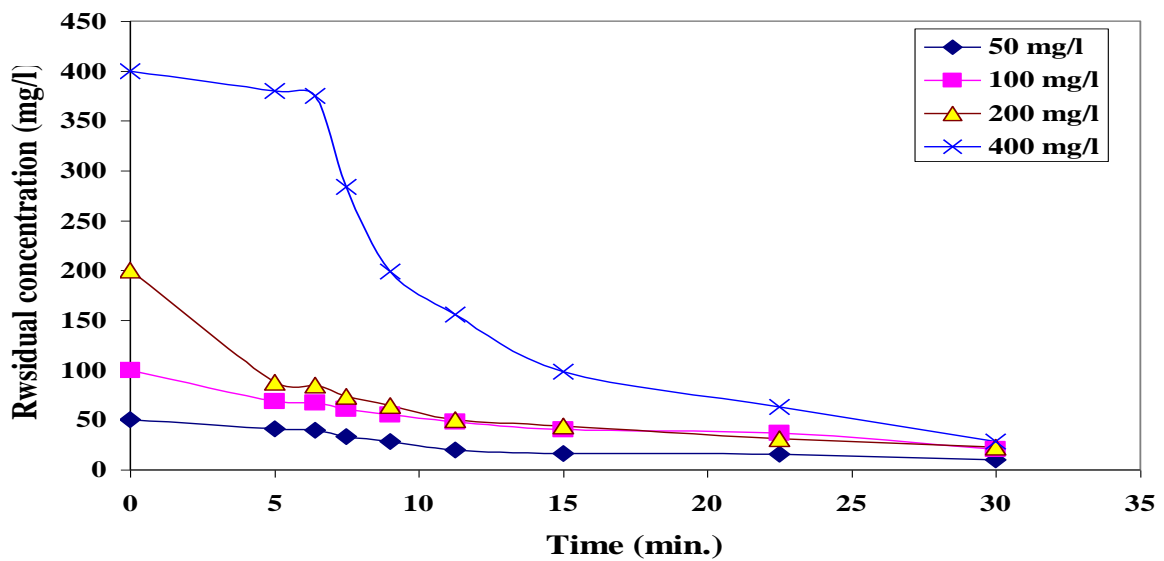


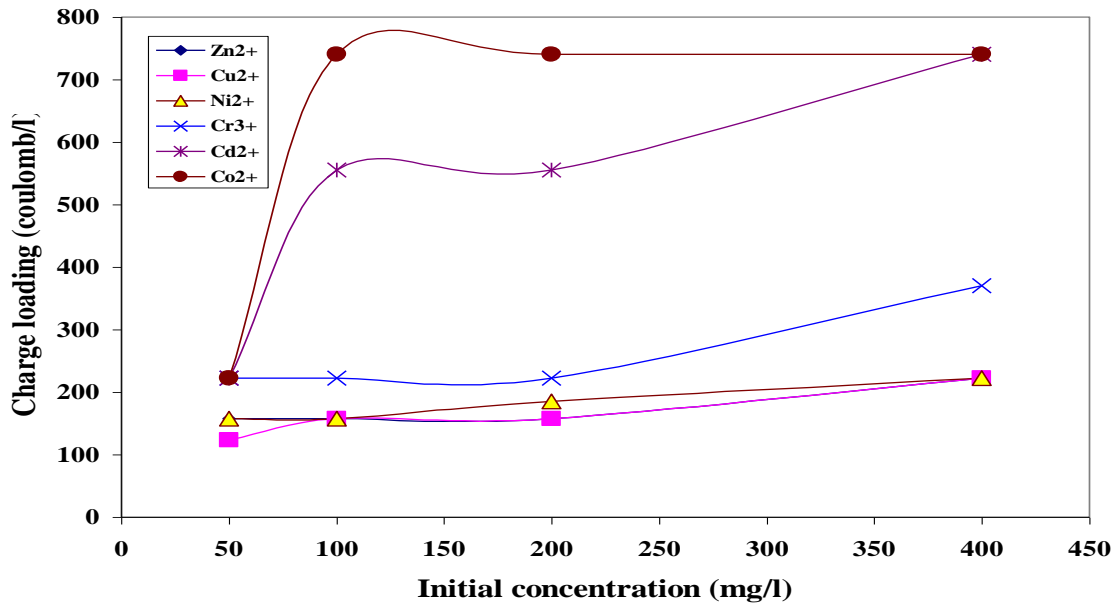
Fig. (16) Effect of initial concentration on the removal efficiency of Cr<sup>3+</sup> ions.  
Current density = 1.35 mA/cm<sup>2</sup>, surface = 1848 cm<sup>2</sup>.



**Fig. (17) Effect of initial concentration on the removal efficiency of Cd<sup>2+</sup> ions.**  
 Current density = 1.35 mA/cm<sup>2</sup>, anode surface = 1848 cm<sup>2</sup>.



**Fig. (18) Effect of initial concentration on the removal efficiency of Co<sup>2+</sup> ions.**  
 Current density = 1.35 mA/cm<sup>2</sup>, surface = 1848 cm<sup>2</sup>.



**Fig. (19) Effect of initial concentration on the charge loadings required for an effective removal of metals ,current density = 1.35 mA/cm<sup>2</sup>, anode surface = 1848 cm<sup>2</sup> residual concentration for Zn, Cu, Ni, Cr < 2mg/l and for Cd, Co < 30 mg/l.**

#### 4. CONCLUSIONS

This study investigate the performance of a new continuous-flow, perforated tube electrocoagulation system for treating synthetic solutions containing zinc, copper, nickel, trivalent chromium, cadmium and cobalt using iron anodes materials. The results show the following:

- The removal efficiency of all studied ions decreased significantly upon decreasing initial pH and maximum removal efficiency at the pH of 7.
- At initial pH of 7, the removal efficiency reached value as high as 99% for zinc, copper, Cr (VI) and nickel, while it is about 83% and 80% for cadmium and cobalt.
- The final pH is always higher than initial pH.
- The removal rate of all studied metal ions increased upon increasing current density.
- The highest current (1.35 mA/cm<sup>2</sup>) produced the quickest removal rate, with a 99%, concentrations reduction occurring after 6.4 min for zinc, copper and chromium and after 9 min for nickel. While the removal rate with 87% and 80% concentration reduction occurring just after 30 min for cadmium and cobalt respectively.

- The removal rate of zinc and copper is three times faster than that of chromium and nickel.
- The volumetric electrical charges ensuring 96% removal of zinc and copper were 37, 44.42 coulomb/l respectively; while to achieve the same removal efficiency for chromium and nickel was 148.1 coulomb/l. For cadmium and cobalt, the charge loading to achieve 70% removal yields were 111 coulomb/l.
- An increase of charge loading is observed for all metals ions, when current density was varied in the range 0.27-1.35 mA/cm<sup>2</sup>.
- At lowest current density (0.27 mA/cm<sup>2</sup>), The optimum charge loading are 31.6, 37 and 44.4 coulomb/l for zinc, copper and nickel respectively and it is 55.5 coulomb /l for each of chromium, cadmium and cobalt.
- The removal efficiencies of all studied ions increased with charge loading (Qe).
- The removal rate has decreased upon increasing initial concentration.
- The amount of iron delivered per unit of pollutant removed is not affected by the initial concentration.
- Longer electrolysis times are necessary for chromium, cadmium and cobalt.

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<http://www.its.monash.edu.au/policies/>

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