



REMOVAL OF LEAD FROM SIMULATED WASTEWATER BY ELECTROCOAGULATION METHOD

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ABSTRACT

The separation of lead ions from wastewater was carried out in an electrocoagulation cell which has a set of electrodes, aluminum anode and stainless steel cathode. The effect of several working parameters such as pH, current density, initial lead concentration, electrodes surface area, gap between electrodes and sodium chloride concentration on the performance of electrocoagulation cell were examined.

From the experiments found that the higher removal efficiency achieved at pH 9, with increasing current density and decreasing gap between electrodes the removal efficiency enhanced and the treatment time decreased. Using a flowrate of 0.025 l/min after (7min) electrolysis, the Pb(II) concentration decay from (250mg/l) to only (2.5mg/l) corresponding to a 99% removal efficiency.

Key words: heavy metals, wastewater, electrocoagulation.

الخلاصة

أيونات الرصاص في المياه الصناعية الملوثة فصلت داخل خلية التختير الكهروكيميائي التي تحتوي على قطب انود من الألمنيوم وقطب كاثود من الحديد المقاوم للصدأ. عدة متغيرات والتي لها تأثير على كفاءة الإزالة مثل الدالة الحامضية، كثافة التيار، تركيز الرصاص الأولي، درجة الحرارة، تركيز كلوريد الصوديوم، المسافة بين الأقطاب، المساحة السطحية للأقطاب ونوعيتها تم دراستها.

من التجارب وجد ان أعلى كفاءة ازالة تتحقق عندما تكون الدالة الحامضية 9، وبزيادة كثافة التيار التيار وتقليل المسافة بين الأقطاب تتحسن كفاءة الأزالة ويقل وقت المعالجة. كذلك وجد ان كفاءة الأزالة تتحسن عند تقليل معدل الجريان.

INTRODUCTION

One of the main causes of industrial pollution is the discharge of effluents containing heavy metals. Disposal of industrial wastewater has always been a major environmental issue. Pollutants in industrial wastewater are almost invariably so toxic that wastewater has to be treated before its reuse or disposal in water bodies [1].

Lead ion is one of the most toxic species, it's a natural constituent of the earth's crust, and it is present in many wastes as a result of its wide spread use. Because of its chemical properties, resistance to corrosion, ability to form desirable alloys and acceptable electrical conductivity, lead is used in a variety of application in the construction, communications,

energy production and distribution, pigments, dying and transport industries. An important use of lead is in lead-acid batteries [2].

Lead ions not biodegradable and tend to accumulate in living organisms, causing various health problems. According to the world health organization, the acceptable range of Pb^{2+} in water is 0.01ppm [3].

Various techniques have been employed for the treatment of heavy metals including precipitation, adsorption, ion-exchange, and reverse osmosis.

For many years the conventional treatment method for polluted water still used all-over the world without significant change. It includes dosing the chemical coagulant, such as aluminum sulfate and ferric chloride, the metal ions agglomerate the pollutants causing them either to sink to bottom or become sufficiently large that they can be filtered out or floated out using dissolved air flotation.

This method of treatment has certain drawbacks like handling large quantities of chemicals and production large volume of sludge causing disposal problem. Therefore there is an urgent need to develop innovative and more effective techniques for treatment of wastewaters. Electrochemical techniques have attracted, in this case, a great deal of attention because of their versatility, safety, selectivity, amenability to automation and environmental compatibility [4].

Electrocoagulation appears to be one of the most effective approaches. An electro coagulation reactor is an electrochemical cell wherein a sacrificial metal anode usually aluminum but occasionally iron is used to dose polluted water with a coagulating agent [5]. In this process, the treatment is done without adding any chemical coagulant or flocculent, thus reducing the amount of sludge which must be disposed [6]. The electrocoagulation has been successfully used to treat heavy metal containing solutions [4,7,8], dye-containing solutions with a removal efficiency as high as 99% [9], potable water[10], urban and restaurant wastewater[11], oil-water emulsions [12] and phenolic compounds [13]. Electrocoagulation compared with other techniques has many advantages, such as fast rate of removal pollutant particles, simple equipment and easy operation, reduction or absence of equipment for adding chemicals, and a decreased amount of precipitated or sludge. However the most disadvantages of EC is the sacrificial electrodes are dissolved into wastewater streams as a result of oxidation and need to be regularly replaced.

The objective of the present work were (1) to examine the applicability of electrocoagulation process for removal of lead from simulated wastewater and (2) to determine the effects of various parameters such as pH, current density, initial lead ion concentration, sodium chloride concentration, electrolysis time, electrode surface area, gap between electrodes and solution flowrate on the removal efficiency.

- EQUIPMENT AND MATERIALS

Materials

Synthetic polluted water samples with various concentrations of lead were prepared by dissolving lead nitrate $Pb(NO_3)_2$ (fluka products) without any further purification in deionized water. The required mass of $Pb(NO_3)_2$ were calculated as follows:

$$W = V \times C_i \times \frac{M.wt}{At.wt} \dots\dots\dots(1)$$

Where:

W: Weight of $Pb(NO_3)_2$ (g)

V: Volume of solution (3L)

C_i : Initial concentration of lead ions in solution (g/L)

M.wt: Molecular weight of $Pb(NO_3)_2$ (331.21g/mole)

At.wt: Atomic weight of lead (207.21g/mole)

In order to increase the conductivity of the solution, sodium chloride was added to the solution before injecting it into the cell. The chloride salt added to the solution can also prevent the formation of oxide layer on the anode and therefore reduce the passivation problem of the electrode.

The initial pH of the solutions was adjusted by adding either (1M) hydrochloric acid or (1M) sodium hydroxide.

The standard solutions used in the atomic absorption analysis were prepared using a Titrisol standard solution from merck.

Reactor design and procedure for Pb(II) removal

The experimental work was performed in two parts (batch and continuous modes). The effect of pH, current density, lead ions concentration, NaCl concentration, electrolysis time, surface area and gap between electrodes were studied.

A schematic diagram of the experimental set-up is shown in fig.(1).

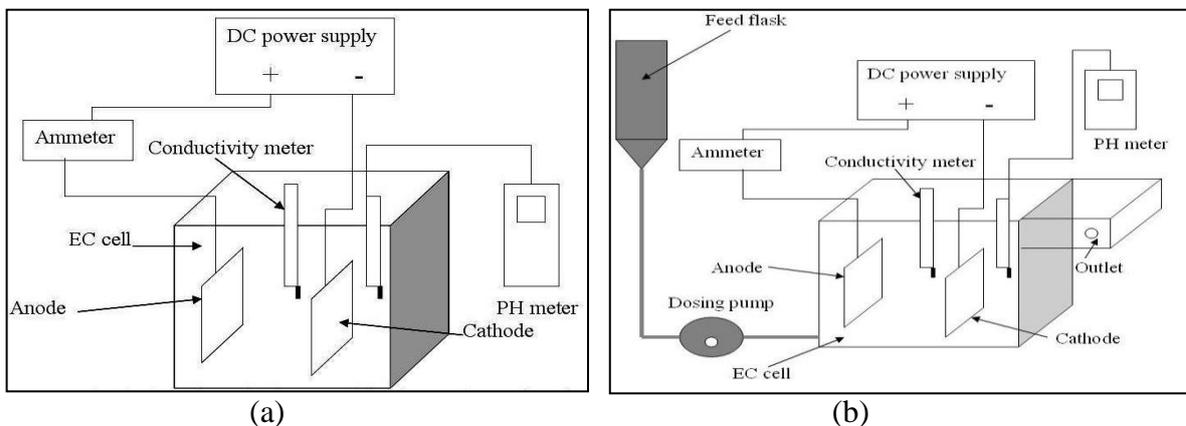


Fig.(1): Schematic diagram of batch and continuous experimental.

(a): Batch mode, (b): continuous mode

The batch electrocoagulation cell (fig 1-a) was constructed from 6mm thickness of glassy material with a square cross section and effective volume of (4L). 3L of polluted water was introduced into EC cell for each experiment. The cell comprised of two parallel plate electrodes, Al as anode and St.St. as cathode of 99% purity.

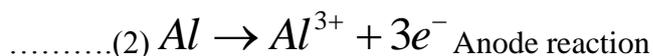
The two electrodes dipped in wastewater with a variable distance (1-4)cm between them. The electrodes were connected to the terminals of a DC power supply and the electrical circuit switched on as soon as the electrodes were covered by the wastewater. The desired current was achieved by altering the voltage of the electrical circuit.

Samples of 5ml withdrawn from the cell each (3min) and then these samples were filtrated and taken to be analyzed. At the end of each run, the system was washed several times with water and once with HCl to remove any solids tended to cling at the inside walls of the cell

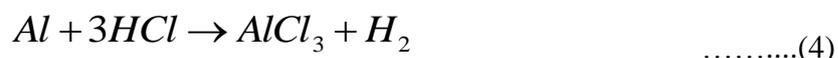
and to avoid passivity of the electrodes. The same procedure was applied in continuous mode (fig.1-b) where the EC cell of (3.5L) effective volume and divided into two compartments with dimensions of (9*12*30cm) and (9*12*9cm). The first compartment is provided with two electrodes Al as anode and St.St. as cathode. This compartment receives the polluted water from a conical flask by using the regulator of dosing pump. While, the effluent undergoes settling the suspended solids at the second compartment, where the samples were collected.

BRIEF DESCRIPTION OF ELECTROCOAGULATION MECHANISM

The main reaction occurring during the electrolysis in the electrochemical cell produced aluminum ion at anode and hydroxide as well as hydrogen ions at cathode as shown below:



In addition the active metal cation (Al^{3+}) react with hydroxide ions (OH^{-}) to form a metal hydroxide $\text{Al}(\text{OH})_3$ which then acts as a coagulant with the pollutant particles and metal hydroxide forming layer aggregates which may settle out or be carried to the surface by hydrogen bubbles produced at the cathode [14]. The equilibrium for the aluminum water system occurs as a result of passivation (i.e. formation of an oxide layer) and corrosion is identified. The presence of the chloride ion in solution has been reported to decrease passivation and thereby increase electrocoagulation treatment efficiency. The mechanism for chloride ion reducing passivation of the oxide layer formed on aluminum as shown in equations below:



RESULTS AND DISCUSSION

In order to examine the efficiency of electrocoagulation process for removing lead ions. Several operating parameters such as pH, current density, initial lead concentration, electrodes surface area, gap between electrodes and sodium chloride concentration have been explored.

Effect of initial pH

pH has a considerable effect on the performance of electrocoagulation process [11], also the pH of the medium change during the process. This change depends on the type of electrode material and initial pH. In this study a series of experiments were performed, using solutions containing Pb^{2+} of (250 mg/l) each, with an initial pH varying in the range (3-10). The effect of initial pH on the removal efficiency is shown in figure (2), it can be seen that the removal efficiency (Re) after (20 min) electrolysis time at (5.49 mA/cm²) current density reached values as high as 99% when pH equal 9. At pH of 10, the removal rate was slower by about (60 min), however it showed a good removal rate later. In contrast, when the initial pH

is decreased, a dramatic decrease of the removal efficiency is observed (40%) after (120 min) at pH equal to 3. The decrease of removal efficiency at a pH less than 5 was attributed to an amphoteric behavior of $\text{Al}(\text{OH})_3$ which lead to soluble Al^{3+} cations when the initial pH is low and to monomeric anions $\text{Al}(\text{OH})_4^-$ when the initial pH is high [15]. These soluble species are useless for water treatment. When the initial pH was kept in the range (5-9), all aluminum cations produced at the anode formed polymeric species $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ [16], and precipitated $\text{Al}(\text{OH})_3$ leading to a more effective treatment.

The treatment induced an increase in pH by about (1-2) unit at the first (2-3 minutes) and then decreased. This might be explained by the excess of hydroxyl ions produced at the cathode in sufficiently acidic conditions and by liberation of OH^- due to occurrence of a partial exchange of Cl^- with OH^- in $\text{Al}(\text{OH})_3$ [7].

As a result of the previous discussion of the effect of pH on the removal efficiency, the initial pH was adjusted to 9 for all subsequent studies.

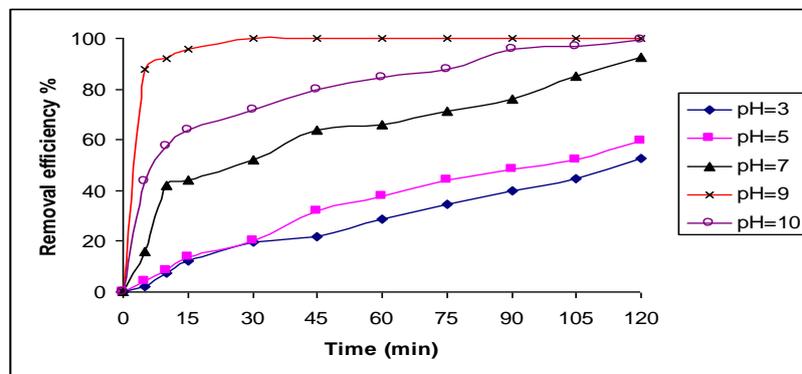


Fig. (2): Variation of lead removal efficiency with different pH.
(Vertical Al/St.St electrodes, $i=5.49\text{mA}/\text{cm}^2$, $[\text{lead}]=250\text{ppm}$,
 $[\text{NaCl}]=200\text{ppm}$, $\text{gap}=2\text{cm}$, $T=20^\circ\text{C}$).

Effect of current density

Current can be directly controlled in batch electrocoagulation runs. It is significant because it directly determines both coagulant dosage and bubble generation rate, also influences both mixing and mass transfer at the electrodes [5].

In this study, the current intensity was varied in the range (0.25-1.5) Ampere which linearly corresponds to (0.915-5.49 mA/cm^2) current density defined as current divided by electrode active area in an attempt to investigate the influence of this parameter on the removal efficiency of lead.

The variation of removal efficiency with different current density (0.915-5.49 mA/cm^2) is shown in figure (3). From this figure it can be noticed that the removal efficiency increased upon increasing current density. The highest current density (5.49 mA/cm^2) produced the quickest removal rate with a 99% concentration reduction occurring just after (20min).

This behavior is explained by the excess amount of aluminum and hydroxide ions generated at a given time within the electrocoagulation cell which are related to the current flow using Faraday's law [7].

$$W = \frac{ItM}{zF} \dots\dots(6)$$

Where: W is the amount of aluminum dissolving (g/cm²), I is the current density, t is the time, M is the molecular weight of aluminum (g/mol), z is the number of electrons transferred in the reaction and F is the Faraday's constant (96486 C/mol) which leads to increase the floc production, also bubbles density increase and their sizes decrease resulting in a more efficient and faster removal. The relationship between current density and amount of aluminum released is shown in figure (4).

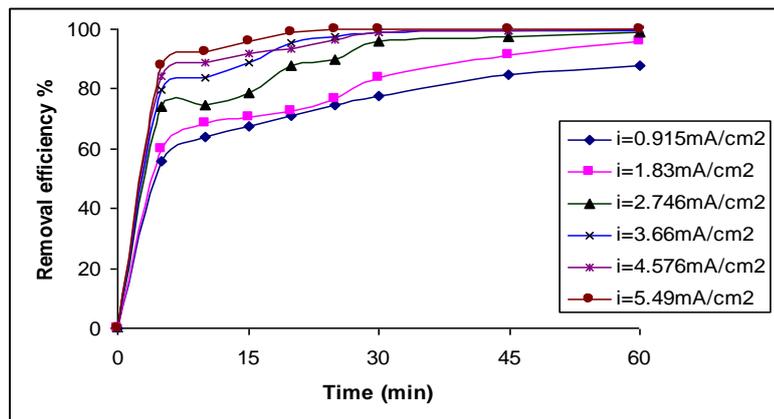


Fig.(3):Variation of lead removal efficiency with different current density. (Vertical Al/St.St electrodes, pH=9, [lead] =250ppm, [NaCl] =200ppm, gap=2cm, T=20°C).

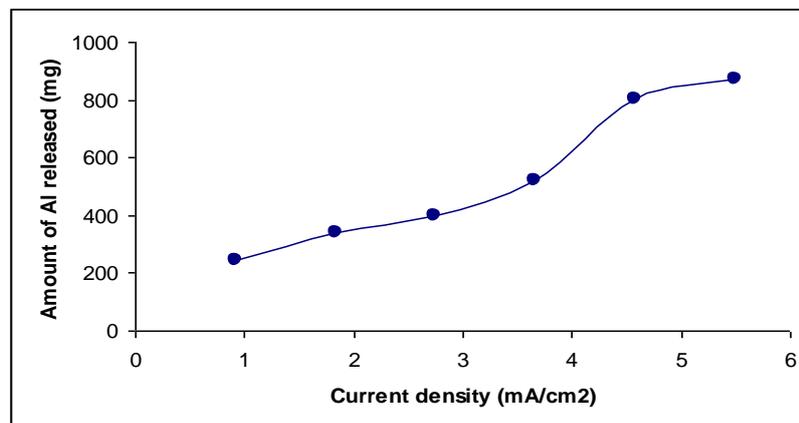


Fig.(4):Relation between current density and Al released. (Vertical Al/St.St electrodes, pH=9, [lead] =250ppm, [NaCl]=200ppm, gap=2cm, T=20°C).

Effect of initial lead concentration

The effect of various lead concentrations (50-250ppm) on the removal efficiency in the electrocoagulation cell is investigated and plotted in figure (5). As expected, it appears that the removal efficiency decreased upon increasing initial concentration. It is clear from figure (4) that in higher concentrations, longer time is needed for removal of lead, but higher initial

concentration of lead were reduced significantly in relatively less time compared to lower concentrations.

The time taken for reduction thus increase with the increase in concentration. This decreased is explained by the theory of dilute solution. In dilute solution, formation of the diffusion layer at the vicinity of the electrode causes a slower reaction rate, but in concentrated solution the diffusion layer has no effect on the rate of diffusion or migration of metal ions to the electrode surface [17], however 20 min was necessary to achieve 99% removal efficiency.

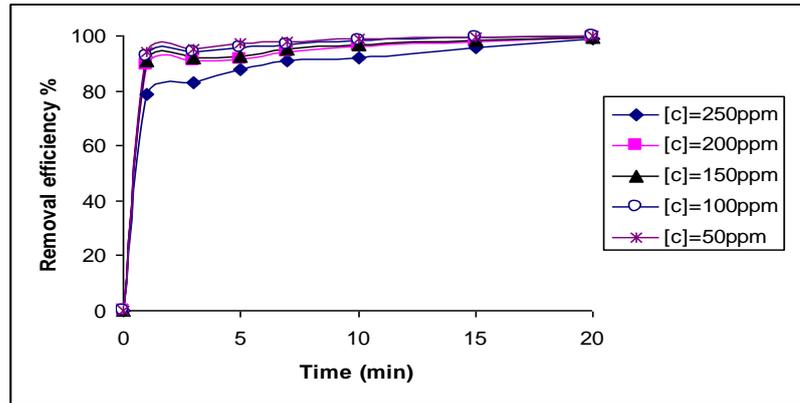


Fig.(5):Variation of lead removal efficiency with different initial lead concentration.(Vertical Al/St.St electrodes, pH=9, $i=5.49$ mA/cm², [NaCl] =200ppm, gap=2cm, T=20°C).

Effect of sodium chloride concentration

Sodium chloride concentration was varied in the range (100-400 ppm) to evaluate the impact of solution conductivity on the electrocoagulation efficiency. As shown in figure (6), the highest NaCl concentration produced the quickest removal rate with (99%) removal efficiency occurring just after 15min; however 20min was necessary to achieve the efficient removal of lead.

This behavior is attributed to the change in the ionic strength effects on the solution which leads to destabilization between charged species and lead ions during the treatment [4].

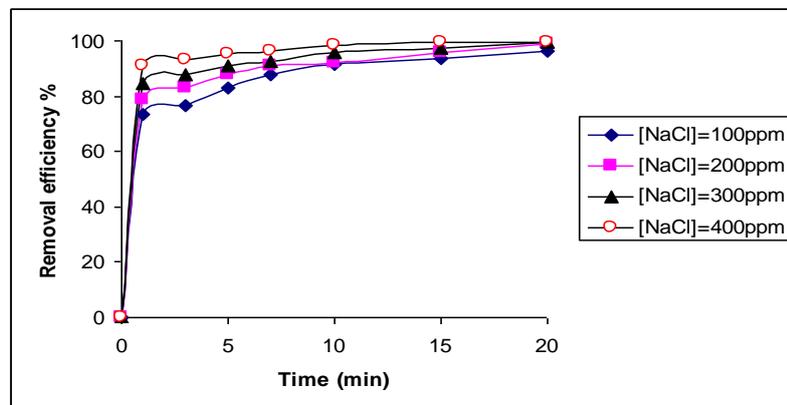


Fig. (6): Variation of lead removal efficiency with different NaCl concentration (Vertical Al/St.St electrodes, pH=9, [lead] =250ppm, gap=2cm, $i=5.49$ mA/cm², T=20°C).

Effect of electrodes spacing

The effects of electrodes spacing on the removal efficiency is shown in figure (7). It seems from this figure that faster removal happened with decreasing electrodes gap, and this is due to increase the current passage through the cell which lead to increase the amount of Al^{3+} released in the solution (The resistance of the solution decrease with decreasing the gap).

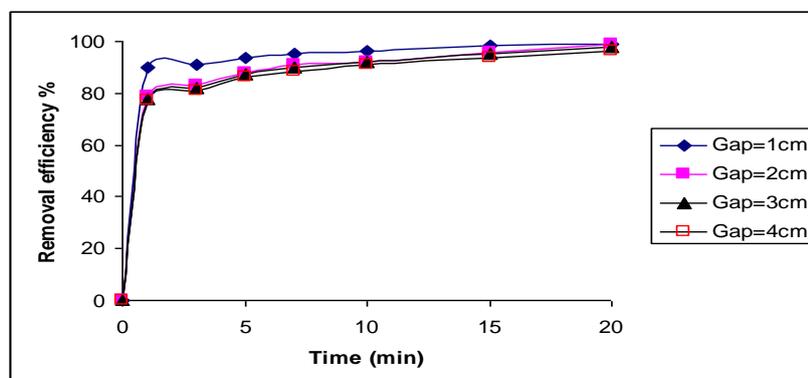


Fig. (7): Variation of lead removal efficiency with different gap.
(Vertical Al/St.St electrodes, pH=9, [lead] =250ppm,
[NaCl] =200ppm, $i=5.49\text{mA}/\text{cm}^2$, $T=20^\circ\text{C}$).

Effect of electrodes surface area

Two electrodes sizes with different types (Al/St.St and Al/Al) are used to investigate their effect on the electrocoagulation efficiency. The results are shown in figures (8) and (9) respectively.

Figure (8) indicate that increasing the active area from (101.95 to 273.12 cm^2) enhanced the removal efficiency and reducing the treatment time required, the explanation of this phenomena as follows: larger electrode surface area resulted in a great dispersion of bubbles throughout the reactor, whereas a smaller electrode surface area resulted in a concentrated source of bubbles within the reactor, and with increasing the dispersion of bubbles in the reactor, probability of collision between the bubbles and coagulant increased leading to increase the removal efficiency.

Figure (9) shows that the removal efficiency influences with different electrodes type. From this figure, it can be seen that Al/Al electrodes produced the quickest removal rate with a 99% concentration reduction occurring just after 5min. However 20min was necessary for Al/St.St to achieve nearly the same removal efficiency for Al/Al electrodes. This is due to that with using Al/Al electrodes both anode and cathode release Al^{3+} , thus increased the amount of aluminum hydroxide which lead to enhanced the removal efficiency.

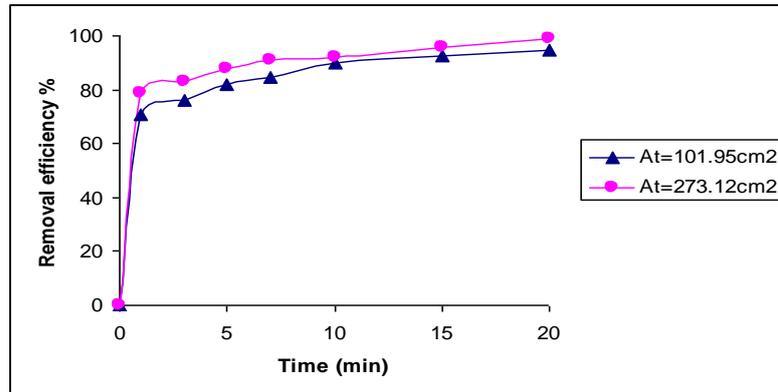


Fig.(8):Variation of lead removal efficiency with different electrodes surface area (Vertical Al/St.St electrodes, pH=9, [lead] =250ppm, [NaCl]=200ppm, gap=2cm, I=1.5A/T=20°C).

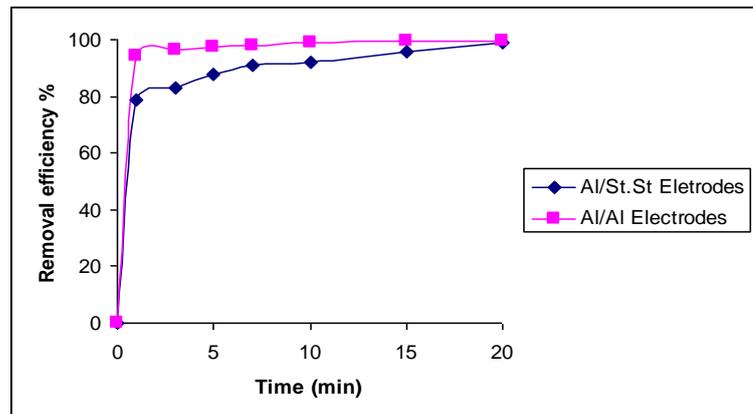


Fig.(9):Variation of removal efficiency with different electrodes. (pH=9, [lead] = 250ppm, [NaCl] =200ppm, gap=2cm, $i=5.49\text{mA/cm}^2$, T=20°C).

Continuous mode

Effect of wastewater flowrate

To investigate the effect of liquid flowrate containing lead ions on the electrocoagulation efficiency, a series of experiments carried out on solutions containing a constant lead concentration (250mg/l) where the initial pH was fixed at 9, flowrate being varied from 0.025-0.15 l/min at 5.49 mA/cm² current density by using (Al/St.St) electrodes.

Figure (10) represent the relationship between removal efficiency and treatment time for different flowrate. It is noted from this figure that the removal efficiency decreased upon increasing solution flowrate. This reduction in efficiency is explained by the decrease of residence time in the electrocoagulation cell with increasing solution flowrate. Indeed the amounts of aluminum and hydroxide ions generated at a given time is constant since the current density is constant.

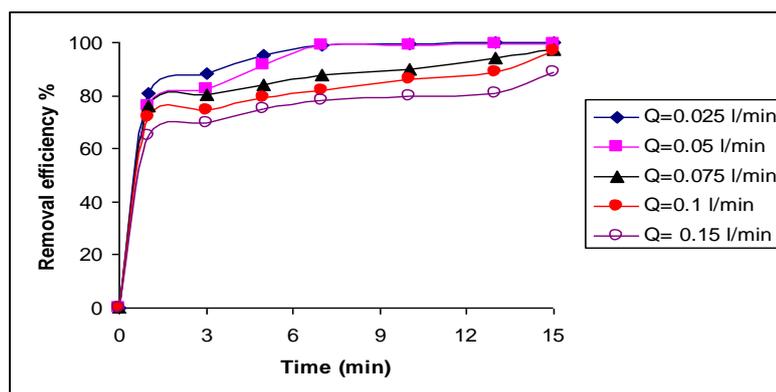


Fig.(10): Variation of lead removal efficiency with different flowrate.
(Vertical Al/St.St electrodes, pH=9, [lead] =250ppm, [NaCl] =200ppm,
gap=2cm, $i=5.49\text{mA/cm}^2$, $T=20^\circ\text{C}$).

CONCLUSIONS

In the present study the applicability of electrocoagulation process in the treatment of polluted water containing lead ions has been investigated. The effect of different operating parameters (pH, current density, initial lead concentration, electrodes surface area, gap between electrodes and sodium chloride concentration) on the electrocoagulation efficiency have been studied and the results can be summarized as follows:

- With regard to pH, the highest removal efficiency with shorter time achieved at pH 9.
- The removal rate was shown to increase upon increasing the current density. While the removal rate decrease with increasing initial lead concentration.
- The removal efficiency increased and the treatment time decreased with increasing sodium chloride concentration.
- An aluminum electrodes were preferable for electrocoagulation treatment of lead due to higher removal efficiency (99.08%) in 10min compared with 99% in 20min for St.St cathode.
- With respect to electrode size the best removal obtained at the higher electrode surface area and lower spacing between the electrodes due to the greater dispersion of bubbles throughout the reactor.
- With increasing the initial lead concentration the time required to achieve the highest efficiency increased but that higher initial concentration of lead was reduced in relatively less time than the lower concentrations.
- With respect to solution flowrate the removal efficiency decreased with increasing flowrate.



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