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Removal of Cadmium from Industrial Wastewater using Electrocoagulation Process

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ABSTRACT

Cadmium is one of the heavy metal found in the wastewater of many industries. The electrocoagulation offers many advantages for the removal of cadmium over other methods. So the removal of cadmium from wastewater by using electrocoagulation was studied to investigate the effect of operating parameters on the removal efficiency. The studied parameters were the initial pH, initial concentration, and applied voltage. The study experiments were conducted in a batch reactor with $(10 \times 10 \times 15)\ cm$ with two pairs of aluminum electrodes with dimension $(8 \times 8)\ cm$ and 2mm in thick with 1.5 cm space between them. The optimum removal was obtained at pH =7, initial concentration = 50 mg/L, and applied voltage = 20 V and it was 90%.
Keywords: Electrocoagulation, cadmium, wastewater.

ازالة الكادميوم من المياه الصناعية الملوثة باستخدام عملية التخثر الكهربائي

الخلاصة

الكادميوم يعتبر واحد من العناصر الموجود في المياه الخارجة من العديد من الصناعات. تعتبر عملية التخثر الكهربائي من العمليات التي ابرزت مزايا عديدة بالمقارنة مع الطرق الاخرى لازالة الكادميوم. أزالة الكادميوم من المياه الملوثة تم دراسته باستخدام التخثر الكهربائي لدراسة تاثير ظروف التشغيل على نسبة الازالة. تم دراسة كل من درجة الحامضية الابتدائي و التركيز الابتدائي وفرق الجهد المسلط . تم اجراء التجارب في مفاعل بابعاد (10*10*15) سم (طول * عرض * ارتفاع) باستخدام زوجين من اقطاب الالمنيوم بابعاد (8*8) سم وسمك 2 ملم وبتباعد 1.5 سم بين الاقطاب. تم الحصول على افضل ازالة باستخدام درجة حموضة ابتدائية للمحلول = 7 وتركيز ابتدائي 50 ملغم/لتر و فرق جهد = 50 فولت ليعطي نسة ازالة %90 .
الكلمات الرئيسية : التخثر الكهربائي ، الكادميوم ، المياه الملوثة.

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1. INTRODUCTION

The progressive of the industry and its entry as an essential element in all joints of life, Led to several big problems that emerged as a result of the wastes of these industries. Some of them led to major problems such as global warming and desertification and the lack of drinking water, **(Jorgensen, et. al. 1979)**.

The heavy metals are one of the most pollutants found in industrial wastewater. Arsenic, mercury, cadmium, chromium, copper, nickel, silver, and zinc are the most commonly found toxic heavy metal in wastewater. The presence of large quantities of these pollutants leads to environmental problems and may lead to higher treatment cost and other problems, **(Fernandez and C.J. Cerjan, 2000)**.

Among the different heavy metals, cadmium is one of the most toxic pollutants. Cadmium is found naturally and enters in large number of industries, plant soils, and from smoking. Due to low permissible dose to humans, excessive exposure may occur even with small quantities of cadmium are found, **(U.S. Geological Survey, 2018)**.

Cadmium is in the form of soft silver-white metal. Cadmium is found usually as an impurity in lead or zinc, and therefore production of Cd is primarily as a byproduct of Pb or Zn smelting. Cd compounds solubility in water is range from soluble to practically insoluble**, (ATSDR,1997)**.

Commercially, Cd enters in many industries such as paint pigments, batteries, cosmetics, in galvanizing steel, as a barrier in nuclear fission, The United States is the world's first producer with 600 metric tons, and US import about 150 metric tons (**U. S. Geological Survey, 2018)**.

The world health organization determined that the maximum quantity in drinking water is 0.005mg/L**, (Youssef, et al., 2004).**

There are many different ways to remove cadmium from industrial wastewater. The most common method are ion exchange, adsorption, chemical coagulation, electrocoagulation, and others, (**M. Singanan, 2011).** Electrocoagulation (EC) is one of the methods used for the treatment of wastewater and deal with large number of pollutants**,(Naje and Abbas, 2013).**

Electrocoagulation is a simple way to treat wastewater. The electrocoagulation process works on the principle of that the cations produced by the electrode corrosion, and it is in most cases aluminum and/or iron anodes which is responsible for the increase of the coagulation of pollutants in the aqueous solution. In the other half of the cell the hydrogen is produced which capable for the pollutant removal flotation or sedimentation**, (Chaturvedi, 2013).**

Electrocoagulation is one of the methods used for removing heavy metals from contaminated wastewater. The process involves an electrical cell with two electrodes. The process is done by applying an electrical current one the cell to the anode (sacrificial electrode) which is usually made from aluminum or iron. The electrodes are arranged in the treatment tank which is filling with contaminated water**, (Emamjomeh, 2006)**.

Electrocoagulation is used since the early 20th century. Electrocoagulation remains unused in industrial scales in the first period because the high operation cost and electricity cost. These points make electrocoagulation to retreat in front of other treatment methods. The costs of electricity, as well as the power sources, are lowered that make EC available again**, (Chen, 2004).**

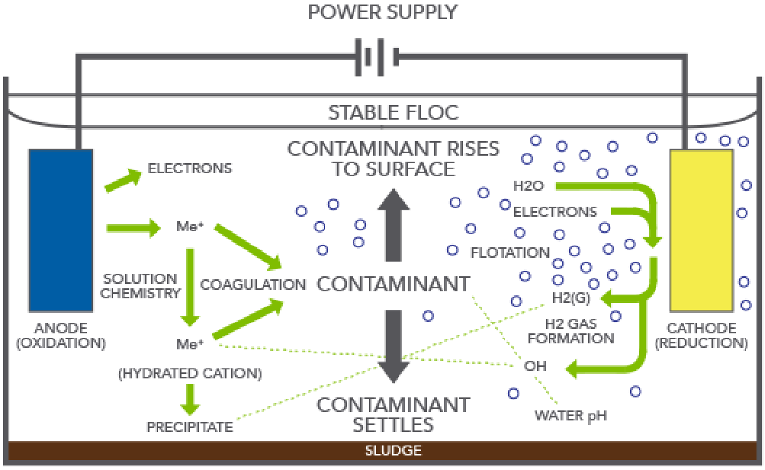

Figure 1. Schematic diagram of simple EC cell.

Electrocoagulation is a technology combining the benefits and functions of three processes the chemical coagulation, flocculation, and the electrical chemistry in wastewater treatment**, (Holt, et al., 2005)**.
The process is based on the dissolution of the anode and is automated. In the other half of the cell at the cathode hydrogen gas bubbles generate rises and help in aggregations formation.
EC achieved by applying a direct current between the anode and cathode, which are impressed in wastewater. The dissolution of the anode (aluminum or/and iron) takes place due to the applying of electrical current. The following reaction is taking place in the anode, (**Mollah, et al., 2001)**:

$$M \rightarrow M^{+} + e^{-} \qquad (1)$$

$$Al_{(s)} \rightarrow Al_{aq}^{+3} + 3e^{-} \quad E_o = +1.66\,V \qquad (2)$$

At the other half of the cell, the water is hydrolyzed to form hydrogen gas by the following reaction :

$$\mathbf{2H_2O_L + 2e^{-} \rightarrow H_{2_g} + 2\,OH^{-}\ E_o = -0.83\,V} \quad (3)$$

As well as the above reaction, a different side effect may occur in the EC cell such as a direct reduction of metal ions on the cathode**.** Usually aluminum, iron stainless steel are used as the material electrodes. The use of these materials is due to their availability, free of toxicity, low cost, and they give high efficiencies**, (Kumar, 2004)**. Some other materials such as magnesium (Mg) are also used sometimes as an electrode**, (Vasudevan, et al., 2010)**.
The study used aluminum as an electrode. The most common and best form of aluminum electrode is called Keggin cation $Al_{13}O_4(OH)_{24}{}^{+7}$, which is considered as the main source of precipitate and soluble complexes is known as Al13 ion. The Keggin structure with radius of 2.5 nm is formed of tetrahedral AlO_4 at the center surrounded by 12 octahedral AlO_6 attached with H_2O. The ion is used to reach the maximum charge neutralization. Thus it is represented as the controller and the more stable polymeric for wastewater treatment**, (Sarpola, 2007)**.

2. Experimental work

2.1Apparatus

The cell consisted of DC laboratory power supply with voltage range (0-30) V and a current range (0-5 A), reactor made from Perspex sheet with dimensions (10 cm width * 10cm length * 15 cm height), with aluminum electrodes of dimensions (8 cm * 8 cm) and thickness of 2 mm. A schematic diagram of the cell is shown in **Fig. 2.**

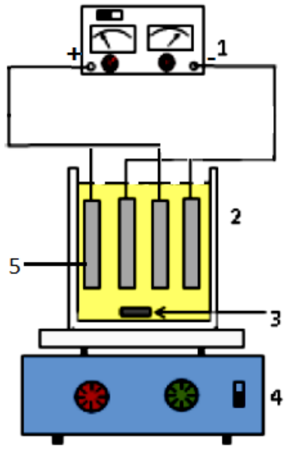

Figure. 2 Schematic diagram of the cell 1) power supply 2) EC cell 3) stirrer bar 4) magnetic stirrer 5) electrode.

2.2 Simulated solution

Stock solution with 1000 mg/L of cadmium was prepared by dissolving (1.9512) of $CdCl_2.2H_2O$ in 1000 ml of distilled water. The preparation of solution with different concentration is by dilution of the stock solution according to **Eq. 4** to get the desired concentration for each experiment.

$$V_1C_1 = V_2C_2 \qquad (4)$$

2.3 Experiment procedure

The experimental work is done with a range of operating conditions as shown in **Table 1**. For each run, one liter of simulated wastewater is used in the reactor. The surface to volume ratio was equal to $26.88 m^2/m^3$. The initial pH adjusted by using different doses of HCl and NaOH and as electrolyte NaCl was used (10 g/l). All experiments were conducted at room temperature which was approximately about $25^oC \pm 1$

Table. 1 the range of operation condition.

Property	**Range**
pH	5-9
Initial concentration (ppm)	50-250
Voltage range (V)	10-30

The process started after preparation of the initial sample, and the voltage was kept constant. The hydrogen gas H_2 was generated at the cathode during the process The samples were taken using of pipette from about 3 cm from the surface of the ample to avoid the floating flocs or the sediments.
Samples of 10 ml were taken by using pipette at the initial and after each 15 min of the process, let it settle and then filtered to measure the Cd content.
After each experiment, the electrodes were cleaned and washed with HCl to remove the precipitate on the surfaces of electrodes that reduce the efficiency of electrodes. The electrocoagulation process samples are tested by using atomic absorption spectroscopy in the Ministry of Industry.

3. RESULTS AND DISCUSSION

3.1 Results

Three different values of initial pH, initial concentration, and applied voltage were used in the present study. The total time of each run is (60) min and at each 15 min Cd concentration was measured and shown with the removal efficiency for each run in **Table 2**.

Table. 2 Remaining cadmium and removal efficiency.

Run	**pH**	**Initial concentration (ppm)**	**Voltage (V)**	**Remaining cadmium (ppm)**	**Removal efficiency**
Run	pH	Initial concentration (ppm)	Voltage (V)	Remaining cadmium (ppm)	Removal efficiency
1	5	50	10	20	60
2			20	15	70
3			30	15	70
4		100	10	45	55
5			20	40	60
6			30	30	70
7		250	10	125	50
8			20	100	60
9			30	90	64
10	7	50	10	10	80
11			20	5	90
12			30	5	90
13		100	10	30	70
14			20	20	80
15			30	15	85
16		250	10	75	70
17			20	60	76
18			30	55	78
19	9	50	10	15	70
20			20	10	80
21			30	10	80

22		100	10	35	65
23			20	30	70
24			30	20	80
25		250	10	110	56
26			20	95	62
27			30	70	72

3.2 Effect of operation parameters:

The electrocoagulation process is affected by many factors. The three factors studied in this research were: initial pH, initial concentration, and applied voltage. These factors are chosen as the most factors that effected the removal efficiency of the process.

3.2.1 Effect of initial pH

The pH of solution played an important role in the chemical and electrochemical coagulation process**, (Liu, et al., 2010)**. The initial pH of solution is adjusted to get the desired pH by using hydrochloric acid and sodium hydroxide. The results after 60 min are shown in **Fig. 3.**

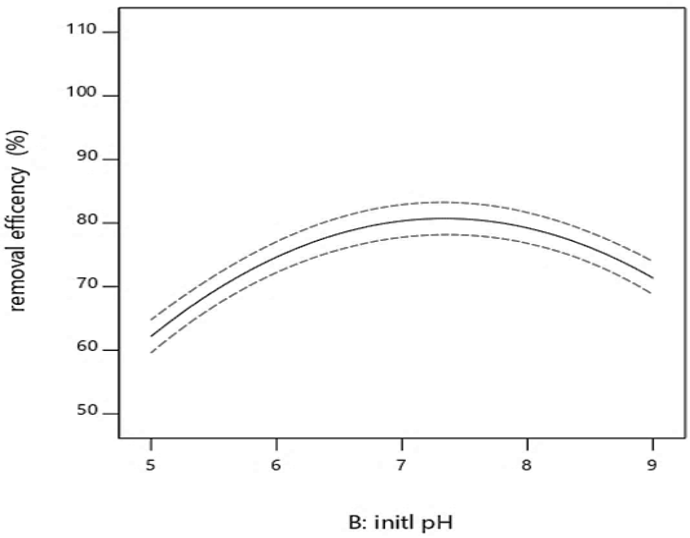

Figure. 3 the effect of initial pH on the removal efficiency of cadmium.

The pH of the solution is varied during the process, and the change depends upon three main factors the type of electrodes, initial pH and alkalinity**, (Riyad, et al., 2008)**. The above figure shows that as the pH value of the initial solution increases, the removal efficiency of cadmium is increased as the initial pH of solution increase from 5 to 7. It is due to the formation of the OH^- ions. On the other hand, for a pH more than 7, the removal efficiency decreases.

At pH below 7, the anode (Al) ion and hydroxides that formed such as $Al^{+3}, Al(OH)^{2+}, and\ Al(OH)_2^+$ is with a positive charge. They work by compression of the electrical double layer or by nebulization of its charge to remove pollutant**, (Zhen, et al., 2016)**.

At pH about 7 the aluminum is transformed mainly to form $Al(OH)_3$ which remove cadmium by adsorption**.** The increase of pH above 7 will led to the producing of a species such as $Al(OH)_4^-$, $Al(OH)_5^{-2}, Al(OH)_6^{-3}, and\ AlO_2^-$ in the solution which reduces the removal of cadmium.

As seen, the best initial pH is equal to 7 which gave maximum removal efficiency of Cd from wastewater which is in agreement with most of studies of cadmium removal using EC process**, (Mahvi and Bazrafshan, 2007, Escobar, et al., 2006, Vasudevan, et al., 2009).**

B. Effect of the applied voltage

The applied voltage plays an important role in the electrocoagulation process. The applied voltage is related directly with rate of bubble produced, the floc size and growth, and coagulant dosage rate. These are related to the speed of removal of pollutants.

A range of voltage is used to study the effect of this parameter on the removal efficiency of cadmium from wastewater. Three values of applied voltage (10, 20, and 30) were used and the results are shown in **Fig. 4**.

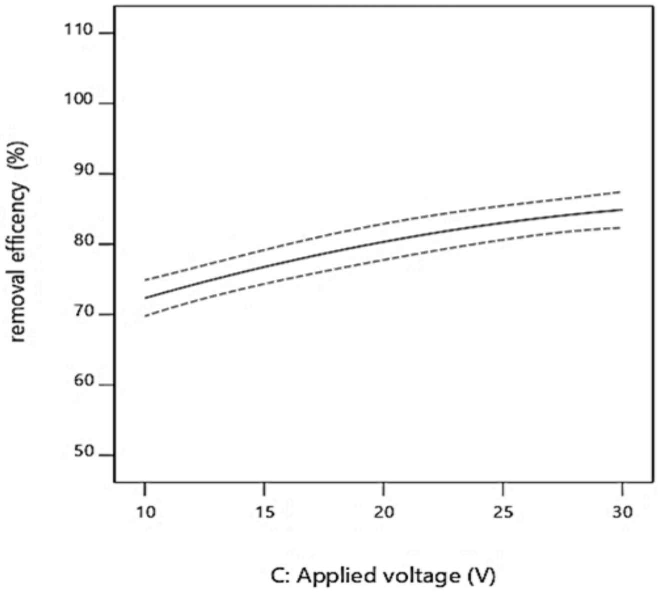

Figure. 4 the effect of applied voltage on removal efficiency of cadmium.

As seen in the figure above that the cadmium removal efficiency increases with increasing the applied voltage. The highest cadmium removal efficiency is achieved at the highest voltage (30V) for an EC time 60 min.

This increase is explained by:

i) As the voltage is increased the rate of Al^{+3} productions at the anode increases too. This led to an increase in the production of aluminum hydroxides which work as a coagulant. The increase in this hydroxide will help in the removal of cadmium by adsorption, which led to flocs formation that can be removed by filtration or it could be precipitate.

ii) At the same time an increase in the rate of hydrogen formation at the cathode, which helps in two ways. It improved the mixing process of Al^{+3} with cadmium particles and increased the movement of flocs to the top surface to float and form flocculants**, (Tir and Mostefa, et al., 2008)**.

iii) The increasing in applied voltage leads to an increase in OH^{-} producing with time**, (Abbas, et al., 2011).**

iv) The more Al^{+3} and OH^{-} is divided into the system and faster Cadmium concentration decrease

As a result with high applied voltage (high current density) the highest rate of dissolution of anodes is occurring in the EC cell according to faradays law**, (Guo, et al., 2006)**. This gives high chance for particle re-stabilized which caused by reversed charge due to particle adsorption of excess Al^{+3}. It seems that an optimal current density lowers electrical consumption and reduce the investment cost. The range of applied voltage is between (20-30 V)**,(Zhen, et al., 2016).**

C. Effect of initial concentration

The initial concentration of the prepared cadmium solution was attended with a range of concentrations (50-250) mg/l treated with EC. **Fig. 5** shows the effect of initial concentration on the cadmium removal efficiency.

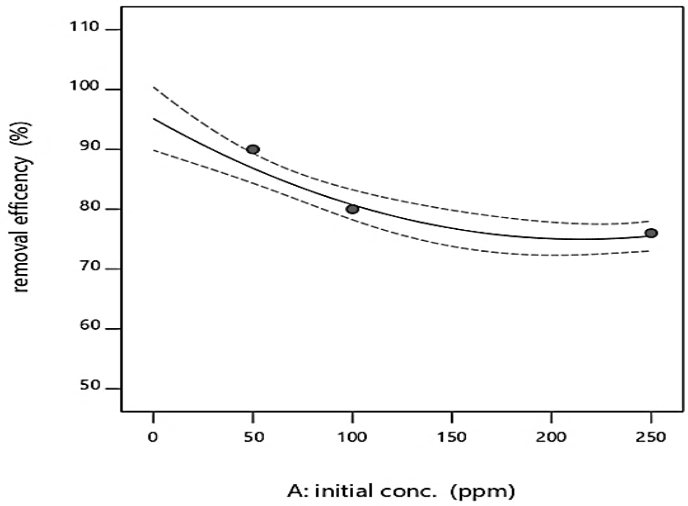

Figure. 5 The effect of initial concentration on the removal efficiency of cadmium.

The above figure shows that the removal efficiency is increased as the initial concentration of cadmium decreased.

This phenomenon could be caused by two main causes:

i) The higher concentration of Cd^{+2} could tend to passivate the anode chemically.

ii) Under this condition, $Al(OH)_3$ coagulant is limited, and their active surface is totally saturated with cadmium ions which make no more active area to adsorb more cadmium ions.

Obviously, the removal of cadmium is limited by the generation of Al^{+3} and to remove higher concentration longer time is used. On the other hand, higher initial concentrations were relatively reduced faster than for lower concentration this make the

EC process more active at the beginning of the process for higher initial concentration than at the end for the process**, (Mansour and Hasieb, 2012)**.

4. CONCLUSIONS

Here are the main conclusions and recommendations for future research

- The removal of cadmium by using the electrocoagulation process is successfully achieved. And it shows a dependence on initial pH, initial concentration and applied voltage.
- The optimum is achieved by using an initial pH equal to 7, initial concentration 50 mg/L, and with applied voltage 30V
- The best removal was equal to 90% of cadmium
- The variables studied shows a different performance. The initial pH increase from 5-7 led to increase in the removal efficiency of cadmium, but for pH more than 7 the removal efficiency was decreased.
- The initial concentration shows that with the increase in the initial concentration the removal efficiency was decreased.
- The applied voltage shows the increase in the applied voltage led to an increase in removal efficiency.

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NOMENCLATURE

`v1, v2: is the initial and final volume (ml)

C1, C2: is the initial and final concentration respectively (Mg/L)

V = applied voltage (volt)

t= time (min)