

# REMOVAL OF HEAVY METALS IN WASTEWATER BY ELECTROCHEMICAL TREATMENT

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**D**uring the last decade, there has been increasing social preoccupation in industrialized countries with respect to environmental protection, resulting in progressively tougher legislation regarding waste deposits. The presence of heavy metals in wastewater constitutes one of the most important problems in environmental engineering today,<sup>[1]</sup> fundamentally due to their high toxicity and cumulative character. Contamination by heavy metals is principally a problem characteristic of industrial effluents, and the activities that generate dumps of this kind of contaminated material are both numerous and diverse: metallurgical processes, industries involving metal plating, pigmentation and dyes, and producers of cellulose acetate, accumulators and batteries, printed circuits, etc. Given that the great majority of metallic ions can be electrodeposited in a metallic form on a cathode, electrochemistry offers a way of treating almost all of these types of wastewater.<sup>[1-4]</sup>

On the other hand, when treating effluents it is normal to work with low concentrations of heavy metals in solution (less than 1000 ppm). When two-dimensional electrodes are used as cathodes, the low concentration originates transport problems of these ions to the cathode at high current densities. This fact makes it necessary to design electrochemical reactors capable of treating these types of effluents in an efficient way; that is to say, obtaining an almost total recuperation of the metal.

One very interesting option concerns the use of three-dimensional electrodes.<sup>[5-7]</sup> The principal characteristic of this type of electrode is that when it extends to three dimensions, it has a high active area on which the electrochemical reaction can take place; in our case, depositing of the metallic ion. The direct consequence of the high active area that these electrodes have is a decrease in the real current density when the deposit reaction takes place, even when working at

high current intensities. This minimizes the problem of transport of the reagent to the electrode and permits almost total elimination of the metallic ions in the effluent to be treated.

The laboratory experiment described in this paper was developed for advanced students in chemical engineering or chemistry. It was designed for groups of three students each to perform during two periods of four hours each. The students must present a full report on the experiment at its end, including a description of the experiment's objective, the experimental plan, a description of the experimental system, a brief summary of the theory behind the experiment, presentation and treatment of experimental data, discussion of the results, and finally, any suggestions that might improve the experiment and a discussion of the sources of error.

The main objective of the experiment is to demonstrate an

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electrochemical application for solution of the very real problem of removing heavy metals in effluents. In addition, and following a predominantly applied method, the economic parameters of the experiment are calculated. At the end of the experiment, the students must understand and be familiar

with the different electrochemical processes (oxidation and reduction reactions, Faraday's laws, etc.), parameters, and magnitudes (current density, cell voltage, etc.).

The experiment concerns elimination via electrochemical treatment of the cation  $\text{Cu}^{2+}$  in a synthetic effluent, using a three-dimensional electrode as the cathode. Later, treatment of the effluent was carried out using a two-dimensional electrode and comparing the results obtained in both experiments. Finally, the economic parameters of the process (current efficiency, energy consumption, etc.) were calculated for the experiment carried out with the three-dimensional cathode.

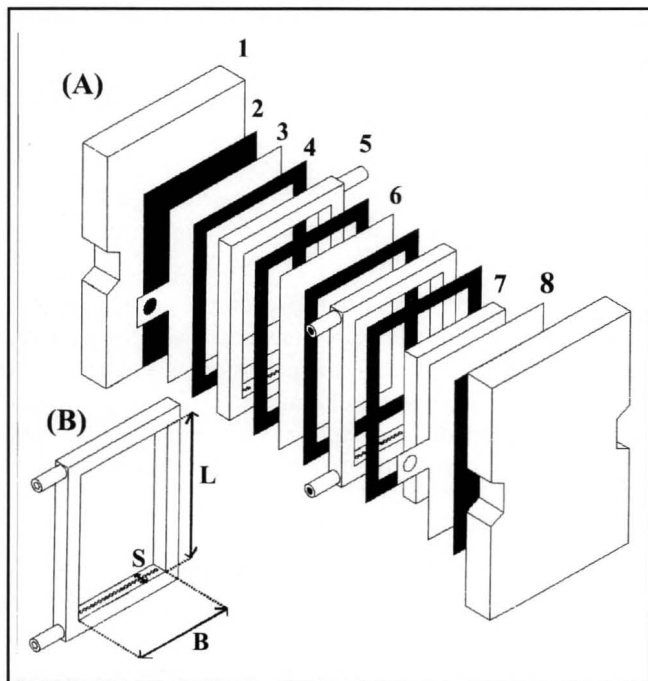
## EXPERIMENTAL PROCEDURE

### *Description of the Experimental Assembly*

The electrochemical reactor used was a filter-press-type reactor (see Figure 1) with separate anodic and cathodic compartments. Reactor dimensions were: length (L), 9 cm; width (B), 7 cm; height (S), 1 cm. As can be seen in the figure, this kind of reactor has a sandwich-type structure where the electrodes are placed at the reactor extremes. Each compartment consists of a flow distributor (made of polypropylene) where the solution flows parallel to the electrodic surfaces. The anodic and cathodic compartments are separated by a membrane. The figure shows how all the described elements are separated by sealing sheets to prevent the escape of solution.

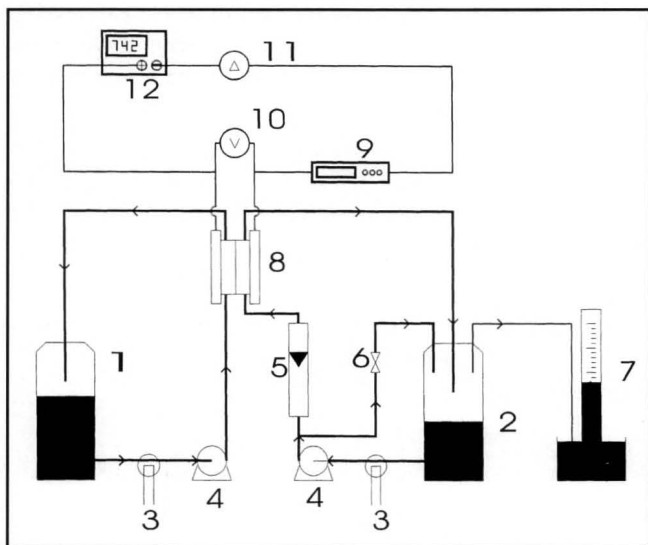
The cathodes are a carbon felt (supplied by Carbone Lorraine) with an active electrode area per unit volume of  $221 - 7 \text{ cm}^2/\text{cm}^3$  as the three-dimensional cathode and a graphite plate as the two-dimensional cathode. In the experiment with the three-dimensional electrode, the graphite plate is used as a current collector. As the anode, a DSA- $\text{O}_2$  electrode (Dimensionally Stable Anode for oxygen evolution) supplied by METAKEM (Usingen, Germany) was used in both experiments. The separator was a SIBRON 3457 anionic exchange membrane supplied by Ionac Chemical Company (New Jersey). The whole structure is placed between two steel plates where it is pressed to avoid solution escape. As shown in the figure, the only difference between the configuration of the reactor employed in the two experiments is the introduction of the three-dimensional electrode.

Figure 2 shows a simplified diagram of the experimental system. It includes a filter-press cell, electrolyte tanks, and magnetically driven pumps. The system permits control and measurement of the temperature and the catholyte flow by means of two heat exchangers and a flowmeter, respectively. The gases generated over the cathode were collected in an inverted burette to measure their volume. To prevent gas escape, the cathodic branch of the system was hermetically sealed. This branch also had a bypass to secure complete homogenization of the catholyte solution. The necessary electrical instrumentation consisted of a 3A-30V DC power



**Figure 1.** (A) Filter-press reactor scheme: 1. Back plates; 2. Insulator sheet; 3. DSA- $\text{O}_2$ ; 4. Sealing sheet; 5. Solution frame; 6. Anionic-exchange membrane; 7. Carbon felt; 8. Graphite plate.

(B) Scheme of the filter-press reactor dimensions.



**Figure 2.** Scheme of the experimental system: 1. Anolyte tank; 2. Catholyte tank; 3. Heat exchanger; 4. Pumps; 5. Flowmeter; 6. Bypass; 7. System for gas measuring; 8. Filter-press reactor; 9. Coulombimeter; 10. Voltmeter; 11. Ammeter; 12. Current feeder.

supply, two multimeters to measure the intensity flowing and the cell voltage, and a coulombimeter with a 0.1-1A shunt to measure the charge passed.

Analysis of the  $\text{Cu}^{2+}$  concentration in the samples was made using the ICP (Inductive Coupled Plasma) with an ICP Perkin-Elmer Optima 3000. Since most undergraduates do not have an ICP readily available, they could also analyze the  $\text{Cu}^{2+}$  concentration with the colorimetric method of the Bicinchoninate.<sup>[8]</sup>

### Carrying out the Experiments

The experimental conditions under which the two experiments were carried out are shown in Table 1. Prior to each practice session, the professors must prepare the anolyte and catholyte solutions and register the calibration curve of the ICP analyzer in order to facilitate analysis of the samples that will be taken by the students. The  $\text{Cu}^{2+}$  calibration curve is linear over the entire concentration range of  $\text{Cu}^{2+}$  (0 - 1000 ppm  $\text{Cu}^{2+}$ ), and it is not necessary to dilute the samples taken during the experiments.

**First Session** • In this session, the students must carry out the elimination using a three-dimensional cathode. Before the experiment starts, it is helpful for the professor to show the students a disabled filter-press reactor so they can better comprehend the structure and method of operation of a filter-press reactor.

First, a sample of 1 ml of catholyte must be taken before its introduction into the system in order to know the exact initial concentration of the  $\text{Cu}^{2+}$ ; this sample is labeled "sample 0." After that, the anodic and cathodic branches must be filled and washed with distilled water. Then the system is emptied. The catholyte and anolyte solutions can then be introduced into the corresponding deposits and the pumps connected; the catholyte flow is adjusted to the required value, and after a few minutes the system reaches the working temperature of 30°C. At that moment, a 1-ml volume sample of the catholyte solution is extracted and labeled "sample 1." After that, current (0.63A) is made to flow through the system.

The experiment is carried out for approximately one hour. Every five minutes, 1-ml-volume samples are taken until the end of the experiment at 2500 C of passed charge (this charge is rather more than the 150% charge necessary to deposit the 0.5g  $\text{Cu}^{2+}$  initially present in the catholyte, thus assuming a 100% current efficiency in the copper-deposit reaction). For each sample, note is taken of the values of time, cell voltage, quantity of charge circulated, and the volume of gas originated onto the cathode. At the end of the experiment, the volumes of the anolyte and catholyte are measured and a sample of the anolyte solution is taken to check the presence of  $\text{Cu}^{2+}$  that may

have passed through the membrane separator. After that, the system is washed several times with distilled water. The electrochemical reactor must be filled with water until the next session.

Hydrogen is a flammable gas. Although the volume of  $\text{H}_2$  generated during the experiments is small, care is necessary and the burette where the  $\text{H}_2$  is collected must not be exposed to heat.

During the session, the  $\text{Cu}^{2+}$  concentration of the samples must be measured. The catholyte solution initially has a light-blue color due to the presence of ions  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  in solution. As copper is deposited on the cathode, the solution gradually loses its blue color until it is completely colorless at the end of the experiment.

**Second Session** • Prior to the second session the professors must remove the three-dimensional electrode from the reactor and prepare the system. During this session, the students must carry out the elimination of  $\text{Cu}^{2+}$  using a two-dimensional cathode. The experiment is carried out by using the same procedure as was used in the first session.

## RESULTS AND DISCUSSION

1. The most important charge-transfer processes that take place inside the electrochemical reactor can be seen in Figure 3.
2. At this point, it is possible to observe the differences found between using a three-dimensional and a two-dimensional cathode to remove  $\text{Cu}^{2+}$ . Figure 4 shows  $\text{Cu}^{2+}$  concentrations in the catholyte vs time. When the three-dimensional carbon felt cathode was used, the final  $\text{Cu}^{2+}$  concentration in the catholyte was less than 1 ppm. On the other hand, when the two-dimensional graphite cathode was used, the final  $\text{Cu}^{2+}$  concentration in the catholyte was approximately 50% of the initial concentration.

Table 2 shows the values of time, concentration of  $\text{Cu}^{2+}$  in the catholyte, volume of  $\text{H}_2$  generated, charge passed, and the average cell voltage at different times of electrolysis. The results up to now show how well a three-dimensional electrode behaves in the elimination of heavy metal ions

**TABLE 1**  
Experimental Conditions of the  $\text{Cu}^{2+}$  Removal Experiments

Operation Mode	Galvanostatic
Catholyte (V:0.51)	$8 \times 10^{-3}\text{M CuSO}_4$ (1g/l $\text{Cu}^{2+}$ ) + 0.5M $\text{Na}_2\text{SO}_4$ + 0.05M $\text{H}_2\text{SO}_4$
Anolyte (V:0.51)	0.5M $\text{Na}_2\text{SO}_4$
Temperature	30°C
Current Density	10 mA/cm <sup>2</sup> (current: 0.63 A)
Catholyte Flow	50 l/h
Total Electrical Charge	2500C

in solution versus the use of conventional two-dimensional electrodes in which the reaction of the formation of  $H_2$  in the cathode is very important and the  $Cu^{2+}$  concentration decreases very slowly, as explained at the beginning of this article.

Table 3 shows the charge balance with respect to the electrodeposited Cu and generated  $H_2$  at different times of electrolysis. Moreover, it is interesting in the experiment with the three-dimensional cathode to do the calculations at the point where the copper is eliminated, at approximately 45 minutes.

From the difference in  $Cu^{2+}$  concentration between sample 0 and sample 1, we may calculate the real volume of catholyte. It is interesting to note that the initial  $Cu^{2+}$  concentration in the experiment with the two-dimensional cathode is higher than the initial  $Cu^{2+}$  concentration measured in the experiment with the three-dimensional cathode. This fact can be explained because the carbon felt used as a three-dimensional electrode has a high porosity and retains a high volume of distilled water in the preliminary washing stage.

The principal error during the calculation of the charge balance is caused by the charge employed in the reduction of the  $O_2$  present in the catholyte, which is not experimentally measured by the students. But this error is not too high due

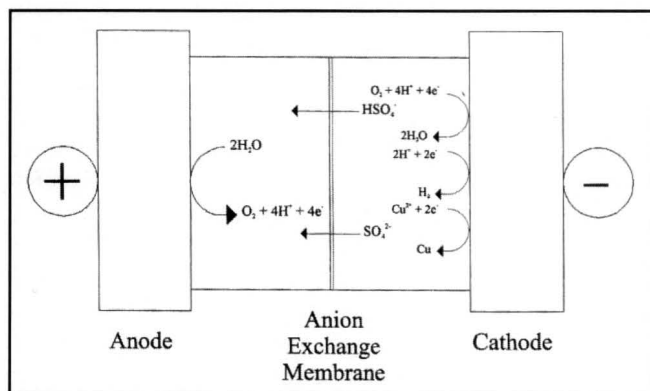


Figure 3. Charge transport processes inside the filter-press reactor.

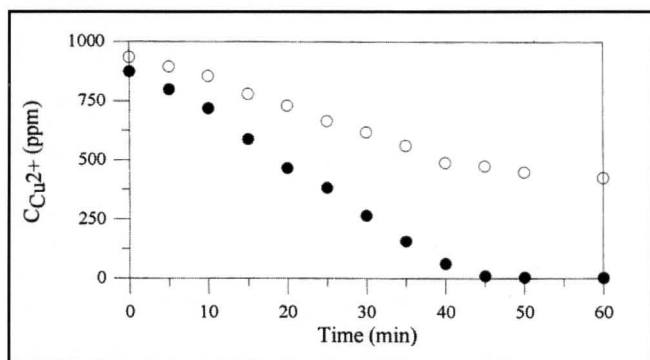


Figure 4. Representation of  $Cu^{2+}$  concentration (ppm) vs. time (min) during the experiments. ● - carbon felt; ○ - graphite plate

to the low concentration of  $O_2$  in solution, and therefore it can be disregarded. Other optional methods are: give this value to the students, or before the experiment eliminate the  $O_2$  in solution by bubbling the catholyte with  $N_2$  for approximately 45 minutes, increasing the duration of the practice session in this way.

One of the most important experimental errors appears in the charge balance if the cathodic system is not hermetically closed—the measure of volume of generated  $H_2$  will be incorrect. Close attention must be paid to this, especially during the sampling, to avoid any type of gas escape.

On the other hand, in the analyses of the anolyte samples taken at the end of the experiments, the presence of  $Cu^{2+}$  ions was not detected. This fact indicates that during the experiments, these ions did not pass through the membrane separator. This is logical due to the short duration of the experiments and the use of an anionic-exchange membrane.

Finally, the calculations corresponding to the economic parameters of the process for the experiment using the three-

TABLE 2  
Parameters Measured in the  $Cu^{2+}$  Removal Experiments

Time (min)	Charge passed (C)	$Cu^{2+}$ concentration (ppm)	Volume of $H_2$ (ml)	$V_{cell}$ (V)
<i>Three-Dimensional Cathode</i>				
sample 0	-	995	-	-
sample 1	-	873	-	-
20	760	485	0	2.06
40	1520	81	11	2.16
45	1750	5.2	24	2.39
60	2280	1.3	78	2.42
<i>Two-Dimensional Cathode</i>				
sample 0	-	1010	-	-
sample 1	-	934	-	-
20	760	735	40	3.22
40	1520	511	87	3.27
60	2280	405	158	3.32

TABLE 3  
Charge Balances of the  $Cu^{2+}$  Removal Experiments

Time (min)	Charge passed (C)	Charge Used in $Cu^{2+}$ reduction (C)	Charge Used in $H_2$ generation (C)
<i>Three-Dimensional Cathode</i>			
20	760	683	-
40	1520	1380	87
45	1750	1510	190
60	2280	1515	620
<i>Two-Dimensional Cathode</i>			
20	760	343	317
40	1520	716	690
60	2280	892	1254

dimensional electrode are shown in Table 4. The following expressions are used to calculate the characteristic economic parameters of this electrochemical process.

**Current Efficiency** • This parameter relates the total charge passed with the charge used in depositing copper.

Current Efficiency Cu(CE%) = (Charge used in depositing copper/Charge passed) × 100

**Energy Consumption** • This is the energy necessary to deposit a certain amount of copper. It is normally expressed in kilowatt-hour (kWh) per kilogram (kg) of product obtained.

$$\text{kWh} = V_{\text{cell}}(\text{V}) \times I(\text{A}) \times T(\text{s}) \times \frac{1 \text{ kW}}{10^3 \text{ W}} \times \frac{1 \text{ h}}{3600 \text{ s}} =$$

$$V_{\text{cell}}(\text{V}) \times Q(\text{C}) \times \frac{1 \text{ kW}}{10^3 \text{ W}} \times \frac{1 \text{ h}}{3600 \text{ s}}$$

$V_{\text{cell}}$  changes along the experiment. The correct expression of this parameter is

$$V_{\text{cell}} = \frac{1}{T} \int_0^T V(t) dt$$

Nevertheless, the variation of  $V$  during the experiment is not very important, and to simplify the calculation of kWh, an average value can be used.

$$\text{kg}_{\text{Cu}} = \text{number of deposited moles of Cu} \times \text{At}_{\text{wt}}\text{Cu}(\text{g}) \times \frac{1 \text{ kg}}{10^3 \text{ g}} =$$

$$Q(\text{C}) \times \frac{b}{n} \times \frac{\text{CE}\% \times 10^{-2}}{F} \times \text{At}_{\text{wt}}\text{Cu}(\text{g}) \times \frac{1 \text{ kg}}{10^3 \text{ g}}$$

The expression for energy consumption is

$$\frac{\text{kWh}}{\text{kg}_{\text{Cu}}} = \frac{2680.55 \times V_{\text{cell}}}{\text{At}_{\text{wt}}\text{Cu} \times \text{CE}\% \times \frac{b}{n}}$$

where  $Q$  is the charge passed,  $I$  is the current,  $T$  is the time of electrolysis,  $V_{\text{cell}}$  is the average value of the electrochemical reactor voltage,  $\text{At}_{\text{wt}}\text{Cu}$  is the atomic weight of copper,  $b$  is the stoichiometric coefficient of metallic copper in the deposit reaction (in our case 1, Figure 3), and  $n$  is the number of electrons exchanged in the reaction (in our case 2).

It can be seen in Table 4 that the two calculated parameters are quite constant until 45 minutes. By this time, all the copper is deposited over the cathode. At that time, the formation of  $\text{H}_2$  becomes important and the economics parameters become worse.

## STUDENT REPORTS

1. First, the students must give a description of the experimental system and a brief summary of the theory behind the practice.

**TABLE 4**  
Current Efficiency and Energy Consumption of the  $\text{Cu}^{2+}$  Removal Experiment with a Three-Dimensional Cathode

Time (min)	Current efficiency %	Energy consumption (kWh/kg <sub>Cu</sub> )
20	87	2.00
40	90	2.03
45	86	2.34
60	68	3.00

2. The students must have a clear comprehension of the charge-transfer processes that take place inside the filter-press reactor. In this way they must sketch a scheme similar to Figure 3. At this point, the professor can ask them some additional questions such as “Why do we use an anionic-type exchange membrane as the separator?” and “What will happen if we use a cationic-exchange membrane?”.

3. The next step is to compare and explain the differences found between using a three-dimensional cathode and a two-dimensional cathode with respect to the recovery of copper. The students must represent Figure 4 and do the charge balance using the measured experimental data in the same way as mentioned previously. At this point, the question “What will happen if we bubble  $\text{N}_2$  inside the catholyte solution?” can help the students detect the influence of the dissolved  $\text{O}_2$ .
4. Then the students should calculate the economic parameters of the experiment.
5. The last point is a critical evaluation of the practice and discussion of the sources of error.

## SUMMARY

Student reaction to the experiment has been very satisfactory. The main importance of the practice session is that it tackles the real problem of treating effluents containing heavy metals. It also achieves the goals mentioned in the first paragraphs of this article. The students assimilated the basic theoretical concepts of electrochemistry (charge balances, charge and mass transport processes, Faraday’s laws, etc.) and they familiarized themselves with the use of the instruments used in applied electrochemistry (power supplies, multimeters, coulombimeters, etc.).

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