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## Electrochemical Simultaneous Removal of Copper and Zinc from Bimetallic Solution Using Packed-Bed Cathode Made of Carbon Particles - Kinetic Study.

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### ABSTRACT

The simultaneous electrochemical removal of copper and zinc from a bimetallic solution containing their ions differs significantly, quantitatively and qualitatively, from their removal from monometallic solutions. In this work, a kinetic study is presented about the simultaneous electrochemical removal of copper and zinc from simulated bimetallic solutions containing different mass ratios of copper to zinc using a packed-bed cathode made of carbon particles. Results revealed that:

- The value of rate constant,  $k_{Cu}$ , decreased linearly with increased mass ratio of Cu to Zn.
- The value of the rate constant,  $k_{Zn}$ , was found to be independent of the mass ratio of copper to zinc.
- The value of both,  $k_{Cu}$  and  $k_{Zn}$  increased linearly with increasing intensity of applied current.

**Keywords:** Copper and zinc; Simultaneous removal; Electrolytic reactor; Electrochemical Kinetics.

### Nomenclature

$C_t$ : concentration of metal ion at time  $t$ ,  $mg/dm^3$

$C_0$ : the initial concentration of metal ion,  $mg/dm^3$

$k$ : reaction rate constant,  $min^{-1}$

$I$ : intensity of applied electric current, A.

$t$ : electrolysis time, min.

$X$ : Cu to Zn mass ratio.

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## INTRODUCTION

In some applications, the simultaneous removal/recovery of multiple heavy metals from waste solutions containing their ions is of practical importance; e.g. the recycling of precious metals from electronic wastes. The electrodeposition of a less active metal, e.g. copper, from a bimetallic solution containing its ions and ions of more active metal, e.g. zinc, differs significantly, quantitatively and qualitatively, from the electrodeposition from a monometallic solution containing ions of the less active one. This is basically attributed to the metal displacement reaction between the deposited atoms of the more active metal and ions of the less active metal; i.e. the cementation of the two metals are not independent.

Ascensão et al. [1] performed experiments on the electrolytic recovery of Cd, Cu, Pb and Zn ions from monometallic and multi-metallic solutions. They reported that the recovery of copper showed different behaviors for solutions containing just copper ions and those containing copper ions with other metals ions at the same applied potential and using the same experimental setup. However, they neither considered the selective removal of the metals nor performed any kinetic analysis.

Grimshaw et al. [2] experimentally studied the co-electrodeposition of copper and nickel from a bimetallic solution. Their results indicate that the presence of nickel enhanced the rate of copper deposition and attributed this enhancement to the displacement reaction between the deposited  $\text{Ni}^0$  and  $\text{Cu}^{2+}$  in solution. They presented a model to simulate the co-electrodeposition of the two metals with pH and temperature; however, the model did not include the effect of changing the mass ratio of  $\text{Ni}^{2+}$  to  $\text{Cu}^{2+}$  on the kinetics of removal of either metal.

Gustafsson et al. [3] investigated the successive removal and recycling of copper, indium and gallium from hydrochloric acid solutions of dissolved selenium-depleted material by applying suitable potentials for reduction of copper and indium. The authors reported that the time of complete separation of copper was shorter for copper than that of indium. However, they neither considered the order of the deposition reactions nor how the rate constant of the deposition of each metal was quantitatively affected by the presence of the three metals together in one solution.

Santos et al. [4] investigated the removal of cadmium, lead and copper, using an electrolytic cell from aqueous solutions. Most probably they did not consider the removal of the three metals from a solution mixture containing the three metals and, therefore, they reported nothing about the effect of the presence of the three metals on the kinetics of removal of each of them.

For the simultaneous electrolytic removal of copper and zinc from bimetallic solution, Alebrahim [5] reported that copper deposited first and zinc second; a behavior which is consistent with their respective standard reduction potentials. Also, they concluded that the presence of zinc with copper, at different mass ratios, did not negatively affect the removal of copper while the removal of zinc was delayed; the duration of the delay decreased with either increasing the mass ratio of zinc to copper or the intensity of the applied electric current.

All previously mentioned researches did not include any kinetic study that quantitatively expresses the effect of the presence of an active metal with another less active on successive electrochemical removal of the two from a solution containing both of them. Also, to our knowledge, no other one has performed such kinetic study. Therefore, the work presented in this manuscript was intentionally directed to perform a kinetic study on the successive electrochemical removal of copper (the less active metal) and zinc (the more active metal) from their bimetallic solution. The data analyzed in the current paper were taken from the doctoral thesis presented at the University of Surrey by one of the authors [6].

## EXPERIMENTAL WORK AND METHODOLOGY

All about the experimental apparatus and methodology of research are available elsewhere [5].

RESULTS AND DISCUSSION

1- Effect of Cu to Zn ratio on kinetics of simultaneous removal of Cu and Zn

1.1 Kinetics of copper removal

The effect of the mass ratio of copper to zinc, present in the treated solution, on the kinetics of copper removal is depicted in Figure (1). These runs were done under the following experimental condition: applied current intensity, initial pH and flow rate were, kept constant at, 3 A (i. e. corresponding to a superficial current density of 3.82 A/dm<sup>2</sup>), 2.65 and 0.065 L/s, respectively. The plotted results indicate that the copper removal increased with decreasing the ratio of copper to zinc and followed first order kinetic model with respect to the bulk concentration of copper; i.e. the decay of copper concentration in bulk solution is represented by the equation:

$$\ln \frac{C_t}{C_0} = -k_{Cu} t \quad (1)$$

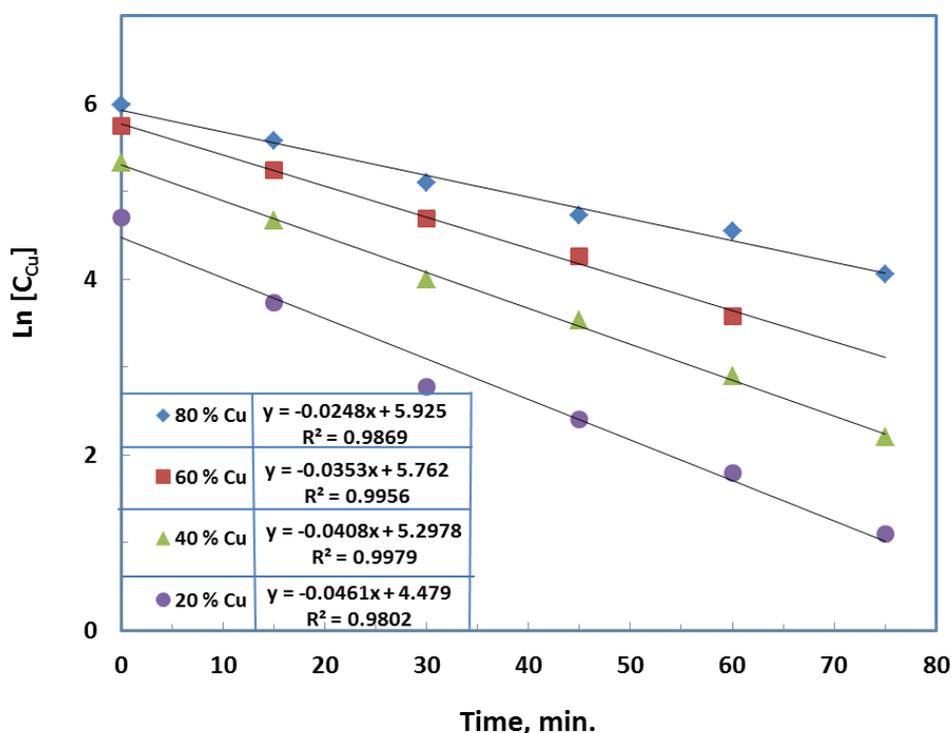
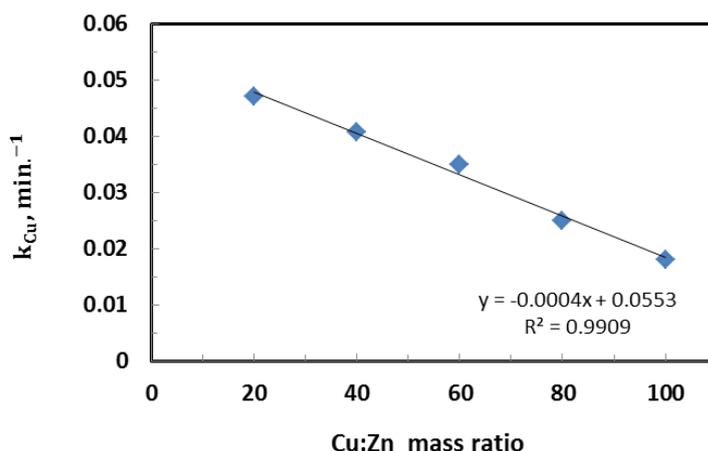


Figure 1: Plot of Ln [C<sub>Cu</sub>] versus time for different values of copper to zinc ratios.

The value of the rate constant,  $k_{Cu}$ , decreased with increased mass ratio of copper to zinc; i.e. with increased initial copper concentration which agrees well with the results presented by Alebrahim et al. [7] when copper was removed from a monometallic solution. From another point of view, it can be said that increasing zinc ratio enhanced the removal of copper. In order to quantitatively describe this observation, Figure (2) was constructed where the values of  $k_{Cu}$ , taken from Figure (1), were plotted against Cu:Zn mass ratio. It is important to mention that the value of  $k_{Cu}$  at 100% Cu, under the previously mentioned experimental condition, was calculated from a correlation given by Alebrahim et al. [7].

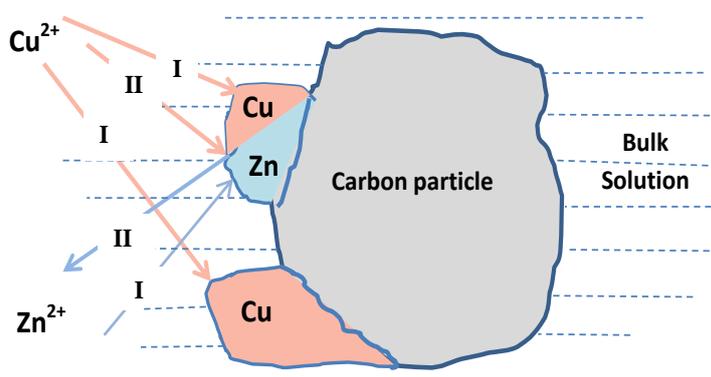


**Figure 2: Effect of Cu to Zn mass ratio on the rate constant of Cu removal.**

The data presented in Figure (2) were found to be best fitted by the following linear function

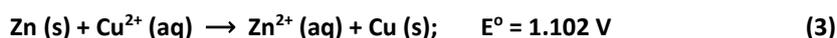
$$k_{Cu} = - 0.0004X + 0.0553 \quad (2)$$

Where X stands for Cu to Zn mass ratio. It is of significance to mention that, when using Eq. 2 to predict a value of  $k_{Cu}$ , the type of the electrolytic reactor and the values of the operating parameters, at which the values of  $k_{Cu}$ , plotted in Fig. (2), were obtained, should be taken into account.



**Figure 3: Electrodeposition of Cu and Zinc from bimetallic solution**

The enhancement of copper deposition with increasing the ratio of zinc can be interpreted in view of Figure (3). Both  $Cu^{2+}$  and  $Zn^{2+}$  ions can be electrolytically discharged, step I, and deposit on the surface of carbon particle as long as the applied potential can overcome the overpotentials needed to electrodeposit both metals. During the progress of the process,  $Cu^{2+}$  comes in contact with the deposited zinc and the metal displacement reaction, represented by Eq. 3, occurs; especially in the presence of sufficient concentration of  $Cu^{2+}$  in bulk solution; this is denoted by step II.



According to this interpretation, copper ions are discharged and deposit via two steps and, therefore, lead to enhancement of copper deposition. On the other hand, the quantity of deposited zinc is the resultant of steps I and II. If the rate of step I is larger than that of step II, the deposited zinc layer will be sustained.

### 1.2 Kinetics of zinc removal

Figure (4) shows the kinetics of zinc removal under the same experimental conditions of Figure (1). As the figure illustrates, the deposition of zinc from monometallic solution, 0.0 % Cu, occurred straightforward following first order kinetics with respect to bulk concentration of zinc. However, in the presence of copper with zinc in bimetallic solutions, removal of zinc showed two distinct time periods. The first period is shown to have a slope of 0.00, i.e.  $k_{Zn} = 0.00$ , at all Cu:Zn ratios. During this period no detectable removal of zinc was observed. This period of time decreased with increasing zinc ratio.

The second period, for all zinc ratios, reveals the decay of zinc ions concentration in bulk solution followed, as was observed for copper, first order kinetic model. However, the value of the rate constant  $k_{Zn}$  is almost independent of the mass ratio of copper to zinc; as the lines representing  $\ln [C_{Zn}]$  versus time are almost parallel. Figure (5) illustrates the variation of  $k_{Zn}$  with copper to zinc ratio. The average value of the apparent rate constant is  $0.00796 \text{ min}^{-1}$  with standard deviation of 0.0037. These results indicate that the presence of copper ions with zinc ions in a single solution did not show a drawback effect on the rate of zinc removal during the second period.

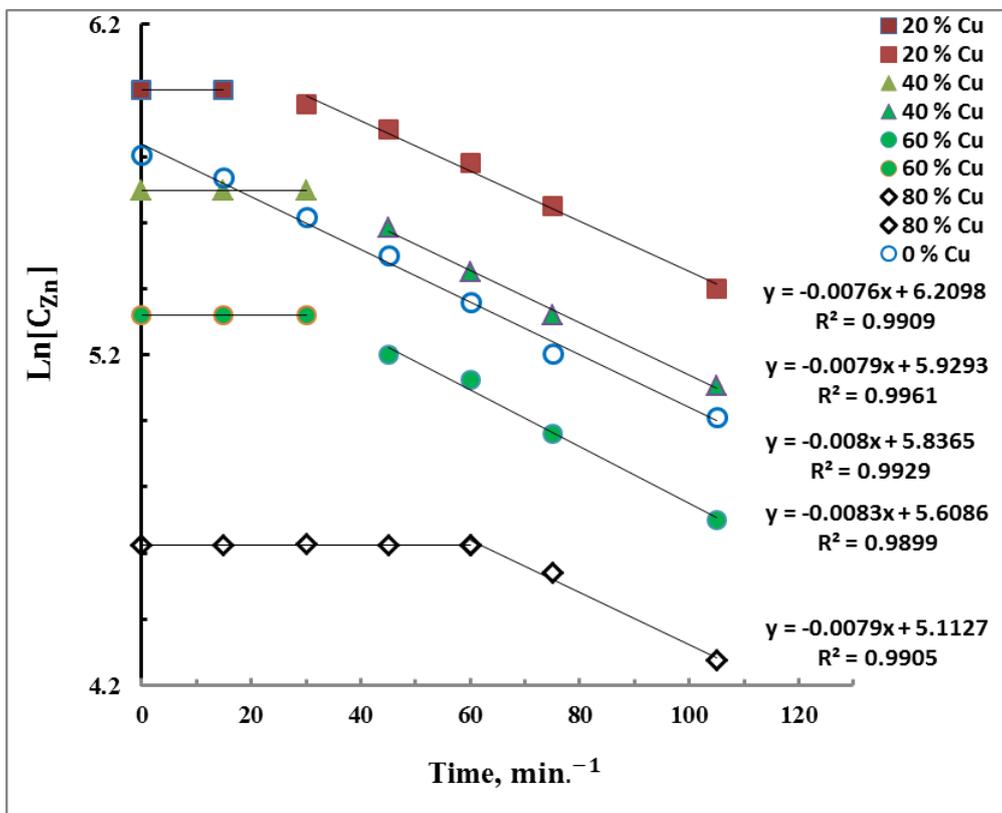


Figure 4: Effect of Cu to Zn mass ratio on the rate constant of Zn removal.

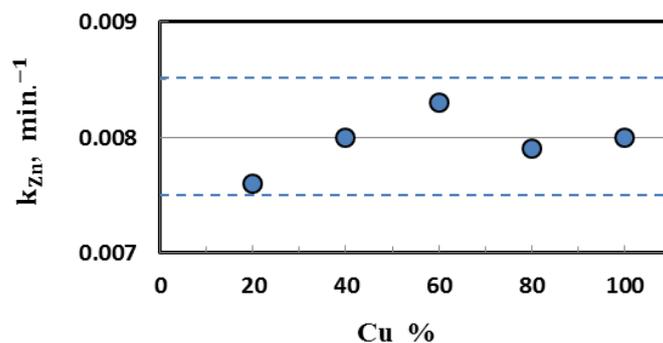


Figure 5: Variation of k of Zn removal with Cu:Zn mass ratio

## 2- Effect of current intensity on the kinetics of simultaneous removal of copper and zinc

In order to investigate the effect of the applied current intensity on the kinetics of simultaneous removal of copper and zinc, the two bimetallic solutions containing 60 % and 40 % Cu were treated at applied current intensities of 5 and 6 A while keeping constant flow rate of 0.065 L/s and constant pH<sub>0</sub> (=2.65).

### 2.1 Solution containing 60 % copper

#### 2.1.1 Kinetics of copper removal

The results presented in Figure (6) indicate that the decay of copper concentration follows the model described by Eq. (1) and the value of  $k_{Cu}$  increased with increasing the current intensity; a result which agrees well with the results presented by Alebrahim et al. [8] for the removal of copper from monometallic solution.

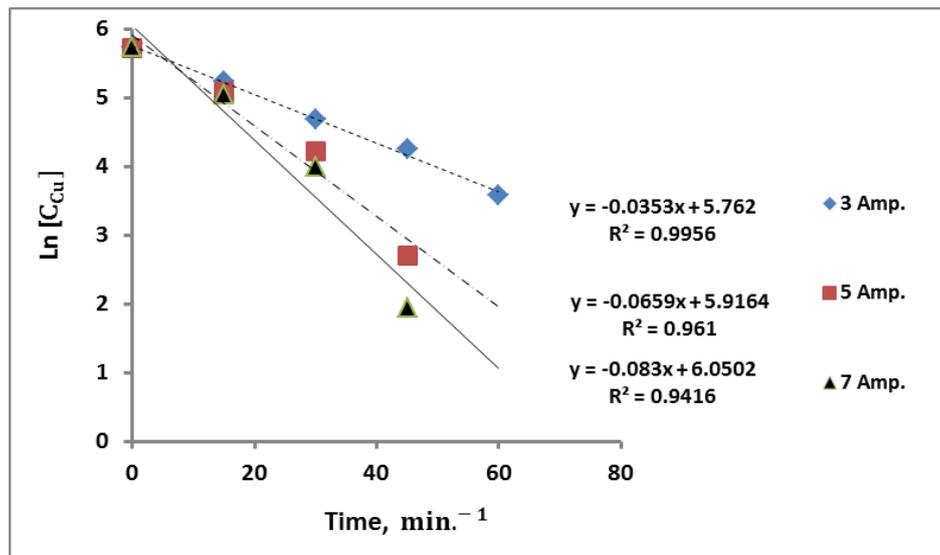


Figure 6: Effect of current intensity on kinetics of copper removal (60 % Cu)

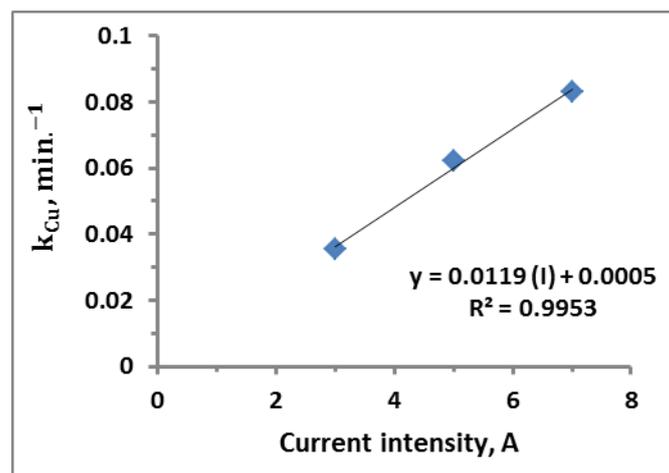


Figure 7: Relation between  $k_{Cu}$  and applied current intensity for Cu-(60 % Cu)

The effect of increasing applied current intensity,  $I$  (A), on  $k_{Cu}$  is shown in Figure (7). This effect is well described by the linear function

$$k_{Cu} = 0.0119 (I) + 0.0005 \quad (2)$$

### 2.1.2 Kinetics of zinc removal

Figure (8) illustrates as well that the removal of zinc comprised two distinct time periods. The first period is shown to have a slope of 0.00, i.e.  $k_{Zn} = 0.00$ , at all values of the applied current intensity. The duration of this period, however, decreased with increased current intensity.

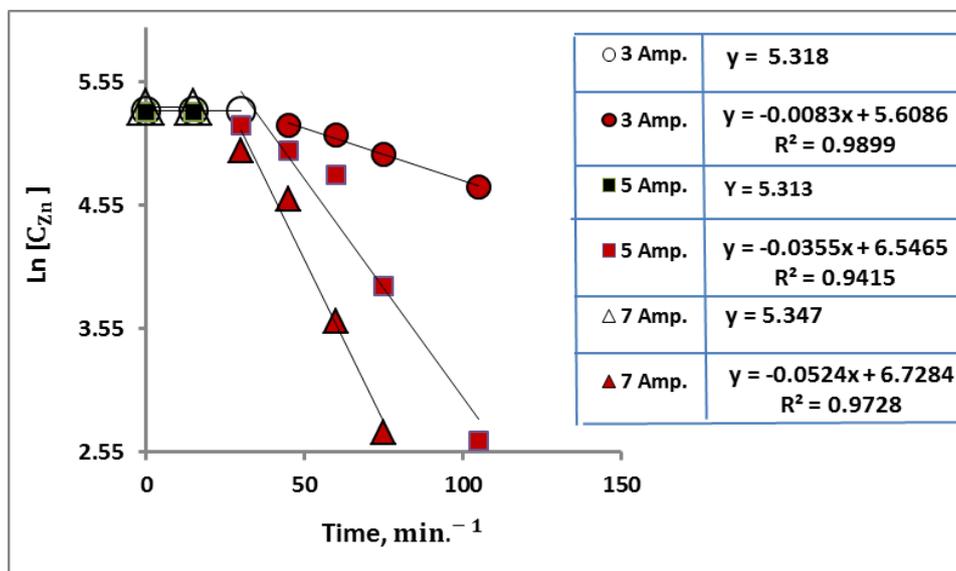


Figure 8: Effect of current intensity on kinetics of zinc removal-(60 % Cu)

The second period, for all current intensities, exhibits straight line with negative slope; i.e. the removal of zinc follows first order kinetics with respect to bulk concentration of zinc ions in solution. The relation between  $k_{Zn}$  and current intensity is shown in Figure (9). The relation is best described by the linear equation

$$k_{Zn} = 0.011(I) - 0.0231 \quad (3)$$

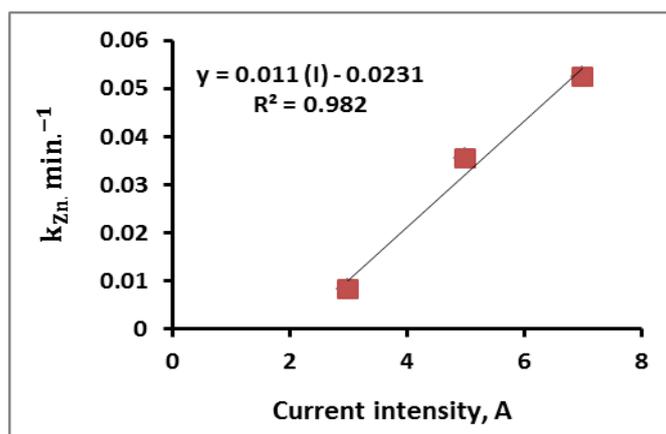


Figure 9: Relation between  $k_{Zn}$  and applied current intensity for Zn-(60 % Cu)

## 2.2 Solution containing 40 % copper

### 2.2.1 Kinetics of copper removal

According to the data presented in Figure (10), the value of the rate constant,  $k_{Cu}$ , increased with increasing intensity of the applied current. This **observation** is well agreed with the observation mentioned in 2.1.1.

Additionally, when comparing the values of  $k_{Cu}$ , at the same value of the intensity of the applied electric current, one can find that the value of  $k_{Cu}$  for the 40% solution is larger than its value for the 60% solution, which agrees well to what has been observed when copper was removed from monometallic solution; as  $k_{Cu}$  was reported, by Alebrahim et al. [8], to decrease with increasing the bulk concentration of  $Cu^{2+}$  ions.

On plotting the values of  $k_{Cu}$ , obtained from Fig. (10), versus current intensity, a strong linear relationship, shown in Fig. (11), was obtained.

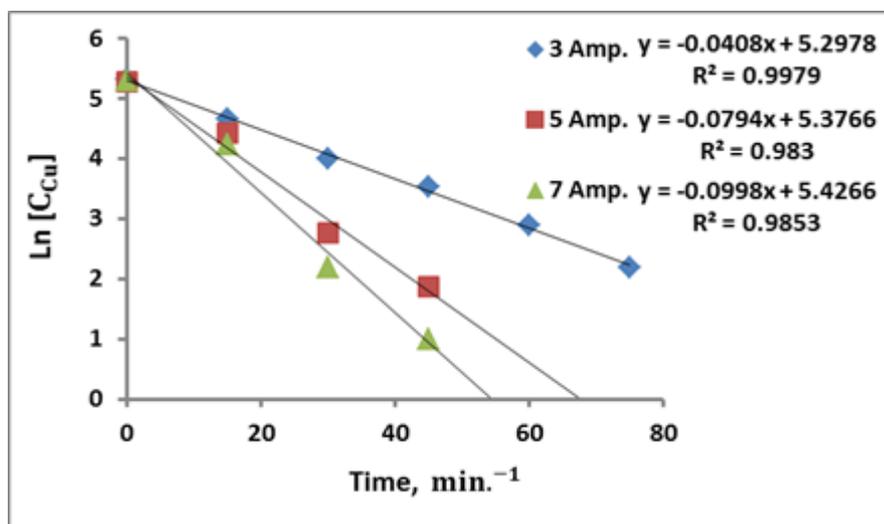


Figure 10: Effect of current intensity on kinetics of copper removal-(40 % Cu)

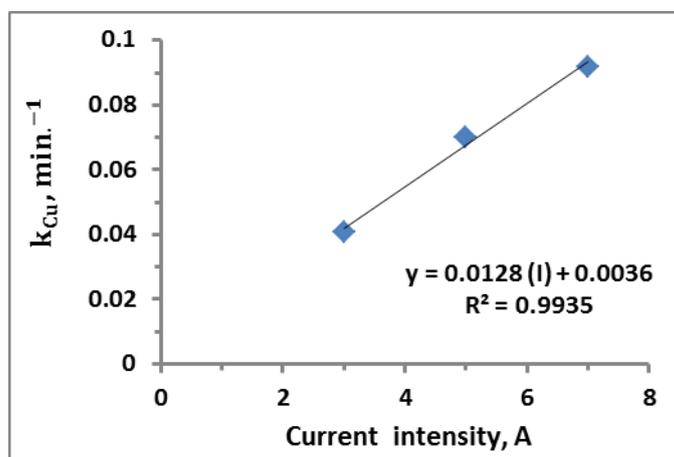


Figure 11: Relation between  $k_{Cu}$  and applied current intensity for Cu-(40 % Cu)

### 2.2.2 Kinetics of zinc removal

The results presented in Figure 12 illustrate the presence of three cases to the process of zinc electrochemical deposition:

- 1- At the applied current of 3 Ampere, the electrochemical removal of zinc followed the behavior aforementioned in 2.1.2.
- 2- At the applied current of 5 Ampere, the electrochemical removal of zinc was achieved via two time periods; i.e. the first period lasted for 30 minutes from the start and then the second period started thereafter. In these two periods the removal of zinc followed first order kinetic model with respect to

bulk concentration of zinc. As indicated in the figure, the value of the observed rate constant of the first period,  $0.0188 \text{ min}^{-1}$ , is smaller than that,  $0.0357 \text{ min}^{-1}$ , of the second period. The reason behind this observation might be interpreted according to what follows. In view of Fig. 3, the net rate of zinc deposition is the resultant of the two rate processes I and II and as is reported in the sub-section 1.1, if the rate of step I is larger than that of step II, the deposited zinc layer will be sustained. As, for copper and zinc, the rate of step I (electrochemical deposition) increased with increasing intensity of the applied current and the rate of the second step (cementation) decreased with the decrease in bulk concentration of copper ions, i.e. less zinc dissolution (an observation reported by Heba et al. [9], the difference between the two rates becomes in favor for zinc deposition.

- 3- At the applied current of 7 Ampere, the deposition of zinc started straight forward from the start in a single regime and followed first order kinetics with respect to the bulk concentration of zinc ions.

There is another important observation which is that the values of  $k_{Zn}$  is independent of the initial value of zinc concentration as long as the applied current intensity is constant which confirms what has been previously reported in 1.2. The relation between  $k_{Zn}$  and current intensity is still best described by the linear equation that is shown in Figure (13).

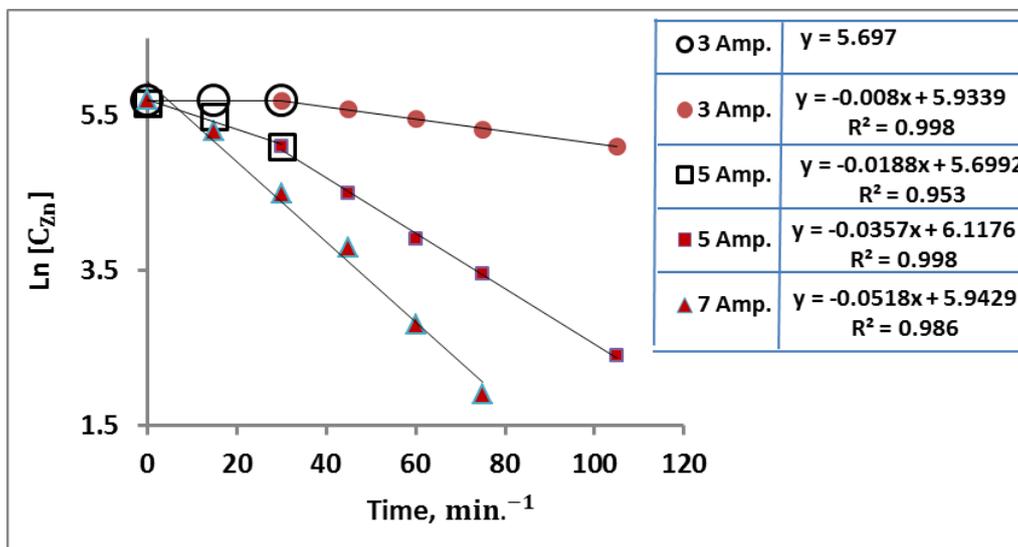


Figure 12: Effect of current intensity on kinetics of zinc removal-(40 % Cu)

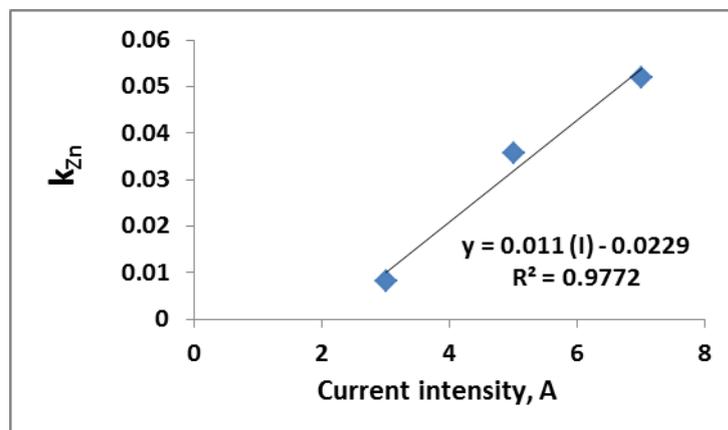


Figure 13: Relation between  $k_{Zn}$  and applied current intensity for Zn-(40 % Cu)

## CONCLUSIONS

The copper removal increased with decreasing the ratio of copper to zinc and followed first order kinetic model with respect to the bulk copper concentration in solution. The value of rate constant,  $k_{Cu}$ , decreased linearly with increased mass ratio of Cu to Zn.

The decay of zinc concentration, in solution, followed, as well, first order kinetic model with respect to the bulk concentration of zinc. However, the value of the rate constant,  $k_{Zn}$ , was found to be independent of the mass ratio of copper to zinc.

The value of both,  $k_{Cu}$  and  $k_{Zn}$  increased linearly with increasing intensity of applied current.

Selection of the intensity of the electric current to be applied depends on the aim of the removal process. If the primary goal is just the removal of copper and zinc, the intensity of electric current which enables removing process to be accomplished within short time, as practically possible, should be used. But if the primary goal is to remove and recover heavy metals, it is necessary to use the appropriate intensity of electric current to remove copper first then the removal of zinc is done at a later stage.

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