

# Removal of Copper From Wastewater By Cementation From Simulated Leach Liquors

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## Abstract

Every year, tons of precious and/or toxic metals are thrown away in industrial liquid effluents and most frequently directly in natural environment. The recovery of those metals in dilute solutions is an everyday problem associating both ecology and economy. Copper is among the most prevalent and valuable metal used by industry. Cementation is one of the most effective and economic techniques for recovering toxic and or valuable metals from industrial waste solution and from leach liquors obtained by leaching low grade copper ore. The present study was carried out to investigate the removal of copper metal ions from synthetic waste water by cementation using a rotating iron cylinder. The study covered the effect of different parameters in batch mode which are: Initial copper concentrations, pH values, rotational speed, and reaction temperature on the rate of cementation. The rate of cementation was found to increase with increasing rotational speed, temperature, and pH till a value of 2.1 and then starts to decrease. On the other hand as the initial copper ions concentration increases from 0.2 to 0.4 M the rate of copper ions removal increase. The rate of copper recovery ranged from 10% to 90% per hour depending on the operating conditions Rates of cementation which can be expressed in terms of the rate of mass transfer were correlated to the controlling parameters by dimensionless equation:

$Sh=0.18 SC^{0.33} Re^{0.961}$ . This equation can be used in the design and operation of high-productivity cementation reactor.

**Keywords:** Waste Water; Leach liquors; Cementation; Electrodialysis

## Introduction

The importance of environmental pollution control has increased significantly in recent years. Environmental lists are primarily concerned with the presence of heavy metals in aqueous effluents due to their high toxicity and impact on human and aquatic life [1]. Copper, which is very detrimental for both, aquatic life and biological treatment of wastewater can be found in many wastewater sources including printed circuit board manufacturing, metal finishing industry e.g. pickling of copper and its alloys, electroplating and electro less plating, electro polishing, paint manufacturing, wood preservatives and printing operations [2]. A number of technologies were developed over the years to remove copper from wastewater. The most important of these technologies include adsorption [3], chemical precipitation [4], ion exchange [5], reverse osmosis [6] and electrodialysis [7], but all of them have drawbacks. Cementation is one of the most effective and economic techniques for recovering toxic and/or valuable metals from industrial waste solutions [8]. The process has been largely used in industry for a long time, not only in hydrometallurgy but also in the purification process of stream and waste waters [9]. Cementation method has some advantages, such as recovery of metals in relatively pure metallic form, simple control requirements, low energy consumption and is in general low cost process. The main disadvantages of the technique are excess sacrificial metal consumption [10]. Cementation is used as a general term to describe the process whereby a metal is precipitated from a solution of its salts by another electropositive metal by spontaneous electrochemical reduction to its elemental metallic state, with consequent oxidation of a sacrificial metal for the recovery of more expensive and more noble dissolved metal species present in aqueous solutions [11]. The general reaction for a cementation process is given by [12]



where N represents the noble metal and M the reductant metal. This process has been applied in metallurgy, to recover metals from dilute leach liquors [13-18]. It is also exploited in metal finishing industry to recover noble metals such as copper from some waste solutions, etc. This article is concerned with the study of copper cementation in batch reactor containing rotating iron cylinder. Copper has been selected for a double interest: removal of toxic metals whose effects on the environment have been clearly proven beside the fact that copper is a valuable saleable product. Iron has been chosen as a sacrificial metal because of its availability and its low cost. In addition the present technique is used to recover copper from leach liquors obtained from low grade copper ores. Since copper cementation on less noble metal is diffusion controlled process [19], the aim of the present work is to enhance the rate of cementation of copper on iron by using a rotating iron cylinder. The rate of the copper (II)/iron cementation reaction in the presence of surfactant was determined by measuring the rate of cementation of copper on a rotating iron cylinder from a copper sulfate solution in the absence and the presence of surfactant were investigated by El-Batouti [20]. She reported that the rate of cementation reaction is decreased by an increasing concentration of surfactant, temperature and number of rotation. Sulka et al [21]. Who studied the kinetics of the cementation of silver ions onto copper from acidic sulphate solutions

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in a rotating cylinder system; they reported that the rotational speed leads to a considerable increase in the rate of cementation. Previous studies on Cu cementation have deal with wastewater which contains low  $\text{Cu}^{++}$  concentration [20, 21]. The present work deals with solutions containing relatively high  $\text{Cu}^{++}$  concentrations such as those obtained by leaching low grade copper ores or exhausted copper oxide catalyst. High  $\text{Cu}^{++}$  concentrations differ from dilute solution in their tendency for interionic attraction which affects properties such as electrical conductivity, diffusivity and ion activity [22]. In addition high  $\text{Cu}^{++}$  concentrations cause the formation of rough deposits which alters the hydrodynamics of rotating cylinders [23-26].

## Experimental part

The experimental set-up used in this study as well as the materials utilized will be presented. Properties evaluation methods are also shown

### Experimental set up

The experimental set-up is schematically shown in (Figure 1). It consists of 2 liters beaker and a rotating iron cylinder of 10 cm length and 2cm diameter that was positioned in the center of the beaker at a distance equal 2cm from the beaker. An iron cylinder was connected to multi speed agitated motor and was insulated with teflon.

### Materials

Before each run a stock solution of copper sulfate was prepared by dissolving the copper sulfate analytical reagent in distilled water. The experimental desired concentrations were obtained by successive dilutions with distilled water. The pH of the solution was adjusted by adding 0.1N hydrochloric acid solution each experiment. The pH- meter (Hana, Model pH211) was used to measure the pH of the solutions. The analytical determination of copper sulfate solutions was carried out by iodometry using standard solution of sodium thiosulfate [27].

### Experimental Procedure

Copper solutions were prepared from the stock solution by successive dilution to the desired concentrations. In each run 1750 ml of synthetic solution placed in the reactor cell. The pH of the solutions was adjusted by adding 0.1 N hydrochloric acid solutions for each experiment. Before each run cylinder rotation speed was adjusted at the required value, rotation speed was measured by an optical tachometer. During experiments, 10 ml samples were collected every 10 minutes from fixed location and analyzed for the percentage removal of copper ions. The rate of copper removal was determined under different parameters. Table 1 gives a summary of all studied parameters and their ranges. The physical properties of copper sulfate solution such as density and viscosity were measured experimentally using density bottle and Ostwald viscometer; whereas the diffusivity was calculated from literature (Table 2) [28].

## Results and discussion

### Effect of time

The effect of initial copper concentration on the rate of cementation was studied using 0.2, 0.3 and 0.4 M of copper ions (Figure 2). The data were assumed to fit the equation [29]:

$$V \ln(C_0/C) = KAt \quad (2)$$

Where:

V Volume of solution containing copper ions ( $\text{cm}^3$ ),

$C_0$  Initial concentration of copper ions (M),

C Concentration of copper ions at time t (M),

K Mass transfer coefficient for the smooth cylinder

A Active surface area of the rotating iron cylinder ( $\text{cm}^2$ ), and

t Time (s).

The mass transfer coefficient of copper cementation on iron (k) was calculated from the slope ( $kA/V$ ) of the plot  $\ln C_0/C$  vs t. It is clear from (Figure 2) that as the initial copper ions concentration increases from 0.2 to 0.3 M the percentage removal increases. According to the electrochemical theory of cementation which postulates that cementation takes place through the galvanic cell: Fe/ electrolyte/ Cu, increasing the cathode area via copper powder formation would decrease polarization and consequently would increase the rate of cementation. This phenomenon was also observed by AH Elshazly [30] in the case of copper cementation onto zinc plates. (Figure 3) shows that the present data fit equation (2) i.e. The reaction is first order with respect to  $\text{Cu}^{++}$  concentration, this finding is consistent with previous studies [20,21] on extremely dilute solutions i.e the concentration range of  $\text{Cu}^{++}$  does not alter the mechanism of the reaction.

### Effect of rotational speed

Figure 4 shows the effect of cylindrical rotation speed on the rate of cementation the mass transfer coefficient under different initial concentration of  $\text{Cu}^{++}$  was calculated from the slope ( $kA/V$ ) of the plot  $\ln C_0/C$  vs t., the mass transfer coefficient under different initial concentration of copper ions was calculated. The effect of rotational speed on the rate of reaction can be used to determine whether a reaction is diffusion or chemically controlled. If the rate of reaction increases with increasing the rotational speed, then the reaction is diffusion controlled. If the rate of the reaction is independent of the rotational speed, then the reaction is completely chemically controlled [20]. The diffusion controlled nature of the reaction was confirmed by the fact that the mass transfer coefficient increases systematically with increasing the speed of rotation, from 200 to 400, as shown in (Figure 4). The 400 rpm seems to be the optimum rotational speed, but 350 is better to save the power. Increasing the speed of rotation reduces the diffusion layer thickness across which copper has to diffuse to reach

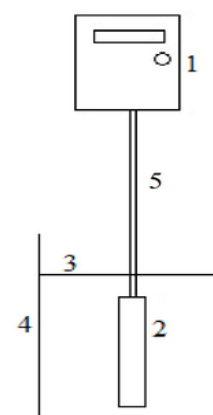


Figure 1: Schematic diagram of the experimental set-up. (1) variable speed motor, (2) Rotating iron cylinder, (3) Copper sulfate solution level, (4) 2L beaker.,(5) Motor shaft

Parameter	Range
Initial copper sulfate concentration (M)	0.2- 0.4
Cylindrical Rotational speed (rpm)	250 - 400
Temperature (oC)	25-55
pH	1.1- 4.1

Table 1: Summary of all studied parameters and their ranges

Cu <sup>++</sup> Concentration(M)	$\rho(\text{kg/m}^3)$	$\mu(\text{kg/m.s}) \times 10^3$	$D(\text{m}^2/\text{s}) \times 10^{10}$
0.2	1029	1.129	5.85
0.3	1051	1.221	5.41
0.4	1062	1.276	5.182

Table 2: Physical properties of copper sulfate solutions measured at 25°C

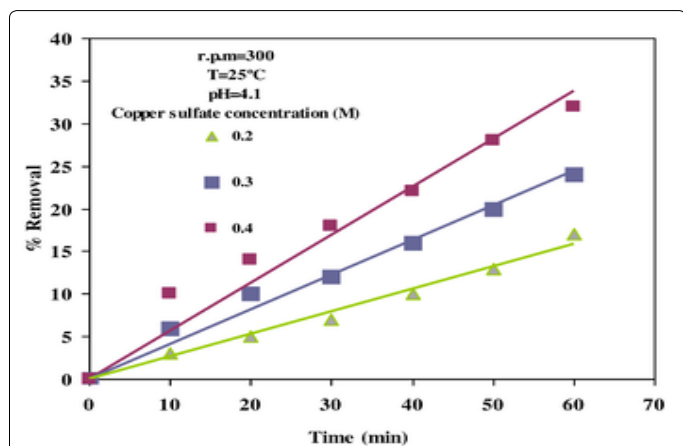


Figure 2: Effect of cementation time on the percentage removal of different copper sulfate concentrations

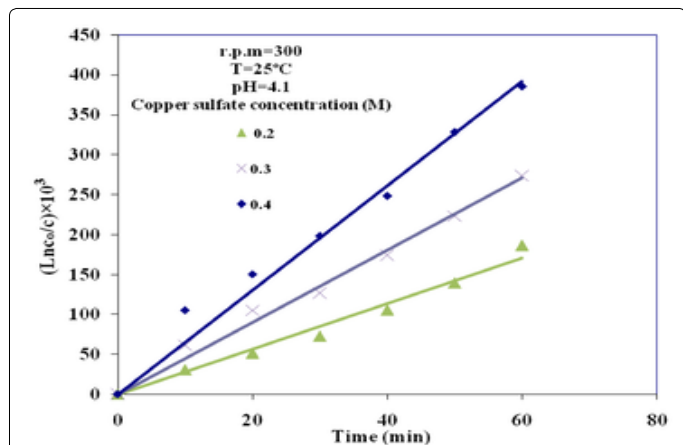


Figure 3:  $\ln(C_0/C_t)$  vs. cementation time at different copper sulfate concentration

the iron surface with a consequent increase in the rate of copper ions deposition. This phenomenon was also observed by S. A. Nosier [31] in the case of cadmium cementation onto a cylindrical zinc sheet.

### Effect of Initial pH of the Solution

It has been established that pH is an important operating factor influencing the performance of cementation process. In this work, the examination of the pH effect on the cementation process was studied for pH ranging from 1.1 to 4.1. Copper cementation onto iron substrate in an acid medium is accompanied by the simultaneous iron dissolution in acid that produces hydrogen and implies an over-consumption

of iron. The generated hydrogen bubbles increases local turbulence which enhances the rate of mass transfer [32]. So, from (Figures 6 and 7), it was observed that the mass transfer coefficient and the rate of cementation increases slightly from pH 1.1 to 2.1. However, for pH higher than 2.1, ferric hydroxide are produced, blocking the active surface and leading to more significant decrease of k value and the rate of cementation [33]. Therefore, a copper sulfate solution of pH= 2.1 is the optimum value.

### Effect of temperature

It has been found in many studies reported previously that the effect of temperature onto cementation reactions is significant. The variation of  $\ln(C_0/C_t)$  with cementation time t showing the effect of temperature (ranging from 25 to 55°C) is presented in (Figure 8). The values of the cementation rate constant k, calculated from the slopes of the curves by using Eq. (2). It can be seen from these results that the cementation rate increased greatly with the increase of temperature from 25 to 55°C. This last value of temperature seems to be the optimal one. The increase in the rate of cementation with temperature may be attributed to the increase in the diffusivity (D) of Cu<sup>++</sup> across the concentration boundary layer surrounding the rotating cylinder as a result of decreasing the solution viscosity ( $\mu$ ) according to the Stokes-Einstein equation [34]

$$\frac{\mu D}{T} = \text{constant} \quad (3)$$

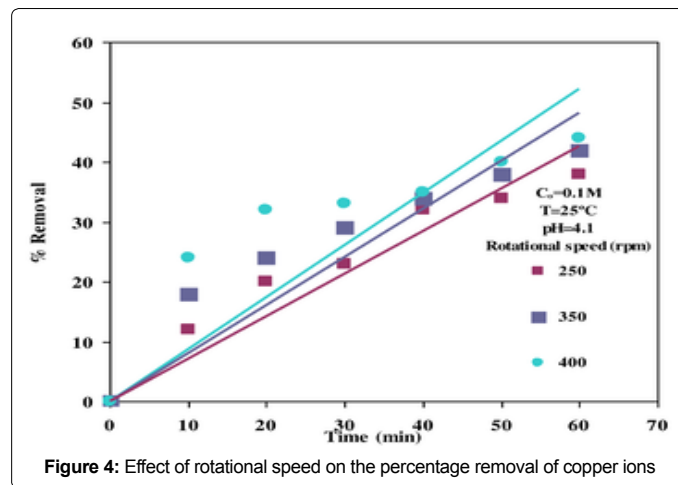


Figure 4: Effect of rotational speed on the percentage removal of copper ions

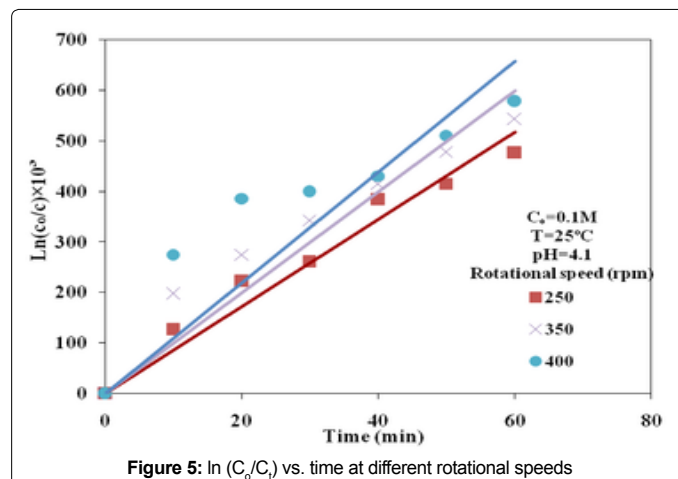


Figure 5:  $\ln(C_0/C_t)$  vs. time at different rotational speeds

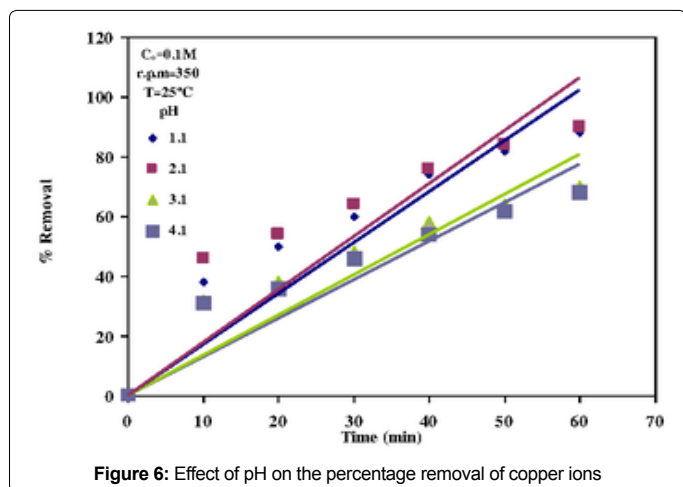


Figure 6: Effect of pH on the percentage removal of copper ions

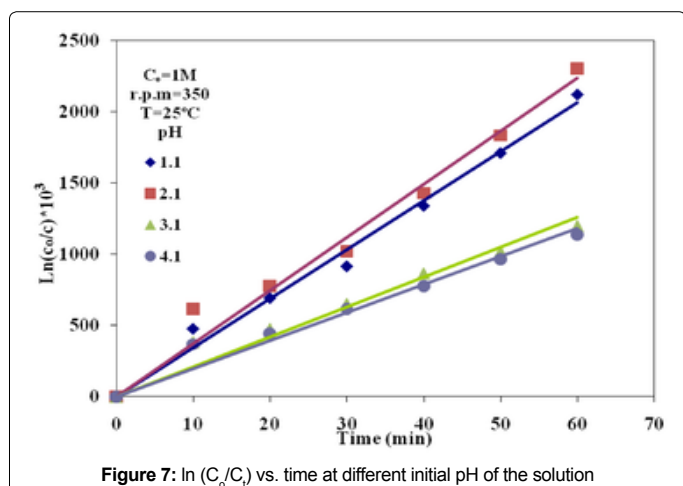


Figure 7:  $\ln(C_0/C_t)$  vs. time at different initial pH of the solution

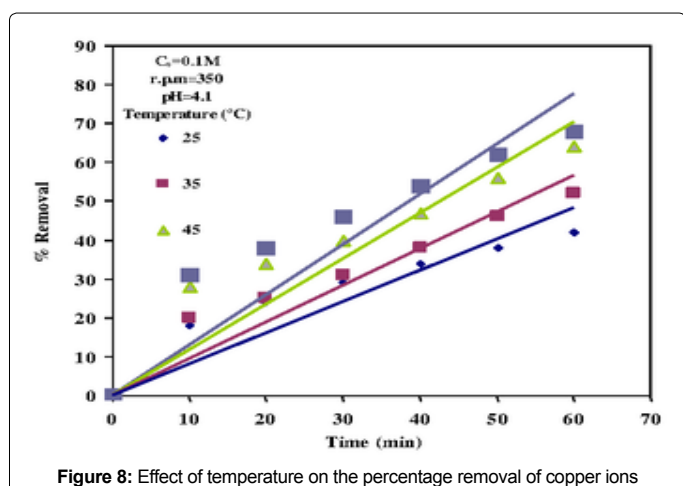


Figure 8: Effect of temperature on the percentage removal of copper ions

From Figure 10, according to Arrhenius equation:

$$K = A \exp(-E/RT) \quad (4)$$

Where  $E$  is the activation energy (kcal/mole),  $R$  is the universal gas constant (cal/mole.k).  $A$  is the frequency factor and  $T$  is the Kelvin temperature, we found that the value of the activation energy is 4.556. So, we can deduce that the reaction between the solution and the rotating cylinder is a diffusion controlled reaction.

The following dimensionless mass transfer equation was found to correlate the mass transfer coefficient to these variables:

$$Sh = 0.18Sc^{0.33}Re^{0.961} \quad (5)$$

Where  $Re$  is the Reynolds number ( $=\rho r \omega d^2/\mu$ ),  $Sc$  is the Schmidt number ( $\mu/\rho D$ ),  $Sh$  is the Sherwood number ( $Kd/D$ ),  $d$  is the iron electrode diameter (m),  $D$  is the copper iron diffusivity ( $m.s^{-2}\pi$ ),  $\omega$  is the rotation per second (Rps),  $\mu$  is the absolute viscosity ( $Kg.m/s$ ) and  $\rho$  is the density of solution ( $Kg/m^3$ ).

The exponent of  $Sc$  was fixed at 0.33 following previous theoretical and experimental studies in mass transfer. The exponent 0.961 was obtained by plotting  $\log Sh$  versus  $\log Re$  (Figure 11), for the conditions:  $1166 < Re < 5840$ ,  $Sc = 1744 - 35$ . The value 0.18 was obtained by a  $Sh$  versus  $Sc^{0.33}Re^{0.961}$  (Figure 12). Previous studies on mass transfer at rotating cylinder [23] have shown that for smooth rotating cylinders  $Sh$  increases with 0.7 power of  $Re$ . The exponent 0.96 obtained in this work may be attributed to the surface roughness induced by the deposited copper [23-26]. The above equation can be used in the design and operation of high-productivity cementation reactor.

## Conclusion

The majority of previous studies on the cementation have deal with extremely dilute solutions typical of waste water. The present study is concerned with cementation of copper from relatively high concentration of  $CuSO_4$  similar to solutions obtained by leaching low

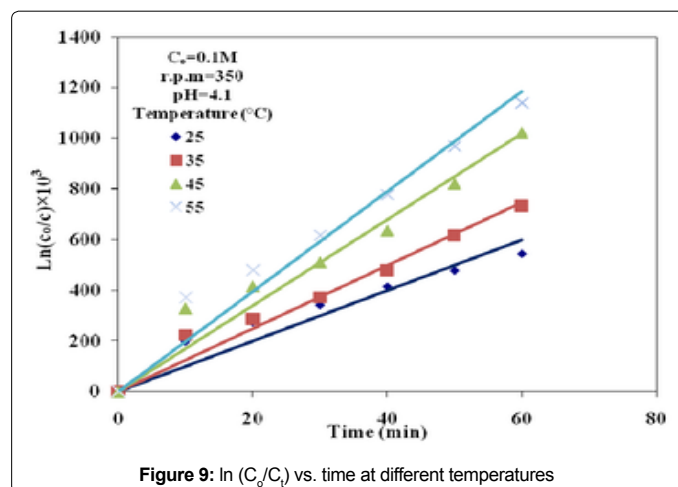


Figure 9:  $\ln(C_0/C_t)$  vs. time at different temperatures

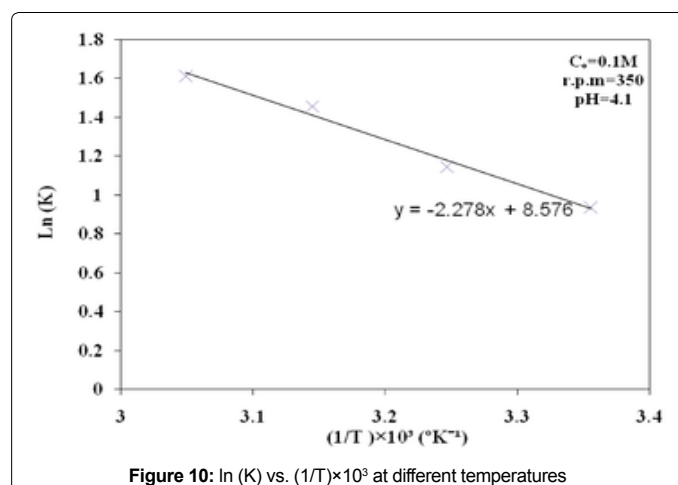


Figure 10:  $\ln(K)$  vs.  $(1/T) \times 10^3$  at different temperatures

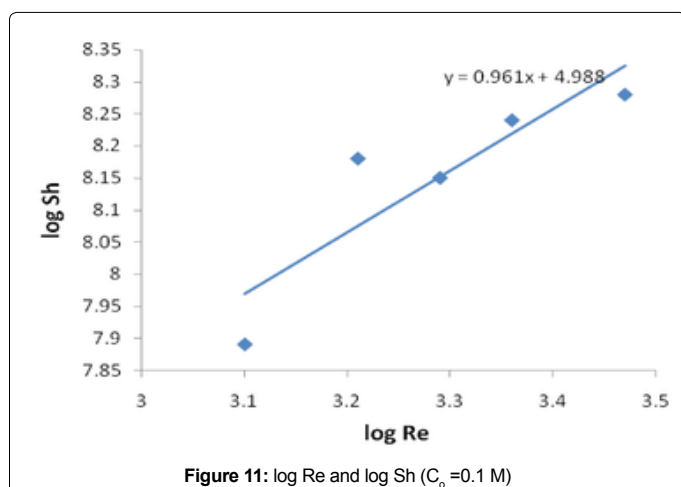


Figure 11: log Re and log Sh ( $C_0 = 0.1$  M)

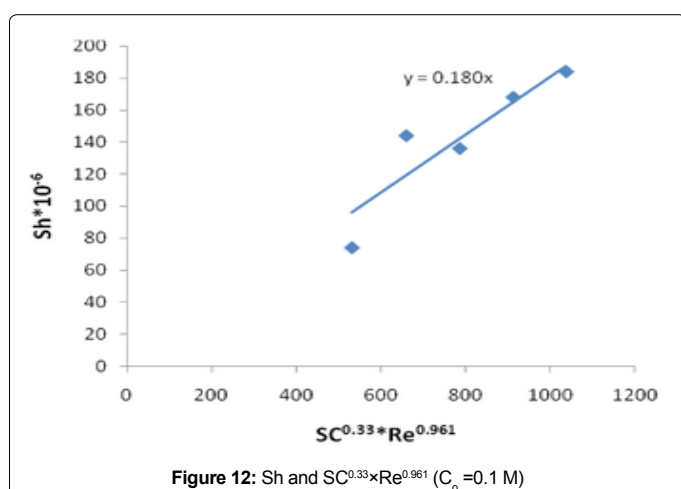


Figure 12: Sh and  $SC^{0.33} \times Re^{0.961}$  ( $C_0 = 0.1$  M)

grade ores and exhausted copper oxide catalyst on the rotating iron cylinder. This design offers high copper ions removal rate owing to the high degree of turbulence prevailing at the surface of the rotating cylinder even at low speed of rotation. The influence of variables such as cylinder rotational speed, initial metal ion concentration, initial pH of the solution and temperature were investigated. The results showed that the rate of copper removal increases with increasing rotational speed and temperature. It was also observed that as the initial copper concentration increases from 0.2 to 0.4 M the rate of copper ions removal increases. Another point worth mentioning is that the copper ions removal rate increases with increasing pH till a value of 2 and then starts to decrease. The optimum conditions for the cementation process by using the present cell based on maximum copper ions removal was rotational speed of 350 rpm, 55°C, pH of 2.1 and 0.2 M of copper ions. The rate of Cu recovery ranged from 0% to 90% per hour depending on the operating conditions.

## List of Symbols

N: the noble metal; M: the reductant metal; K: Mass transfer coefficient for the smooth cylinder; d: Iron electrode diameter (m); D: Copper iron diffusivity(m.s<sup>-1</sup>); v: Rotation per second (Rps); Re: Reynolds number ( $=\rho v d^2/\mu$ ); Sc: Schmidt number ( $=\mu/\rho D$ ); Sh: Sherwood number ( $=Kd/D$ ); V: Volume of solution containing copper ions (cm<sup>3</sup>); C: Concentration of copper ions at time t (M); Co: Initial concentration of copper ions (M); A: Active surface area of the rotating

iron cylinder (cm<sup>2</sup>), t: Time(s), E: the activation energy (kcal/mole), R: the universal gas constant(cal/mole.k) A: the frequency factor, T: the Kelvin temperature (°K).

## Greek letters

$\mu$ : Absolute viscosity (Kg.m/s);  $\rho$ : Density of solution (Kg/m<sup>3</sup>)

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