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Experimental Investigation of Mass Transfer for Copper Reduction by Weight Difference Technique

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Abstract

An experimental analysis was included to study and investigate the mass transport behavior of cupric ions reduction as the main reaction in the presence of 0.5M H_2SO_4 by weight difference technique (WDT). The experiments were carried out by electrochemical cell with a rotating cylinder electrode as cathode. The impacts of different operating conditions on mass transfer coefficient were analyzed such as rotation speeds 100-500 rpm, electrolyte temperatures 30-60 ℃, and cupric ions concentration 250-750 ppm. The order of copper reduction reaction was investigated and it shows a first order reaction behavior. The mass transfer coefficient for the described system was correlated with the aid of dimensionless groups as follows:

$$Sh = 3.77\, Re^{0.533}\, Sc^{0.356} \qquad 4075 < Re < 34088$$

Key words: Mass transfer coefficient, Electrodeposition of cupric ions, Weight difference technique (WDT).

Introduction

In the past years there was a special apprehension for the recovery / removal of copper from different types of waste (waste water with low or high amount of copper, waste printed circuit boards from dismantling electrical and electronic equipment, used batteries, ash from the burning of leftover) [1]. To get rid of large amounts of electronic remainders is causes environmental pollution and loss of precious resources [2, 3]. There are various techniques used for recovery of heavy metals and treatment of dilute metal impure water as a superfluity from mineral processing [4].

Contaminants are existing in certain concentrations in the environment as a result of human actions, having a significant negative influence on it. Due to the difficulty and the great cost of the methods for their management, a detailed analysis to determine the best techniques for their removal is required. The major sources of contamination with metal ions are the remainders from industrial activities in the following regions [5]:

- Metallurgy (etching, polishing).
- Mining (primary output of ores, mine waters).
- Hydroelectrometallurgy (exhausted electrolytes), istry (depleted electrochemical sources – batteries and accumulators).
- Electroplating, electrodeposition, (polluted baths).

- Chemistry (catalysts, chemical reagents, dyes).
- Leather (tanning).

It must be revealed that in every industrial unit wastewater encompassing metal ions are attained [5, 6]. Metal recovery from recyclable waste is a less energy consuming process than obtaining the metal from raw mineral resources (also taking into consideration the increasing restriction of resources). According [7], metal recycling processes involves diminished radiations of greenhouse gases – thus appreciably participate to the environmental safeguard.

Water is the basis of survival, the essential obligation for health and vital need for industrial development. This is the most precious item for the humanity. Water accessibility is reducing and for this reason it is essential to preserve the water quality.

Disposal of metal ions from water is a main regard because these pollutants can be collected in humans and their presence clear long-term influences and several illnesses. The common metal ions that have significant influences on human health are cadmium, lead, and copper [8].

All copper compounds are actually poisonous. Human can be subjected to copper by air inhalation, and water swallowing. A portion of copper poisonousness is due to the creation of monovalent ions that have the capability to produce greatly interactive free roots. Copper can bring illnesses influencing the brain, liver, and neural system. An amount of copper in sea water above acceptable restrictions could destruct marine life. This affects fish and other marine organisms [8].

Copper may approach the environment from mines, plantations, industrial plants by wastewater thrown into rivers. Copper can be reached also in the air from natural sources such as volcanoes, decomposing plants, and forest fires. Drinking water can comprise high amounts of copper if the pipes through which is pumped are made of copper. Rivers has been handled with copper composites to govern algae growing, or water seeping from power plants and soils may encompass great content of copper [8].

The aim of the present work is to design and construct a copper recovery cell so as to study the effect of various operating parameters on the mass transfer coefficient.

Theory

Mass transfer plays an important role in chemical and electrochemical operations. It is the motion of materials from one situation in the solution to another emerges from variation in concentration, electrical or chemical potential at the two situation. The reaction of cathodic copper deposition is used to study mass transfer at the rotating cylinder electrode (RCE) [9].

In general, the mechanism of mass transfer depends upon the dynamics of the system in which it occurs. There are two distinct modes of mass transport, molecular diffusion mass transfer and convective mass transfer, are analogous to conduction heat transfer and convective heat transfer [10].

Molecular diffusion mass transport is a slow process in which the transfer of matter is due to random motion, from high concentration region to low concentration region, of stationary molecules by influence of their thermal energy or from fluids moving in laminar flow independent of any convection effects, although it is nevertheless show even in turbulent flow. The net flow of each molecular species occurs in the direction of a negative concentration gradient and hence increase the mass transfer rate [10].

Convective mass transfer encompasses the transfer of material between a boundary surface and an moving fluid, or between two immiscible moving fluids, this category of transfer based on the transport properties and the dynamic of the flowing fluid. The mechanical agitation has generated fast motion of large portion of fluids called eddies from the position to another. These eddies make transport in turbulent region more rapid than in laminar region [10].

By retaining to the Fick's first law which is used to define mass transfer rate (flux):

$$N_j = k_m \Delta C_j \qquad \ldots(1)$$

$$k_m = \frac{N_j}{\Delta C_j}$$

It is obviously clear that by calculating the mass transfer rate N_j and the difference in the concentration ΔC_j, the mass transfer coefficient can be determined.

N_j can be calculated by dividing the weight of the specimen before and after the experiment (ΔW) by the area of specimen, time of experiment, and atomic weight of copper as shown by the following equation:

$$N_j = \frac{\Delta W}{A \times t \times A_w} \qquad \ldots(2)$$

$\Delta C_j = C_o - C_f$, can be measured from knowing the cupric ions concentration before experiment C_o, and the cupric ions concentration after experiment C_f which was calculated by atomic absorption device, type Analytikjena, German origin.

For the recovery of Cu^{+2} in electrolyte contain H_2SO_4, under convection, mass transfer can be described by a dimensionless group correlation of the following expression [11]:

$$Sh = aRe^{b}Sc^{0.356} \qquad \ldots(3)$$

Experimental Work

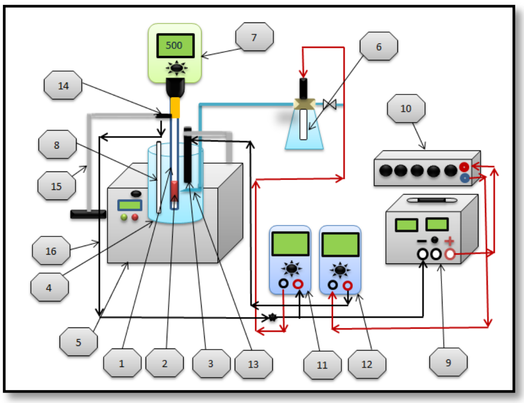
1. Materials

In this study the electrolyte solution used was composed of:

- Annular grade sulfuric acid provided by SD Fine–Chem Limited company (purity > 98 wt%, sp.gr. 1.84) is used. Sulfuric acid is diluted by distilled water to prepare 0.5M H_2SO_4 solution.
- Copper sulfate petahydrate ($CuSO_4.5H_2O$) provided by ROMA company is used as redox system to give various concentrations of cupric ions 250, 500, and 750 ppm.

2. Cell and Circuit

The experimental apparatus which were used for performing the present work is shown in Figure 1. The cell consisted of beaker of capacity 2 liter, the anode was a compressed graphite cylindrical bar (insoluble) is an electrical conductive material used for copper recovery, which had 28 mm diameter and 15 cm length, rotating cylinder electrode (RCE) used as the working electrode (cathode) made of copper having 25 mm outside diameter and 20mm inside diameter and 3.2cm length. The rest of rotating electrode (shaft) was made of teflon, the distance between electrodes is 3cm. The electrical circuit consisted of 6V DC power supply, connected in a series with cell and ammeter. A voltmeter was connected in parallel with the reference electrode and cathode.



1. Rotating shaft, 2. Working electrode (specimen), 3. Graphite electrode (anode), 4. Beaker, 5. Water bath, 6. Reference electrode (SCE), 7. Digital stirrer, 8. Thermometer, 9. Power supply, 10. Resistance box, 11. Voltmeter, 12. Ammeter, 13. Luggin capillary tip, 14. Brush, 15. Stand, 16. Electric wires.

Fig. 1: Schematic diagram of experimental setup

3. Electrochemical Reaction

In this stud the reduction of cupric ions was considered as shown in the following equation in order to determine k_m for this process with the aid of weight difference technique.

$$Cu^{+2} + 2e^{-} \xrightarrow{\quad\quad} Cu \qquad \ldots(4)$$

Results and Discussion

Table 1 shows the determined mass transfer coefficient k_m by weight difference technique under different operating conditions.

Figure 2 describe the effect of rotation rate on mass transfer coefficient k_m calculated by WDT. It is clear from these figures that by increasing the rotation rate resulting in rises k_m as presented for a given temperature. This can be ascribed to the increase in the transfer rate of cupric ions near to the electrode surface by eddy transport. Increasing velocity leads to decrease the diffusion layer thickness at the surface due to eddies break through diffusion layer diminishing its thickness which exhibits the attraction resistance to copper transfer [12].

Table 1: k_m by WDT under different operating conditions

T, ℃	Rotation rate (rpm)	$k_m \times 10^3$ *(cm/s)* for 250 ppm Cu^{+2}	$k_m \times 10^3$ *(cm/s)* for 500 ppm Cu^{+2}	$k_m \times 10^3$ *(cm/s)*for 750 ppm Cu^{+2}
30	100	4.266196	4.315825	6.247023
	200	5.297857	5.832570	7.481934
	300	6.515114	7.894590	8.971969
	400	8.040995	9.870073	10.86129
	500	8.916118	11.21638	12.67958
45	100	4.670039	5.891485	7.294601
	200	5.770343	7.535745	8.357544
	300	7.281437	9.178956	10.13139
	400	8.692206	10.73127	11.88552
	500	9.527953	11.68249	14.10500
60	100	5.465652	6.837334	8.253200
	200	7.320438	8.681214	10.31207
	300	8.624342	9.951418	12.00958
	400	10.59190	11.61391	13.82989
	500	11.68399	12.61508	15.02930

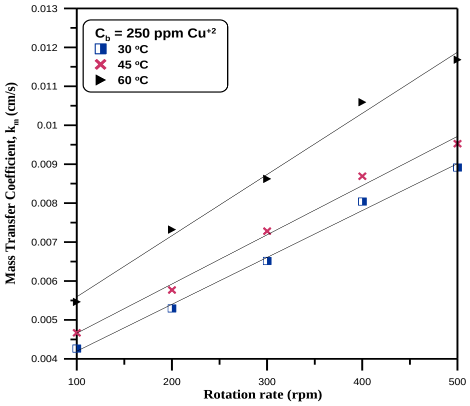


Fig. 2: k_m vs. rotating rates at different temperatures for electrolyte containing 250 ppm Cu^{+2}

It is obvious from Figure 3 that as of the temperature increases k_m increases. This is due to the fact that by increasing temperature it will accelerate reaction rate. Furthermore, increasing temperature will increase the diffusion coefficient of electroactive species (cupric ions) [12, 13], which causes a slight increase in solution conductivity and decreases the viscosity and hence increase the diffusion rate of cupric ions to the electrode surface [14].

It can be presented from Figure 4 that increasing cupric ions concentration leads to increase the mass transfer coefficient. This can be attributed to the fact that by increasing the cupric ions it will increase the driving force (concentration difference) and in the same time it will increase the electrical conductivity of solution and lowerers the solution resistivity for the current flowing between electrodes, i.e. this assists the copper removal from solution and its precipitated on cathode [14].

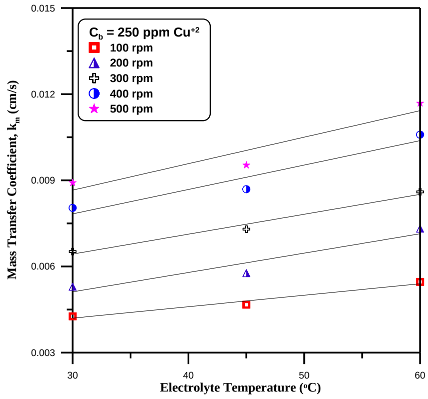


Fig. 3: k_m vs. electrolyte temperatures at different rotation rates for electrolyte containing 250 ppm Cu^{+2}

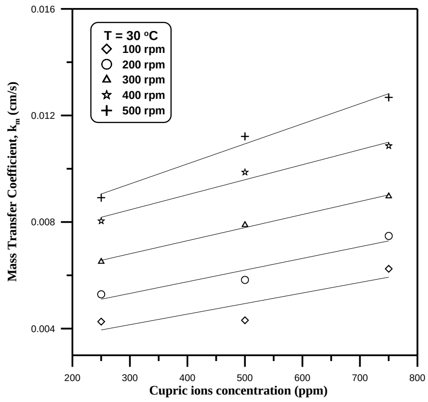


Fig. 4: k_m vs. cupric ions concentration at different rotation rates and 30 ℃

Figure 5 displays the plot of *log* $Sh/Sc^{0.356}$ vs. *log Re* at various operating conditions for WDT technique, an upright line was obtained, its slope is ***b***, while the intercept is ***a***.

From the above figures ***a*** and ***b*** were found for WDT technique as presented in the following equation:

$$Sh=3.77\,Re^{0.533}\,Sc^{0.356} \qquad \ldots(5)$$

For the range $4075 < Re < 34088$

Figure 6 presents cupric ions concentration against time so as to examine the order reaction for copper reduction. It can be seen from the above figures that the concentration of cupric ions decreased in a nonlinear way, so the reduction reaction of copper which is under mass control is first order reaction and that is a good agreement with [15] as show in Figure 7. It can also be observed that removal of cupric ions increased with increasing rotation rates and electrolyte temperature. For a constant temperature, it can be noticed the removal of cupric ions was achieved at 500 rpm higher than at 100 or 300 rpm due to the increase in rotation rate resulting in rising the copper reduction rate.

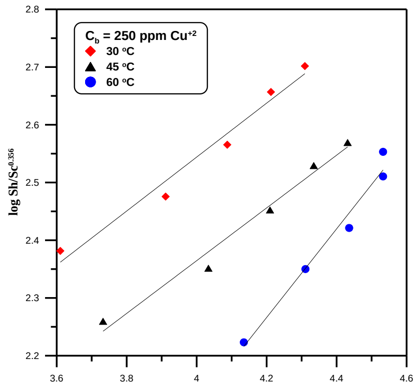


Fig. 5: The relation between *log* $Sh/Sc^{0.356}$ against *log Re* for electrolyte solution contains 250 ppm Cu^{+2}

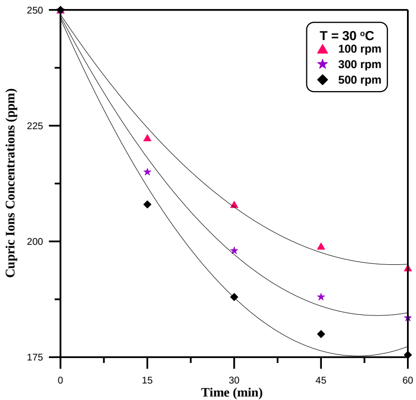


Fig. 6: Cu^{+2} concentrations against time for electrolyte contains 250 ppm Cu^{+2} at 30 ℃

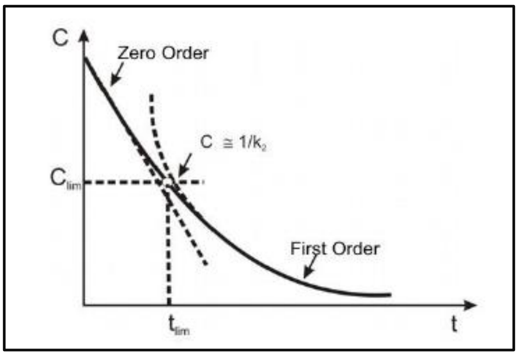


Fig. 7: Behavior of a variable-order reaction [15]

Conclusions

1. The most effective parameter on k_m is the rotation rate and the smallest effective parameter is the cupric ions concentration.
2. The reduction reaction of copper is a first order reaction.
3. The mass transfer coefficient increased with the increasing in electrolyte temperature for both techniques.
4. RCE proved useful for rapid heavy metal ions removal studies.

Nomenclature

A = Cathode area, cm^2

a = constant used in Eq. 3

b = constant used in Eq. 3

C_o = initial concentration of cupric ions, mol/cm^3

C_f = final concentration of cupric ions, mol/cm^3

d = diameter, cm

D = diffusion coefficient, cm^2/s

k_m = mass transfer coefficient, cm/s

N_j = diffusional flux of electroactive species, $mol/s.cm^2$

Re = Reynold number, U d/v

Sh = Sherwood number, k_m d/D

Sc = Schmidt number, v/D

T = temperature, ℃

U = velocity, cm

ΔC = concentration difference between initial concentration and final concentration, mol/cm3

v = kinematic viscosity of cupric ions, cm^2/s

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