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Cementation of Copper with Zinc Metal from Monometallic Sulphate Solution Using Stirred Reactor.

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ABSTRACT

This manuscript deals with the cementation of copper from monometallic sulfate solution onto zinc sheet in a simple stirred reactor. Firstly, the effects of initial copper ions concentration, initial pH of the solution, stirring speed, reaction temperature and mass of zinc sheet on copper removal were investigated. Secondly, a kinetic study was carried out in order to shed light on the effect of each parameter on the rate constant of the reaction. Thirdly, a correlation for predicting the rate constant was obtained using a statistical and least square multivariate regression technique. R^2 of the obtained correlation was 97.4%.

Keywords: Wastewaters; Heavy metals; Cementation kinetics; Copper removal

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INTRODUCTION

Heavy metals (HMs) are classified among the most persistent pollutants in wastewater; i.e. they cannot be destroyed or degraded. Most of these metals become toxic at high concentrations due to their ability to accumulate in living tissues [1]. Wastewaters may contain heavy metal ions, such as Ag, Au, Cd, Co, Cr, Cu, Ni, Pb, and Zn ions, up to the concentration of 1000 mg/l [2]. They must be adequately treated before being discharged into waste streams or better recycled within the processing plant. The driving forces behind removing and better recycling (HMs) include:

- Economic; many of (HMs) are valuable such as Ag, Cu and Ni.
- Environmental; i.e. reduces the environmental impact and health risks.
- Energy and resource conservation; removal and recycling of (HMs) is important from the perspective of saving energy; for instance the recycle of copper saves 85 % of energy consumption of that used to get copper from its ore [3].

Various methods are employed to remove or recover the undesired metal impurities from wastewaters streams, such as neutralization with acid or base solution, chemical precipitations, cementation, crystallization, solvent extraction, flotation, ion exchange, adsorption onto different adsorbents, reverse osmosis, electro-dialysis, electro-winning and electro-deposition [4, 5, 6, 7 and 9]. These methods have some drawbacks. For example, chemical precipitation requires extremely long settling time; ion exchange and adsorption processes are slow and expensive, and may require frequent regeneration for adequate performance; reverse osmosis, electro-dialysis, electro-winning and solvent extraction methods are very expensive, and have high operating costs [10]. Alebrahim M. F. [8] used electrochemical deposition technique and recovered copper as Cu_2O not as Cu metal.

Cementation is one of the most effective techniques for removing/recovering toxic and valuable metals from industrial waste streams [11]. Cementation is a metal-replacement process in which a solution containing ions of less active metal, e.g. Cu^{+2} , comes in contact with a more active metal such as zinc. A spontaneous electrochemical occurs leading to the reduction of the ions to its elemental metallic state and oxidation of the neutral atoms to its ionic form. It has been applied for the removal/recovery of toxic and valuable metals from waste solutions; [12].

Literature survey on cementation process indicates that the process is mainly affected by several parameters. Some parameters are related to the physical properties of the treated solution; i. e. the initial pH (pH_0) and the initial concentration (C_0) of the metal to be removed and/or recovered. Some others, operating parameters, are temperature, flow condition, and type of sacrificial metal and its geometrical shape.

Some authors did not study the effect of pH_0 , [13, 6, 14, 15 and 16]. Stankovic et al. [17] Using a packed-bed column filled with brass particles, i.e. Zn was the sacrificial metal, reported the decrease of copper cementation rate with increasing pH_0 . The data presented by [18], however, indicate that the cementation of copper on granular zinc increased with increasing pH_0 and the maximum cementation rate was obtained at the free pH (= 4), this is the natural pH of the copper chloride solution used in their experiments.

For the effect of $(C_0)_{\text{Cu}}$, Young et al. [19] did not study its effect, Stankovic et al. [17] and Donmez et al. [20] claimed that low cupric ion concentrations are in favor of a high cementation rate, HOR and Mohamed [14] reported that the initial concentration had no significant influence on the copper removal rate. Also Demirkiran and Kunkul [21] and Ekmekyapar et al. [22] reported that the removal copper increased as the concentration of copper ions is increased. The effect of flow was studied by several authors; [16, 17 and 22] they reported that increasing turbulence condition enhances the removal of Cu. Considering the effect of temperature on removal of copper, some researchers [6 and 16] did not study its effect and some others [15, 21 and 22] reported the increase of removal rate with temperature.

Based on this shortened review, there is a need to investigate explicitly the effect of the previously mentioned parameters on copper removal/recovery from monometallic solutions containing it. Therefore, the main aim of this work is to investigate the removal/ recovery of copper from monometallic solutions by cementation on zinc; by fulfilling the following research objectives:

- To investigate the effect of pH_0 , C_0 , solution temperature, agitation speed and mass of chemically active metals on removal/recovery of copper from simulated monometallic solutions.
- After performing the experimental part, attention was directed towards the assessment of cementation kinetics. Multiple regression analysis method was utilized in order to get a correlation for predicting the apparent rate constants of the process.

EXPERIMENT WORK

1. SET UP

Figure (1) shows a schematic drawing of the experimental set-up. It consisted of cylindrical glass container (reactor) of 10.5 cm internal diameter and had a capacity of 1L. At the central axis of the container a paddle impeller of 4 cm outer diameter, made of 316 S.S. was positioned 4 cm above the bottom of the container. The impeller was connected to a variable speed motor via 316 S.S. shaft of 0.5 cm diameter. Both the impeller and the shaft were covered with epoxy resin so that to be isolated from the treated solution to avoid their participation in the cementation process. A thermometer was placed inside the container to adjust and follow the temperature of the treated solution. The container and its contents were immersed in a rectangular water bath that enabled manual adjustment of its temperature and consequently the temperature of processed solution. In order to keep the water content of the treated solution, a vertical water condenser was mounted at the top of the container to condense evolved water vapor.

2. MATERIALS

All used chemicals, shown in Table (1), were analytical grade and purchased from El-Gomhouria Company for Trading Chemicals and Medical Appliances; Egypt.

Table 1 Chemicals used in the experimental work

Item No.	Species name	Chemical formula	Purity/ Concentration
1	Copper sulfate	$CuSO_4 \cdot 5H_2O$	98.5 %
2	Sulfuric acid	H_2SO_4	98 %
3	Sodium hydroxide Pellets	NaOH	98 %
4	Acetone	C_3H_6O	99 %
5	Iron sheet	Fe	99 %
6	Zinc sheet	Zn	99.9 %

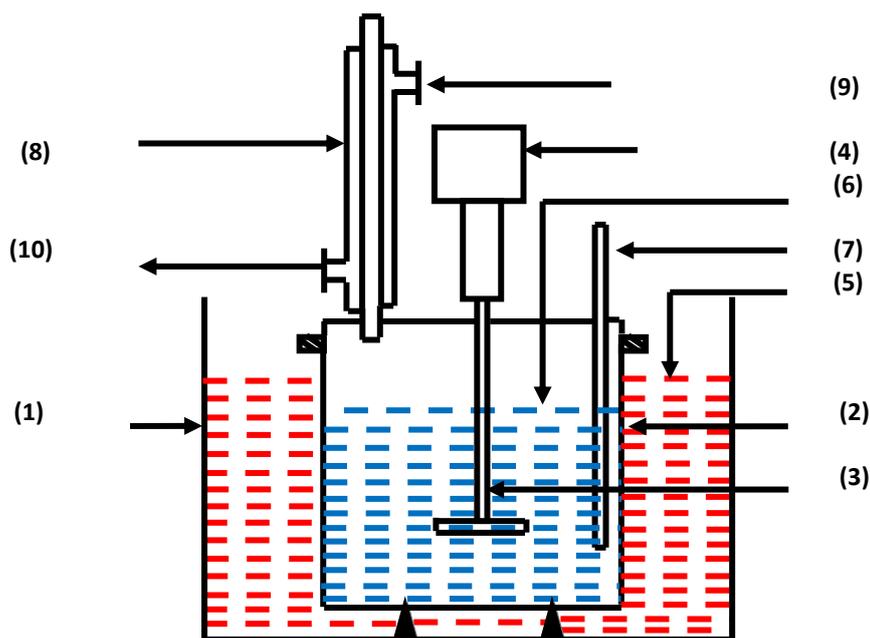


Figure (1) Experimental apparatus:

- | | |
|--------------------------------|------------------------|
| 1. Rectangular water bath | 6. Electrolyte level |
| 2. Cylindrical glass container | 7. Thermometer |
| 3. Agitator | 8. Condenser |
| 4. Variable speed motor | 9. Input cooling water |
| 5. Water level | 10. Output water |

3. METHODOLOGY

Before the commencement of a set of experiments, a solution of the metal to be removed was prepared, at a specified concentration of the metal ions; by dissolving its metal salt in freshly distilled water. Using (JENWAY, 3505 pH meter of accuracy ± 0.02), the initial pH of the solution was adjusted by adding drops of an acid or (0.1 M) sodium hydroxide solution. A sample of the solution was taken to measure the initial concentration by atomic absorption spectrophotometer (Perkin Elmer 2280). The surfaces of a precipitant metal sheet were degreased with acetone, cleaned from any adhered oxides by using emery paper of grit size 320 CAMI (Coated Abrasive Manufacturers Institute), etched in diluted HCl to remove any remained oxides, thoroughly washed with distilled water and then dried.

In each run 500 ml of the synthetic solution were placed in the reactor. The rotational speed of the impeller was selected and the motor was turned on. Into the agitated solution a specified mass of precipitant metal (sheet) was added. At fixed time intervals 2 ml samples were withdrawn by a pipette. The pH and copper concentration were measured. The removal of copper was determined under different parameters in order to find the most appropriate removal conditions. Table (2) shows all the studied parameters and their ranges. In another experiment, iron (sheet) was used instead of zinc under the observed appropriate conditions; in order to assess the effect of changing the precipitant metal on removal of copper.

Table 2: Studied parameters and their ranges

Parameter	Range
Initial copper concentration (mg/l)	200, 300, 800
Rotational speed (rpm)	300, 500, 700
Temperature (°C)	30, 40, 50, 60
pH	1, 2, 2.98, 3.22, 5.22
Mass of Zn (g)	0.5, 1.7, 2.4

RESULTS AND DISCUSSION

1. Effect of various parameters on the cementation of copper on zinc sheet

The cementation reaction between copper ions containing solution and metallic zinc occurs according to the following reaction:



E° for this reaction is 1.1 V which is greater than 0.36 V; hence diffusion of Cu^{+2} to Zn surface controls the above reaction [23].

1.1 Effect of initial concentration

Figure (2) depicts the effect of initial copper concentration on the rate of cementation. This set of experiments was accomplished at 40 °C, 500 rpm, 1.7g Zinc and pH of 3.22. It is obvious that the cementation of copper increased as the C_o of Cu^{2+} was increased; which agrees with the previous observations [21 and 22]. In these two manuscripts the authors attributed the increase of copper cementation, with increasing C_o , solely to the porous nature of the deposited copper and the ease of Cu^{2+} ions diffusion through it. Meanwhile, they ignored the increase of concentration difference between that in the bulk solution and the concentration at the surface of Zn with increasing C_o . This concentration difference is the driving force for diffusion.

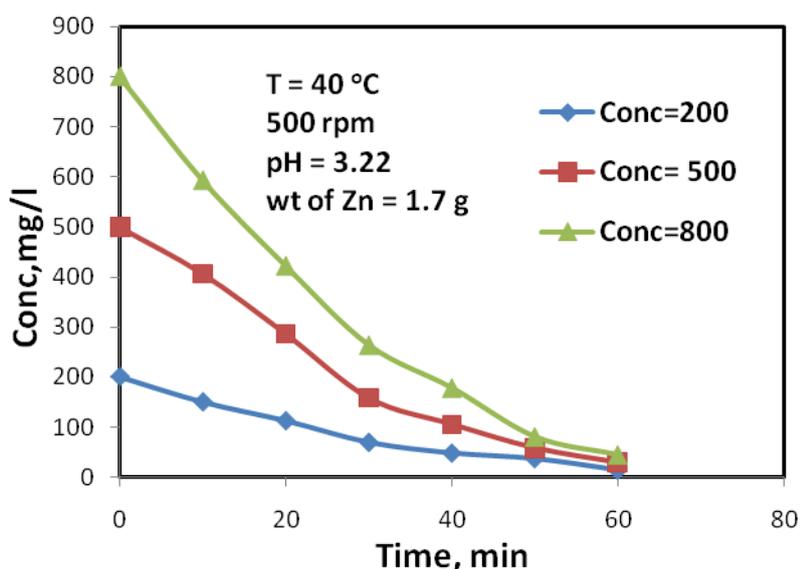


Figure (2) Concentration of copper ions vs. time at different initial concentrations of copper

1.2 Effect of rotational speed

To determine the effect of stirring speed on cementation of copper, experiments were carried out at the concentration of 500 mg/l, temperature of 40 °C, mass of Zn 1.7g and pH value of 3.22. The results are illustrated in Figure (3). The results elucidate that the rate of cementation of copper increased with increasing stirring speed; i.e. increased turbulence. Increasing the rotation speed decreased the thickness of the diffusion layer across which copper had to pass through to reach the zinc surface, this lead to decreased diffusion resistance and consequent increased copper deposition rate. This observation was also reported by several authors using different experimental setups [6, 15, 24, 21 and 25]. The same behavior was reported by Nosier S. A. [26] in the case of cadmium cementation onto a cylindrical zinc sheet.

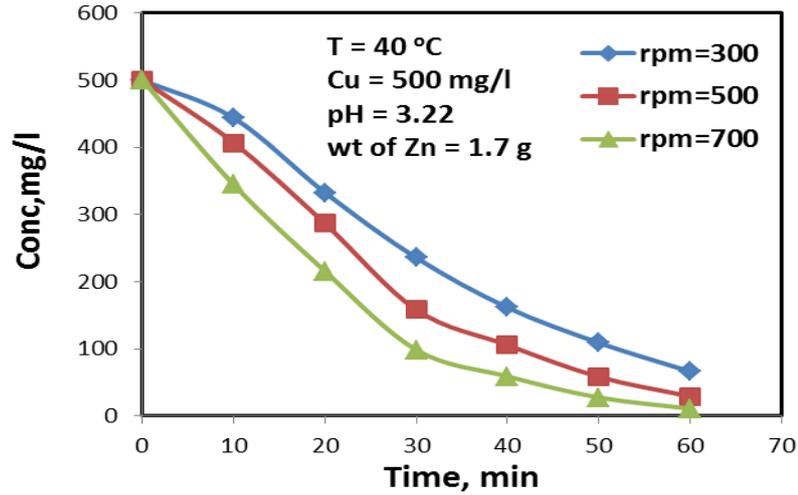


Figure (3) Concentration of copper ions vs. time at different stirring speed

1.3 Effect of temperature

The effect of temperature was examined (ranging from 30 to 60 °C). In these experiments other parameters were hold constant at the initial concentration of 500 mg/l, stirring speed of 500 rpm, Zn mass of 1.7g and initial pH value of 3.22. The effect of temperature is presented in Figure (4). The cementation rate increased with the increase of temperature from 30 to 60 °C. The increase in the rate of cementation with temperature is a consequent of the increase in the diffusivity (D) of Cu²⁺ with increasing temperature as expressed by the well known Stokes-Einsten equation:

$$D_{T_2} = D_{T_1} \frac{T_2}{T_1} \frac{\mu_{T_1}}{\mu_{T_2}} \quad (2)$$

Where T is the absolute temperature and μ is the viscosity of liquid solvent. When $T_2 > T_1$, then $\mu_{T_2} < \mu_{T_1}$ and consequently $D_{T_2} > D_{T_1}$. This behaviour was reported by several authors [15, 24, 21 and 22].

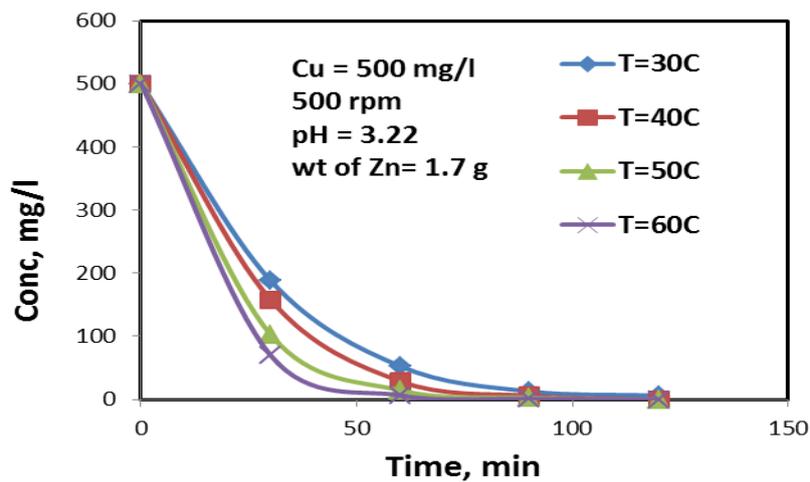


Figure (4) Concentration of copper ions vs. time at different temperature

1.4 Effect of Initial pH of the Solution

Inspection of the pH₀ effect on the cementation of copper on zinc was investigated under different pH₀ values ranging from 1 to 5.22 (free pH). The initial concentration of solution, stirring speed, Zn mass and temperature in these experiments were 500 mg/l, 500 rpm, 1.7g and 30 °C, respectively. The results are shown in Figure (5). It is obvious that the cementation rate of copper increased with increasing pH₀. This behavior is

directly related to the decrease of H^+ concentration with increasing pH_0 . The following reactions are competitive to the cementation of copper on zinc:



The rates of these two reactions, certainly, decrease with decreasing H^+ concentration and, therefore, more copper ions are discharged.

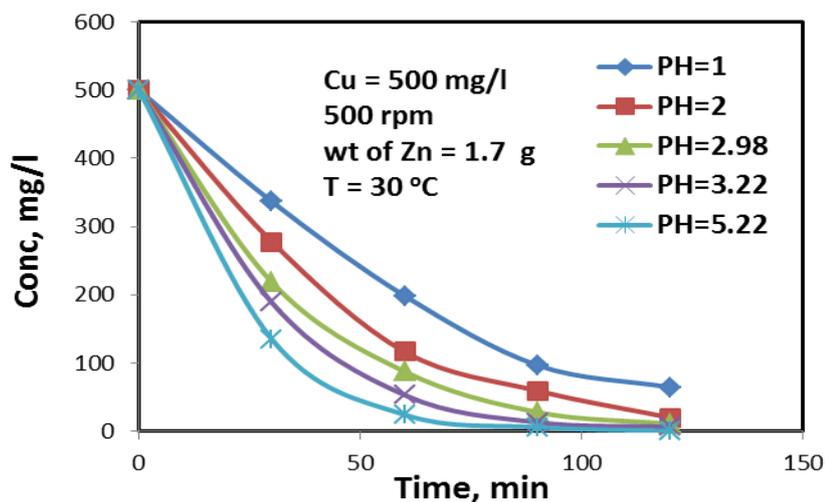


Figure (5) Concentration of copper ions vs. time at different pH values

1.5 Effect of mass of zinc sheet

To elucidate the role played by mass of zinc sheet, i.e. surface area of zinc, on cementation rate. Experiments were carried out by changing mass of zinc from 0.5 to 2.4 g while keeping other operating at constant values; i.e. temperature = 30 °C, stirring speed = 500 rpm, pH = 5.22 (free pH) and Cu^{2+} concentration = 500 mg/l. The choice of the free pH was necessary in order to minimize as much as possible the dissolution of zinc at lower pH values. Figure (6) shows the obtained results. It can be seen that the rate of cementation of copper increased with increasing of zinc mass. As the mass of zinc sheet increases, there will be larger surface area of zinc sheet per copper ion which results in increasing cementation rate of copper.

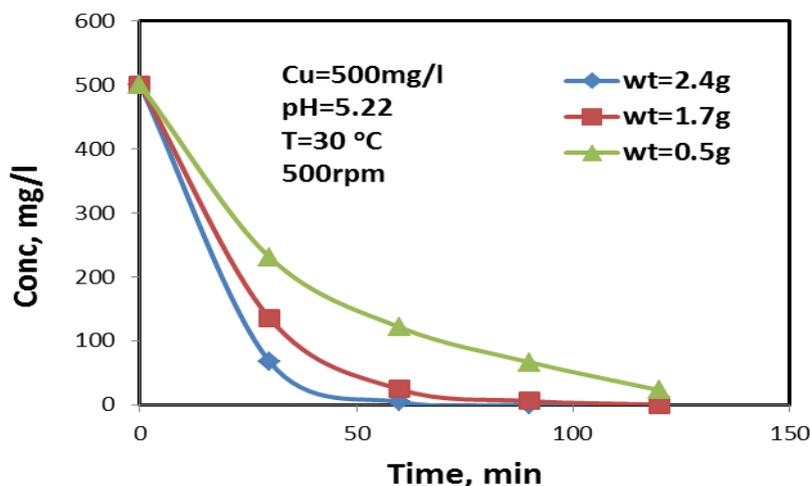


Figure (6) Concentration of copper ions vs. time at different zinc masses

It is important to mention that as the mass of zinc was increased the curves, describing the rate of cementation, got closer and it may coincide after a certain mass of zinc.

2. The cementation of copper by iron sheet

Iron can also be used to cement copper according to Eq. (5).



E^0 of this reaction is 0.777 V which is less than that of reaction (1) and as a consequent Zn is stronger than Fe for removing copper. Figure (7) illustrate comparison between the cementation of copper by iron and zinc sheets. It is clear that the use of zinc sheet resulted in higher removal of copper. The removal percentage of copper ions by using Zn sheet was 100% in less than 2 hr but by using iron, it was 82% under the same conditions of initial concentration, rotational speed, pH, temperature and mass of Zn or Fe. This gives the opportunity to tailor the process of copper removal; for instance, if the treated solution contains copper and iron, then iron will be the sacrificial metal.

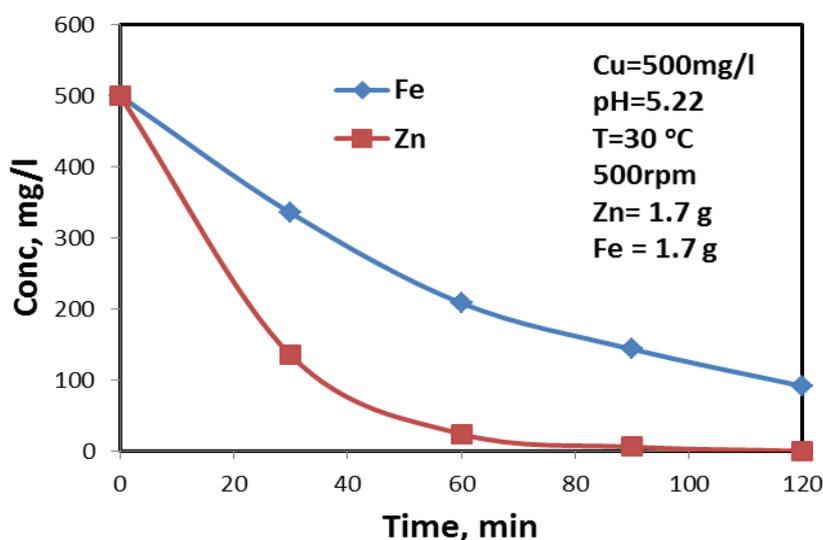


Figure (7) Concentrations of copper ions vs. time using iron and zinc sheets

KINETIC ANALYSIS

Cementation of copper with zinc is a heterogeneous electrochemical reaction. As mentioned in the section of results and discussion, the process is affected by several operating parameters. Therefore, this section was directed to determine the order of reaction, to assess the effect of each operating parameter on the reaction rate constant and finally to find a correlation for predicting the rate constant.

Figure (8) shows a plot of $\ln(C)$ versus time for different initial copper concentrations (C_0) under constant values, indicated in the figure, of other operating parameters. The plotted results indicate that the cementation reaction follows a first order kinetics and the value of the rate constant (k) increases with increasing initial concentration of copper. On plotting values of k versus C_0 a linear relationship was obtained as shown in Figure (9). For elementary reactions, it is acknowledged that the rate constant is independent of the initial concentration of the reactant. Such behavior was not observed in the current work and, therefore, it can be stated that the cementation reaction follows a pseudo first order kinetics.

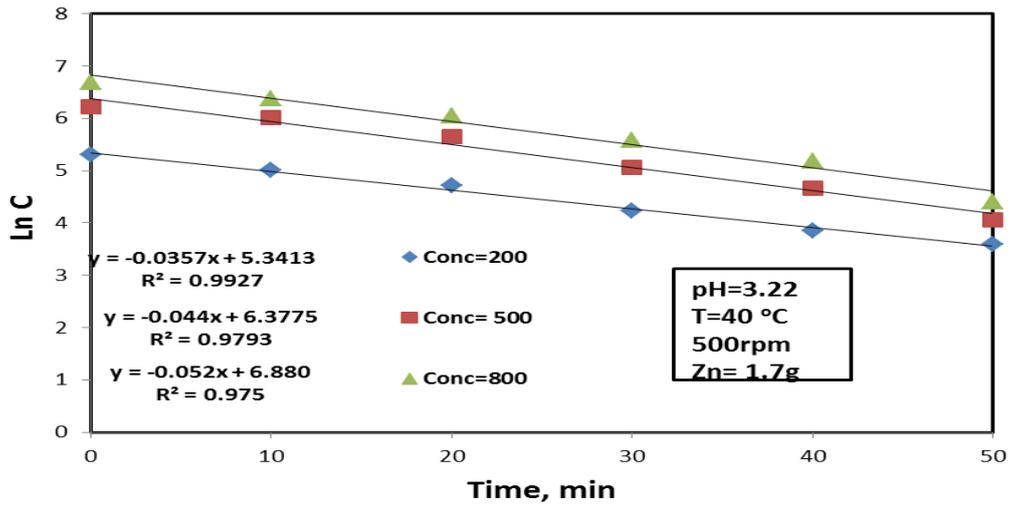


Figure (8) In [C] vs. Cementation time at different initial copper concentration

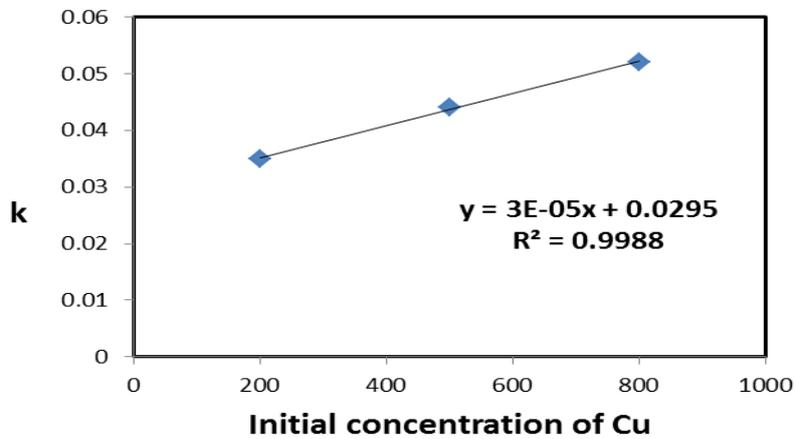


Figure (9) Rate constants vs. initial concentration of copper

The effect of the rotational speed on the kinetics of copper cementation is shown in Figure (10). The results, as well, indicate the first order kinetics of the process and k increases linearly with the rotational speed of the agitator as indicated by Figure (11).

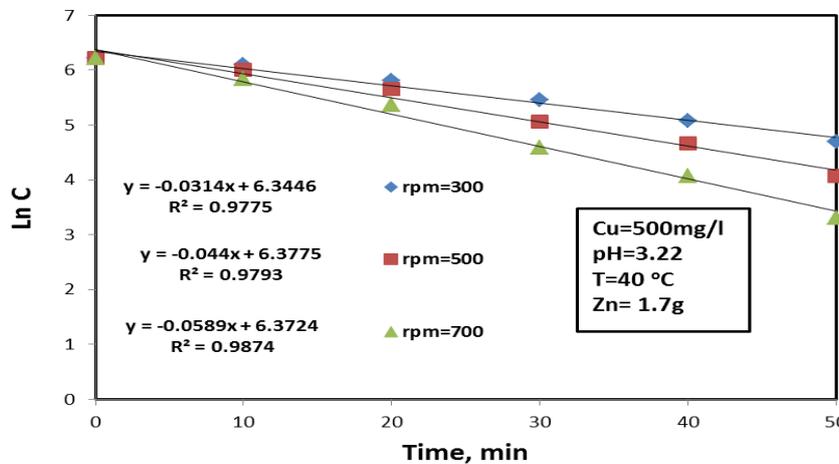


Figure (10) In [C] vs. Cementation time at different rotational speeds

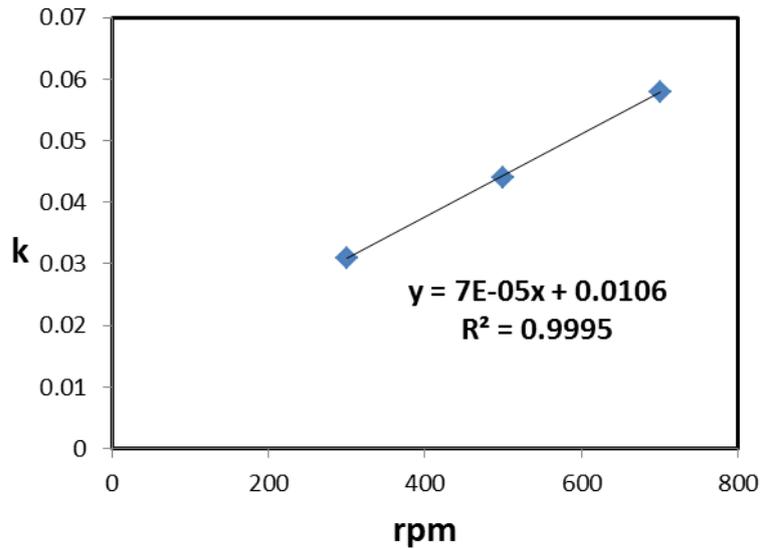


Figure (11) Rate constants vs. rpm

The effect of the initial pH of the treated solution on the kinetics of copper removal is shown in Figure (12). For all values of pH₀, linear relationships between ln (C) and time were obtained and the slope of a line, the reaction rate k, increased with increasing pH₀ under similar operating conditions. On plotting values of k with pH₀, Figure (13), a linear relationship was also obtained.

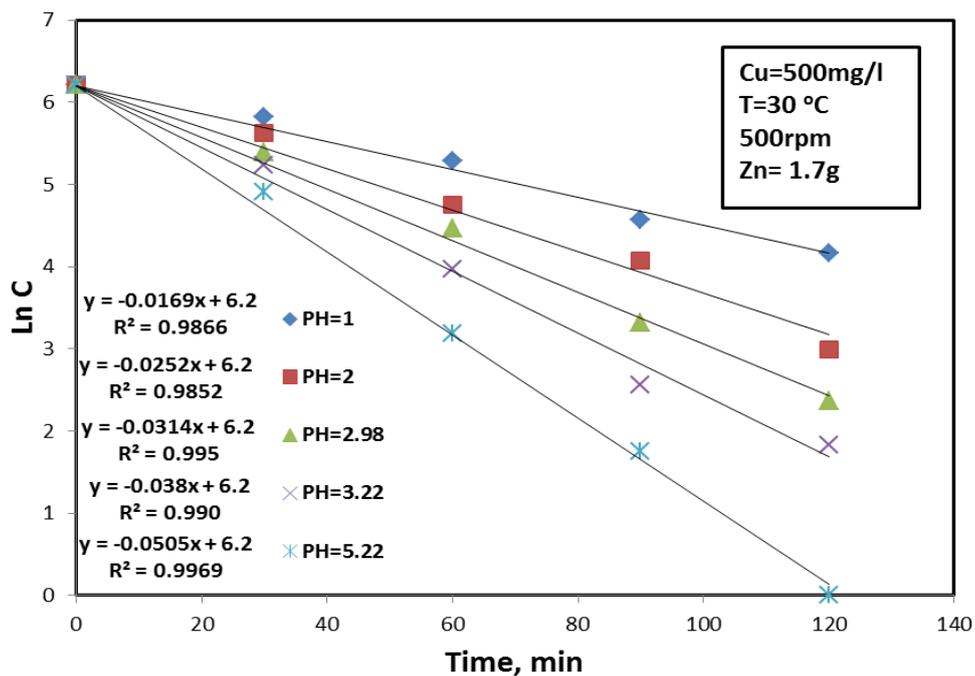


Figure (12) ln [C] vs. cementation time at different initial pH of the solution

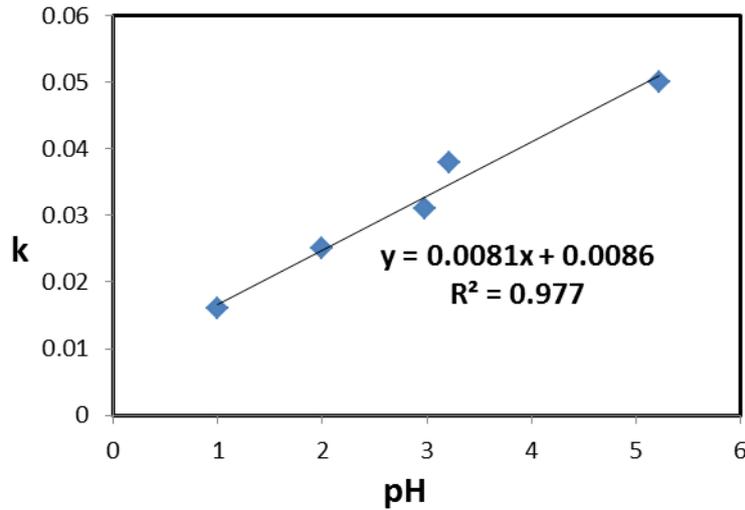


Figure (13) Rate constants vs. pH

The effect of changing temperature, while keeping other operation parameters at constant values, of the treated solution on the kinetics of copper removal was investigated. The results presented in Figure (14) confirm, as well, the first order kinetics of the process and the increase of rate constant k with increasing the temperature of reaction.

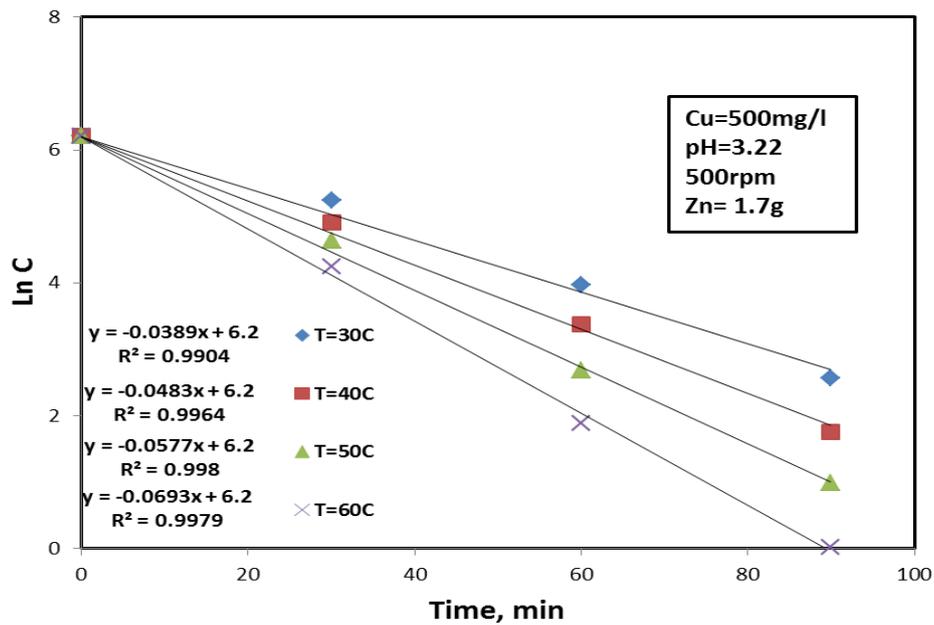


Figure (14) $\ln [C]$ vs. cementation time at different temperatures

Arrhenius plot, Figure (15), was constructed between $\ln(k)$ and the reciprocal of absolute temperature. The figure illustrates that the process proceeds in a single mode with an activation energy of 16.304 kJ/mol. It is interesting to find that Amin et al. [27] reported an activation energy of 3.99 kcal/mol (16.67 kJ/mol) for the cementation of cadmium on granular zinc using a rotating fixed bed reactor and Donmez et al. [20] reported 14.1 kJ/mol for cementation of copper with aluminum.

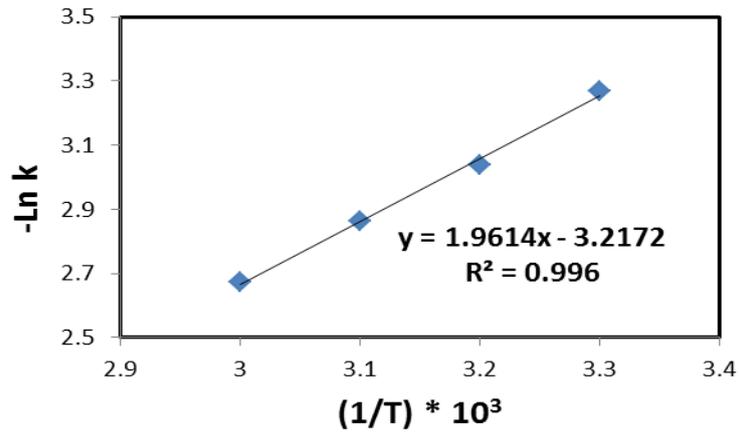


Figure (15) Arrhenius plot for copper cementation reaction

The effect of zinc mass on the kinetics of copper removal is shown in Figure (16). It might be observed that reaction rate constant increased with increasing the mass of zinc sheet. According to Figure (17) a linear relationship correlates k with the mass of zinc sheet. The increase of k with increasing mass of zinc, however, might not exist at after a certain value of zinc mass as was previously pointed out in 1.5.

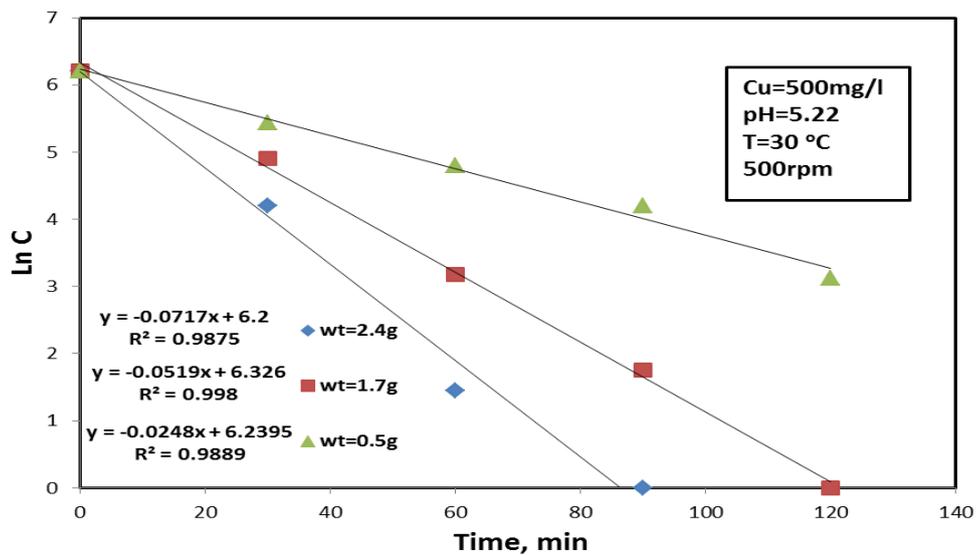


Figure (16) $\ln [C]$ vs. cementation time at different zinc masses

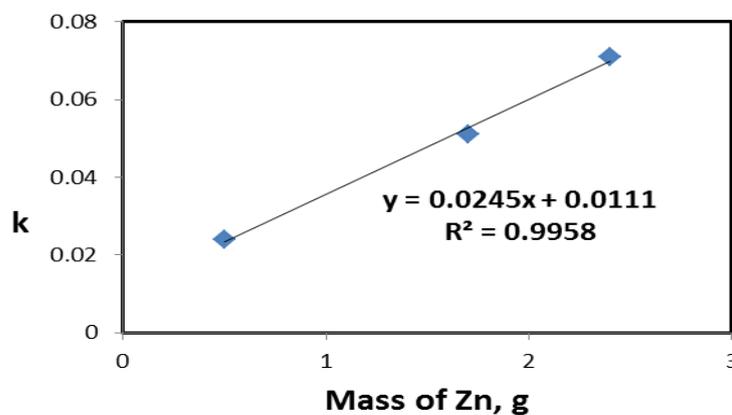


Figure (17) Rate constants vs. mass of zinc

CORRELATION FOR PREDICTING k

To represent the influence of the operating parameters on the rate constant *k* of cementation of copper on zinc, a mathematical correlation must be proposed. Statistical and least square multivariate regression techniques are frequently employed for modeling and analysis of problems in which a response of interest dependent variable is influenced by several independent variables. The presented results in section of kinetic analysis indicate that *k* depends on *C*₀, pH₀, rotational speed (RS), temperature (T) and mass of zinc. The effect of zinc mass was ignored due to the reason over mentioned in 1.5. The model takes the following form.

$$k = b_0 + b_1 \text{pH}_0 + b_2 T + b_3 C_0 + b_4 \text{RS} + \epsilon \tag{6}$$

Where *b*₀ to *b*₄ are the coefficients of the correlation, *C*₀ is the initial copper concentration (mg/l), RS is the rotational speed (rpm), pH₀ is the initial pH of solution, T is the reaction temperature (K) and ϵ is the error which is the difference between the observed experimental values and the correlation prediction values. The values of *k* obtained from Figures (8, 10, 12 and 14), given in Table (3), were used to get the correlation. The values and p-values of the coefficients are given in Table (4). All the p-values are less than 0.001 which means that each term of the correlation is significant.

Table 3: The apparent rate constants and their correlation coefficients

Parameters	First order kinetic model	
	k, min ⁻¹	R ²
Concentration, mg/l		
200	0.035	0.992
500	0.044	0.979
800	0.052	0.975
Temperature, K		
303	0.038	0.990
313	0.048	0.996
323	0.057	0.998
333	0.069	0.997
Rotation speed, rpm		
300	0.031	0.977
500	0.044	0.979
700	0.058	0.987
pH		
1	0.016	0.986
2	0.025	0.985
2.98	0.031	0.995
3.22	0.038	0.990
5.22	0.050	0.996

Table 4: Value and p-value of each term coefficient

Coefficients	Values	p-values
<i>b</i> ₀	- 0.375852203	4.18464 * 10 ⁻¹¹
<i>b</i> ₁	0.007708421	7.5217 * 10 ⁻⁷
<i>b</i> ₂	0.001150249	6.51387 * 10 ⁻¹¹
<i>b</i> ₃	2.08034 * 10 ⁻⁵	1.32855 * 10 ⁻⁵
<i>b</i> ₄	4.96376 * 10 ⁻⁵	1.07604 * 10 ⁻⁶

Coefficients *b*₁, *b*₂, *b*₃ and *b*₄ of the independent parameters pH₀, T, *C*₀ and RS, respectively, are positive which results in an increase in *k* with increasing their level, i.e. increase of Cu cementation.

Figure (18), on the other hand, shows the normal probability of standardized residuals and the mean of correlation errors is equal to zero. The linear distribution of the residual errors indicates that the errors are normally distributed which means that the predictions of the model are not biased.

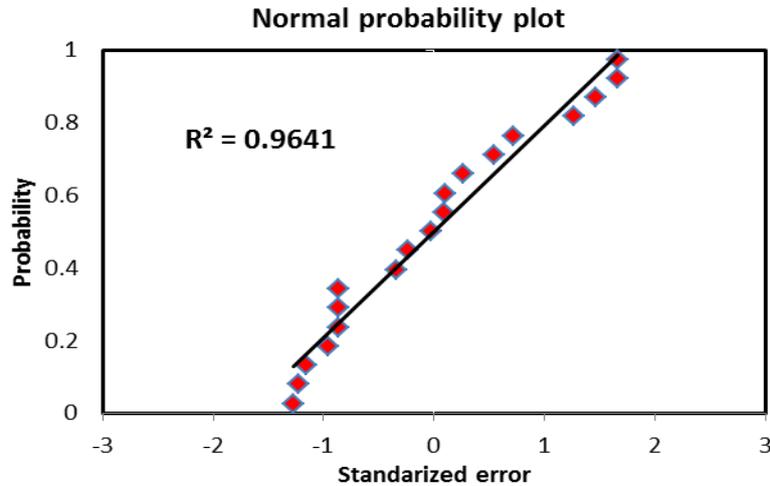


Figure (18) Normal probability of standardized errors

According to table (4) the effect of the operating parameters on k , in a decreasing order is $pH_o > T > C_o > RS$.

Figure (19) shows a comparison between the experimentally observed data and correlation predictions. The figure shows a good agreement between them. It can be claimed that the present correlation well fits the experimental data and consequently we can use it to predict values of k when zinc sheet as sacrificial metal.

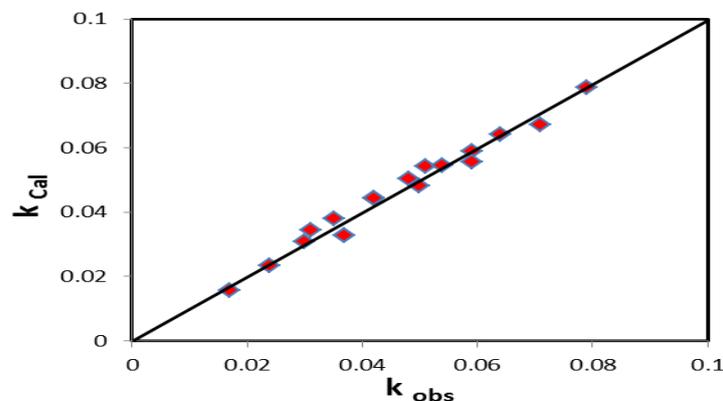


Figure (19) Calculated k vs. observed k

CONCLUSIONS

- Removal of copper from monometallic solution by cementation on zinc was efficiently done in a simple-agitated reactor. Complete removal of copper was possible in less than 60 minutes operating time.
- Cementation reaction is heterogeneous in nature and follows a pseudo first order kinetics. The rate constant was found to be a function of pH_o , T , C_o and RS .
- The cementation of copper on zinc is a single-regime process and has activation energy of $16.304 \text{ kJ mol}^{-1}$.
- A correlation for predicting the rate constant was obtained by applying least square multivariate regression technique. The obtained correlation has the form

$$k = -0.376 + 0.0077 pH_o + 0.00115 T + 2.08 \cdot 10^{-5} C_o + 4.96 \cdot 10^{-5} RS$$

- The effect of the operating parameters on k , in a decreasing order is $pH_o > T > C_o > RS$.

NOMENCLATURE

C_0	Initial concentration of copper, mg/l
T	The reaction temperature, K
pH_0	The initial pH of solution
k	Apparent rate constant, min^{-1}
D	Diffusivity
μ	Viscosity of liquid solvent
ϵ	The error which is the difference between the observed experimental values and the correlation prediction values
b_0 to b_4	The coefficients of the correlation
E°	Electrode potential
E_a	The activation energy of reaction, kJ/mol

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