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Removal Of Toxic Cu^{++} In Presence Of Amino Acids



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ABSTRACT

The rate of copper II/iron cementation reaction in presence of aminoacids as glycine, alanine, and phenyl alanine was measured at different temperatures using atomic absorption spectrophotometer. It was found that, the rate of cementation decreases with increasing the percentage of composition of amino acids and increases by increasing temperature and the number of rotation. Thermodynamic parameters ΔH^* , ΔG^* and ΔS^* were calculated. © 2007 Trade Science Inc. - INDIA

INTRODUCTION

Cementation is one of the most effective and economic techniques for recovering toxic and valuable metals from industrial waste solution^[1]. Cementation is also used in purifying leach liquor prior to electrowining of metal^[2]. From its solution by a loss noble metal which is usually cheap and non toxic. Cementation reaction are also used in purification of solution for example in the process of steam purification in the addition of zinc powder to zinc electrolyte in order to eliminate cations such as copper and cadmium which would otherwise reduce the current efficiency of the subsequent step of zinc elec-

trodeposition^[3]. More recently effect of surfactant on the removal of Cu^{++} from waste water.

Heavy metals such as copper, nickel, chromium, mercury and cadmium, etc. are present in many industrial waste waters and must be removed prior to discharge. The presence of these toxic ions in the waste water effluents causes severe pollution problems. Various treatment processes have been developed to remove heavy metals from waste water^[1]. The cementation processes has been used in industry for a long time not only in metallurgy^[2] but also in the purification of processes cams and wastewater^[3-6]. The cementation reaction is an electrochemical process by which a more noble metal precipi-

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tated from solution and is replaced in solution by a metal higher in electromotive forces. The removal of heavy metals such as copper and lead by cementation has been studied by a number of researchers^[7]. The lead removal from waste water by cementation using a fixed bed of iron spheres^[8]. Furthermore, the cementation of copper from dilute copper sulphate solution on fixed bed of iron powder. The surface geometry used was a zinc cylinder. Previous studies have shown that cementation reactions are diffusion controlled^[9]. The advantages of cementation process include its relative simplicity, ease of control, low energy consumption and recovery of valuable or toxic metals.

The aim of the present work is devoted to study the kinetics of copper cementation on rotating iron cylinder in the presence of amino acids as glycine, alanine, and phenyl alanine at different temperatures.

EXPERIMENTAL

The apparatus

The apparatus which permits the rotation of clamping iron cylinder assembly arranged such as that only the peripheral surface of pure Fe was exposed to solution and 200 ml covered reaction vessel. The cylinder was rotated in experimental solution with variable speed motor. The frequency of rotation recorded as revolution per second was counted by an optical tachometer. The reaction vessel was set in a constant $\pm 0.05^\circ\text{C}$ ultrathermostate.

Kinetic measurements

Reagent-grade chemicals and redistilled water were used in the preparation in the experimental and stock of CuSO₄ solution was prepared from BDH analar CuSO₄, five different solutions of CuSO₄ have conc. 6.25, 31.75, 63.56, 95.27 and 127 ppm. Assuming that, copper ion concentration is negligibly low at iron/solution interface. [C: copper concentration (M l⁻¹) in solution at time t (sec), k: the rate constant of cementation or mass transfer coefficient which depends upon fluid flow, temperature and concentration (cm sec⁻¹), A: exposed area (cm²) of iron/cm² solution and V: volume of solution (cm³)].

Thus the rate of copper cementation is propor-

tional to copper concentration of solution, the exposed iron area and the specific rate constant k.

The reaction proceeds as follow^[10,11]:



This reaction is diffusion controlled whose rate at batch reactor can be represented by equation (2)

$$-V \frac{dc}{dt} = -kAc \quad (2)$$

Equation (2) can be integrated to:

$$V \ln \frac{C_0}{C} = kAT \quad (3)$$

where V is the volume of solution containing copper ions and C₀ is its initial concentration.

Figure 1 gives the relation between log C₀/C against time for cementation of copper sulphate concentration from which the rate constant k were calculated and given in TABLE 1.

The values of k×10² (cm.sec⁻¹) at different CuSO₄ concentration and at different temperatures are given in table (1).

Figure 1 shows that, the concentration of Cu²⁺ decreases as cementation process proceeds.

Figure 2 also indicated that the cementation reaction is a first order reaction which was verified by other authors^[11-15]. It is clear from TABLE 1 that,

TABLE 1: Values of k·10³ at different CuSO₄ concentration at different temperature

CuSO ₄ ppm T°C	6.25	31.3	63.5	95.25	127
25	3.3	4.2	4.35	5.43	5.88
30	3.9	4.91	5.001	6.83	7.3
35	4.021	5.48	5.95	7.31	8.02
40	4.35	5.90	6.10	8.45	9.36

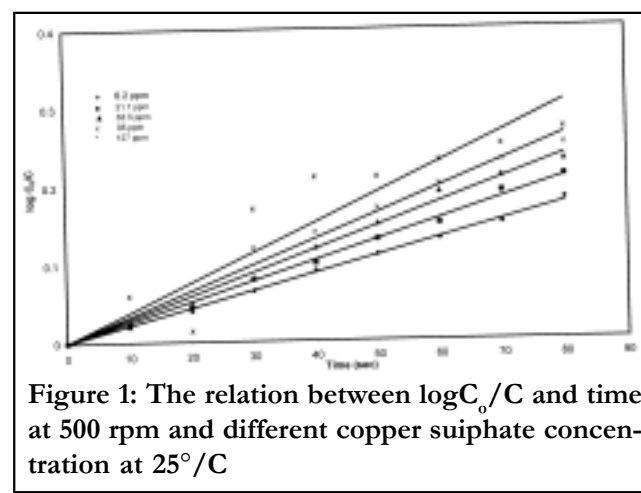


Figure 1: The relation between log C₀/C and time at 500 rpm and different copper sulphate concentration at 25°C

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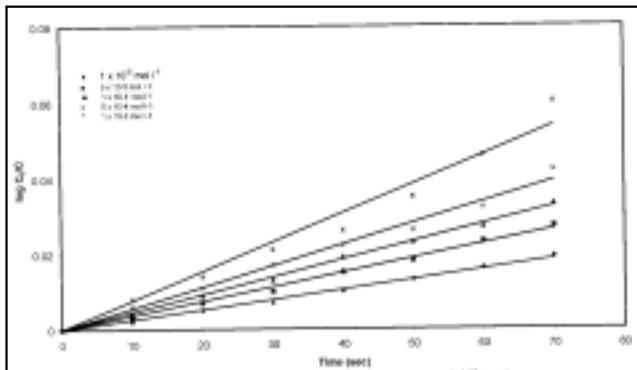


Figure 2: The relation between $\log C_0/C$ and time at 500 rpm and different glycine concentration at 25°C

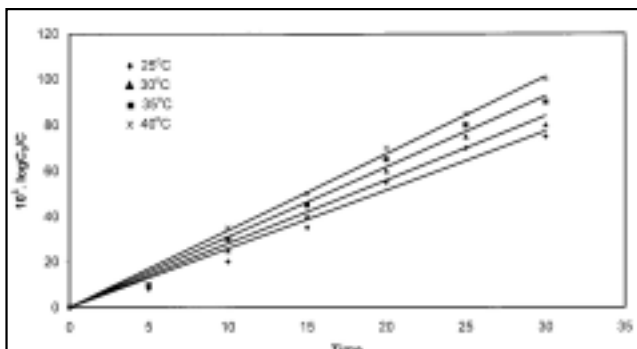


Figure 3: The relation between $\log C_0/C$ and time for Cu^{++} at different temperatures for glycine

the rate of cementation reaction is increased by increasing concentration i.e. cementation rate increases in the direction of precipitation of copper and increases also by increases the temperatures. Figure 3 shows the relation between $\log C_0/C$ against time for different temperatures at constant $CuSO_4$ concentration (95.25 ppm.) for glycine as example. The plots pass through origin, which prove that the cementation reaction is a first order in presence of amino acids. The rate of reactions for different inhibitor composition is calculated from the slopes of time lines. TABLE 2 summarizes the obtained results at different temperatures. It is found that cementation process is inhibited by addition of amino acids. The percentage of inhibition for cementation reaction is calculated from the following relation:

$$\% \text{inhibition} = \frac{k - \bar{k}}{k} \cdot 100$$

k rate of reaction when blank solution used (95.222 mg/l) Cu^{++}

\bar{k} rate of reaction in presence of amino acids.

TABLE 2: First order rate constant ($k \cdot 10^4 \text{ sec}^{-1}$) for the cementation on iron metal in presence of glycine at zero rotation speed and 63.5 ppm $CuSO_4$

$C \times 10^5 \text{ mol l}^{-1}$	1	5	10	50	100
T°C					
<u>Glycine</u>					
25	3.61	2.81	2.23	2.18	1.62
30	4.38	3.52	2.88	2.76	1.82
35	4.68	5.18	3.42	3.75	2.13
40	5.21	5.78	3.85	4.32	2.38
<u>Alanine</u>					
25	1.38	1.42	1.20	0.67	0.6
30	2.10	1.52	1.35	0.64	0.68
35	2.35	1.6	1.48	0.82	0.79
40	2.98	2.21	1.85	0.95	0.59
<u>Phenyl alanine</u>					
25	1.62	1.12	0.92	0.56	0.42
30	2.0	1.52	1.005	0.75	0.63
35	2.10	1.43	1.12	0.81	0.70
40	2.62	2.08	1.90	0.92	0.84

TABLE 3: The relation between % inhibition and concentration for all amino acids at 25°C

$C \times 10^5 \text{ mol l}^{-1}$	1	5	10	50	100
Compounds		% inhibition			
Glycine	35.2	35.4	45.73	50	63
Alanine	57	67	72	84	86
Phenyl alanine	63	74	79	87	90

TABLE 3 gives the relation between the percentage of inhibition in the rate of cementation reaction and amino acids cementation. It was found that the % inhibition ranged from 35.2% to 98% depending on the type of amino acid and its concentration. The order of cementation inhibition is

blank < glycine < alanine < phenyl alanine.

Amino acids may form a thin film on the iron metal which leads to decrease the rate of cementation reaction; also, adsorption of acids on the surface depends mainly on the structure.

Phenyl alanine has longer hydrocarbon chain therefore it adsorbed on surface of metal more than glycine and alanine smaller adsorbs on the iron surface^[15]. The decrease in the diffusion coefficient (D); of Cu^{++} solution containing amino acids which is due to the increases in the interfacial viscosity η in accordance to Stokes-Einstein^[16, 17]:

$$\eta \frac{D}{T} = \text{constan t}$$

where T is the absolute temperature.

The increase in the interfacial viscosity is caused

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by the adsorption of amino acid molecules at the iron surface.

In those amino acids the nitrogen atom was considered as the active center of their attraction with the metal surface. Accordingly, it is most likely that phenyl alanine is the most inhibitor and the efficiency of inhibition increases in order

Glycine < alanine < phenyl alanine

Where substitution of hydrogen atoms e.g. in glycine by nucleophilic group as methyl or phenyl group leads to an increases in electron density on -NH₂. This might lead to more convenient electron transfer from functional group to metal with subsequent coordination, hence great adsorption and inhibition efficiency^[17].

Effect of stirring on the reaction

The rate of cementation is calculated at the following different rpm: 50, 100, 200, 300, 400, 500, and 600 revolution/minute. The values of k are given in TABLE 4. Reaction using CuSO₄ has concentration 63.5 ppm.

From the above TABLE it is obvious that the rate of cementation reaction in presence of amino acid was increased by increasing rpm TABLE 5. The effect of rotational speed on the rate of reaction can also be used to determine whether the reaction is diffusion controlled or chemically controlled. If the rate of reaction increases with increasing stirring speed, then the reaction is diffusion controlled. If the reaction is independent on the stirring speed then

TABLE 4: This gives effect of rpm on reaction rate

Rpm	50	100	200	300	400	500	600
k.10 ³ cm sec ⁻¹	6.1	7.2	8.1	9.1	12.0	15.1	19.2

TABLE 5: Effect of rpm on reaction rate at different rpm, 1×10⁻⁴ mol l⁻¹ amino acid and 25°C

Rpm	k·10 ³						
	50	100	200	300	400	500	600
Glycine	3.4	5.1	6.8	8.2	10.1	13.1	15.3
Alanine	3.1	4.6	6.0	7.1	9.02	11.3	13.2
Phenyl alanine	2.9	4.1	5.4	6.3	7.80	9.8	11.3

the reaction is chemically controlled. The data shown in this table proved that, the cementation reaction is diffusion controlled^[18].

Thermodynamic treatment of the results

From the integrated form of Arrhenius equation:
 $\ln k = -E/RT + \ln A$ (4)

where R is the gas constant [8.314 kJ mol⁻¹]

E is the activation energy and A is the frequency factor. The values of E are given in TABLE 6. These values for the enthalpy of activation ΔH*, entropy of activation ΔS* and free energy of activation ΔG* can be obtained using equation:

$$\Delta H^* = E - RT \quad (5)$$

$$\Delta S^*/R = \ln A - \ln BTe/h \quad (6)$$

$$\Delta G^* = \Delta H^* - T \Delta S^* \quad (7)$$

where B is the Boltzman constant, e is 2.7186, h is Plank's constant.

The increase in the heat of adsorption lead to an

TABLE 6: Thermodynamic parameters of activation at different amino acid composition

C × 10 ⁵ mol l ⁻¹	1	5	10	50	100
<u>a) Glycine</u>					
ΔE*	18.16±2.66	20.36±0.96	36.66±3.2	39.66±3.26	39.49±5.4
ΔH*	15.68±2.66	17.88±0.96	34.19±3.2	36.2±3.26	37.1±5.4
-ΔS*	238±8.7	238±3.1	181±10.5	171±10.6	169.6±10.6
ΔG*	86.98±8.7	88.96±1.90	88.1±6.39	88.19±8.01	87.57±10.7
<u>(b) Alanine</u>					
ΔE*	20.33±8.51	21.28±7.21	21.53±3.29	24.27±1.5	37.69±6.26
ΔH*	82.71±7.21	18.78±7.21	19.08±3.29	19.08±1.5	32.22±0.96
-ΔS*	245±2.7	236.8±2.6	237±2.6	230 ± 2.5	181±20.0
ΔG*	91.34±16.8	89.39±12.3	89.74±10.3	89.0±9.0	89.19±12
<u>(c) Phenyl alanine</u>					
ΔE*	23.14±3.7	23.81±3.7	27.85±9.1	34.03±6.58	35.1±6.58
ΔH*	20.66±3.7	21.34±3.7	25.36±9.1	31.6±6.58	32.7±6.58
-ΔS*	225±12.1	235±20.0	216±2.4	203±21	193±21
ΔG*	88.91±7.3	91.41±12.5	89.81±17.0	42.12±13	90.58±12

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increase in the energy of adsorption forces, however raising of the temperature acts in the reverse direction, increasing the kinetic energy of the molecules, facilitating desorption (consequently in physical adsorption). In absence of acids the activation energy = 25 kJ mol⁻¹ which is smaller than when acid is used as inhibitor. Thus the high values of activation energies show that:

- (1) The rate of cementation of copper increased by addition of acid at temperature above 20°C.
- (2) The adsorption process is physical adsorption^[9].

TABLE 4 shows that the entropy ΔS^* possesses high negative values indicating a highly ordered organic species in the solution under investigation. This is explained by the formation of more stable transition state.

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