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Kinetic Study of Copper Deposition on Zinc by Cementation Reaction and Effects of Some Amino Acids

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The results of the rate of cementation of Cu^{2+} in $CuSO_4$ solution and in presence of different concentration of amino acids at different ppm of Cu^{2+}, different temperatures and different rpm are given. The energy of activation as well as thermodynamic parameters ΔH^*, ΔG^* and ΔS^* are discussed. It is found that the cementation reaction is first orders and rate controlling step is found to be diffusion of copper ions to zinc cylinder. It is found that the rate of cementation increases in presence of amino acids.

Key Words: Cementation reaction, Wastewater, Copper deposition and amino acids.

INTRODUCTION

Cementation is one of the most effective and economic technique uses for recovery toxic and valuable metals from industrial wastewater stream. The specific contaminants leading to pollution in water include a wide spectrum of chemicals, pathogens and physical or sensory changes such as elevated temperature and discolouration. While many of the chemicals and substances that are regulated may be naturally occurring (calcium, sodium, iron, manganese, *etc.*) the concentration is often the key in determining what is a natural component of water and what is a contaminant. High concentrations of naturally-occurring substances can have negative impacts on aquatic flora and fauna[1].

Alteration of water's physical chemistry includes acidity (change in pH), electrical conductivity, temperature and eutrophication. Eutrophication is an increase in the concentration of chemical nutrients in an ecosystem to an extent that increases in the primary productivity of the ecosystem. Depending on the degree of eutrophication, subsequent negative environmental effects such as anoxia (oxygen depletion) and severe reductions in water quality may occur, affecting fish and other animal populations[2].

Some of the pollutants like lead, arsenic, mercury, chromium specially hexavalent chromium, nickel, barium, cadmium, cobalt, selenium, vanadium, oils and grease, pesticides, *etc*. are very harmful, toxic and poisonous even in ppb range. There are some minerals which are useful for human and animal health in small doses beyond which these are toxic. Zinc, copper, iron, *etc*. fall into this category. For agriculture, some elements like zinc, copper, manganese, sulphur, iron, boron, together with phosphates, nitrates, urea, potassium, *etc*. are useful in prescribed quantities. There are some compounds like cyanides, thiocyanides, phenolic compounds, fluorides, radioactive substances, etc which are harmful for humans as well as animals[3].

Copper as a pollutant: Wastewater pollution in industrial areas is one of the most important environmental problems. Heavy metals pollution especially copper is a serious problem which affects all ecosystems and human health directly or indirectly as in food chain. The maximum limit value of copper in wastewater is 0.05 mg/L as reported in World Health Organization (WHO)[4].

EXPERIMENTAL

AnalaR grade potassium dichromate ($K_2Cr_2O_7$) in presence of sulphuric acid and copper sulphate ($CuSO_4.5H_2O$) supplied by BDH Chemicals Ltd. was used in preparation of experimental solution.

Apparatus and techniques: The apparatus in Fig. 1 is used in recovery of copper ion (Cu^{2+}) from the solution which permits the relation of immersed zinc or iron cylinder in a 250 mL glass beaker containing 200 mL of experimental solution.

The zinc cylinder used in each run is a 7 cm length while the iron cylinder used in each run is a 6.5 cm length and variable diameters only the peripheral surface of pure zinc or iron was exposed to the solution.

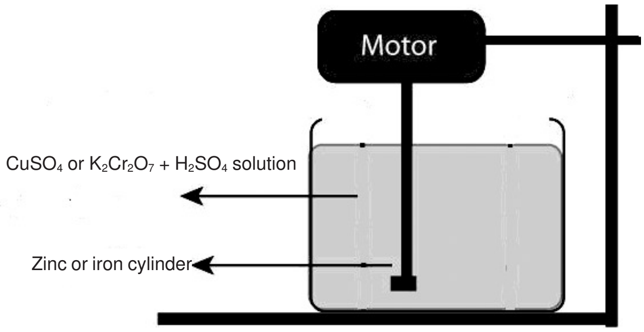
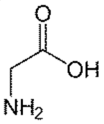


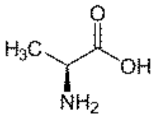
Fig. 1. Schematic diagram of the apparatus

The cylinder was rotated in experimental solution by laboratory stirrer and its angular velocity monitored by means of an optical tachometer. The reaction vessel was set in a constant ± 0.05 ºC ultra thermostat.

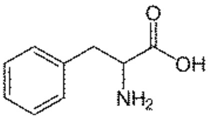
Amino acids additives:



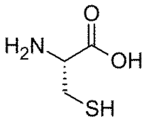
Glycine



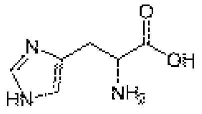
Alanine



Phenyl alanine



Cysteine



Histidine

Kinetic measurements: Analar copper sulphate and deionized water were used in the preparation of blank solution (100 ppm) as well as in the presence of different six concentration of organic compounds [1, 5, 10, 50, 100 and 500 ppm].

The reaction rate was determined at four temperatures [25, 30, 35 and 40 ºC] as well as at rotation speed [125, 250, 375, 500 and 700 rpm].

Through the proceeding reaction, at different time (minutes) interval, 0.2 mL of sample was taken from reaction solution and diluted by deionized water. The concentration of Cu^{2+} ions in the sample after dilution lies practically in limit of atomic absorption spectrophotometer method (AAS).

Correcting for the change in reactant volume as result of sampling was considered unnecessary since each sample taken was only 0.2 mL, which was 0.1 % of total reactant volume. The determination of copper ion concentration was carried out using Perkin-Elmer atomic absorption spectrophotometer.

Determination of densities and viscosities: The density was determined by using DA-300 Kyoto electronic at 25, 30, 35 and 40 ºC. An oscillation period of the measuring cell will vary depending on density of sample contained in the cell. The oscillation period at the time will be given as follows:

$$\eta = 2\pi\,(dV_c + Mc/Z)^{0.5}$$

where d: Density of the sample contained in the cell (g cm^{-3}); V_c : Volume of the cell contained in the cell (cm^3); Mc : Mass of sample contained in the cell (g); Z : Constant.

$$d = (Z/4Vc\pi^2)\,T^2 - (Mc/Vc)$$

A cell factor (f) will be calculated from the oscillation frequencies (T_a and T_w) of two different densities of standard substances (d_a and d_w) as the following equation:

$$F = Z/4Vc\,\pi^2 = d_a - d_w/T_a^2 - T_w^2$$

A density of unknown sample (d) will be provided if its oscillation frequency (T) is analyzed as shown in the following equation:

$$d = d_a - F(T_a^2 - T^2)$$

The viscosity is measured using Koehler viscosity bathing (model K23400 kinamatic baths) at 25, 30, 35 and 40 ºC.

RESULTS AND DISCUSSION

Cementation is one of the most effective and economic techniques for recovering toxic and/or valuable metals from industrial waste solution. 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. The process has been largely used in industry for a long time not only in hydrometallurgy but also in the purification process of wastewaters[5-12].

The cementation reactions are considered as heterogeneous processes limited by diffusion through the mass boundary layer. The rate of cementation not only depend on the prevailing hydrodynamic conditions but also depends on the nature of the deposited metal, powery non coherent deposits may enhance the rate of cementation while smooth coherent deposit may inhibit the rate of cementation.

Mechanistic studies of cementation reactions have revealed that cementation is electrochemical in nature which takes place through a galvanic cell[13-15].

For the present case where Cu^{2+} ions are cemented on Zn, the galvanic cell is:

$Zn/CuSO_4/Cu$, the cell reaction

$$\text{Anode}: Zn \rightarrow Zn^{2+} + 2e \quad e_o = 0.763\ V$$

$$\text{Cathode}: Cu^{2+} + 2e \rightarrow Cu \quad e_o = 0.337\ V$$

E_o is the standard cell potential where:

$$E_o = e_{o\text{-ve}} + e_{o\text{+ve}} = 0.763 + 0.337 = 1{:}1V$$

The extent to which Cu^{2+} can be removed by cementation on Zn can be determined from the equation:

$$\Delta G_o = RT\ \ln K$$

where: ΔG_o is the standard free energy of the cell reaction

$$Zn + Cu^{2+} = Zn^{2+} + Cu$$

K is the equilibrium constant of the reaction

$$K = [Zn^{2+}]/[Cu^{2+}]$$

So,

$$\Delta G_o = -ZE_oF/K \text{ therefore } E_o = (RT/ZF)\ \ln K$$

$$1{:}1 = (0.059/2)/\ln K \qquad K = 1.56 \times 10^{16}$$

The high value of the equilibrium constant K shows that cementation of Cu^{2+} by Zn can lower Cu^{2+} concentration in waste solution below the maximum permissible value.

The removal of Cu^{2+} by cementation has been studied by a number of researchers who used different less noble metals such as Zn, Fe and Al and different methods to enhance the rate of cementation such as the rotating disc, the rotating cylinder agitated vessels, gas sparing, fixed and fluidized beds and surface pulsation[16-21,5].

In most cases the cementation reactions from dilute solutions have been found to follow first order diffusion controlled kinetics[22].

The most studies are used widely in the chemical process industry to conduct processes such as mixing drying, cooling, enhancement of diffusion controlled processes such as electroplating, electrochemical machining, etching, *etc*.[23-26]

Variation of rate constant of cementation of copper: Cementation reaction requires a transfer of electrons between the dissolving zinc and the precipitating copper. This requirement causes the copper to cement on the zinc surface rather than remaining in the bulk of the solution. The kinetics of copper cementation has been studied extensively. It was agreed that the rate controlling step was the diffusion of copper ion to zinc surface. In such case the rate of change of copper concentration in the leach solution was followed.

The overall cementation reaction was preceded as follows:

$$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$$

This reaction is diffusion controlled whose rate in a batch reactor can be represented by following equation:

$$\ln C_o/C = kAt/V$$

where k is rate constant (sec^{-1}), A is area of cylinder, t is the time, V is volume of solution contained Cu^{2+} concentration and C is concentration.

log C_o/C was plotted against time for different concentrations of copper ion and at different temperature as shown in Figs. 2-6. The values of rate constants represented in Table-1 show that the rate of mass transfer increased by increasing concentration and temperature *i.e.*, cementation rate increases in the direction of precipitation of copper indicating that cementation reaction is a first order reaction as verified before. The result is consistent with the previous studies conducted under different conditions[5,22-27].

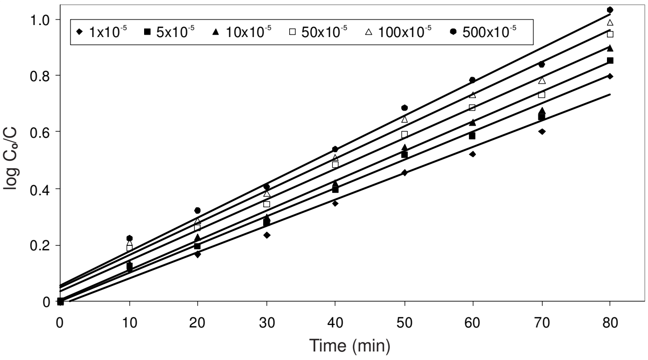


Fig. 2. Relation between log C_o/C and time (min) for histidine at different concentrations of copper ion

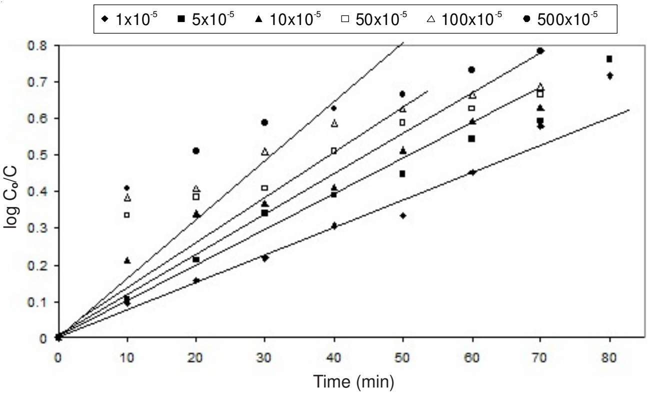


Fig. 3. Relation between log C_o/C and time (min) for cysteine at different concentrations of copper ion

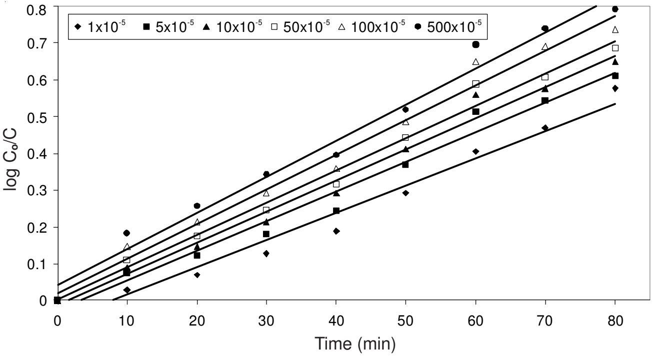


Fig. 4. Relation between log C_o/C and time (min) for phenylalanine for different concentrations of copper ion

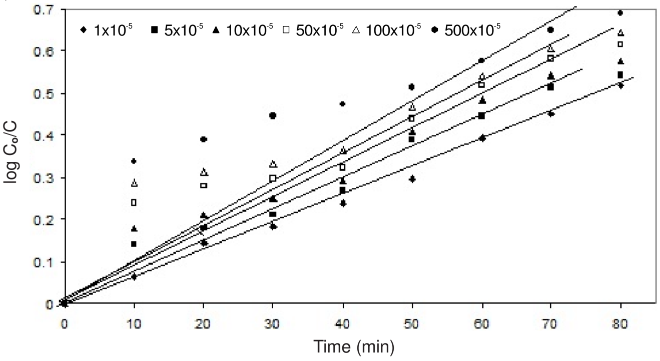


Fig. 5. Relation between log C_o/C and time (min) for alanine for different concentrations of copper ion

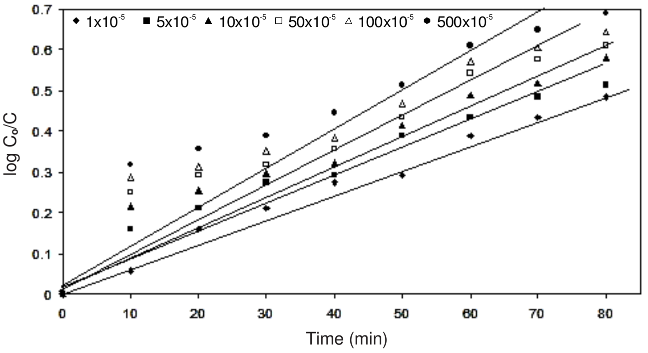


Fig. 6. Relation between log C_o/C and time (min) for glycine for different concentrations of copper ion

TABLE-1
VALUES OF RATE CONSTANT, k sec^{-1} AT 500 rpm, 100 ppm

Organic compounds	Histidine	Phenylalanine	Cysteine	Alanine	Glycine
$C \times 10^5$ (mol.l^{-1})	k sec^{-1}				
1	0.0194	0.0057	0.0136	0.0027	0.0022
5	0.0196	0.0067	0.0167	0.0030	0.0028
10	0.0222	0.0073	0.0186	0.0032	0.0030
50	0.0224	0.0079	0.0208	0.0035	0.0035
100	0.0230	0.0090	0.0260	0.0038	0.0038
500	0.0233	0.0105	0.0264	0.0041	0.0041

Effect of organic compounds: In present study, the rate of reaction (k) values in the presence and absence of organic compounds were estimated. It is found that, the presence of organic compounds accelerate the rate of the reaction as shown in Table-2.

TABLE-2
RELATION BETWEEN % ACCELERATION AND CONCENTRATION OF AMINO ACIDS AT 25 ºC

Organic compounds	Histidine	Phenylalanine	Cysteine	Alanine	Glycine
C×10^5 (mol.l^{-1})	% acceleration				
1	17.40	26.01	32.60	29.20	39.13
5	23.90	30.43	36.10	32.17	41.30
10	25.22	34.78	37.10	34.10	43.47
50	26.01	39.13	42.17	39.13	45.11
100	27.03	43.47	45.10	41.30	47.82
500	30.10	45.10	47.82	43.47	52.17

According to the obtained results from the reduction of Cu^{2+} on surface of zinc cylinder, we can summarize our conclusion as follows: The degree of acceleration has increased by increasing the concentrations of the used organic compound.

The percentage acceleration for different concentrations of the studied additives is estimated at 25 ºC as shown in Table-2.

The percentage of acceleration is represented as following:

$$\% \text{ acceleration} = (k_{organic} - k_{blank})/k_{blank} \times 100$$

where: k_{blank} = rate constant for blank solution; $k_{organic}$ = rate constant in presence of organic compounds.

Inspection of Table-2 shows that the percentage acceleration of the studied compounds increases in the following order:

Histidine > cysteine > phenylalanine > alanine > glycine

The increase in the rate of cementation with increasing initial copper ion concentration is the resultant of the following effects of initial copper ion concentration.

[i] As the initial copper ion concentration increases the diffusivity of (Cu^{2+}) decreases as a result of the decrease in solution viscosity and inters ionic attraction between ions, this effect tends to increase the rate of mass transfer.

[ii] Copper ions are transferred from the bulk solution to the zinc surface during cementation by (1) copper ions are transferred from the bulk solution to the zinc surface during cementation by (1) diffusion across the diffusion layer (δ) present at the zinc surface and (2) electrostatic attraction (electrical migration) between the positively charged copper ions and negatively charged zinc anode of the galvanic cell: Zn/electrolyte/Cu through which cementation takes place. It is well known that both the rate of diffusion and the rate of ion transfer by electrical migration increase with increasing reactant bulk concentration, which leads to a consequent increase in the mass transfer coefficient[28].

[iii] With increasing the initial Cu^{2+} concentration the porous copper deposits grows rapidly with a consequent increase in the cathode area. Since the reaction rate is controlled by the cathodic process it follows that the rate of cementation as well as the mass transfer coefficient should increase with initial Cu^{2+} concentration[13].

Effect of viscosity on the rate of Cu^{2+} cementation: Viscous flow should be visualized as the movement of one layer of molecules with respect to another layer involving transition as well as rotation motion of the molecules, with an energy required to pass over a hindrance potential energy barrier. Kanzmann and Eyring showed that the viscosity of a liquid can be expressed by the following equation:[29]

$$\eta = (N/V) \exp(-\Delta S^*/R) \exp(-\Delta H^*/RT)$$

where, (N/V) is the molecular value of the liquid. ΔH^* is the enthalpy of activation. ΔS^* is the entropy of activation. R is the gas constant (8.32 J.mol^{-1}.K^{-1}) and T is the absolute temperature. Tables 3-7 shows the decrease of viscosity of the solution by increasing the temperature and that can be expressed by Arrhenius equation:[30]

Where η is the viscosity of the solution, A is a pre-exponential factor, E^* is activation energy of the flow Cu^{2+} to the energy barrier, R is the gas constant and T is absolute temperature in Kelvin. The next equation represents Stockes-Ilkovic equation where, the product of the rate constant and the square root of viscosity of the show that, the product of $K\eta^{1/2}$ for various solutions is almost constant which indicates that, the Stokes-Ilkovic relation is valid for these solutions and this

TABLE-3
VALUES OF DENSITY (ρ) AND VISCOSITY (η) FOR THE SOLUTION IN THE PRESENCE OF DIFFERENT CONCENTRATIONS OF HISTIDINE AT DIFFERENT TEMPERATURES. [(ρ = g cm^{-3}), (η = g cm^{-1} s^{-1})]

Temp (ºC)	25 ºC		30 ºC		35 ºC		40 ºC	
C×10^3 (mol L^{-1})	ρ	η	ρ	η	ρ	η	ρ	η
0.00	1.160	2.210	1.130	2.120	2.110	2.040	1.070	1.980
0.26	1.107	1.020	1.080	0.990	1.064	0.970	1.050	0.940
0.53	1.082	1.082	1.035	1.010	1.012	0.980	1.030	0.950
0.79	1.042	1.042	0.210	1.040	0.987	0.990	0.980	0.960
1.05	1.016	1.016	0.995	1.050	0.970	1.000	0.960	0.960
1.30	1.005	1.005	0.966	1.060	0.960	1.010	0.955	0.970
1.50	1.003	1.003	0.960	1.080	0.955	1.020	0.950	0.970
1.80	1.002	1.002	0.961	1.100	0.950	1.030	0.940	0.970

TABLE-4
VALUES OF DENSITY (ρ) AND VISCOSITY (η) FOR THE SOLUTION IN THE PRESENCE OF DIFFERENT CONCENTRATIONS OF CYSTEINE AT DIFFERENT TEMPERATURES

Temp (ºC)	25 ºC		30 ºC		35 ºC		40 ºC	
C×10^3 (mol L^{-1})	ρ	η	ρ	η	ρ	η	ρ	η
0.00	1.160	2.210	1.130	2.120	1.110	2.040	1.070	1.980
0.26	1.050	1.030	1.020	0.980	1.000	0.960	0.990	0.930
0.53	1.020	1.050	1.010	0.990	0.990	0.970	0.980	0.940
0.79	1.001	1.070	0.960	1.010	0.950	0.990	0.975	0.950
1.05	0.980	1.090	0.950	1.020	0.950	1.000	0.960	0.960
1.30	0.975	1.110	0.950	1.050	0.940	1.010	0.950	0.960
1.57	0.971	1.130	0.960	1.070	0.940	1.020	0.945	0.970
1.82	0.970	1.170	0.960	1.090	0.930	1.030	0.940	0.970

TABLE-5
VALUES OF DENSITY (ρ) AND VISCOSITY (η) FOR THE SOLUTION IN THE PRESENCE OF DIFFERENT CONCENTRATIONS OF PHENYLALANINE AT DIFFERENT TEMPERATURES [(ρ = g cm^{-3}), (η = g cm^{-1} sec^{-1})]

Temp (ºC)	25 ºC		30 ºC		35 ºC		40 ºC	
C×10^3 (mol L^{-1})	ρ	η	ρ	η	ρ	η	ρ	η
0.00	1.160	2.500	2.130	2.200	2.110	2.150	2.070	1.970
0.24	1.066	2.450	1.003	2.170	0.995	2.020	0.984	1.820
0.48	1.021	2.200	1.001	2.030	0.987	1.850	0.958	1.680
0.71	1.005	2.150	0.984	1.960	0.967	1.830	0.944	1.660
0.94	0.980	2.000	0.964	1.820	0.952	1.660	0.932	1.540
1.17	0.952	1.850	0.942	1.720	0.931	1.520	0.930	1.370
1.40	0.945	1.660	0.940	1.520	0.930	1.410	0.922	1.310
1.63	0.940	2.210	0.927	2.120	0.923	1.040	0.910	1.980

TABLE-6
VALUES OF DENSITY (ρ) AND VISCOSITY (η) FOR THE SOLUTION IN THE PRESENCE OF DIFFERENT CONCENTRATIONS OF ALANINE AT DIFFERENT TEMPERATURES

Temp (ºC)	25 ºC		30 ºC		35 ºC		40 ºC	
$C\times10^3$ (mol L^{-1})	ρ	η	ρ	η	ρ	η	ρ	η
0.000	1.160	2.350	1.130	2.120	1.110	2.010	1.070	1.800
0.530	1.074	2.290	1.070	2.080	1.053	1.860	1.000	1.690
1.050	1.040	2.150	1.028	1.950	1.007	1.800	0.977	1.610
1.570	1.022	2.080	1.005	1.860	0.985	1.730	0.962	1.590
2.100	1.005	1.970	0.982	1.740	0.961	1.630	0.940	1.470
2.600	0.973	1.630	0.982	1.480	0.941	1.390	0.930	1.270
3.100	0.960	1.190	0.960	1.370	0.940	1.290	0.920	1.610
3.600	0.957	2.210	0.945	2.120	0.930	2.040	0.916	1.980

TABLE-7
VALUES OF DENSITY (ρ) AND VISCOSITY (η) FOR THE SOLUTION IN THE PRESENCE OF DIFFERENT CONCENTRATIONS OF GLYCINE AT DIFFERENT TEMPERATURES

Temp (ºC)	25 ºC		30 ºC		35 ºC		40 ºC	
$C\times10^3$ (mol L^{-1})	ρ	η	ρ	η	ρ	η	ρ	η
0.000	1.160	2.500	1.130	2.250	1.110	2.100	1.070	1.980
0.340	1.080	2.420	1.032	2.150	1.010	2.030	0.984	1.830
0.670	1.046	2.190	1.020	2.020	0.985	1.860	0.962	1.640
1.007	1.005	2.150	0.984	1.950	0.961	1.810	0.940	1.610
1.330	0.981	2.000	0.973	1.800	0.936	1.660	0.934	1.520
1.660	0.961	1.810	0.947	1.670	0.936	1.570	0.923	1.370
1.990	0.956	1.630	0.940	1.510	0.930	1.410	0.920	1.300
2.300	0.941	2.210	0.931	2.120	0.922	2.040	0.910	1.980

confirms the suggestion that, the reaction is controlled by diffusion of Cu^{2+} from bulk to zinc surface[31].

Effect of stirring on the rate of cementation

A series of experiments were performed to investigate the effect of stirring speed on the reaction rate. The stirring speed used was 125, 250, 375, 500, 625 and 750 rpm as shown in Figs. 7 -11. The effect of rotational speed on the rate constant (k) can be used to determine whether a cementation reaction rate is diffusion controlled or chemically controlled, since if the rate constant increases with increasing stirring speed. Then the reaction is diffusion controlled. However k is independent of stirring speed then the reaction is likely to be chemically controlled. Figs. 7-11 show the variation of log C_o/C against time, for cementation reactions rate constant of 100 ppm Cu^{2+}, at different speed of rotation (rpm) of zinc cylinder and show that the rate constant increases by increasing the speed of rotation and this indicated that the cementation reaction is a diffusion controlled reaction.

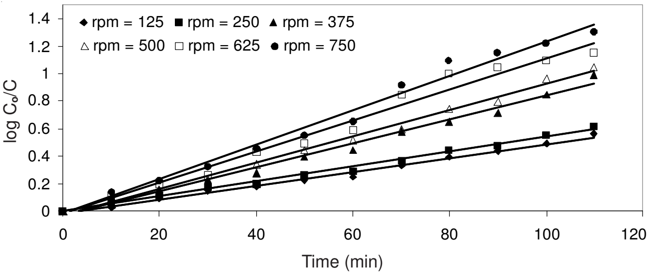


Fig. 7. Relation between log C_o/C and time (min) for histidine at different rpm

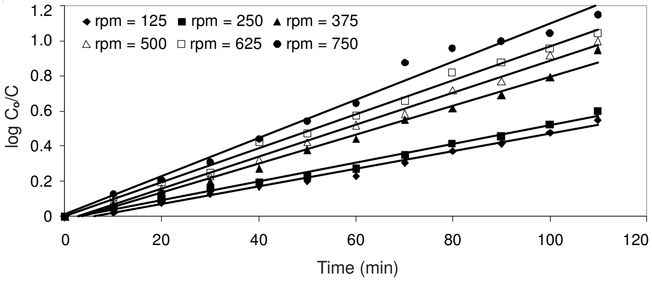


Fig. 8. Relation between log C_o/C and time (min) for cysteine at different rpm

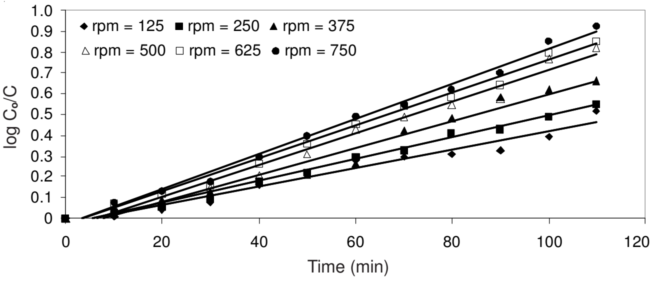


Fig. 9. Relation between log C_o/C and time (min) for phenylalanine at different rpm

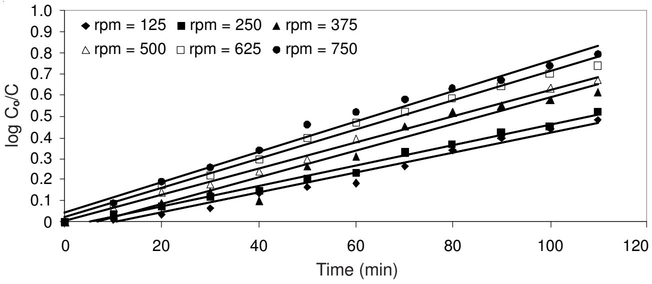


Fig. 10. Relation between log C_o/C and time (min) for alanine at different rpm

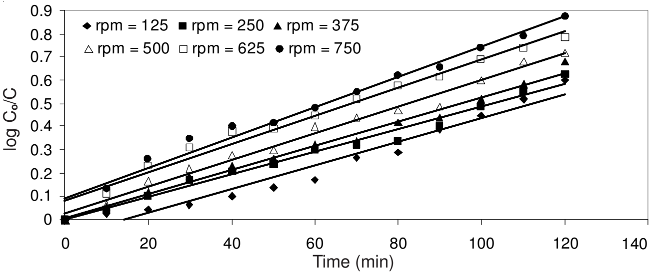


Fig. 11. Relation between log C_o/C and time (min) for glycine at different rpm

Effect of temperatures on cementation reaction: Figs. 12 -17 gives the relation between log C_o/C against time (min) for blank solution and solutions in presence of amino acids at 25, 30, 35 and 40 ºC.

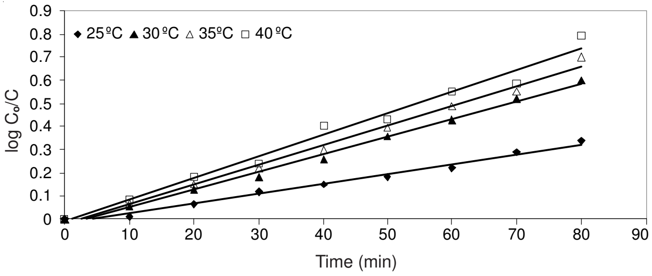


Fig. 12. Relation between log C_o/C and time (min) for blank at different temperatures

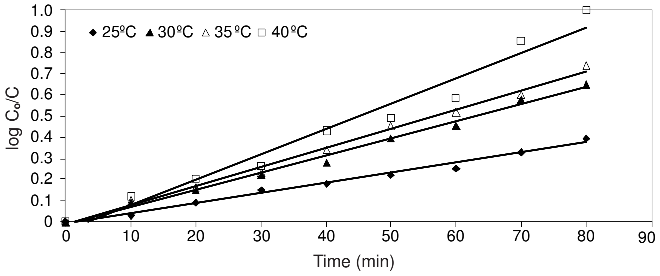


Fig. 13. Relation between log C_o/C and time (min) for histidine at different temperatures

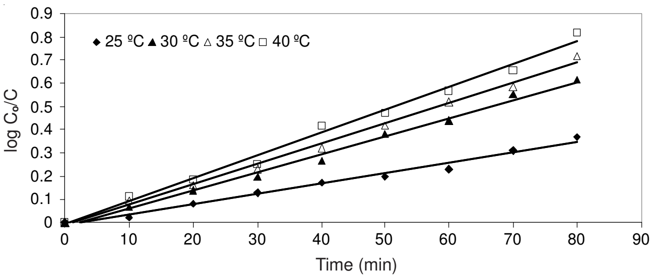


Fig. 14. Relation between log C_o/C and time (min) for cysteine at different temperatures

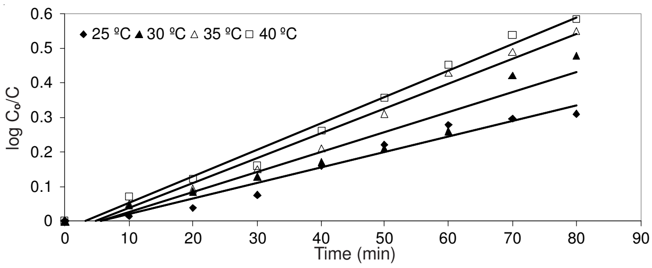


Fig. 15. Relation between log C_o/C and time (min) for phenylalanine at different temperatures

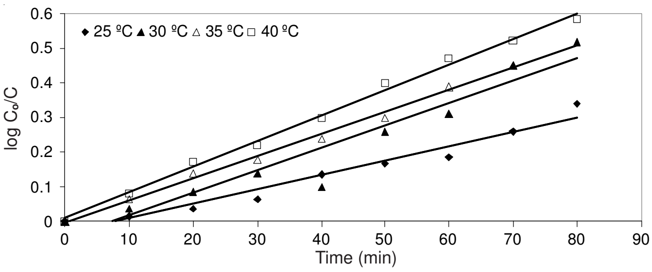


Fig. 16. Relation between log C_o/C and time (min) for alanine at different temperatures

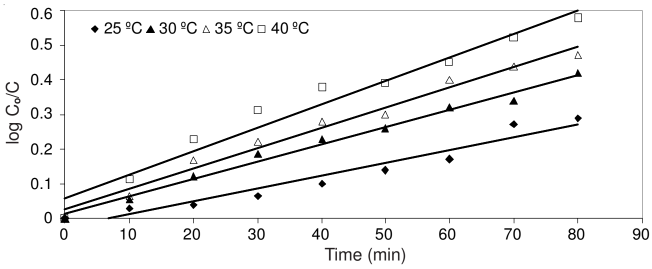


Fig. 17. Relation between log C_o/C and time (min) for glycine at different temperatures

It can be summarized that, the increase of mass transfer under forced conditions (*i.e.* rotating zinc cylinder) may be caused by several distinct situations: [i] Increased diffusion rates as a consequence of increased solution temperatures; [ii] Increased cathode surface area caused by electrodeposits roughening (*i.e.* surface roughness of the precipitated metal); [iii] Increased agitation, which decreases the cathode diffusion layer thickness; [iv] The transfer of metal ions from the solution bulk by electrical migration in addition to convection and diffusion (in our case electrical migration takes place through the attraction of the positively charged metal ions to the negatively charged metal deposited on the cylinder which act as a cathode in the galvanic cell).

Thermodynamic treatment of the reactions: The activation energy of the process is an important parameter for determining the rate controlling step.

The apparent activation energy E for a given cementation reaction can be obtained from the temperature dependence of the constant K by using Arrhenius equation:

$$K = A \exp(-E^*/RT)$$

where K is the rate constant, A is a pre-exponential factor, E^* is the activation energy. R is the gas constant and T is the absolute temperature.

$$\ln k = -E/RT + \ln A$$

The activation energy of the process is an important parameter for determining the controlling step.

If boundary layer diffusion of the aqueous species is the rate controlling step. E^* is generally < 28 KJ mol^{-1}, while if adsorption of the species on the reaction surface and subsequent chemical reaction takes place the E values usually > 43 KJ mol^{-1}. The values for the enthalpy of activation ΔH^*, entropy of activation ΔS^* and free energy of activation ΔG^* can be obtained by using the following equations:

$$\Delta H^* = E - RT$$

$$\Delta S^*/R \ln A - \ln(\alpha Te/h)$$

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

where a is the Holtzman's constant, e is the electronic charge (e = 2.7183) and h is Plank's constant.

The activation energy ΔE^*, the free energy ΔG^*, enthalpy ΔH^* and entropy ΔS^* of activation were calculated by least squares procedure and values are given in Table-8 together with their standard deviations. It is obvious that the value of E^* < 28 KJ mol^{-1}, this indicates that the cementation reaction is controlled by diffusion processes. It is noticed also that all the values of ΔS^* are highly negative values indicating a more ordered systems and non random distribution of ions on the zinc rod.

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TABLE-8
THERMODYNAMIC PARAMETERS FOR THE SOLUTION IN THE PRESENCE OF DIFFERENT CONCENTRATIONS OF ALL ORGANIC COMPOUNDS AT 25 ºC

C × 10^5 (mol L^{-1})	Thermodynamic parameters	Histidine	Cysteine	Phenylalanine	Alanine	Glycine
1	E_a (kJ mol^{-1})	8194.05	8194.05	8194.05	8194.05	8194.05
	ΔH^* (kJ mol^{-1})	5715.23	5715.23	5715.23	5715.23	5715.23
	ΔS^* (J mol^{-1} k^{-1})	-177.03	-177.03	-177.03	-177.03	-177.03
	ΔG^* (kJ mol^{-1})	58498.30	58498.30	58498.30	58498.30	58498.30
5	E_a (kJ mol^{-1})	9164.49	8140.67	8649.87	8898.49	9737.33
	ΔH^* (kJ mol^{-1})	6685.67	5661.85	6171.05	6419.67	7258.51
	ΔS^* (J mol^{-1} k^{-1})	-174.78	-178.44	-175.99	-175.41	-173.41
	ΔG^* (kJ mol^{-1})	58798.58	58865.59	58643.85	58719.98	58963.42
10	E_a (kJ mol^{-1})	4934.27	6516.78	9164.49	7661.03	7509.20
	ΔH^* (kJ mol^{-1})	2455.45	4037.96	6685.67	5182.21	5030.38
	ΔS^* (J mol^{-1} k^{-1})	-189.25	-184.279	-174.78	-179.85	-181.77
	ΔG^* (kJ mol^{-1})	58881.66	58980.98	58798.58	58806.59	59227.00
50	E_a (kJ mol^{-1})	6744.58	5459.28	7905.19	9737.33	7251.72
	ΔH^* (kJ mol^{-1})	4265.76	2980.46	5426.37	7258.51	4772.90
	ΔS^* (J mol^{-1} k^{-1})	-183.67	-188.36	-179.24	-173.41	-183.43
	ΔG^* (kJ mol^{-1})	59027.32	59142.81	58869.07	58963.42	59463.54
100	E_a (kJ mol^{-1})	5868.66	6104.03	8680.04	5459.28	6618.14
	ΔH^* (kJ mol^{-1})	3389.84	3625.21	6201.22	2980.46	4139.32
	ΔS^* (J mol^{-1} k^{-1})	-187.63	-187.18	-177.34	-188.36	-186.18
	ΔG^* (kJ mol^{-1})	59333.38	59434.60	59076.11	59142.81	59649.94
500	E_a (kJ mol^{-1})	18679.20	6618.14	7793.81	6104.03	6913.68
	ΔH^* (kJ mol^{-1})	16200.38	4139.32	5314.99	3625.21	4434.86
	ΔS^* (J mol^{-1} k^{-1})	-146.15	-186.18	-181.41	-187.18	-185.57
	ΔG^* (kJ mol^{-1})	59777.78	59649.94	59405.29	59434.60	59765.14

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