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Cementation of Cu (II) by zinc electrode in presence of carbohydrates and its application on samples of industrial wastewater

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Abstract

The cementation of copper ions (ii) from aqueous solution onto zinc electrode was investigated. The rate of copper (ii) removal was studied as a function of initial copper concentration, speed of rotation, temperature, and the addition of certain carbohydrates. The rate of cementation of copper on zinc cylinder is enhanced by increasing initial copper concentration, stirring and temperature. It was found that mannose improves the rate of copper cementation, while starch, maltose, sucrose and fructose inhibit it. The adsorption isotherm data obtained from the present study were analyzed in the light of Langmuir and Temkin isotherms. Activation parameters and isokinetic relationship were calculated and discussed. The cementation process was successfully applied to recover Cu^{2+} spiked into two an industrial wastewater samples. The recovery percentage of Cu^{2+} increases in the presence of mannose about (95.6 %) and (98.3 %) for the samples (I) and (II), respectively.

Keywords: Cementation; Copper ion; Carbohydrates; Isotherms models.

1. INTRODUCTION

In the recent years, public health concern has been focused increasingly on the more insidious risks, and therefore those more difficult to quantify, associated with long-term exposure of man and animals to continuous relatively small amounts of potentially toxic chemicals, especially the heavy metals [1].

Copper is recognized to be one of the heavy metal wide spread heavy metal contaminants of the environment [2]. Dilute copper containing solutions are encountered in chemical industries as wastes from the electroplating, pickling and the textile industries [1, 3]. Copper ion as pollutant doesn't accumulate in the human body, while upon exposure to massive amounts of copper can cause illness or even death [1]. So, several techniques have been developed and used to remove and/or recover a wide range of micro pollutants from water and a variety of industrial effluents [4].

Cementation is one of the most effective and economical techniques used for recovering toxic and valuable metals from industrial wastewater [5, 6]. Cementation is also used widely to purify leach liquors from more noble impurities in electrowinning of metals before electrolysis. Metal cementation is a process by which metal ions are precipitated from solution on the surface of a cementing agent (e.g. metallic iron, zinc and aluminium). Removal of heavy metals, especially copper, by cementation has been studied by a number of researches [1, 7- 13].

The present work is aimed to study the removal of copper ions from aqueous solutions by a cementation process using rotating zinc cylinder in presence of carbohydrates (fructose, glucose, mannose (monosaccharides), sucrose, maltose, (disaccharides) and starch (polysaccharides)). The choice of the carbohydrates is based on the following considerations (1) natural products, (2) non-toxic compounds, (3) low price, (4) easy available, (5) environmentally friendly compounds, (6) play a key role in the immune system, fertilization, preventing pathogenesis, blood clotting, and development and (7) play a major role in a number of industries as (the food industry, the textile industry, the pharmaceutical industry and (d) the chemical industry). [14,15]. The rate of cementation of copper ion from copper sulphate solution on rotating zinc cylinder was studied as a function of Initial concentration of

copper ion, Speed of rotation of zinc cylinder, Temperature, the activation parameters and isokinetic relationship, The addition of carbohydrates and physical parameters of solution such (density and viscosity). Rotating cylinder has used as a mean of enhancing the rate of cementation.

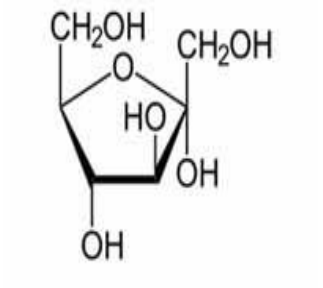
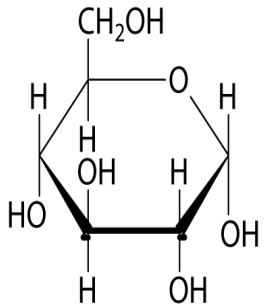
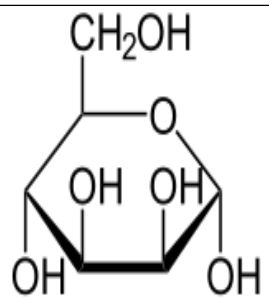
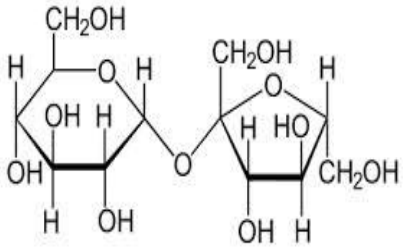
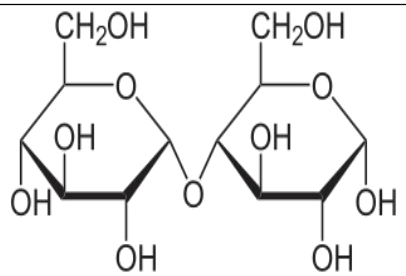
A batch cementation test was performed to determine the optimum operating conditions for copper cementation using a sample of industrial wastewater.

2. Experimental

2.1. Materials

Analar grade copper sulphate ($CuSO_4.5H_2O$) supplied by BDH chemicals Ltd., was used in preparation of experimental solutions.

The organic additives selected in the present work are fructose, glucose, mannose (monosaccharides), sucrose, maltose (disaccharides) and starch (polysaccharides) supplied by BDH chemicals Ltd. The chemical structures of these additives were represented in Figure (1)

		
D-Fructose	**D-Glucose**	**D-Mannose**
(a) (Monosaccharides)		
		
Sucrose	**Maltose**	

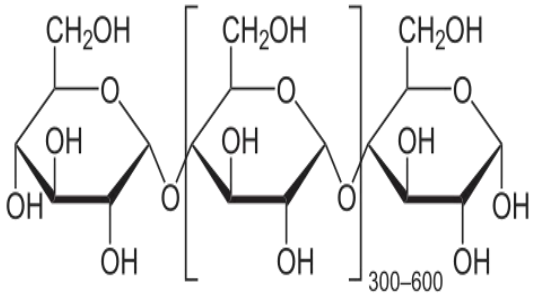
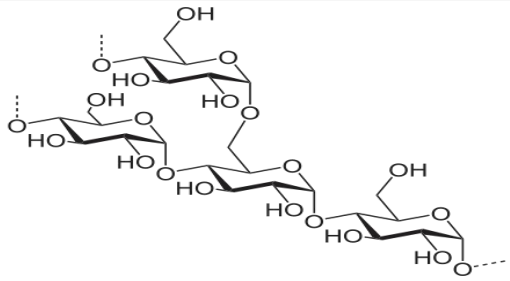
(b) (Disaccharides)	
	
Structure of the amylose molecule	**Structure of the amylopectin molecule**
Starch	
(c) (Polysaccharides)	

Figure (1): (a) (Monosaccharides), (b) (Disaccharides) and (c) (Polysaccharides).

2.2. Apparatus

The apparatus (Figure 2) which permits the rotation of the clamping Zn cylinder assembly (purity > 99.99%) was arranged so that only the peripheral surface of pure Zn was exposed to the solution and the 250 ml covered reaction vessel. The cylinder was rotated in the experimental solution with a variable-speed motor. The frequency of rotation was monitored by means of an optical tachometer. Temperature control was maintained for the reaction by containing the apparatus setup in a constant ±0.05°C ultrathermostat.

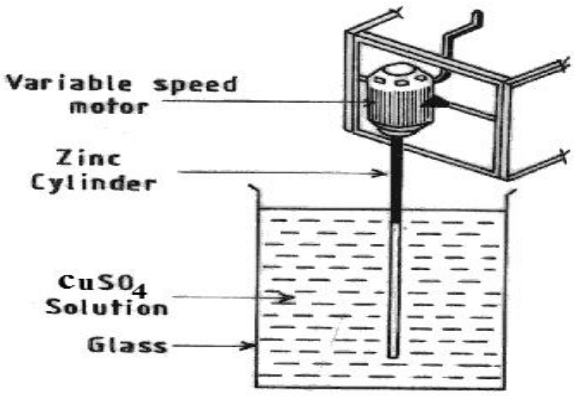


Figure (2): A schematic diagram of the apparatus.

2.3. Procedure

Analar copper sulphate and deionized water were used in the preparation of solutions. Fresh solutions with concentrations of 50, 100, 150, 200, 300 mg/l Cu^{2+} were prepared. Six different concentrations of the organic compounds are (0.5, 1.0, 1.5, 2.0, 3.0 and 4.0) × 10^{-5} mol/1.

The zinc cylinder used in each run is a 7.0 cm length and variable diameters. Before each run 2cm of zinc cylinder was insulated by Taflon and the active surface of the zinc cylinder was polished by fine emery paper, degreased with trichloroethylene, washed with alcohol, and finally rinsed in distilled water. The reaction vessel used consists of a 250 ml glass beaker containing 200 ml $CuSO_4.5H_2O$ solution or $CuSO_4$-organic additive mixture purged with nitrogen gas via a dispersion tube to maintain an oxygen free environment in all studies. Nitrogen gas was bubbled for at least 20 min prior to the beginning of each experiment. The rate of cementation of Cu^{2+} ions was determined in the absence and presence of organic additive at different concentrations of Cu^{2+}, different temperatures, 298, 303, 308 and 313 and rotation speeds ranging from 125 to 750 rpm. Samples of 0.5 ml were taken from the reaction solution at time intervals of 10, 20, 30… minutes, and diluted to 5 ml with deionzed water. The concentration of Cu^{2+} ions in the sample after dilution lies practically in the limit of atomic absorption spectrophotometer. Correcting for the change in reactant volume as result of sampling was considered unnecessary since each sample taken was only 0.5ml, which was 0.25% of total reactant volume. The sample was analyzed for its copper content using a Perkin-Elmer 2380 atomic absorption spectrophotometer (Cu wave length (λ) 324.8 nm). The solution pH was adjusted at 5.3 by the using portable digital pH meter (Model 201/digital). The density was determined by using DA-300 Kyoto electronic at 298, 303, 308 and 313 K. The viscosity was measured using Koehler viscosity bathing (model K23400 kinematic baths) at 298, 303, 308 and 313 K. The accuracy of the instrument is 2%. Diffusivity of $CuSO_4$ was taken from literature [11, 16] and was corrected for the change in temperature using Stokes-Einstein equation

3. Results and discussion

3.1. Kinetic study of cementation

For any cementation reaction the general reaction equation can be written as follows:

$$nA^{a+} + mB^{o} \longrightarrow nA^{o} + mB^{b+} \quad (1)$$

where n, m, A, B, a^+, and b^+ represent the stoichiometric coefficients, the noble and reductant metals, and valences of the noble and reductant metal, respectively [17].

The overall reaction for copper cementation on zinc is expressed by the following equation:

$$Cu^{2+} + Zn \longrightarrow Cu + Zn^{2+} \quad (2)$$

In most systems, cementation reactions have been found to be controlled by boundary layer diffusion, and the reaction is first order with respect to the cementation of noble metal ions, which in the case of copper cementation could be expressed by the following equation [3]:

$$dC/dt = -k'C \quad (3)$$

where,

$$k' = DA / \delta V = k\,A/V \quad (4)$$

where C is concentration of the copper ions (mg/l), t is reaction time (sec), K is a mass transfer coefficient (cm sec^{-1}). D is the diffusion coefficient the copper ions (cm^2 sec^{-1}), δ is diffusion layer thickness (cm), A is reaction surface area (cm^2), and V is volume of solution (cm^3).

The integrated form of the first-order equation can be described as:

$$\log C_o/C = (k\,A/2.303V)\,t \quad (5)$$

where,

C_o: initial concentration of copper ions (mg/l),

C: concentration of copper ions at time t (mg/l).

3.2. Effect of initial concentration of Cu^{2+}

Figure (3) shows the relation between log C_o/C and time for different concentrations of copper sulphate from which the mass transfer coefficients (k) were calculated as given in Table (1). Figure (3) also indicates that cementation reaction follows the first-order kinetics with respect to the noble metal which was verified by other authors [7, 8, 11-13].

It is clear from Table (1) that the rate of mass transfer coefficient increases with increasing copper ion concentration, i.e. cementation rate increases in the direction of precipitation of copper which in agreement with reported results [1,7]. During the cementation reaction the deposited copper accumulates onto the surface of the zinc cylinder and a product layer (metallic copper) appears on the cylinder surface. This surface deposit shows a resistance to the diffusion of copper ions. Depending on the nature of the surface deposit its presence can enhance or diminish the cementation rate. If the metallic layer formed on the reductant metal is a coherent deposit the cementation rate decreases with increasing deposit mass. This case was observed at low initial copper ion concentration conditions. If the surface deposit formed on the reductant metal is a porous metallic layer the cementation rate may increase when the

deposit layer thickness increases. When the initial copper ion concentration is high a coarse and porous precipitate on the metal cylinder surface appears. Under such conditions the diffusion of copper ions from the bulk of the solution to the cylinder surface occurs through the porous layer easily and the cementation rate can increase with the increase of the layer thickness [19, 20]. Comparable experimental results were reported by several researchers [1, 8, 21] for various cementation reaction.

Table (1): Values of mass transfer coefficient (k) at different initial concentrations of $CuSO_4$ at 125 rpm, pH 5.3 and T = 298K.

Concentration mg/l	$k\times 10^4$ cm.sec $^{-1}$
50	7.51
100	8.56
150	9.48
200	11.41
300	12.70

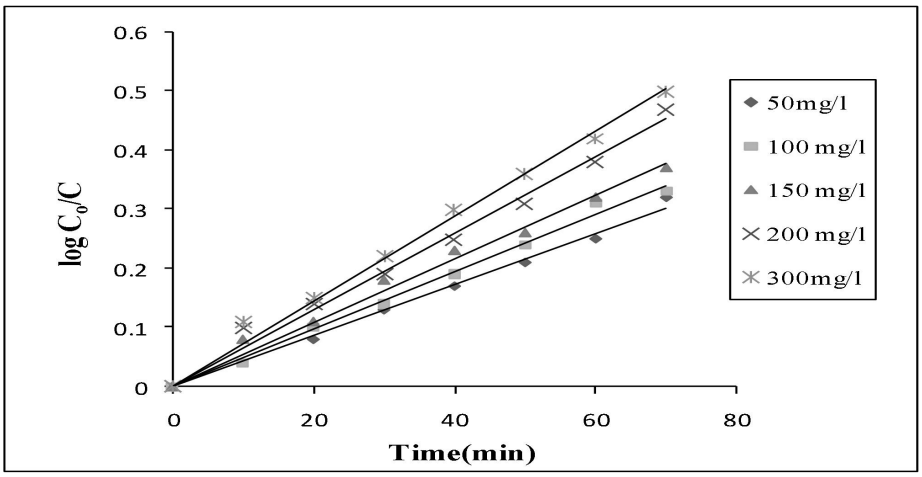


Figure (3): Relation between log Co/C and time for CuSO4 solution at different initial concentrations of Cu2+ at 125 rpm, pH 5.3 and 298 K.

3.3. Effect of rotation speed on the rate of cementation

Figure (4) shows the relation between log C_o/C and time at different speeds of rotation (rpm) of the zinc cylinder in absence of carbohydrates (Figure 4a) and presence of fructose (Figures

4b,4c) from which the mass transfer coefficients (k) are calculated as given in Table (2). Figure (4) also indicates that cementation reaction is first-order in the absence and presence of fructose. It is evident from Table (2) that the rate of cementation of copper on zinc cylinder is enhanced by stirring; this indicates that the copper cementation rate is the diffusion controlled [7, 22]. This behavior may be explained as follows:

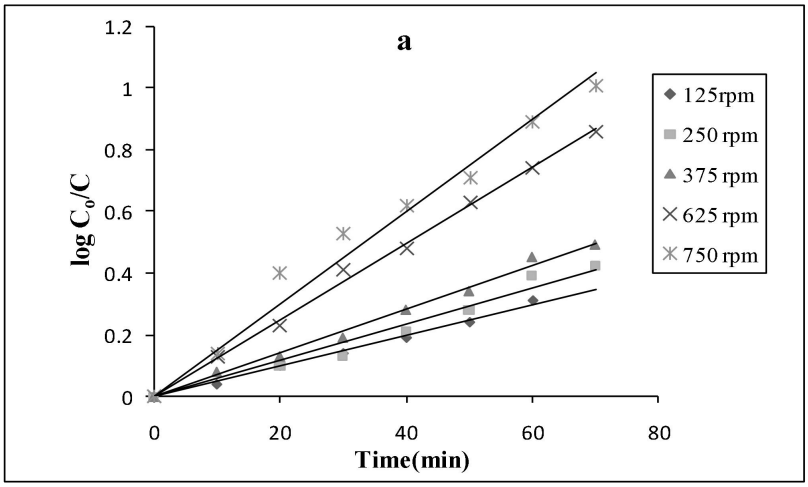
i The higher the rotating speed, the higher the solution flow and thinner the diffusion layer; thus giving a higher rate of transfer of copper ions to the zinc surface and at the same time, through the porous deposit layer formed on the zinc cylinder which, in turn, enhances the rate of cementation reaction [1, 7, 21].

ii During cementation reaction, a deposit layer of metallic copper is formed onto the surface of zinc cylinder. If the rotation speed of the cylinder is strong enough, the deposit formed onto the cylinder can peel off from zinc surface. This fact can facilitate the diffusion of ions towards the metal cylinder surface, and thus the rate of cementation of copper increases as the rotation speed of the cylinder increases [19, 23].

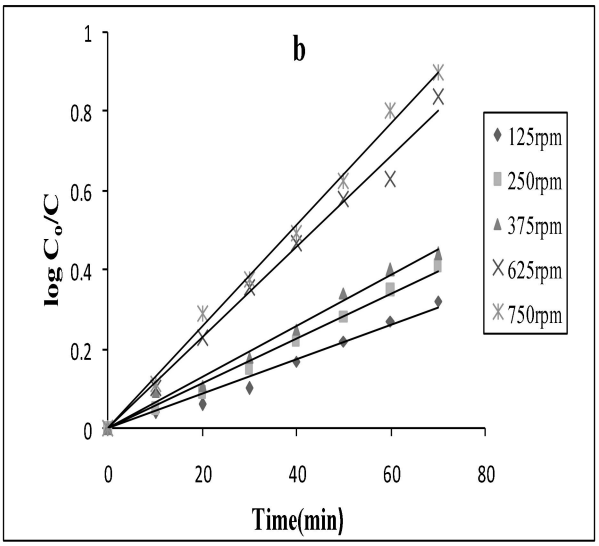
iii Furthermore, the diffusion layer thickness decreases as the rotation speed of the cylinder increases, which facilitate the diffusion of copper ions towards cylinder surface which would lead to increase in the mass transfer coefficient, which is related to the diffusion layer thickness by the equation [11, 19, 24].

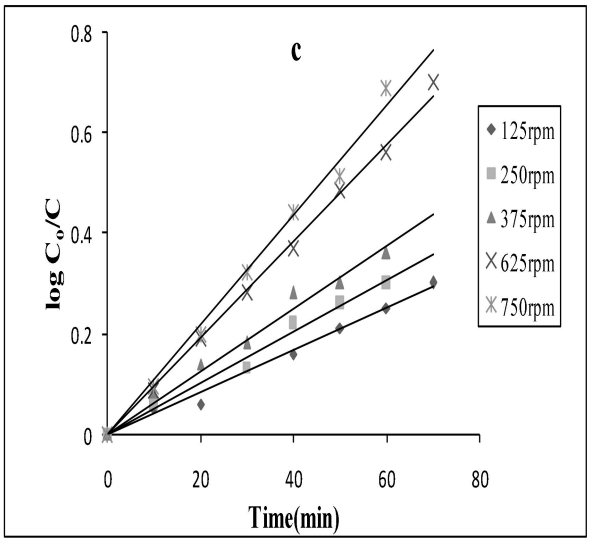
$$k = d / \delta \qquad (6)$$

iv Because the contact of copper ions with zinc cylinder increases per unit time, the rate of cementation will increase as the rotating speed increases [1].



a) in absence of carbohydrate





b) in presence of 0.5 x10^{-5} mol/l fructose **c) in presence of 1 x10^{-5} mol/l fructose**

Figure (4): Relation between log C_o/C and time at 100ppm$CuSO_4$, 298 K and different rotation speeds:

Table (2): Values of mass transfer coefficient (k) at different rotation speeds, 100ppm CuSO4, pH 5.3 and 298 K for different carbohydrates.

carbohydrates	blank	Fructose		Glucose		Mannose		Sucrose		Maltose		Starch	
C×10^5 mol/l	0	0.5	1	0.5	1	0.5	1	0.5	1	0.5	1	0.5	1
rpm	k×10^4 cm. sec $^{-1}$												
125	8.56	7.94	7.58	13.36	12.45	16.25	15.35	7.76	7.40	7.58	7.22	5.24	4.33
250	10.23	10.30	9.21	16.80	15.18	17.17	16.45	10.12	8.67	9.58	8.50	6.51	5.42
375	12.47	11.74	11.20	20.96	16.26	20.97	18.98	11.38	11.20	11.21	10.85	8.50	6.51
625	22.32	20.80	17.36	27.13	23.51	29.13	23.89	20.44	15.92	19.72	15.56	10.13	7.60
750	27.14	23.33	19.71	28.58	27.49	30.76	27.87	22.97	18.63	22.80	18.46	11.40	9.41

A plot of log k (mass transfer coefficient) against log ω (angular velocity) in absence and presence of different carbohydrates is linear, as shown in Figure (5), this supports the conclusion that the cementation is mass transfer limited or diffusion controlled [7, 19] and it is clear that the mass transfer coefficient increased with increasing the angular velocity, according to the following equations:

For blank solutions:

$$k \alpha (\omega)^{0.762} \quad (7)$$

For solutions containing carbohydrates:

$$k \alpha (\omega)^{n} \quad (8)$$

Where the values of the velocity exponent (n) ranged from (0.572 to 0.816) depending on the type of carbohydrates added as shown in Table (3).The values of exponent (n) for mannose and glucose were higher than that observed in blank solution, this indicated that these additives (mannose and glucose) were accelerated the rate of the cementation reaction while the values of exponent (n) for other carbohydrates (fructose, sucrose, maltose, and starch) were lower than that observed in blank solution, this indicated that these additives were inhibited the rate of the cementation reaction.

Table (3): Values of (n) for CuSO4 solution in absence and presence of carbohydrates.

Carbohydrates	n
Blank	0.762
Mannose	0.816
Glucose	0.792
Fructose	0.736
Sucrose	0.717
Maltose	0.698
Starch	0.572

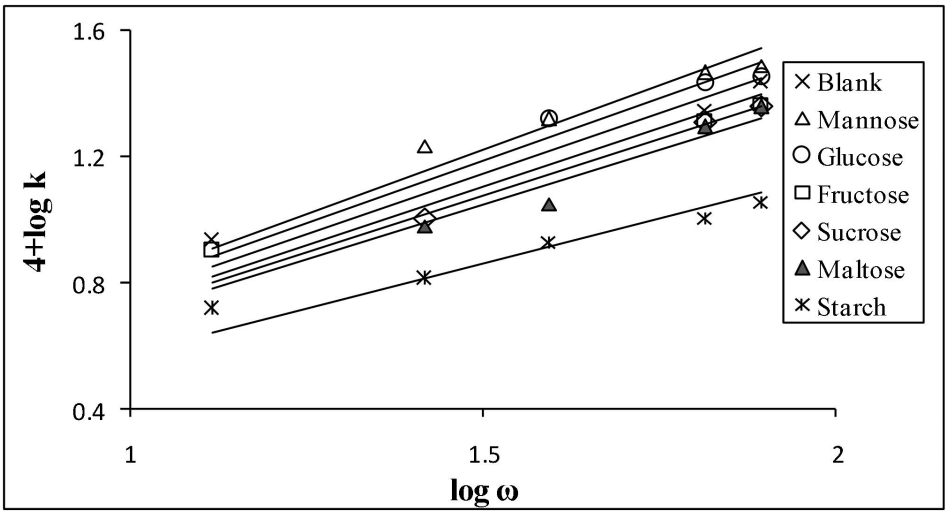


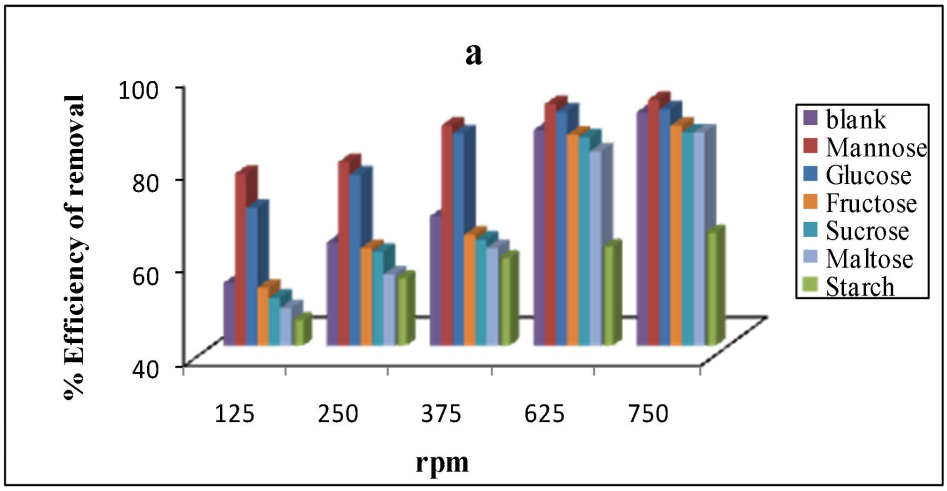
Figure (5): Effect of rotation speeds on the mass transfer coefficient at 100ppm CuSO4, 298 K and at 0.5 x10-5 mol/l of carbohydrates.

The efficiency of copper removal at different rotation speeds in absence and presence of carbohydrates was calculated from the relation [1]:

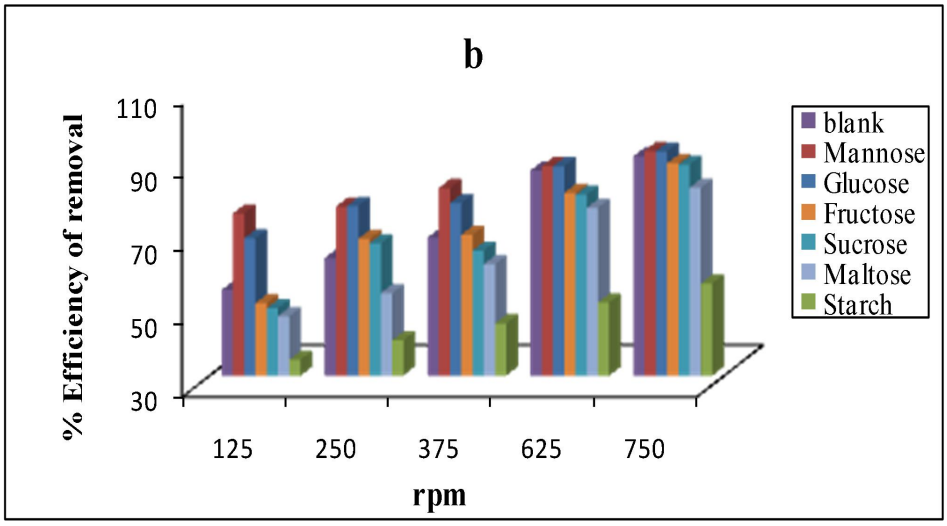
$$\% \text{ efficiency of removal} = [C_o - C_e / C_o] \times 100 \qquad (9)$$

where C_o: is the initial concentration of copper and C_e: is the concentration of copper at end of experiment.

Figure (6) shows the efficiency of copper removal at 70 min in absence and presence of carbohydrates at different rotation speeds (rpm), it clarify that more than 90% of copper removal was accomplished by zinc cylinder in blank and in presence of glucose and mannose at stirring speed 750 rpm while 55-64% of copper removal was accomplished by zinc cylinder in presence of starch at stirring speed 750 rpm.



a) 0.5 x10^{-5} mol/l



b) 1 x10^{-5} mol/l

Figure (6): Relation between efficiency of copper removal and different rotation speeds (rpm) at 100ppm CuSO4, 298K and in presence of different carbohydrates at:

3.4. Effect of temperature on the rate of cementation

In order to investigate the effect of the reaction temperature on the copper cementation from the actual solutions some experiments were performed in the temperature range of 298- 313 K. Figures (7, 8) show the relation between log C_o/C and time at different temperatures in absence and presence of different carbohydrates. The plots pass through origin, which proves that cementation reaction is first order. The mass transfer coefficients (k) for blank and different additives were calculated from the slopes of the linear plots. Table (4) summarizes the obtained results at different temperatures.

The results showed that the elevation of solution temperature increase the mass transfer coefficients for different concentrations of carbohydrates. This may be attributed to the fact that:

i As the temperature increases the solution viscosity decreases and hence the diffusivity [D] of Cu2+ increases according to Stokes-Einstein equation [1, 7, 25]:

$$D\eta / T = \text{constant} \qquad (10)$$

where; D is the diffusion coefficient; η is the solution viscosity; and T is the absolute temperature.

ii High temperature helps to decrease the thickness of hydrodynamic boundary layer, the diffusion layer and hence the mobility and the diffusivity of Cu^{2+} increase [1, 8, 25].

Furthermore, it was observed from these results that the deposit (metallic copper layer) formed on the surface of the zinc cylinder was coherent at low temperature, and therefore the cementation reaction proceeds at a slower rate [19].

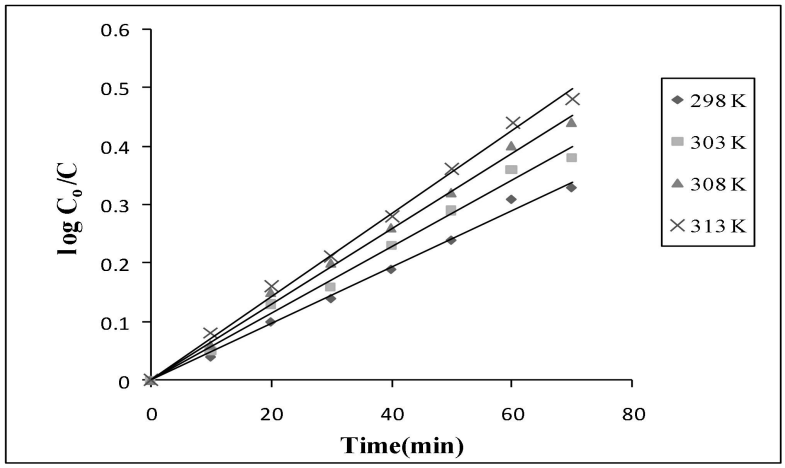
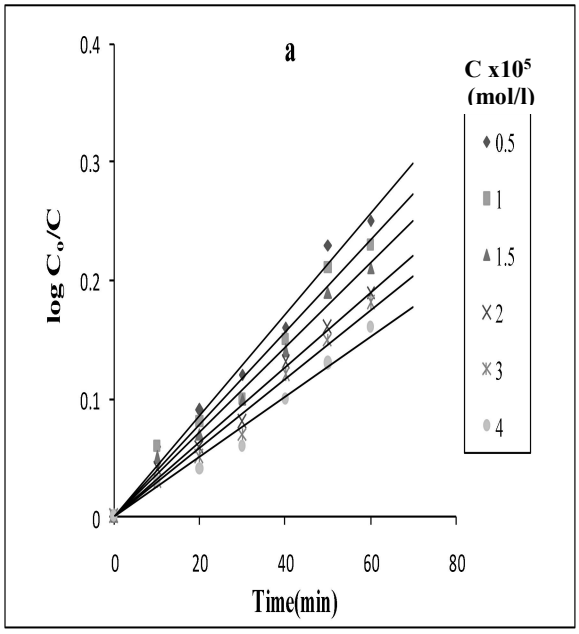
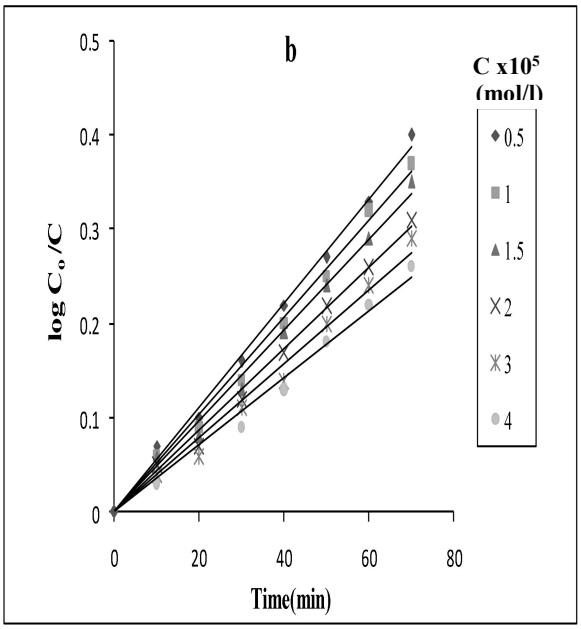


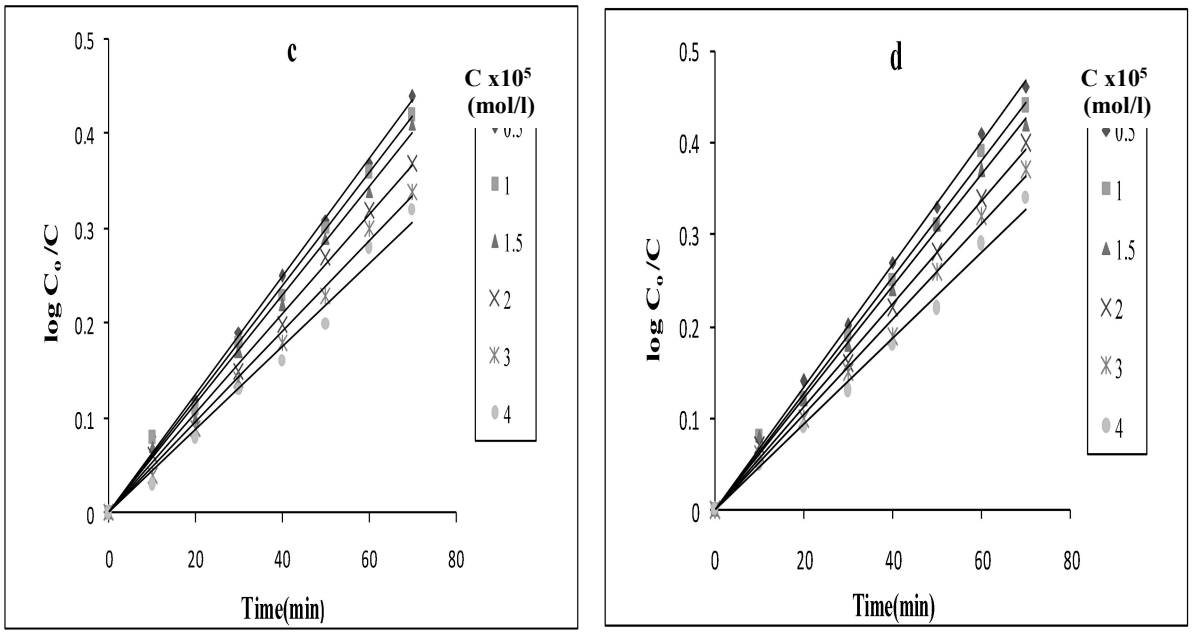
Figure (7): Relation between log C_o/C and time for different temperatures at 100ppm $CuSO_4$, pH 5.3 and 125 rpm.



a) 298 K



b) 303 K



c) 308 K **d) 313 K**

Figure (8): Relation between log Co/C and time for different concentrations of fructose at 100 ppm CuSO4, 125 rpm and at different temperatures:

Table (4): Values of mass transfer coefficient (k) at different temperatures for100 ppm CuSO4, 125 rpm and at different concentrations of carbohydrates.

Fructose								Glucose							
C×10^5 mol/l	**0.0**	**0.5**	**1**	**1.5**	**2**	**3**	**4**	**C×10^5 mol/l**	**0.0**	**0.5**	**1**	**1.5**	**2**	**3**	**4**
T (K)	**k× 10^4 cm.sec^{-1}**							**T (K)**	**k× 10^4 cm.sec^{-1}**						
298	8.56	7.82	7.17	6.62	5.73	5.36	4.64	**298**	8.56	13.23	12.58	12.01	11.35	10.51	9.85
303	10.34	10.23	9.66	8.94	8.01	7.28	6.72	**303**	10.34	14.67	13.84	12.96	12.38	11.49	10.87
308	11.82	11.58	11.27	10.70	9.95	9.06	8.33	**308**	11.82	17.70	16.63	15.57	14.68	13.88	12.31
313	12.92	12.68	11.96	11.58	10.69	9.92	9.02	**313**	12.92	18.81	17.58	16.67	15.60	14.92	13.61
Mannose								**Sucrose**							
C×10^5 mol/l	**0.0**	**0.5**	**1**	**1.5**	**2**	**3**	**4**	**C×10^5 mol/l**	**0.0**	**0.5**	**1**	**1.5**	**2**	**3**	**4**
T(K)	**k× 10^4 cm.sec^{-1}**							**T(K)**	**k× 10^4 cm.sec^{-1}**						
298	8.56	13.61	12.70	12.41	11.64	10.94	9.91	**298**	8.56	7.68	7.14	6.56	5.63	5.24	4.48
303	10.34	15.57	14.73	13.87	12.92	12.13	11.16	**303**	10.34	10.12	9.56	8.78	8.00	7.14	6.55
308	11.82	17.71	16.55	15.82	14.65	13.68	12.38	**308**	11.82	11.11	10.58	10.24	9.43	8.73	7.92
313	12.92	19.82	18.33	17.40	16.16	15.22	13.72	**313**	12.92	12.39	11.85	11.23	10.45	9.83	9.00
Maltose								**Starch**							
C×10^5 mol/l	**0.0**	**0.5**	**1**	**1.5**	**2**	**3**	**4**	**C×10^5 mol/l**	**0.0**	**0.5**	**1**	**1.5**	**2**	**3**	**4**

T(K)	k× 10^4 cm.sec $^{-1}$							T(K)	k× 10^4 cm.sec $^{-1}$						
298	8.56	7.60	6.78	6.20	5.58	5.02	4.39	**298**	8.56	5.99	5.53	5.03	4.54	4.03	3.54
303	10.34	8.57	7.32	6.71	6.08	5.68	5.05	**303**	10.34	6.58	6.10	5.84	5.33	4.59	4.08
308	11.82	9.89	8.89	8.26	7.62	6.86	6.00	**308**	11.82	8.41	7.68	6.91	6.42	5.91	5.16
313	12.92	12.00	11.21	10.56	9.73	9.08	8.24	**313**	12.92	11.86	10.57	9.31	8.28	7.30	6.52

The values of apparent activation energy (E_a) were calculated from the slope of the linear plot of ln k against (1/T) according to the equation:

$$\ln k = - E_a/RT + \ln A \quad (11)$$

The values for the enthalpy of activation ΔH*, entropy of activation ΔS* and free energy of activation ΔG* can be obtained using the equations:

$$\Delta H^* = E_a - RT \quad (12)$$

$$\Delta S^*/R = \ln A - \ln (BTe/h) \quad (13)$$

$$\Delta G^* = \Delta H^* - T\,\Delta S^* \quad (14)$$

where k is the mass transfer coefficient, A is a frequency factor, E_a is the activation energy, R is the gas constant (8.314 J/K mol), T is the absolute temperature (K), B is the Boltzmann's constant (1.38×10^{-23} $J.K^{-1}$), e is the electronic charge (2.7183), and h is Plank's constant (6.626×10^{-34} J.s) [8, 11].

The activation energy E_a, enthalpy ΔH*, entropy ΔS* and free energy ΔG*of activation were calculated by least squares procedures, and are given in Table (5) together with their standard deviations.

It can be seen from Table (5) that the values of E_a of cementation process ranged between 16.8 and 35.5 kJ mol^{-1}, which indicates that the copper cementation reaction by rotating zinc cylinder is diffusion controlled mechanism. This result is consistent with the fact that the rate of cementation increases with increasing speed of rotation (section 3.3). This finding is consistent with previous studies for various cementation systems [1, 21, 26]. It is also clear that the values of E_a in presence of fructose, sucrose, maltose and starch are higher than that of blank indicating that the cementation of copper is inhibited by these compounds, hence supports the phenomena of physical adsorption. On other hand the values of E_a in presence of glucose and mannose lower than that measured at blank solution indicating that the cementation process is accelerated by glucose and mannose [21].

It is noticed also that the ΔS* possesses highly negative values indicating a highly ordered system with less spontaneity and the charge of cations (Cu^{2+} ion) imposes order on the zinc cylinder [27].

Further going over Table (5) it is found that higher values of ΔH* in presence of fructose, sucrose, maltose and starch than that value of ΔH* for blank solution, this revealing that the addition of these additives increase the height of energy barrier of the cementation process to

an extent depend on the type of carbohydrates. On other hand, ΔH* for the solution containing glucose and mannose are lower than that blank, this implies that the addition of two carbohydrates decrease the height of energy barrier of the cementation reaction of copper [1].

The ΔG* values show limited increase with rise in the concentration of carbohydrates revealing weak dependence of ΔG* on the composition of the carbohydrates can be attributed to the general linear compensation between ΔH* and ΔS*. The compensation effect may be attributed to the changes in solution structure as a result of the addition of the carbohydrates [7, 8, 19]. Since the cementation reaction is a diffusion controlled process, as gained from the values of E_a, the activation parameters are expected to be strongly affected by the variation of properties of the medium such as viscosity and density, as a result of adding organic carbohydrates by affecting the diffusivity and activity of the metal ions [7].

3.5. Isokinetic relationship

The isokinetic relationship is a linear relationship between ΔH*(the enthalpy of activation) and ΔS* (the entropy of activation) and the slope in this linear relationship is the temperature at which all reactions that confirm to the line occur at the same rate, (β) is therefore known as the isokinetic temperature represented in Kelvin [7].

Figure (9) shows that the plot of ΔH* versus ΔS* for different carbohydrates was found to be linear. The isokinetic temperature (β) computed from the slope of this plot is 357 (the linear correlation coefficient is 0.999) which is higher than the experimental temperature; this indicated that the reaction is enthalpy-controlled. Moreover, the good linear correlation of the isokinetic relationships for the different carbohydrates indicates that they all have the same reaction mechanism. This finding is agreed with previous studies for various cementation systems such as cementation of Cu^{2+} with zinc and Cd^{2+} with zinc [7, 21].

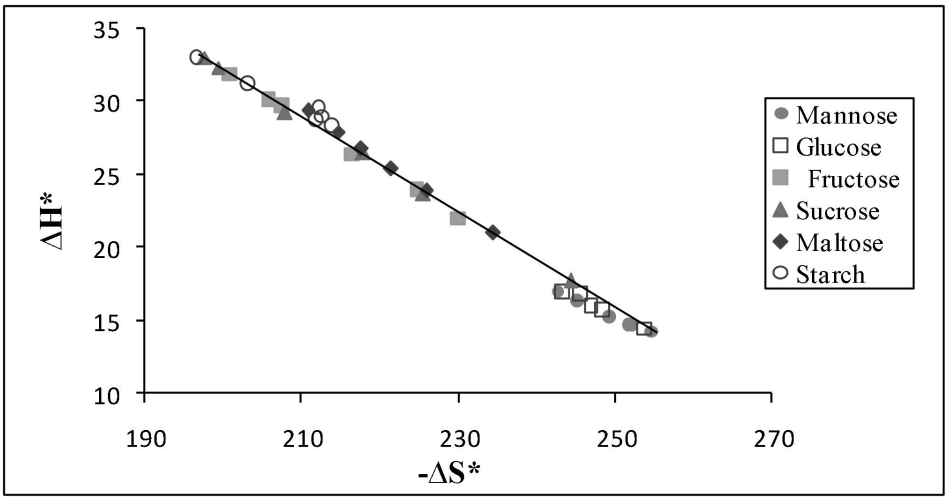


Figure (9): Isokinetic relationship for different carbohydrates.

Table (5): Activation parameters in absence and presence of different concentrations of carbohydrates.

	Fructose				Glucose				Mannose			
C×10^{5} mol/l	**E_a kJ mol^{-1}**	**ΔH* kJ mol^{-1}**	**-ΔS* J mol^{-1} K^{-1}**	**ΔG* kJ mol^{-1}**	**E_a kJ mol^{-1}**	**ΔH* kJ mol^{-1}**	**-ΔS* J mol^{-1} K^{-1}**	**ΔG* kJ mol^{-1}**	**E_a kJ mol^{-1}**	**ΔH* kJ mol^{-1}**	**-ΔS* J mol^{-1} K^{-1}**	**ΔG* kJ mol^{-1}**
0.0	**21.3±2.20**	**18.8±2.20**	**240.0±7.30**	**90.5±4.40**	**21.3±2.20**	**18.8±2.20**	**240.0±7.30**	**90.5±4.40**	**21.3±2.20**	**18.8±2.20**	**240.0±7.30**	**90.5±4.40**
0.5	24.5±4.29	22.1±4.29	230.0±14.1	90.6±8.48	19.4±2.56	16.9±2.56	243.4±8.38	89.5±5.06	19.5±0.36	17.0±0.36	242.6±1.17	89.4±0.71
1	26.4±5.61	23.9±5.61	224.6±18.37	90.8±11.09	18.5±2.50	16.0±2.50	246.9±8.20	89.6±4.95	18.9±0.96	16.4±0.96	245.1±3.13	89.5±1.89
1.5	29.0±5.14	26.5±5.14	216.6±16.83	91.0±10.16	18.1±2.45	15.6±2.45	248.5±8.01	89.7±4.83	17.8±0.66	15.3±0.66	249.2±2.16	89.6±1.30
2	32.6±6.13	30.1±6.13	205.6±20.08	91.4±12.12	19.3±5.48	16.8±5.48	277.4±17.93	89.5±10.83	17.24±0.54	14.8±0.54	251.6±1.77	89.8±1.07
3	32.2±4.98	29.7±4.98	207.5±16.30	91.6±9.84	19.26±2.39	16.79±2.39	245.7±7.82	90.0±4.72	17.2±0.43	14.76±0.43	252.1±1.40	89.9±0.85
4	34.5±6.79	32.0±6.79	200.9±22.22	91.9±13.41	17.0±0.59	14.5±0.59	253.8±1.94	90.2±1.17	16.8±0.27	14.3±0.27	254.5±0.88	90.2±0.53
	Sucrose				**Maltose**				**Starch**			

C×10^5 mol/l	E_a kJ mol^{-1}	ΔH* kJ mol^{-1}	-ΔS* J mol^{-1} K^{-1}	ΔG* kJ mol^{-1}	E_a kJ mol^{-1}	ΔH* kJ mol^{-1}	-ΔS* J mol^{-1} K^{-1}	ΔG* kJ mol^{-1}	E_a kJ mol^{-1}	ΔH* kJ mol^{-1}	-ΔS* J mol^{-1} K^{-1}	ΔG* kJ mol^{-1}
0.0	**21.3±2.20**	**18.8±2.20**	**240.0±7.30**	**90.5±4.40**	**21.3±2.20**	**18.8±2.20**	**240.0±7.30**	**90.5±4.40**	**21.3±2.20**	**18.8±2.20**	**240.0±7.30**	**90.5±4.40**
0.5	20.2±1.95	17.7±1.95	244.3±6.37	90.6±3.85	23.5±2.06	21.0±2.06	234.4±6.75	90.9±4.08	35.5±6.53	33.0±6.53	196.4±21.37	91.6±12.90
1	26.2±1.99	23.7±1.99	225.5±6.50	91.0±3.93	26.4±4.18	23.9±4.18	225.9±13.68	91.2±8.26	33.6±5.80	31.2±5.80	203.3±18.99	91.8±11.46
1.5	32.0±1.97	29.3±1.97	207.9±6.46	91.3±3.90	27.9±4.49	25.5±4.49	221.3±14.71	91.5±8.88	31.2±4.16	28.7±4.16	212.0±13.61	91.9±8.22
2	29.0±1.22	26.5±1.22	217.9±4.01	91.4±2.42	29.3±4.41	26.8±4.41	217.6±14.42	91.7±8.70	30.8±2.67	28.4±2.67	214.0±8.73	92.2±5.27
3	34.4±0.89	32.4±0.89	199.2±2.91	91.5±1.76	30.5±4.18	28.0±4.18	214.6±13.67	92.0±8.25	31.6±2.94	29.1±2.94	212.6±9.62	92.5±5.39
4	35.5±0.93	33.1±0.93	197.6±3.05	92.0±1.84	31.9±4.84	29.4±4.84	210.8±15.84	92.3±9.56	32.0±2.79	29.6±2.79	212.1±9.13	92.8±5.51

3.6. Effect of carbohydrates on the rate of cementation

The effect of concentrations of various carbohydrates compounds on the mass transfer coefficients calculated from the plots log C_o/C against time at different concentrations are given in Tables (6, 7). Table (6) shows that the presence of monosaccharides (as fructose), disaccharides (as sucrose and maltose) and polysaccharides (as starch) retarded the rate of cementation of Cu^{2+} ions and it gives also the relation between the percentage of inhibition in the rate of the cementation reaction and different concentrations of these carbohydrates. It was found also that the percentage of inhibition ranged from 8.65 to 58.65% depending on the type of carbohydrates and their concentrations. The percentage of inhibition for the cementation reaction is calculated from the relation [8]:

$$\% \text{ inhibition} = [(k_o - k) / k_o] \times 100 \qquad (15)$$

where k_o, k are the rate of cementation in absence and in presence of carbohydrates.

Inspection Figure (10) shows that the relation between the percentage of inhibition in the rate of the cementation reaction and different concentrations of carbohydrates at 100 ppm $CuSO_4$, 125 rpm and 298 K. It is obvious that:

i. The percentage of inhibition increases as the concentration of carbohydrates increases.

ii. The order of decreasing inhibition is as follows:

Polysaccharides (starch) > disaccharides (maltose > sucrose) > monosaccharides (fructose).

It is clear from Table (6) and Figure (10) that the experiments conducted in the presence of various amounts of starch, maltose, fructose and sucrose between 0.5×10^{-5} mol/l and 4×10^{-5} mol/l, the mass transfer coefficients decreases with gradually increasing the concentrations of these additives. This may be attributed to:

i Adsorption of these additives on zinc surface, which leads to form a film (adsorbed layer) at zinc surface. After forming that layer, the diffusivity of Cu2+ ions to zinc surface decrease due to the presence of adsorbed layer and diffusion layer, which leads to decrease the rate of cementation. Also adsorption of these additives on zinc surface depends mainly on the structure [1, 21, 28].

ii The increase in the viscosity of solutions containing these additives (Table 8) which is due to steric hindrance, bulkness effect of molecules

and the relatively large numbers of glycosidic bonds would require more energy to be ruptured, which leads to decrease the mobility and the diffusivity of Cu2+, with a consequent decrease in the rate of cementation [7].

iii The chemical structure of starch is differ than other additives, where the structure of starch consists of the relatively large number of D-glucose units connected by glycosidic bonds, the relatively large numbers of glycosidic bonds and large numbers of hydroxymethyl groups [29].

iv The presence of large numbers of (OH) groups in case of starch leading to formation the hydrogen bond formed with water molecules would required more energy to be ruptured [7].

Table (7) shows that the presence of mannose and glucose enhanced the removal of Cu^{2+} ions from aqueous solution by cementation and it also shows the relation between the percentage of acceleration in the rate of the cementation reaction and different concentrations of these carbohydrates. It was found also that the percentage of acceleration ranged from 15.07 to 59.00 % depending on the type of carbohydrates and their concentrations. The percentage of acceleration for the cementation reaction is calculated from the relation [1]:

$$\% \text{ acceleration} = [(k - k_o) / k_o] \times 100 \qquad (16)$$

where k_o, k are the rate of cementation in absence and in presence of carbohydrates.

Inspection Figure (11) shows that the relation between the percentage of acceleration in the rate of the cementation reaction and different concentrations of carbohydrates at 100 ppm $CuSO_4$, 125 rpm and 298 K. It is observed that:

i The percentage acceleration increases as the concentration of carbohydrates decreases.

ii The order of acceleration of the studied compounds is:

Mannose > Glucose

From Table (7) and Figure (11) it is also apparent that the experiments conducted in the presence of mannose and glucose between 0.5×10^{-5} $moll^{-1}$ and 4×10^{-5} $moll^{-1}$, the mass transfer coefficients increases at lower concentrations of mannose and glucose. This may be attributed to the following:

i The presence of ring oxygen atom which has lone pair of electrons is a great probability for Zn^{2+} ions which produces through dissolution of zinc metal to interact or adsorb electrostatically on oxygen atom lone pair by a sort of coordinate bond. The amount of Zn^{2+} ions decrease due to formation of a coordinate bond between Zn^{2+} ions and these additives, i.e. more zinc metal will dissolve and rate of cementation increases [1].

ii The terminal hydroxyl groups of these additives are interacting with Zn^{2+} ions also by a sort of coordinate bond. Therefore, the amount of Zn^{2+} ions decrease due to formation of a coordinate bond between Zn^{2+} ions and the terminal hydroxyl groups, i.e. the consumption of zinc metal was increased and hence the rate of cementation increases [1, 30].

iii The decrease in the viscosity of solutions containing these additives as in Table (13) which is due to high solubility of these additives, which leads to increase the mobility and the diffusivity of Cu^{2+} ions, with a consequent increase in the rate of cementation [1, 7].

iv The beneficial structure effect of mannose giving the advantage to increase the strength of coordinate bond with Zn^{2+} through the presence of bulky hydroxymethyl group and two (OH) groups in axial position [1].

Therefore, one can conclude that the performance of these additives has been ascribed to the type and strength of interaction with Zn^{2+} ions at solutions [1, 7].

Further, increase of mannose and glucose concentrations gradually decreases the removal of Cu^{2+}ions from aqueous solution by cementation; however the cementation rate could still be higher than blank. This may be explained on the basis that:

i. The hydroxyl groups have another mode of interaction leading to attack Cu^{2+} ions [1, 31].

ii. Changes of activity of Cu^{2+} ions in the solution brought by the increase in additives concentrations [32].

iii. In presence of excess concentration of additives there is possible adsorption of these additives on the zinc surface, thus; reducing the active area of the zinc surface [1, 21].

iv. At higher concentration of additives the transfer of Cu^{2+} ions is gradually interfered by thick, porous, and amorphous layer of metal deposits, this is in agreement with the previous studies for various cementation systems [1, 26].

v. The formation of hydrogen bonds with water molecules via the presence of three (OH) groups in equatorial position in case of glucose would required higher energy to broke [7].

It is concluded from these results of the present study that the improvement in the cementation performance was caused by adding 0.5×10^{-5} $moll^{-1}$of mannose, this associated drop in the viscosity of the solution, which allow Cu^{2+} ions to move more freely in the solution and hence the rate of cementation increases, this finding is in agreement with other authors [1, 21, 26].

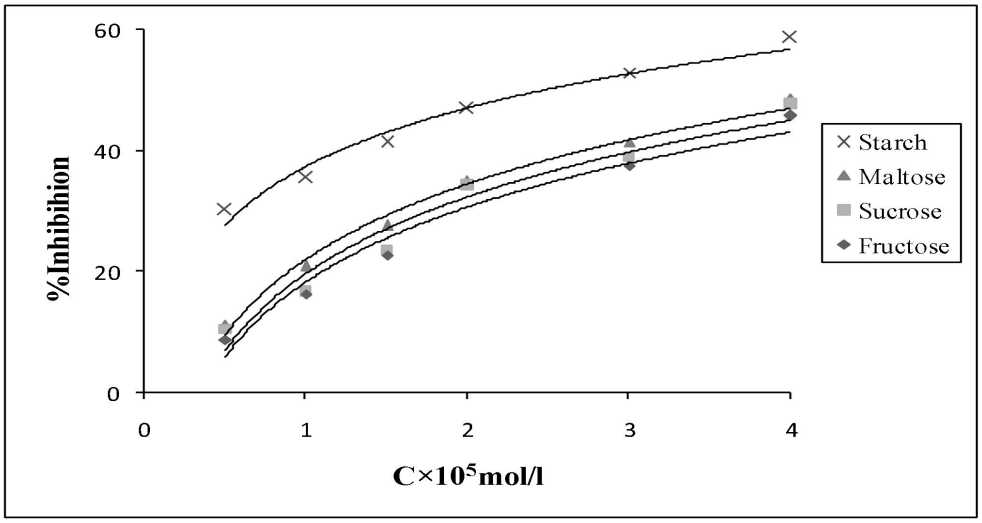


Figure (10): Relation between % inhibition and concentrations of carbohydrates at 100ppm $CuSO_4$, 125 rpm and 298 K.

Table (6): Effect of concentration of carbohydrates on the % inhibition of mass transfer coefficient (k) at 100ppm CuSO4, 125 rpm and 298 K.

Fructose							
$C\times10^5$ mol/l	**0.00**	**0.5**	**1**	**1.5**	**2**	**3**	**4**
$k\times10^4$ cm. sec^{-1}	**8.56**	7.82	7.17	6.62	5.73	5.36	4.64
% inhibition	**0.00**	8.65	16.24	22.66	33.06	37.38	45.79
Sucrose							

C×10^5 mol/l	0.00	0.5	1	1.5	2	3	4
k×10^4 cm. sec^{-1}	8.56	7.68	7.14	6.56	5.63	5.24	4.48
% inhibition	0.00	10.28	16.59	23.37	34.23	38.79	47.66
Maltose							
C×10^5 mol/l	0.00	0.5	1	1.5	2	3	4
k×10^4 cm. sec^{-1}	8.56	7.60	6.78	6.20	5.58	5.02	4.39
% inhibition	0.00	11.22	20.79	27.57	34.81	41.36	48.72
Starch							
C×10^5 moll^{-1}	0.00	0.5	1	1.5	2	3	4
k×10^4 cm. sec^{-1}	8.56	5.99	5.53	5.03	4.54	4.03	3.54
% inhibition	0.00	30.02	35.40	41.24	46.96	52.92	58.65

Table (7): Effect of concentration of carbohydrates on the % acceleration of mass transfer coefficient (k) at 100ppm CuSO4, 125 rpm and 298 K.

Glucose							
C×10^5 mol/l	0.00	0.5	1	1.5	2	3	4
k×10^4 cm. sec^{-1}	8.56	13.23	12.58	12.01	11.35	10.51	9.85
% acceleration	0.00	54.57	46.96	40.30	32.59	22.78	15.07
Mannose							
C×10^5 mol/l	0.00	0.5	1	1.5	2	3	4
k×10^4 cm. sec^{-1}	8.56	13.61	12.70	12.41	11.64	10.94	9.91
% acceleration	0.00	59.00	48.37	44.98	35.98	27.80	15.77

Table (8): Physical parameters (viscosity η and diffusion coefficient D) at different concentrations of carbohydrates for 100 ppm CuSO4, 125 rpm at different temperatures.

	Fructose								**Glucose**								**Mannose**							
T (K)	**298**		**303**		**308**		**313**		**298**		**303**		**308**		**313**		**298**		**303**		**308**		**313**	
C× 10^{-5} mol /l	**η cm poise**	**D× 10^{6} cm² sec⁻¹**	**η cm poise**	**D× 10^{6} cm² sec⁻¹**	**η cm poise**	**D× 10^{6} cm² sec⁻¹**	**η cm poise**	**D× 10^{6} cm² sec⁻¹**	**η cm poise**	**D× 10^{6} cm² sec⁻¹**	**η cm poise**	**D× 10^{6} cm² sec⁻¹**	**η cm poise**	**D× 10^{6} cm² sec⁻¹**	**η cm poise**	**D× 10^{6} cm² sec⁻¹**	**η cm poise**	**D× 10^{6} cm² sec⁻¹**	**η cm poise**	**D× 10^{6} cm² sec⁻¹**	**η cm poise**	**D× 10^{6} cm² sec⁻¹**	**η cm poise**	**D× 10^{6} cm² sec⁻¹**
0.5	1.17	11.7	1.13	10.8	1.12	9.63	1.10	8.57	1.15	11.9	1.12	10.9	1.10	9.80	1.08	8.73	1.13	12.1	1.11	11.0	1.09	9.89	1.07	8.81
1	1.19	11.5	1.15	10.6	1.14	9.46	1.12	8.42	1.13	12.1	1.11	11.0	1.08	10.0	1.07	8.81	1.11	12.3	1.09	11.2	1.07	10.1	1.05	8.98
1.5	1.21	11.3	1.19	10.3	1.15	9.38	1.14	8.27	1.11	12.3	1.10	11.1	1.07	10.1	1.06	8.89	1.10	12.4	1.08	11.3	1.06	10.2	1.04	9.06
2	1.25	10.9	1.23	9.93	1.20	8.99	1.18	7.99	1.10	12.4	1.08	11.3	1.06	10.2	1.04	9.06	1.08	12.6	1.06	11.5	1.04	10.4	1.02	9.24
3	1.3	10.5	1.2	9.54	1.2	8.56	1.2	7.60	1.0	12.6	1.0	11.6	1.0	10.4	1.0	9.24	1.0	12.9	1.0	11.7	1.0	10.6	1.0	9.33

	0		8		6		4		8		5		4		2		6		4		2		1	
4	1.36	10.3	1.34	9.11	1.30	8.29	1.26	7.48	1.06	12.9	1.03	11.9	1.02	10.6	1.00	9.43	1.04	13.1	1.02	12.0	1.01	10.7	0.98	9.62

	Sucrose								**Maltose**								**Starch**							
T (K)	**298**		**303**		**308**		**313**		**298**		**303**		**308**		**313**		**298**		**303**		**308**		**313**	
C× 10^{-5} mol/l	**η cm poise**	**D× 10^6 cm^2 sec^{-1}**	**η cm poise**	**D× 10^6 cm^2 sec^{-1}**	**η cm poise**	**D× 10^6 cm^2 sec^{-1}**	**η cm poise**	**D× 10^6 cm^2 sec^{-1}**	**η cm poise**	**D× 10^6 cm^2 sec^{-1}**	**η cm poise**	**D× 10^6 cm^2 sec^{-1}**	**η cm poise**	**D× 10^6 cm^2 sec^{-1}**	**η cm poise**	**D× 10^6 cm^2 sec^{-1}**	**η cm poise**	**D× 10^6 cm^2 sec^{-1}**	**η cm poise**	**D× 10^6 cm^2 sec^{-1}**	**η cm poise**	**D× 10^6 cm^2 sec^{-1}**	**η cm poise**	**D× 10^6 cm^2 sec^{-1}**
0.5	1.25	10.9	1.23	9.93	1.21	8.91	1.14	8.27	1.42	9.60	1.34	9.11	1.26	8.56	1.16	8.13	1.44	9.47	1.35	9.05	1.32	8.17	1.20	7.85
1	1.28	10.7	1.26	9.69	1.24	8.70	1.16	8.13	1.50	9.09	1.36	8.98	1.28	8.42	1.18	7.99	1.50	9.09	1.40	8.72	1.34	8.05	1.22	7.73
1.5	1.30	10.5	1.28	9.54	1.26	8.56	1.18	7.99	1.53	8.91	1.39	8.78	1.30	8.93	1.20	7.85	1.60	8.52	1.45	8.42	1.36	7.93	1.24	7.60
2	1.40	9.74	1.38	8.85	1.30	8.29	1.21	7.79	1.56	8.74	1.50	8.14	1.36	7.93	1.23	7.66	1.66	8.22	1.52	8.03	1.40	7.70	1.26	7.48

3	1.62	8.42	1.41	8.66	1.32	8.17	1.25	7.54	1.65	8.27	1.55	7.88	1.40	7.70	1.26	7.48	1.76	7.75	1.56	7.83	1.42	7.60	1.28	7.36
4	1.65	8.27	1.51	8.09	1.41	7.65	1.28	7.36	1.74	7.84	1.60	7.63	1.44	7.49	1.30	7.25	1.81	7.54	1.64	7.45	1.45	7.44	1.32	7.14

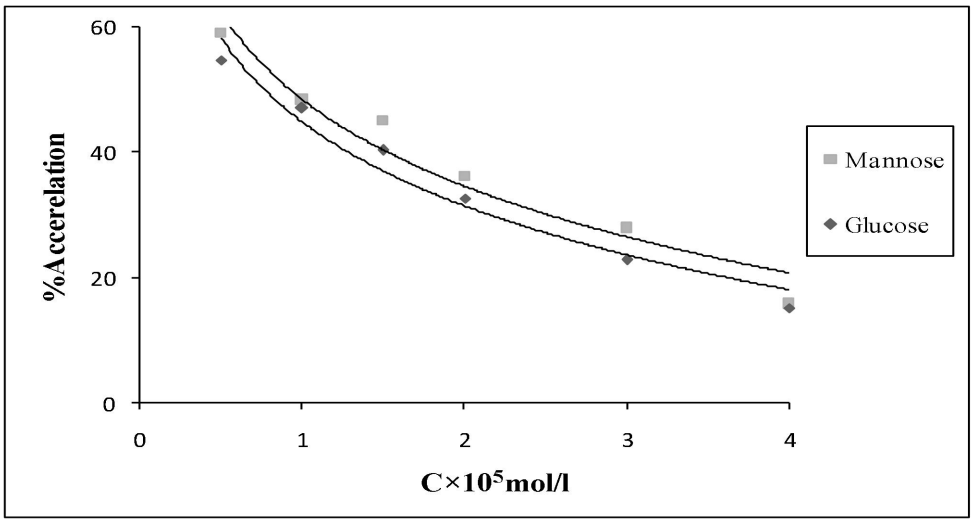


Figure (11): Relation between % acceleration and concentrations of carbohydrates at 100ppm $CuSO_4$, 125 rpm and 298 K.

3.7. Adsorption isotherm

The electrochemical processes on the metal surface were caused by the adsorption of organic additives [33], and the degree of surface coverage (θ) for different concentrations of organic additives. The adsorption depends on the chemical structure of organic additives [34].

The adsorption isotherm data obtained from the present study were analyzed in the light of Langmuir and Temkin isotherms. The Langmuir adsorption isotherm has been used in the form as follows [35]:

$$\theta / 1 - \theta = KC \qquad (17)$$

Rearrangement of equation (17) gives

$$C / \theta = 1/K + C \qquad (18)$$

where K is the equilibrium constant of adsorption process, C is the concentration of organic additives and θ is the surface coverage.

The degree of surface coverage (θ) was determined in the form of equation as follows [36]:

$$\theta = (k_{blank} - k_{organic})/k_{blank} \qquad (19)$$

where k_{blank} is the rate of cementation of blank and $k_{organic}$ is the rate of cementation in presence of organic additives.

Figure (12) shows that the relation between C/ θ and C for carbohydrates at 298 K which gives straight line with intercepts (1/K). The values of (K) for this system were calculated

from the intercept of the Figure (12) and the data were provided in Table (9). It is apparent that the linear correlation coefficients (R^2) are very good and the slope in case of maltose was equal one. This supports the applicability of the Langmuir adsorption isotherm indicating that the adsorption of maltose onto zinc surface may be governed by physisorption [27], and the Langmuir isotherm is valid for monolayer adsorption onto metal surface with a finite number of identical sites [37]. On other hand the slopes values in case of fructose and sucrose were not close to equal one but in case of starch the slope was more than one. This deviation may be refer to the interaction among adsorbed spices on the zinc surface but such adsorbed spices such as large molecules (as carbohydrates) interact by mutual repulsion or attraction. This meaning that the adsorption of fructose, sucrose and starch does not accord with the Langmuir adsorption isotherm. In order to determine the mechanism of cementation, the experimental data were applied to Temkin adsorption isotherm [27, 38].

The Temkin isotherm has generally been applied in the following linear form [39]:

$$\theta = (\ln K/-2a) + (\ln C/-2a) \qquad (20)$$

where a is the lateral interaction term describing the molecular interactions in the adsorption layer and the heterogeneity of the metal surface.

Figure (13) shows that the Temkin adsorption isotherm plotted as θ vs. ln C for carbohydrates at 298 K which yields straight line with slope (1/-2a) and intercepts (ln K/- 2a). The value of (a) for this system was calculated from the slope of the Figure (13) and the data was provided in Table (9) and it is apparent that (R^2) is very good. Table (9) shows that all the values of (a) are smaller than zero (i.e. the values of (a) are negative), indicating that the repulsion exists in the adsorption layer [38].

It is well known that the standard free energy of adsorption (ΔG^o_{ads}) is related to the equilibrium constant of adsorption (K) and (ΔG^o_{ads}) can be calculated in the form of equation as follows [40]:

$$\Delta G^o_{ads} = - RT \ln (55.5\ K) \qquad (21)$$

where the value (55.5) is the concentration of water in solution in ($moll^{-1}$) [41].The other symbols have the definitions mentioned previously.

The calculated adsorption free energies are listed in Table (9). In all cases, the ΔG^o_{ads} values are negative. The negative values of ΔG^o_{ads} indicate the feasibility of the reaction and the spontaneous adsorption of the inhibitor [42]. It is found that ΔG^o_{ads} values are more positive

than -40 kJ mol^{-1} indicating that the inhibitors are physically adsorbed on the metal surface (i.e. the adsorption by inhibitors was governed by physisorption) [8,27].

Table (9): Parameters of Langmuir and Temkin isotherms and ΔGoads for carbohydrates in presence of 100 ppm CuSO4, 125rpm and 298 K.

Carbohydrates	Langmuir			Temkin				
	K	Slope	R^2	Slope	-a	K	R^2	$-\Delta G^o_{ads}$ $kJmol^{-1}$
Fructose	18726.59	0.865	0.997	0.180	2.78	53.61	0.967	19.82
Sucrose	20833.33	0.940	0.955	0.182	2.75	54.81	0.969	19.87
Maltose	26595.74	1.11	0.989	0.180	2.78	55.30	0.988	19.89
Starch	78125.00	1.43	0.987	0.166	3.01	58.25	0.997	20.02

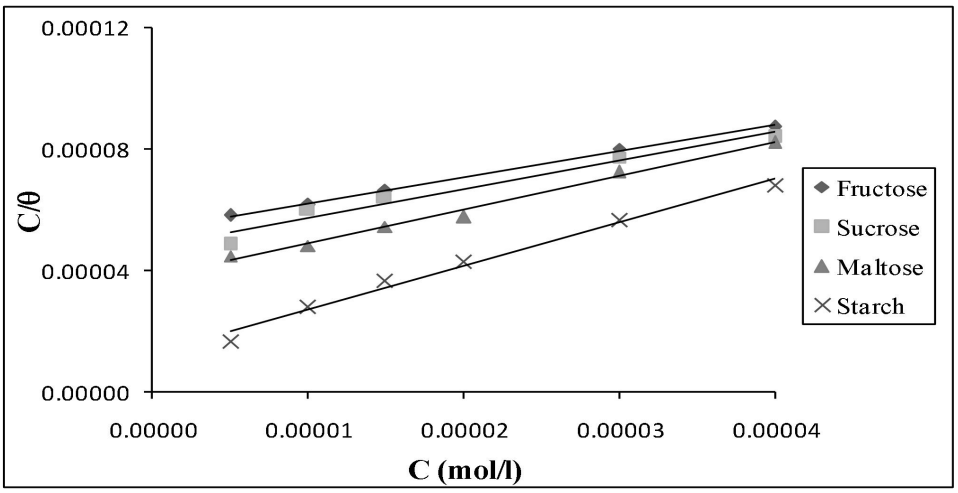


Figure (12): Langmuir adsorption isotherm for carbohydrates at 100ppm CuSO4, 125 rpm and 298 K.

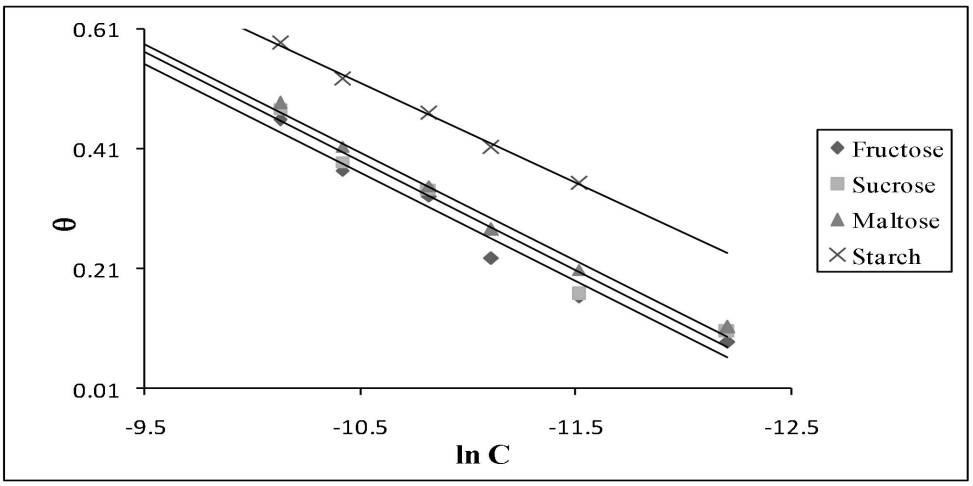


Figure (13): Temkin adsorption isotherm for carbohydrates at 100ppm CuSO4, 125 rpm and 298 K.

3.8 Application of cementation process on samples of industrial wastewater

A cementation reaction is applied to two filtered samples collected from El-Beda waste (sample I, located at Kafr El-Dawar in Behaira Governorate, Alexandria, Egypt) and Rakta company waste (sample II, located at Tabia region in Alexandria, Egypt) spiked with internal standard solution consisted of 10 mg/l Cu^{2+}. The original concentrations of copper in the filtered samples were 11.58 and 9.16 (µg/l) respectively. The cementation reaction rate of Cu^{2+} in the two samples in the absence and in the presence of mannose is estimated. The following reaction conditions were as follows: 625 rpm, 313 K, and 6 hours reaction period. The exposed surface areas of zinc cylinder for the sample (I) were 29.47 cm^2 and 29.36 cm^2 in absence and presence of mannose; respectively, while the exposed surface areas of zinc cylinder for the sample (II) were 29.36 cm^2 and 29.25 cm^2 in absence and presence of mannose; respectively. After 1 h Cu^{2+}concentration (sample (I) in the absence of mannose was found to be 8.71 ppm, i.e. Cu^{2+}concentration decreased by 12.9%. While after 2 h it became 4.27 ppm, i.e. 57.3% is recovered from the initial concentration. At the end of the experiment, the concentration of copper reached 1.00 ppm, i.e. about 90.0% is recovered from the sample (I) (Table 10). The mass transfer coefficient for Cu^{2+} is calculated from Figure (15) as $6.78x10^{-4}$cm sec^{-1}. In case of the sample (II) in the absence of mannose the concentration of Cu^{2+} after 1h, was found to be 4.72 ppm, i.e. Cu^{2+} concentration decreased by 49.9%. While after 2 h it became 2.54 ppm, i.e. 73.0% is recovered from the initial concentration. At the end of the experiment, the concentration of copper reached 0.44 ppm, i.e. about 95.3% is recovered from the sample as shown in Table (11). The mass transfer coefficient for Cu^{2+} is calculated from Figure (16) as $10.99x10^{-4}$ cm sec^{-1}. In the presence of mannose sample (I),

Cu^{2+} concentration after 1 h decreased by 48.5% and after 2 hour the recovery of Cu^{2+} was found to be 75.9%, while at the end of the reaction it reached 0.31 ppm i.e. 95.6% of initial Cu^{2+} concentration is completely recovered as shown in Table (10). Mass transfer coefficient is found to be 10.73×10^{-4} cm sec^{-1}as given in Figure (15). While in case of the sample (II) and after 1 h, the concentration of Cu^{2+} decreased by 64.5% and after 2 h the recovery of Cu^{2+} was found to be 80.0%, while at the end of the reaction it reached 0.134 ppm i.e. 98.3% of initial Cu^{2+} concentration is completely recovered as given in Table (11). Mass transfer coefficient is found to be 14.44×10^{-4} cm sec^{-1} as shown in Figure (16). It is clear that the presence of mannose increases the recovery percentage of Cu^{2+} and also reduces the time recovery (95.6%, 5 h) and (98.3%, 5 h) relative to that in absence of mannose (90.0%, 5.5 h) and (95.3%, 5.5 h) for the samples (I) and (II), respectively. This is a good and satisfactory result from the environmental point of view as an original concentration of Cu^{2+} of 11.58 ppb will become 0.51 ppb i.e. 95.6% removal and the original concentration of 9.16 ppb will become 0.16 ppb i.e. 98.3% removal for the samples (I) and (II), respectively. These concentrations will be negligible or become zero when the samples are subjected to dilution before dumped on the aquatic system.

Table (10): Relation between log C_o/C and time for sample (I).

In absence of Mannose			In presence of Mannose		
Time (min)	**C (ppm)**	**log C_o/C**	**Time (min)**	**C (ppm)**	**log C_o/C**
0	**10**	**0.00**	**0**	**7.11**	**0.00**
30	**9.12**	**0.04**	**30**	**3.91**	**0.26**
60	**8.71**	**0.06**	**60**	**3.66**	**0.29**
90	**4.90**	**0.31**	**90**	**2.83**	**0.40**
120	**4.27**	**0.37**	**120**	**1.71**	**0.62**
150	**3.16**	**0.50**	**150**	**1.37**	**0.72**
180	**2.82**	**0.55**	**180**	**1.08**	**0.82**
210	**2.69**	**0.57**	**210**	**0.85**	**0.92**
240	**2.34**	**0.63**	**240**	**0.67**	**1.03**

270	2.29	0.64	270	0.64	1.05
300	1.86	0.73	300	0.31	1.36
330	1.00	1.00	330	0.31	1.36
360	1.00	1.00	360	0.31	1.36

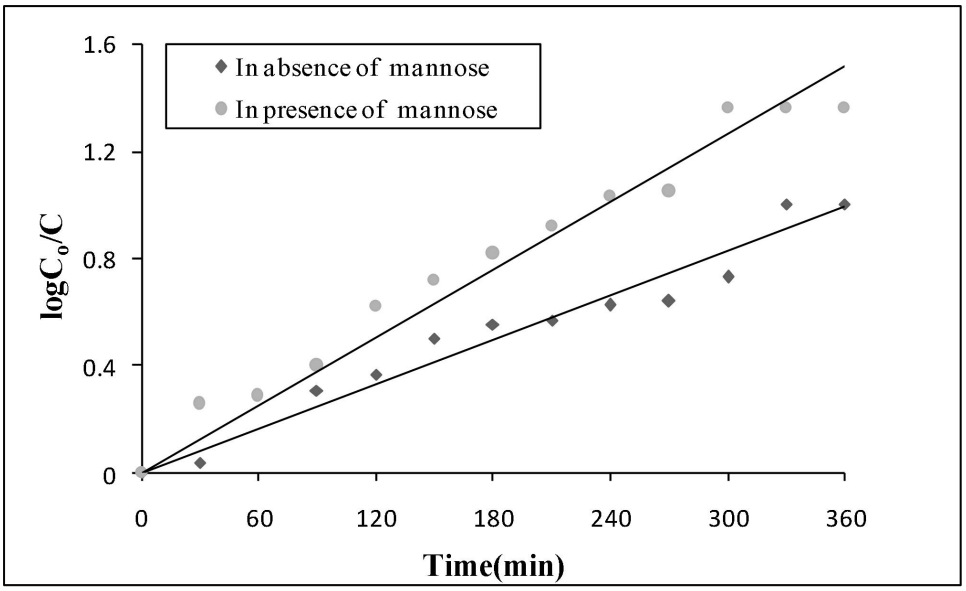


Figure (15): Relation between log Co/C and time for sample (I) in absence and presence of 0.5x10-5mol/l of mannose at 625 rpm and 313 K.

Table (11): Relation between log Co/C and time for sample (II).

In absence of Mannose			In presence of Mannose		
Time (min)	C (ppm)	log C_o/C	Time (min)	C (ppm)	log C_o/C
0	9.42	0.00	0	7.7	0.00
30	6.67	0.15	30	3.84	0.30
60	4.72	0.30	60	2.73	0.45
90	3.34	0.45	90	2.17	0.55
120	2.54	0.57	120	1.54	0.70

150	**2.01**	**0.67**	**150**	**0.84**	**0.96**
180	**1.49**	**0.80**	**180**	**0.52**	**1.17**
210	**1.19**	**1.02**	**210**	**0.38**	**1.31**
240	**0.65**	**1.16**	**240**	**0.29**	**1.42**
270	**0.61**	**1.19**	**270**	**0.273**	**1.45**
300	**0.59**	**1.20**	**300**	**0.134**	**1.76**
330	**0.44**	**1.33**	**330**	**0.134**	**1.76**
360	**0.44**	**1.33**	**360**	**0.134**	**1.76**

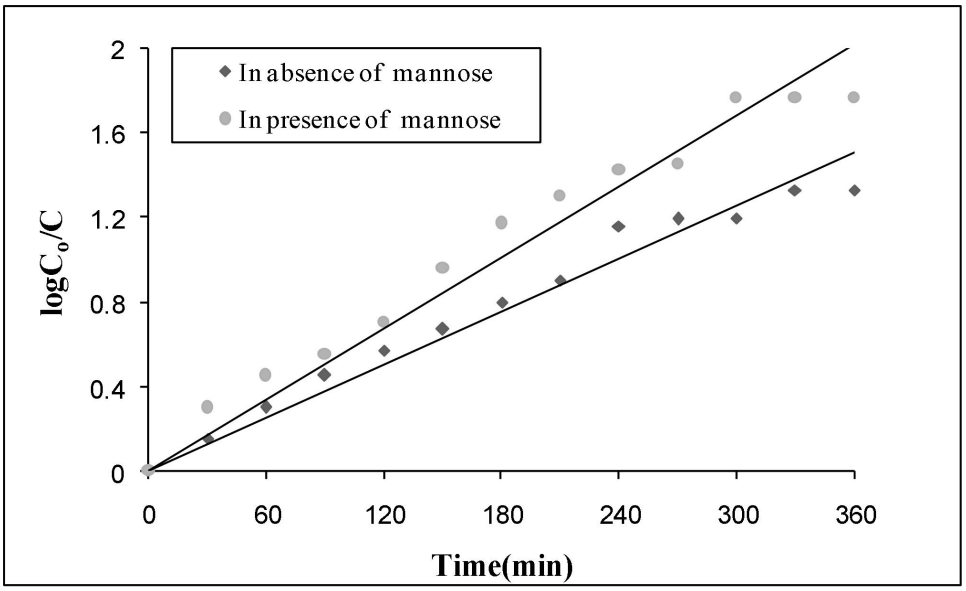


Figure (16): Relation between log Co/C and time for sample (II) in absence and presence of 0.5x10-5mol/l of mannose at 625 rpm and 313 K.

4. Conclusions

1. Cementation is an efficient technique by which pollution due to cupric ion can be readily decreased.
2. For Cu^{2+} / Zn cementation system, the mass transfer coefficient (k) increases with the increasing initial copper ions concentration, rotational speed of zinc cylinder and temperature.

3. The presence of monosaccharides (as fructose), disaccharides (as sucrose and maltose) and polysaccharides (as starch) retarded the rate of cementation of Cu^{2+} ions, the order of decreasing inhibition is as follows:

   Polysaccharides (starch) > disaccharides (maltose > sucrose) > monosaccharides (fructose).

4. The presence of mannose and glucose enhanced the removal of Cu^{2+} ions from aqueous solution by cementation, the order of acceleration of the studied compounds is: Mannose > Glucose

5. An acceptable rate of metal removal is obtained by using small concentration of mannose.

6. The adsorption isotherm data obtained from the present study were analyzed in the light of Langmuir and Temkin isotherms.

7. The cementation reaction was applied to two samples (I,II) of wastewater spiked with Cu. It is clear that the presence of mannose increases the recovery percentage of Cu^{2+} and also reduces the time recovery (95.6%, 5 h) and (98.3%, 5 h) relative to that in absence of mannose (90.0%, 5.5 h) and (95.3%, 5.5 h) for the samples (I) and (II), respectively.

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