

# Removal of chelated cupric ions from industrial effluents by cementation on zinc using a rotating cylinder batch reactor

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Rate of  $\text{Cu}^{++}$  removal from simulated industrial effluents by cementation on rotating zinc cylinder was studied in presence of chelating agents. Parameters studied were, initial  $\text{Cu}^{++}$  concentration, type of chelating agents (citric and tartaric acid), speed of rotation, temperature and pH. It was found that the presence of chelating agents inhibits the cementation reaction by a percentage ranging from 9.89 % to 34.4 % at 20 °C. Citric acid has a higher inhibition effect than tartaric acid. The cementation reaction kinetic follows first order kinetics. At  $\text{pH} \leq 2$  the chelating agent has a negligible effect on the cementation rate. The activation energy lies between 3.7 to 9.3 kcal/mol indicating a diffusion-controlled cementation mechanism even in the presence of chelating agents.

تم دراسة معدل إزالة أيونات النحاس الناتجة من محاكاة المخلفات الصناعية السائلة عن طريق الإحلال الفلزى وذلك باستخدام إسطوانة من الزنك الدوارة في وجود عوامل تكوين المتراكبات. ولقد تم دراسة العوامل التالية: التركيز الابتدائي لأيون النحاس. نوع عوامل تكوين المتراكبات (حامض الستريك وحامض الطرطريك)، سرعة دوران الإسطوانة، درجة الحرارة، الرقم الهيدروجيني للمحلول. ولقد وجد أن وجود تلك العوامل يعرقل من سرعة تفاعل الإحلال بنسبة مئوية تتراوح بين 9.89 إلى 34.4 عند درجة حرارة 20 °م. ولقد لوحظ أن تأثير حامض الستريك أكبر من تأثير حامض الطرطريك على سرعة التفاعل. كما وجد أن حركية التفاعل من الرتبة الأولى. كذلك وجد أن عند رقم هيدروجيني أقل من 2. فإن تأثير هذه العوامل يمكن إهماله على معدل الإحلال الفلزى. وقد تم تعيين طاقة التنشيط للتفاعل ووجد أنها تتراوح بين 3.7 إلى 9.3 كيلو سعر حرارى لكل مول، مما يؤكد أن التفاعل محكوم بخطوة الإنتشار.

**Keywords:** Cementation, Chelated heavy metals, Rotating cylinder, Wastewater treatment

## 1. Introduction

Wastewater discharged from electroless plating, metal finishing industries, pharmaceutical industry, food industry and pulp and paper industry may contain a considerable portions of strong chelating agents such as ethylene diaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), citric and tartaric acids. These chelating agents form an equimolar chelates with many heavy metals. These chelated heavy metal species are very stable over a wide range of pH beside their strong buffering capacity. Consequently conventional precipitation/coagulation treatment which a pH dependent process will be ineffective for heavy metal removal from these waste streams. Thus the need for more effective alternative technique to remove such chelated heavy metal species is essential. Within literature, many approaches have been investigated such as adsorption [1], ion exchange [2], membrane process [3] and

electrochemical methods [4] to treat wastewater containing chelated heavy metal species. Although some of these methods may be effective in the removal of chelated species from wastewater, however the economic consideration is still uncertain.

Breaking the metal chelate species into free metal and free chelating agent, followed by recovering of heavy metals in insoluble form is another approach which has also been studied [5]. Chemicals such as dithiocarbamate, hydrosulfite, sulfide iron salts are often effective in lowering metal concentration and meeting discharge requirements. However they are dangerous and generate wastes that may still require further processing. Cementation on the other hand appears to be an effective alternative to conventional treatment methods due to its simplicity in operation, ease of control, low cost, and the possibility of recovering valuable metals. Cementation is a process by which the more noble metal is precipitated from its salts by another less

noble metal. Removal of heavy metal from waste water by cementation has been studied by many authors [6-12]. Some authors studied the effect of the presence of organic compounds such as surfactants [13-18] and alcohols [19] on the rate of cementation of heavy metals. It has been found that the presence of anionic surfactants during cementation can enhance the rate of cementation [17-18]; however alcohols have a negative effect on the cementation rate [19].

The aim of the present work is to investigate the effect of the presence of chelating agents on the rate of cupric ion cementation on rotating zinc cylinder. The effect of the chelating agent type, speed of rotation, temperature and pH on the rate of cementation reaction have also been studied.

## 2. Experimental technique

The experimental setup consisted of one liter Pyrex glass vessel of 14 cm height and 9 cm diameter. A zinc cylinder of 7 cm height and 2 cm diameter was placed in the middle of the vessel at 3 cm distance from the bottom of the glass container. The zinc cylinder was connected to a variable speed motor by a steel shaft. Precautions were taken to avoid any vibrations during runs. Cylinder rotational speed was controlled by means of a variac and was measured by an optical tachometer.

The temperature of the solution was adjusted using a thermostat. Solution pH was measured and recorded. Solutions were prepared using distilled water and A.R grade chemicals. Before each run the zinc cylinder was cleaned using emery paper followed by etching in 10 % HCl to remove any oxides from the surface followed by washing using distilled water.

Before each run 1000 ml of  $\text{CuSO}_4$  of known concentration were placed in the vessel and the speed of rotation was adjusted at different values. Equinormal solution of cupric ions and chelating agents were prepared to study the effect of the chelating agents on rate of cementation.

The kinetics of the reaction was followed by withdrawing 5 ml of the solution every 5 minutes for copper analysis using iodometry [20] during the course of the run. Table 1

shows the range of the values of different parameters studied in the present work.

## 3. Results and discussion

Rates of cementation of copper ions on zinc were expressed in the present work in terms of the mass transfer coefficient which was obtained under different conditions from the batch reactor equation:-

$$-V(dC/dt) = kAC. \quad (1)$$

This upon integration yields:

$$V \ln(C_0/C) = kAt. \quad (2)$$

Fig. 1, shows the relation between  $\log C_0/C$  against time at different copper sulphate concentrations in absence of chelating agents, the mass transfer coefficients were calculated from the slope  $kA/V$ . Fig. 1 also confirms the fact that cementation reaction is a first order reaction as found by other authors [6-9, 12, 14, 16, 19].

Fig. 1 also shows that increasing initial  $\text{Cu}^{++}$  concentration increases the mass transfer coefficient. This finding can be explained by the presence of rough deposits at high concentration. These rough deposits act as turbulence promoters and consequently increase rate of cementation.

Figs. 2-4 show the effect of rpm on the rate of cementation for copper sulfate without chelating agent, and in presence of citric and tartaric acid respectively. It is noted that, in all cases the increase of rpm increases the rate of cementation which indicates the diffusion-controlled nature of the reaction even in the presence of chelating agents. As the speed of rotation increases, the degree of turbulence increases which creates eddies and hence decreases boundary layer thickness and enhances rate of cementation.

Table 1  
Values of different variables studied in the present work

Parameters	Range
RPM	60, 100, 200, 300, 400, 500r.p.
Concentration of $\text{Cu}^{++}$	.05, 0.1, 0.15, 0.2, 0.25, 0.3 N
Temp	20, 30, 40 ° C
Type of chelating agent	Citric acid and tartaric acid
PH (citric acid)	2, 4, 6, 8,10

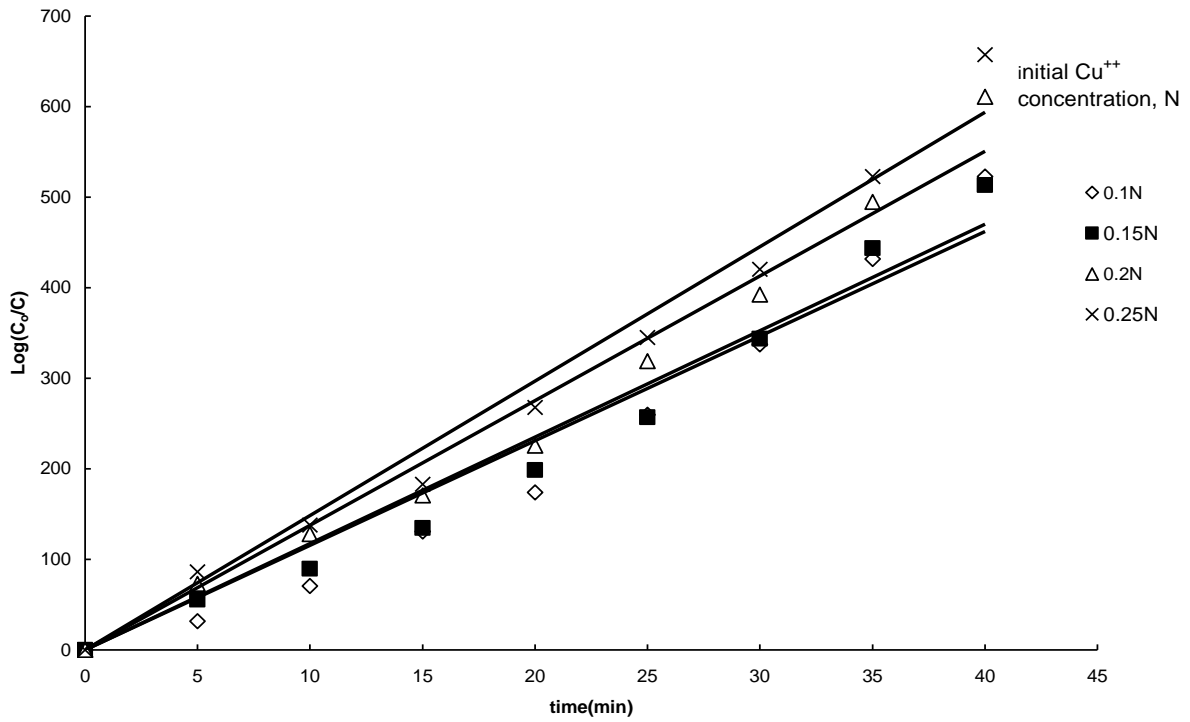


Fig. 1. Effect of initial cupric ion concentration on cementation rate (rpm=650, temp=20° C).

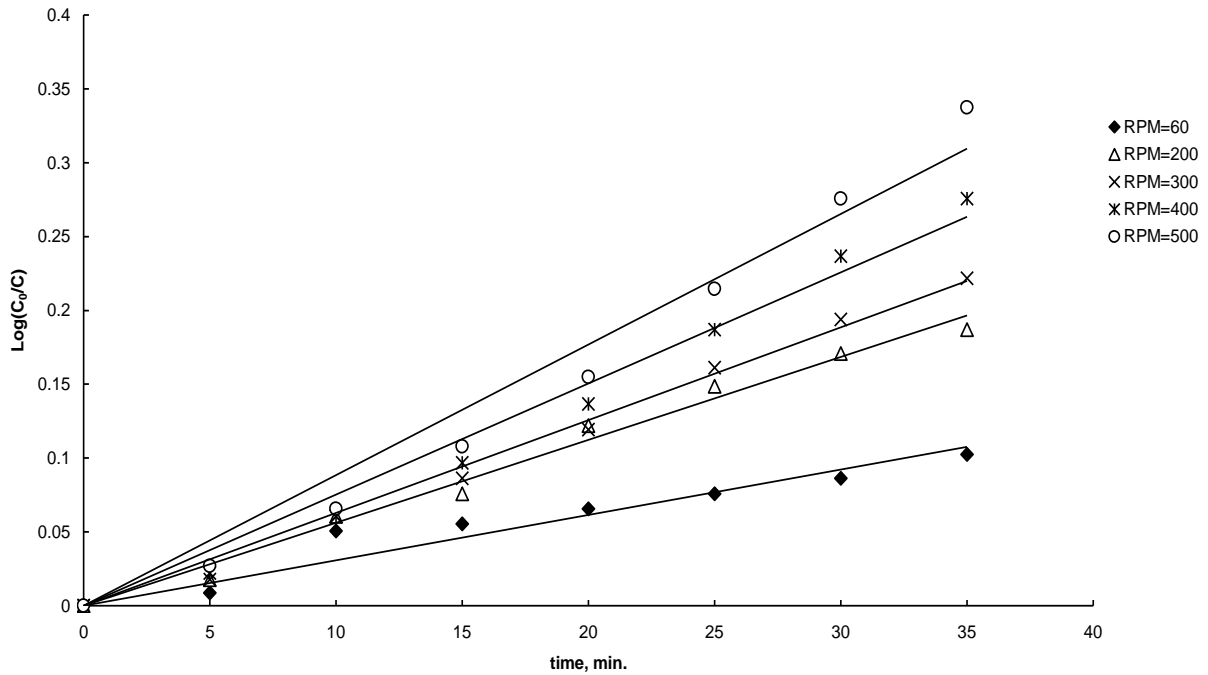


Fig. 2. Effect of rpm on the rate of copper ion cementation on zinc in absence of chelating agents. (initial Cu<sup>++</sup> concentration=0.1 N, Temp=20 °C).

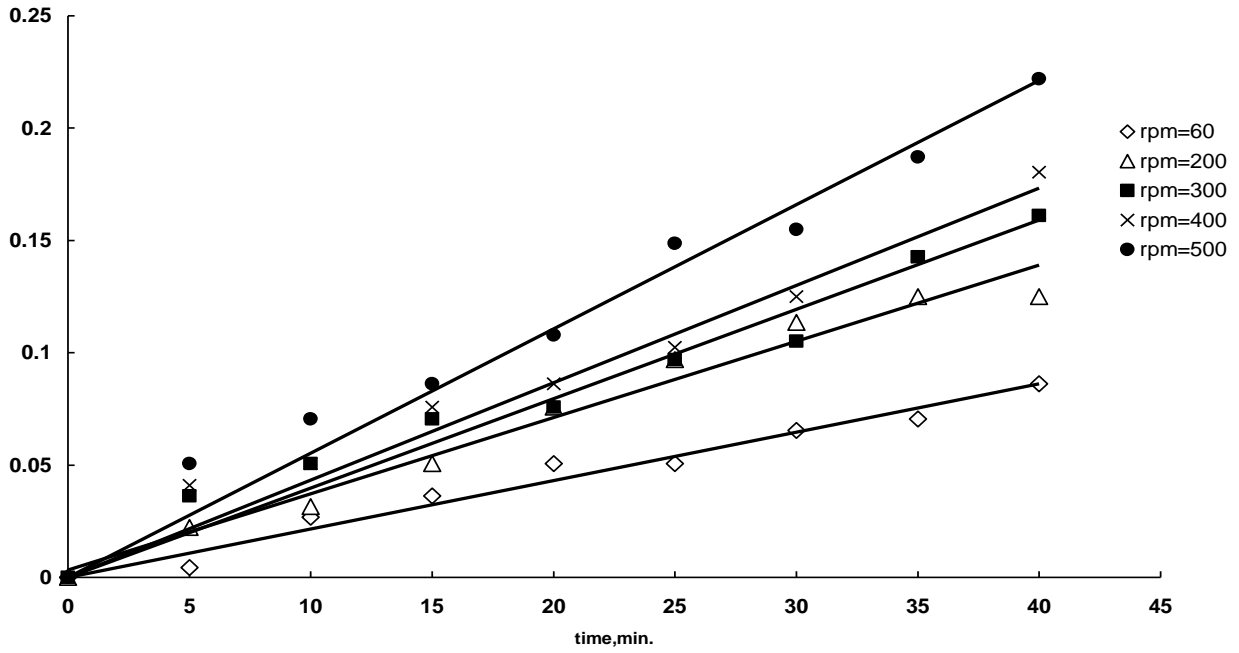


Fig. 3. Effect of rpm on the rate of copper ion cementation in the presence of citric acid (initial  $Cu^{++}$  concentration=0.1 N, citric acid concentration=0.1N, temp=20 °C).

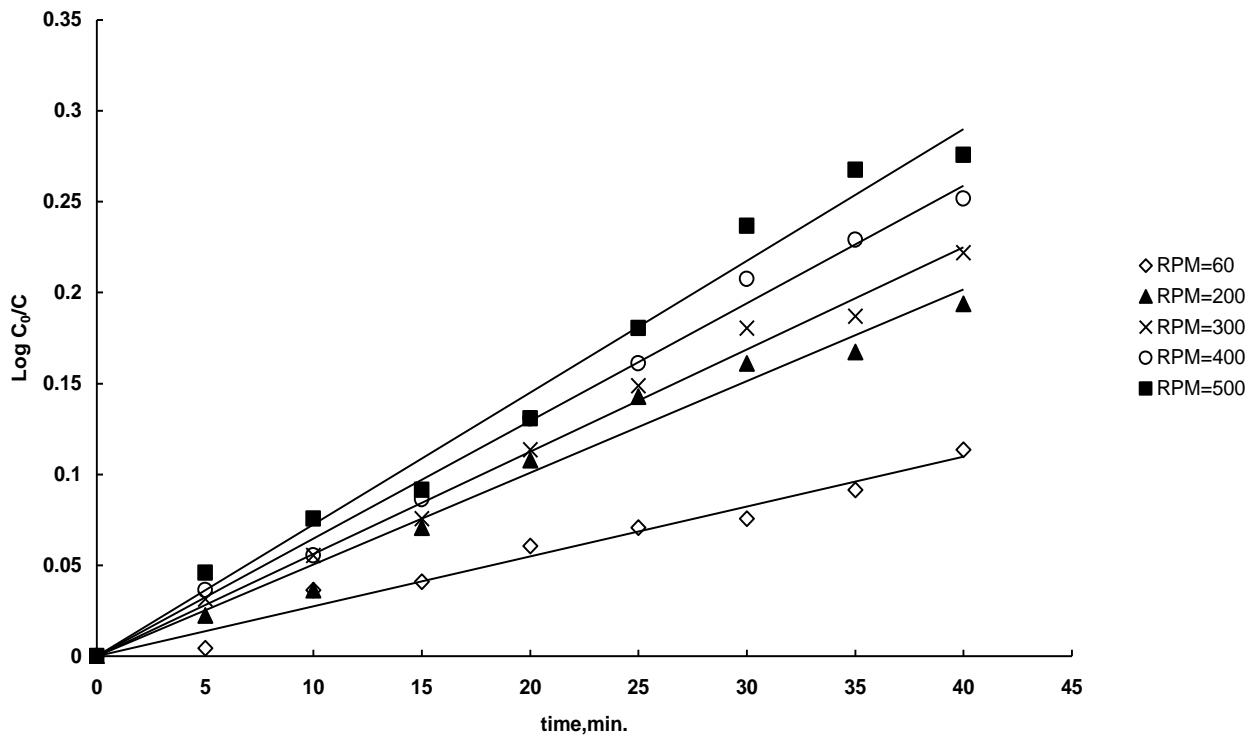


Fig. 4. Effect of rpm on copper ion cementation in the presence of tartaric acid. (initial  $Cu^{++}$  concentration=0.1 N, Tartaric acid concentration=0.1 N, temp=20° C).

Fig. 5 shows that mass transfer coefficient depends on rpm according to the following equation:

$$k \propto (\text{rpm})^{0.52} \quad \text{for chelating agent free solution,} \quad (3)$$

$$k \propto (\text{rpm})^{0.5} \quad \text{for tartaric acid,} \quad (4)$$

$$k \propto (\text{rpm})^{0.47} \quad \text{for citric acid,} \quad (5)$$

The relatively low rpm exponent (0.52) may be attributed to the relatively low range of cylinder rotational speeds. The values are fairly consistent with the exponent obtained by different authors who used relatively low rotational speeds [20]. The relatively low exponent (0.52) may also explained by the fact that under the present conditions mass transfer of the ions involved in the cementation reaction takes place across a solution boundary layer and a porous layer of copper deposit. While mass transfer across the liquid phase boundary layer is sensitive to cylinder rotation, diffusion of the ions across the porous copper layer adherent to the zinc

cylinder is not sensitive to cylinder rotation. Authors who obtained higher exponent obtained the mass transfer coefficient by measuring the limiting current of the cathodic reduction of  $\text{K}_3\text{Fe}(\text{CN})_6$  or the cathodic deposition of a compact copper where mass transfer takes place only across the liquid phase boundary layer [20]. Fig. 5 shows that chelating agents reduce the rate of cementation. The percentage inhibition of chelating agent on the rate of cementation calculated from the equation:

$$\% \text{ inhibition} = \left( \frac{k - k^-}{k} \right) \times 100. \quad (6)$$

Where  $k$ : mass transfer coefficient in chelating agent free solution,  
 $k^-$ : mass transfer coefficient in presence of chelating agent.

Table 2 summaries the results for % inhibition efficiency for both citric and tartaric acid. The % inhibition varies between 29.17 to 34.4% for citric and 9.89 to 13.98% for tartaric acid.

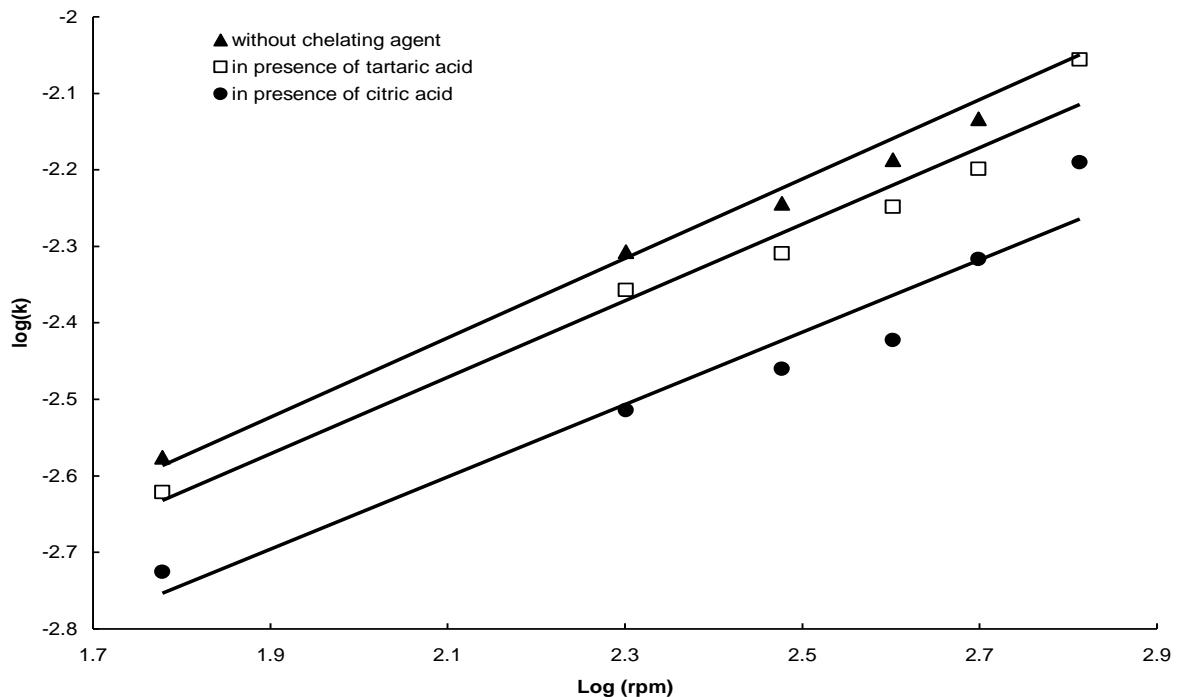


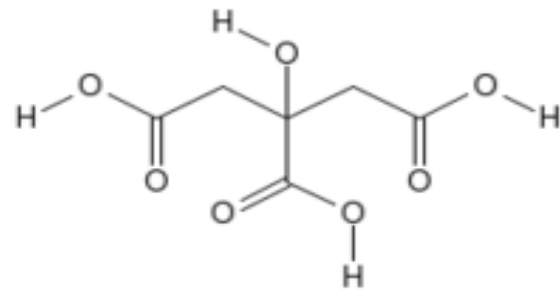
Fig. 5. Effect of rpm on the mass transfer coefficient (Initial  $\text{Cu}^{++}$  concentration=0.1 N, citric acid concentration=0.1 N, tartaric acid concentration=0.1 N, temp=20 °C).

The inhibition effect of chelating agents can be attributed to that the chelation reduces the diffusivity of cupric ions in solution and slows down the rate of cementation. Due to this slowness in the reaction rate a uniform and smooth porous deposits were obtained in presence of chelating agent, compared to rough and non uniform deposit was obtained in case of chelating agent free solution.

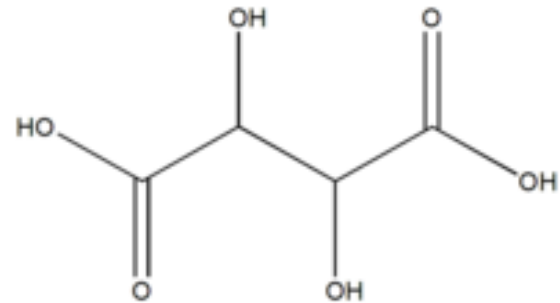
It is noted from the above results that the decrease in the rate of cementation is more pronounced in case of citric acid than tartaric acid, and this can be explained as follows:

1. The extent of chelation is a function of the number of donating groups or atoms in a chelating agent, since citric acid contains seven oxygen atoms compared to six in case of tartaric acid, it is expected that the chelation by citric acid is stronger than by tartaric acid [21]. Chemical structure of both citric and tartaric acid is shown in fig. 6.

2. In general the overall formation constants for chelation of cat ion and anion ligand of citric acid are greater than that of tartaric acid, as it obvious from table [3].



(a)



(b)

Fig. 6. Chemical structure: (a) citric acid, (b) tartaric acid.

Table 2  
% inhibition efficiency at equinormal concentration of Cu<sup>++</sup> and chelating agents at 20° C

RPM	Citric acid	Tartaric acid
60	29.17	9.89
100	25.26	11.39
200	37.90	10.81
300	39.18	13.99
400	41.90	13.23
500	34.40	13.98

Table 3  
Overall formation constant for chelation of Ligand (L) at 298 K and zero ionic strength [1]

species	L <sup>-3</sup> (citrate)	L <sup>-2</sup> (tartarate)
H <sup>+</sup>	HL (6.4)	HL (4.37)
	H <sub>2</sub> L (11.16)	H <sub>2</sub> L (7.44)
	H <sub>3</sub> L (14.29)	
	CuL (7.2)	
	CuHL (10.7)	
Cu <sup>++</sup>	CuH <sub>2</sub> L (13.8)	CuL (3.97)
	CuOHL (16.4)	
	Cu <sub>2</sub> L <sub>2</sub> (16.3)	

However it seems that the effect of tartaric acids is selective i.e. it depends on the type of metal ions which has been indicated by the work by Bóckman et al. [15]. They found that a high concentration of tartrate in the solution causes a reduced cementation rate. Their results revealed that the cementation rates of Cu<sup>+2</sup>, Sb<sup>+3</sup>, and Cd<sup>+2</sup> are reduced, but not to the same extent as the cobalt ion cementation.

The observed effect of chelating agents in the present study is in agreement with the results of Ku et al. [22]. They have found that the presence of ethylene diaminetetracetic acid (EDTA) in aqueous solutions inhibited the removal of cadmium by zinc. They attributed that effect to the possible formation of Cd-EDTA chelates, which possess higher redox potential than that of free cadmium ions.

Fig. 7 shows that the rate of cementation increases with temperature according to Arrhenius equation:

$$k = A e^{-\frac{E}{RT}} \quad (7)$$

With an activation energy ranging from 3.7 to 9.3 kcal/mol for all cases indicating the diffusion-controlled characteristics of the cementation reaction even in the presence of chelating agents.

Fig. 8 shows the role of pH on the rate of cementation of  $\text{Cu}^{++}$  on zinc in presence of citric acid as a chelating agent. It is evident that pH has a significant role on the rate of cementation especially in the presence of citric acid. As pH increases, the rate of cementation decreases. This result is in agreement with the result obtained by Ku et al. [22]. They studied the effect of pH on the rate of cementation of copper ions on iron powder in presence of a strong chelating agent EDTA. They found that for highly acidic conditions  $\text{pH} \leq 2$ , the predominant copper species are the free copper ions  $\text{Cu}(\text{II})$ . However the protonated copper chelate,  $\text{CuHEDTA}$  and very stable

copper chelates  $\text{CuEDTA}$  form over a broad range from 3 to 11.

#### 4. Conclusions

- The presence of chelating agents on industrial effluents retards the cementation rate of  $\text{Cu}^{++}$  ion on zinc.
- The extent of the inhibition by chelating agent is a function on its structure, rpm, pH and temperature.
- Tartaric acid shows less % inhibition compared to citric acid.
- For  $\text{pH} \leq 2$ , the effect of chelating agent is negligible.
- Activation energy values are in the range of 3.7 to 9.3 kcal/mol, which indicates that the cementation reaction is diffusion controlled one.

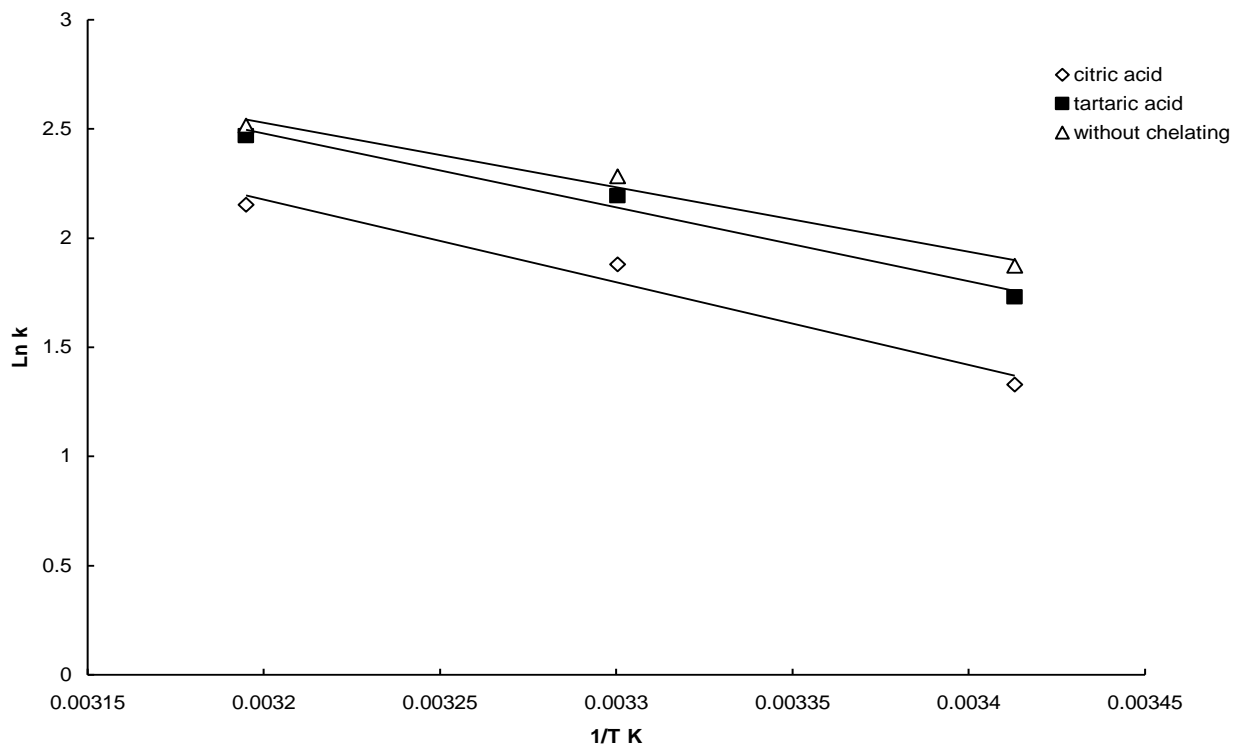


Fig. 7. Plot of Arrhenius equation in presence and absence of chelating agents. initial copper ion concentration=0.1 N , rpm=400).

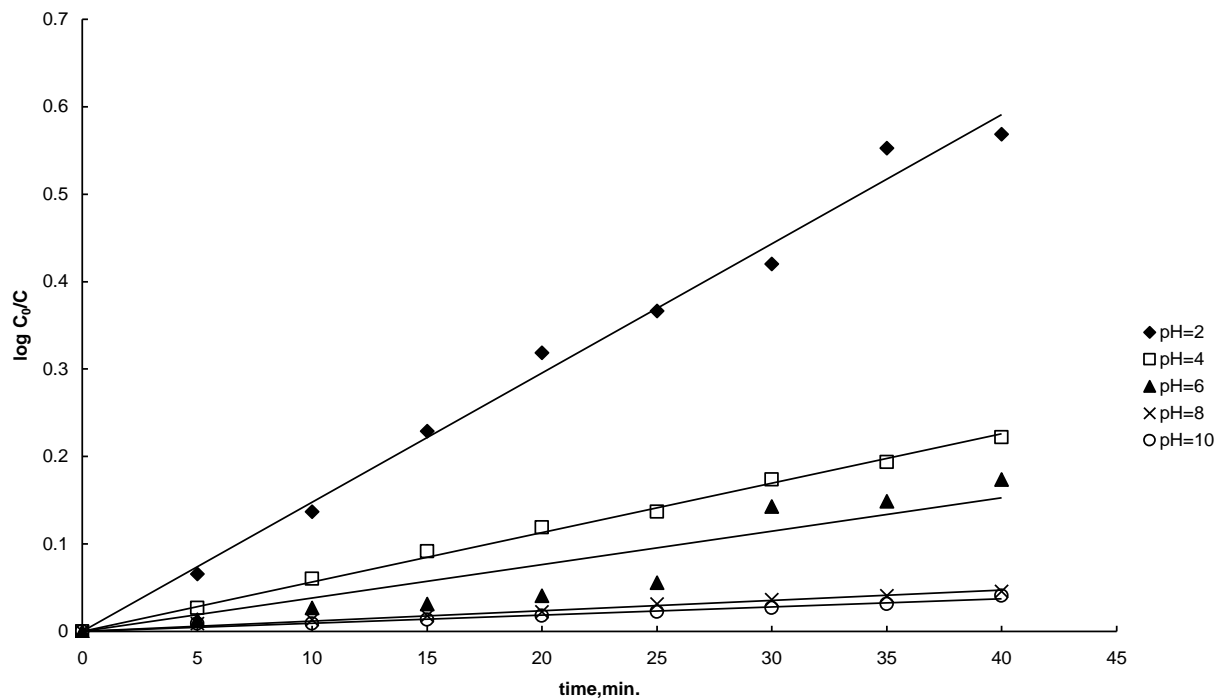


Fig. 8. Effect of pH on the rate of copper ion cementation on zinc on the presence of citric acid (Cu<sup>++</sup> initial concentration=0.1 N, citric acid concentration=0.1 N, rpm=500, temp=20° C).

**Nomenclature**

- A is the active area of the rotating cylinder, cm<sup>2</sup>,
- A is the frequency factor cm/s,
- C is the final concentration of the solution, N,
- C<sub>0</sub> is the initial concentration of the solution, N,
- E is the activation energy Kcal/mol,
- k is the mass transfer coefficient in absence of chelating agents, cm/s,
- k<sup>-</sup> is the mass transfer coefficient in presence of chelating agent cm/s,
- R is the gas constant cal/mol.°K,
- T is the absolute temperature °K,
- t is the time of cementation, s, and
- V is the volume of solution, cm<sup>3</sup>

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