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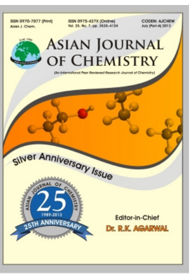

Removal of Toxic Lead Ions in Presence of Cationic Surfactants

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The removal of toxic Pb^{2+} from waste water by cementation on rotating zinc cylinder takes place in absence and in presence of cationic surfactants as cetyl trimethylammonium bromide (CTAB) and cetyl pyridinium bromide (CPYB). The rate of removal of Pb^{2+} was studied under different conditions of rotation speed, initial Pb^{2+} concentration, temperature and different types of cationic surfactants. It was found that, the rate of removal of Pb^{2+} increases with increasing rotation speed (rpm) and temperatures. The presence of surfactants was found to decrease the rate of cementation. The decrease in the rate of cementation was ranged from 29 to 78 % depending on the type of surfactants and its concentration. Thermodynamic parameters ΔG^*, ΔH^* and ΔS^* were calculated.

Key Words: Removal, Lead, Surfactant.

INTRODUCTION

Lead is one of the common and toxic pollutants released into the natural water from various industrial activities such as metal plating, oil refining, paint and pigment producing and battery manufacturing[1]. Lead can enter the human body through inhalation, ingestion or skin contact. As a result when the body is exposed to lead it can act as a cumulative poison. Lead accumulates mainly in bones, brain, kidney and muscles and may cause many serious disorders like anemia, kidney disease, nervous disorder and sickness even death[2-4]. Lead can replace calcium, which is an essential mineral for strong bones and teeth, while play important role in sympathetic actions of nerve and blood vessel for normal functioning of nervous system. It also acts as an enzyme inhibitor in body, *e.g.*, replaces essential element zinc from heme enzyme. The high level of lead damages cognitive development especially in children[5]. Due to toxic effects of lead ions, the removal of them from waters and wastewaters is important in terms of protection of public health and environment[6]. The conventional methods for heavy metal removal from water and wastewater include oxidation, reduction, precipitation, reverse osmosis, ion exchange, electrolysis and adsorption.

Lead is one such toxic substance and is widely used in industrial raw material for storage battery manufacture, printing, paint, dying processes, photographic material, matches and explosive manufacturing. The storage battery industry is the largest use of lead[1]. Concentrations from 0.400 ppm have been reported from some of the preceding industrial sources[7,8].

There are several methods that can remove Pb^{2+} from waste water such as chemical precipitation, ion exchange adsorption, reverse osmosis and electro dialysis, all of which have drawbacks, *e.g.* chemical precipitation requires extremely long settling times; both ion exchange and carbon adsorption are very expensive and may require frequent regenerations for adequate performance. Reverse osmosis and electro dialysis require expensive equipments and have high operating costs[9].

Cementation is used as a general term to describe solution of its salts by another electropositive metal. The cementation technique has been used in industry for long time, not only in hydrometallurgy but also in the purification process of streams and waste water. The advantages of cementation process include its relative simplicity, ease of control and redox potential of the sacrificing metals limit the application of this process.

Agelidis *et al.*[10,11] studied Pb^{2+} removal from waste water using fixed bed of iron spheres and iron powder. Lead ion concentration approach 200-500 mg dm^{-3} in the industrial wastewater[12], this value is very high in relation to the standard of the water quality and it should be reduced. Many applications have been reported in industry[13-17] for the recovery of metals and purification of electrolyte solution. Almost all the authors have reported that electrochemistry at room temperature is diffusion control[18-25].

The object of the present work is to investigate how surface-active substances such as cetyl trimethyl ammonium bromide and cetyl pyridinum bromide affect the rate of cementation of lead from diluted lead nitrate solution using rotating zinc cylinder.

EXPERIMENTAL

AnalaR grade $Pb(NO_3)_2$ supplied by BDH chemicals Ltd were used. Cationic surfactants used in the present work were cetyltrimethyl ammonium bromide (CTAB) and cetyl pyridinum bromide (CPYB) BDH AnalaR. The composition of surfactant ranged from 5×10^{-5} to 1.25×10^{-3} mol L^{-1}.

Experimental technique: A zinc cylinder of 1.30 cm diameter and 8 cm height was rotated in 200 cm^3 solution. The cylinder was driven by 0.25 horse power variable speed motor connected to the cylinder (Fig. 1). Cylinder rotation speed was controlled by a variac and was measured by an optical tachometer. The reaction vessel was placed in a constant temperature water bath.

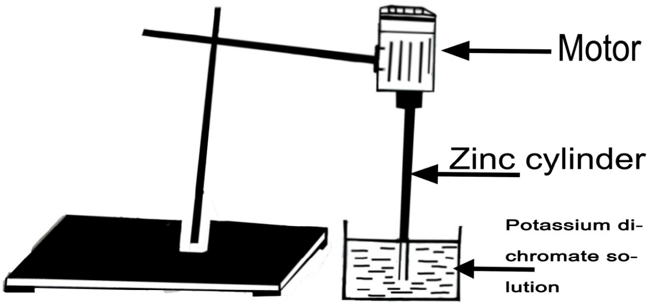

Fig. 1. Diagram of apparatus

The cylinder was rotated in a solution with variable speed motor (Fig. 1). The frequency of rotation recorded as revolution per second was counted by an optical tachometer. The reaction vessel was set in a constant ± 0.05 ultrathermostate.

The rate of cementation of lead ions on zinc metal was determined at different temperatures 25, 30, 35 and 40 ºC and at different rotations 100,250,400,500,700 and 900 rpm.

Reagent-grade chemicals and redistilled waster were used in the preparation of experimental and stock Pb $(NO_3)_2$ solution. Before each run, the upper 3 cm of Zn cylinder was insulated with poly styrene lacquer to avoid the vortex and the active surface of the zinc was polished with a fine emery paper, degreased with tri chloroethylene, washed with alcohol and finally rinsed in distilled water. The lower flat bottom of the cylinder was also isolated.

The reaction vessel was 250 mL glass beaker containing 200 mL $Pb(NO_3)_2$ solution or $Pb(NO_3)_2$ surfactant mixture in which the rotating cylinder was immersed. All chemical analysis was carried out using Perkin-Elmer atomic absorption spectrophotometer. Solution pH was fixed at 5.5 for solutions.

RESULTS AND DISCUSSION

Before testing the effect of different variables on the rate of cementation of Pb^{2+} on Zn. it would be of interest to determine thermodynamically the extent to which the reaction:

$$Zn + Pb^{2+} = Zn^{2+} + Pb \tag{1}$$

can proceed in the indicated direction to make sure that this technique can reduce Pb^{2+} concentrations to extremely low values. Applying the vant-Hoff isotherm to the above reaction[24].

$$\Delta G^o = -Z\,E^o\,F \tag{2}$$

where Eº is the standard e.m.f of the galvanic cell through which the cementation reaction takes place according to the modern electrochemical theory of cementation[19]. The galvanic cell made of Zn with Pb electrodes has Eº = 0.632 volt. Therefore 0.632 = 0.059/2 log K, from which the equilibrium constant = 2.653×10^{23} which is the final ratio between Zn^{2+} and Pb^{2+}, *i.e.* cementation of Pb^{2+} on Zn would proceed almost to complete under favourable Kinetic conditions. Fig. 2 shows the rate of Pb^{2+} deposition [represented by plotting log C/C_o *vs.* time] at different temperatures for blank solution. Also, the rate of Pb^{2+} removal increases with increasing temperature.

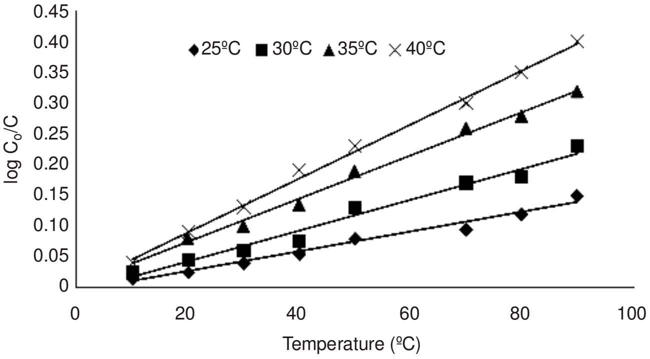

Fig. 2. Relation between log C_o/C and t for blank solution and 250 rpm at different temperature

The rate of lead cementation with zinc can be expressed in terms of the disappearance of Pb^{2+} from the solution by the equation.

$$\frac{dC}{dt} = -\frac{kAC}{V} \tag{3}$$

which upon integration yields

$$\ln\frac{C_o}{C} = \frac{kAt}{V} \tag{4}$$

where C is the lead concentration (ppm) in solution at time t, k is the rate of cementation reaction (min^{-1}); V is the volume of solution containing Pb^{2+} ions (cm^3), C_o is the initial concentration and A is exposed area (cm^2).

Figs. 3 and 4 show the effect of concentration of surfactant on the rate of cementation. A linear plot of log C_o/C *vs.* t is verification that the cementation rate is first order with respect to Pb^{2+}. The rate of the reaction (k) was obtained from the slope log C_o/C *vs.* t. It is clear from Tables 1 and 2, that, the rate of the reaction is decreased by increasing concentration of the surfactant.

The cementation process is inhibited by addition of cationic surface active substance. The percentage of inhibition for cementation reaction is calculated from the following relation:

$$\text{Inhibition }(\%) = \frac{k - k'}{k}100 \tag{5}$$

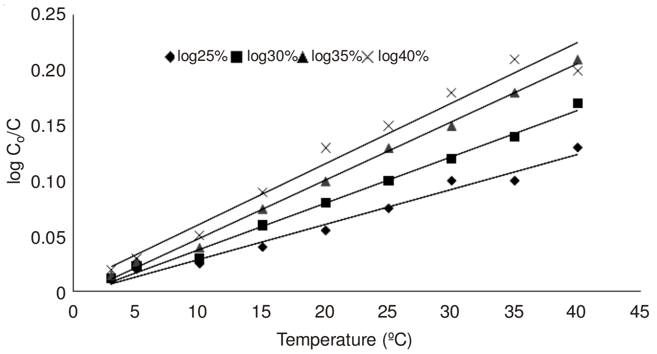

Fig. 3. Relation between log C_o/C and t for CTAB at 250 rpm and 2×10^{-4} CTAB

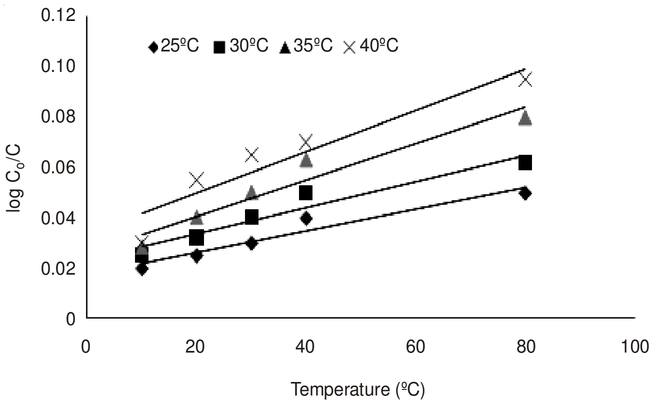

Fig. 4. Relation between log C_o/C and for CPYB at 250 rpm and 2×10^{-4} mol L^{-1} CPYB

TABLE-1
FIRST ORDER RATE CONSTANTS ($k \times 10^3$ sec^{-1}) FOR CEMENTATION ON ZINC METAL IN PRESENCE OF CPYB AT DIFFERENT TEMPERATURE AND 250 rpm

Temp. (ºC)	Concentration of CPYB × 10^{-5}					
	0	10	20	30	50	100
25	5.33	3.77	2.86	2.33	2.05	1.45
30	6.2	4.58	3.60	2.82	2.80	1.85
35	7.3	5.85	5.30	3.60	3.20	2.31
40	8.3	7.90	5.89	5.11	4.80	3.31

TABLE-2
FIRST ORDER RATE CONSTANTS ($k \times 10^3$ sec^{-1}) FOR CEMENTATION ON ZINC METAL IN PRESENCE OF CTAB AT DIFFERENT TEMPERATURE AND 250 rpm

Temp. (ºC)	Concentration of CTAB × 10^{-5}					
	0	10	20	30	50	100
25	5.33	3.20	2.60	2.15	1.96	1.40
30	6.20	3.89	3.40	2.80	2.66	1.70
35	7.30	5.52	4.80	3.18	3.11	2.20
40	8.30	6.90	5.46	4.88	4.62	2.80

where k is reaction rate constant in blank solution [250 rpm]. k = rate constant of the reaction in the presence of cationic surface active substance. Table-3 and Fig. 5 gives the relation between the percentage of inhibition of the rate of cementation and cationic surface active substance concentration at 25 ºC. The % inhibition depends on the types of cationic surface active substance and its concentration. The order of cementation inhibition is blank < CPYB < CTAB.

TABLE-3
RELATION BETWEEN THE PERCENTAGE INHIBITION OF CATIONIC SURFACE ACTIVE SUBSTANCE AND CONCENTRATION AT 250 rpm AT 25 ºC

Concentration × 10^{-5} M	10	20	30	50	100
CPYP	29.26	46.34	56.30	61.50	71.80
CTAB	39.96	51.30	59.66	63.20	73.73

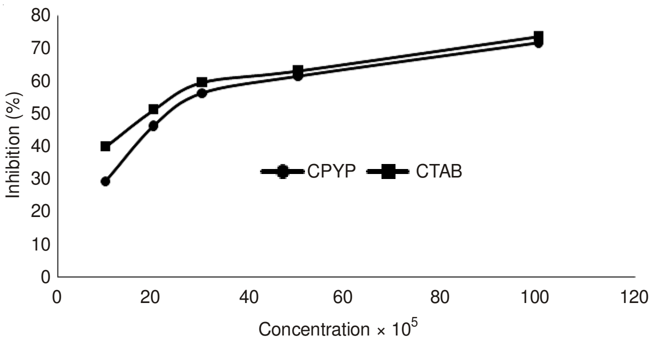

Fig. 5. Relation between percent of inhibition and concentration of cationic surface active substance at 250 rpm

Effect of stirring on the rate of cementation: The effect of rotational speed on the rate constant k can be used to determine whether a cementation reaction is diffusion controlled or chemically controlled[23]. If the rate constant increase 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. Fig. 6 and Table-4 show that, the rate of reaction k increases by increasing rpm of zinc cylinder at 298 ºC in case of blank and as solutions which indicate that, cementation reaction is diffusion controlled[20].

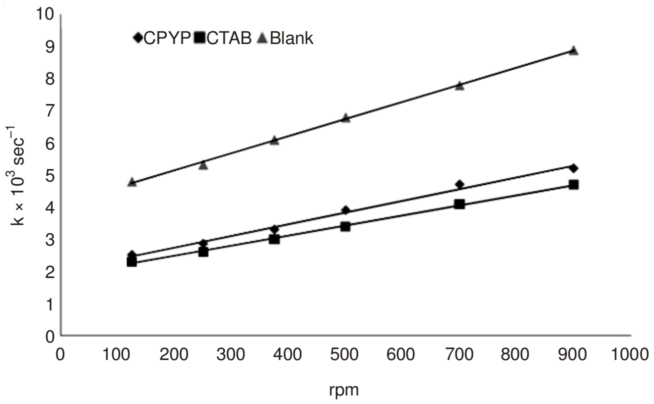

Fig. 6. Relation between rpm and rate of the reaction

TABLE-4
EFFECT OF RPM ON THE CEMENTATION RATE OF LEAD ON ROTATING ZINC CYLINDER AT 25 ºC FOR BLANK AND IN THE PRESENCE OF CATIONIC SURFACE ACTIVE SUBSTANCE (20×10^{-5} mol L^{-1})

rpm	Values of $k \times 10^3$ sec^{-1}		
	CTAB	CPYB	Blank
100	1.7	1.6	1.3
250	3.0	2.5	2.6
500	2.8	3.6	4.15
600	3.7	4.0	5.2
800	4.0	4.6	6.0
1000	5.0	5.8	7.4

The decrease in the rate of cementation in the presence of cationic surface active substance may be attributed to:

(i) Cationic surface active substance may form a thin adsorbed film on the zinc metal which leads to decrease the cementation rate of reaction; also adsorption of cationic surface active substance on the surface depends mainly on the structure. CPYB which has aromatic ring which are adsorbed on the surface of the metal more than CTAB which is aliphatic.

(ii) The decrease in the diffusion coefficient (D) of Pb^{2+} in solutions containing cationic surface active substance is due to the increase in the interfacial viscosity η in accordance to Stokes-Einstein equation[25].

$$\eta\frac{D}{T} = \text{constant} \tag{6}$$

where T is the absolute temperature. The increase in the interfacial viscosity is caused by the adsorption of cationic surface active substance molecules on the zinc surface. CPYB is more inhibitor than CTAB because it has more than one functional group.

The effect of binary mixture of surface active compounds of surfactants has been studied in several cases. In many industrial applications surfactants are invariable mixtures as they are produced from feedstock containing mixed hydrocarbon chain length. It not only exhibits superior properties as compared to only singular surfactant but also can be produced at relatively lower cost.

The surfactants used in practical application are usually mixture of surface-active components due to: (i) the very high costs of pure substances production. (ii) the surfactants mixture in many practical applications has much better properties than those of their individual components.

The values of rate of cementation k for mixed surfactants. Table-5 illustrated that the rates of reduction of Pb^{2+} on rotating zinc cylinder decreases on addition one surfactants to other due to synergism[25].

The values of synergism parameter S_1 were calculated by using the relationship given by Aramaki and Hackerman[26].

$$S_1 = \frac{I_{mix} - I}{\acute{I} - I} \tag{7}$$

where I_{mix} is the rate of reduction in the presence of mixed surfactants, Í is rate of reduction in presence of single surfactant and I is rate of reduction of blank.

Effect of temperature: The effect of temperature on the rate of cementation reaction in presence and in absence of surfactants was determined in temperature range of 25-40 °C and illustrated in Table-1. It was observed that the cementation rate increases with temperature for different concentrations of surfactants.

Thermodynamics treatment of the reaction: From the integrated form of Arrhenius equation:

$$\ln(k) = \frac{-E}{RT} + \ln(A) \tag{8}$$

where R is the gas constant, E is the activation energy and A is the frequency factor. The values of E are given in Table-6.

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

TABLE-5
EFFECT OF MIXED SAS ON THE RATE OF REMOVAL OF Cr^{6+} AT 25 °C

$C_{CPYB} \times 10^5$ mol L^{-1}	$C_{CTAB} \times 10^5$ mol L^{-1}	$K_{blank} \times 10^3$	K in presence of mixed SAS	Reduction (%)
10	10	5.53	1.65	70.28
	20		1.56	70.9
	30		1.48	72.38
	50		1.42	73.50
	100		1.38	7.25
20	10	5.53	1.43	73.32
	20		1.39	74.06
	30		1.30	75.74
	50		1.18	78.00
	100		1.10	79.50
30	10	5.53	1.40	73.58
	20		1.31	76.00
	30		1.20	77.61
	50		1.11	79.29
	100		1.08	79.85
50	10	5.53	1.32	74.76
	20		1.23	77.00
	30		1.16	78.31
	50		1.10	79.40
	100		0.95	82.24
$C_{CTAB} \times 10^5$ mol L^{-1}	$C_{CPYB} \times 10^5$ mol L^{-1}	$K_{blank} \times 10^3$	K in presence of mixed SAS	Reduction (%)
10	10	5.53	1.98	63.60
	20		1.89	65.65
	30		1.74	67.53
	50		1.68	68.65
	100		1.60	70.14
20	10	5.53	1.82	66.00
	20		1.70	68.28
	30		1.65	69.21
	50		1.54	71.26
	100		1.48	72.35
30	10	5.53	1.72	67.91
	20		1.68	68.65
	30		1.60	70.14
	50		1.51	71.81
	100		1.41	73.60
50	10	5.53	1.60	70.90
	20		1.52	71.58
	30		1.43	73.23
	50		1.32	75.33
	100		1.21	77.30

SAS = Cationic surface active substance

$$\Delta H^* = E - RT \tag{9}$$

$$\frac{\Delta S^*}{R} = \ln(A) - \ln\left(\frac{\alpha Te}{h}\right) \tag{11}$$

where α the Boltzmann constant, e is 2.7183 and h is Plank's constant.

Although the change in free energy of activation, ΔG*, with the cationic surface active substance concentration for all used cationic surface active substance is only small values (Table-6) and variations occur in the enthalpy of activation values ΔH* and entropy of activation ΔS*, with cationic surface active substance concentration where in all these cases ΔH* and ΔS compensate each other to produce little changes in ΔG*.

However all the values of ΔS* are highly negative values, indicating a more ordered system and non-random distribution

TABLE-6
THERMODYNAMIC PARAMETER OF
DIFFERENT SAS AT 25 ºC

Conc.10^5 mol L^{-1}	ΔG^*	ΔH^*	ΔS^*	E
CTAB				
1	96.137±3.8	24.02±0.66	242±2.19	26.5±0.66
5	105.6±10.2	35.841±2.16	235±9.50	38.34±1.16
10	105.06±8.12	36.52±1.21	230±1.67	38.39±1.16
50	97.69±6.12	24.981±4.0	244±1.15	27.5±0.4
CPYB				
Conc. mol L^{-1}	ΔG^*	ΔH^*	ΔS^*	E
1	95.952±1.66	22.92±0.66	235±2.12	25.4±0.66
5	99.652±3.65	31.118±1.86	230±3.12	33.6±1.8
10	103.57±2.89	36.521±2.52	225±2.16	39±2.52
50	97.441±5.30	24.921±4.20	240±3.15	25±4.2
Blank				
Conc. mol L^{-1}	ΔG^*	ΔH^*	ΔS^*	E
	92.73±6.72	37.42±3.4	185.53±11.1	40±3.4

ΔG^* and ΔH^* in KJ mol^{-1} and ΔS^* in J mol^{-1} degree^{-1}

of the cationic surface active substance and the number of the substituent present in each cationic surface active substance.

In general, the values of E and ΔH^* decreases as the cationic surface active substance concentration decreases Table-6,which may be attributed to that; the cationic surface active substance increases the local solution viscosity at the Fe surface with a consequent decrease in the diffusivity of Cr^{6+} ion. The cationic surface active substance molecules decreases the natural convection flow arising from the density difference between the bulk solution and the solution at the electrode surface due to the repulsion force between the Fe and the NH_4^+ group of the cationic surface active substance, leading to decrease the rate of oxidation.

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