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Carrier mediated transport of toxic elements, part II Transport modeling for extraction of Pb (II) by Cyanex302/xylene as carrier from nitrate medium using SLM

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Abstract:

The facilitated transport of Pb (II) through cellulose triacetate as polymeric support, Cyanex302/xylene as carrier is investigated. The influence of some factors e.g. the aqueous , membrane and strip concentrations on the permeability of Pb(II) were studied. The maximum flux obtained with these membranes is 4.2×10^{-7} mol m^{-2} s^{-1}. Aqueous and membranes resistances were determined from a model that describes the transport mechanism across the membranes using the stoichiometric relationship Pb/Cyanex302 and the extraction equilibrium constant value of 8.1×10^{-5}determined independently by liquid–liquid extraction. An activation energy of 65.2 kJ mol^{-1} was also determined for Pb(II) migration, which suggest that the transport of Pb (II) is controlled by a membrane diffusion mechanism A mathematical model was suggested and validated by experimental result.

Keywords: diffusion Facilitated transport; Lead; Cyanex302/xylene ; cellulose triacetate; reaction mechanism, Transport modeling.

I. Introduction

Accumulation of heavy metals in soils and their consequent transfer to aquifers through the soil matrix are known to cause serious threats to the environment. In recent years, technologies dealing with soil remediation have received considerable attention [1]. Among the available processes, electro kinetic extraction appears as a promising in-situ strategy for soil decontamination. Laboratory and pilot-scale experiments have demonstrated the effectiveness of the process to remove a wide variety of heavy metals. The removal of toxic ions from waste waters is of great significance due to environmental and economical aspects. The so-called heavy metals have been recovered with separation methods based on solvent extraction (SX), which consumes large amounts of organic extraction processes liquid membranes have been used because of their high transport rates, selectivity factors, and minimization of the required organic components [2]. Single-stage extraction and back-extraction of a number of species with liquid membranes have been investigated for about 30 years. Among the different liquid membranes modalities, the supported liquid membranes (SLMs) have been widely used for the separation of a number of species [3]. Whereas their lack of stability, which might prevent upscale applications, has also been reported [4]. Recently, cellulose-based polymeric inclusion membranes (PIMs), first introduced by Sugiura [5], have received increasing attention as an alternative to SLM. Extraction of a number of species has been reported by several groups [6–9]. PIMs have been reported to have better mechanical properties than traditional SLMs and good chemical resistance [10]. The addition of plasticizers is reported to improve the compatibility of the carrier with the polymer, and additionally improve the brittleness and elasticity by creating a polymeric solution [11]. Lead is a trace heavy metal of major interest in environmental protection owing to its cumulative toxicity. Lead is still emitted into the biosphere in considerable amounts owing to its application as a fuel additive. Environmental lead results in a serious and well known health risk to animals and humans [12,13]. The presence of trace amounts of lead in many industrial streams is also undesirable mainly because it may eventually be passed on to a food or other product used or consumed by people [14]. Hence, the development of new methods for selective separation, concentration and determination of lead in sub-micron levels is still a challenging task. Lead is one of the most ubiquitous elements in the environment and recognized as a major health risk to humans and animals [15,16]. Solid phase extraction procedures for lead have been reported using various solid supports such as activated carbon [17], silica gel [18], cellulose [19], Amberlite XAD series resins [20-25], Chromosorb resin [26], Ambersorb resin [27] and polyurethane foam [28]. Two methodologies were commonly practiced for solid phase extraction of lead. One was based on chemical reactions either for synthesis of a selective ligand 22 [14] or its covalent coupling to support material [20,23&24] and other for functionalization of the solid support itself [18,21&25]. These methods were somewhat lengthy and time-consuming. A relatively simple alternative for preparation of the solid phase is

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based upon the impregnation of reagents on solid supports. Interesting studies using acidic organophosphorous extractant such as DEHPA (di-(2-ethylhexyl) phosphoric acid), Cyanex 272 (bis(2,4,4-trimethyl pentyl)[1] phosphinic acid), Cyanex302 (bis(2,4,4-trimethylpentyl) monothiophosphinic acid), Cyanex301(bis(2,4,4-trimethylpentyl) dithio phosphinic acid) and PC-88A or IONOQUEST 801 (2-ethylhexyl hydrogen 2-ethylhexyl phosphonate) impregnated on a solid support have been reported [29-34]. Mechanism and kinetics of the sorption of cadmium (II) with Cyanex302 [31] and Cyanex301 [32] was undertaken. The extent of impregnation of Cyanex302 [33] and PC-88A [34] on different Amberlite XAD series resins was found to influence the extractability of cadmium(II) and copper(II) [33] and ytterbium(III), terbium(III), samarium(III) and lanthanum(III) [32]. Selective separation of iron(III), cadmium(II) and nickel(II) was achieved using Cyanex272 and Cyanex302 impregnated on Amberlite XAD-2 by controlling aqueous phase pH [32]. While the decontamination of ground water for some heavy metals was possible due to the high sorption capacity of Cyanex302 impregnated on Amberlite IRA-96 [33]. Extraction of lead with DEHPA, Cyanex272 and IONOQUEST 801 impregnated on Amberlite XAD-7 was influenced by the pH of aqueous phase and type of extractant [34]. No attempts have been made for selective separation and concentration of lead to facilitate its determination from complex matrices using Cyanex302 impregnated on C18 disc. Solid phase extraction methods using columns with a narrow internal diameter limit the usable flow rates to a range of 1–10 cm^3 min^{-1} resulting in long time for enrichment from large sample volumes. While C18 discs enable much higher flow rates [35]. In view of this the extraction of lead with Cyanex302 impregnated on C18 disc and determination by FAAS was systematically studied. This type of solid phase overcomes the limitations of solvent extraction, over use of large quantities of organic solvents while high specificity and selectivity of a liquid cation exchanger can be achieved by controlling the sorption and elution parameters. N.El-said etal studied the transport of Cd(II) from high salinity chloride medium through supported liquid membrane ,part (I)[38].We conducted the work to cover a great area of other toxic elements such as pb (II),Cr(III),etc.

II. Experimental

Cyanex302 from Aldrich, DTPA (diethylene triamine tetra acetic acid) from Fluka Switzerland, lead chloride (99%) from Merck. Other chemicals are analytical grade from Fluka. Atomic absorption/Emission Spectrophotometer 210/VGP, Buck scientific, USA, was used for determination of cadmium concentration. The apparatus used for membrane extraction is shown in Fig.1. It is composed of two cylindrical vessels made of Teflon and Plexiglas. They are arranged both coaxially and vertically. The liquid membrane was fixed on Sartorius SM cellulose acetate microporous carrier (thickness 65 mm, diameter of pores 0.2 mm, porosity 70%, effective area 6.25 cm^2); placed at the bottom of the inner vessel. The carrier was washed and dried with acetone, then saturated with the membrane phase. The volumes of the solutions placed in the outer (feed phase, F) and inner (receiving phase, S) vessels, were 50 and 25 cm^3, respectively Fig.1.show the scheme of Pertraction apparatus: (1) double shield glass outer vessel, (2) Plexiglas inner tube, (3) Teflon cross stirring blade, (4) Teflon holder, (5) silicon rubber ring, (6) niobium holder, (7) titanium holder, (8) magnet. basis of numerous experiments at various stirring rates, stirring rate of 150 rpm in the counter-current mode, using a cross shaped Teflon stirrer was found to be optimal. The distance of stirrer from the membrane was fixed at about 3 mm, the level of both phases were the same, small volumes of both phases were taken out at various time intervals for measuring lead(II) concentration.Unless otherwise stated experiments were performed at 25 °C.

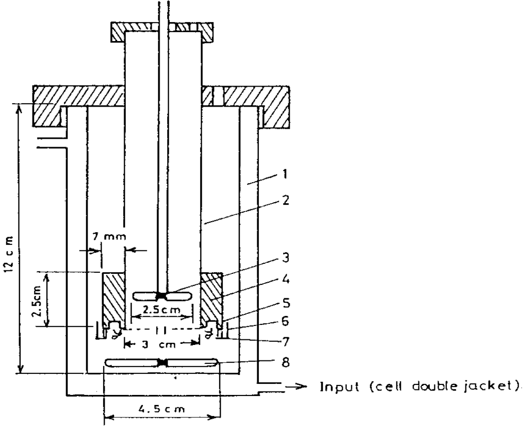

Fig.1.Scheme of Pertraction apparatus: (1)double shield glass outer vessel, (2)Plexiglas inner tube, (3) Teflon cross stirring blade, (4) Teflon holder, (5) silicon rubber ring, (6) niobium holder, (7) titanium holder, (8) magnet

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III. Results and discussion

The transport of Pb(II) from chloride medium through SLM containing Cyanex302 was investigated as a function of the feed and membrane composition. It was found that the transport behavior, although from relatively high initial concentration of Pb(II) in the feed, is in good accordance with the above-described model [35,36]. The processes that can occur as interfering factors responsible for hydrochloric acid and water transport was described [38]. Under the assumptions of steady state and linear concentration gradients with very low values of K_{ds}/K_{dF}, ratio, where K_{ds} and K_{dF} are the distribution ratios of metal species between the membrane, the strip and the feed solution. Providing, instantaneous interfacial chemical reactions between metal species and the carrier, and low metal concentration, the following equation was derived for metal transport through a flat-sheet of SLM [36, 37].

$$\ln\frac{C_F}{C_{OF}} = -\frac{S}{V}Pt\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

where, *t* is the time (s) elapsed since the beginning of the permeation process, C_F and C_{0F} are the metal ion concentration at *t* and zero time, respectively, V_F is the feed volume (cm^3), *S* is the effective membrane area (cm^2) and *P* is the permeability coefficient (cm/s).The interfering factors can be described [38] as the following equations:

$$Pb(II) + 2NO_3^- + \overline{2S} \underset{M-S}{\overset{F-M}{\rightleftarrows}} \overline{Pb(NO_3)_2.2S}\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

$$H^+ + NO_3^- + \overline{nS} \underset{M-S}{\overset{F-M}{\rightleftarrows}} \overline{HCl.nS}\ldots\ldots\ldots\ldots 3$$

$$H_2O + +\overline{mS} \underset{M-S}{\overset{F-M}{\rightleftarrows}} \overline{H_2O.mS}\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where S is denotes, the solvent, TBP and the bar indicates organic phase. Also, the symbols ‘F-M’ and ‘M-S’ above and below the arrow in expressions (1), (2), (3) and (4) denote ‘feed membrane’ interface and ‘membrane-strip’ interface. At these respective interfaces, the complexation reaction and decomplexation (i.e. reverse) reaction occurs, respectively. SLM is considered to be stable when its ability to mediate active mass transport in the system investigated conserved for a sufficiently long Pertraction time.

3.1. Influence of aqueous phase acidities

Effect of the feed solution acidity pH from 1–3, having high concentration "0.1-3M" of $NaNO_3$ on the transport of Pb(II) was studied. The initial metal concentration in the feed was 0.01M much lower than the carrier concentrations (0.3M). A solution of 0.02M DPTA, was used as the stripping phase. Transport of Pb(II) courses are shown in Fig.2. Transport of Pb(II) in all systems investigated can be described by reaction (R-1). In the time interval from 0.5 to 1 h and feed metal concentration C_{FD} 0.01 M, when $[HNO_3]_{0F}$ 0.1M and the feed acidity decreased to pH~2, the nitric acid transport from the feed into the strip solution decreased. Consequently, the acid concentration gradient in the feed diffusion layer decreased due to the transport of HNO_3 and caused an increase of K_{dF} of Pb(II). On the other hand, an increase in K_{dS} Pb(II) can be demonstrated at pH= 4–5, in consequence of increasing significance of the solvation mechanism [7]. Both of these effects led to the decrease of P_F of Pb(II) at 0.1M [HCl]F, where K_{dS} decreases rapidly with increasing $[HNO_3]_F$.As in Fig.2. it is obvious that *P* of Pb(II) increases with decreasing $[HNO_3]$.

3.2. Effect of carrier (Cyanex302) concentration

Based on the above results, a composition of 0.01M Pb(II) in 0.3M $NaNO_3$ at pH= 3, for the feed solution was chosen. Unless otherwise stated, the composition of strip solution remained at 0.02M DPTA, 0.1M $NaNO_3$, and pH 4–5, Fig.3 depicts the effect of membrane concentration on the extraction of Pb(II). It shows the transport kinetics in terms of $\ln(C_F/C_{0F})$ versus time curves. It was noticed that there is no deviation from linearity in the pertraction process. It is obvious that moderate increase in cyanex302 concentration, leads to an increase in initial flux of the metal through the membrane and exhibits a maximum at 0.5M cyanex302.While the value of distribution ratio continues to increase progressively. For instance, by changing the cyanex302 concentration from 0.1 to 0.3 M, the distribution ratio of Pb(II) was increased by 40 times. The calculated values of the effective permeability coefficients for the extracted complex of Pb(II) in the membrane lie in a relatively wide interval, as shown in Fig.4,the permeability coefficients of the metal investigated through SLM calculated from the slopes of the linear parts of the $\ln(C_F/C_{0F})$ versus time plot. It is clear that, there is an effective increase of permeability coefficient upon increasing cyanex302 concentration from 0.1 to 0.3 M in membrane phase. The permeability coefficient of Pb(II) increased as cyanex302 concentration increased from 0.1 to 0.3M membrane concentration, due to higher distribution coefficient with increasing cyanex302 concentration in the membrane phase. This is probably due to the potential gradient of pH’s between the feed and the strip. Steady increase of permeability coefficients is observed upon increasing cyanex302 concentrations from 0.1 to 0.3M. After 0.5h pertraction, the metal yield in the strip was 45% with further increase upon increasing time. This equilibrium state was achieved after 1 h for 0.3M cyanex302, this linearity occurs after about 2 h pertraction Fig.5. After 0.5 h of pertraction, about 45% of initial amount of Pb(II) was accumulated in the stripping phase. But the transport of Pb(II) appeared to be stopped after 1 h pertraction with 85% yield in the strip phase which may be due to membrane stability and linear concentration gradient resulting in equilibrium between feed and strip, this fact is confirmed by the significant a small decrease of pH of the stripping phase.

3.3. Influence of strip concentration

Figs.4 and 6, shows the influence of strip concentration from (0.005–0.02M DPTA). It is interesting to note that the effects of changing strip concentration onto the transport of Pb (II) were different. With increasing strip concentration, from 0.005 to 0.02M DPTA the transport of Pb(II) increased, with no deviation from linearity upon further increase, from 0.005 to 0.02M DPTA. This may be due to the low transport of HNO_3 alone and the low transport of water from the phase with the higher value of thermodynamic activity into the other with the lower one that could occur in principle by an extraction mechanism [16] according to R-4. This is confirmed by slightly decreasing the measured pH values of strip phase after 2 h and longer time of per traction. The ratio between transport rates of HNO_3 acid and that of metal plays an important role, i.e. when the metal transport is faster, it is preferentially accumulated in the strip and the extraction efficiency is high. While, if the metal transport rate is slower than the acid transport rate, the acid is transported preferentially into the strip phase causing low extraction efficiency.

3.4. Effect of temperature

Figs.(7 and 8), shows that there is an increase in the permeability coefficient by increasing temperature up to 298 K. At fixed stirring rate, the natural logarithm of the rate constant was found to be linear with respect to 1/*T* (Fig.9), which allowed estimating the activation energy of the slope of the straight line according to the Arrhenius and Eyring equations. The activation energies from temperature range 278–298K for the studied system was calculated to be 65 k cal/mol at our hydrodynamic conditions. The estimated activation energy falls in the suggestion that the transport of Pb(II) is likely controlled by chemical reaction controlled process.

Pertraction model

In order to have a quantitative description of the transport across the membranes, a model was developed based on a simplified method described elsewhere [18] and the following assumptions:

(1)- The higher stability and lower transport of acid and water
(2)- The chemical reactions are fast at the interface [19].
(3)- The linear concentration gradients across the aqueous boundary layers
(4)- The species concentration are the same in the interface as in the bulk.
(5)- Negligible of metal concentration at the membrane.

The extraction process [20] at the source membrane interface can be represented by the following reaction:

$$Pb^{2+}_{sm,i} + 2HA_{2(ms,i)} \leftrightarrow Pb(HA)_{(ms,i)} + 2H_{+sm,i} \ldots\ldots 5$$

$$k^{q}_{ex} = \frac{[Pb(HA)_{(ms,i)}][H_{+sm,i}]^{2}}{[Pb^{2+}_{sm,i}] + [(HA2)_{2(ms,i)}]^{\frac{(2+q)}{2}}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 6$$

Where HA represents the cyanex302 species and the subscripts m, membrane phase; i, interface; s, source solution. Hence, the flux of Pb(II) across the membranes can be described applying Fick’s first law to the diffusion of metal across the different interfaces. The metal flux at the source/membrane interface, J_a, is defined as

$$J_a = -D_a \frac{d[M(n)}{dx} = \Delta_a^{-1}([M(n)_b] - [M(n)_{a,i}]) \ldots\ldots\ldots 7$$

$$J_a = -D_a \frac{d[M(n)}{dx} = J_{\max} - \Delta_a^{-1}([M(n)_{a,i}]) \ldots\ldots\ldots\ldots\ldots\ldots 8$$

Where the subscript b stands for bulk concentrations. The metal flux at the membrane phase, J_m, is defined by the following equation:

$$J_m = -D_m \frac{d[M(n)}{dx} = \Delta_m^{-1}([M(n)_{ms,i}] - [M(n)_{r,i}]) = \Delta_m^{-1}[M(n)_{m,s,i}] \text{.......9}$$

The terms Δ_m and Δ_a represent the resistances across the membrane phase and the aqueous phases, respectively. With $\Delta_m = \delta_m/D_m$ and $\Delta_a = \delta_a/D_a$, δ_m is the thickness of the membrane layer, and δ_a the thickness of the queous boundary layer, whereas D_m represents the apparent iffusion coefficient and D_a represents the true aqueous diffusion coefficient. At steady state, $J_m = J_a = J$, and thus, combining Eqs.(6), (7) and (9), considering the diffusion of mainly one species in the membrane phase, the overall flux J is given by:

$$J = \frac{J_{\max} \Delta_a k_{ex} [(HA)_{2,ms,i}]^{(2+q)/2}}{\Delta_m [H_{sm,i}]^2 + \Delta_a k_{ex} [(HA)_{2,ms,i}]^{(2+q)/2}} \text{...........10}$$

Or, if we consider the transport to occur under first-order kinetics, we can express the transport of lead in terms of permeability, this is, the velocity at which the metal is transported as:

$$P = \frac{k_{ex}[(HA)_{2,ms,i}]}{\Delta_m [H_{sm,i}]^2 + \Delta_a k_{ex}[(HA)_{2,ms,i}]} \text{...........11}$$

This equation shows the dependence that permeability has with several parameters, which contain valuable information on the limiting processes of the diffusion and chemical reactions that are actually occurring in the membrane. The aforementioned information is contained in (a) the maximum theoretical flux in the membranes ($J_{\max}$), (b) the aqueous and organic resistances and (c) the complex stoichiometry (depending on q) and extraction constant. Transform of equation, therefore

$$\frac{1}{P} = \frac{\Delta_m [H_{sm,i}]^2}{k_{ex}[(HA)_{2,ms,i}} + \Delta_a \text{...........................12}$$

$$-\log P = \log \frac{k_{ex}}{\Delta_m} + \log \frac{[H_{sm,i}]^2}{[(HA)_{2,ms,i}} + \Delta_a \text{...........13}$$

by neglecting Δ_a since it is very small and taking $k_{ex} = \Delta_m$ arbitrary for approximation, so $\log \frac{k_{ex}}{\Delta_m} \to 0$, therefore, equation (14)is a linear relation as postulated in assumption (3)

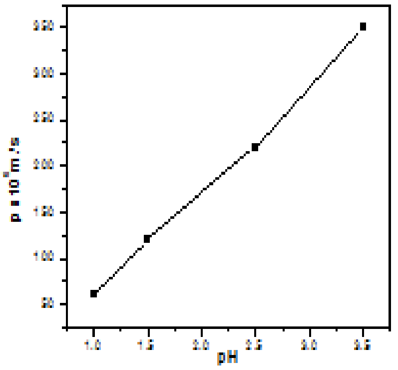
$$-\log P = \log \frac{[H_{sm,i}]^2}{[(HA)_{2,ms,i}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 14$$

$$-\log P = 2l\,\text{og}[H_{sm,i}] - \log\ [(HA)_{2,ms,i} \ldots\ldots\ldots\ldots\ldots\ldots 15$$

the previous suggested **model by N.El-Said** in equations (14 or 15) can be represented by three dimension optimization, Figs (9,10 ,11and 12).

IV. Conclusion

A pertraction membrane can be designed for pertraction of Pb from nitrate medium by cyanex302/xylene using DPTA as stripping agent. The activation energy calculated was found to be 65 kcal/mol for the studied system. Under the same hydrodynamic conditions, a simple pertraction permeable model was evaluated in a good agreement with experimental results



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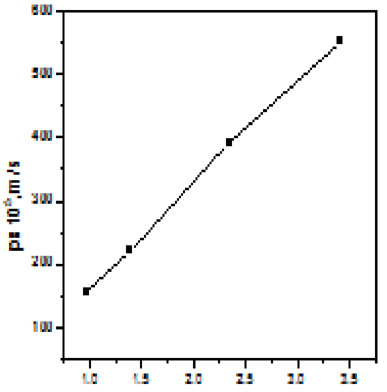

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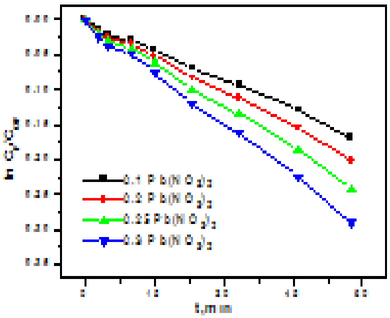

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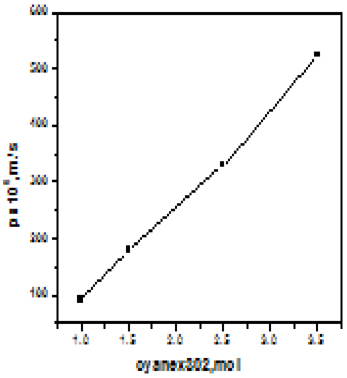

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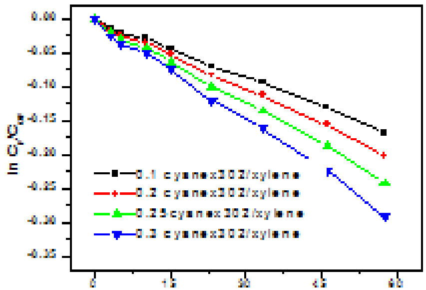


Fig.4 Semilogarithmic plots of ln CF/C0F against time, min different carrier concentrations. F: 0.1M NaNO3+0.1M Pb(NO3)2 M: xM cyanex302/xylene, S:0.03M DTPA, 1M NaCl.

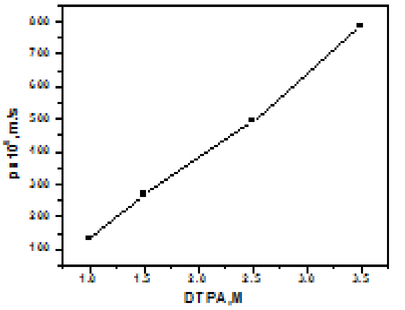


Fig.3. Influence of carrier concentration on permeability coefficient pa10⁶ m/s of Pb(II), F: 0.1M NaNO3, 0.03M Pb(II), M: x cyanex302/xylene. S:0.03M DTPA, 1M NaCl

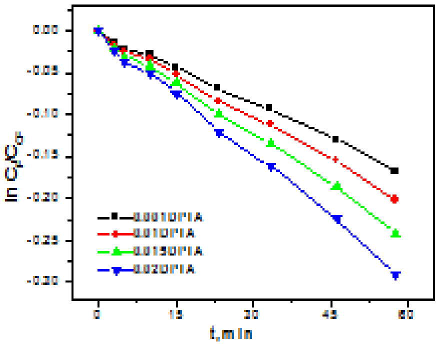


Fig 5 Semilogarithmic plots of ln CF/C0F against time, min different strip concentrations. F: 0.1 M NaNO3, 0.03M Pb(II), M: xM cyanex302/xylene, S:0.03M DTPA, 0.1M NaNO3.

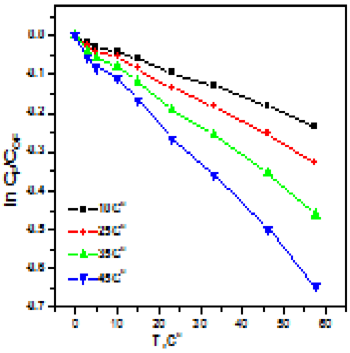


Fig.6 Semilogarithmic plots of ln CF/C0F against temperature of Pb(II) F: 0.1M NaCl, 0.03M Pb(II) pH=4, M: 0.2M cyanex302/xylene. S: 0.03M DTPA, 0.1M NaNO3.

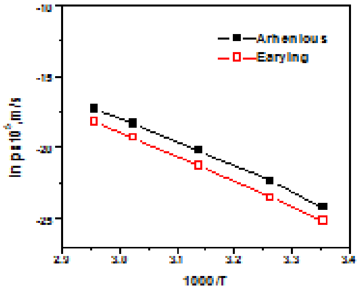


Fig.10 Influence of temperature on permeability coefficient Linear plot of Arrhenius and Eyring of Pb(II) F: 0.1M NaCl, 0.03M Pb(II) pH=4, M: 0.2M cyanex302/xylene. S: 0.03M DTPA.

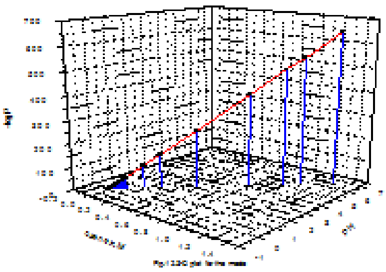
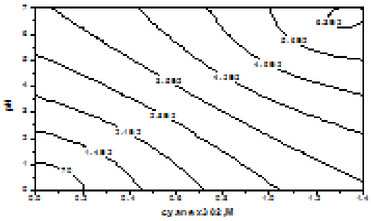


Fig.12 3D plot for the model



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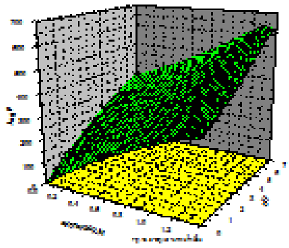

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