

Application of emulsion liquid membranes for removal of Cd, Co, Ni and Pb from Ismailia Canal, red sea, El Manzala lake, tape waters

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Abstract: The paper points to the presence of heavy elements such as cobalt, nickel, lead and cadmium ratios of small but very harmful to the environment as well as health harmful if used by people for agricultural purposes, etc. This is the heavy elements harmful if it exceeds the limit as it is then used as components of the value after the extract has found these elements mentioned sources such as Ismailia Canal - Manzala Lake and the Red Sea, has been used as comparison tap water ELM for the separation of these elements has been selected cobalt (III) dicarbolyde Span surfactant 80/85 and the use of acid silicon tungestic stage stripping effect concentrations of the carrier and the amendment, has been selected Co(III) dicarbolyde because metal organic compound with a larger surface area and the distinction between the structure of certain net structure.

Key words: cobalt (III) dicarbolyde; Ismailia Canal - Manzala Lake; acid silicon tungestic; Span surfactant 80/85.

I. Introduction

Water pollution with heavy metals is a very important problem all over the world. Nickel, lead and cadmium are three typical widespread heavy metal pollutants in the natural water environment. The main anthropogenic pathway which nickel, lead and cadmium entering environment is via wastes from industrial processes such as electroplating, alloy manufacturing, pigments, batteries and textile operations⁽¹⁻⁸⁾, Nickel entering body could cause cancers of the lungs, nose and bone^(1,2). Cadmium entering body could cause serious damages of the kidneys, lungs, bones and type tension, Lead could cause brain damage^(4,5) in children even at extremely low concentration⁽⁶⁻⁸⁾. The extraction of Cadmium (II) ions from aqueous solutions by emulsion liquid membrane (ELM) technique was investigated, Co (III) dicarbolyde in xylene using the. As stripping agent, nitroacetic acid (NTA) was used. Experimental results for the batch extraction of Cd (II) ions using a surfactant 80/85 are presented. The effects of various parameters such as feeding phase, membrane phase, stripping phase concentrations and the pH of the external phase were investigated. It was found that the most effective parameters in the extraction of Cd ion are pH of the external phase and concentration of the stripping agent in the internal phase. A simple empirical model was deduced to predict the rate of pertraction in such system⁽⁸⁾. For the study of Nickel and Cobalt together. The process An ELM process using tri-n-octylphosphine oxide (TOPO) to extract Cobalt from the Zinc plant acidic thiocyanate leach solutions containing Cobalt and Nickel has been presented. ELM consists of a diluent (kerosene), a surfactant (SPAN 80), and a carrier (TOPO). 6 M HNO₃ solutions have been used as stripping solution. These parameters are membrane type and composition, mixing speed, pH and thiocyanate concentration of feed solution, surfactant and extractant concentrations, and HNO₃ concentration of the stripping solution, phase and treatment ratios. The parameters mentioned were investigated and optimum conditions were determined. It is possible to selectively extract 99% of cobalt at the optimum conditions. The separation factors of Cobalt with respect to Nickel, based on initial feed concentration, have experimentally found to be of as high as 480 for about equimolar Co–Ni feed solutions⁽⁹⁻²³⁾. Extraction of Cadmium (II) ions from aqueous solutions by Co(III)dicarbolyde in xylene using the emulsion liquid membrane (ELM) technique was investigated. As stripping agent, nitroacetic acid (NTA), was used. Experimented for the batch extraction of Cd (II) ions using a surfactant 8/85 are presented. The effects of various parameters such as feeding phase, membrane phase, stripping phase concentrations and the pH of the external phase were investigated. It was found that the most effective parameters in the extraction of Cd ion are pH of the external phase and concentration of the stripping agent in the internal phase. A simple empirical model was deduced to predict the rate of pertraction in such system. Emulsion liquid membranes (ELM) with di-2-ethylhexylphosphoric acid in n-alkane, and dipicrylamine and Cobalt(III)dicarbolyde in nitrobenzene stabilized in double emulsions by SPAN 80/85 surfactant were used for preconcentration^(8,11) of radioactive fission products (¹³⁷Cs, ⁹⁰Sr, ¹³⁹Ce, and ¹⁵²Eu) from slightly acidic nitrate solutions. The efficiency of sulfuric, phosphotungstic and silicotungstic acids as stripping agents, and picric acid as the bulky anion additive was investigated. A group separation of the fission products is possible by the ELM technique and can be considered

for their removal from waste water solutions. Extraction processes using emulsion liquid membrane (ELM) have received significant attention due to their potential as an effective technique for treatment of industrial liquid wastes. However, the need to obtain desired level of stability is very important in order to overcome the obstacle of the application of ELM at industry.

1.1. MATERIALS AND METHODS

1.1.1. Sampling sites

Samples were collected from different water sources, for example, the Red Sea - Ismailia Canal and Manzala Lake downloaded from the same source temperatures were determined in different sources separately and sent these samples to analysis Laboratory) Ministry of agriculture (Cairo).

1.1.2. Sample collection

Samples were collected different water sources, which we have mentioned Month in October-November- October 2012 using 1L (one liter) [poly ethylene] [PE] bottles that were soaked in the previous 10% solution of nitric acid and rinsed thoroughly with water several times, and finally bidistilled with a portion of the water sample, and they were all water samples from source sealed and immediately transferred to the laboratory for analysis. Lab named the samples for analysis of heavy metals immediately filtered using a filter paper in order to maintain metals were then stored in the refrigerator until use at 25° C.

II. Experimental

2.1. Chemicals and Reagents:

2.1.1. Preparation

Co (III) dicarbonyl/xylene, the surfactants of Liquid Emulsion Membrane SPAN 80 and 85 (sorbitol mono- and trioleate) and/or other chemicals were analytical grade. A turbine type impeller was used for preparation of the liquid membrane with organic; water volume ratio $r_1 = 1$ and at a mixing rate 4000 – 6000 rpm for 5 – 10 min. Some emulsions remained stable for months. When breakage of emulsions was desired alcohols were used. The extraction of multiple W/O/W emulsion was performed in a multi stages double-Jackets cell thermostated temperature 25°C by stirring with magnetic bar (50x10 mm) stirrer at 300-700 rpm usually with 50 ml of outer (feed) solution. The extraction was followed by sample taking (0.5-1.0ml) from solution and measuring the extraction was followed by sample taking (0.5-1.0ml) from solution and measuring by the (ICP-OES) of ARL type model 3520, Buck Scientific, USA, was used for determination of cadmium concentration. The pH values were measured using a pH-meter of the type B-417 HANA instrument. Hydrogen ion concentrations in solutions were measured using a digital pH-meter of type CG-820 Schott Gerate from Germany a connected to a combined electrode which was standardized by suitable standard buffer solutions. The deviations in the readings were in the range of ± 0.02 at the laboratory temperature 25 ± 2 °C. The cell used in pertraction of toxic elements using ELM is shown 1. on the. 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. 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 cadmium concentration. Unless otherwise stated experiments were performed at 25 °C.

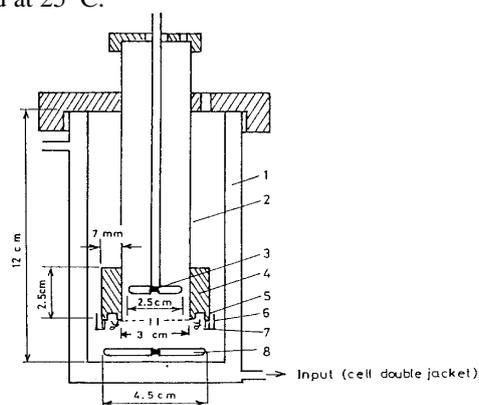


Fig.1. Scheme of pertraction apparatus: (1) double shield glass outer vessel, (2) Plexiglas inner tube, (3) Teflon cross stirring blade, (4) Teflon holder, (5) silicon rubber ring, (6) niobium holder, (7) titanium holder, (8) magnet

2.1.2. Co (III) dicarbolid characterisation [(B₉C₂H₁₀)₂S₂CH] Co (III)

Co (III) dicarbolid is a well. Studied Ni (II), Co (II), Cd (II) and Pb (II) extractant from acidic, aqueous media such as HNO₃ form of nitrated cobalt (III) dicarbolid is a strong acid in polar, organic diluent, the density and viscosity of the organic phase are suitable for processing applications. Where the density 1000-1020Kg^m³. And viscosity 30-50mpas (20°C).

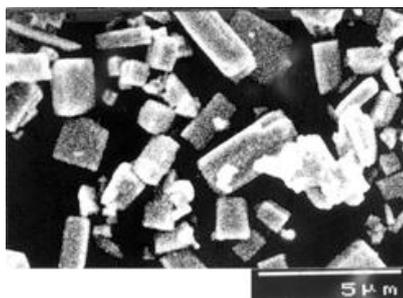
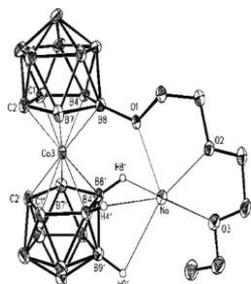


Fig (2): Co (III) dicarbolid coordinating sphere

Fig (3): SEM of Co (III) dicarbolid

2.1.4. Particle size measurement:

Particle size was measured using Malvern Particle Size Analyzer. The particle size is in the colloidal range and ranged from 247.6 nm to 518.2 nm using 4.5% and 9.5% Compritol respectively. Increasing the emulsion content in the prepared Co (III) dicarbolid resulted in increased mean particle size. This increase in particle size with increasing emulsion concentration may be due to the reduction of homogenization efficiency with increasing dispersed membrane phase^(24, 25).

2.1.5. Limits of detection for heavy metals (Cd, Ni, Pb and Co)

A sensitive and simple method for the simultaneous preconcentration of nutritionally important minerals in real samples has been reported. The method is based on the formation of metal complexes by Co (III) dicarbolid. The metals content on the complexes are then eluted using 5 mL 2 M HNO₃ in xylene, which are detected by An inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) of ARL type model 3520, was used for element analysis where argon is used and the power was 1.5 kilo Watt and the temperature of the plasma was about 6000~All elements were found in the effluent except palladium. An inductively coupled Plasma-Optical Emission Spectrometry (ICP-OES) of ARL type model 3520, was used for element analysis where argon is used and the power was 1.5 kilo Watt at resonance line. In this procedure, minerals such as Cd, Ni, Pb and Co could be analyzed in one run by caring out the simultaneous separation and quantification of them. At optimum condition the response are linear over concentration range of 0.04–1.1 go mL⁻¹ for Ni²⁺ and 0.04–1.0 μg mL⁻¹ for Cd²⁺, Pb²⁺ and Co²⁺. The detection limits of each element are expressed as the amount of analytes in ng mL⁻¹. The sorption capacity was determined by saturating 0.5 g solid phase. The loading capacity is 0.59, 0.51, 0.67 and 0.48 mg g⁻¹ for Ni²⁺, Co²⁺, Cd²⁺ and Pb²⁺. The ability of method for repeatable recovery of trace ion is 99.0, 96.9, 97.2 and 97.8. Of 1.2, 1.1, 0.98 and 1.2 for Ni²⁺, Co²⁺, Cd²⁺ and Pb²⁺. The low detection limits of these elements in this technique make it a superior alternative to (ICP-OES) of ARL type model 3520.

2.6. Samples analysis

In the feeding phase we used different samples from Ismailia Canal, red sea, El Manzala Lake, tape waters which were analyzed in table (1).

Table. (1): Water analysis according to Chemical analysis Laboratory) Ministry of agriculture:

- A is a sample water from Ismailia Canal.
- B is sample water from red sea.
- C is sample water from El Manzala Lake.
- D is a sample from tape water.

no	pH	E.C	E.C	Soluble Cations				Soluble Anions				S.A.R	R.S.R	S.S.P%
				Ca ⁺²	Mg ⁺²	Na ⁺¹	K ⁺¹	CO ₃ ⁻²	HCO ₃ ⁻¹	Cl ⁻¹	SO ₄ ⁻²			
Meq/L														
A	7.7	0.42	268.8	1.6	1.4	0.68	0.2	0	2.2	1.5	0.36	0.7	-0.8	21
B	7.6	55.7	35648	20	115	422	0.61	0	3.6	420	134.81	51.4	-131.4	75
C	7.9	2.62	1676	2.2	9.8	14	0.22	0	4	18	4.3	5.77	-8	53
D	7.7	0.5	320	1	2	2.15	0.26	0	2	2	1.4	1.76	-1	39

no	Mn	Fe	Zn	Cu	Co	Mg	Pb	Cd	Ni
ppm									
A	-	0.053	0.007	0.03	1	12.4	0.048	-	0.005
B	-	0.047	0.02	0.02	1	1600	-	0.047	-
C	-	0.095	0.05	0.005	0.01	125	-	0.072	0.024
D	-	0.105	0.007	-	0.02	90	0.021	0.059	0.045

III. Results and discussion

3.1. Extraction the metals from wastewaters using emulsion liquid membrane:

Studied the extraction of Co (II), Ni (II), Cd(II) and Pb(II) with emulsion liquid membrane. Further data were reported for Co(II),Ni(II),Cd(II) and Pb(II) with different carrier/extractants,study the optimized version of the extraction protocol provided a 99.8% recovery of Co(II) in the internal phase of the emulsion liquid membrane after a one stage extraction process, but Ni(II) was the dominant metal ion in the raffinate from the extraction surfactant concentration as the parameter controlling emulsion liquid membrane stability such as span 80/85 the ratio 3:1 due to increasing the affinity of water stripping solution was (STA) . In the experiments 300ml of simulated industrial waste water 50ml of ELM mixed inside the cell double jacket used stripping Silicon tungstic acid the stirring speed of the 4000-6000rpm.

3.2. Kinetic study.

At a constant interface area in double emulsion system and when the concentration of separated element in feed solution is much lower than the concentration of carrier in membrane and their chemical interaction does not change the concentration of carrier at interphase substantially, most of the results on membrane extraction (pertraction) can be approximated by a pseudo-first order kinetic law:

$$\log\left(1 - \frac{R}{R_{\infty}}\right) = -Kt \dots\dots (1)$$

$$R = R_{\infty}(1 - e^{-kt}) \dots\dots(2)$$

or

Where R is the yield of recovery (dimensionless fraction) at time t_5 and R_{∞} is the yield at pseudo-equilibrium and k is effective rate constant of membrane extraction (min^{-1}), which consists from a hydro dynamically influenced part and distribution dependent part .Therefore, all results were statistically treated by standard least-square method on a (programme Computer)(PC) to obtain the parameters R_{∞} and k. This work aims to remove the toxic elements from waters.Cd, Co, Ni and Pb by ELM using double jacket cell while the feed compartments of the cells are connected and opened together.

$$K = \frac{2pD_1}{R_{\infty}(2p - 1)} \dots\dots\dots (3)$$

$$p = 1 + \frac{1}{D_{II}r_{II}} \dots\dots\dots (4)$$

Where D_I is distribution ratio on the membrane/feeding solution interface and P is the pertraction factor determined by distribution ratio D_{II} on the membrane/stripping solution interface at organic: aqueous volume ratio r_{II} ($r_{II} = 1$ in our experiments). Thus, pertraction factor p varies within interval from 1 (at an unefficient stripping agent, $D_{II} \gg 1$) to infinity (the external masking effect of stripping agent, $D_{II} \gg 1$) and the dramatic changes are to be expected in the region, when extraction to membrane is relatively low (when $D_I r_{II} < 1$). At the practically important values of R_{∞} (say $R_{\infty} > 0.5$), regardless on the way how the value is obtained (i.e. by an efficient membrane extraction or depressing activity coefficient in stripping solution) and the efficient rate constant varies within the interval from $k = D_I$ (when $p = \infty$ and $R_{\infty} = 1$) to $k = 4 D_I$ (if $p = 1$ and $R_{\infty} = 0.5$). Hence, the effect of a strong stripping agent on pertraction parameter is positive in respect of increasing R_{∞} , but it influences the rate constant k in opposite direction. Obviously, the experimental arrangement used in our work and the expected precision of received kinetic data does allow confirming this kinetic model in details. Figs (4-7) show clearly that ,at the experimental conditions using 0.1 M

Co(III)dicarbolid /xylene, and 0.01 M silicon tungestic acid(STA) as stripping phase .And the Feeding water is a real water from different types. In the feeding phase we used different samples from Ismailia Canal, red sea, El Manzala lake, tape waters which were analyzed in table (1).Water analysis according to Chemical analysis Laboratory) Ministry of agriculture.: A. is sample water from Ismailia Canal. B is sample water from red sea. El Manzala Lake is a sample from tape water. The fraction yield calculated by plotting $\ln(1-R)$ against $t \cdot \text{min}^{-1}$ reaches a maximum values for Cd,(II),Co(II) Ni(II) and Pb(II) from the four types of waters ~80-99% .By plotting the pertraction rate K^{-1} against stripping phase .It is found that that the rate differs from one water to the other depending on the chemical composition of water and its salt content .from afro mentioned above ,that is means that the major process depending on the global effect of membrane type and concentration, Fig.(4-7).

3.3. Effect of pertraction rate

In order to evaluate its influence on the different sources transport rate, the initial concentration of heavy metals in the feed solution was varied 1–2.5 g/l. The results are shown in Fig (8-11). . It is observed that at high initial concentrations, the amount of metals which dissolved in nitric acid that crosses the membrane is relatively high, so it is easy to monitor the process by following the heavy metals concentration in the feed phase. On the other hand, lower initial concentration results in a lower amount of Silicone tungestic acid as stripping phase transported. It is reasonable to observe increases in extraction time by increasing the feed concentration in the external phase. This is true for all extraction processes.

3.5. Determination of recovery yield for toxic elements

The recovery yield for toxic elements from waters in different sources was shown in Fig(12) from this result we can use the Co(III)dicarbolid and stripping phase silicon tungestic acid Span 80/85 for preconcentration of these toxic elements. The recovery data were analyzed using a kinetic model and they are founding to be (99.9-99.7-94.5 and 92%) for tap water, Ismailia canal, Manzala Lake and red sea respectively. for tap water, Ismailia canal, Manzala Lake and red sea respectively.

IV. Conclusion:

A global efficiency for this type of membrane Co(III) dicarbolid with Silicon tungestic acid as stripping phase and surfactant Span 80/85 can be used for complete recovery of some toxic elements from waters and analysis by using pseudo-first order kinetic model .

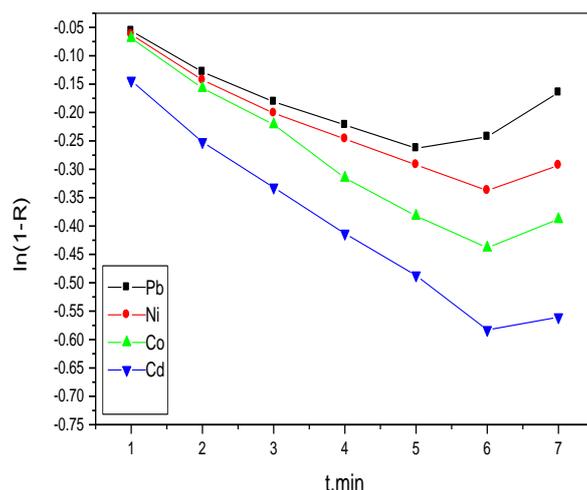


Fig.(4).Kinetic pertraction of toxic elements from tape water with ELM,
M=0.1 M Co(III)dicarbolid/xylene,F=tape water B,S=0.01
STA,3%SPAN 80/85(3:1), $\ln(1-R)$ vs t,min

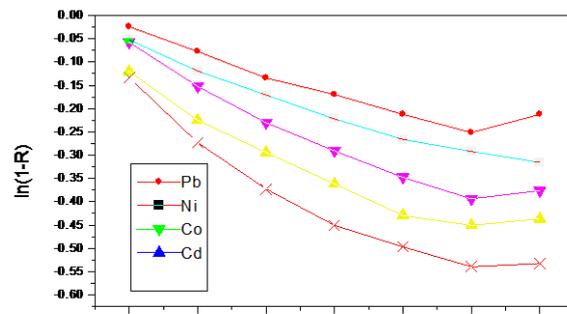


Fig.(5) Kinetic pertraction of toxic elements from lake water with ELM, M=0.1M Co(III)dicarbolide/xylene, F= lake sample water c, S=0.01 STA, 3%SPAN 80/85(3:1), ln(1-R) vs t, min

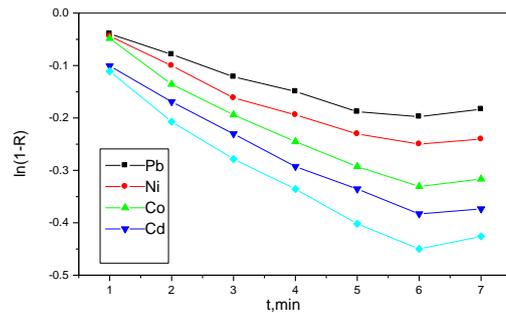


Fig.(6) Kinetic pertraction of toxic elements from canal water with ELM, M=0.1M Co(III)dicarbolide/xylene, F=sample canal water sample A, S=0.01M STA, 3%SPAN 80/85(3:1), ln(1-R) vs t, min

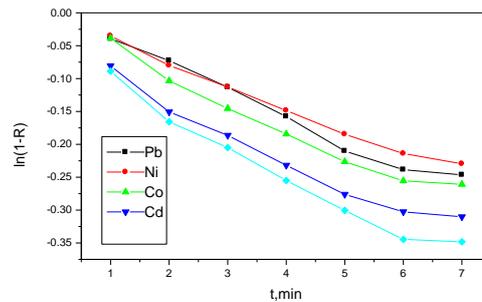


Fig.(7) Kinetic pertraction of toxic elements from Red sea water with ELM, M=0.1M Co(III)dicarbolide/xylene, F=sample red sea water D, S=0.01M STA, 3%SPAN 80/85(3:1), ln(1-R) vs t, min.

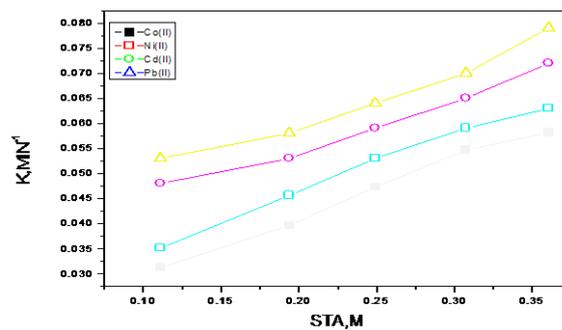


Fig.(8) Pertraction rate of toxic element K, min^{-1} , from tape water with ELM, M=0.1 M Co(III)dicarbolide/xylene, F=tape water B, S=0.01 STA, 3%SPAN 80/85(3:1), ln(1-R) vs t, min

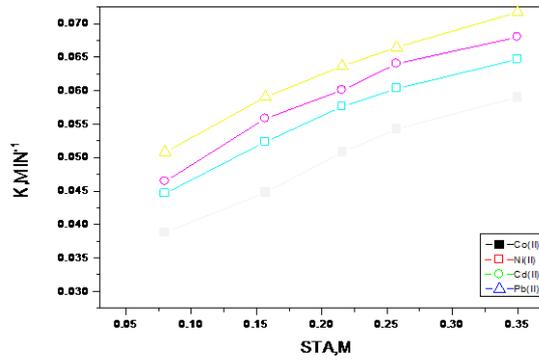


Fig.(9). Pertraction rate of of toxic element K, min^{-1} , from lake water with ELM, $M=0.1 \text{ M Co(II)dicarbolide/xylene}$, $F=\text{lake water B}$, $S=0.01 \text{ STA, 3\%SPAN 80/85(3:1), ln(1-R)}$ vs t, min

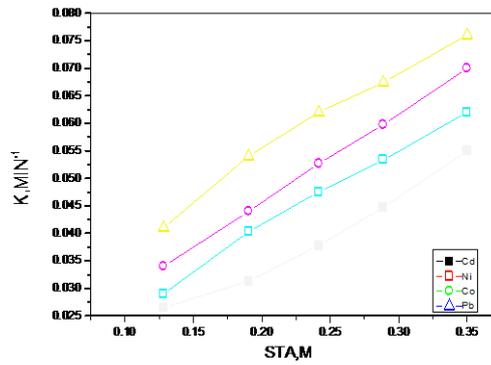


Fig.(10) Pertraction rate of of toxic element K, min^{-1} , from Canal water with ELM, $M=0.1 \text{ M Co(II)dicarbolide/xylene}$, $F=\text{canal water B}$, $S=0.01 \text{ STA, 3\%SPAN 80/85(3:1), ln(1-R)}$ vs t, min

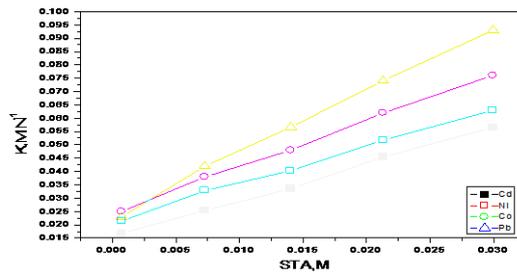


Fig. (11). Pertraction rate of of toxic element K, min^{-1} , from Red Sea water with ELM, $M=0.1 \text{ M Co(II)dicarbolide/xylene}$, $F=\text{Red Sea B}$, $S=0.01 \text{ STA, 3\%SPAN 80/85(3:1), ln(1-R)}$ vs t, min

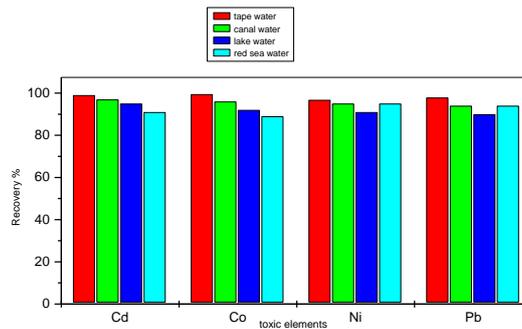


Fig.(12).The recovery yield of toxic elements using ELM, $M=0.1 \text{ M Co(II)dicarbolide/xylene}$ Strip= 0.01 M STA , $F=X$ water

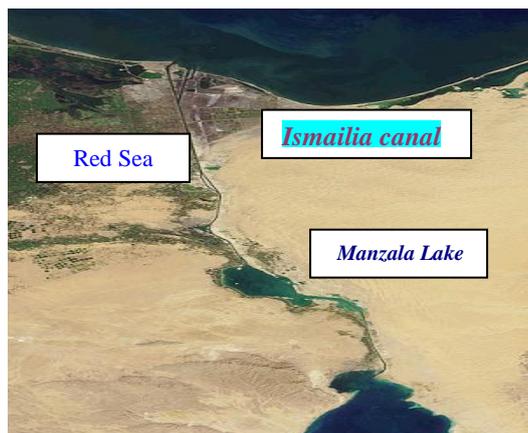


Fig (13): map to obvious some sources in the paper such as red sea, Manzala Lake and Ismailia canal

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