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Recovery of Cd(II), Co(II) and Ni(II) from Chloride Medium by Solvent Extraction Using CYANEX 923 and CYANEX 272

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ABSTRACT

The paper aims to study the extraction and separation of Cd(II), Co(II) and Ni(II) from their mixtures in hydrochloric acid medium with CYANEX 923 in kerosene. Preliminary investigations showed that only Cd(II) is extracted with CYANEX 923 while Co(II) and Ni(II) are not extracted. Different parameters affecting the extraction of Cd(II) with CYANEX 923 such as hydrochloric acid, hydrogen ion, extractant and metal concentrations, temperature investigations were also investigated. The stoichiometry of the extracted metal species investigated was found to be $HCdCl_3$.2CYANEX 923. The stripping of the extracted Cd(II) species is obtained with 0.1 M HCl solution. Co(II) was found to be extracted with CYANEX 272 at pH 5.8 leaving Ni(II) in the solution.

A developed process for the sequential of Cd(II), Co(II) and Ni(II) from therir mixture in hydrochloric acid medium is proposed.

Keywords: Extraction, Cd(II), Co(II), Ni(II), CYANEX 923, CYANEX 272, Chloride medium.

INTRODUCTION

Cadmium finds its way to water bodies through waste water from metal plating industries, nickel cadmium batteries, phosphate fertilizers, mining, pigments, stabilizers, ceramics, metallurgical and photographic products and alloys.[(1-3)] However**,** due to its high toxicity the public have been pressing to reduce or even eliminate the use of cadmium in many countries. Although the consumption of cadmium in every day life seems to decrease slowly, potential new applications as thin photovoltaic films of CdSe and CdTe appear useful for solar energy generation[(4)]. Cadmium is used in nuclear reactors as control rods and as a shield to absorp neutrons, resulting in the formation of various isotopes including cadmium-113, which is present in spent nuclear fuel and radioactive wastes associated with operating nuclear reactors and fuel reprocessing plants. Nickel is found in industrial waste solutions resulting from electroplating and spent catalysts and one of the composition of intermediate level active waste [(5)]. Cobalt is used in pigments, ceramics, glass, paints and fertilizers. Artificial isotope ^{60}Co is radioactive and is used in radiotherapy by neutron irradiation. **Ahmed** [(6)] studied the sequential separation of Co(II), U(VI), Zn(II), Cr(III) and Cr(VI) from 1 M $(NH_4)_2SO_4$, $(NH_4)Cl$ and $(NH_4)NO_3$ using CYANEX 272 in kerosene**.** The extraction and separation of Co(II) from its mixture with U(VI),

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Nd(III), Fe(II) in nitrate medium using CYANEX 301 in kerosene was possible by monitoring the concentration of sulphuric acid stripping solution. [7] **Almela and Alizade**[8] reported that in the extraction of Cd(II) from chloride medium by bis(2,4,4 trimethylpentyl) monothiophosphinic acid (CYANEX 302) in kerosene, the extracted species are $CdR_2(HR)$ and $CdR_2(HR)_2$, HR being the active component in the commercial extractant CYANEX 302. **Reddy et al.,**[9] studied the extraction of cadmium(II) from sulphate solutions using TOPS 99 (an equivalent of di-2-ethylhexyl phosphoric acid), PC88A, CYANEX 272 and their mixtures. It was found that the extraction of cadmium increases with the equilibrium pH of the aqueous phase and the extractants concentrations. The extraction took place via cation exchange mechanism with the formation of 1:3 metal to reagent complex. The separation of cadmium from nickel was possible. **Gupta et al.,** [10] studied the extraction of cadmium from 1 M HCl using CYANEX 923 in toluene. The authors found that the exraction of cadmium increases with acid molarity, extractant and chloride concentrations. The extracted species was found to be $CdCl_2$.2CYANEX 923. They also reported that CYANEX 923 can be used to extract and separate cadmium from other metal impurities from some natural ores. **Reddy and Priya** [11] studied the solvent extraction of cadmium, nickel and cobalt from chloride leach liquor of spent nickel-cadmium batteries with CYANEX 923 and CYANEX 272. They found that the extraction of cadmium increases with CYANEX 923 and chloride concentrations while nickel and cobalt are separated using CYANEX 272 via cationic exchange mechanism.

The aim of this paper is to study the extraction of Cd(II), Co(II) and Ni (II) by both CYANEX 923 and CYANEX 272 in kerosene from chloride medium to learn about the parameters affecting their extraction. Based on the difference in the extraction and stripping behavior of the investigated metals, a process for their separation from their mixture in HCl medium is proposed.

EXPERMENTAL

Chemicals and Reagents

Most of the used chemicals were of analytical grade. The commercial extractant CYANEX 923 and CYANEX 272 were kindly offered by Cytec Inc. and used as received; kerosene was obtained from Misr Petroleum company, Egypt.

Procedure

The batch experiments were carried out by equilibrating in stoppered glass bottles equal volumes of 0.06 M CYANEX 923 in kerosene and 0.01 M Cd(II), 1.7×10^{-3} M Co(II), 0.5 M Ni(II) in 1 M HCl for 5 min. After equilibration and phase separation, a suitable volume of the aqueous phase was spectrophotometrically measured.

Cadmium and cobalt concentrations were spectrophotometrically determined using 4-(2-pyridylazo) Resorcinol (PAR) [12] at λ = 492 nm using Shimadzu UV/VIS. double beam recording spectrophotometer, Model 160-A, Japan. The hydrogen ion concentration for the solutions was measured using a digital pH meter of Hanna instruments type at the ambient laboratory temperature 25± 1^{o}C. During batch experiments a good mixing for the two phases was achieved using a thermostated water bath shaker of the type Julabo SW-20C, Germany controlled within ± 1^{o}C.

The concentration of the metal in the organic phase was calculated from the difference between its concentration in the aqueous phase before and after extraction. The distribution ratio D was calculated as the ratio of the concentration of the metal in the organic phase to its concentration in the aqueous phase.

Result and Discussion

Extraction of Cd(II), Co(II) and Ni(II) by CYANEX 923 in kerosene

Investigations were carried out to know the optimum conditions for the extraction of 0.01 M Cd(II), 1.7×10^{-3} M Co(II) and 0.5 M Ni(II) using 0.06 M CYANEX 923 in kerosene. Preliminary experiments showed that the extraction of Co(II) and Ni(II) from 1 M HCl solution is negligible, therefore detailed study on their extraction with CYANEX 923 was not carried out in the present work.

The different parameters affecting the extraction of Cd(II) were separately investigated. Stripping investigations of cadmium from the loaded organic phase were also carried out.

Effect of hydrochloric acid concentration

The effect of hydrochloric acid concentration on the extraction of 0.01 M Cd(II) using 0.06 M CYANEX 923 in kerosene was investigated in the range 0.5 - 4 M. The results represented in Fig.(1), show that the extraction percentage of cadmium increases with HCl concentrations up to 2.5 M then remains constant with further increase in the acid molarity.

Effect of chloride concentration

The influence of chloride concentration on the extraction of 0.01 M Cd(II) by 0.06 M CYANEX 923 was investigated in the range 1 -3 M at constant hydrogen ion concentration of 1 M. The results presented in Fig.(1), show that the extraction of Cd(II) increases with the increase in chloride concentration due to salting out effect of chloride ions .

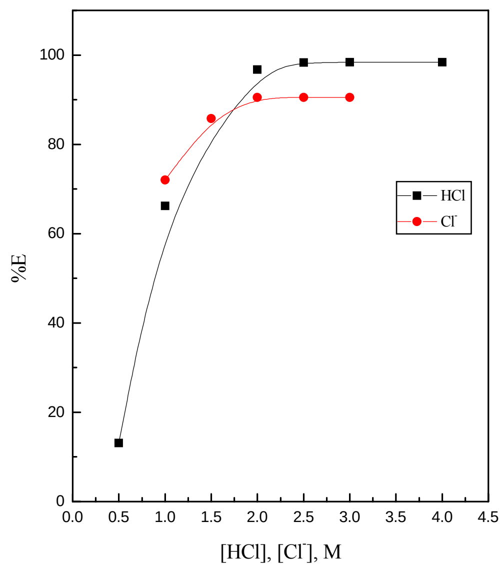

Fig. (1) : Effect of [HC] or [Cl$^-$] on the extraction of 0.01 M Cd(II)by 0.06 M CYANEX 923 in kerosene, Temp. = 25^{o}C, Shaking time = 5 min.

Effect of hydrogen ion concentration

The effect of hydrogen ion concentration on the extraction of 0.01 M Cd(II) using 0.06 M CYANEX 923 in kerosene was investigated over the range 0.1 - 1 M at constant chloride ion concentration of 1.0 M. When log D is plotted versus log H^+ concentration Fig.(2), a linear relation of slope ≈ 1.0 is obtained within the investigated acid concentration range which indicates that one mole of H^+ participates in the extraction.

Effect of CYANEX 923 concentration

The effect of CYANEX 923 concentration on the extraction of 0.01 M Cd(II) from 1 M HCl solution was investigated in the range 0.01- 0.06 M. The plot of log D against the corresponding log CYANEX 923 concentration gives a linear relation of slope 2 which indicates that 2.0 moles of CYANEX 923 participate in the extracted species, Fig.(2).

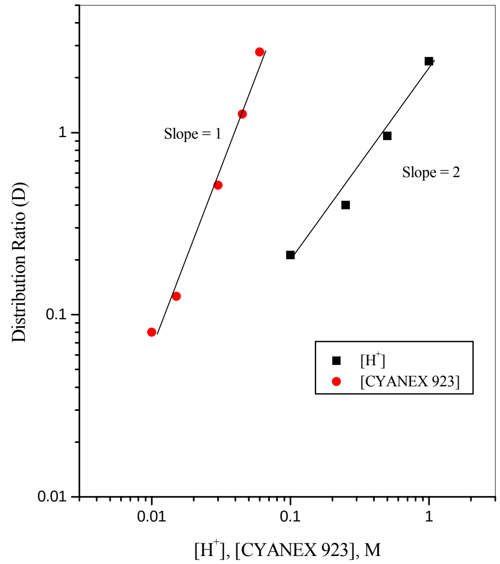

Fig. (2) : Effect of [H^+] or [CYANEX 923] on the extraction of 0.01 M Cd(II) by CYANEX 923 in kerosene, Temp. = 25^{o}C, Shaking time = 5 min.

Extraction equilibrium

Based on the above slope analysis results, the extracted species is expected to be the acidocomplex of the type $HCdCl_3$.The extraction of 0.01 M Cd(II) from HCl solution can be represented by :

$$H^+ + CdCl_3^- + \overline{2CYANEX\,923} \rightleftarrows \overline{HCd_3.2CYANEX\,923} \quad (1)$$

$$K_{ex} = \frac{D}{[H^+]\,\overline{[CYANEX\ 923]}^2} \quad (2)$$

Where bars indicate organic species, and K_{ex} represents the extraction constant. The average value of K_{ex} at different [H^+] and [CYANEX 923] is 566 ±22 M^{-3}.

Effect of Temperature

The effect of temperature on the extraction of 0.01 M Cd(II) from 1.0 M HCl solution using 0.06 M CYANEX 923 in kerosene was studied in the range 15 - 50^{o}C, Fig. (3). The thermodynamic parameters calculated and tabulated in Table (1) show a negative value of (ΔH) which indicates that the extraction process is exothermic; the positive value of (ΔG) indicates that the process is spontaneous and the negative value of (ΔS) indicates a decrease in the randomness of the system.

Table (1) : Thermodynamic parameters of 0.01 M Cd(II) extracted by 0.06 M CYANEX 923 in kerosene

from 1 M HCl solution.

Thermodynamic parameter	Calculated Value
Enthalpy Change (ΔH)	-43.61 ± 4.08 kJ $mole^{-1}$
Free Energy Change (ΔG)	15.70 ± 0.02 kJ $mole^{-1}$
Entropy Change (ΔS)	-199 ± 4 J $mole^{-1}$ K^{-1}

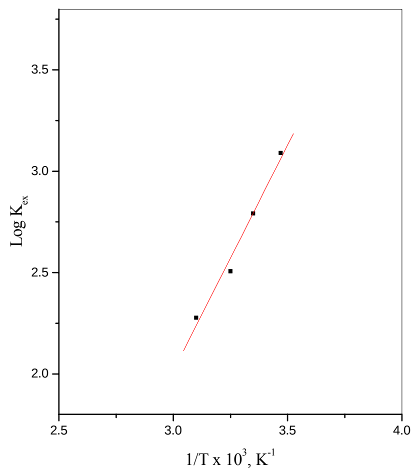

Fig. (3) : Effect of temperature on the exraction of
0.01 M Cd(II) by 0.06 M CYANEX in
kerosene from 1 M HCl solution .
Shaking time = 5 min. A : O = 1 : 1

Effect of cadmium concentration

The effect of Cd(II) concentration on its extraction was studied cover the range 0.01 - 0.1 M from 1.0 M HCl solution by 0.06 M CYANEX 923 in kerosene. The results obtained and represented in Fig.(4), show that the extraction of Cd(II) increases with the increase in the initial Cd(II) concentration up to 0.05 M then remains constant with further increase in its concentration.

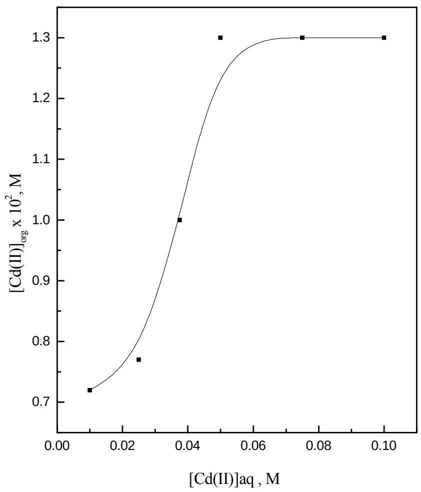

Fig. (4) : Effect of Cd(II) concentration on its extraction by 0.06 M CYANEX 923 in kerosene from 1 M HCl soluion .

Shaking time = 5 min. A : O = 1 : 1

Temp. = 25^{o}C

Loading capacity

The loading capacity of CYANEX 923 was carried out by contacting 0.01 M Cd(II) from 1.0 M HCl solution with CYANEX 923 in kerosene solution at (A/O) phase ratio of 1:1; the two phases were separated, Cd(II) concentration was determined, and the same organic phase was used again for the extraction with fresh Cd(II) solution. The results represented in Fig.(5) indicate that the maximum concentration of Cd(II) in the organic phase was found to be 0.013 M and reached after 5 extraction stages. The loading capacity is 0.218 M Cd(II) per 1 mole CYANEX 923.

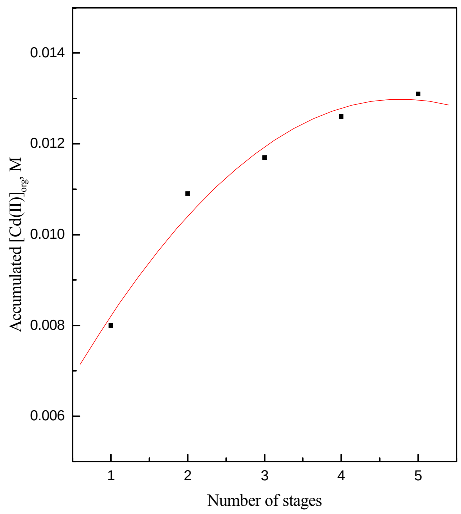

Fig. (5) : Effect of number on the extraction of 0.01 M Cd(II) by 0.06 M CYANEX 923 in kerosene from 1 M HCl solution.

Shaking time = 5 min. A : O = 1 : 1

Temp. = 25^{o}C

Effect of phase ratio

The effect of phase ratio on the extraction of 0.01 M Cd(II) from 1 M HCl solution by CYANEX 923was investigated at different organic: aqueous phase ratios in the range 0.25 to 2.0. The extraction percentage of Cd(II) obtained are plotted against the corresponding phase ratio as shown in Fig.(6) which shows that the extraction percentage of Cd(II) reaches 99% at organic to aqueous phase ratio of 1.5.

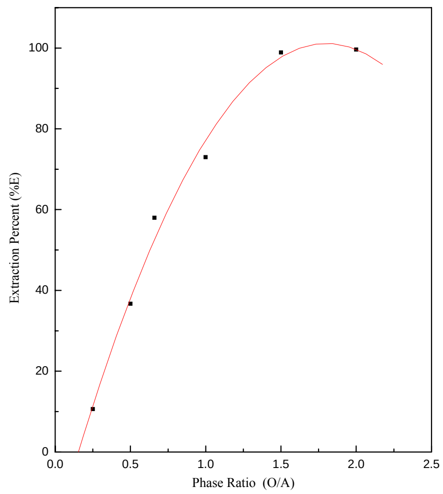

Fig. (6) : Effect of phase ratio on the extraction of 0.01 M Cd(II) by 0.06 M CYANEX 923 in kerosene from 1 M HCl solution.

Shaking time = 5 min. Temp. = 25^{o}C

The extraction behavior of Co(II) using CYANEX 272 studied in previous work[6] and show that the extraction start at pH 4.0 whereas the extraction of Ni(II) start at pH 6.0, therefore the separation of Co(II) and Ni(II) is suggested to be at pH 5.8 .

Separation of Cd(II), Co(II) and Ni(II) from 1 M HCl solution by CYANEX 923 and CYANEX 272

The extraction investigations on the solvent extraction of Cd(II), Co(II) and Ni(II) by CYANEX 923 and CYANEX 272 led us to the following conclusion that a selective extraction of Cd(II) by CYANEX 923 in kerosene where Co(II) and Ni(II) were not extracted and Cd(II) was recovered from the organic phase by 0.1 M HCl. Extraction with CYANEX 272 showed that Co(II) was extracted by 2% CYANEX 272 in kerosene at pH 5.8 where, Ni(II) was not extracted. The extracted cobalt was stripped from the loaded CYANEX 272 solution with 3 M H_2SO_4 solution. Extraction with CYANEX 272 showed that Ni(II) was recovered as nickel chloride salt, Fig. (6)

Cd(II), Co(II), Ni(II) from 1 M HCl Solution

Extraction by 0.06 M CYANEX 923

O/A =1

Organic Aqueous

Cd(II) Co(II) and Ni(II)

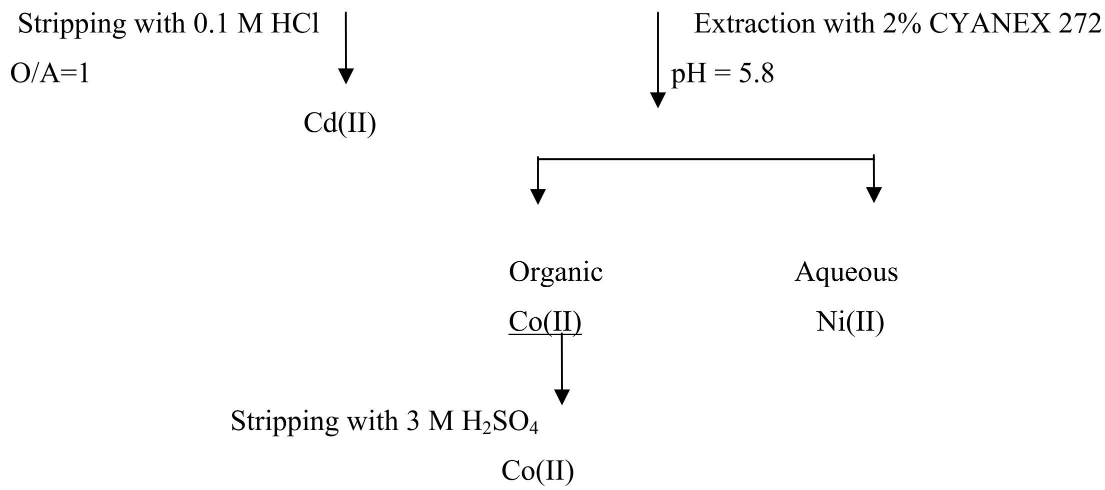

Fig. (6) : A conceptual flow diagram for the recovery of Cd(II), Co(II) and Ni(II) from 1 M HCl solution by CYANEX 923 and CYANEX 272 in kerosene.

CONCLUSION

-CYANEX 923 could extract Cd(II) from 1 M HCl solution while Co(II) and Ni(II) are nearly not extracted.

-The increase in hydrochloric acid, hydrogen ion, chloride ion and CYANEX 923 concentrations increased the extraction of Cd(II).

-The extraction equilibrium of Cd(II) by CYANEX 923was reached after 5 min.

- The increase in temperature decreased the extraction of Cd(II) with CYANEX 923.

- Stripping investigations showed that 0.1 M HCl solution is effective for the quantitative stripping Cd(II).

- Co(II) was found to be extracted with CYANEX 272 at pH 5.8 leaving Ni(II) in the solution.

- 3 M H_2SO_4 is effective for stripping Co(II) from its loaded CYANEX 272 solution.

-The difference in the extraction and stripping behavior of Cd(II), Co(II) and Ni(II) from chloride medium could be used for their sequential separation from their mixture.

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