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Full Length Research Paper

Extraction of Eu(III) from nitrate medium by CYANEX921 using solvent extraction technique

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The extraction of Eu(III) was investigated from nitrate medium by CYANEX921 (C921). It was found that the chemical formula of the main extracted species in the organic phase is $Eu(NO_3)_3$.3[C921] for extraction by C921. It was found that the Eu(III) percent extracted from toluene, n-hexane, cyclohexane and kerosene was nearly similar but with faster phase separation in favor of toluene. The relation between the shaking time and the percent of extracted C921 (%E) was studied at different pH. It was found that the best shaking time is 20 min at pH between 0.5-1.0, whereas at pH 2.0 the best shaking time is 15 min. The maximum extraction of Eu(III) was found to be after 5 min at pH 3.0. The extraction of Eu(III) increase with increasing of pH, however, the extraction precent increase from 28.5% at pH 0.5 to 98% at pH 3.0 The calculated average for the extraction constant is 6.58 at pH 3.0 under various C921 concentrations. From the data obtained, it was found that arsenazoIII (AIII) is a good stripper for Eu from organic phase which reach to 65% at pH 2. The stripping of Eu decreased from 57% to 2% when rising the pH from 0.5 to 11.

Key word: Solvent extraction / europium(III)/CYANEX921/ nitrate media /stripping.

INTRODUCTION

The organophosphorus compounds are mainly employed as extractants for many metal ions. Cytec Industries Inc. Company has manufactured produced some of these compounds under the name of CYANEX®. These compounds are characterized by their selective extraction power, stability and low cost, (Thornton, 1992). CYANEX 921 is considered as a commercial product of tri-n-octylphosphine oxide (TOPO). It is a mixture of three different trialkyl phosphine oxides, one of them is TOPO which contributes ~ 93% in CYANEX921. It found some applications in TOPO as commonly used as separation and recovery of some metal ions in industrial and nuclear fields. In previous works , CYANEX 921 was used as an extractant for separation of U(VI) and Th(VI) from nitric acid medium, (El-Reefy and Awwad (1997)." It was also used for separating U(VI) and Fe(III) from commercial phosphoric acid, (Awwad et al., 2002). CYANEX301(C301) or C921 and their binary mixtures have been used to extract uranium (VI) from aqueous HNO_3 and H_2SO_4 media , (Awwad et al., 2005). From the nitric acid medium the order of extraction efficiency of uranium is (C301+ C921) > C921 > C301. In case of H_2SO_4 medium uranium extraction takes the order, C301 > C921 ≈ (C301+ C921). Extraction of Am(III) and Eu(III) from the NO_3^-, ClO_4^-, SCN^- and NO_3^- + ClO_4^- media with TOPO in xylene has been carried out at temperature of 15, 25, 30 and 35°C respectively, (Suresh et al., 2003) . Under the extraction conditions, the species $M(NO_3)_3{\cdot}3TOPO$, $M(SCN)_3{\cdot}4TOPO$, $M(ClO_4)_3{\cdot}4TOPO$ and $MNO_3(ClO_4)_2{\cdot}4TOPO$ are predominantly extracted at all the temperatures whereas (M = Am or Eu)."

Sorel's cement is mixture of MgO powder or calcined magnesite powder as a major component and $MgCl_2$ solution of a certain concentration in the MgO- $MgCl_2$ – H_2O system. The major reaction products of magnesium oxychloride (MOC) pastes have long been revealed to be exist in four crystalline phases, F2, F3, F5 and F9, (Maravelaki-Kalaitzaki and Moraitou, 1999)": $2Mg(OH)_2.MgCl_2.4H_2O$(F2); $3Mg(OH)_2.MgCl_2.8H_2O$(F3); $Mg(OH)_2.MgCl_2.8H_2O$(F5); and $Mg(OH)_2.MgCl_2.5H_2O$(F9). According to the phase diagram, the ternary oxychloride phases are dependent on $MgO/MgCl_2$ molar ratio. The potential use of Sorel's cement as a good adsorbent material for treatment of thorium, uranium and chromium contaminated water has been reported, (Daifullah and Awwad, 2003); (Awwad

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Table 1. Effect of diluent on the extraction of 500 mg/l Eu(III) from nitrate solution with 0.2 M C921.

Diluent	D (distribution ratio)
toluene	46.2
cyclohexane	36
n-hexane	41
Kerosene	40

and Daifullah, 2005); (Hassan et al., 2006).

Hence, this work is directed to study the extraction of Eu(III) from nitrate media by using soft doner ligand CYANEX 921/ toluene to obtain the optiumum condition for extraction of Eu(III). The wastewater produced which have the dyes of Arsenazo(III) complexed with Eu was purified to clear solution before discharge to sewage. Sorel's cement as adsorbent was used for this process.

MATERIALS AND METHODS

Preparation of Eu (III) solutions

A stock solution of pure eurobium (99.99%) with concentration of 1000 mg/l was prepared. The pH was adjusted to 3±0.1. Working solutions of different concentrations were prepared by diluting stock solution with 0.1 M $NaNO_3$.

Preparation of organic solutions

C921 was given by Cytec and purified in a (v/v (1:1) ratio at 25°C for 15 min) using 0.5M C921 in toluene contacted with 0.5 M ammonium carbonate. White Precipitation of ammonium phosphine oxide was crytalized, and then dissolved in acetone. Purified product was obtained after evaporation of acetone at 70°C. A stock solution of 0.5 M of the organic extractant, C921, in toluene was prepared. Organic extractant solutions with the required con-centrations were prepared from the stock solution by dilution with toluene.

Preparation of sorel's cement as adsorbent material

Sorel's cement, F3 type, was prepared using commercial grade of MgO and $MgCl_2$ (supplied by ADWEC, Egypt). Magnesium oxide (2.4 g) was dissolved in 8 ml of aqueous 1.78 M MgCl2 solution at 75℃ to neutralize the free hydrogen ions formed by the hydrolysis of MgCl2. A precipitate was separated by centrifugation and washed thoroughly with ethanol. The solid product was dried under IR lamp, stored in a desiccator and kept at 75°C for 4 h. The dry solid precipitate was grinded and sieved to a particle size of 50 mesh.

Extraction procedure

Extraction of Eu(III) was carried out at 25 ± 1°C with exception in the study of temperature). In this work, equal volumes (5 cm^3) of aqueous solution containing a known concentration of the element under investigation and organic solution with known extractant concentration were equilibrated by shaking for 20 min. with the exception the studying of shaking time in stoppered glass tubes in a thermostated mechanical shaker. After equilibration, and separation of the two phases, the concentration of Eu in aqueous phase was spectrophotometrically measured using a Shimadzu UV visible spectrophotometer model UV-160A. Europium concentrations were determined in the aqueous phase through the color of the AIII–Eu complex at 655 ± 2 nm, Marzenko (1982). The concentration of the investigated metal in the organic phase was calculated by the difference between its concentration in the aqueous phase before and after extraction.

The distribution ratio (D) for each sample was calculated from the relation:

$$D = \frac{\text{Concentration of U(VI) in the organic phase}}{\text{Concentration of U(VI) in the aqueous phase}} \quad (1)$$

The percentage extracted, % E, was calculated by the following equation:

$$\%E = \frac{100D}{D + 1} \quad (2)$$

With the aim of separating of Eu(III), the liquid-liquid extraction of Eu was studied from aqueous solutions by C921 in toluene. The investigated parameters are the effect of C921, metal ion concentrations, pH, and temperature. The results obtained are analyzed and the equilibria encountered are proposed.

Extraction of Eu(III)

The extraction of Eu(III) was performed with 0.2 M C921 in toluene, n-hexane, cyclohexane and kerosene. It was found that the extracted Eu(III) percent extracted in both cases was nearly similar but with faster phase separation in toluene (Table 1). Therefore, toluene was used as suitable diluent for C921 in the extraction of Eu. For the extraction of Eu(III), samples of pH at 0.5 , 1.0, 2.0, and 3.0 ±0.1 containing 500 mg/l Eu(III) were dissolved in 0.1 M sodium nitarte solutions were prepared and shaken with 0.20 M C921 in toluene at 25°C for different time intervals between 5-30 min. The relation between the shaking time and the percent of extracted C921 (%E) is studied at each pH. At pH 0.5 and pH 1.0, the best shaking time is 20 min , whereas at pH 2.0, the best shaking time is 15 min. The maximum extraction of Eu(III) at pH = 3.0 was found to be after 5 min.

Studies on the extraction of 500 mg/l Eu(III) from nitric acid media with 0.2 M C921 in toluene was carried out. The obtained results are given in Table 2. Extraction was proven as an increase with the decrease in acid concentration.

Based on these preliminary experiments, investigations on the factors affecting the extraction of 500 mg/l Eu(III) was performed using C921 in toluene from nitrate medium at shaking time 20 min at pH 3 at 25°C. Unless otherwise stated, the aqueous phase contains 500 mg/l Eu(III) in 0.1 M nitrate medium and the organic phase was 0.2 M C921 in toluene.

Effect of metal ion concentration

Samples containing different concentrations of Eu(III) within the range 100 to 1000 mg/l dissolved in 0.1 M nitrate solutions at pH of 0.5 , 1.0, 2.0, and 3.0 were prepared, respectively. The extraction was studied by 0.2 M C921 in toluene at 25°C. The results obtained are represented in Table 2 as a relation between the equilibrium concentration of Eu in the aqueous phase and in the organic phase. The concentration of Eu in the organic phase decreases with increasing its concentration in the aqueous phase at all pHs. How-

Table 2. Effect of 0.2M C921 on the removal of different concentration of Eu(III) at differents pH at 25^{o}C.

Eu(III) (mg/l)	pH 0.5		pH 1.0		pH 2.0		pH 3.0	
	D	%E	D	%E	D	%E	D	%E
100	3.4	77.3	23	95.8	56	98.2	147	99.3
300	1.2	54.5	7.0	87.5	40	97.5	132	99.2
500	0.4	28.6	2.0	66.6	28	96.5	46.2	97.9
800	0.09	8.25	0.5	33.3	3.5	77.7	7.51	88.2
1000	0.02	1.96	0.3	23.0	0.9	47.4	4.6	82.1

Table 3. Effect of pH on the extraction of 500 mg/l Eu(III) from nitrate solution with 0.2 M C921 in toluene at different temperature.

pH	25℃		35℃		55℃	
	D	%E	D	%E	D	%E
0.5	0.4	28.5	0.13	11.5	0.03	2.9
1.0	2.0	66.6	0.89	47.0	0.25	20
2.0	28	96.5	2.0	66.7	0.95	48.7
3.0	46.2	97.9	3.5	77.8	1.2	54.5
>3.4	Precipitation of Eu(III) started					

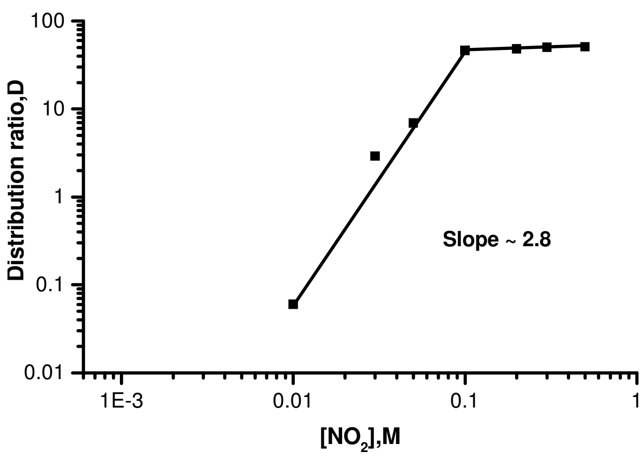

Figure 1. Effect of nitrate ion concentration on the extraction of Eu(III) by 0.2M C921/toluene at pH 3.

ever, the extraction of Eu(III) at 1000 mg/l increase from 1.96% at pH 0.5 to 82.1% at pH 3.0

Effect of pH

A series of 0.1 M nitrate solutions with 500 mg/l Eu(III) but varies hydrogen ion concentrations giving pH values in the range 0.5 - 3.4 were used. Table 3 shows the relation between the pH and the respective percent of extracted Eu(III) at different temperatures. The extraction percent increases sharply with the increasing pH from 0.5 to 2.0, then slightly increase with further increase in pH from 2 to 3 for different temperature. The disolution of Eu(III) start at more than pH 3.4. The extraction of Eu was also found that it decreases with increasing temperature, which confrims the processes of extraction is exothermic.

Effect of nitrate ion concentration

Different nitrate ion concentrations covering the range from 0.01 to 0.50 M was used. Log-log relation between the nitrate concentrations in the aqueous phase and the corresponding distribution ratios (D) is given in Figure 1. At high nitrate ion concentration (0.1 - 0.5), it has no effect on the extraction of Eu(III). While at low concentration of nitrate, the distribution ratio of Eu(III) increase sharply with the increase in nitrate ion concentration in the range between 0.01 to 0.1 M. This is also supported by the presence of active band of NO_2^- in the IR spectrum of the extracted Eu species.

Effect of C921 concentration

Various concentrations of C921 in toluene was used to extract Eu(III) in 0.1 M nitrate solutions at pH 3.0. The extractant concentrations used covered the range 0.03-0.30 M. The C921 concentrations were plotted against the corresponding distribution ratios of Eu(III) between the two phases as log-log relation in Figure 2. The extraction of Eu increases with the increases in C921 concentration from 0.03 to 0.1 M. The slight increase in the distribution ratio with increasing the extractant concentration from 0.1 to 0.3, may be due to the competition of water molecules and the C921 molecule. A linear relation, log D- log C921 was plotted with slope ≈2.9 was obtained. This value suggested that the extracted species contains three C921 molecules per Eu ion.

Extraction equilibrium

Based on the above studied parameters, the equilibrium of Eu(III) extraction by C921 in toluene at pH 3.0 can be

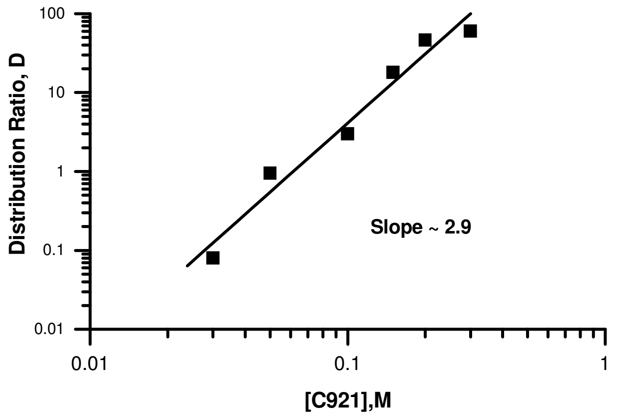

Figure 2. Effect of C921 concentration on the extraction of Eu(III) from 0.1M nitrate solution at pH 3.

Table 4. Extraction constants of Eu(III) from 0 .1M nitratemedium at differents concentration of C921.

[C921](M)	Log K_{ex}
0.03	6.47
0.05	6.8
0.1	6.4
0.15	6.7
0.2	6.76
0.3	6.35

represented by:

$$Eu^{3} + 3NO_3 + 3\overline{C921} \rightleftharpoons [Eu(NO_3)_3].3C921 \quad (3)$$

where bars refer to organic species.

Therefore, within the pH range 0.5 to 3.0, the extraction constant of this equation is given by:

$$K_{ex} = \frac{\overline{[Eu(NO_3)_3.3\ C921]}}{[Eu]^{+3}\ [NO_3]^{-3}\ \overline{[C921]}^{3}} \quad (4)$$

or,

$$K_{ex} = \frac{D}{[NO_3]^{-3}\ \overline{[\ C921]}^{3}} \quad (5)$$

Taking logarithms on both sides of equation (5), the following relation is obtained:

$$\log K_{ex} = \log D - 3\log [NO_3] - 3\log [C921] \quad (6)$$

The extraction constant was calculated at pH 3.0 at different concentrations of the C921 and the results obtained for K_{ex} are almost constant, see Table 4.

Table 5. Thermodynamic parameters for the extraction of Eu from nitrate solution with 0.2M C921/toluene at different temperature

ΔH (kJ mol^{-1})	ΔG(kJ mol^{-1})	ΔS(J $K^{-1}mol^{-1}$)
-118.67	-38.54	-269

Effect of temperature

The effect of temperature on the extraction efficiency of Eu is demonstrated as shown in in Figure 3. The reaction between the 0.2 M C921/toluene and Eu is a chemical exothermic reaction. From the data obtained, the extraction decreases with increasing of temperature. Thermodynamic parameter were calculated. The change of the extraction equilibrium constant (k_{ex}) with temperature is expressed by as follows:

$$\log K_{ex} = -\Delta H/2.303RT + \Delta S/2.303R$$

where, ΔH as (extraction enthalpy), T as (temperature), ΔS as (extraction entropy) and R as (gas constant).

A plot of log K_{ex} against 1/T gives a straight line of slope -ΔH/2.303R and the intercept of ΔS/2.303R (Figure 3). The values of ΔH and ΔS are listed in Table 5. The free energy of complexation (ΔG) could be calcualted by using the following equation:

$$\Delta G = \Delta H - T\ \Delta S$$

From the thermodynamic data, it could be concluded that the magnitude and sign of the enthalpy change (ΔH) associated with the extraction process. The entropy change of the extraction of Eu by C921 / toluene is more disorder. The negative values of ΔG indicated a spontaneous nature for the extraction of Eu(III).

IR investigation

To learn about the coordination of Eu(III) with C921 in the organic phase, the IR spectra of the extractant in kerosene before and after loading with Eu(III) were measured.The main feature of the IR spectrum of the extractant in toluene before loading by Eu(III) is characterize by a strong sharp band at 1158 cm^{-1} corresponding to the P=O bonds.

Comparing the spectrum with that of the extractant in toluene after loading with Eu(III) it was found that the intensity of the P=O band present at 1158 cm^{-1} decreased and convert from single band to doublet which indicates that cleavage may occur in the double bond giving P–O– bond. Also, appearance of a new two strong band at 1122 and 1250 cm^{-1} corresponding to P–O– bonds

Table 6. Stripping of the extracted Eu(III) from loaded 0.2M C921/ toluene at pH 2.0

Strip Solution(M)	[Stripper], (%)			
	0.05	0.1	1.0	2.0
	% Stripped			
HCl	12	20	65	70
HNO_3	19	26	80	77
H_2SO_4	8	16	52	65
Na_2CO_3	2	7	11	12
NaOH	3	6.5	12.8	15
EDTA	0.0	0.0	0.0	0.0
AIII	22	29	47	65

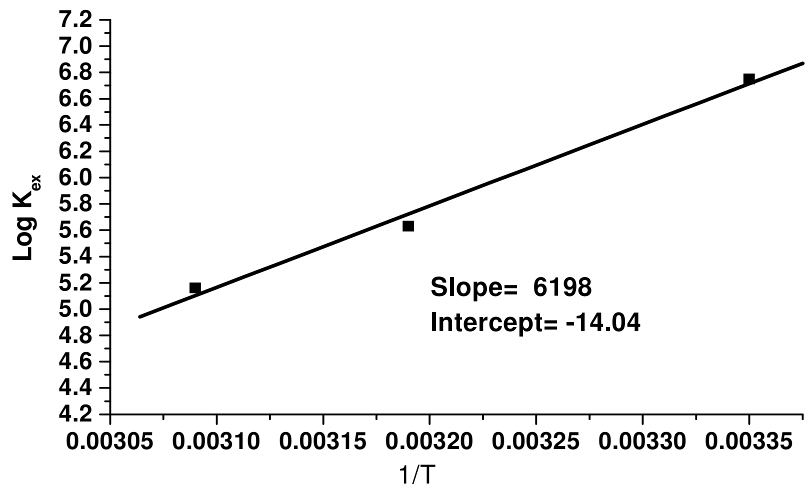

Figure 3. Effect of temperature on the extration of Eu concentration by C921/toluene.

bonds. Appearance of a new band at 650 cm^{-1} corresponding to the Eu–O bonds suggests that the extracted Eu(III) is coordinated to oxygen of the P–O– group, in addation, to appearance of the same band of nitrate NO_2 as strong band at 1357 in the IR spectrum of the extracted Eu species indicate that NO_2 take parts in mechanisum of extraction.

Stripping investigations

The stripping investigations were observed to select appropriate strip solutions for the Eu(III) extraction by 0.2 M C921 in toluene at phase ratio (org : aq = 1:1). HCl, HNO_3, H_2SO_4, NaOH, and Na_2CO_3 with EDTA and AIII were used as strippers respectively. The obtained results are represented in Table 6 as a relation between the type and concentration of the stripper and the corresponding stripping percent of Eu(III). From tables it is clear that mineral acid and AIII are good strippers of Eu(III) than bases.

The effect of number of stages on the stripping of Eu(III) from saturated organic solution , 57% Eu(III) stripped with 0.05 M AIII at pH 0.5 was investigated. It was found that Eu(III) was stripped quantitatively by 0.05% arsenazo(III) after three stages with A/O phase ratio 1:1, while at phase ratio 1:2(A/O) the number of stages decreased to one at temperature 25°C, Table 7. It was found that the pH have remarkable effect on the stripping of Eu from the C921, however % of Eu stripped by 0.05 M arsenazo(III), decresing from 57 to 2% when reasing the pH from 0.5 to 11 , Table 7.

Treatment of wastewater produced

The wastewater produced which have the dyes of Arsenazo(III) complexed with Eu was purified to clear solution before discharge to sewage for reduction of waste obtained and save the environmental from the toxic and hazrodous waste. Sorel's cement was used for this process.

In this study, the form of F3 was used for treatment of the dyes of AIII complexed with Eu from wastewater eff-

Table 7. Effect of pH on the stripping of Eu(III) by 0.05M AIII) from C921 at 25°C for 15 min shaking.

0.5M Strip Solution	**pH**			
	0.5	**1.0**	**5.0**	**11.0**
	% Stripped			
AIII	57	51	10	2

effluents due to its ability to adsorb a variety of inorganic and organic aggregates; (Sorel, 1867). Advantages of Sorel's cement used for this process including its ease of synthesis, low cost, good efficiency, and fast kinetics for removal of metals and dyes.

The color removal of the dyes of AIII complexed with Eu from wastewater was investigated via measurement the absorbance before and after shaking with sorel's cement using UV160A spectrophotometer. Chemical oxygen demand (COD) value before treatment with Sorel's cement is 523 mg O_2/l and reaches to 18 mg O_2/l after treatment while Eu decrease from 500 to 15 ppm indicating an efficiency of Sorel's cement for removal of dyes of AIII reaches to 97%. Its was found that 1.0 g of Sorel's cement is enough to treatment of one liter of the dye of arsenazo(III) complexed with Eu and becomes save to discharge to sewage.

Conclusion

The extraction of Eu(III) from nitrate medium by C921/toluene was investigated. From the date obtained, it was found that the extraction of Eu(III) increase with increasing of pH, however, the extraction precent increase from 28.5% at pH 0.5 to 98% at pH 3.0. Sorel's cement used as adsorbent material for treatment of wastewater produced due to its ease of synthesis, low cost, in addition, has a fast kinetics and good efficiency for removal of metals and dyes from wastewater before discharge to sewage.

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