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## RESEARCH ARTICLE

### Extraction and Separation of Nano-Sized Zirconia from Nitrate medium using Cyanex921

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#### Abstract

Zirconium nitrate solution obtained from alkali fusion of Egyptian Rosetta zircon concentrate was subjected to zirconium extraction using liquid-liquid extraction technique. Zirconium was effectively extracted from nitrate medium using 6% Cyanex921 dissolved in kerosene as diluent. The relevant factors controlling the extraction process of zirconium using Cyanex921 were studied. These factors include Cyanex921 concentration, A:O phase ratio, contact time and diluent type. More than 99.6% of Zr was extracted by 6% Cyanex921 at contact time 10 minutes, phase ratio O:A (v:v) 2:1 and the diluent was kerosene. Third phase formation was studied and dissolving it by using decanol as modifier was also done. Stripping of zirconium from loaded Cyanex921 has been carried out using 4M H<sub>2</sub>SO<sub>4</sub> as an effective stripping agent. The feasibility of using Cyanex921 for separation of zirconium was assisted by stripping studies. The loaded zirconium onto Cyanex921 has been stripped by stripping efficiency 94.18% when using 4M H<sub>2</sub>SO<sub>4</sub> as an efficient eluting agent at 10 minutes contact time and phase ratio O:A (v:v) 1:1.

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#### Introduction

Zirconium metal generally exist in nature in two minerals, zircon (Zirconium silicate-ZrSiO<sub>4</sub>) and baddilite (Zirconia-ZrO<sub>2</sub>) (Elvers et al., 1989). The mineral zircon is widely distributed in the earth's crust as a component of igneous, metamorphic and sedimentary rocks and found in the form of heavy residues of rocks or beach sand. In fact, the beach sand zircon is usually associated with ilmenite, rutile, magnetite and monazite (Abdel-Rahim, 2005). The major commercial sources of zircon are beach deposits which recovered from the processing of heavy-mineral bearing sand, these deposits are mainly found in Australia, Brazil, South Africa, Ceylon, India, Madagascar, USA and Egypt (Saberyan et al. 2010). Furthermore, Australia is the major world producer and exporter of zircon sand (Hoddinott, 1995). The typical composition of zircon beach sand is in Wt%: ZrO<sub>2</sub>, SiO<sub>2</sub>, HfO<sub>2</sub>, FeO, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub> (62.8, 31.7, 1.2, 0.3, 0.25, 0.2 and 0.12% respectively) (MacDonald et al., 1982). On the other hand, the less abundant mineral like baddilite contains 73% of ZrO<sub>2</sub> and 0.4-1.7% of HfO<sub>2</sub> (Suriyachat, 1992).

Zirconium is used in the nuclear industry as a structural material for nuclear reactors due to its excellent corrosion resistance and low neutron capture cross section, it is also used as cladding material for fuel rods in nuclear reactors. Furthermore zirconium has many industrial applications such as the ceramic industry, enamels, refractory materials, glazes, foundry mold and abrasive grits dye pigments and catalyst in organic reactions (Rajmane et al., 2006). Due to strategic importance of zirconium in various fields, it is important to select a chemical method for separation of Zirconium from its concentrates. For extraction of zirconium, numerous methods have been employed include: fractionated crystallization, precipitation, reduction, sublimation or distillation, absorption chromatography and ion exchangers. The distribution of solute between two immiscible solvents (liquid-liquid extraction) has been regarded as one of the most promising operation to separate the metallic elements due to its great technical ease of carrying out the continuous mode (Ritcey, 1979). Many studies were made for the extraction of zirconium from nitrate

medium using organophosphorus compounds includes TBP (Aliakbari et al., 2014), TOPO (Banda et al., 2013), TRPO (trialkylphosphine oxide) (Xu et al., 2012), Cyanex301 & 302 (Saberyan et al., 2008), Cyanex272 (Taghizadeh et al., 2009), Cyanex923 (Taghizadeh et al., 2011) and D2EHPA (Taghizadeh et al., 2009) that shows a great results for the extraction of zirconium.

In this study, solvent extraction technique was used for the extraction of zirconium from as-prepared Zirconium nitrate solution resulted by alkali fusion of Egyptian Rosetta zircon. The extraction process was done by using Cyanex921 and Factors affecting on the extraction process were evaluated. These factors include O: A phase ratio (v:v), Cyanex921 concentration, contact time and diluent type. In addition, the third phase formation during the extraction process was also studied. The factors affecting on stripping of zirconium from loaded Cyanex921 like A:O phase ratio, contact time, type of stripping agent and stripping agent concentration, were studied to determine the optimum conditions for extraction and separation of zirconium using Cyanex921.

### Materials and methods:

All chemicals used in the experiments were purchased and used as received without further purification. Materials used in this work alizarin red S, Zirconyl chloride octahydrate ( $\text{Cl}_2\text{OZr}\cdot 8\text{H}_2\text{O}$ , 98%), ethanol, butanol, pentanol, octanol, decanol, Hydrochloric acid, sodium hydroxide and nitric acid, Cyanex921 were from Sigma–Aldrich. Egyptian Rosetta zircon mineral (97%) with chemical composition that  $\text{ZrO}_2+\text{HfO}_2$  (66.42%),  $\text{SiO}_2$  (32.23%),  $\text{Fe}_2\text{O}_3$  (0.14%),  $\text{TiO}_2$  (0.22),  $\text{ThO}_2$  (0.02%),  $\text{U}_3\text{O}_8$  (0.04%),  $\text{MgO}$  (0.02%),  $\text{CaO}$  (0.01%), RE Oxides (0.07%),  $\text{Al}_2\text{O}_3$  (0.06%),  $\text{K}_2\text{O}$  (<0.01%),  $\text{Na}_2\text{O}$  (<0.01%) and  $\text{P}_2\text{O}_5$  (0.13%).

### Preparation of zirconium nitrate solution

A sample of 250g of Egyptian Rosetta zircon was mixed with 312g of sodium hydroxide pellets and charged to a 316-L stainless steel crucible. The crucible was then fed to the electric furnace where the fusion reaction took place. The reaction temperature was adjusted at  $650\text{ }^\circ\text{C}$  for 2h. The fusion product was mixed with (4 times of its weight) distilled water at  $60\text{ }^\circ\text{C}$  and stirred for 2 hrs to remove sodium silicate solution. The residue ( $\text{Na}_2\text{ZrO}_3\cdot\text{H}_2\text{SiO}_3$ ) was dissolved in concentrated HCl at  $90\text{ }^\circ\text{C}$  with stirring for 2 hrs then immediately filtrated giving residue which mainly composed of unreacted zircon,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ThO}_2$  and  $\text{H}_2\text{SiO}_3$ . The filtrate was crystallized at low temperature giving zirconyl chloride hydrate crystals which then filtrated and dissolved in 1M hydrochloric acid and pH was adjusted to 9 using ammonia solution to precipitate  $\text{Zr}(\text{OH})_4$ . The obtained zirconium hydroxide was dissolved in certain volume of nitric acid to form of zirconium nitrate solution.

### Extraction of zirconium using Cyanex921

A mixture of 10 ml of as-prepared  $\text{Zr}(\text{NO}_3)_4$  solution ( $4.11\text{ g/l Zr}^{+4}$ ) and volumes of diluted Cyanex921 (keeping the required phase ratio) was stirred vigorously in 50 ml beaker using magnetic stirrer at room temperature for certain contact time. The mixture then transferred to a separating funnel and allowed to be settled down for 20 minutes. The aqueous and organic phases were separated and the aqueous samples were analyzed. The factors which control the extraction process were studied in details like; phase ratio (O: A) v:v, solvent concentration, contact time and the effect of diluents used. In addition the third phase formation during the extraction process was also studied and the usage of alcohols for solving this problem was done by using different types of alcohols.

### Stripping of zirconium from loaded Cyanex921

All the experiments were performed on the pregnant organic solution Cyanex921, a mixture of 10 ml of the loaded organic ( $3.35\text{ g/l of Zr}^{+4}$ ) and certain volume of stripping agent (keeping the required phase ratio) was stirred vigorously in 50 ml beaker using magnetic stirrer and at room temperature for certain contact time. The mixture then transferred to a separating funnel and allowed to be settled down for 20 minutes. The aqueous and organic phases were separated and the aqueous samples were analyzed. The factors controlling the stripping process were studied as, the effect of the type of stripping agent, the concentration of the stripping agent, the contact time and the effect of phase ratio (A:O) v:v.

### Chemical analysis of Zirconium

Zirconium was analyzed in all aqueous phases using alizarin red S method (Furman 1962; Elshehy 2011). Absorbance of the formed zirconium alizarin complex was measured at 520nm against proper standard solutions using a Lambda 3 UV/VIS spectrophotometer (PerkinElmer, USA).

### Characterization of ZrO<sub>2</sub> product

For characterization of the produced ZrO<sub>2</sub> was done using number of techniques. UV-visible absorbance spectra were recorded using a HP-8453 spectrophotometer. The morphology was studied using transmission electron microscopy (TEM). TEM images were obtained using a JEOL JEM-1230 TEM operating at 120 kV. Samples for TEM imaging were prepared by suspending a Formar carbon-coated, 300 mesh copper grid (Ted Pella) in ethanol-diluted samples for approximately 2 minutes and X-ray diffraction (XRD) patterns of the product was collected at room temperature using an X'Pert Philips Materials Research Diffractometer with CuK<sub>α1</sub> radiation. Also Inductively Coupled Plasma –Mass Spectrometry Model Scan-16-ICP-MS. Thermo, USA was used to determine impurities elements in the produced ZrO<sub>2</sub>.

## Results and discussion:

### Effect of organic solvent (O) : Aqueous solution (A) ratio

The effect of organic solvent (O) to aqueous solution ratio was evaluated at different O: A ratio (from 3:1 to 1:5) using 2% Cyanex921 in kerosene and contact time 5 minutes. Figure (1) shows that the extraction efficiency of zirconium slowly increased from O:A 1:5 till 1:2 (E% increased from 6.9 to 17.2%) but after 1:2 the extraction efficiency highly increased from O:A 1:2 till 2:1 (E% increased from 17.2 to 58.66%), then slowly increased after 2:1, so that the best phase ratio for the extraction of zirconium from nitric acid medium using Cyanex921 was found to be 2:1 (O: A) (v:v).

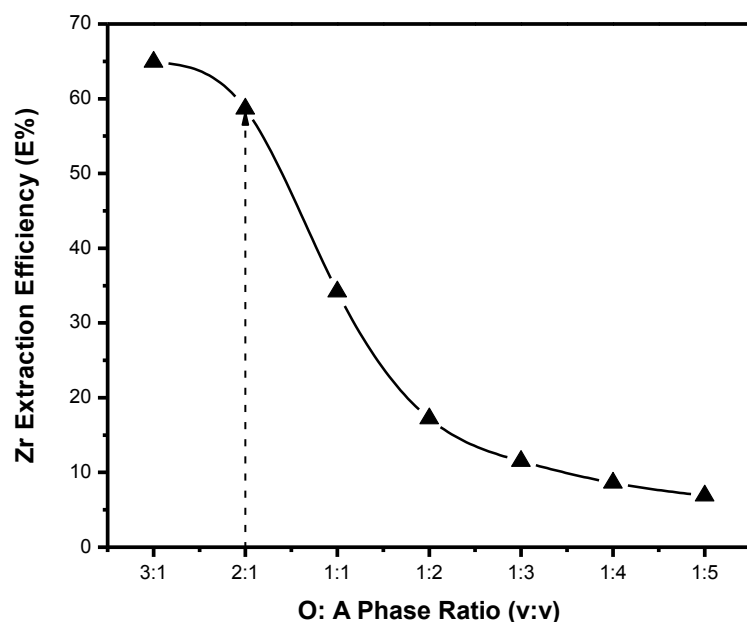


Fig. 1. Effect of O: A phase ratio on the extraction of zirconium from nitrate medium using Cyanex921.

### Effect of organic solvent concentration

Experiments have been done to study the effect of organic solvent concentration on the extraction of zirconium using Cyanex921 organic solvents while the other variables were kept constant thus O:A phase ration is 2:1, diluent is kerosene and contact time 5 minutes. The obtained results (Table 1 and Figure 2) show that the extraction efficiency of zirconium was highly increased with increasing the concentration of Cyanex921 till concentration 6% (E% increased from 58.66 to 96.46%). But after the concentration 6% the extraction efficiency became stable, so that the best organic solvent concentration is 6%.

### Effect of contact time

The contact time needed for the extraction of zirconium from nitric acid medium was determined by making experiments at contact time range from 1 to 30 minutes using 6% Cyanex921 in kerosene and phase ration (O:A) 2:1. Figure (3) and Table (2) shows that The extraction efficiency of zirconium was increased with increasing contact time from 1 minute to 10 minutes (E% increased from 94.61 to 99.6%), but after 10 minutes the extraction

efficiency became constant. Finally the best contact time for the extraction of zirconium from nitrate medium is 10 minutes.

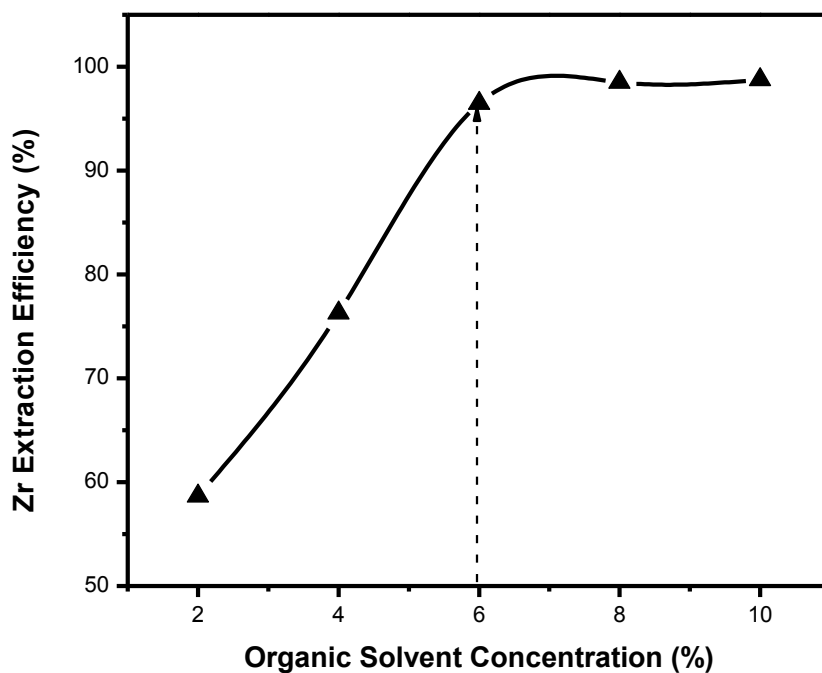
**Table 1.** Effect of organic solvent concentration on the extraction of zirconium using Cyanex921

Cyanex921 conc., (%)	Zr(A), g/l	Zr(O), g/l	D(Zr)	Extraction efficiency, %
2	1.70	1.21	0.71	58.66
4	0.97	1.57	1.61	76.27
6	0.14	1.98	14.14	96.46
8	0.060	2.02	33.66	98.5
10	0.051	2.03	39.80	98.75

Zr(A), Zirconium concentration in aqueous phase

Zr(O), Zirconium concentration in organic phase (Cyanex921)

D(Zr), Distribution coefficient for zirconium ( $D(Zr) = Zr(A)/Zr(O)$ )



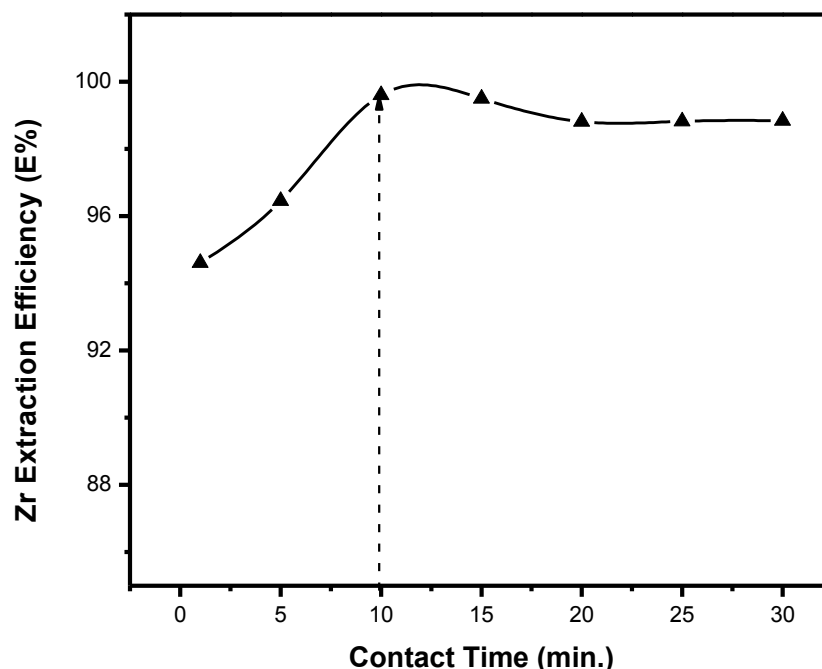
**Fig. 2.** Effect of Cyanex921 concentration on the extraction of zirconium from nitrate medium.

#### Effect of diluent type

The effect of diluent type was studied by using four types of diluents (Benzene, Toluene, Carbon tetrachloride and kerosene) while the other variables were kept constant like 6% Cyanex921, O:A ratio 2:1 and 10 minutes contact time. Figure (4) shows that zirconium extraction efficiency depends on the diluent type and the best diluent for Cyanex921 and gave the highest extraction efficiency was kerosene (E% is 99.46%).

**Table 2.** Effect of contact time on the extraction of zirconium using Cyanex921.

Contact Time, (min.)	Zr(A), g/l	Zr(O), g/l	D(Zr)	Extraction efficiency, %
1	0.22	1.94	8.8	94.61
5	0.14	1.98	14.14	96.46
10	0.015	2.05	136.6	99.6
15	0.020	2.04	102	99.5
20	0.048	2.03	42.29	98.81
25	0.22	1.94	8.81	98.82
30	0.14	1.98	14.14	98.84

**Fig. 3.** Effect of contact time on the extraction of zirconium using Cyanex921 from nitrate medium.**Effect of using different modifiers for dissolving the third layer**

The third phase formation is troublesome to the both extraction and stripping processes because it change the mass transfer and phase separation, and this decrease the extraction efficiency. Extensive studies have been conducted on the third phase formation in various extraction systems to understand the kinetics of third phase formation and they found that low temperature and high concentration of nitric acid greatly facilitate the formation of the third phase(Xu and Wang, 2012). In addition the metal concentration in the aqueous phase and the type of organic solvent also has great effect on the third phase formation(Liao 2002; Liao 2002; Jia 2003; Kedari 2005).

Series of experiments were done using various types of alcohols like Ethanol, Butanol, Pentanol, Octanol and Decanol. The obtained results show that Ethanol, Butanol and Pentanol react with nitric acid in aqueous phase with the evolution of nitrogen oxides as reddish brown color. On using Octanol and Decanol third phase dissolved and the ratio of Octanol to Cyanex921 (v:v) was 2:10 and thus of decanol to Cyanex921 was 1:10, so that the best modifier used in this work was Decanol because less amount of Decanol will be enough to dissolve third layer.

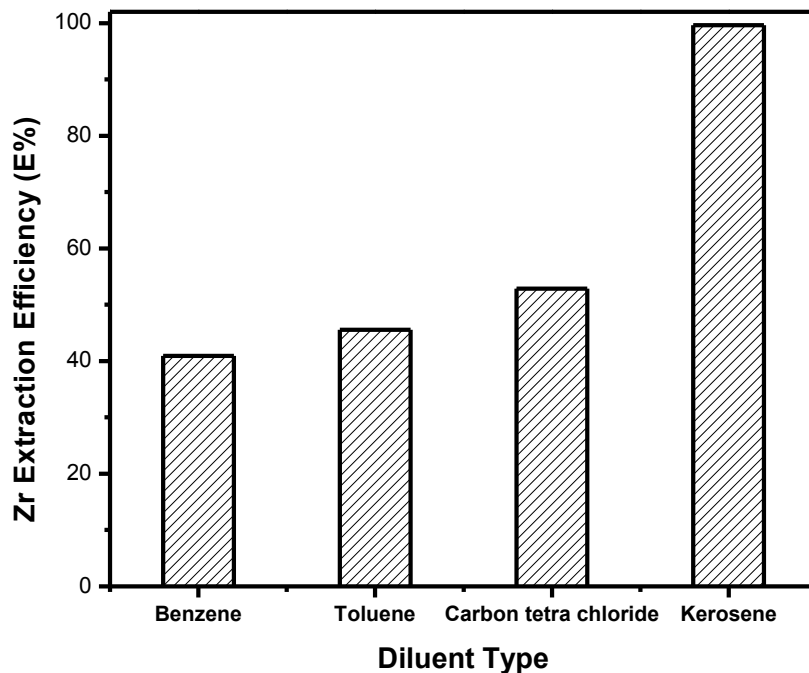


Fig. 4. Effect of diluent type on the extraction of zirconium using Cyanex921 from nitrate medium.

#### Distribution isotherm equilibrium curve

Distribution isotherm is a plot of the equilibrium concentration of the extracted species of zirconium in the extracted phase against its concentration in the raffinate layer. Distribution isotherm can be prepared for either the extraction process (and in this case it is called extraction isotherm) or the stripping process (which called stripping isotherm). Data for the extraction isotherm could be easily obtained from either “phase ratio variation” single contact of a fixed volume of aqueous feed (input leach liquor) with different volumes of organic solvent or else by “saturation process”. Repeated contact of one and the same aliquot of the organic solvent with several aliquots of fresh input leach liquor. McCabe-Thiele diagram is a composite plot of the distribution isotherm and the operating line. The operating line could be established by only one point, which corresponds to the final raffinate composition and the ratio of the aqueous to organic phases that determines the slope of the line, as it is a straight line. The diagram can be used to evaluate the approximate number of theoretical stages required for the extraction process.

In this study, different volumes of the organic solvents (6 % Cyanex921 in kerosene) were contacted with different volumes of the aqueous feed (nitrate solution) at the optimum conditions previously determined as, contact time 10 minutes, O: A ratio 2:1 and the diluent is kerosene, the aqueous and organic phases were separated and then analyzed for amount of zirconium extracted. The equilibrium line is then established by plotting the concentration of zirconium in the organic phase versus its concentration in the aqueous phase as in Table (3) and as represented in Figure (5) (Robbins, 1981). The next step is construction of McCabe-Thiele diagram. It is clear that two theoretical stages are quite suitable for zirconium extraction using Cyanex921.

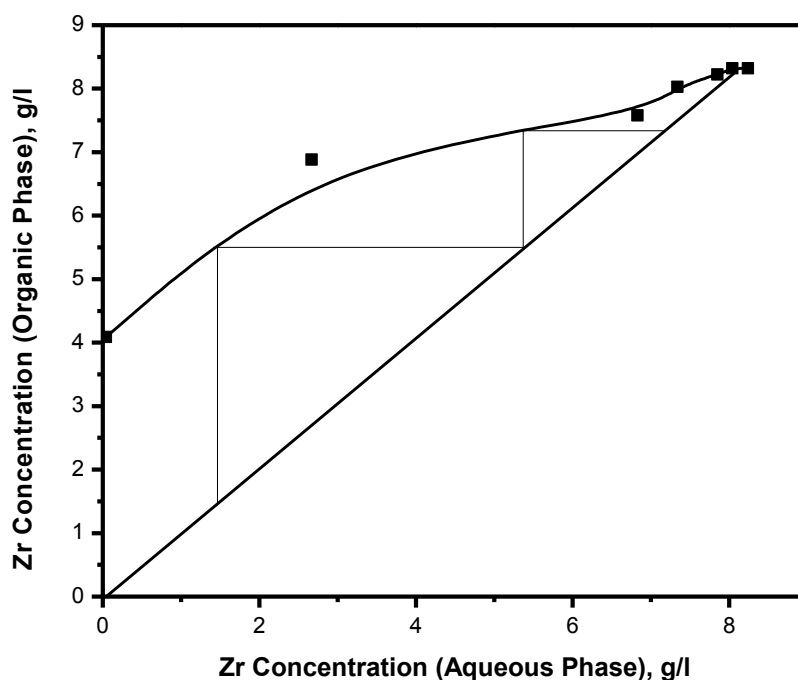
#### Stripping of the loaded zirconium Cyanex921 in nitrate acid medium

Experiment of extraction using the optimum conditions was done for studying the factors affecting on the stripping efficiency of zirconium from loaded Cyanex921. The amount of loaded zirconium on Cyanex921 after the extraction process was found to be 3.35 g/l with extraction efficiency 97.56%.

**Table 3.** The obtained data for construction of McCabe-Thiele diagram for Zirconium extraction using Cyanex921.

No	Zr(A), g/l	Zr(O), g/l	Zr(O) total, g/l
1	0.042	4.09	4.09
2	2.67	2.78	6.88
3	6.83	0.70	7.58
4	7.34	0.44	8.03
5	7.85	0.19	8.22
6	8.04	0.09	8.32
7	8.24	-	8.32

*Zr(O) total, Total zirconium loaded on Cyanex 921*

**Fig. 5.** McCabe-Thiele diagram for the extraction of zirconium using Cyanex921

#### Effect of stripping agent

The effect of stripping agent was studied by using different stripping agents ( $\text{H}_2\text{O}$ , NaCl 10%, HCl 1M,  $\text{H}_2\text{SO}_4$  1M and  $\text{HNO}_3$  1M) and the other factors kept constant thus A:O phase ratio 1:1 and contact time 5 minutes. Figure(6) shows that the stripping efficiency of zirconium from loaded Cyanex921 greatly depends on the type of stripping agent thus the best stripping agent was found to be 1M  $\text{H}_2\text{SO}_4$  (S% was 41.74%) and stripping factor ( $S_{\text{Zr}}$ ) was 0.72 this mean great distribution of zirconium from loaded Cyanex921 to 1M  $\text{H}_2\text{SO}_4$ .

#### Effect of acid molarity

The effect acid molarity was studied using different molar concentration of  $\text{H}_2\text{SO}_4$  at contact time 5 minutes and A:O phase ratio 1:1. Figure (7) shows that the stripping efficiency increases with increasing the molarity of acid

from 0.5 to 4M (S% increased from 20.54 to 72.1%) and then decreased, so that 4M  $\text{H}_2\text{SO}_4$  is sufficient for stripping of zirconium from loaded Cyanex921.

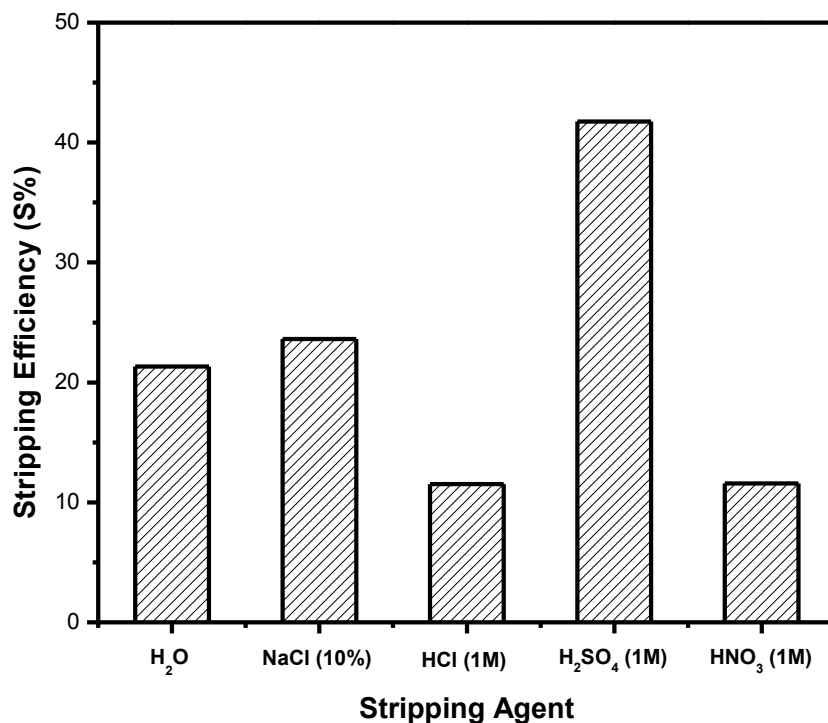


Fig. 6. Effect of stripping agent on the stripping of zirconium from loaded Cyanex921.

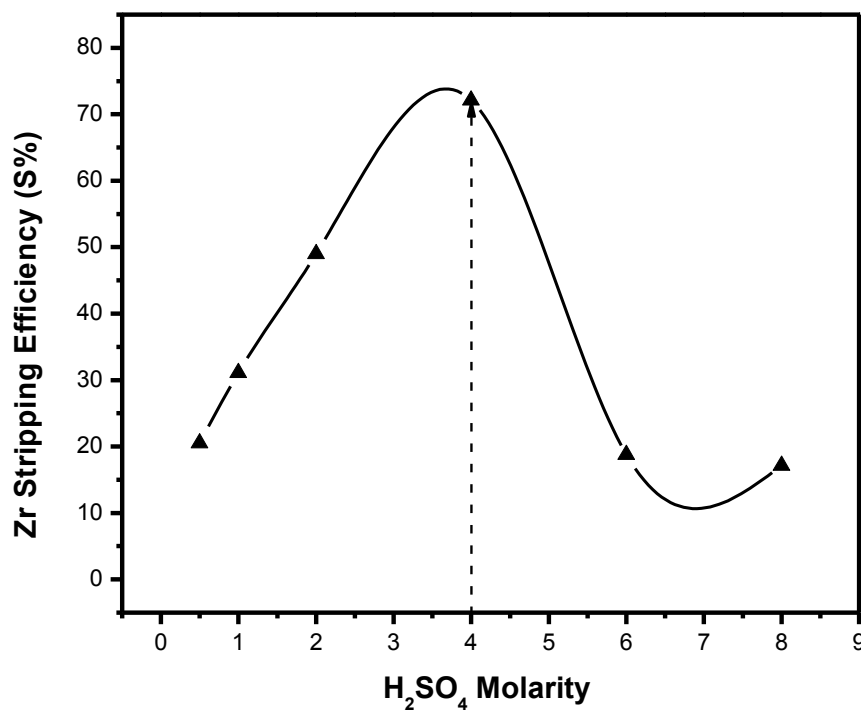


Fig. 7. Effect of stripping agent concentration on the stripping of zirconium from loaded Cyanex921.

### Effect of A: O phase ratio

The effect of A: O (v:v) phase ratio was studied at range 5:1 to 1:3, the contact time was 5 minutes and 4M H<sub>2</sub>SO<sub>4</sub>. Figure (8) shows that The stripping efficiency of zirconium from loaded Cyanex921 was slowly increased from phase ratio A:O 5:1 till reach 3:1 (S% increased from 23.46 to 31.13%), and after 3:1 the stripping efficiency highly increased till 1:1 (S% increased from 31.13 to 72.09%), but after 1:1 the stripping efficiency decreased, thus the best phase ratio is 1:1

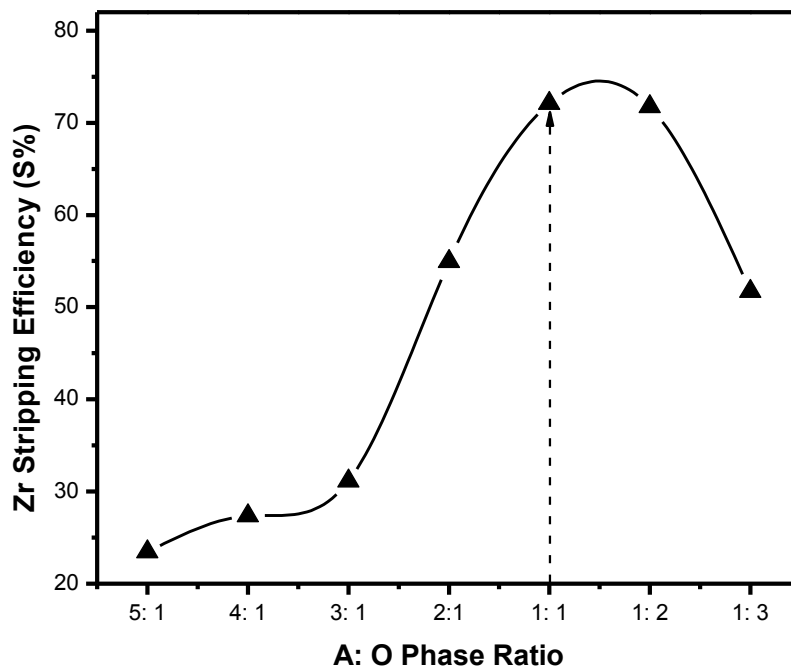


Fig. 8. Effect of A:O phase ratio on the stripping of zirconium from loaded Cyanex921.

### Effect of contact time

The effect of contact time on the stripping of zirconium from loaded Cyanex921 in nitrate medium was studied at different contact time from 5 to 30 minutes while other factors kept constant thus A:O phase ratio 1:1 and 4M H<sub>2</sub>SO<sub>4</sub> stripping agent. The stripping efficiency was increased from contact time 5 minutes to 10 minutes (S% increased from 72.1 to 94.18%) then it decreased (Figure 9). It is clear that the best contact time for the stripping of zirconium from loaded Cyanex921 is 10 minutes.

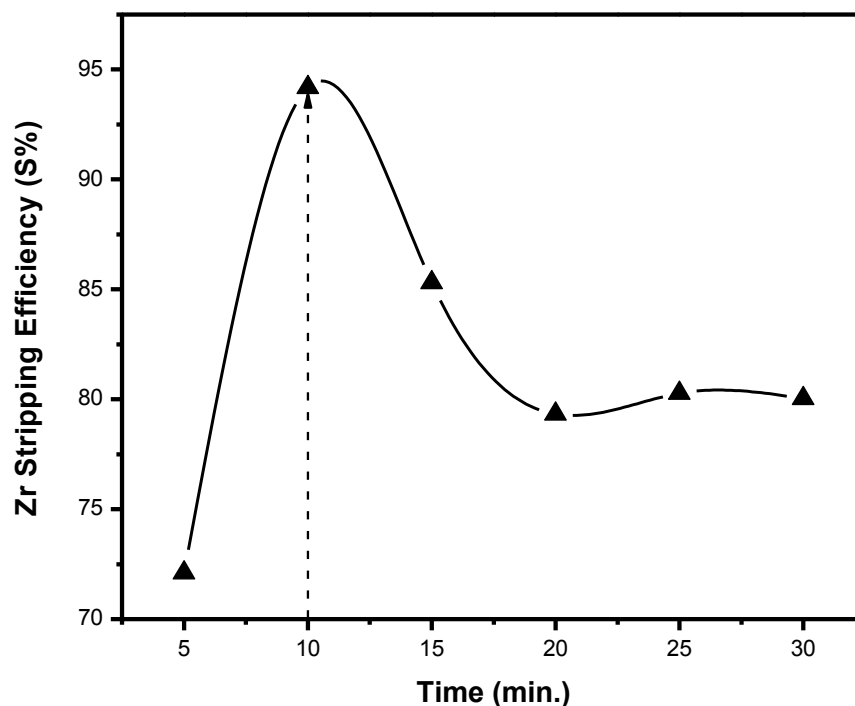
### Distribution isotherm equilibrium curve

Fixed volume of the aqueous phase (4 M H<sub>2</sub>SO<sub>4</sub>) were contacted for 10 minutes with different volumes of the loaded Cyanex921 until equilibrium is obtained keeping fixed phase ratio (A:O) 1:1. A measured portion of the aqueous phase was taken for Zirconium analysis. The results shown in Table (4) and represented in Figure(10). By construction of McCabe-Thiele diagram for stripping of zirconium from the loaded Cyanex921, it is clear that three stages are sufficient for the stripping of zirconium from loaded Cyanex921.

After stripping process, the stripping agent loaded with zirconium was adjusted by ammonia solution to pH 9 to precipitate zirconium as Zr(OH)<sub>4</sub> which filtrated and dried at 60 °C overnight, then burned at 550 °C for 3 hours to form ZrO<sub>2</sub> which used for complete characterization.

### Characterization of ZrO<sub>2</sub> product

As shown in Figure (11-a) The X-ray diffractograms for zirconia sample shows the presence of tetragonal phase (t) of zirconium oxide as the major phase (JCPDS-17-923) with four characteristic peaks of the (101, 110, 112 and 211) facets at 2θ=30.3835.436, 50.95 and 60.36 respectively. In addition Figure (11-b) shows that the particle size of the formed zirconia from solvent extraction using Cyanex921 was ranged between 15 – 20 nm this because Cyanex921 in this experiments acts as extractor for zirconium and surfactant for the preparation of zirconium nanoparticles.



**Fig. 9.** Effect of contact time on the stripping of zirconium from loaded Cyanex921.

#### Analysis of $ZrO_2$ using ICP (Inductively Coupled Plasma)

Zirconia sample was analyzed for impurities using ICP and the results show the formation of pure zirconia using Cyanex921, Thus the concentration of  $HfO_2$  after solvent extraction became 105ppm,  $SiO_2$  was found to be 99ppm,  $Al_2O_3$  76ppm,  $TiO_2$  48ppm,  $Fe_2O_3$  880ppm,  $MgO$  23ppm,  $CaO$  23ppm and  $P_2O_5$  87ppm. It is clear that all the procedures used in preparation of zirconium nitrate solution then solvent extraction Cyanex921 gave zirconium oxide approximately free of all other metals like  $HfO_2$ ,  $SiO_2$ ,  $Al_2O_3$ ,  $TiO_2$ ,  $Fe_2O_3$ ,  $MgO$ ,  $CaO$  and  $P_2O_5$ .

**Table 4.** The obtained data for construction of McCabe-Thiele diagram for stripping of zirconium from loaded Cyanex921.

No	Zr(A) total, g/l	Zr(A), g/l	Zr(O), g/l
1	0.31	3.06	0.29
2	0.58	2.76	0.58
3	0.86	2.79	0.56
4	0.99	1.35	1.99
5	1.08	0.83	2.52
6	1.11	0.30	3.04
7	1.12	0.13	3.22
8	1.13	0.07	3.27
9	1.13	0.04	3.31
10	1.13	0	3.35

*Zr(A) total, Total zirconium stripped in aqueous phase.*

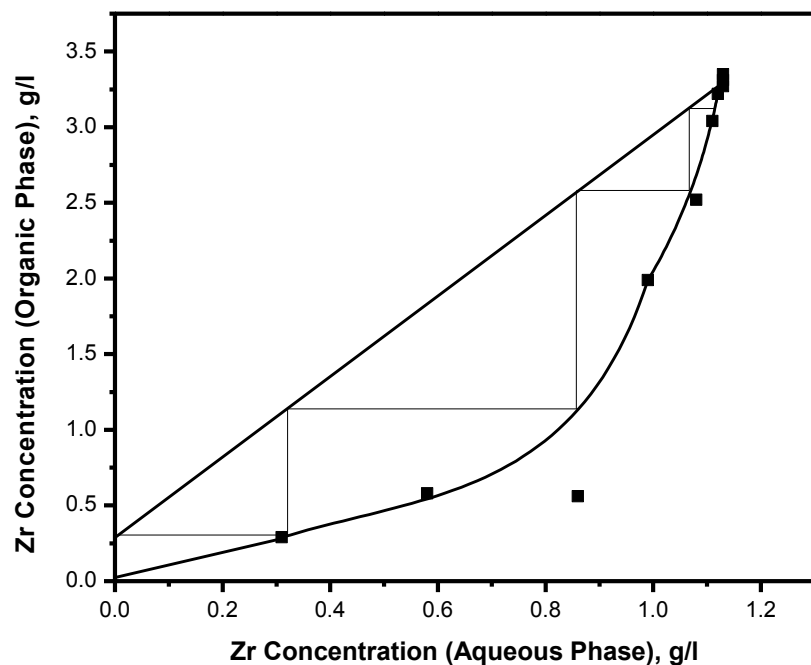


Fig. 10. McCabe-Thiele diagram for the stripping of zirconium from loaded Cyanex921.

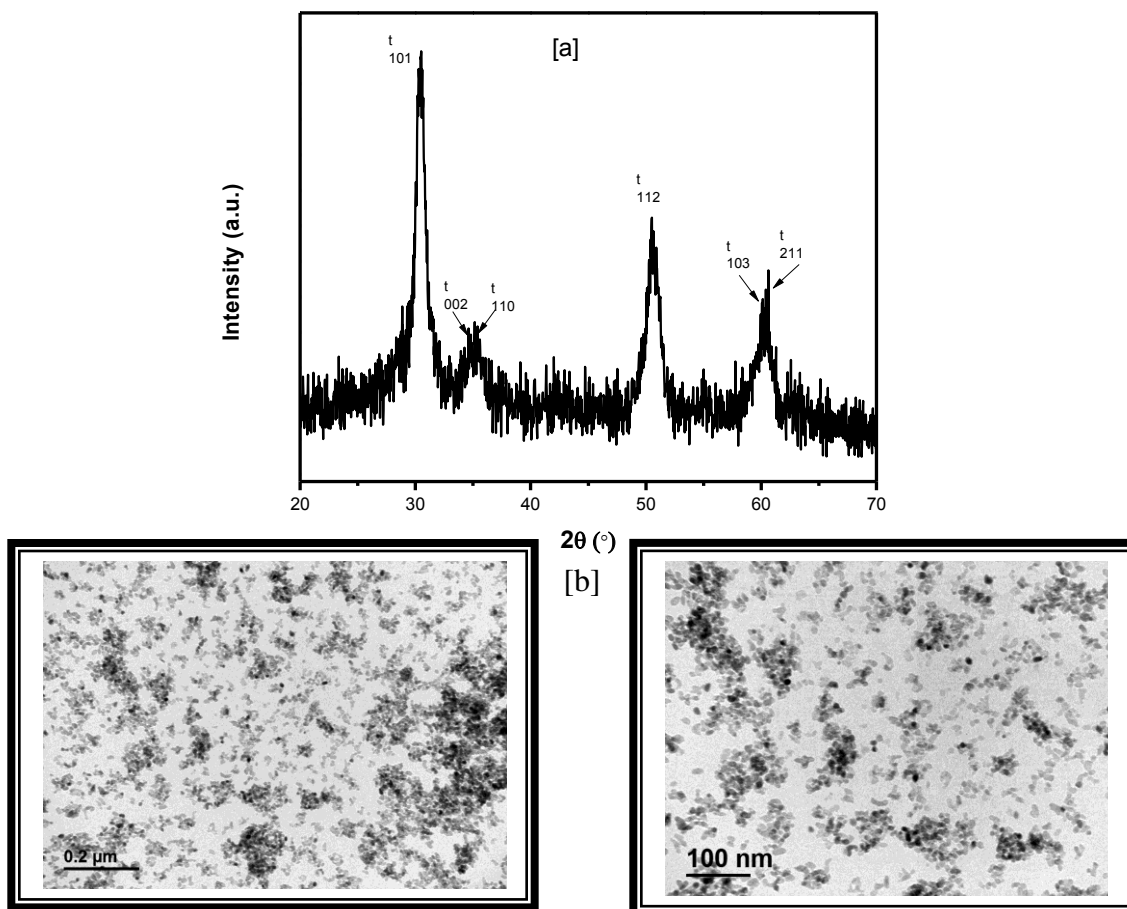


Fig. 11. Characterization of the as-prepared ZrO<sub>2</sub> using (a) XRD, (b) TEM.

## Conclusions:

The extraction and separation of zirconium using Cyanex921 was studied with respect to various factors. These factors were the effect of Cyanex921 concentration, contact time, diluents used, phase ratio (O:A) v:v and HNO<sub>3</sub> concentration. It was found that the optimum conditions for extraction of zirconium from the nitric medium were 6% Cyanex921 in kerosene and 10 minutes contact time at phase ratio (2:1). The obtained results also show that the extraction efficiency for Zr<sup>+4</sup> at these optimum conditions was 99.6%. Additionally Decanol was chosen to be the best modifier for solving third phase problem.

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