



Potentiality of some Synthesized Benzimidazolo-quinazolinone and Pyrimido-benzimidazole Ligands for Selective Extraction of the Rare Earth Elements

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Abstract

Three synthesized multidentate organic solvents; namely 1,2-dihydro-3H-benzimidazolo [1,2-a] quinazolin - 4 - one (4a), 1,2 - dihydro - 2, 2 dimethyl benzimidazolo [1,2-a] quinazolin - 4 (3H) - one (4b) and 3 - (cyclohexane - 1 - on - 2yl) pyrimido [1,2-a] benzimidazole (4c) were examined for their extractive potentiality of the rare earth elements from Kadabora sulfate leach liquor. The influential parameters controlling the extraction process including the extractant type, the sulfuric acid concentration, the contact time, the organic/aqueous ratio and the solvents concentration were determined. It was also found that the extractability of the synthesized multidentate organic compounds (4a, 4b and 4c) for rare earths decreases in the order $4a > 4b > 4c$. The effects of the stripping agent type, concentration, contact time and O/A ratio on the stripping efficiency of the rare earth elements from the loaded extractants were also tested. A rare earth cake was finally obtained from the strip solution by the addition of oxalic acid as a precipitating agent.

Keywords: Rare earths, extraction, benzimidazoloquinazolinone, pyrimidobenzimidazole, stripping, precipitation.

Introduction

The rare earth elements are attracting increased attention because they have been widely utilized in metallurgy, glass, ceramics, as well as the recent advances in superconductivity, laser applications, magnetostrictive materials and hydrogen storage materials^{1,2}. For instance, Y and Sm have an interesting application in the field of nuclear technology due to their low cross-section for neutron capture and the high temperature stability of their oxides. Cerium oxide is uniquely suited as a polishing agent for glass. Permanent magnet technology has indeed been revolutionized by alloys containing Nd, Sm, Gd, Dy, or Pr^{3,4}.

Separation of the rare-earth elements by solvent extraction has actually been widely employed in various fields from analytical chemistry to hydrometallurgy which is the technology of extracting metals from ores by aqueous methods⁵. Accordingly, the separation of rare-earth elements by solvent extraction is an interesting subject to attract a number of researchers. This is because of its simplicity, rapid rate as well as convenience to both tracer and macro amounts of metal ions.

Preparation of proper macrohetero cyclic compounds would thus act as extractants for recovering valuable metals from the leach liquors of their corresponding economic minerals. Quinazolines are indeed a big family of heterocyclic compounds, which have shown broad variety of biological activity profiles^{6,7}, e.g. analgesic, narcotic, diuretic, antihypertensive, antimalarial, sedative, hypoglycaemic, antibiotic, antitumoral and many others. Quinazoline and its related skeletons are presented as an important class of

heterocycle scaffolds occurring in a large number of bioactive molecules for a variety of biological targets⁸. Benzimidazoles are very useful intermediates/subunits for the development of molecules of pharmaceutical or biological interest. Substituted benzimidazole derivatives have found applications in diverse therapeutic areas including antiulcers, antihypertensives, antivirals, antifungals, anticancers, and antihistaminics⁹. 3,4,4a-5-tetrahydro - 3,3,4a- trimethyl 1 - 7 - (substituted) - pyrimido (1,6-a) benzimidazole-1-thiol (la-c) has been explored as a new reagent for the separation, extraction and determination of palladium. Isopropylphosphonic acid 1-hexyl-4-ethyloctyl ester is a newly developed extractant, with a pKa value of 5.49, which has been used to extract transition metals and rare earths¹⁰.

The structure of the organic extractants plays actually an important role in determining the effectiveness of the extraction. In this regard, Preston and Du Preez¹¹ have described the effect of some bifunctional ligands containing S=O, C=O or P=O groups on the extraction of the trivalent rare earths from chloride media by solutions of some alkylsalicylic acids. As a matter of fact, synergistic extraction systems show promise in the field of solvent extraction¹².

Several studies were done to utilize the triazolo-pyrimidine heterocycles as water immiscible solvents suitable for bridging metal atoms to form dinuclear or polynuclear species^{13, 14}. The heterocyclic nitrogen compounds such as ($\alpha - \omega$ bis 5(hydroxy pyrazol - 4 - oyl alkanes) were proven to selectively extract the rare earth elements Lu(III), Eu(III) and La(III) from 0.1 M nitrate media¹⁵.

In the present work, the corresponding synthesized ligands were used as possible organic extractants to detect their potentiality in extracting the rare earths. For this purpose, a representative sulfate leach liquor was prepared from the multiple oxide mineralization (mainly REE, U, Ta, Nb) in Kadabora Batholith in the Central Eastern Desert of Egypt. This liquor was then subjected to several extraction experiments to test the efficiency of the prepared synthesized organic solvents¹⁶ under several conditions.

Material and Methods

Preparation of the Extractants: Three multidentate organic compounds that would be suitable to act as organic extractants for the rare earth elements were prepared. However, the three compounds 2 - ((dimethyl amino) methylene) cyclohexane - 1,3 - dione (1a), 2 - ((dimethyl amino) methylene) 5,5dimethyl cyclohexane-1,3-dione (1b) and (E)-2-(3-dimethyl amino) acryloyl cyclohexanone (1c) were selected as the starting materials. These enamindiones (1a, 1b and 1c) were reacted with 2-amino-benzimidazole (2) in refluxing pyridine to afford, in each case, only one isolable product (as examined by TLC) identified as 1,2-dihydro-3H-benzimidazolo [1,2-a] quinazolin - 4 - one (4a), 1,2 - dihydro - 2, 2 dimethyl benzimidazolo [1,2-a]

quinazolin - 4 (3H) - one (4b) and 3 -(cyclohexane-1-on-2yl)pyrimido[1,2-a]benzimidazole(4c).

To a mixture of (1a), (1b) and (1c) (10 mmol) and the appropriate heterocyclic amine (2-aminobenzimidazole) (10mmol) in pyridine (25 ml) was refluxed for 12 h, then left to cool. The solvent was evaporated in *vacuo* and the residual solid was taken in ethanol then collected by filtration, washed with water, dried and finally recrystallized from suitable solvent to afford the corresponding products.

The formation of these compounds (4a, 4b and 4c) are assumed to take place via an initial Michael - type addition of the imino function (endocyclic nitrogen)¹⁷ in compound 2 to the double bond in the enamindiones 1a, 1b and enamindione 1c to give the acyclic non - isolable intermediates 3a, 3b and 3c. The non - isolable intermediates undergo intramolecular cyclization and subsequent aromatization via the loss of dimethylamine and water molecular to afford the final isolable products 4a, 4b and 4c as represented in the following Schemes (I, II and III). The spectral data of the synthesized compounds are illustrated in table-1.

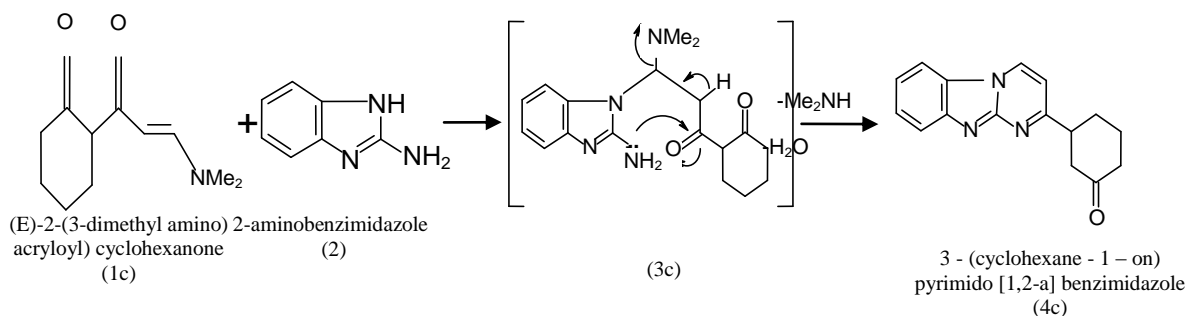
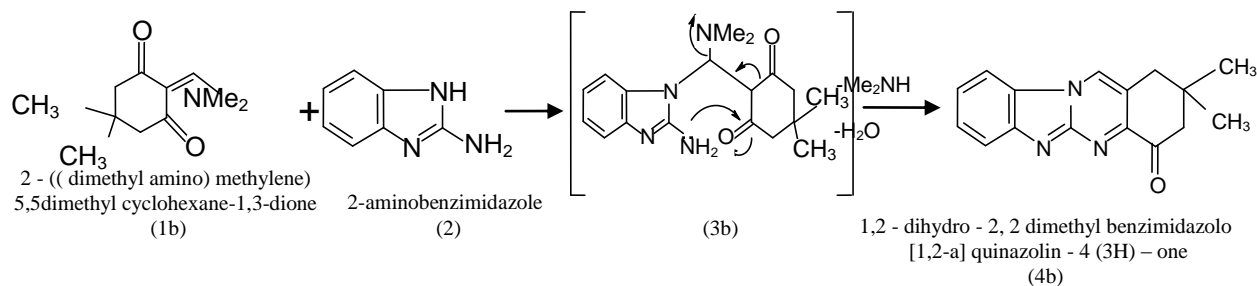
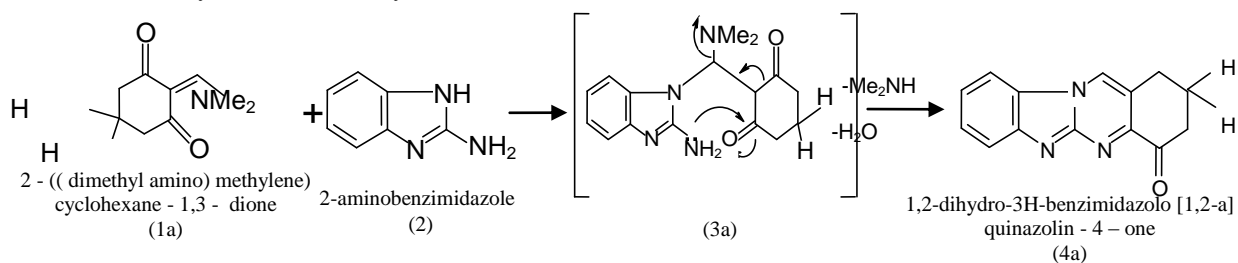


Table -1
Spectral data of the synthesized compounds (4a, 4b and 4c)*

| Compound | Type | | Analysis |
|---|--|---|--|
| 1,2-Dihydro-3H-benzimidazo[1,2-a]quinazolin-4-one (4a) | Yield 95%; mp. 263°C. (ethanol/dioxane) | IR (KBr) $\gamma_{\max}/\text{cm}^{-1}$ | 1686.5 (C=O), 1616.8 (C=N), 1608.4 (C=N) |
| | | ^1H NMR (DMSO-d6) | δ 2.32 (t, 2H, CH ₂), 2.70 (m, 2H, CH ₂), 3.76 (t, 2H, CH ₂), 7.47-8.35 (m, 4H, Ar H), 9.09 (s, 1H, CH) |
| | | Chem. NMR ^{13}C estimation | 22.5(CH ₂), 36.3 (CH ₂), 193.9 (C=O), 161.9 (C=N), 133.1 (C), 31.1 (CH ₂), 150.0 (C=N), 157.1 (CH), 126.9 (C), 143.5 (C), 119.1 (CH), 112.1 (CH), 123.0 (2CH) |
| | | MS (m/z) | 237 (M ⁺), 154, 103, 53 |
| | Analysis of imperial formula C ₁₄ H ₁₁ N ₃ O M.WT(237.26) | Calculated Found | C, 70.87; H, 4.67; N 17.71 % C, 70.84; H, 4.70; N 17.73% |
| 1,2-Dihydro-2,2-dimethylbenzimidazo[1,2-a]quinazolin-4(3H)-one (4b) | Yield 93%; mp. >300°C. (ethanol/DMF) | IR (KBr) $\gamma_{\max}/\text{cm}^{-1}$ | 1712.5 (C=O), 1606.2 (C=N), 1615.4 (C=N) |
| | | ^1H NMR (DMSO-d6) | δ 1.20 (s, 6H, 2CH ₃), 2.60 (s, 2H, CH ₂), 3.68 (s, 2H, CH ₂), 7.47-8.37 (m, 4H, Ar H), 9.06 (s, 1H, CH) |
| | | Chem. NMR ^{13}C estimation | 33.2 (C), 28.2 (2CH ₃), 35.5 (CH ₂), 193.9 (C=O), 161.9 (C=N), 133.1 (C), 48.8 (CH ₂), 157.1 (CH), 150.0 (C), 143.5 (C), 119.1 (CH), 123.0 (2CH), 112.1 (CH), 126.9 (C) |
| | | MS (m/z) | 265 (M ⁺), 209, 154, 103, 53 |
| | Analysis of imperial formula C ₁₆ H ₁₅ N ₃ O M.WT(265.31) | Calculated Found | C, 72.43; H, 5.69; N 15.84% C, 72.40; H, 5.65; N 15.80% |
| 3-(Cyclohexan-1-on-2yl)pyrimido[1,2-a]benzimidazole (4c) | Yield 86%; mp. 260°C. (ethanol/dioxane) | IR (KBr) $\gamma_{\max}/\text{cm}^{-1}$ | 1727 (C=O), 1631 (C=N), 1582 (C=N) |
| | | ^1H NMR (DMSO-d6) | δ 1.52-1.56 (m, 4H), 1.64-1.69 (m, 2H), 1.80-1.83 (m, 2H), 3.23 (m, 1H), 6.16 (d, 1H, J = 4.2 Hz, pyrimidine-6-CH), 6.90-7.32 (m, 4H), 8.81 (d, 1H, J = 4.2 Hz, pyrimidine-5-CH) |
| | | Chem. NMR ^{13}C estimation | 26.8 (CH ₂), 27.4 (CH ₂), 42.7 (CH ₂), 210.2 (C=O), 55.1 (CH ₂), 34.6 (CH ₂), 168.9 (C=N), 150.0 (C=N), 143.5 (CH), 119.1 (C), 123.0 (2CH), 112.1 (C), 126.9 (C), 135.8 (CH), 118.4 (CH) |
| | | MS (m/z) | 265 (M ⁺), 209, 154, 103, 53 |
| | Analysis of imperial formula C ₁₆ H ₁₅ N ₃ O M.WT(265.31) | Calculated Found | C, 72.43; H, 5.7; N 15.84% C, 72.39; H, 5.67; N 15.80% |

* Analyzed in Cairo University (Micro Analysis Lab.).

Recovery Procedure: The leach liquor previously prepared¹⁶ from Kadabora ore sample was analyzed where the REEs were found to assay 2043 ppm table-2. This sulfate leach liquor was subjected to solvent extraction for its REEs content by shaking with the synthesized organic multidentate organic compounds (4a, 4b and 4c) dissolved in carbon tetrachloride. Extraction experiments have been made under different conditions to achieve their highest extraction efficiency. Several stripping experiments have also been performed under different conditions to attain the highest efficiency. For the preparation of the RE₂O₃ product, a corresponding oxalate product was first prepared before ignition at 900°C.

Analytical Methods: The spectrophotometric analyses of the rare earth elements were performed with a double beam UV-VIS recording Shimadzu UV160A spectrophotometer. The concentration of the rare earth elements whether in the prepared leach liquors or in the aqueous raffinate solutions (after extraction) or else, in the stripping solutions was all the time

analyzed by arsenazo (III) without any preliminary separation¹⁸. on the other hand, a Shimadzu FTIR 8101 PC infrared spectrophotometer was used for analyzing the synthesized heterocyclic compounds (extractants), the extracted organometallic complex (after extraction) as well as the stripped complex (after stripping) (Cairo University, Egypt). For pH measurements, a Cheker-1 pH meter provided with HI1270 combination electrode from HANNA instrument was always used.

Table -2
Analysis of some elements of interest in Kadabora sulfate leach liquor

| Element | Concentration, ppm |
|---------|--------------------|
| Ti | 558 |
| U | 810 |
| Ta | 1065 |
| REE | 2043 |
| Nb | 3189 |
| Fe | 1608 |

Results and Discussion

Results of the Extraction Conditions: Effect of the Extractant Type: Both the starting multidentate organic compounds (4a, 4b and 4c) (schemes I, II and III) were dissolved in carbon tetrachloride to obtain 0.2% concentrations. These compounds were then stirred with the prepared 0.44 mol/L sulfuric acid leach liquor at an O/A ratio of 1/1 for 15 minutes. The obtained extraction efficiencies of the rare earth elements are tabulated in table-3.

Table-3

Effect of the extractant type (0.2%) on the extraction efficiency of the rare earth elements from Kadabora 0.44 M sulfuric acid leach liquor (O/A ratio of 1/1 for 15 minutes contact time)

| Type of Extractant | REE's Extraction Efficiency, % |
|--------------------|--------------------------------|
| 4a | 96.8 |
| 4b | 88.5 |
| 4c | 76.3 |

It is clear from these results the prepared extractants has greatly affected the extraction efficiency of the rare earth elements.¹⁵ It has also to be mentioned that it is clearly evident that the formed complex between a REE metal and ligand would take place by the reaction of oxygen and nitrogen atoms in a manner to form the five membered ring which is more stable, more planar and not be sterically hindered with oxygen than the six membered with lower stability^{19,20,21} Accordingly, the ability of compound (4a) to extract the rare earth elements was higher than the two compounds (4b and 4c).

Effect of Sulfuric Acid Concentration: To examine the effect of sulfuric acid concentration of leach liquor upon the extraction efficiency of the rare earth elements by 0.2% of the prepared solvents, The concentration of the former was increased from 0.44 to 0.88 and 1.76M/L. The latter three liquors were then shaken with equal volumes of solvents (4a, 4b and 4c) for 15 minutes. From the obtained results shown in table-4, it was found that the extraction efficiency of the rare earth elements is higher at lower acid concentration where by increasing the acid concentration from 0.44M to 1.76M, the extraction efficiency decreased from 96.8% to 74.8% in case of 4a and from 88.5% to 63.5% in case of 4b while it decreased from 76.3% to 50.9% in case of 4c. It can thus be inferred that increasing the acid concentration might result in competition for the complexation sites. Rahmani et al.²² reported that sulfate ions bridged the metal ion that is bonded to (4a, 4b and 4c) through the nitrogen atom and oxygen atom.

Effect of Contact Time: To study this effect, equal volumes of the sulfate leach liquor of 0.44 mol/L and 0.2% concentration of the prepared solvents (4a, 4b and 4c) in carbon tetrachloride were shaken for various time periods ranging from 1 to 30 min. From the obtained results shown in figure-1, it was found that

loading the rare earth elements starts to occur within few minutes, In other words, the extraction efficiency is gradually increased by increasing the contact time and reached the constant values of 96.8%, 88.5% and 76.3% after 15 minutes by using (4a, 4b and 4c) respectively.

Table -4

Effect of sulfuric acid concentration of Kadabora leach liquor on the extraction efficiency of the rare earth elements with 0.2% of the synthesized extractants (O/A ratio of 1/1 for 15 minutes contact time)

| H ₂ SO ₄ Conc., M | REE's Extraction efficiency, % | | |
|---|--------------------------------|------|------|
| | 4a | 4b | 4c |
| 0.44 | 96.8 | 88.5 | 76.3 |
| 0.88 | 83.2 | 72.3 | 63.7 |
| 1.76 | 74.8 | 63.5 | 50.9 |

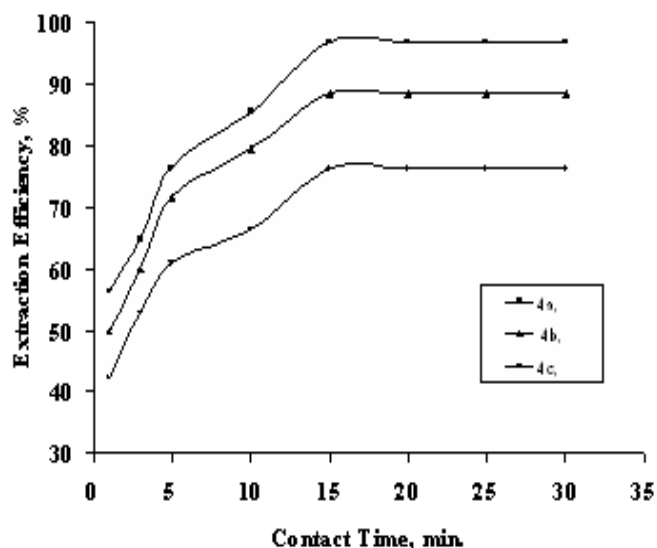


Figure -1

Effect of contact time on the extraction efficiency of the rare earth elements from Kadabora leach liquor with the synthesized extractants (0.2%)(O/A ratio of 1/1, leach liquor acidity of 0.44 mol/L)

Effect of Organic/Aqueous Ratio: This factor was studied in the range from an O/A = 4/1 to 1/4 figure-2. Contacting equal volumes of the organic and aqueous solutions for 15 minutes leads to 96.8%, 88.5% and 76.3% extraction efficiency of rare earth elements respectively. By increasing the organic phase ratio, the REEs percentage extraction efficiency decreased. This phenomenon may be due to the ions competition on the complexation sites. On the other hand, By increasing the aqueous volume of 0.44M sulfate leach liquor over the organic volume of 0.2% compounds (4a, 4b and 4c), the REE extraction efficiency remained constant after an O/A ratio of 1, indicating that an O/A ratio of 1/1 would be considered the suitable ratio for an efficient REEs extraction.

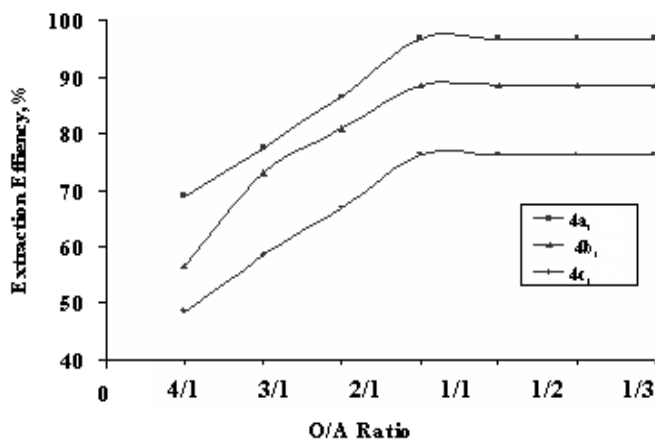


Figure -2

Effect of O/A ratio on the extraction efficiency of the rare earth elements from Kadabora leach liquor with the synthesized extractants(0.2%)(leach liquor acidity of 0.44M,contact time 15 min.)

Effect of the Extractants Concentration: To study this factor, the concentration of the synthesized extractants (4a, 4b and 4c) in carbon tetrachloride was varied from 0.01% up to 0.4% whereas the other extraction conditions were fixed as an O/A ratio of 1/1, a shaking time of 15 minutes and using the working leach liquor of 0.44 mol/L H₂SO₄ acid.

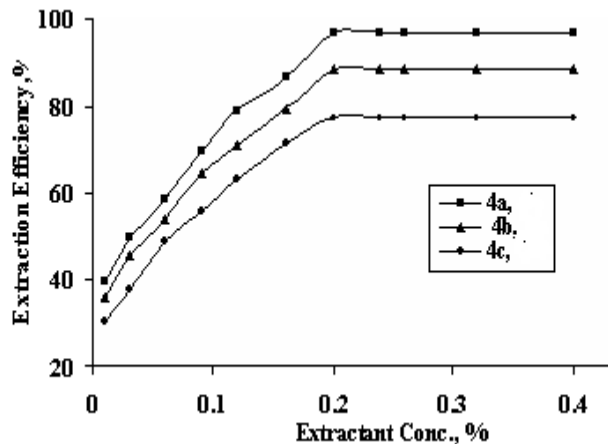


Figure -3

Effect of concentration of the synthesized extractants (4a, 4b and 4c) on the extraction efficiency of the rare earth elements from Kadabora sulfate leach liquor (O/A ratio of 1/1, leach liquor acidity of 0.44 M, contact time 15 minutes)

From the obtained results shown in figure-3, it is clear that as the (4a, 4b and 4c) concentration increased, the extraction efficiency of the REEs gradually increased until reaching 96.8%, 88.5% and 76.3% REE respectively at 0.2% concentration and above which no further extraction occurred. In other words, it can be mentioned that by increasing the

solvent's concentrations, the distribution coefficient increases until a concentration of 0.2% after which no further increase occurred as shown in the log-log plot figure-4. Comparing the different obtained equations, it can be seen that using solvent 4a for extraction of the REEs, it gives the highest slope and in turn the highest increase in the distribution coefficient with the increase of its concentration up to 0.2%.

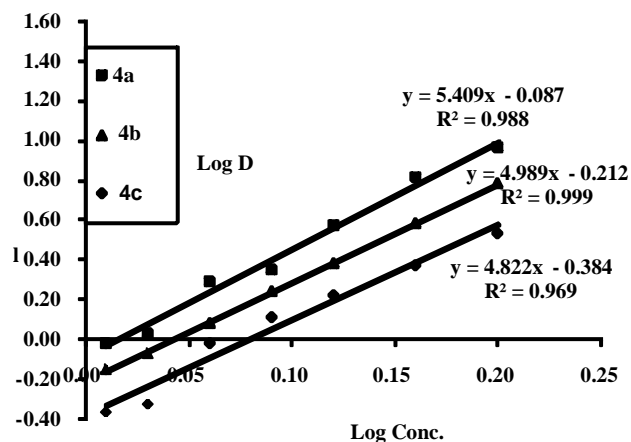


Figure -4

The log-log plot of the distribution coefficient of the REEs versus solvents (4a, 4b and 4c) concentration (O/A ratio of 1/1, leach liquor acidity of 0.44 M, contact time 15 minutes)

Results of the Stripping Conditions: At 0.2% concentration of the synthesized three extractants (4a, 4b and 4c), loading was achieved to the extent of 2027, 1897 and 1675 ppm rare earth elements respectively to study the conditions of their back extraction (stripping) into a proper stripping agent. The relevant factors of the latter were then studied to find out the stripping characteristics of the studied rare earth elements.

Determination of the Proper Stripping Agent (4a, 4b and 4c): Different acids and alkalis were shaken with the prepared loaded solvents at an O/A ratio of 1/1 for 15 minutes in an endeavor to define their stripping efficiencies. Both the alkali solutions KOH and NaOH at 5% concentration besides 9M sulfuric acid have resulted in REEs stripping efficiency in the range from about 60 to 86%. As shown in table-5, 5% KOH solution exhibited the highest stripping efficiency of the rare earth elements from the loaded solvent. In the meantime, both sulfuric and nitric acids in a concentration of up to 2.0M as well as 4% oxalic acid have not yielded any stripping result.

It can thus be inferred that the ability of the rare earth elements to be stripped and dissolved in the alkali hydroxide solutions may be interpreted as due to the presence of organo hydroxyl acids that would hinder precipitation of the rare earth elements as their hydroxides.²³ Small quantities of the organo hydroxyl acids might have possibly been formed as a result of contacting the solvents (4a, 4b and 4c) with the sulfate leach liquor and which have next been transferred into the alkali hydroxide strip alkali solutions.

Table -5

Effect of the stripping agent type on the stripping efficiency of the rare earth elements from the loaded extractants (4a, 4b and 4c) at 0.2% concentration (O/A ratio of 1/1 for 15 minutes contact time)

| Stripping Agents | REEs Stripping Efficiency, % | | |
|---|------------------------------|------|------|
| | 4a | 4b | 4c |
| HNO ₃ (0.5,1 2, 2.5, 3 mole/L) | - | - | - |
| H ₂ SO ₄ (0.5,1,2,2.5,3 mole/L) | - | - | - |
| H ₂ SO ₄ (10.0 mole/L) | 75.3 | 67.9 | 62.5 |
| Oxalic acid (1,3,5%) | - | - | - |
| NH ₄ OH (35%) | 58.7 | 42.3 | 41.9 |
| NaOH (5 %) | 78.7 | 71.6 | 68.8 |
| KOH (5 %) | 85.6 | 78.9 | 70.8 |

Effect of Potassium Hydroxide Concentration: Potassium hydroxide solutions of concentrations varying from 5 and up to 25% were contacted with equal volumes of the working loaded solvents (4a, 4b and 4c) for 15 minutes. As shown in figure-5, the stripping efficiency of the rare earth elements attained maximum values of 96.6, 86.6 and 78.0% from the loaded solvents 4a, 4b and 4c respectively at 15% KOH concentration.

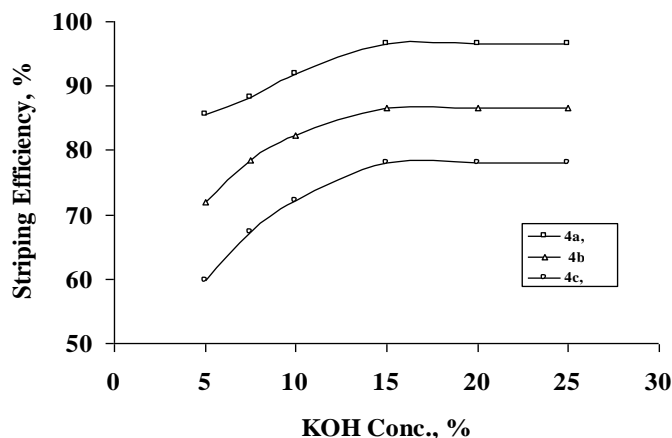


Figure -5

Effect of KOH concentration on the stripping efficiency of the rare earth elements from the loaded extractants(4a,4b and 4c)at 0.2% concentration(O/A ratio of 1/1 for 10 minutes contact time)

Effect of Contact Time: Potassium hydroxide of 15% concentration was used to strip the rare earth elements from the working loaded solvents (4a, 4b and 4c) by shaking equal volumes of both phases for different stirring time periods ranging from 1 to 30 minutes. From figure-6, it was found that the maximum REEs stripping efficiency of 96.7%, 86.7% and 78.3% using (4a, 4b and 4c) respectively was obtained after 10 minutes contact time.

Effect of Organic/Aqueous Ratio: Different volume ratios of O/A of the loaded solvents (4a, 4b and 4c) together with 15% potassium hydroxide concentration were shaken for 10 minutes.

The studied O/A ratios were varied from 4/1 to 1/4. The maximum stripping efficiencies of the REEs of 96.6%, 86.6% and 78.0% from the loaded (4a, 4b and 4c) respectively were obtained by decreasing the O/A ratio till 1/1 and which remained constant below the latter figure-7. It is also worthy to mention that the rare earth elements were almost completely stripped in case of the loaded 4a extractant after one contact with fresh 15% potassium hydroxide solution. However, in case of the loaded 4b and 4c extractants, 98.8% and 98.5% REEs were stripped selectively after two and three contacts using fresh potassium hydroxide solution. From the a forementioned results, it can be concluded that the synthesized 1,2-dihydro-3H-benzimidazolo [1,2-a] quinazolin-4-one(4a),1,2-dihydro-2,2dimethylbenzimidazolo [1,2-a] quinazolin-4(3H)-one (4b) and 3-cyclohexane-1-on-2yl) pyrimido [1,2-a] benzimidazole (4c) in carbon tetrachloride have successfully been used as effective extractants for the rare earth elements from the sulfate leach liquor of Kadabora ore sample. These elements were then almost completely released by potassium hydroxide strip solutions in successive 2 to 3 contacts.

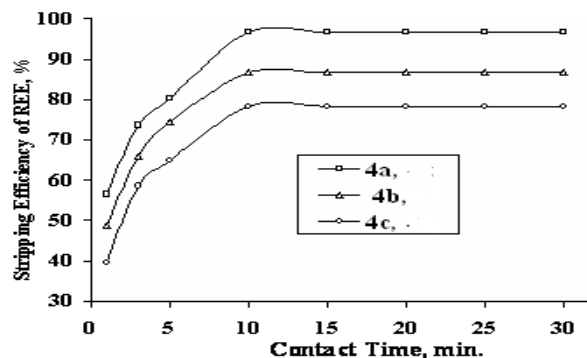


Figure -6

Effect of contact time on the stripping efficiency of the rare earth elements from the loaded extractants (4a, 4b and 4c) at 0.2% concentration (O/A ratio of 1/1 for 15 % KOH concentration)

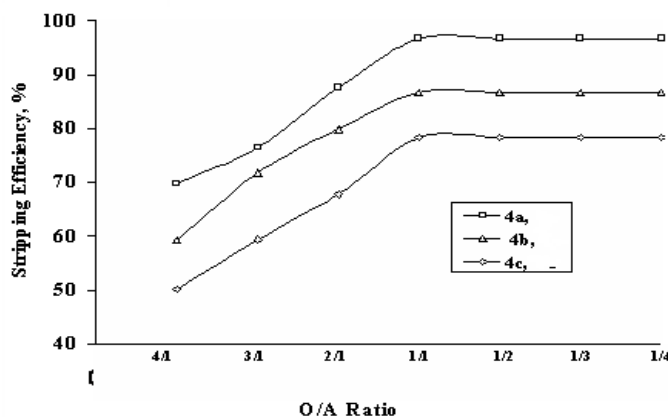


Figure -7

Effect of O/A ratio on the stripping efficiency of rare earth elements from the loaded extractants (4a, 4b and 4c) at 0.2% concentration (15% KOH concentration, 10 minutes contact time)

Mechanism of the REEs Recovery: In order to define the mechanism of the REEs recovery by the synthesized multidentate ligands, it was found necessary to subject the studied compounds to IR-analysis. This analysis has included the three prepared 4a, 4b and 4c extractants in CCl_4 i.e. before REEs extraction (freshly prepared in their free-state) as well as after their extraction (loaded-extractants) and stripping (regenerated-extractants) as shown in table-6. From the obtained results, it has been realized that some characteristic peaks representing the major groups of the three studied extractants (4a, 4b and 4c) such as the aliphatic C-H, C=O and C=N groups have sharp intensity that turned to medium intensity after the extraction and stripping experiments. This indicates that the studied extractants are able to form complexes with metal ions in the sulfate leach liquors. Accordingly, the sharp C=N peaks at 1618.8, 1606.2 and 1630.5 cm^{-1} and the C = O peaks at 1686.5, 1712.5 and 1720.7 cm^{-1} present in (4a, 4b and 4c) spectra have decreased after extraction but increased again after stripping; a matter which is most probably due to the formation of the metal complexes. It is thus possible to mention that the three synthesized extractants; namely 1,2-dihydro-3H-benzimidazolo [1,2-a]quinazolin-4-one (4a), 1,2-dihydro-2,2dimethyl benzimidazolo [1,2-a] quinazolin-4(3H)-one (4b)

and 3-(cyclohexane-1-on-2yl) pyrimido [1,2-a] benzimidazole (4c) can be considered as multidentate agents with many donor atoms. The latter exhibit indeed good affinities towards the REE ions in sulfate leach liquors. It can thus be cited that the rare earth elements have most probably been complexed to these extractants through binding to the nitrogen and oxygen atoms in the extraction step and to be released by stripping with a strong alkali.

It has also to be mentioned that it is clearly evident that the formed complex between a REE metal and ligand would take place by the reaction of oxygen and nitrogen atoms in a manner to form the five membered ring which is more stable, more planar and not be steric with oxygen so producing more yield in case of 4a complex. In case of 4b, the formed complex between REE metal and ligand is to be cited in the reaction of oxygen and nitrogen atoms which give low yield than 4a complex because the presence of two methyl groups made steric hindrance. In case of 4c complex, it produces low yield due to the formed ring which is six membered with lower stability than 4a and 4b complexes¹⁹⁻²¹. These reactions can be represented as follows:

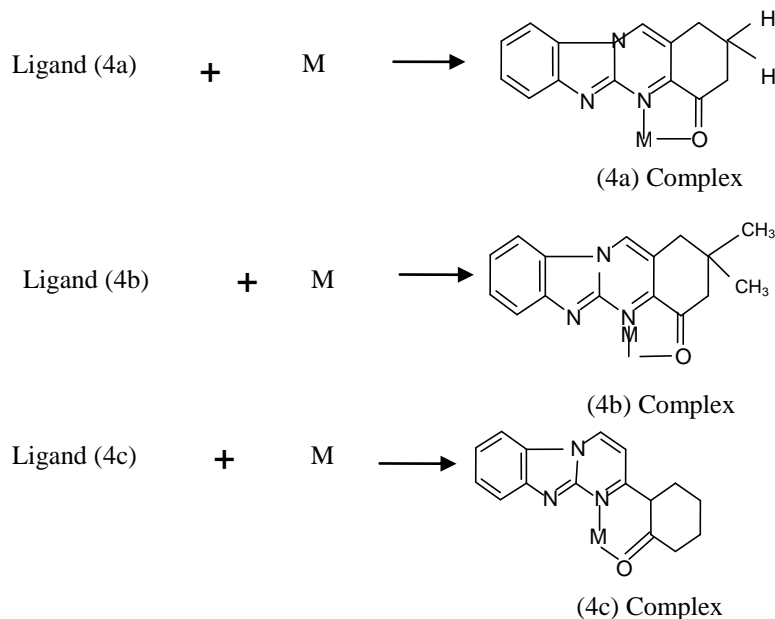


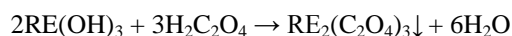
Table -6
Infrared spectra of the fresh, loaded and regenerated synthesized extractants (4a, 4b and 4c)

| Major groups | 4a | | | 4b | | | 4c | | |
|------------------|----------------------------------|---------------------------------------|--------------------------------------|----------------------------------|---------------------------------------|--------------------------------------|----------------------------------|---------------------------------------|--------------------------------------|
| | Extractant cm^{-1} (vs) | after extraction cm^{-1} (m) | after Stripping cm^{-1} (m) | Extractant cm^{-1} (vs) | after extraction cm^{-1} (m) | after Stripping cm^{-1} (m) | Extractant cm^{-1} (vs) | after extraction cm^{-1} (m) | after Stripping cm^{-1} (m) |
| Aliphatic | | | | | | | | | |
| C – H | 2863.9 | 2864.1 | 2865.3 | 2866.3 | 2864.7 | 2865.7 | 2883.5 | 2884.6 | 2882.9 |
| C = O | 1686.5 | 1680.2 | 1685.7 | 1712.5 | 1704.4 | 1713.1 | 1720.7 | 1715.3 | 1721.0 |
| C = N | 1618.8 | 1600.0 | 1618.8 | 1606.2 | 1586.2 | 1606.2 | 1630.0 | 1610.0 | 1631.5 |
| C = N | 1608.4 | 1582.6 | 1608.4 | 1615.4 | 1600.2 | 1615.4 | 1582.0 | 1500.3 | 1580.9 |

vs: very strong; m: moderate

Behavior of the Associated Ions: As previously mentioned, it was found that Kadabora sulfate leach liquor contains some interesting metal values besides the REEs (table 1). These involve Nb and Ta to the extent of 3189 and 1065 ppm respectively together with U assaying 810 ppm while Ti and Fe assay 558 and 1608 ppm respectively. Concerning the behavior of these metal ions during REEs extraction with the synthesized multidentate extractants 4a, 4b and 4c, it has indeed been ascertained that Nb, Ta and U are co-extracted with the REEs to the extent of 50, 43 and 20% respectively under the studied optimum conditions. In the meantime, the three extracted metal values have been co-stripped with the REEs by 5% KOH at an A/O ratio of 1/1 for 15 minutes shaking time. The purpose was to define the peak's positions on one hand and to compare the differences in the latter and their intensities, on the other hand. In the mean time, it is so interesting to indicate that both Ti and Fe interfere in the extraction process, however, they have not been detected in the final product that has been obtained through stripping of the loaded extractants with 15% KOH solution.

Preparation of the Rare Earths Product: Oxalic acid was used as the precipitating agent of the studied rare earth elements from their strip solution²⁴. It was added with continuous stirring to potassium hydroxide solutions (collected from different contacts) at a solid /liquid ratio of 1/5. This reaction can be expressed by the following equation:



The rare earth elements have thus been precipitated with an efficiency of about 95.4% and the obtained oxalate precipitate was filtered and thoroughly washed before ignition at 900° C to obtain the RE₂O₃ final product. The latter was then analyzed using the Scanning Electron Microscope (SEM) for its chemical composition and as shown in table-7, the obtained total REEs product attains a purity of 86%.

Table -7
SEM elemental analysis of the ignited oxalate precipitate formed from the alkali strip solution of the working extractant 4a

| Elements | Concentration,*(wt%) |
|----------|----------------------|
| Si | 2.6 |
| S | 6.6 |
| Ca | 4.4 |
| La | 12.8 |
| Ce | 35.6 |
| Nd | 8.6 |
| Sm | 2.9 |
| Eu | 2.5 |
| Y | 23.6 |
| U | 0.4 |

*Philips SEM - Research section lab - NMA - Egypt

Conclusion

Using the three synthesized extractants for rare earth extraction from Kadabora sulfate leach liquor, it was revealed that extraction is governed by the sulfuric acid concentration, the contact time, the aqueous to organic ratio as well as the solvents (4a, 4b and 4c) concentration in carbon tetra chloride. The extraction efficiencies of 96.8%, 88.5% and 76.3% total REE were thus obtained under the optimum conditions of contacting equal volumes of 0.44M sulfate leach liquor with 0.2% of the prepared extractants (4a, 4b and 4c) respectively, for 15 minutes contact time. The complex formation through both the nitrogen and oxygen atoms of the synthesized extractants was confirmed by IR analysis.

The extractability of the three synthesized organic multidentate compounds (4a, 4b and 4c) for the rare earths was found to decrease in the order 4a > 4b > 4c. It was also indicated that the solvent 4a gives the highest increase in the distribution coefficient with the increase of its concentration. In the meantime, it was also found that in case of the 4a extractant, complete stripping of the rare earth elements was achieved after one contact using 15% potassium hydroxide solution at an A/O ratio of 1/1 for 10 minutes. In case of the extractant 4b, the rare earth elements were stripped with an efficiency of 98.8% after two contacts using 15% KOH solution while in case of the extractant 4c, 98.5% of the rare earth elements were stripped after three contacts.

Finally, it has to be indicated that the purity of the final obtained RE₂O₃ product from Kadabora ore sample by the extractant 4a has attained a purity of 86%.

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