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Solvent Extraction of Gallium (III) from Acid Media by Adogen-464 in Toluene

T.A. Lasheen, A.T. Kandil, E.A. Manaa, El. A. Nouh and W.S. Hafez
Nuclear Materials Authority, Cairo, Egypt

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ABSTRACT

Adogen-464 (Methyltrialkyl (C_8-C_{10}) ammonium chloride)/toluene has been utilized for the liquid-liquid extraction of gallium (III) ions from the acidic aqueous media. In this context, the effect of different variables such as pH, Adogen-464 concentration, contact time, organic/aqueous (O/A) phase ratio and diluents type on the extraction efficiency of Ga (III) were studied and optimized. About 97% of gallium ions were extracted from aqueous solution at pH 2.75 using 10% (v/v) of Adogen-464/toluene after 15 minutes shaking time, in presence of 2 M NaCl and O/A phase ratio of 2:1. The stripping of the extracted Ga(III) species was successfully done and optimized using 0.5M HCl acid, 10 minutes contact time and A/O phase ratio; 1:1. The investigation also included the extraction of Ga (III) from leach liquor of a selected silicate sample.

Key words: Gallium, Solvent extraction, Adogen-464, PADAP, silicate sample.

INTRODUCTION

Gallium has emerged as an important industrially useful metal. It is extensively used in the manufacture of semiconductor devices for photovoltaic cells and computers since it provides efficient optical transitions as well as high electron mobility [(1-3)]. Thus all these applications have put great pressure on the availability of pure gallium in large amounts. Gallium occurs in very small amounts in rocks and ores of other metals and mostly associated with aluminum, zinc and germanium. Acid solutions from hydrometallurgical production of zinc are important sources of gallium, in addition to alkaline Bayer solutions for aluminum where it is recovered as a by-product [(4,5)].

Extraction of gallium ions from aqueous solutions is commonly achieved by chemical precipitation[(6)], complexation [(7)], ion exchange [(8-11)] and solvent extraction. Each of these techniques except solvent extraction has its merits and limitations in application. However, solvent extraction has attracted a significant attention due to its ability to selectively recover low concentration of metals. Solvent extraction is an efficient approach for gallium recovery from leach liquor. It has the advantages of a simple flow-sheet and a high gallium recovery ratio. In addition, it does not destruct the composition of the circulating solution.

In recent years several extractants of different classes have been used for the extraction of Ga (III). Among these, the chelating agents 8-hydroxyquinoline is one of the most studied extractants [(12-14)]. Some carboxylic acids are potential extractants for Ga (III), but the studies are mainly confined to the mechanism of extraction [(15-17)]. Different high molecular weight amines have also been used for achieving the separations of gallium ions [(18-20)]. Great efforts have been also made for the extraction of Ga(III) using D_2EHPA and TOPO, however, the use of these extractants has many limitations including long equilibration time and modifiers addition [(21-26)]. In the last two decades some alkyl-phosphines of the Cyanex series have emerged as useful gallium extractants. Cyanex 301 was used for the recovery of Ga (III) ions from Bayer liquor [(27)]. However, the use of this extractant for the recovery of Ga (III) from copper containing matrices was limited. On the other hand, Cyanex 923 has been established as a well-known extractant with several inherent advantages. It was reported that Cyanex 923 or Cyanex 925 in kerosene could extract Ga(III) species from aqueous chloride solution favoring Cyanex 925 as it has higher loading capacity under the same extraction conditions [28]. The extraction increased with the increase in the extractant and chloride concentrations. The use of amines and their quaternary salts for metal ions extraction has received considerable attention during the last decades. Several types of quaternary ammonium salts were used for the extraction of Ga (III) ions with different extraction efficiencies e.g. Aliquat-336 [18], Adogen-364 [29,30] and cetyldimethylbenzyl-ammonium chloride [31]. The extraction behavior of several metals using adogen-464 has already been reported [32,33]. However, very little information is available on the extraction of Ga (III) by adogen-464. In this context, the current work aims to study the applicability of the latter reagent as a new extractant for Ga (III) ions from acidic aqueous media. For this purpose, the effect of different parameters affecting the extraction process such as the nature of diluent, pH, extraction time, concentration of extractant and the presence of several foreign ions have been investigated with particular emphasis on their possible applications to extract Ga(III) from acidic leach liquor of silicate rock sample.

EXPERIMENTAL

1. Chemicals and Reagents

All chemicals and reagents used in the present work were of analytical reagent grade (*A.R.*). Double distilled water was used to prepare different aqueous solutions. The extractant Adogen-464 (methyl trialkyl ammonium chloride) (*Sigma-Aldrich, Germany*) shown in **Fig. (1)** diluted by toluene (*Dop organic , Turkey*) was used in the preparation of the organic phase. 2-(5-bromo-2-pyridylazo)-5-(diethylamino) phenol (PADAP) (*Merck, Germany*) was used for determination of Ga (III) ions. A stock solution of Ga(III) (standard solution of atomic absorption, *Merck*) was used.

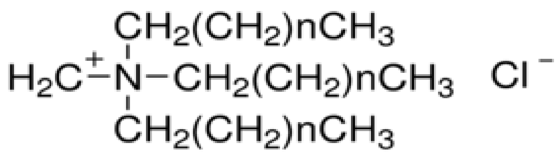

Fig. (1): Adogen-464structure

2. Apparatus

UNICAM UV-visible spectrophotometer (*England*) with quartz cells of a cm path length was used for recording absorption spectra and absorbance measurements at the selected wavelength. GFL 3006 mechanical shaker, (*Germany*) was used for shaking .

3. Extraction and Stripping Procedures

All the extraction experiments were carried out by equilibrating desired volumes of aqueous and organic phases in separating funnels for 15 min at room temperature. Unless otherwise mentioned, the composition of the organic phase was 10% (v/v) Adogen-464/ toluene. After phase disengagement both phases were separated. Stripping of Ga (III) from the loaded organic phase was achieved by equilibrating the organic phase with 0.5 M HCl for 10 min at O/A (1:1).

4. Analysis

The silicate sample used in the application was subjected to major elemental analysis using standard methods of analysis [34], **Table (1)**. Gallium ions were determined in all the experiments during the extraction and stripping stages using the recommended spectrophotometric procedure using PADAP method [35]. Trace elements were determined using ICP-AES technique at ACMA lab, Canada.

Table (1): Major and trace elements analysis of quartz sample, Wadi Sikait, South Eastern Desert, Egypt.

Major	SiO_2		Al_2O_3		P_2O_5		TiO_2		Fe_2O_3		CaO		Mg	Na_2	K_2
Wt %	73.4		11.7		0.06		0.08		1.4		1.3		0.5	5.6	5.4
Trace	Th	Cu	Co	Cd	Cr	Mn	V	Ni	Mo	***G***	Zn	Pr	Au		
ppm	36.	3.	0.	0.0	34.	14.	3.	23.	17.	***56***	30.	6.	0.1		

RESULTS AND DISCUSSIONS

1. Effect of Variables

1.1. Effect of Diluent

The effect of benzene, toluene, kerosene, chloroform and octanol diluents on the extraction of Ga (III) was studied using 10% Adogen-464 and shaking time 10 min. The extraction efficiency of Adogen-464 in different diluents is in the order: kerosene < octanol < chloform < benzene < toluene, **Fig. (2)**. The variation in the extraction efficiencies might be due to the difference in the solubility (polarity) of the used diluents. In this respect, the decrease in polarity of diluents was followed by an increase in the extraction efficiency [36]. In the light of the obtained results, toluene was a more superior diluent than others.

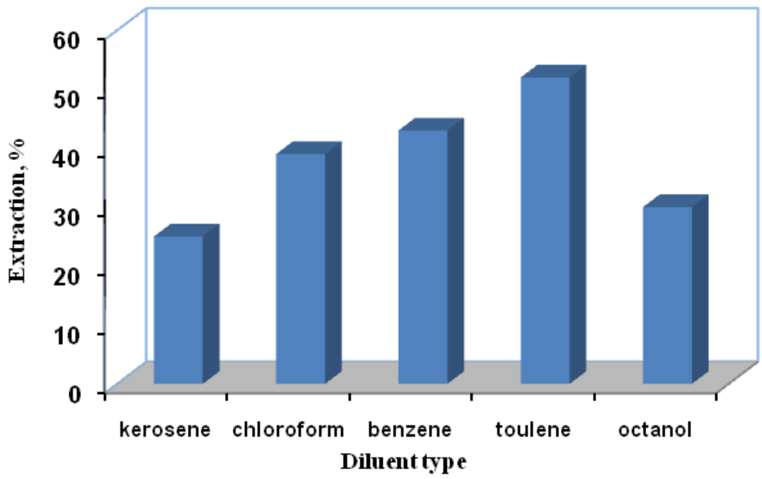

Fig. (2): Effect of diluents on Ga (III) extraction efficiency, Adogene-464 10%, shaking time 10 min, Ga (III) 10 µg mL^{-1}, pH 2.75, A/O 1:1.

1.2. Effect of pH

The effect of pH on the extraction efficiency of Ga (III) with 10% Adogen-464/toluene was studied in the pH range of 2.0-5.0. The obtained results shown in **Fig. (3)** indicated that, the most favorable condition was at pH 2.75. More than the latter pH value the extraction efficiency of Ga (III) was decreased due to the precipitation of gallium species [7]. At higher pH > 4.5 the soluble complex $Ga(OH)^{-}_{4}$ becomes predominant and the extraction of Ga decreases. Plotting of log D vs. pH gave a straight line with a slope of 0.48.

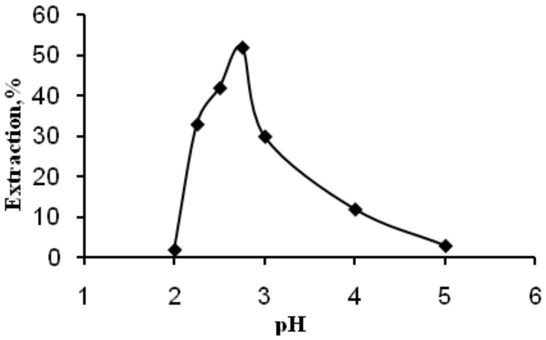

Fig.(3): Effect of pH value on Ga(III) extraction efficiency. Adogene-464 10%, shaking time 10 min, Ga (III) 10 µg mL^{-1}, A/O 1:1.

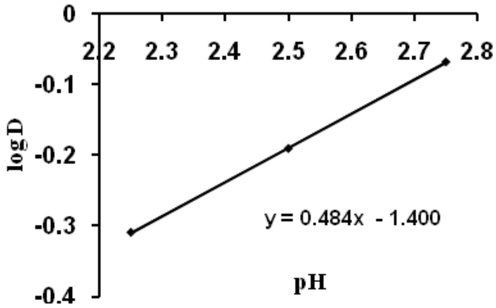

Fig:(4): Plot of log D vs. pH

1.3. Effect of Adogen-464 Concentration

In order to ascertain the optimum concentration of Adogen-464/toluene required for the quantitative extraction of Ga (III), a series of experiments were conducted by varying the concentration of Adogen-464 in the range from 2.5 to 15 % (v/v) with aqueous solution containing 10 µg mL^{-1} of Ga (III) at pH 2.75 for 15 min. The results presented in **Fig.(5)** showed a progressive improvement in the extraction efficiency of Ga(III) by increasing Adogen-464 concentration from 2.5 to 10%. More than 10% Adogen-464, the extraction efficiency did not show any additional increment in the extraction efficiency of Ga (III). Therefore, 10% Adogene-464 in toluene is adequate and considered the optimum concentration for Ga (III) extraction. Based on the relationship between log D vs. log [Adogen-464] of Ga (III) extraction results plot in **Fig. (6),** a straight line (R^2 = 0.99) with a slope of 0.89 was obtained. This suggests the association of one mole of the extractant with each mole of the extracted metal ion species in the formed complex.

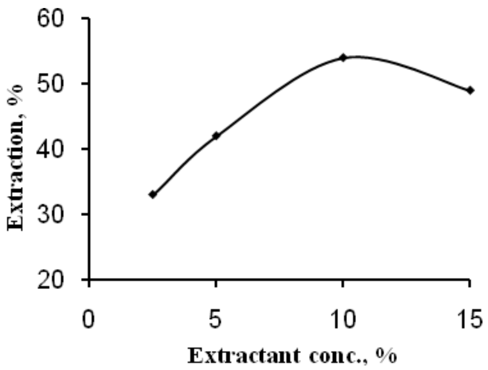

Fig. (5): Effect of extractant concentration on Ga (III) extraction efficiency. Shaking time 15 min, Ga (III) 10 µg mL^{-1}, pH 2.75, A/O 1:1.

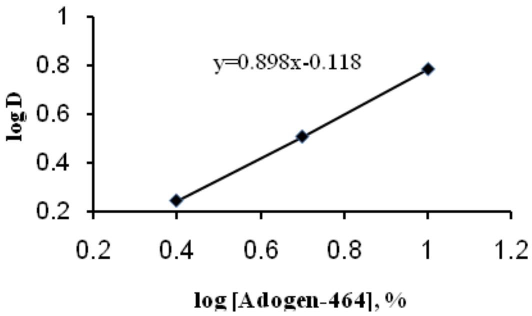

Fig. (6): Plot of log D vs. log [Adogen-464]

1.4. Effect of Time

The effect of shaking time on the extraction of Ga (III) from aqueous medium at pH 2.75 using 10% Adogen-464/toluene was investigated at various mixing periods of time ranging from 5 to 25 min. It was observed, **Fig. (7)** that, the extraction efficiency of Ga (III) reached 55% in a short contact period of 15 min under previous mentioned conditions. Therefore, 15 min was adequate and considered as the optimum time.

1.5. Effect of Organic/Aqueous Phase Ratio

To recover Ga (III) from the aqueous solution containing 10 µg mL^{-1} Ga (III), the solution was equilibrated with 10% Adogen-464/toluene at O/A ratios within 1/3 to 3/1 while keeping the total volume of phases constant. The obtained results in **Table (2)** indicate that the phase O/A of 2:1 is the suitable ratio for Ga (III) extraction under the studied conditions. The McCabe-Thiele plot in **Fig. (8)** proves that, two stages are required for extraction of 87% of Ga(III) from aqueous phase at O/A (2:1).

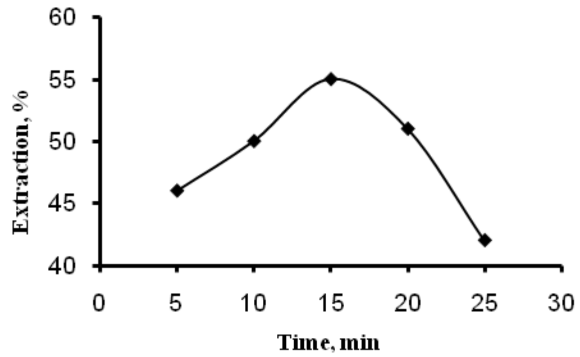

Fig.(7): Effect of equilibration time on Ga(III) extraction efficiency. Adogene-464 10%, Ga(III)10 µg mL^{-1}, pH 2.75, A/O 1:1.

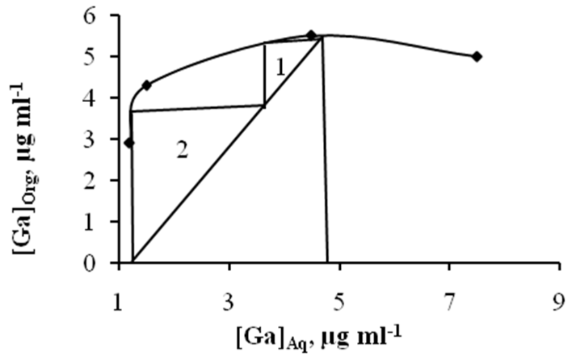

Fig. (8): McCabe-Thiele plot for Ga(III) extraction.

Table (2): Effect of organic/aqueous ratio on 10 µg mL^{-1} Ga (III) extraction efficiency by 10% Adogen-464/toluene solution from aqueous medium of pH 2.75.

O/A ratio	Extraction, %
1/3	20
1/2	29
1/1	54
2/1	87
3/1	84

1.6. Effect of Salts

The effect of NaCl and KCl salt solutions on the extraction of Ga (III) was investigated under the optimized conditions to improve the extraction efficiency (salting out effect). The concentrations of the two salt solutions in the aqueous phases was varied within the range from 0.5 to 3.0 M. A noticeable improvement in the extraction efficiency of Ga (III) was observed, and NaCl solution showed more Ga extraction, **Fig.9.** This behavior might be related to the decrease of Na ionic radius than K. It is well known that the salting out effect increases with lowering of the ionic radii for ions of the same charge(37). Using 2 M NaCl solution, the extraction efficiency of Ga (III) increased to 97% in one stage.

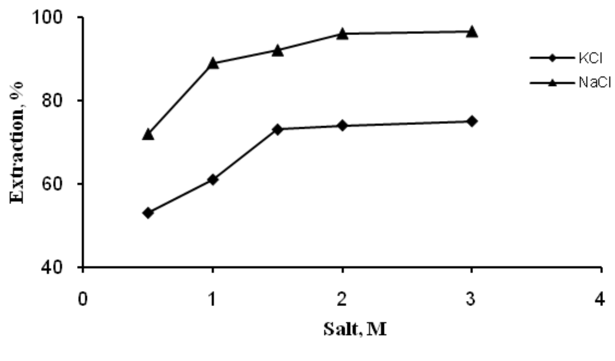

Fig. (9): Effect of some salts on the extraction of Ga (III). Adogene-464 10%, shaking time 15 min, Ga (III) 10 µg mL^{-1}, pH 2.75, A/O 1:1.

2. Fourier Transformation Infra Red Spectra of Adogen-464 and Ga (III) Loaded Adogen-464

The infra red spectra of Adogen-464 and Ga(III) loaded Adogen-464 were recorded to know the interaction between the extractant and the metal ion. The spectra of extractant and its complex with Ga(III) are shown in **Fig. (10)**. They demonstrate that C-H symmetric and asymmetric deformation vibration and stretching vibration for pure and Ga(III) loaded Adogen-464 are identical. The peak at 1461.9 cm^{-1} characteristic to quaternary amine $(CH_3)N^+$ was also observed in both spectra. However the peak at 1380.9 cm^{-1} due to C-N stretching vibration for Adogen-464 was shifted to 1373 cm^{-1} in Ga(III) loaded Adogen-464 indicating the possibility of bonding between Ga(III) and Adogen-464**[38,39]**. The bands at 1639 Cm^{-1} and 29277 Cm^{-1} are due to C-N and C-H aliphatic stretching vibration, respectively. The band at 29727.2 Cm^{-1} is due to C-H aromatic stretching vibration of toluene.

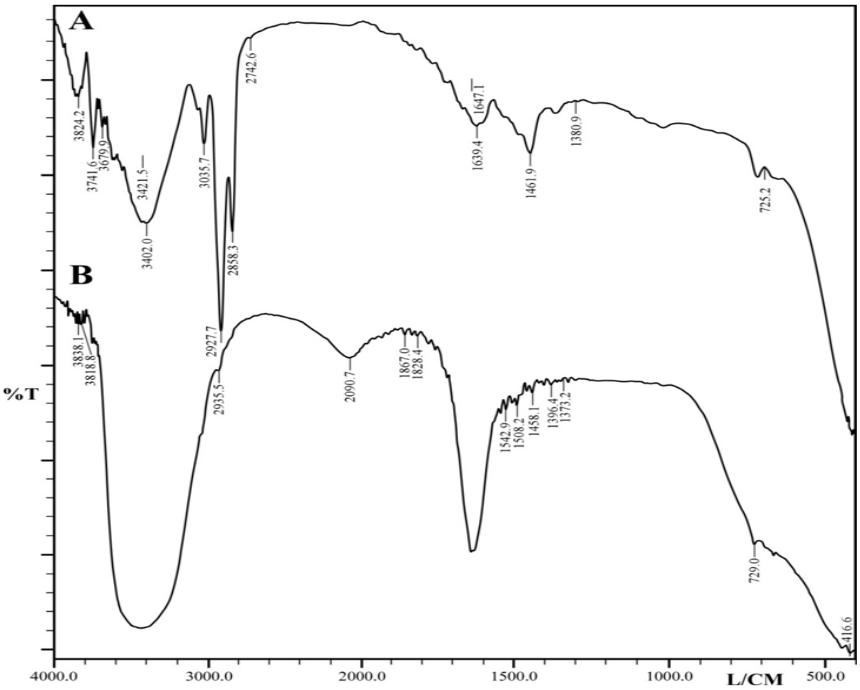

Fig. (10): FTIR spectra of (A) extractant, (B) extractant loaded Ga (III).

3. Effect of Foreign Ions on Ga (III) Extraction

The effect of competing ions which are probably present in the aqueous solution on the extraction of 10µg ml^{-1} Ga (III) was studied. The tolerated limits of interfering ions were established and summarized in **Table (3)**. The translated data show that Co^{+2} ions have a marked effect on the extraction of gallium species even at low concentrations (0.5 µg mL^{-1}). UO_2^{+2} and Tl^{+3} species were tolerated up to 15 µg ml^{-1} while Ni^{+2} and Th^{+4} ions were tolerated to 10 µg mL^{-1} and increased to 40 µg mL^{-1} in case of Fe^{+3} ions. On the other hand, Na^+, K^+, Ca^{+2} and Mg^{+2} cations were tolerated to 100 µg mL^{-1} where Al^{+3} and Si^{+4} cations were tolerated to 200 µg mL^{-1}.

Table (3): Tolerated limit of foreign ions on the extraction of 10 µg mL^{-1} Ga (III)**.**

Foreign ions	Tolerated limit, µg mL^{-1}
Co^{+2}	0.5
Ni^{+2}, Th^{+4} ,	10
UO_2^{+2}, Tl^{+3}, In^{+3}	15
Fe^{+3}	40
Na^+, K^+ , Ca^{+2}, Mg^{+2}	100
Al^{+3}, Si^{+4}	200

4. Stripping Investigations

The effect of 0.5 M HCl, HNO_3, NaOH, NH_4OH, acetic acid solutions beside hot water was studied for stripping Ga (III) from the organic phases at A/O ratio of 1:1and shaking for 15 min. The data presented in **Fig. (11)**, reveal that hydrochloric acid solution is more favorable for Ga (III) stripping than Adogen-464/toluene solvent. In order to determine the required concentration of hydrochloric acid for stripping of Ga (III), a series of experiments were conducted by varying the concentration of HCl in the range from 0.05 to 1.0 M at A/O ratio of 1:1. The results presented in **Fig. (12)** demonstrate that, 0.5 M is an adequate concentration for the stripping of Ga(III).

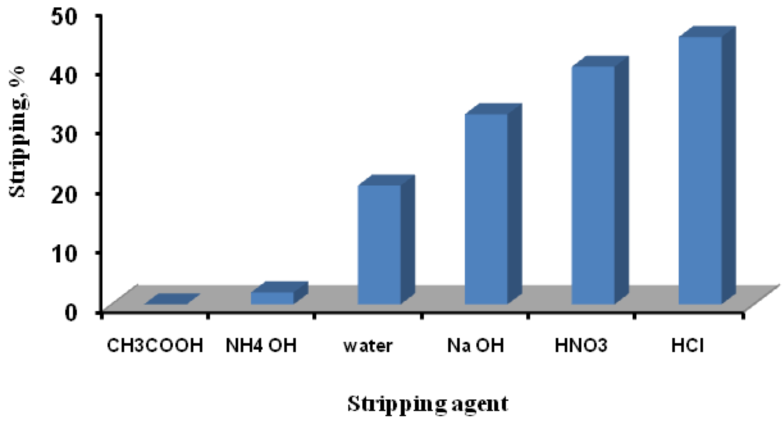

Fig. (11): Effect of stripping agent on gallium (III) stripping efficiency.

The effect of contact time on Ga (III) stripping efficiency was investigated using 0.5 M HCl at A/O phase ratio of 1:1 from 5 to 15min. The obtained data in **Fig. (13)** show that the stripping efficiency of Ga(III) increased with the increase in contact time to reach a maximum at 10 min. Therefore, 10 min was a suitable time to strip Ga (III) from the loaded organic phase.

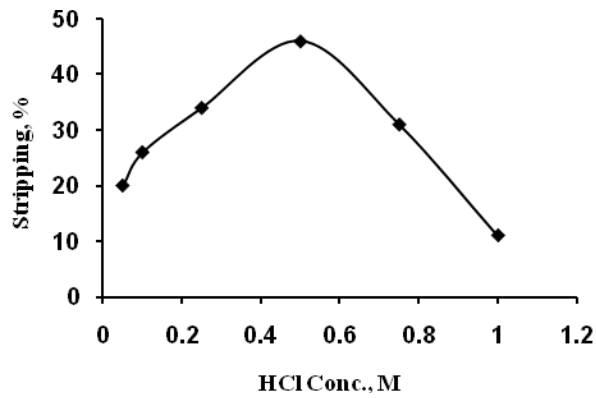

Fig. (12): Effect of HCl concentration on Ga(III) stripping efficiency.

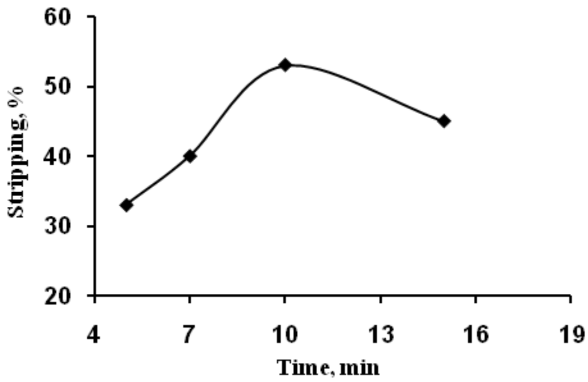

Fig. (13): Effect of contact time on Ga(III) stripping efficiency.

Finally the optimized extraction procedure was applied on the extraction of Ga (III) ions from leach liquor of a chosen silicate sample collected from Wadi Sikait, South Eastern Desert, Egypt. The sample sized at -200 mesh size was leached using 2 M HCl acid at solid/acid solution phase ratio of 1/6 for 2h at 65 C° digestion temperature followed by filtration step [40]. Under the previous leaching conditions, the leach liquor contains about 50 µg ml^{-1} gallium ions; it was subjected to extraction step using 10% Adogen-464/toluene solvent in presence of 2M NaCl at O/A phase ratio of 2:1 for 15 min extraction time. The obtained results showed about 97% extraction efficiency in one stage. The organic phase was then subjected to stripping process using 0.5 M HCl solution at A/O phase ratio of 1:1 after 10 min shaking time. The obtained product was devoted from the contamination whereas most of these elements were tolerated during extraction step.

CONCLUSION

Gallium (III) was efficiently extracted from aqueous solution using Adogen-464/toluene solvent. It was found that, 87% of Ga (III) ions can be extracted from the aqueous media in two stages using an O/A phase ratio of 2:1 and 10% Adogen-464/toluene. On the contrary, about 97% of Ga (III) can be extracted in one stage in presence of NaCl solution. Several ions did not interfere during the extraction of Ga (III) such as Na, K, Ca, Mg, Al. Stripping of Ga (III) from the loaded organic phase has easily done by 0.5 M of HCl using 1:1 A/O phase ratio for 10 min. The procedure was successfully applied to leach liquor of silicate sample.

REFERENCES

(1) B. Gupta, N. Mudhar and I. Singh, Sep. Purif. Technol. 57, 294 (2007).

(2) A.R. Peaker, Properties of Gallium Arsenide. EMIS Data Reviews Series 2.INSPEC, Inst. Electrical Engineers, London and New York (1990).

(3) R.R. Moskalyk, Miner. Eng. 16, 921(2003).

(4) J.E. Hoffmann, 24th Sir Julius Wemher Memorial Lecture. Extraction Metallurgy, 89, 5 (1989).

(5) I. Mihaylov and P.A. Distin, Hydrometallurgy 37 (2), 221 (1995).

(6) M. Sadeghi and L. Mokhtari, J. Radional . Nucl . Chem . 284, 471(2010).

(7) R. Dumortier, M. E. Weber and J. H. Vera, Hydrometallurgy, 76, 207 (2005).

(8)Y. Kataoka, M. Matsuda, H. Yoshitake and Y. Hirose, Method for recovery of gallium, US Patent (1984).

(9) G. Cote and, D. Bauer, Proceedings of the International Solvent Extraction Conference (ISEC'86), Munich, pp. 463 (1986).

(10)J.M. Lamerant, Process for extracting and purifying gallium from Bayer liquors, US Patent (1992).

(11) T. Yotsuyanagi and Y. Nishiyama, Method for recovering gallium, US Patent (1986).

(12) K. Ohashi, R. Iwata, S. Mochizuki, H. Imura, K. Hiratani and H. Sugihara, Talanta 43, 1481(1996).

(13) S.Y. Choi and K. Ohashi, 2000, Anal. Sci., 16, 169-176.

(14) H. Hoshino, A. Ohashi and K. Ohashi, Bunseki Kagaku 52, 775 (2003).

(15) H. Yamada and Y. Taguchi, Analytical Science, 13, 355(1997).

(16) X. Zhang, and G. Yin, Solv. Extr &Ion Exch., 20, 115(2002).

(17) X. Zhang, G. Yin and Z. Hu, Talanta, 59, 905 (2003).

(18) M.A. Karve and S.M. Khopkar, Chem. Anal., (Warsaw), 38, 469 (1993).

(19) J. Mukherjee and S.P. Bag, Chem. Enviro. Res. 4, 211(1995).

(20) J. Mukherjee and S.P. Bag, Chem. Environ. Res. 6, 57(1997).

(21) K. Inoue, Y. Baba and K. Yoshiuka, Solv. Extr. &Ion Exch. 6, 381(1988).

(22) T. Sato, T. Nakamura and S. Ishikawa, Solv. Extr. &Ion Exch., 2, 201 (1984).

(23) T. Sato, H. Yasumura, Y. Mizuno and T. Nishimura, 1996, Solvent extraction of trivalent gallium, indium and thallium from hydrochloric acid solutions by TOPO and TBP. In: Shallcross, D., Paimin,R., Prvcic, L.M. (Eds.), Proc. Int. Solvent Extr. Conf., Melbourne, Australia, vol. 1. University of Melbourne Press, pp. 559-564.

(24) T. Sato, K. Sato, Y. Noguchi and I. Ishikawa, Shigen to Sozai 113, 185 (1997).

(25) D.C. Nambiar, J. S. Gandh and V.M. Shinde, Talanta, 41, 1951(1994).

(26) S. Nishihama, T. Hirai and I. Komasawa, Ind. Eng. Chem. Res., 38, 1032 (1999).

(27) B. Gupta, N. Mudhar and S.N. Tandon, Ind. Eng. Chem. Res. 44, 1922 (2005).

(28) I.M. Ahmed, Y.A. El-Nadi and N.E. El-Hefny, Hydrometallurgy, 131-132, 24 (2013).

(29) E. Rodrıguez de San Miguel, J.C. Aguilar, M.T.J. Rodrıguez, and J. de Gyves, Hydrometallurgy, 57, 151(2000).

(30) Sh. A. Shefjf, A.S. Abdel-Gawad and A.M. El-Wakil, Talanta, 17, 137 (1970).

(31) K. Yamamoto and N. Katoh, J. Soc. Anal. Chem., 15, 1013(1999).

(32) A. Chatterjee and S. Basu, Journal of Radio analytical and Nuclear Chemistry, 150,177(1991).

(33) S. Biswas and S. Basu, Journal of AOAC International, 82, 1257(1999).

(34) G.H. Jeffery, J. Bassett, J. Mendham and R.C. Denney, Vogel's textbook of quantitative chemical analysis. 5th ed. Wiley J.& Sons, New York (1989).

(35) A.T. Kandil, T.A. Lasheen, N. Abd-El-Atty, W.S. El-Naggar and W. S. Hafez, Arab Journal of Nuclear Science and Applications, 47(2), 68 (2014).

(36) L. Yuxin, W. Yundong and D. Youyuan, Chinese J. Chem. Eng., 12(1) 143 (2004).

(37) T. Bhat and S. Sundararajan, Journal of the Less-Common Metals, 12, 231(1967).

(38) K. Nakamoto, Infrared and Raman spectra of inorganic and co-ordination compounds. 5th ed., Wiley, New York (1997).

(39) G. Socrates, Infrared and Raman characteristic group frequencies: tables and charts. 3rd ed., Wiley, New York (2000).

(40) Z. Fang and H. Gesser, Hydrometallurgy, 41, 187(1996).