



Separation of Iridium from Hydrochloric Acid Medium Using Microspheres Containing 2-Ethylhexyl Benzimidazolyl Sulfoxide

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The extraction of iridium(IV) from hydrochloric acid medium was carried out using the microsphere containing 2-ethylhexyl benzimidazolyl sulfoxide as the extractant. The sorption was found to be fast, equilibrium was reached within 6 min. When the concentration of Ir(IV) was 200 mg L⁻¹, nearly all of the Ir(IV) (> 99 %) was adsorbed by the microspheres in 4 mol L⁻¹ HCl medium. The sorbed Ir(IV) ions were desorbed with 0.5 wt. % sodium hydroxide solution. The sorption data could be well interpreted by the Freundlich isotherm model with the maximum adsorption capacity of 80 mg g⁻¹ (25 °C) of Ir(IV) on the microsphere. Iridium(IV) and rhodium(III) could be separated completely with a separation coefficient of Ir(IV) and Rh(III) (1.36×10^4) using the optimal separation parameters. The microspheres can be reused at least in 20 cycles of extraction-stripping process.

Keywords: Iridium, Solid phase extraction, Microspheres, 2-Ethylhexyl benzimidazolyl sulfoxide.

INTRODUCTION

Iridium is known to be an important platinum group metals and widely used in the making of precise alloys, apparatus, plug electrodes and in the automobile, chemical and electronics industries owing to its specific physical and chemical properties¹⁻⁵. Iridium usually associate with rhodium in the ores. Rhodium and iridium are located at the same row in the periodic table. It has been known that separation of Rh(III) and Ir(IV) is one of the most difficult process in hydrometallurgy owing to their similar structures and chemical behaviours. Thus it is urgent to develop efficient approaches for the recovery and separation of iridium and rhodium. The hydrometallurgical methods, including solvent extraction⁶, ion exchange resin⁷ and the reduction of precious metal precipitate by reagents⁸, are more applicable to separation of iridium. Generally solvent extraction has been considered as a most efficient technique for the recovery and separation of iridium from hydrochloric acid solutions. Solvent extraction methods of Ir(IV) recently reported include tributyl phosphate⁹, tributyl phosphate added stannous chloride¹⁰, dihexyl sulfoxide¹¹ and chromogenic calixarene¹². The solvent extraction method has a high selectivity and is easy to scale-up, but the solvent extraction method increases environmental pollution due to the use of toxic organic solvents.

Solid phase extraction has achieved widespread use because of its simple procedure, higher preconcentration factor, rapid

phase separation and combination with different detection techniques. However, the literature studies on the adsorption efficiency of sorbents for Ir(IV) are limited^{13,14}. Interest is increasing on microspheres as sorbent for separation of platinum group metals owing to its effectiveness¹⁵. To the best of our knowledge, until now there is no report on the application of microspheres containing sulfoxide for separating Ir(IV) ions in aqueous solution. In this paper, microspheres containing 2-ethylhexyl benzimidazolyl sulfoxide as sorbent was used for adsorption and separation of Ir(IV) ions from solution. The optimum conditions for separation of Ir(IV) ions were obtained from the batch experiments.

The goal of the present study was to provide a rapid, simple efficient and environmentally friendly method for recovery iridium. In the present work, a new sorbent, the microspheres containing 2-ethylhexyl benzimidazolyl sulfoxide (EHBMSO) have been evaluated for the extraction of Ir(IV) ions from hydrochloric acid medium. The effect of various parameters such as time, concentration of hydrochloric acid and separation coefficient of Ir(IV) and Rh(III) have been studied.

EXPERIMENTAL

A ICP-1000 II inductively coupled plasma atomic emission spectrometer (ICP-AES, Shimadzu, Japan) was used to measure the concentration of Ir(IV). A Z-2000 polarized zeeman atomic absorption spectrophotometer (Hitachi High-

Technologies Corporation, Japan) was used to measure the concentration of Rh(III), Fe(III), Cu(II), Co(II) and Ni(II). The operating conditions were carried out according to the recommendations of manufacturer.

Ethylene glycol dimethacrylate (EGDMA), methyl methacrylate, cyclohexane, azobisisobutyronitrile (AIBN), polyvinyl alcohol and sodium dodecyl benzene sulfonate (SDBS) (analytical grade) were purchased from Beijing Chemical Reagent Co. Stock solution of iridium was prepared by diluting H_2IrCl_6 in ultra-pure water. 2-Ethylhexyl benzimidazolyl sulfide (EHBMS) was synthesized in our laboratory as literature¹⁶. Other chemicals were all commercially available reagents of analytical grade.

Synthesis of 2-ethylhexyl benzimidazolyl sulfoxide (EHBMSO): 2-Ethylhexyl benzimidazolyl sulfide was synthesized according to the following procedure: 2-ethylhexyl benzimidazolyl sulfide (12 g), acetone (30 mL) and acetic acid (80 mL) was placed in a round-bottomed flask fitted with a mechanical stirrer and condenser. H_2O_2 (30 %, 8 mL) was added gradually through a dropping funnel and the reaction mixture was stirred for 2 h at room temperature. It was poured into ice-water, the organic phase was collected and the acetone was further removed by distillation. The yellow crude product was obtained (yield: 71.3 %). Its structure (Fig. 1) was verified by ^1H NMR, ^{13}C NMR and mass spectra. ^1H NMR (300 MHz, CDCl_3) 12.88 (1H, s), 7.79 (1H, d, $J = 6.90$ Hz), 7.58 (1H, d, $J = 6.60$ Hz), 7.33-7.27 (2H, m), 3.35-3.28 (2H, m), 2.10 (1H, t, $J = 12.90$ Hz), 1.63-1.20 (8H, m), 0.98-0.77 (6H, m) ppm; ^{13}C NMR (75 MHz, CDCl_3), δ : 153.26, 143.82, 134.67, 124.26, 123.10, 120.09, 112.23, 60.76, 34.46, 32.38, 28.38, 25.77, 22.76, 13.94, 10.46 ppm; HRMS(ESI) m/z found (%): 279.1521 ($\text{M} + \text{H}$)⁺; calc: (%): 279.1532 ($\text{M} + \text{H}$)⁺.

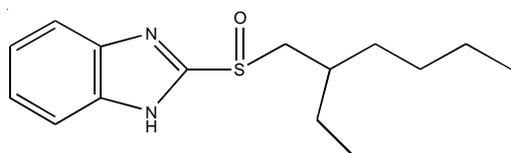


Fig. 1. Structure of 2-ethylhexyl benzimidazolyl sulfoxide (EHBMSO)

Preparation of the microspheres: The microspheres containing EHBMSO were prepared by suspension polymerization technique. In a typical procedure, the organic phase was prepared by dissolution of methyl methacrylate and EHBMSO in cyclohexane. Furthermore, the ethylene glycol dimethacrylate (EGDMA) and azobisisobutyronitrile (AIBN) were also added into this organic phase mixture. Continuous phase (dispersion or suspension medium) was prepared by dissolution of polyvinyl alcohol and sodium dodecyl benzene sulfonate (SDBS) as stabilizers in distilled water. These two phases were combined in the reactor and then heated at 75 °C with stirring at 200 rpm for 4 h under the nitrogen atmosphere. The prepared microspheres were collected by filtration, washed with distilled water, dried under vacuum and sieved to get particles from 150 to 180 μm .

Static batch method: Solid phase extraction of iridium was performed in batch manner using a series of 150 mL Erlenmeyer flasks containing 200 mg the microspheres and 50 mL of 200 mg L^{-1} Ir(IV) solution. 2-Ethylhexyl benzimidazolyl

sulfoxide content of the microspheres is 30 % (w/w) and particle size of from 150 to 180 μm . Hydrochloric acid concentration of the adsorption medium was 4 mol L^{-1} . If necessary, the acidity of the solutions was adjusted by adding HCl or NaOH solution before the addition of the microspheres. These samples were shaken at room temperature using a shaker at 200 rpm for 6 min. After this time adsorbent was separated with filter paper, the final solution concentration was analyzed using ICP-AES.

These results were further used to estimate the extraction efficiency of Ir(IV) ions. The amount of extracted Ir(IV) ions was calculated according to the differences in the Ir(IV) ions concentrations of the aqueous phase between, before and after the extraction. Adsorption capacities of the microspheres for Ir(IV) ions were calculated by following equation:

$$Q = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where Q is the loading capacity of the microspheres (mg g^{-1}) C_0 and C_e is the concentrations of the Ir(IV) ion in the initial solution and in the aqueous phase after adsorption, respectively (mg L^{-1}); V is the volume of the aqueous phase (L); and W is the amount of the microspheres (g).

Separation coefficient of Ir(IV) and Rh(III) ($\beta_{\text{Ir/Rh}}$) was expressed as:

$$\beta_{\text{Ir/Rh}} = \frac{D_{\text{Ir}}}{D_{\text{Rh}}} = \frac{q_e(\text{Ir}) \times C_e(\text{Rh})}{q_e(\text{Rh}) \times C_e(\text{Ir})} \quad (2)$$

where D is distribution coefficient of metal ion in the solid and aqueous phase; q_e is the solid phase metal ion concentration at equilibrium (mg g^{-1}); C_e is the equilibrium liquid phase concentration of metal ion (mg L^{-1}).

RESULTS AND DISCUSSION

Effect of sorbent amount: In order to attain the optimal amount of the microsphere containing EHBMSO for the adsorption of Ir(IV) ions, 50, 100, 150, 200, 250, 300, 350 mg of the microspheres were added to a series of 50 mL Ir(IV) solution, respectively. Condition of the adsorption were as follows: Ir(IV) concentration, 200 mg L^{-1} ; HCl concentration, 4 mol L^{-1} ; contact time, 6 min. The results are plotted in Fig. 2, which shows that the amount of the microsphere has a remarkable effect on the extraction efficiency. When the amount of the microsphere exceeded 200 mg, the adsorption percentage of Ir(IV) on the microsphere was close to 100 %. Therefore, 200 mg of the microsphere was the optimum amount for the adsorption of Ir(IV).

Influences of hydrochloric acid concentration: In industrial application for extraction of Ir(IV), the acidity of the adsorption medium usually influences significantly. The acidity of the sample solution is one of the important factors affecting the formation of $(\text{EHBMSO} \cdot \text{H}_3\text{O}^+)_2\text{IrCl}_6^{2-}$ ion-pairs and the subsequent solid phase extraction. Hydrochloric acid concentration of the adsorption medium was changed from 0.1 to 6 mol L^{-1} . In the study, initial Ir(IV) ion concentration was used as 200 mg L^{-1} and the saturation time was defined as 6 min. Ir(IV) ion adsorption values are shown in Fig. 3. The adsorption percentage of Ir(IV) on the microspheres was very low at lower acidity.

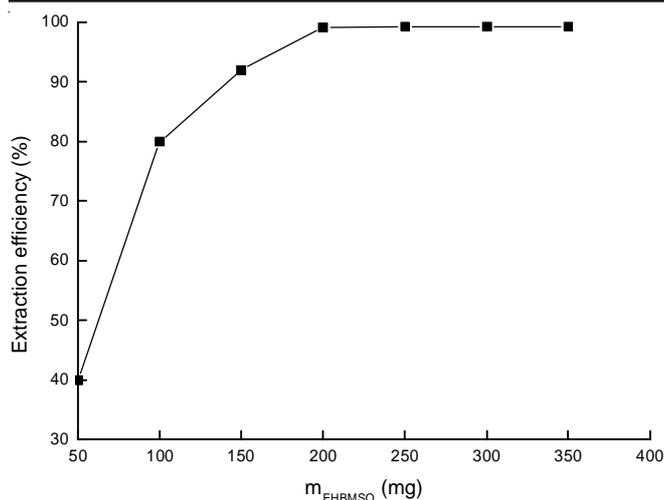


Fig. 2. Effect of the amount of the microspheres over the Ir(IV) ion adsorption; sample volume: 50 mL, Ir(IV) concentration: 200 mg L⁻¹, HCl concentration: 4 mol L⁻¹, contact time: 6 min

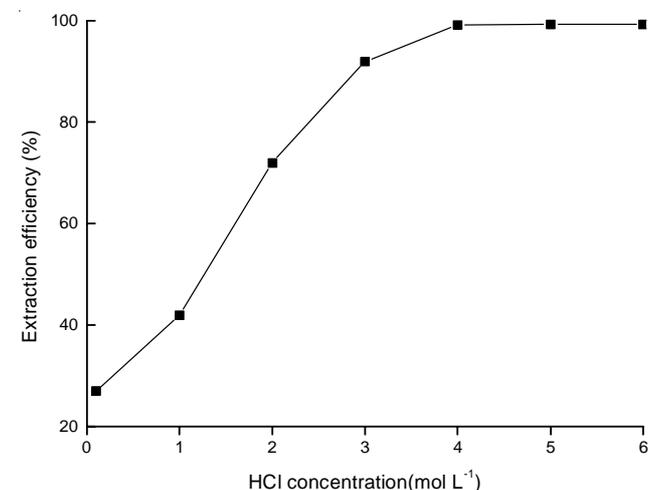


Fig. 3. Effect of the acidity over the Ir(IV) ion adsorption; sample volume: 50 mL, the amount of the microspheres: 200 mg, Ir(IV) concentration: 200 mg L⁻¹, contact time: 6 min

The result indicated that the adsorption percentage of Ir(IV) on the microspheres increased with increasing HCl concentration from 0.1 to 4.0 mol L⁻¹. Further increase of HCl concentration from 4 to 6 mol L⁻¹, the adsorption percentage kept constant (> 99 %). Therefore, quantitative extraction of Ir(IV) occurred at 4 mol L⁻¹ HCl and 4 mol L⁻¹ HCl was adopted in all subsequent experiments.

Effects of contact time: To extract Ir(IV) efficiently by controlling an optimal contact time, the experiments were carried out with different contact time at other fixed extraction parameters. The adsorption of Ir(IV) by the microspheres containing EHBMSo as a function of time is shown in Fig. 4. Contact time was determined by measuring the metal content in the aqueous phase as a function of time until the metal concentration in the aqueous solution did not vary. The two phases were shaken for a period ranging from 1 to 10 min. the adsorption percentage of Ir(IV) on the microspheres increased with increasing contact time from 1 to 6 min. Further increase of contact time from 7 to 10 min, the adsorption percentage kept constant. Therefore, the minimum period of equilibration required for the quantitative extraction of Ir(IV) was found to be about 6 min.

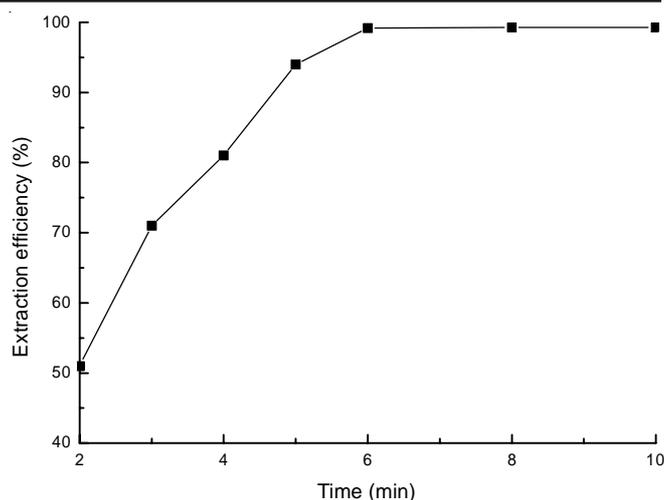


Fig. 4. Effects of contact time over the Ir(IV) ion adsorption; sample volume: 50 mL, Ir(IV) concentration: 200 mg L⁻¹, the amount of the microspheres: 200 mg, HCl concentration: 4 mol L⁻¹

Desorption studies: In the following experiments, hydrochloric acid concentration of the adsorption medium was 4 mol L⁻¹, initial Ir(IV) ion concentration was 200 mg L⁻¹. The volumes of the adsorption and desorption media were both kept constant as 50 mL. Desorption time was fixed as 5 min. The results show that sodium hydroxide solution can be used as the effective stripping agent. As can be seen from Fig. 5, by increasing sodium hydroxide concentration from 0.1 to 0.5 wt. %, the percentage stripping of Ir(IV) increased from 49.1 to 99 %. By further increasing concentration of sodium hydroxide from 0.6 to 0.8 wt. %, the percentage stripping of Ir(IV) kept constant. The stripping was quantitative when 0.5 wt. % sodium hydroxide solution was used.

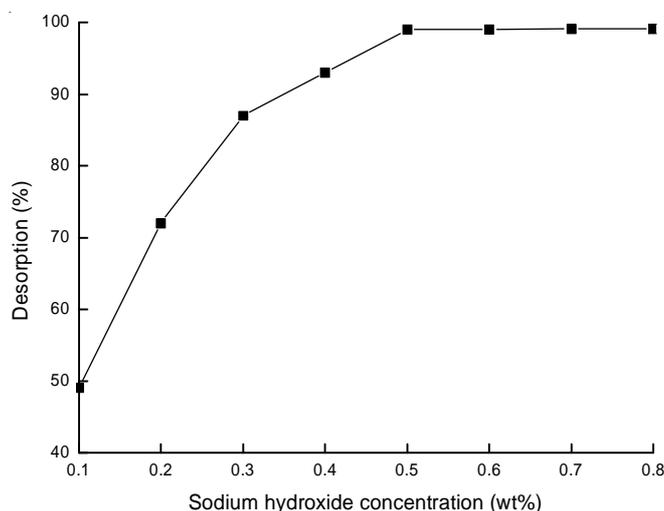


Fig. 5. Influence of sodium hydroxide concentration on the elution of Ir(IV) from the microspheres. (elution volume: 50 mL, desorption time: 5 min)

Microspheres stability tests: Reusability of the adsorbents is one of the most important considerations in the adsorption and removal studies of the Ir(IV). At the end of the adsorption-desorption steps, the microspheres were washed with distilled water for three times for 3 min. The microspheres stability was tested by subjecting the microspheres to several loading and elution batch operations. The sorbent is highly

stable and can be used repeatedly. There was no decrease in sorption capacity under static conditions even after 20 cycles of operation. The microspheres showed good reusability and stability towards Ir(IV).

Adsorption isotherm and adsorption capacity: To conduct the adsorption isotherm experiments, a suitable amount of the microsphere (200 mg) was added to a series of 150 mL Erlenmeyer flasks with Ir(IV) (50 mL, 200-350 mg L⁻¹). Hydrochloric acid concentration of the adsorption medium was 4 mol L⁻¹. Subsequently, the Erlenmeyer flasks were placed in a thermostatic shaker for 1 h at 200 rpm and kept the temperature at 25 °C. After this time adsorbent was separated with filter paper, the final solution concentration was analyzed using ICP-AES. Adsorption capacity of the microsphere for Ir(IV) at 25 °C can be obtained by the adsorption isotherm (Fig. 6).

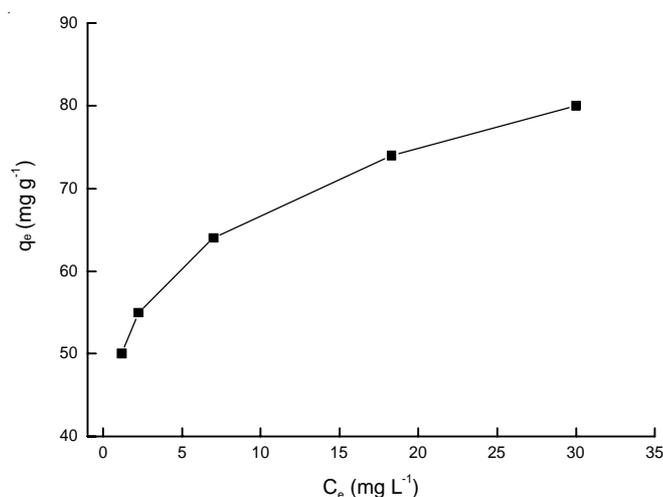


Fig. 6. Isotherm of Ir(IV) adsorption on the microsphere at 25 °C; the microsphere: 200 mg; the initial Ir(IV) concentration range was 200-350 mg L⁻¹

It illustrates that the maximum adsorption capacity of Ir(IV) ions on the microsphere was 80 mg g⁻¹ at 25 °C. The adsorption process can be explained by Freundlich isotherms. The Freundlich isotherms is expressed as:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (3)$$

where q_e is the amount of adsorbate that can be adsorbed at equilibrium (mg g⁻¹), k_f is the Freundlich adsorption constant (mg g⁻¹)(L mg⁻¹)^{1/n} and C_e is the equilibrium liquid phase concentration (mg L⁻¹). Fig. 7 shows the detailed information of the constant k_f and $1/n$ which can be determined by a plot of $\log q_e$ versus $\log C_e$ at 25 °C. The obtained isothermal constants and the correlation coefficients are presented in Table-1.

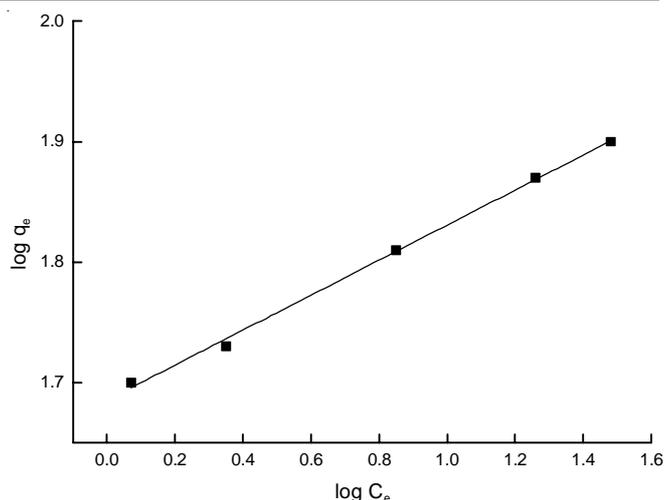


Fig. 7. Freundlich linear plots for adsorption isotherm of the microsphere at 25 °C

It is found that the correlation coefficient R^2 of the sample is as high as 0.9972, which shows that the adsorption isotherms are well fitted with the Freundlich isotherm model.

Separation of Ir(IV) and Rh(III) from impurities:

Based on the above independent extraction experiments of Ir(IV), the desirable extraction parameters of Ir(IV) from hydrochloric acid solution without impurity were obtained. The as-obtained extraction parameters need to be verified if they are or not workable in practical application for the separation of Ir(IV) and Rh(III) from impurities in hydrochloric acid solution. A synthetic stock solution containing Rh(III), Fe(III), Cu(II), Co(II) and Ni(II) was prepared and its compositions were shown in Table-2. Under the optimum conditions, the sorption of Ir(IV) ions at 200 mg L⁻¹ concentration level in the presence of a large excess of diverse ions were examined. The results revealed that 99.1 % Ir(IV) but only 0.8 % Rh(III) were extracted on the adsorbents. By calculation, the separation coefficient of Ir(IV) and Rh(III) ($\beta_{Ir/Rh}$) reached 1.36×10^4 , indicating Ir(IV) and Rh(III) were separated completely. In the other hand, the ones of Fe(III), Cu(II), Co(II) and Ni(II) was below 0.5 %, which suggested the Fe(III), Cu(II), Co(II) and Ni(II) remained in the solution.

Conclusion

In this paper, the adsorption behaviour of Ir(IV) ions on the microsphere containing 2-ethylhexyl benzimidazolyl sulfoxide was investigated. The main advantages of the procedure are its ease and the fast creation of the phase equilibration. The equilibrium is achieved within 6 min. The experimental results indicate that the microsphere can effectively separate Ir(IV) ions from aqueous solutions in 4 mol L⁻¹ HCl medium and has high adsorption capacity for Ir(IV) ions. The adsorption

TABLE-1
FREUNDLICH ISOTHERM PARAMETERS OF THE MICROSPHERE AT 25 °C

Sample	k_f (mg g ⁻¹)(L mg ⁻¹) ^{1/n}	n	R ²	Maximum adsorption capacity
Microsphere	48.42	6.88	0.9972	80 mg g ⁻¹

TABLE-2
COMPOSITION OF THE MIXED SOLUTION

Metal ions	Ir(IV)	Rh(III)	Fe(III)	Cu (II)	Co(II)	Ni(II)
Concentration (mg L ⁻¹)	200	300	50	80	60	70

percentage of Ir(IV) exceeds 99 %. The adsorption isotherms could be well fitted applying the Freundlich isotherm model. Finally, the microsphere sorbents was successfully applied to the separation Ir(IV) ions from the mixed solution with complex matrix. The technology has shown a promising application in the separation of Ir(IV) and Rh(III) from hydrochloric acid medium.

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REFERENCES

1. C.S. Kedari, M.T. Coll, A. Fortuny, E. Goralska and A.M. Sastre, *Sep. Sci. Technol.*, **40**, 1927 (2005).
2. V. Druskovic, V. Vojkovic and S. Miko, *Talanta*, **62**, 489 (2004).
3. B. Tang, F. Han and G.Y. Zhang, *Talanta*, **56**, 603 (2002).
4. C. Locatelli, *Talanta*, **85**, 546 (2011).
5. M.A. Taber, S. Puri, R.K. Bansal and B.K. Puri, *Talanta*, **45**, 411 (1997).
6. A. Mhaske and P. Dhadke, *Hydrometallurgy*, **63**, 207 (2002).
7. D.G. Pearson and S.J. Woodland, *Chem. Geol.*, **165**, 87 (2000).
8. G. Schreier and C. Edtmaier, *Hydrometallurgy*, **68**, 69 (2003).
9. P.P. Sun and M.S. Lee, *Hydrometallurgy*, **105**, 334 (2011).
10. L.H. Zou, J. Chen and Y. Huang, *Hydrometallurgy*, **72**, 31 (2004).
11. N.G. Afzaletdinova, E.R. Ibatova and Y.I. Murinov, *Russ. J. Inorg. Chem.*, **51**, 971 (2006).
12. A. Kumar, P. Sharma, L.K. Chandel, B.L. Kalal and S. Kunsagi-Mate, *J. Incl. Phenom. Macrocycl. Chem.*, **62**, 285 (2008).
13. L.S. Wu and M.Z. Zhao, *Chinese J. Anal. Chem.*, **22**, 877 (1994).
14. L. Zhang, N. Li, P. Fan, X.J. Chu, S. An, J. Zhang and X. Wang, *Hydrometallurgy*, **127-128**, 8 (2012).
15. C. Li, Z.J. Huang and J. Chen, *Asian J. Chem.*, **25**, 10270 (2013).
16. S.P. Feng, Z.J. Huang and P.W. Li, *Asian J. Chem.*, **23**, 2605 (2011).