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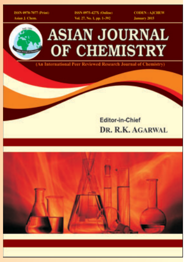

Separation of Palladium from Hydrochloric Acid Medium Using Microspheres Containing Octyl Benzoxazolyl Sulfoxide

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The separation of Pd(II) from hydrochloric acid medium was carried out using the microsphere containing octyl benzoxazolyl sulfoxide as sorbent. The sorption was found to be fast and the equilibrium was reached within 8 min. When the concentrations of Pd(II) and Pt(IV) were 100 mg L^{-1}, nearly all of the Pd(II) (> 99 %) was adsorbed by the microspheres, on the contrary, the one of Pt(IV) was adsorbed was lower (1.8 %) in 0.1 mol L^{-1} HCl medium. Palladium(II) and Pt(IV) can be separated efficiently at a lower acidity. The sorbed Pd(II) ions were desorbed with 0.4 mol L^{-1} thiourea solution. Palladium(II) could be separated completely from a stock solution containing Pt(IV), Cu(II), Fe(III), Zn(II), Co(II) and Ni(II) impurities. Separation coefficient of Pd(II) and Pt(IV) reached 5.4×10^3 using the optimal separation parameters. Kinetic parameters for Pd(II) adsorption on the microsphere were examined. Experimental data was found to be in good agreement with pseudo-second-order kinetics.

Keywords: Palladium, Separation, Microspheres, Octyl benzoxazolyl sulfoxide.

INTRODUCTION

Palladium is a good catalyst and is widely used in hydrogenation and dehydrogenation reactions. Owing to its corrosion resistance properties and easy alloying, palladium and its alloys are also used in chemical industry, medical devices and jewelry manufacturing[1].

Extraction of palladium from ores or spent materials is restricted to leaching in hydrochloric acid media. Palladium usually associate with platinum in the leaching solutions. The separation and purification of platinum and palladium usually are of difficulty owing to their similar structures and chemical behaviours. The hydrometallurgical methods, including solvent extraction, ion exchange resin and the reduction of palladium precipitate by reagents, are more applicable to palladium recovery[2,3]. Generally solvent extraction has been considered as a most efficient technique for the recovery and separation of palladium. A number of studies on the extraction of palladium with solvent extraction methods have been carried out, and many different extraction systems have been examined, including oxime derivatives[4,5], 8-hydroyquinoline derivatives[6], neutral organophosphorus compound[7], pyridine derivatives[8] and phosphonium derivatives[9,10], *etc*. 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[11-15].

Adsorption extraction has achieved widespread use because of its simple procedure, higher preconcentration factor, rapid phase separation and combination with different detection techniques. Some adsorbents such as activated carbon, biosorption and polymers have been used for recover of palladium and platinum[16-18]. However, the literature studies on separation of Pd(II) and Pt(IV) with sorbents are very limited. It was mainly relevant to independent extraction of the two precious metals, and the detailed extraction and separation parameters of Pd(II) and Pt(IV) could not be obtained. To the best of our knowledge, until now there is no report on the application of microspheres containing sulfoxide for separating Pd(II) and Pt(IV) in aqueous solution. In the present work, we have investigated the independent extraction of Pd(II) and Pt(IV) from hydrochloric acid medium with the microspheres containing octyl benzoxazolyl sulfoxide (OBOSO). Based on the independent extraction experiments of Pd(II) and Pt(IV), the desirable separation parameters of Pd(II) and Pt(IV) were selected and were further verified by extracting a synthetic mixing stock solution containing Pd(II) and Pt(IV) and common impurities like Fe(III), Cu(II), Zn(II), Co(II) and Ni(II). The effect of various parameters such as time, concentration of hydrochloric acid and separation coefficient of Pd(II) and Pt(IV) have been studied. The excellent extraction and separation performances of Pd(II) and Pt(IV) suggested the potential application in the future.

EXPERIMENTAL

A Z-2000 polarized zeeman atomic absorption spectrophotometer (Hitachi High-Technologies Corpotation, Japan) was used to measure the concentration of Pd(II), Pt(IV), Fe(III), Cu (II),Co(II), Zn(II) and Ni(II). The operating conditions were carried out according to the recommendations of manufacturer.

Octyl benzoxazolyl sulfide, styrene, ethylene glycol dimethacrylate (EGDMA), methyl methacrylate, divinyl benzene, cyclohexane, azobisisobutyronitrile (AIBN), polyvinyl alcohol and sodium dodecyl benzene sulfonate (SDBS) (analytical grade) were purchased from Beijing Chemical Reagent Co. Palladium(II) and platinum(IV) stock solution (1.0 g L^{-1}) was prepared as described. A weighed portion of palladium or platinum metal was dissolved in aqua regia (120 mL). When the metal was completely dissolved, the solution was evaporated to nearly dryness. Residual HNO_3 was removed by adding 30 mL of 6 mol L^{-1} HCl and evaporated to nearly dryness again and this was repeated 3 times. The solution was transferred into a 250 mL of volumetric flask and the final norm volume was adjusted by adding 0.1 mol L^{-1} HCl solution. Other chemicals were all commercially available reagents of analytical grade.

Synthesis of octyl benzoxazolyl sulfoxide (OBOSO): Octyl benzoxazolyl sulfoxide was synthesized according to the following procedure: octyl benzoxazolyl sulfide (8 g), acetone (5 mL) and acetic acid (10 mL) was placed in a round-bottomed flask fitted with a mechanical stirrer and condenser. H_2O_2 (30 %, 10 mL) was added gradually through a dropping funnel and the reaction mixture was stirred for 3 h at room temperature, then 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: 67.5 %). Its structure (Fig. 1) was verified by ^1H NMR, ^{13}C NMR and mass spectra. ^1H NMR (300 MHz, $CDCl_3$) 7.83 (1H, d, *J* = 6.9 Hz), 7.66 (1H, d, *J* = 6.9 Hz), 7.51-7.42 (2H, m), 3.39-3.32 (2H, m), 1.95(1H, m), 1.77 (1H, m), 1.52-1.48 (2H, m), 1.31-1.26 (8H, m), 0.89 (3H, t, *J* = 6.5) ppm; ^{13}C NMR (75 MHz, $CDCl_3$), δ: 164.44, 151.80, 140.55, 126.96, 125.56, 121.22, 111.51, 53.99, 31.66, 29.01, 28.93, 28.53, 22.57, 21.94, 14.04 ppm; HRMS(ESI) *m/z* found (%): 302.1197 $(M+Na)^+$; calc:(%): 302.1185$(M+Na)^+$.

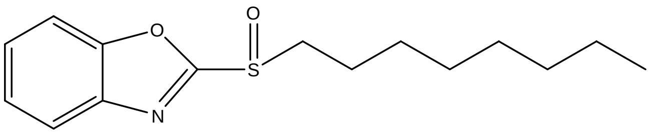

Fig. 1. Structure of octyl benzoxazolyl sulfoxide (OBOSO)

Preparation of the microspheres: The microspheres containing OBOSO were prepared by suspension polymerization technique. In a typical procedure, the organic phase was prepared by dissolution of styrene, methyl methacrylate and octyl benzoxazolyl sulfoxide in cyclohexane. Furthermore, divinyl benzene, 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 80 °C with stirring at 150 rpm for 6 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 120 to 150 µm.

Static batch method: A set of desirable separation parameters were obtained *via* the independent extraction experiments of Pd(II) and Pt(IV). Adsorption extraction of Pd(II) or Pt(IV) was performed in batch manner using a series of 250 mL Erlenmeyer flasks containing 100 mg the microspheres and 50 mL of 100 mg L^{-1} Pd(II) and Pt(IV) solution, respectively. Octyl benzoxazolyl sulfoxide content of the microspheres is 35 % (w/w) and particle size of from 120 to 150 µm. Hydrochloric acid concentration of the adsorption medium was 0.1 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 8 min. After this time adsorbent was separated with filter paper, the final solution concentration was analyzed using AAS.

RESULTS AND DISCUSSION

Effect of the amount of sorbent: In order to attain the optimal amount of the microsphere containing octyl benzoxazolyl sulfoxide for the separation of Pd(II) and Pt(IV) ions, 40, 60, 80, 100, 120, 140,160 mg of the microspheres were added to a series of 50 mL Pd(II) and Pt(IV) solution, respectively. Conditions of the adsorption were as follows: Pd(II) and Pt(IV) concentration, 100 mg L^{-1}, respectively; HCl concentration, 0.1 mol L^{-1}; contact time, 8 min. The results are plotted in Fig. 2.

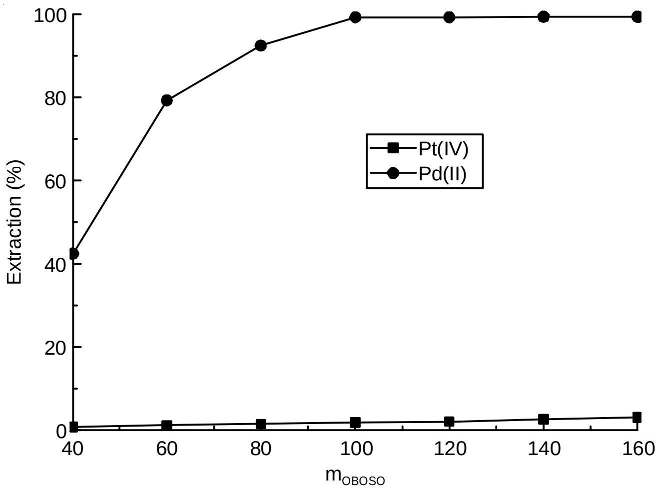

Fig. 2. Effect of the amount of the microspheres on the extraction Pd(II) and Pt(IV). sample volume: 50 mL, Pd(II) concentration: 100 mg L^{-1}, Pt(IV) concentration: 100 mg L^{-1}, HCl concentration: 0.1 mol L^{-1}, contact time: 8 min

As can be seen from Fig. 2, the percentage extraction of Pd(II) increased in the range from 42.5 to 99.3 % while the one of Pt(IV) extraction increased only from 0.8 to 1.8 % by increasing the amount of the microsphere from 40 to 100 mg. Further increasing the amount of the microsphere from 100 mg to 160 mg, the percentage extraction of Pd(II) kept constant, while the one of Pt(IV) had a slight increase (from 1.8 to

3.1 %). The result demonstrated that Pd(II) and Pt(IV) could be separated efficiently with appropriate the amount of the microsphere.

Influences of hydrochloric acid concentration: In industrial application for separation of Pd(II) and Pt(IV), the acidity of stock solution usually influences significantly. Hydrochloric acid concentration of the adsorption medium was changed from 0.1 to 4.0 mol L^{-1}. In the study, initial Pd(II) and Pt(IV) ion concentration was used as 100 mg L^{-1}, respectively, and the adsorption time was defined as 8 min. The results are shown in Fig. 3. As can be seen from Fig. 3, the percentage extraction of Pd(II) kept constant (> 99 %) with increasing HCl concentration from 0.1 mol L^{-1} to 4.0 mol L^{-1}, on the contrary, the one of Pt(IV) had a large increase from 1.8 to 90.5 %. Therefore, Pd(II) and Pt(IV) can be separated efficiently at a lower acidity at other fixed conditions, 0.1 mol L^{-1} HCl was used in all subsequent experiments.

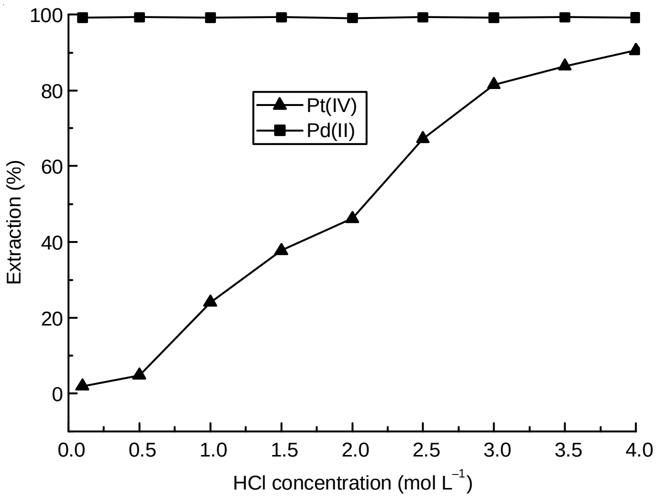

Fig. 3. Effect of H^+ concentration on the extraction of Pd(II) and Pt(IV). sample volume: 50 mL, the amount of the microspheres: 100 mg, Pd(II) concentration: 100 mg L^{-1}, Pt(IV) concentration: 100 mg L^{-1}, contact time: 8 min

Effects of contact time: To extract and separate Pd(II) and Pt(IV) efficiently by controlling an optimal contact time, the experiments were carried out with different contact time at other fixed extraction parameters. The results are shown in Fig. 4. It can be concluded that the adsorption percentage of Pd(II) on the microspheres increased with increasing contact time from 2 to 8 min. Further increase of contact time from 8 to 12 min, the adsorption percentage kept constant (> 99 %). Pt(IV) extraction increased from 1.0 to 1.8 % by increasing contact time from 2 to 4 min. Further increasing contact time from 4 to12 min, the percentage extraction of Pt(IV) kept constant (1.8 %), Pt(IV) extraction was faster than Pd(II) extraction under the same extraction conditions.

Stripping properties of palladium: In the following experiments, hydrochloric acid concentration of the adsorption medium was 0.1 mol L^{-1}, initial Pd(II) ion concentration was 100 mg L^{-1}. The volumes of the adsorption and desorption media were both kept constant as 50 mL. Desorption time was fixed as 10 min. The results show that thiourea solution can be used as the effective stripping agent. As can be seen from Fig. 5, by increasing thiourea concentration from 0.1 to 0.4 mol L^{-1}, the percentage stripping of Pd(II) increased from 37.1 to 99.1 %. By further increasing concentration of thiourea solution from 0.5 to 0.7 mol L^{-1}, the percentage stripping of Pd(II) kept constant (> 99 %). The stripping was quantitative when 0.4 mol L^{-1} thiourea solution was used.

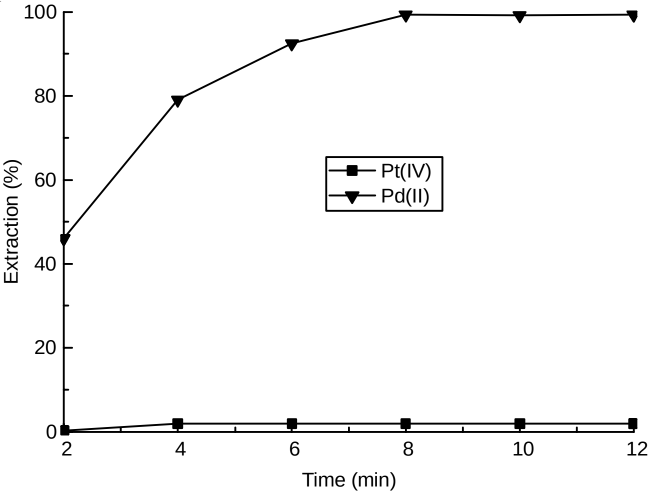

Fig. 4. Effects of contact time on the extraction of Pd(II) and Pt(IV). Sample volume: 50 mL, Pd(II) concentration: 100 mg L^{-1}, Pt(IV) concentration: 100 mg L^{-1}, the amount of the microspheres: 100 mg, HCl concentration: 0.1 mol L^{-1}

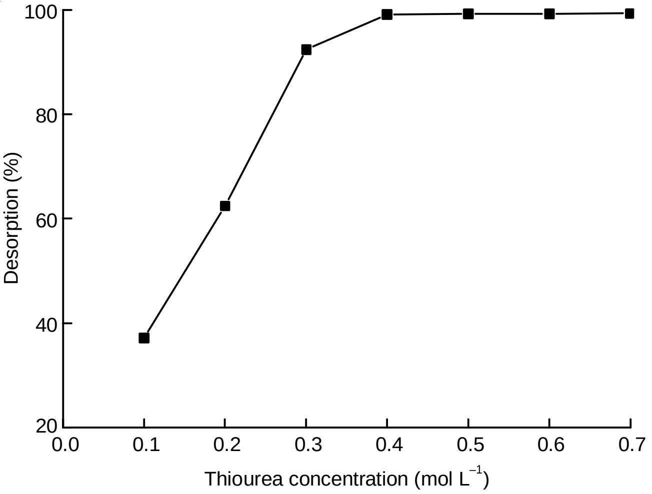

Fig. 5. Influence of thiourea concentration on the elution of Pd(II) from the microspheres. elution volume: 50 mL, desorption time: 10 min

Kinetic for Pd(II) adsorption on the microsphere: In order to investigate of kinetics for Pd(II) adsorption on the microsphere, 50 mg microsphere was added to a series of 250 mL Erlenmeyer flasks with 100 mL Pd(II) solution. Initial Pd(II) solution concentrations is 100 mg L^{-1}. Hydrochloric acid concentration of the adsorption medium was 0.1 mol L^{-1}. Subsequently, the erlenmeyer flasks were placed in a thermostatic shaker at 150 rpm and kept the temperature at 25 °C. At different periods of 1, 2, 4, 6, 8, and 10 min, the solution concentration was analyzed using AAS.

The pseudo-second-order model model is represented as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{1}$$

where, q_e and q_t (mg g^{-1}) are the amounts of Pd(II) adsorbed on unit mass of the microsphere when the concentration is equilibrium and at time t (min), respectively; k_2 (g mg^{-1} min^{-1}) is the rate constant of the pseudo-second-order model model. q_e is calculated by following equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{2}$$

where, C_0 and C_e are the concentrations of the metal 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).

q_t is calculated by following equation:

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{3}$$

where, C_t is the concentrations of the metal ion in any time t. The plot of t/q_t *versus* t (Fig. 6) yields very good straight lines. Table-1 lists the computed results obtained from the second-order equation. The correlation coefficients for the second-order kinetic equation was greater than 0.999. The calculated q_e values also agree very well with the experimental data. These indicate that the adsorption system studied belongs to the second order kinetic model.

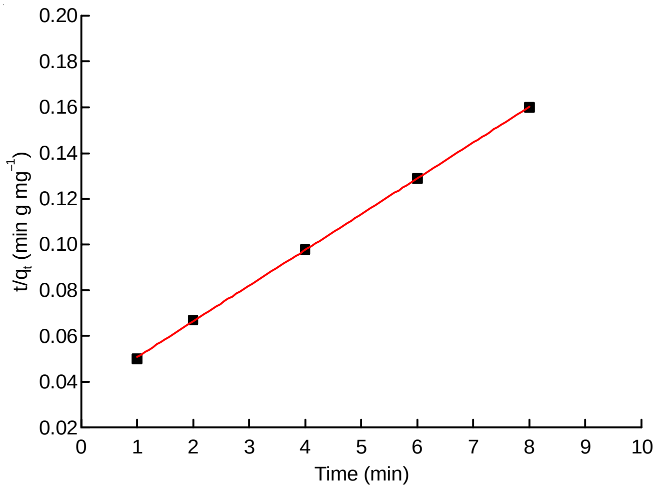

Fig. 6. Pseudo-second-order kinetics for adsorption of Pd(II) on the microsphere. Sample volume: 100 mL, the amount of the microspheres: 50 mg, Pd(II) concentration: 100 mg L^{-1}, temperature: 25 °C

TABLE-1
KINETIC PARAMETERS FOR Pd(II) ADSORPTION ON THE MICROSPHERE AT 298 K

T (K)	$C_{Pd(II)}$ (mg L^{-1})	$q_{e,exp}$ (mg g^{-1})	$q_{e,cal}$ (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2
298	100	64.0	63.9	0.00697	0.9991

Separation of Pd(II) from synthetic sample: Based on Figs. 2-4, when Pd(II) and Pt(IV) existed in the stock solution alone, both of them could be separated efficiently by controlling the amount of the microspheres, HCl concentration and adsorption time. The optimum extraction separation parameters of Pd(II) and Pt(IV) were summarized as the following: the amount of the microspheres, 100 mg, HCl concentration, 0.1 M, adsorption time t = 8 min. These optimized separation parameters need to be verified if they were workable and practical for separation of Pd(II) from a stock solution containing Pt(IV), Cu (II), Fe(III), Zn(II), Co(II) and Ni(II) impurities.

Separation coefficient of Pd(II) and Pt (IV) ($\beta_{Pd/Pt}$) was expressed as:

$$\beta_{Pd/Pt} = \frac{D_{Pd}}{D_{Pt}} = \frac{q_e(Pd)\cdot C_e(Pt)}{q_e(Pt)\cdot C_e(Pd)} \tag{4}$$

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}). The synthetic sample containing Pd(II), Pt(IV), Cu (II), Fe(III), Zn(II), Co(II) and Ni(II) was prepared, and its compositions were shown in Table-2. The results revealed that 99.1 % Pd(II) but only 1.8 % Pt(IV) were extracted on the adsorbents under the optimum conditions. By calculation, the separation coefficient of Pd(II) and Pt(IV) ($\beta_{Pd/Pt}$) reached 5.4 × 10^3, indicating Pd(II) and Pt(IV) were separated completely. In the other hand, the ones of Fe(III), Cu (II), Co(II), Zn(II) and Ni(II) was below 0.6 %, which suggested the Fe(III), Cu (II), Zn(II), Co(II) and Ni(II) could not be adsorpted on the microsphere.

TABLE-2
COMPOSITION OF THE MIXED SOLUTION

Metal ions	Pd(II)	Pt(IV)	Fe(III)	Cu(II)	Zn(II)	Co(II)	Ni(II)
Conc. (mg L^{-1})	100	100	20	35	30	15	25

Conclusion

The microsphere containing octyl benzoxazolyl sulfoxide was effective for separation of Pd(II) and Pt(IV) from hydrochloric acid media using a suitable extraction parameters: HCl concentration, 0.1 M and contact time t = 8 min, the amount of the microspheres, 100 mg. The above parameters were also workable and practical for extraction and separation of Pd(II) from a stock solution containing Pt(IV), Cu (II), Fe(III), Zn(II), Co(II) and Ni(II) impurities. Under the controlled conditions, Pd(II) and Pt(IV) could be separated efficiently and their separation coefficient reached 5.4 × 10^3. The present technology is full of potential application on separation of Pd(II) and Pt(IV) in hydrochloric acid media. The kinetic experiments showed that the adsorption processes of Pd(II) on the microsphere followed well pseudo second-order kinetic at 25 °C (R^2 = 0.9991).

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REFERENCES

1. A. Sari, D. Mendil, M. Tuzen and M. Soylak, *J. Hazard. Mater.*, **162**, 874 (2009).
2. A. Cieszynska and M. Wisniewski, *Hydrometallurgy*, **113-114**, 79 (2012).
3. R. Kumaresan, K.N. Sabharwal, T.G. Srinivasan, P.R. Vasudeva Rao and G. Dhekane, *Solvent Extr. Ion Exch.*, **26**, 643 (2008).

4. Y.F. Shen and W.Y. Xue, *Sep. Purif. Technol.*, **56**, 278 (2007).
5. A. Cieszynska and M. Wisniewski, *Sep. Purif. Technol.*, **73**, 202 (2010).
6. B. Cote and G.P. Demopoulos, *Solvent Extr. Ion Exch.*, **12**, 393 (1994).
7. V.I. Men'shikov, I.Y. Voronova, O.A. Proidakova, S.F. Malysheva, N.I. Ivanova, N.A. Belogorlova, N.K. Gusarova and B.A. Trofimov, *Russ. J. Appl. Chem.*, **82**, 183 (2009).
8. M. Wiœniewski, A. Jakubiak and J. Szymanowski, *J. Chem. Technol. Biotechnol.*, **63**, 209 (1995).
9. S.V. Bandekar and P.M. Dhadke, *Sep. Purif. Technol.*, **13**, 129 (1998).
10. A. Cieszynska and M. Wisniewski, *Sep. Purif. Technol.*, **80**, 385 (2011).
11. J.M. Sanchez, M. Hidalgo and V. Salvado, *Solvent Extr. Ion Exch.*, **22**, 285 (2004).
12. E. Guibal, N. Von Offenberg Sweeney, T. Vincent and J.M. Tobin, *React. Funct. Polym.*, **50**, 149 (2002).
13. Z. Tu, S. Lu, X. Chang, Z. Li, Z. Hu, L. Zhang and H. Tian, *Mikrochim. Acta*, **173**, 231 (2011).
14. J. Traeger, J. Konig, A. Stadtke and H.J. Holdt, *Hydrometallurgy*, **127-128**, 30 (2012).
15. R.K. Sharma, A. Pandey, S. Gulati and A. Adholeya, *J. Hazard. Mater.*, **209-210**, 285 (2012).
16. H. Sharififard, M. Soleimani and F.Z. Ashtiani, *J. Taiwan Inst. Chem. E*, **43**, 696 (2012).
17. P. Ramakul, Y. Yanachawakul, N. Leepipatpiboon and N. Sunsandee, *Chem. Eng. J.*, **193-194**, 102 (2012).
18. N. Das, *Hydrometallurgy*, **103**, 180 (2010).