



Solid Phase Extraction Preconcentration of Platinum with Microspheres Containing Octyl Benzothiazolyl Sulfoxide

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The extraction of platinum(IV) in hydrochloric acid medium was carried out using the microspheres containing octyl benzothiazolyl sulfoxide as the extractant. Adsorption capacities under optimum conditions were determined. According to the results, the optimum operating conditions for platinum extraction by the microspheres were octyl benzothiazolyl sulfoxide content = 35 % (w/w), hydrochloric acid concentration = 4.0 mol L⁻¹ and contact time = 10 min. Under these optimum operating conditions, Pt(IV) ions adsorption capacities increased with increasing initial Pt(IV) ions concentration and it reached the maximum value at 39 mg g⁻¹. Successful stripping of Pt(IV) from the microspheres were achieved with 0.4 wt % sodium hydroxide solution. The microspheres can be reused at least in ten cycles of extraction-stripping process.

Keywords: Platinum, Solid phase extraction, Microspheres, Octyl benzothiazolyl sulfoxide.

INTRODUCTION

Demand for platinum has increased because of its wide range of applications, such as in vehicle catalytic converter systems and electronic industries, vessels for laboratory and valuable equipments including thermocouple elements. The consumption of platinum by the autocatalyst sector is rising by 5 % each year. As a consequence spent automobile catalysts have emerged as a major secondary source of platinum¹⁻³. The conventional methods for the recovery of platinum are chemical precipitation and the solvent extraction. Precipitation process has inherent disadvantages, such as high chemical consumption and high labor requirements involved in the repeated process, slow kinetics and solid-liquid-separation. The chemical precipitation process increases environmental pollution due to use of toxic chemicals. Also, as aqueous chemistry for the extraction and separation of platinum is extremely complicated⁴. 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.

The literature review reveals that a number of extractants are used for solvent extraction of Pt(IV) from acidic solutions. Solvent extraction behavior of Pt(IV) using various phosphorous based extractants like trioctylphosphine oxide⁵, TBP⁶, di(2-ethylhexyl) amino phosphonic acid⁷, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester⁸, bis(2-ethylhexyl) hydrogen phosphate⁹ and bis(2,4,4-trimethylpentyl) monothio-phosphonic acid¹⁰ were studied. Some other methods were

developed for the rapid and selective extraction of platinum with extractants like Alamine 336¹¹, 2-mercaptobenzothiazole¹², N,N-dioctylglycine¹³, tri-octylamine¹⁴, N,N-dioctylsuccinamic acid¹⁵, N,N-dimethyldithiocarbamoyl ethoxy substituted calix[4]arene¹⁶ and P-50 oxime¹⁷.

However, to overcome various problems associated with solvent extraction systems like third phase problem, compatibility issues with the diluent and the corresponding hydrodynamics related problems, solid phase extraction becomes one of the most sought after methods for recovery of platinum from acidic solutions. Many adsorbents such as activated carbon, clays, metal oxides, silica and zeolite have been used for platinum recovery¹⁸.

The aim of the present paper is to develop a simple, efficient and environmentally friendly process for recovery of platinum from hydrochloric acid medium. In the present work, a new sorbent, the microspheres containing octyl benzothiazolyl sulfoxide have been evaluated for the extraction of Pt(IV) from hydrochloric acid medium. The effect of various parameters such as time, octyl benzothiazolyl sulfoxide content, concentration of hydrochloric acid and initial Pt(IV) ions concentration 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 Pt(IV).

Divinylbenzene (DVB), styrene, azobisisobutyronitrile (AIBN), cyclohexane, polyvinyl alcohol and sodium dodecyl benzene sulfonate (SDBS) (analytical grade) were purchased from Beijing Chemical Reagent Co. Pt(IV) stock solution (5 g L^{-1}): A weighed portion of 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. Octyl benzothiazolyl sulfide was synthesized in our laboratory as literature¹⁹. Divinylbenzene and styrene were purified by washing with a 10 % sodium hydroxide aqueous solution. Other chemicals were all commercially available reagents of analytical grade.

Synthesis of octyl benzothiazolyl sulfoxide: Octyl benzothiazolyl sulfoxide (OBTSO) was synthesized according to the following procedure: Octyl benzothiazolyl sulfide (10 mL), 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 %, 15 mL) was added gradually through a dropping funnel and the reaction mixture was stirred for 2 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: 79.5 %). Its structure (Fig. 1) was verified by ^1H NMR, ^{13}C NMR and mass spectra. ^1H NMR (300 MHz, CDCl_3) 8.09-8.02 (2H, m), 7.60-7.47 (2H, m), 3.30-3.13 (2H, m), 2.02 (1H, m), 1.79 (1H, m), 1.77-1.74 (2H, m), 1.46-1.5 (8H, m), 0.96 (3H, t, $J = 6.6$) ppm; ^{13}C NMR (75 MHz, CDCl_3), δ : 177.85, 153.94, 135.96, 126.91, 126.13, 123.91, 122.30, 56.72, 31.68, 29.05, 28.96, 28.57, 22.58, 21.59, 14.06 ppm; HRMS (ESI) m/z found (%): 296.1137 ($\text{M} + \text{H}$)⁺; calcd. (%): 296.1137 ($\text{M} + \text{H}$)⁺.

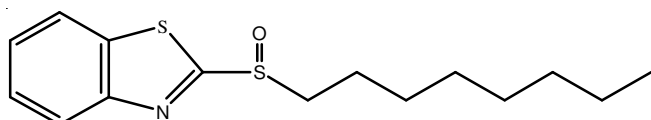


Fig. 1. Structure of octyl benzothiazolyl sulfoxide

Preparation of the microspheres: The microspheres containing octyl benzothiazolyl sulfoxide were prepared by suspension polymerization technique. In a typical procedure, the organic phase was prepared by dissolution of styrene and octyl benzothiazolyl sulfoxide in cyclohexane. Furthermore, the divinylbenzene (DVB) 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 350 rpm for 5 h under the nitrogen atmosphere. The prepared microspheres were collected by filtration, washed with distilled water, dried under vacuum and sieved to get particles lower than $150 \mu\text{m}$.

Static batch method: Solid phase extraction of platinum was performed in batch manner by adding a measured weight of the microspheres in 50 mL of Pt(IV) solution (initial

concentration 1 mg/L) with a known acidity in 150 mL Erlenmeyer flask. These samples were shaken at room temperature using a shaker at 250 rpm for 10 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 Pt(IV) ions. The amount of extracted Pt(IV) ions was calculated according to the differences in the Pt(IV) ions concentrations of the aqueous phase between, before and after the extraction. Adsorption capacities of the microspheres for Pt(IV) ions were calculated by following equation:

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

where Q is the loading capacity of the microspheres (mg g^{-1}); C_0 and C_e are the concentrations of the Pt(IV) ions 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).

RESULTS AND DISCUSSION

Effect of OBTSO contents: The first effective parameter on the Pt(IV) ions adsorption of the microspheres was selected as octyl benzothiazolyl sulfoxide content of the microspheres. During the preparation of the microspheres, the octyl benzothiazolyl sulfoxide content was changed between 0 to 45 % (w/w) for a typical procedure to prepare different the microspheres with different octyl benzothiazolyl sulfoxide contents. Hydrochloric acid concentration of the adsorption medium was 4 mol L^{-1} , initial Pt(IV) concentration was used as 1 g L^{-1} and contact time was fixed as 10 min (this time is the saturation value for Pt(IV) ion adsorption onto the microspheres). The volume of the adsorption medium and the amount of the microspheres were kept as 50 mL and 0.50 g, respectively, in all studies. Adsorption studies were batchwise type and were performed at room temperature. The obtained results are shown in Fig. 2. The result indicated that the adsorption capacity of the microspheres increased with increasing octyl benzothiazolyl sulfoxide content of the microspheres from 0 to 35 %

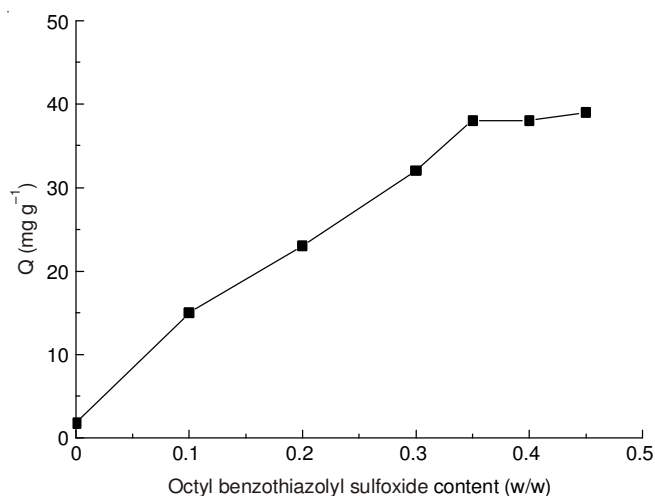


Fig. 2. Effect of octyl benzothiazolyl sulfoxide content over the Pt(IV) ion adsorption. sample volume: 50 mL, Pt(IV) concentration: 1.0 g L^{-1} , HCl concentration: 4.0 mol L^{-1} , the amount of the microspheres: 0.5 g, contact time: 10 min

(w/w). Further increase of octyl benzothiazolyl sulfoxide content from 35 % (w/w) to 45 % (w/w), the adsorption capacity of the microspheres kept constant.

Maximum adsorption for Pt(IV) ions was achieved using the microspheres (*i.e.*, 39 mg g⁻¹ the microspheres) with octyl benzothiazolyl sulfoxide content (*i.e.*, 35 %, w/w) as expected.

Influences of hydrochloric acid concentration: In industrial application for extraction of Pt(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 (octyl benzothiazolyl sulfoxide·H₃O⁺)₂PtCl₆²⁻ 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 Pt(IV) ion concentration was used as 1 g L⁻¹ and the saturation time was defined as 10 min. Pt(IV) ion adsorption values are shown in Fig. 3. The adsorption capacity of the microspheres was very low at lower acidity.

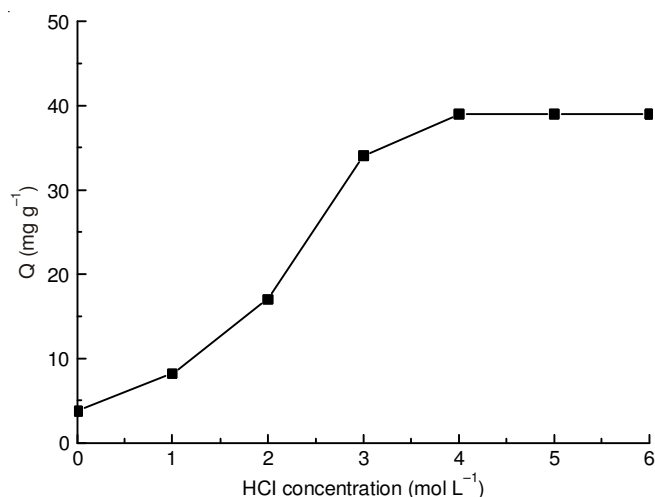


Fig. 3. Effect of the acidity over the Pt(IV) ion adsorption. sample volume: 50 mL, Pt(IV) concentration: 1.0 g L⁻¹, the amount of the microspheres: 0.5 g, octyl benzothiazolyl sulfoxide content: 35 % (w/w), contact time: 10 min

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

Influences of initial metal ion concentration: The effect of initial Pt(IV) ion concentration on the adsorption was evaluated. The microspheres with octyl benzothiazolyl sulfoxide content (*i.e.*, 35 %, w/w) were used in these studies. The obtained adsorption results are shown in Fig. 4. The Pt(IV) ion adsorption capacity increased with increasing the initial Pt(IV) ion concentration from 0.2 to 1 g L⁻¹. It reached the maximum value (*i.e.*, 39 mg g⁻¹ the microspheres) at 1 g L⁻¹ initial Pt(IV) ion concentration. Further increasing the initial Pt(IV) ion concentration from 1 to 1.4 g L⁻¹, the Pt(IV) ion adsorption capacity kept constant. Maximum adsorption was achieved using the microspheres (*i.e.*, 39 mg g⁻¹ the microspheres) with initial Pt(IV) ion concentration (*i.e.*, 1 g L⁻¹) as expected.

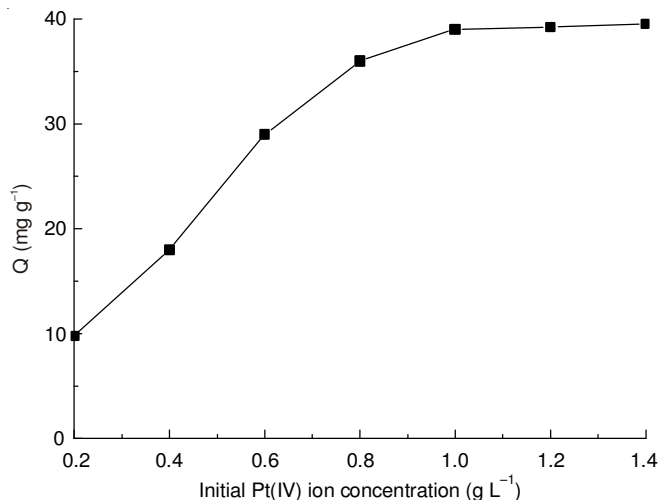


Fig. 4. Effect of the initial Pt(IV) ion concentration over the Pt(IV) ion adsorption. sample volume: 50 mL, HCl concentration: 4.0 mol L⁻¹, the amount of the microspheres: 0.5 g, Octyl benzothiazolyl sulfoxide content: 35 % (w/w), contact time: 10 min

Effects of contact time: To extract Pt(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 Pt(IV) by the microspheres containing octyl benzothiazolyl sulfoxide as a function of time is shown in Fig. 5. 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 15 min. The Pt(IV) ion adsorption capacity increased with increasing contact time from 1 to 10 min. Further increase of contact time from 10 to 15 min, the Pt(IV) ion adsorption capacity kept constant. Therefore, the minimum period of equilibration required for the quantitative extraction of Pt(IV) was found to be about 10 min.

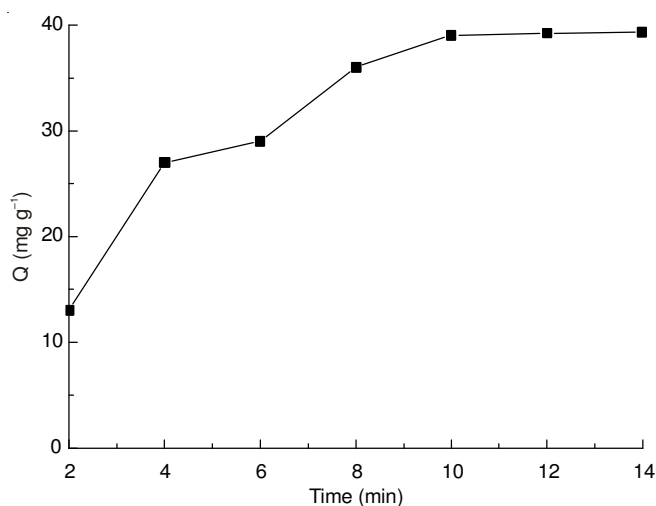


Fig. 5. Effects of contact time over the Pt(IV) ion adsorption. Sample volume: 50 mL, Pt(IV) concentration: 1.0 g L⁻¹, the amount of the microspheres: 0.5 g, Octyl benzothiazolyl sulfoxide content: 35 % (w/w), HCl concentration: 4 mol L⁻¹

Desorption studies: Platinum loaded in the microspheres was stripped with various stripping agents, such as sodium hydroxide, thiourea and nitric acid as stripping agents. In the

following experiments, hydrochloric acid concentration of the adsorption medium was 4 mol L^{-1} , initial Pt(IV) ion concentration was 1 g L^{-1} and octyl benzothiazolyl sulfoxide content of the microspheres was 35 % (w/w) in all experiments of this part of the study. 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 platinum can not be stripped from the microspheres with acid solution and thiourea solution. Sodium hydroxide solution can be used as the effective stripping agent. As can be seen from Fig. 6, by increasing sodium hydroxide concentration from 0.1 to 0.4 wt %, the percentage stripping of Pt(IV) increased from 74.6 to 99.1 %. By further increasing concentration of sodium hydroxide from 0.4 to 0.6 wt %, the percentage stripping of Pt(IV) kept constant. The stripping was quantitative when 0.4 wt % sodium hydroxide solution was used.

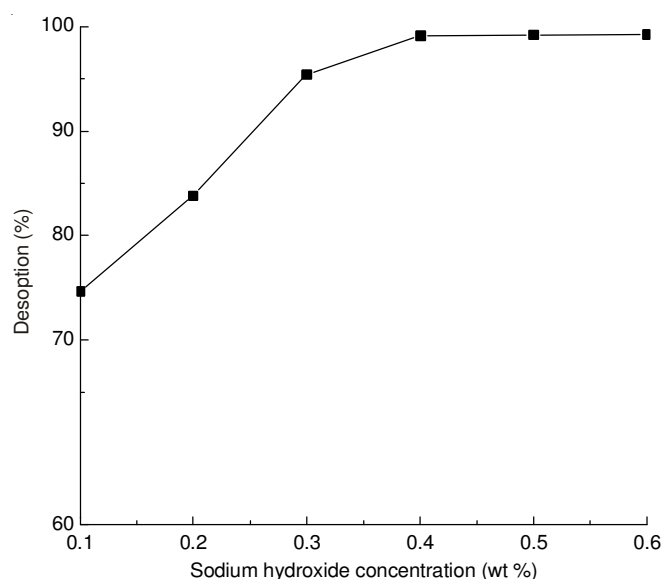


Fig. 6. Influence of sodium hydroxide concentration on the elution of Pt(IV) from the microspheres. Elution volume: 50 mL, desorption time: 5 min

Microspheres stability tests: Reusability of the adsorbents is one of the most important considerations in the adsorption and removal studies of the Pt(IV). At the end of the adsorption-desorption studies, the microspheres were washed with the 0.1 wt % sodium hydroxide solution first and then with distilled water for three times for 5 min in all adsorption-desorption steps. 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 ten cycles of operation. The microspheres showed good reusability and stability towards Pt(IV).

Conclusion

The microspheres containing octyl benzothiazolyl sulfoxide were synthesized and studied as a novel sorbent for Pt(IV) from hydrochloric acid medium. Suspension polymerization method was used in the preparation of microspheres. Extractant capacities of the microspheres for the extractant of Pt(IV) ions from hydrochloric acid solutions under optimum conditions were determined. The Pt(IV) ions extractant capacities increased with increasing initial Pt(IV) ions concentration under the determined optimum conditions. The result showed that the sorption of platinum onto the microspheres is fast, the equilibrium being attained within 10 min. The microspheres were found to be reusable after desorption for several times.

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