

SOLVENT EXTRACTION OF PALLADIUM (II) AND EFFECTIVE SEPARATION OF PALLADIUM(II) AND PLATINUM(IV) WITH SYNTHETIC SULFOXIDE MSO

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Abstract

Extraction performances of Pd(II) and separation behaviors of Pd(II) and Pt(IV) were studied using a synthetic sulfoxide MSO as extractant from hydrochloric acid media. Pd(II) transferring was depended strongly on the MSO and HCl concentration, phase ratio (O/A), contact time, and Pd(II) concentration in stock solution. By controlling MSO and HCl concentration, Pd(II) and Pt(IV) could be separated effectively and the highest separation coefficient reached 758 when MSO and HCl concentration were fixed at 25% (V/V) and 1.5 M, respectively. Pd(II) loaded in organic phase was stripped effectively with a mixed solution containing NH₄Cl and ammonia solutes. The percentage stripping of Pd(II) was 95.1% using 3% (w) NH₄Cl and 3 M NH₃H₂O.

Keywords: MSO; Palladium; Platinum; Separation; Solvent extraction

1. Introduction

It is well known that precious metals which possess special physical and chemical properties are important materials and have been applied widely in industry and technology recently [1-5]. Especially, the demand amount of platinum group metals (PGMs) has increased a lot in industry, furthermore, their demand for higher and even super purity usually is put emphasis on especially as well. To satisfy these demands, new methods for their recovery from ores and spent materials have been prompted [6-8]. However, in consideration of the low natural abundance of the precious metals, traditional production methods, such as precipitation and reducing process methods, do not meet their tremendously increasing demand in industries and other spheres.

Solvent extraction has been proved to be a very efficient and practicable approach for extraction and recovery of the precious metals leached from their low graded sources or spent catalysts [9,10]. Generally, the single extraction of palladium(II) from acidic media is easy and its operating parameters can be controlled simply. Because [Pd(Cl)₄]²⁻ with planar and square structure has lower thermal stability but higher dynamic activity, which is favorable for

[Pd(Cl)₄]²⁻ to have reactions of hydration and ligand exchange in hydrochloric acid media, hence is beneficial to extraction of Pd(I). However, the separation and purification of Pd(II) and Pt(IV) usually is full of difficulty, mainly due to their chemically similar behaviors or synergistic extraction actions in a acidic media, i.e. in hydrochloric acid ambience. So it is necessary and urgent to develop a few applicable extraction and separation processes of palladium and platinum. For decades, much efforts have been made in seeking for high selective extractants used to effectively extract and separate Pd(II) and Pt(IV) [11-15]. Generally, palladium and platinum exist in the same ore thanks to their similar physical and chemical properties. After being leached with nitrohydrochloric acid, Pd(II) and Pt(IV) consist in the same stock solution, which causes tremendous difficulties in separation and purification. A number of extractants have been used to extract and separate Pd(II) and Pt(IV) in the recent years [16-18]. But the main work is still in its early or intermediate study.

In this work, extraction of Pd(II) and separation of Pd(II) and Pt(IV) using synthetic sulfoxide MSO from hydrochloric acid media were investigated. The experiments indicated that efficient extraction of Pd(II) and separation of Pd(II) and Pt(IV) could be realized by mainly controlling extractant and

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hydrochloric acid concentration. The obtained technology can be possibly applied in the separation and purification of Pd(II) and Pt(IV) from hydrochloric acid solution.

2. Experimental

2.1 Materials

The synthesized sulfoxide MSO extractant (R_2SO), which was a mixture and the carbon number of R was $C_5 \sim C_8$ and mass percentage content of S was 10.40%, was used as supplied by South China University of Technology, China. Its important parameters were presented as the following: $d=0.899 \text{ g}\cdot\text{cm}^{-3}$ (28 °C), viscosity $\eta=25 \text{ mPa}\cdot\text{S}$ (25 °C), boiling point $\sim 300 \text{ °C}$ and characteristic absorption of IR of $\nu_{S=O}=1025.34\text{cm}^{-1}$. The IR spectrum of MSO is shown in Fig. 1.

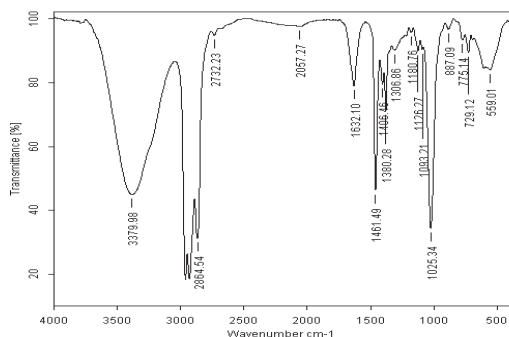
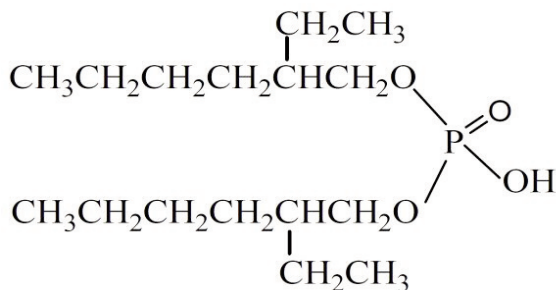


Figure 1. IR spectrum of MSO

The other reagents, except kerosene served as diluted solvent and was of C.A grade, were of analytical reagent grade and used directly as received without any further purification. $PdCl_2$ and H_2PtCl_6 were purchased from Wenda Rare and Precious Reagent Factory in Tianjin, China. The other assisting reagents, including hydrochloric acid, ammonium chloride, ammonia, P204, cupric sulfate, ferrous sulfate and nickel chloride, were purchased from Shanghai Chemical Reagent Co., Ltd, China. The chemical structure of P204 extractant for the base metals is shown as the following:



2.2 Preparation of stock solutions and organic phase

A series of stock solutions containing from 0.2000 to 1.000 $\text{g}\cdot\text{L}^{-1}$ Pd(II) or a mixture with each 1.000 $\text{g}\cdot\text{L}^{-1}$ of Pd(II) and Pt(IV) were prepared by dissolving each $PdCl_2$ and H_2PtCl_6 in 0.1 mol. L^{-1} HCl in the 100 mL of volumetric flask. A synthetic mixing stock solution containing Pd(II) and Pd(IV), as well as Fe(II), Cu(II) and Ni(II) impurities, was prepared by concocting their solutes in 0.1 M HCl. The hydrogen ion (H^+) concentration in all the stock solutions was adjusted using 12 mol. L^{-1} HCl. The organic phases of the desired concentrations were prepared by adding a definite volume of MSO diluted in kerosene into a 50 mL of volumetric flask.

2.3 Extraction of Pd(II) and Pt(IV) with MSO

All experiments were carried out at room temperature ($\sim 303\text{K}$).

For determining the percentage extraction of Pd(II) or Pt(IV), equal volumes (10 mL) of both phases were mixed in a 60 mL of separatory funnel and vigorously shaken for a stipulated time, which was sufficient enough to attain equilibrium in a preliminary experiment. After complete separation of two phases, the metal ion concentration in aqueous solution was determined using an atomic absorption photometer (WFX-110, from Ruili Analysis and Instrument Inc., Beijing, China). The metal concentration in organic phase was obtained by subtraction method.

Percentage extraction (abbreviated as PE%) of Pd(II) or Pt(IV) is calculated as the Eq.(1):

$$PE\% = \frac{[M]_{(o)}}{[M]_{(a, total)}} \times 100 \quad (1)$$

where $[M]_{(o)}$ is the concentration of Pd(II) or Pt(IV) in organic phase, $[M]_{(a, total)}$ is the total concentration of Pd(II) or Pt(IV) in the stock solution before extraction.

Distribution coefficient (D) of Pd(II) or Pt(IV) between the organic and aqueous phases is expressed as the Eq.(2):

$$D = \frac{[M]_{(o)}}{[M]_{(a)}} = \frac{PE\%}{1 - PE\%} \quad (2)$$

where $[M]_{(a)}$ is the concentration of Pd(II) or Pt(IV) in aqueous phase after extraction. Separation coefficient of Pd(II) and Pt(IV) ($\beta_{Pd/Pt}$) is expressed as the Eq.(3):

$$\beta_{Pd/Pt} = \frac{D_{Pd}}{D_{Pt}} = \frac{PE_{Pd}\%(1 - PE_{Pt}\%)}{PE_{Pt}\%(1 - PE_{Pd}\%)} \quad (3)$$

2.4 Separation verification of Pd(II) and Pt(IV) from impurities

The verification experiment was conducted by extracting a mixed solution containing Pd(II) and Pt(IV) as well as Cu(II), Fe(II), and Ni(II) impurities with MSO under the optimized conditions which were obtained by extracting and separating Pd(II) and Pt(IV) only. At first, the mixed solution was contacted with 100 mL of 0.2 M of P204 for 30 min, and the extraction operations were carried out for three stages to remove the impurities. After the two phase separated completely, the extracted aqueous solution was contacted with 100 mL of 25% MSO(V/V) for 5 min, likely the operations were performed for three stages, as a result the Pd(II) was extracted nearly completely. Subsequently, the extracted aqueous solution was adjusted with 12 M hydrochloric acid until its hydrogen ion concentration reached 5.0 M. The resulted solution was contacted with 100 mL of 60% MSO(V/V) for 30 min and the same operations were conducted for four stages.

3. Results and discussion

3.1 Extraction of Pd(II)

In these experiments the following parameters were fixed: $[Pd(II)] = 1.000 \text{ g.L}^{-1}$, hydrochloric acid concentration: 1.5 M, phase ratio $O/A = 1$, contact time $t = 10$ min, to investigate effect of MSO concentration on the extraction of Pd(II) by changing MSO concentration from 5% to 40% (V/V). The results are shown in Fig.2.

From Fig.2, it can be seen clearly that PE% of Pd(II) increased fast as MSO concentration varied from 5% to 25% (V/V), then almost kept constant as the extractant concentration further increased from 25% to 40% (V/V). Under the conditions, PE% of Pd(II) reached 98.9% with 25% (V/V) MSO, which was indicative of that almost all Pd(II) was transferred

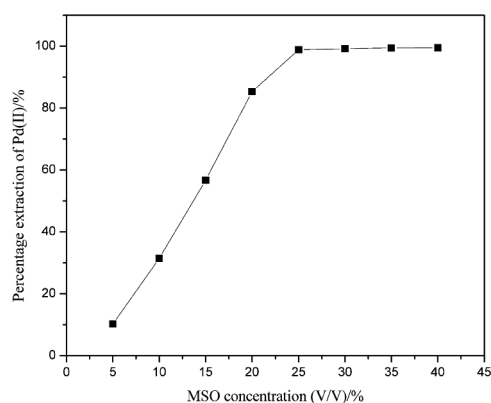


Figure 2. Effect of MSO concentration on the extraction of Pd(II)

from the aqueous solution to the organic phase. The results also demonstrated that Pd(II) could be extracted effectively using 25%(V/V) MSO as the other extracting parameters were fixed.

The contact time of two phases often has a significant effect on the transfer of metal ions. The following experiments were carried out to investigate the contact time of two phases on the extraction of Pd(II) under the other fixed extraction parameters: $[Pd(II)] = 1.000 \text{ g.L}^{-1}$, MSO concentration: 25%(V/V), hydrochloric acid concentration: 1.5 M, phase ratio $O/A = 1$. The results are shown in Fig.3.

From Fig.3, as contact time of two phases varied from 1 to 10 min PE% of Pd(II) had a fast increase first (from 1 to 5 min) then almost kept invariable (from 6 to 10 min). The further experiments exhibited that PE% of Pd(II) had no increase as the contact time further prolonged. The results also displayed that the extraction equilibrium of Pd(II) could be established for 5 min. Hence, the following experiments about Pd(II) extraction all were carried out for 5 min.

The effect of organic/aqueous (O/A) phase ratio on the extraction of Pd(II) was investigated, for it was a significant parameter for the metal extraction and should be provided in extraction technology. The following experiments were conducted using different phase ratios with the other fixed parameters: $[Pd(II)] = 1.000 \text{ g.L}^{-1}$, MSO concentration: 25%(V/V), hydrochloric acid concentration: 1.5 M, contact time $t = 5$ min. The results are shown in Fig.4.

From Fig.4, PE% of Pd(II) increased fast from 41.2 to 98.9% as O/A changed from 0.2 to 1.0 then almost kept constant as O/A varied from 1.0 to 2.0. The results show that it is favorable for Pd(II) extraction using a higher O/A. However, it is unnecessary to use a higher O/A. The suitable O/A should be controlled under 1.0 or so for the efficient extraction of Pd(II).

For the extraction of Pd(II) and Pt(IV) in industry, most of them are carried out in hydrochloric acid media. Furthermore, H^+ concentration can place an important role on the extraction and separation of Pd(II) and Pt(IV). In the following experiments, effect

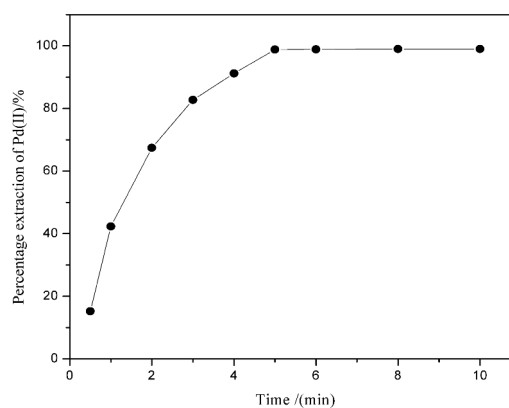


Figure 3. Effect of contact time on the extraction of Pd(II)

of H^+ concentration on the extraction of Pd(II) was determined with the other fixed parameters: $[Pd(II)]=1.000\text{g}\cdot\text{L}^{-1}$, MSO concentration: 25%(V/V), phase ratio $O/A=1.0$, contact time $t=5$ min. The results are shown in Fig.5.

From Fig.5, as a whole, PE% of Pd(II) increased basically with the increasing H^+ concentration. By increasing H^+ concentration from 0.5 to 1.5 M, PE% of Pd(II) varied from 42.6 to 98.9%. As H^+ concentration changed from 1.5 to 3.0 M, PE% of Pd(II) decreased first then increased slowly. Obviously, a “concave” valley curve of PE% of Pd(II) appeared approximately at the corresponding H^+ concentration in the range of 1.5-2.5 M. To further investigate this influence, Pd(II) was extracted with different MSO concentration while H^+ concentration varied from 0.5 to 3.0 M. The results indicated that the similar phenomenon occurred, the same “concave” valley curve of PE% of Pd(II) appeared around at 1.5-2.5 M of H^+ concentration. Our previous work also demonstrated the similar effect in Pd(II) extraction using dibutyl sulfoxide as extractant [14]. We speculated that the concave valley curve of PE% of Pd(II) could be attributed to different extraction mechanisms under different acidity. From Fig.5, Pd(II) can be efficiently extracted by MSO when H^+ concentration controlled at 1.5 M or so.

In addition, the effect of aqueous Pd(II) concentration on PE% of Pd(II) was investigated using 20% (V/V) MSO under the fixed conditions: phase ratio $O/A=1.0$, H^+ concentration: 1.5 M, contact time $t=5$ min. The results are shown in Fig.6.

From Fig.6, PE% of Pd(II) had a clear decreasing tendency as aqueous Pd(II) concentration changed in the range from 0.2000 to 2.000 $\text{g}\cdot\text{L}^{-1}$. However, it decreased slowly (from 98.2 to 85.3%) with Pd(II)

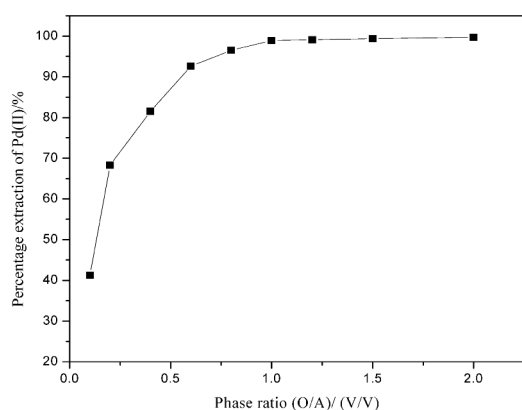


Figure 4. Phase ratio (O/A) on the extraction of Pd(II)

Table 1. Separation coefficient ($\beta_{Pd/Pt}$) of Pd(II) and Pt(IV)

Extractant concentration (%(V/V))	5	10	15	20	25	30	35	40	45	50
Separation coefficient ($\beta_{Pd/Pt}$)	8.2	23.6	37.2	96	758	693	665	629	451	228

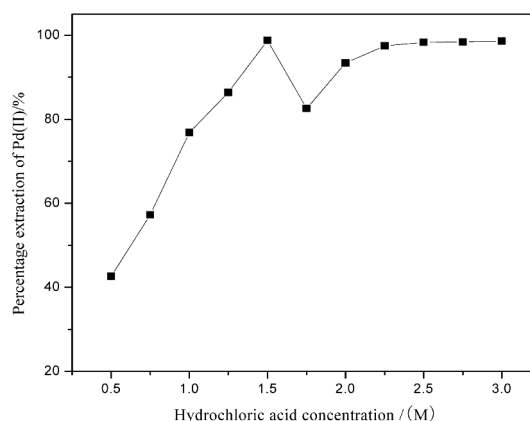


Figure 5. Effect of hydrochloric acid on the extraction of Pd(II)

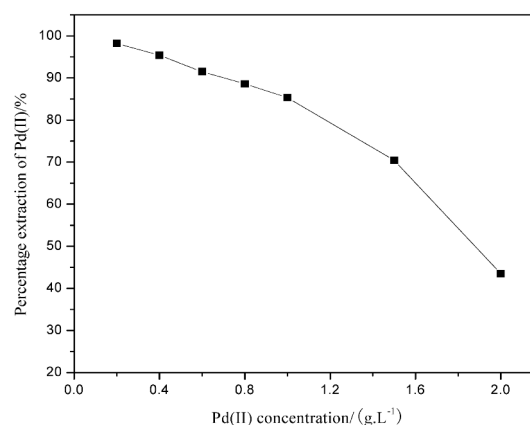


Figure 6. Effect of Pd(II) concentration of aqueous solution on the extraction of Pd(II)

concentration varying from 0.2000 to 1.000 $\text{g}\cdot\text{L}^{-1}$, but it had drastic decrease (from 85.3 to 43.7%) by further increasing Pd(II) concentration from 1.000 to 2.000 $\text{g}\cdot\text{L}^{-1}$. The results show that it was favorable to extract Pd(II) with a lower concentration using a lower concentration of MSO. Of course, the extraction performance of Pd(II) was effective as aqueous Pd(II) concentration was within 0.8000~1.000 $\text{g}\cdot\text{L}^{-1}$ or so even using a lower concentration of MSO.

3.2 Extraction and separation of Pd(II) and Pt(IV) from HCl solution

To investigate the optimal separating parameters of Pd(II) and Pt(IV), the following experiments were carried out by altering MSO concentration with the other fixed parameters: $[Pd(II)]=[Pt(IV)]=1.000\text{g}\cdot\text{L}^{-1}$, hydrochloric acid concentration: 1.5 M, phase ratio:

O/A=1.0, contact time: =5 min. The results display in Fig.7. It can be seen from Fig.7, by increasing MSO concentration, PE% of both Pd(II) and Pt(IV) increased. However the PE% of Pd(II) had a rapid increase but the one of Pt(IV) merely had a slight increment, i.e. PE% of Pd(II) increased in the range from 10.2 to 98.9% while the one of Pt(IV) increased from 1.3 to 10.6% as MSO concentration varied from 5 to 25% (V/V). By increasing MSO concentration continuously from 25 to 65% (V/V), PE% of Pd(II) almost kept constant while the one of Pt(IV) increased greatly from 10.6 to 71.2%. Based on the different tendency of PE% of Pd(II) or Pt(IV) by varying MSO concentration, Pd(II) and Pt(IV) could be separated efficiently with lower concentration of MSO, and its suitable concentration should be controlled within 20-25% (V/V) with the other fixed conditions. In addition, the experimental separation coefficient ($\beta_{Pd/Pt}$) of Pd(II) and Pt(IV) is shown in table 1. From table 1, $\beta_{Pd/Pt}$ increased first (MSO concentration from 5% to 25% (V/V)) then decreased (MSO concentration from 25% to 65% (V/V)), and $\beta_{Pd/Pt}$ reached its maximum experimental value (758). The

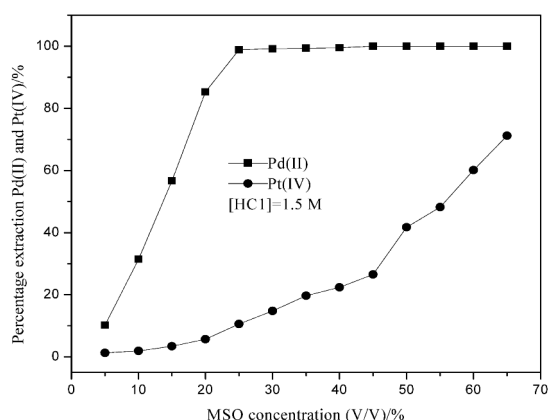


Figure 7. Effect of MSO concentration on the separation of Pd(II) and Pt(IV)

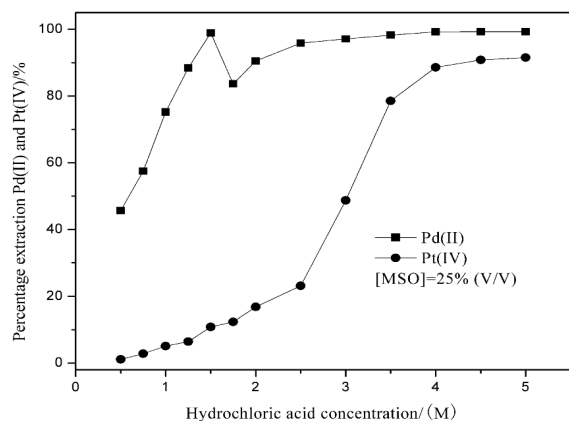


Figure 8. Effect of hydrochloric acid concentration on the separation of Pd(II) and Pt(IV)

results displayed that Pd(II) and Pt(IV) can be separated efficiently with 25% (V/V) MSO.

For the extraction and separation of Pd(II) and Pt(IV) from hydrochloric acid media, the H^+ concentration may place an important role. So following experiments were conducted to investigate the properties of extraction and separation of Pd(II) and Pt(IV) by changing hydrochloric acid concentration with the other fixed parameters: $[Pd(II)]=Pt(IV)]=1.000g.L^{-1}$, MSO concentration, 25% (V/V), phase ratio O/A=1.0, contact time $t=5$ min. The results are shown in Fig.8.

It can be seen from Fig.8 that hydrochloric acid concentration had an important effect on the extraction and separation of Pd(II) and Pt(IV). In a whole, PE% of Pd(II) increased basically with the increasing H^+ concentration, and it reached 99.3% when H^+ concentration was 5 M. Likewise, a concave valley curve of PE% of Pd(II) appeared approximately at the corresponding H^+ concentration at 1.25-2.0 M, which phenomenon was detected when single Pd(II) in aqueous solution was extracted by MSO. In addition, PE% of Pd(II) also reached 98.8% with 1.5 M HCl, which indicated that addition of Pt(IV) had nearly no effect on the extraction of Pd(II). For Pt(IV), its PE% increased continuously by increasing HCl concentration from 0.5 to 5.0 M. But, it had a slow and slight increase from 1.2 to 23.1% accompanying increase of HCl concentration from 0.5 to 2.0 M, but had a fast increase (from 23.1 to 88.6%) with increasing HCl concentration from 2.0 to 4.0 M, then had a slight accretion (from 88.6 to 91.5%) by further increasing HCl concentration from 4.0 to 5.0 M. The results demonstrated that effective separation of Pd(II) and Pt(IV) could be realized by controlling a lower concentration of HCl, such as 1.5 M or so.

3.3 Verification of separating Pd(II) and Pt(IV) from a mixed solution containing Fe(II), Cu(II) and Ni(II) impurities

Based on Fig.7 and 8, when Pd(II) and Pt(IV) existed in the stock solution alone, both of them could be separated efficiently by controlling MSO and HCl concentration. The optimum extraction separation parameters of Pd(II) and Pt(IV) were summarized as the following: MSO concentration, 25%(V/V), HCl concentration, 1.5 M, O/A=1.0, contact time $t=5$ min. These optimized separation parameters should be verified if they were workable and practical for separation of Pd(II) and Pt(IV) from a stock solution containing Fe(II), Cu(II) and Ni(II) impurities. A simulated stock solution containing Pd(II), Pt(IV), Cu(II), Fe(II), Ni(II) and 1.5 hydrochloric acid was prepared as mentioned in the experimental section.

The composition of the solution is shown in Table 2.

Table 2. Composition of the mixed solution

Metal ion	Pd(II)	Pt(IV)	Fe(II)	Cu(II)	Ni(II)
Concentration (mg.dm ⁻³)	250	1000	100	600	300

At first, the mixed stock solution was treated with 0.2 M of P204 for three times. The results are shown in table 3.

From table 3, the percentage extractions of the overall impurity metals were over 93% but Pd(II) and Pt(IV) almost had no transferring, which indicated that the impurity metals had been removed basically. Subsequently, the mixed aqueous solution was extracted with 25% (V/V) MSO when the O/A and contact time was controlled as 1.0 and 5 min respectively for three stages. The results are shown as table 4

From table 4, the gross PE% of Pd(II) reached 99.9%, indicating Pd(II) was extracted completely, while the one of Pt(IV) was only 12.8%. As a result, the separation coefficient of Pd(II) and Pt(IV) reached 6.8×10^3 , suggesting that Pd(II) and Pt(IV) had been separated efficiently.

Subsequently, the residual solution was adjusted with 12 M hydrochloric acid until the HCl concentration reached 5.0 M. Then the solution was extracted with 60% (V/V) MSO when the O/A and contact time were controlled as 1.0 and 30 min respectively for four stages. The experiments show that the gross PE% of Pt(IV) was more than 99%.

Table 4. Residual concentration and percentage extractions of metal ions with 25% (V/V) MSO after three stages

Metal ion	Pd(II)	Pt(II)	Fe(II)	Cu(II)	Ni(II)
Residual concentration (mg.dm ⁻³)	0.2	871	6.3	11.2	5.1
Gross percentage extraction (%)	99.9	12.8	7.4	8.9	5.6

3.4 Stripping properties of palladium

The stripping performances of Pd(II) loaded in organic phase were investigated using a mixture solution composed of NH₄Cl and NH₃·H₂O solutes. Firstly, the effect of NH₄Cl concentration on the stripping percentage stripping of Pd(II) was studied with the following fixed parameters: concentration of Pd(II) loaded in organic phase: 0.988 g.L⁻¹, ammonia concentration: 3 mol.L⁻¹ M, aqueous/organic (A/O) phase ratio: 1.0, contact time $t=30$ min. The experiments were performed with different concentrations of NH₄Cl. The results are shown in Fig.9.

From Fig.9, at fixed ammonia concentration, percentage stripping of Pd(II) increased first (from 85.7 to 95.1%) accompanying increase of NH₄Cl concentration from 1 to 3% (ω) then decreased (from 95.1 to 82.9%) by further increasing NH₄Cl concentration from 3 to 7% (ω). It was obvious that

Table 3. Residual concentration and percentage extractions of ingredients with P204 after three stages

Metal ion	Pd(II)	Pt(IV)	Fe(II)	Cu(II)	Ni(II)
Residual concentration (mg.dm ⁻³)	249	999	6.8	12.3	5.4
Gross percentage extraction (%)	0.4	0.1	93.2	98	98.2

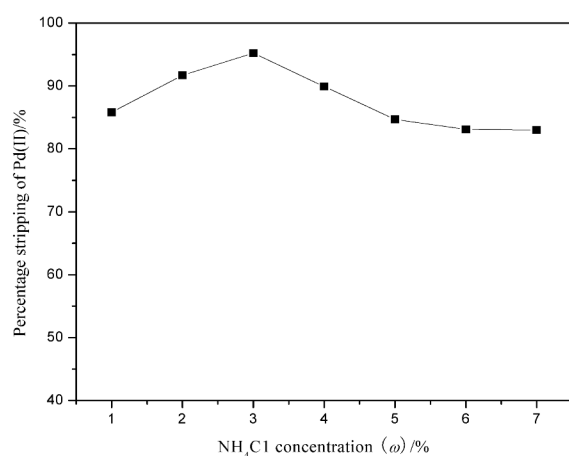


Figure 9. Effect of NH₄Cl concentration on the stripping of Pd(II)

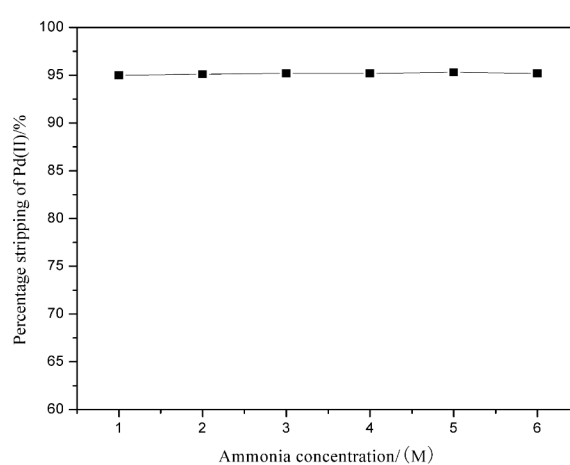


Figure 10. Effect of ammonium hydroxide on the stripping of Pd(II)

the loaded Pd(II) could be effectively stripped with 3% (ω) NH_4Cl solution.

Experiments were carried out to check the effect of ammonia concentration on stripping of Pd(II) at a fixed NH_4Cl concentration (3%) with the other fixed parameters: concentration of Pd(II) loaded in organic phase: $0.988 \text{ g}\cdot\text{L}^{-1}$, NH_4Cl concentration: 3%, aqueous/organic (A/O) phase ratio:1.0, contact time $t=30$ min. The results are shown in Fig.10.

From Fig.10, by altering ammonia concentration in the range from 1 to 6 M, percentage stripping of Pd(II) almost kept invariable and its value was about 95% or so. The experiments demonstrated that the ammonia concentration had no effect on the percentage stripping of Pd(II). However, the interface between the aqueous and organic phases was muddy and full of much foam if no ammonia was added, furthermore, the separation time of two phases prolonged. Nevertheless, the situation could be improved greatly as soon as a certain concentration of ammonia was added to the stripping system.

4. Conclusions

The synthetic sulfoxide MSO diluted in kerosene was effective to extract Pd(II) from hydrochloric acid media using a suitable extraction parameters: $[\text{Pd(II)}]=1.000 \text{ g}\cdot\text{L}^{-1}$, MSO concentration: 25% (V/V), HCl concentration: 1.5 M, phase ratio O/A=1.0, contact time $t=5$ min. The above parameters were also workable and practical for extraction and separation of Pd(II) and Pt(IV) no matter they existed in the stock solution only or with several impurities such as Cu(II), Fe(II) and Ni(II). Under the controlled conditions, Pd(II) and Pt(IV) could be separated efficiently and their separation coefficient reached 758. The present technology is full of potential application on the extraction and separation of Pd(II) and Pt(IV) in hydrochloric acid media.

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