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Solvent Extraction and Stripping of Pd(II) Cyanide in Cetyltrimethylammonium Bromide System

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The solvent extraction of Pd(II) from alkaline cyanide solution by using cetyltrimethylammonium bromide as extractant has been investigated. Palladium(II) was extracted quantitatively with cetyltrimethylammonium bromide in benzene. Ammonium thiocyanate solution could be used as stripping agent. Extraction parameters of Pd(II), including cetyltrimethylammonium bromide concentration, contact time of aqueous and organic phases, organic/aqueous (O/A) phase ratio and NH_4SCN concentration of aqueous phase, were studied. Almost all of the $Pd(CN)_4^{2-}$ (> 99 %) was transferred from the aqueous phase into the organic phase. Most of the Pd(II) in the organic phase can be stripped with ammonium thiocyanate aqueous solutions. The possible mechanisms of extraction and stripping were discussed.

Key Words: Palladium, Solvent extraction, Alkaline cyanide solution.

INTRODUCTION

The solvent extraction technique is one of the most versatile methods used for the removal, separation and concentration of metallic species from mixed metal aqueous media. In recent years, the solvent extraction technique also has become a suitable method for separation of palladium from low concentrated sources. Various reagents have been studied and proposed, including hydroxyoxime, alkyl derivative of 8-hydroyquinoline, neutral organophosphorus compound, ketoxime, hydrophobic amine and dialkyl sulphide and sulphoxide[1-9].

Usually, these extraction systems can extract palladium from weak acid solution, but the industrial cyanide solution is alkaline (pH = 10-11). We have studied the extraction of gold(I) from alkaline cyanide solution using quaternary ammonium salts, such as trialkylmethlammonium chloride (N_{263}) and cetyltrimethylammonium bromide (CTAB)[10-16]. Up to now, no report has been found to make use of this kind of quaternary ammonium salt improve palladium percent extraction.

This work has attempted to study the application of the quaternary ammonium salt, cetyltrimethylammonium bromide (CTAB), in the extraction of Pd(II) from alkaline cyanide solution with the addition of octanol as a modifier. The results showed that almost all of the $Pd(CN)_4^{2-}$ (> 99 %) was extracted into the organic phase during extraction and that most of palladium was transferred from the loaded organic phase into the aqueous phase during the stripping process. This could then provide a potential technique for palladium recovery in industry.

EXPERIMENTAL

A Z-2000 polarized zeeman atomic absorption spectrophotometer (Hitachi High-Technologies Corporation, Japan) was used to measure the concentration of Pd(II). The operating conditions were carried out according to the recommendations of manufacturer. The wavelengths selected were as follows: Pd 247.6 nm.

Cetyltrimethylammonium bromide (CTAB), ammonium thiocyanate (NH_4SCN), octanol and benzene (analytical grade) were purchased from Beijing Chemical Reagent Co. $Pd(CN)_4^{2-}$ was supplied by Yunnan Gold Group Co. Other chemicals were all commercially available reagents of analytical grade.

Cetyltrimethylammonium bromide was dissolved in benzene. Octanol was chosen as a cosolvent and the organic phase used containce 40 % (v/v) octanol in benzene. Cetyltrimethylammonium bromide solutions were made by dissolution in calculated volumes of octanol and benzene. Stock solution of palladium was prepared by diluting $Pd(CN)_4^{2-}$ in ultra-pure water.

General extraction procedure: Equal volumes (10 mL) of both phases were mixed and vigorously shaken for 5 min, which was sufficient enough to attain equilibrium in a preliminary experiment. After phase separation, the concentration of Pd(II) in aqueous solution was determined by an atomic absorption photometer. These results were further used to estimate the extraction efficiency of metal. The amount of extracted metal ion was calculated according to the differences in the metal concentrations of the aqueous phase between, before and after the extraction.

RESULTS AND DISCUSSION

Influences of the extractant concentration: To investigate the effect of cetyltrimethylammonium bromide (CTAB) concentration on the extraction performances of Pd(II), the experiments were performed at the fixed conditions. The results are shown in Fig. 1. As can be seen from Fig. 1, CTAB dissolved in benzene with the extractant concentration varying from 0.0004 to 0.005 mol L^{-1}. The percentage extraction of Pd(II) increased in the range from 23.3-99 % by increasing CTAB concentration from 0.0004 to 0.004 mol L^{-1}. Further increasing CTAB concentration from 0.004 to 0.005 mol L^{-1}, the percentage extraction of Pd(II) kept constant. 0.004 mol L^{-1} CTAB was needed for quantitative extraction of Pd(II) from a alkaline cyanide solution solution containing 0.1 g L^{-1} palladium.

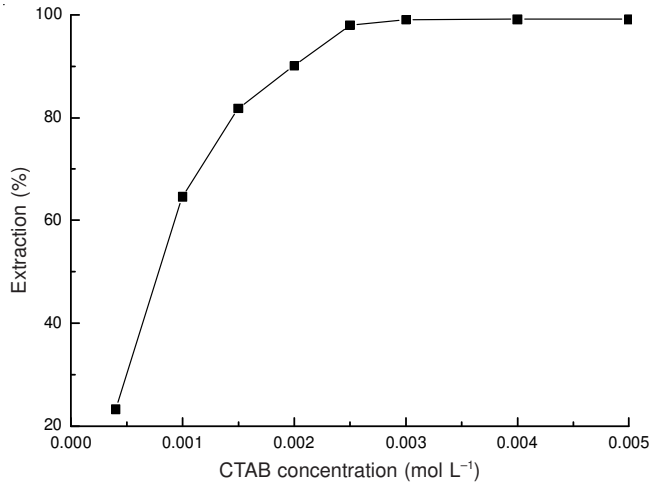

Fig. 1. Effect of extractant concentration on the extraction of Pd(II); $C_{Pd(II)}$: 0.1 g L^{-1}, organic/aqueous: 1.0, contact time: 5 min

Influences of contact time: To extract Pd(II) efficiently by controlling an optimal contact time of aqueous and organic phases, the experiments were carried out with different contact time at other fixed extraction parameters. The results are shown in Fig. 2. 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 0.5 to 10 min. The percentage extraction of Pd(II) increased in the range from 96 to 99 % by in increased of contact time from 0.5 to 5 min. Further increasing contact time from 5 to 10 min, the percentage extraction of Pd(II) kept constant. Therefore, the minimum period of equilibration required for the quantitative extraction of palladium was found to be 5 min.

Influences of organic/aqueous (O/A) phase ratio: To obtain optimal organic/aqueous for extraction of Pd(II), the following experiments were performed at other fixed extraction parameters. The results are shown in Fig.3. As can be seen from Fig.3, by increasing organic/aqueous from 0.5-1.0, the percentage extraction of Pd(II) increased from 97 to 99 %. By further increasing organic/aqueous from 1.0 to 2.0, the percentage extraction of Pd(II) kept constant. Therefore, Pd(II) can be extracted efficiently by controlling organic/aqueous (O/A) phase ratio,1.0.

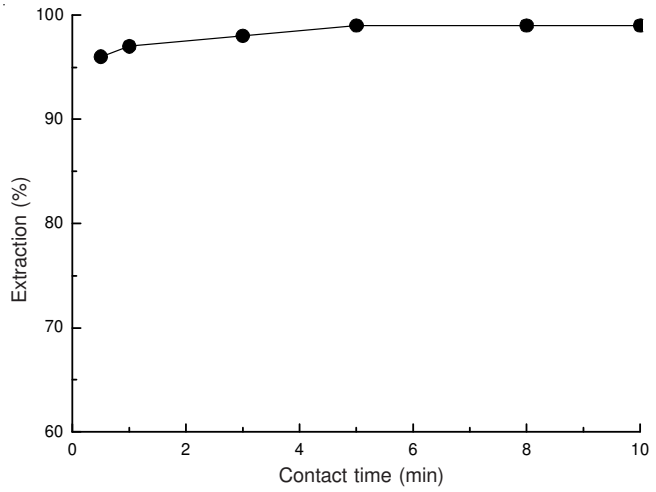

Fig. 2. Effect of contact time on the extraction of Pd(II); $C_{Pd(II)}$: 0.1 g L^{-1}, organic/aqueous: 1.0, C_{CTAB} 0.004 mol L^{-1}

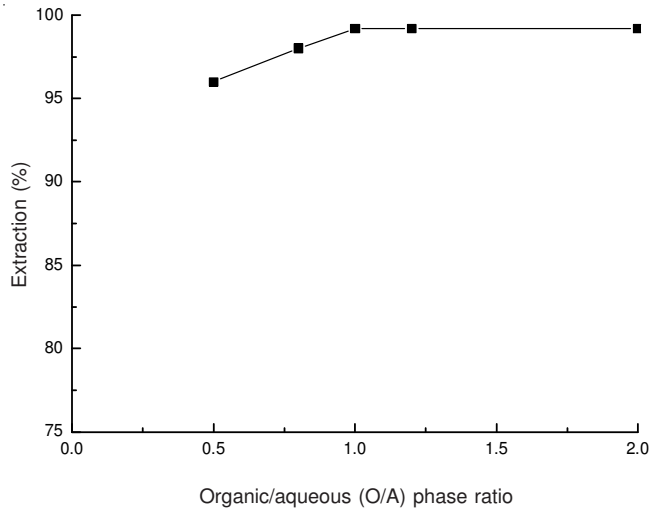

Fig. 3. Effect of organic/aqueous on the extraction of Pd(II); $C_{Pd(II)}$: 0.1 g L^{-1}, contact time: 5 min, C_{CTAB} 0.004 mol L^{-1}

Influences of ammonium thiocyanate concentration on stripping of Pd(II): Fig. 4 shows the effect of ammonium thiocyanate (NH_4SCN) concentration in the aqueous solution on the stripping of Pd(II). With the increase of NH_4SCN concentration, the stripping percentage increases markedly at first and then only slightly. When the NH_4SCN concentration reaches 0.1 mol/L, the stripping percentage is leveled. Maximum stripping was 99 %, which suggests that NH_4SCN is also one of the efficient stripping agents for the separation of Pd(II).

For continuous operation, the organic phase should be reproduced after a stripping process. To investigate the reuse of CTAB- benzene-octanol, an organic phase that had been stripped with a 0.1 mol L^{-1} NH_4SCN aqueous solution was used to extract another alkaline cyanide solution with 0.1 g L^{-1} palladium(II). The results show that most of palladium(II) could be extracted into the recycled organic phase. It is concluded that the reuse of the organic phase for industrial application is possible.

Influences of cosolvent content on the extraction: Pure diluent (benzene) can not extract Pd(II) even with the addition of surfactant. It is very difficult to disengage because the solvent extraction system forms the third phase. When the

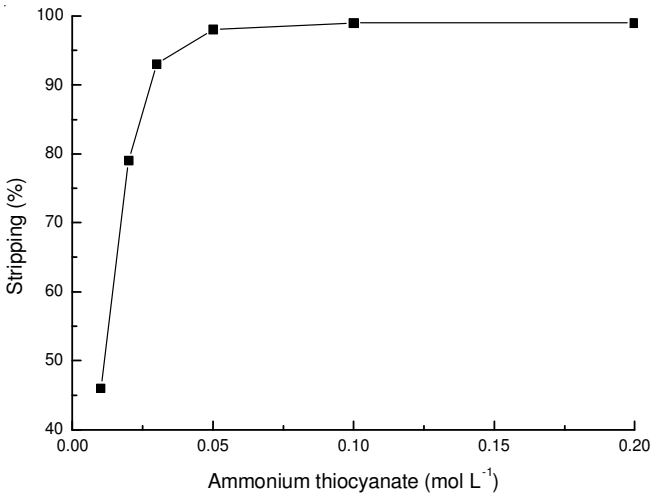

Fig. 4. Effect of stripping reagent concentration on the stripping of Pd(II); $C_{Pd(II)}$: 0.1 g L^{-1}, contact time

volume percentage of octanol is greater than 20 % (v/v), the extraction percentage of palladium is higher than 99 %. When its content in the organic phase is 40 %, the extraction percentage remains essentially unchanged. The palladium was almost quantitatively extracted into the organic phase. It can be seen that the octanol plays an important role during the extraction. Without octanol, practically all palladium remains in the aqueous phase. The addition of octanol remarkably enhances the extraction of palladium. This means that octanol is excellent cosolvent.

Possible mechanism of extraction and stripping: When CTAB is added into alkaline cyanide solution, $Pd(CN)_4^{2-}$ and $CTAB^+$ form electric neutral ion-pair and some of them form white fine precipitates. Electric neutral ion-pair assembling between organic phase and aqueous phase form the third phase. CTAB can be dissolved in benzene to form a w/o microemulsion (reversed micelles) with addition of a cosolvent (*e.g.*, octanol). This microemulsion of CTAB/ octanol/ benzene is used here to extract $Pd(CN)_4^{2-}$. The mechanism of extraction Pd from alkaline cyanide solution follows an ion-association mechanism.

It is well known that the large cation such as $CTAB^+$ tends to combine with a large anion to form an easily extractable ion-pair. SCN^- is such a bulky anion. When aqueous NH_4SCN solution was mixed with the palladium-loaded organic phase, competition occurred between SCN^- and $Pd(CN)_4^{2-}$ for combination wth $CTAB^+$ to form an ion-pair. The mechanism of stripping Pd from palladium-loaded organic phase follows an ion-exchange mechanism.

Conclusion

The solvent extraction of Pd(II) from alkaline cyanide solution was investigated using cetyltrimethylammonium bromide (CTAB) as an extractant. Extraction parameters of Pd(II) were obtained and summarized as the following: CTAB concentration, 0.004 mol L^{-1} ; organic/aqueous (O/A) phase ratio, 1.0; contact time of two phases 5 min. Pd(II) loaded in organic phase could be stripped efficiently using an ammonium thiocyanate (NH_4SCN) solution.

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REFERENCES

1. A. Cieszynska and M. Wisniewski, *Sep. Purif. Technol.,* **73**, 202 (2010).
2. E.A. Mowafy and H.F. Aly, *J. Hazard. Mater.,* **149**, 465 (2007).
3. B. Swain, J. Jeong, S.K. Kim and J.C. Lee, *Hydrometallurgy*, **104**, 1 (2010).
4. J. Traeger, J. Konig, A. Stadtke and H.J. Holdt, *Hydrometallurgy*, **127-128**, 30 (2012).
5. A. Zhang, G. Wanyan and M. Kumagai, *J. Solution Chem*., **33**, 1017 (2004).
6. S. Kiyoyama, S. Yonemura, M. Yoshida, K. Shiomori, H. Yoshizawa, Y. Kawano and Y. Hatate, *React. Funct. Polym*., **67**, 522 (2007).
7. P. Giridhar, K.A. Venkatesan, T.G. Srinivasan and P.R. Vasudeva Rao, *Hydrometallurgy*, **81**, 30 (2006).
8. L. Pan and Z.D. Zhang, *Miner. Eng*., **22**, 1271 (2009).
9. S.P. Feng, Z.J. Huang and M.J. Xie, *Asian J. Chem*., **24**, 3557 (2012).
10. T.X. Zhang, B.G. Huang, W.J. Zhou, H.C. Gao, J. Chen, H.S. Wu and J.G. Wu, *J. Chem. Technol. Biotechnol*, **76**, 1107 (2001).
11. J.Z. Jiang, W.J. Zhou, H.C. Gao, J.G. Wu and G.X. Xu, *Hydrometallurgy*, **70**, 73 (2003).
12. J.Z. Jiang, Y.F. He, H.C. Gao and J.G. Wu, *Solvent Extr. Ion Exch*., **23**, 113 (2005).
13. G. Ma, W.F. Yan, J. Chen, W.J. Zhou, J.G. Wu and G.X. Xu, *Solvent Extr. Ion Exch*., **18**, 1179 (2000).
14. X.J. Pan and J. Chen, *Rare Metals*, **18**, 88 (1999).
15. X.J. Yang, K. Huang, Z.J. Huang, Q.Y. Wei and J. Chen, *Solvent Extr. Ion Exch*., **25**, 299 (2007).
16. X.J. Yang, K. Huang, Q.Y. Wei, Z.J. Huang, J. Chen and J.G. Wu, *Solvent Extr. Ion Exch*., **26**, 556 (2008).