

Direct Extraction of Palladium from Aqueous Solution with Ionic Liquid in Absence of Chelating Agent

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The extraction of palladium(II) chloride by 1-alkyl-3-methylimidazolium hexafluorophosphate [C₄MIM][PF₆] ionic liquids in the absence of a chelating agent was evaluated over a wide range of acidity. Essentially quantitative extraction of trace and macro amounts of palladium is easily accomplished from the pH 4.0 Britton-Robinson buffer solutions by 1.50 g [C₄MIM][PF₆]. Optimum conditions such as shake time and centrifuging time, extraction temperature, aqueous phase acidity, sample volume, dosage of [C₄MIM][PF₆] were established for the extraction of palladium. The proposed method was applied to extract trace amounts of Pd(II) in synthetic samples and the waste water of catalyst of fuel cell with satisfactory results.

Key Words: Extraction, Palladium, Ionic liquids.

INTRODUCTION

Palladium is a metal of economic importance due to its extensive use in jewellery, coating agents, brazing alloys, petroleum, electrical industries and catalytic chemical. Palladium, together with other precious metals, now became also metals of environmental relevance with the introduction of the industrial waster. These metals are emitted into environment and later can be taken up by plants growing and accumulated by aquatic animals. Some of Pd compounds have been reported as a strong human allergens¹⁻⁴.

Therefore extraction and recovery of palladium from and palladium-containing industrial waste streams is important both environmentally and economically. There are various types of processes available such as liquid-liquid extraction^{5,6}, electrochemical preconcentration^{7,8} and co-precipitation^{9,10} to remove or recover palladium. Anion exchange resins^{11,12} as well as the ability to form chelate complexes^{13,14} are also widely used in enrichment procedures based on solid phase extraction (SPE). Ultrasound-dispersion has been successfully employed for the separation and preconcentration of palladium¹⁵.

Room-temperature ionic liquids (ILs) are widely used as a replacement for conventional volatile organic compounds in electrochemical, catalytic reaction, separation and bio-processes¹⁶⁻¹⁷. It is well known that ionic liquids have numerous advantages as a type of green chemical and it is possible to adjust their properties to the requirements of the process¹⁸.

Due to the low flammability and vapor pressure of ionic liquids, in recent years attempts have been made to extract metal ions from aqueous waste solutions using them. But much of these research work was using the ionic liquids with an organic extractant or some improved functional ionic liquids¹⁹⁻²⁴.

In this paper, it is the first time that 'classical' ionic liquids show marked extraction properties towards Pd(II) ions. A 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquids was used to extract the Pd(II) form aqueous solution in the absence of a chelating agent in the ionic liquid phases. The extraction operating factors of Pd(II) by the ionic liquids was also studied by our work.

EXPERIMENTAL

A ZEE nit 700 (Analytik Jena, Germany) atomic absorption spectrometer was used for determining Pd(II). The palladium hollow cathode lamps were run under the conditions recommended by the manufacture. MT-31 YAMATO Touch mixer (Yamato Scientific Co. Ltd.).

All chemicals were of analytical grade and were used without previous purification. The laboratory glassware was kept overnight in a 10 % (v/v) nitric acid solution. Before using, the glassware was washed with deionized water and dried in a dust free environment.

A Pd(II) of 1.0 mg/mL stock solution was prepared by dissolving a weighed amounts of Pd(II) chloride into 5.0 mL

0.1 mol/L hydrochloric acid and diluted to 100 mL with deionized water. 10 µg/mL palladium solution was freshly prepared by appropriate dilution from the 1 mg/mL Pd(II) stock solution.

Britton-Robinson buffer solutions (B-R) were prepared by mixing the mixed acid (composed of 0.04 mol/L H₃PO₄, AcOH and H₃BO₃) with 0.2 mol/L NaOH in proportion. The buffer solutions were prepared to adjust the acidity of the system.

General procedure: Extraction experiments were performed by contacting 1.50 g of ionic liquid and 1.0 mL of Pd(II) solution in B-R buffer solution, pH 4.1. They were kept mixing on the mixer for 5 min at room temperature and centrifuging to separate the two phases. The biphasic system was shaken to ensure it was fully mixed and then centrifuged to separate the two phases after extraction. The upper aqueous phase was taken out and measured with flame atomic absorption spectrometry to determine the concentration of palladium that was left in the aqueous phase. Then Pd(II) ion concentration in ionic liquid was calculated as the difference.

Ionic liquids were synthesized by following a slightly modified reported procedure²⁵. Alkyl bromide was used instead of the corresponding chloride to prepare alkylmethylimidazolium salts. In this way reactions proceeded more rapidly and quantitative yields and nearly colourless final products were obtained.

Extraction efficiency: All measurements were performed at least twice under the same conditions and the relative standard deviations were less than 5 %. The concentration of palladium in the aqueous phase was determined by FAAS and the concentration of Pd(II). In the ionic liquid phase were calculated from the difference between the palladium concentrations in the aqueous phase before and after extraction.

The extraction behavior described in this work was evaluated as extraction efficiency (E %), which is defined as:

$$E (\%) = \left(1 - \frac{C_f}{C_i} \right) \times 100 \%$$

where C_i is the initial concentration of palladium in the aqueous solution before extraction and C_f is the final concentration of palladium remaining in the aqueous solution after extraction.

RESULTS AND DISCUSSION

Effect of equilibration time and centrifugation time on the extraction efficiency: The influence of equilibration time and centrifugation time with a range of 0-20 min was observed. The equilibration time and centrifugation time have no significant effect on the extraction efficiency (E %). So the equilibration time of 3 min and centrifugation time at 3500 rpm of 3 min were selected for the entire procedure, respectively.

Effect of pH on the extraction efficiency: The effect of pH on the extraction efficiency (E %) was recorded in the range pH 2.0-12.0 Fig. 1. As could be seen from Fig. 1. The extraction efficiency (E %) got the maximal value at pH 4.1. So in the subsequent research the pH of the solution was adjusted at 4.1 by using B-R buffer solution.

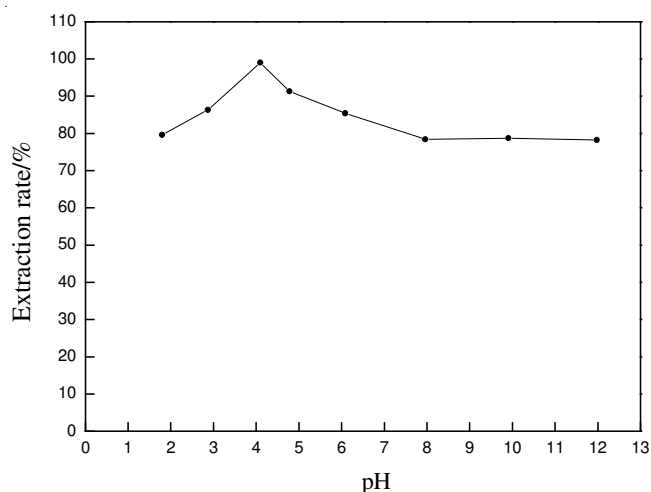


Fig. 1. Effect of pH on the extraction rate (C_{Pd(II)} = 15 µg/mL)

Effect of dosage of [C₄MIM][PF₆] on the extraction efficiency: The effect of the dosage of [C₄MIM][PF₆] in the systems has been investigated on the extraction efficiency (E %) of Pd(II) in the range of 0.25-2.25 g and the results are illustrated in Fig. 2. In this work, [C₄MIM][PF₆] dosage of 1.5 g was adopted.

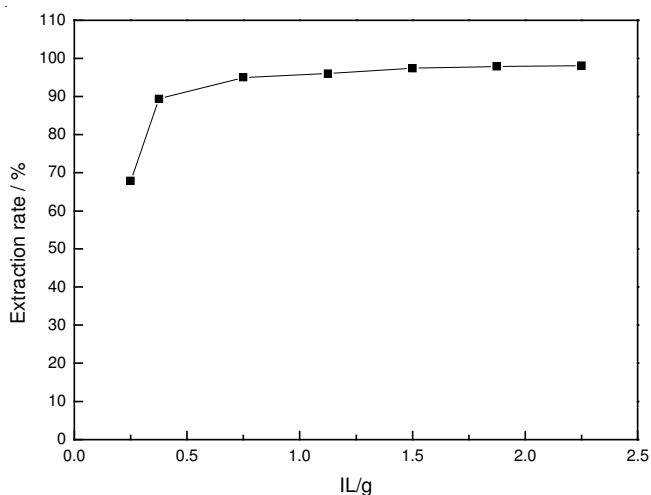


Fig. 2. Effect of dosage of ionic liquids on the extraction rate (C_{Pd(II)} = 15 µg/mL)

Effect of temperature on the extraction efficiency: In this experiment, the extraction efficiency of system at different temperatures (20-50 °C) was studied. The extraction rate was scarcely any variation with temperature raised (C_{Pd(II)} = 15 µg/mL). So the experiment was conducted at room temperature.

Effect of the sample volume: The amount of Pd(II) was fixed at 75 µg and the volume of the sample solution increased from 5.0-50.0 mL. The results were shown in Fig. 3. It could be seen from Fig. 3 that Pd(II) could be extracted quantitatively in the volume of sample 5-25 mL. In this work, the sample volume of 5 mL was adopted.

Extraction capacity of Pd(II): To determine the extraction capacity of the Pd(II), 1.5 g [C₄MIM][PF₆] was equilibrated with 5 mL solution in the range of concentration of Pd(II) (20-350 µg/5 mL). When the concentration of Pd(II) reached 150 µg/5 mL, the extraction capacity arrived at 90 %.

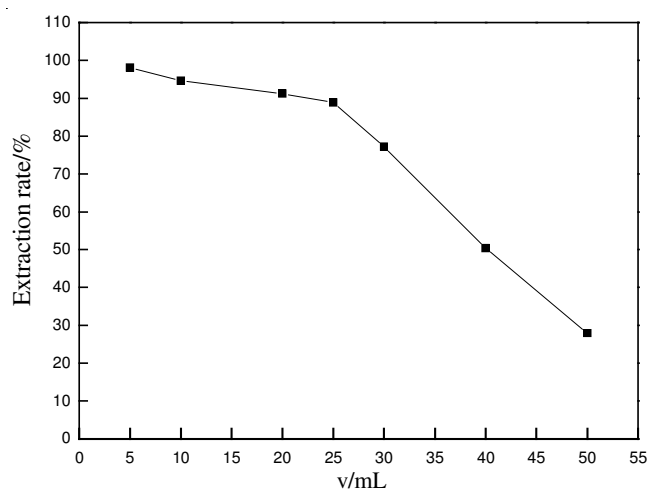


Fig. 3. Effect of sample volume on the extraction rate ($m_{\text{Pd(II)}} = 75 \mu\text{g}$)

So the extraction capacity of $[\text{C}_4\text{MIM}][\text{PF}_6]$ was $100 \mu\text{g g}^{-1}$ ($E \% > 90 \%$).

Selectivity of the extraction method: The selectivity for foreign ions of the proposed method was examined in the presence of various ions. The effect of foreign ions on the determination of Pd(II) by the proposed method was investigated. The tolerance limits for various common foreign ions were studied within a relative error of less than $\pm 5.0 \%$. It was found that 1000 times [ion/Pd(II) (w/w)] of interfering ions, such as K^+ , Na^+ , Ca^{2+} , Zn^{2+} , Mg^{2+} , Ni^{2+} , Cd^{2+} and Fe^{3+} , has no interference to the extraction of Pd(II). The other precious metals, such as $\text{Pt}([\text{PtCl}_6]^{2-})$, $\text{Au}([\text{AuCl}_4]^-)$, $\text{Ir}([\text{IrCl}_6]^{2-})$, were also studied for the extraction of the Pd(II). The tolerance limits (w/w) were as follows: Pt(IV)(2); Ir(IV)(5); $[\text{AuCl}_4]^-$ (100).

Characteristics of the method: Under the optimum conditions, the calibration graph was linear in the range $1.0\text{--}24.0 \mu\text{g mL}^{-1}$. The calibration equation is $A = 0.01002 + 0.0207c$ ($c: \mu\text{g mL}^{-1}$) with a correlation coefficient of 0.9984. The limit of detection (DL), defined as $\text{DL} = 3\text{SB}/m$, was $0.46 \mu\text{g mL}^{-1}$.

Determination of Pd(II) in samples: The proposed method was applied to determination of trace Pd(II) in synthetic samples and the waste water of catalyst of fuel cell. The result was seen in Table-1. There is no significant difference between the found value and the added value for Pd(II) and the recovery was 97.8-101.6 %.

TABLE-1
RESULT OF DETERMINATION OF
GOLD IN STANDARD SAMPLE ($n = 3$)

Sample	Detected ^a ($\mu\text{g/mL}$)	Added ^a ($\mu\text{g/mL}$)	Found ^a ($\mu\text{g/mL}$)	Recovery (%)
Synthetic samples ^b	10.00	5.00	5.08	101.6
		10.00	9.84	98.4
Waste water of catalyst of fuel cell ^c	3.70	5.00	4.89	97.8
		10.00	9.89	98.9

^aAverage value of three determination. ^bIn the synthetic sample: K^+ , Zn^{2+} , Ca^{2+} , Mg^{2+} , Al^{3+} , Ni^{2+} , Fe^{3+} , Cu^{2+} , Co^{2+} 0.4 mg/mL . ^cThe waste water containing Pd(II) was diluted by 12.5 times.

Conclusion

In this study, extractions of Pd(II) ions by $[\text{C}_4\text{MIM}][\text{PF}_6]$ ionic liquids with the absence of chelating agent were performed. A simple, rapid and selective extraction method has been developed and optimized for the extraction of trace Pd(II). The proposed procedure does not need any chelating agent, heating, long incubation time. The proposed method can be applied to the determination of Pd in waste water sample with satisfied result.

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