Using solid carriers impregnated with ammonium ionic liquids for platinum(IV) recovery from chloride solutions

Thuy Thi Le Bui[*,†], **Ha Thi Ngoc Uong**[**,***,****], **Duy Khac Nguyen**[*],
Dung Thi Kim Hoang[***,****], **and Giang Vo-Thanh**[*****,†]

*Oil Refining and Petrochemistry Department, Hanoi University of Mining and Geology,
18-Vien, Duc Thang, Bac Tu Liem, Ha Noi, Viet Nam
**Chemistry Department, University of Medicine and Pharmacy, 227 Hong Bang, Ho Chi Minh City, Viet Nam
***Institute of Chemistry, Vietnam Academy of Sciences and Technology,
18-Hoang Quoc Viet, Nghia Đo, Cau Giay, Ha Noi, Viet Nam
****Institute of Chemical Technology, Vietnam Academy of Sciences and Technology,
1-Mac Dinh Chi street, Hochiminh City, Viet Nam
*****Institut de Chimie Moléculaire et des Matériaux d'Orsay, ICMMO, Université Paris-Saclay,
91405 Orsay Cedex, France

Abstract−Platinum(IV) was extracted from chloride solution using kerosene solution of trioctyl ammonium chloride, methyltrioctylammonium chloride, and tetraoctyl ammonium chloride ionic liquids as solvents in high yields. To increase the Pt(IV) recovery and heterogenize the process for easy handling at industrial scale, these three ionic liquids were directly impregnated on some solid carriers, such as silica gel-60, silica gel-100, Amberlite XAD-7 ion-exchange resin, and Amberlite XAD-7 ion-exchange resin to form sorbents in nature of supported ionic liquid phase. The influence of some factors, such as ionic liquid and solid carrier structure, IL/Pt molar ratio, and ionic liquid loading as well as sorption isotherms, was investigated. The stripping and desorption of Pt(IV) using different eluents and reusability of ionic liquids and supported ionic liquid phases were also evaluated.

Keywords: Ionic Liquid, Pt(IV) Recovery, Sorbent, Supported Ionic Liquid Phase

INTRODUCTION

Platinum with some special properties has a wide range of applications, such as an alloying agent for other metal products, fine wires, medical instruments, jewelry, catalytic converters, air pollution control catalysts, and catalysts for variety of reactions in the chemical and petroleum industry [1].

The oil refinery and transportation industries (catalytic converters of automobiles...) discard a large amount of catalysts containing precious metals, primarily platinum, supported on aluminum oxide (Al_2O_3) every year. According to the Environmental Protection Agency of North American, waste catalysts are classified as poison because they can burn and produce toxic gases [2]. The recovery of precious metals from waste catalysts brings significant benefits, reduces environmental pollution and, therefore, is a valuable topic that has received a great deal of attention for the last decades.

Among steps in recovery of platinum, separation of platinum from leaching solution is complicated because platinum easily forms chemical complex in this medium. Volatile organic phase and hazardous reagents, causing pollution to the environment, are required for hydrometallurgical processes [3]. Therefore, it is important to find an alternative recovery system for separating platinum from secondary waste, including refinery catalysts and automobile exhaust catalysts.

Using solvent impregnated solid carriers increases the separation efficiency and makes the process easy to handle [4]. Some amines have soaked up Amberlite XAD-2 resin to absorb Pt(IV) from solution [5]. Extractant impregnated solid carriers that combine the advantages of both resins and solvent extractants were used as sorbents of Fe(III), Cd(II), Ni(II), and Zn(II) [6-10]. Solid carriers can confine the extractant in a matrix preventing extractant loss, reducing economic constraints and environmental issues. Sorbents have been recently prepared from phosphonium ionic liquids, and biopolymer showed high Pt(IV) sorption performance [11].

Ionic liquids (ILs) offer interesting properties such as high thermal stability, low solubility in water, and very low vapor pressure. They are considered as green and designable solvents and catalysts [12-14] so that they are very suitable for impregnating on solid carriers for sorption of platinum group metals (PGMs). Binnemans et al. performed a great deal of research in extraction of rare-earth using ionic liquids. One of applications is to separate rare-earth and transition metals [15-18]. Tricapryl methyl ammonium chloride ionic liquid was used as solvent for extraction Pt(IV) from chloride solution

[†]To whom correspondence should be addressed.
E-mail: thuykhai2001@gmail.com,
  giang.vo-thanh@universite-paris-saclay.fr

[1]. The optimum conditions in leaching, extraction, and stripping together with the mass balance of the constituents of the spent catalysts in the whole process are being investigated. Some ionic liquids of the Cyphos family have been used for metal recovery in conventional liquid/liquid extraction processes [19]. Recently, some ammonium, phosphonium, and imidazolium ionic liquids were used for selective extraction of Pt(IV) [21-30]. Some ionic liquids have been also used for preparing sorbents by two techniques: (a) impregnation of the resin followed by solvent evaporation [31,32] and (b) immobilization of the IL in biopolymer capsules [33-35] for recovery of metals. A tetra alkyl phosphonium ionic liquid (Cyphos IL-101) was immobilized on different systems (Amberlite XAD-7 resin and alginate biopolymer capsules) [36-39] for Bi(III), Hg(II), Cd(II), and Fe(III) sorption. Impact of the mass transfer properties of the immobilization matrices and the effect of metal speciation on equilibrium and kinetic performance were identified and explained during investigating the different systems. Cyphos IL-101 was also immobilized in biopolymer capsules for Pd and Pt recovery [35,40]. Influence of HCl and chloride ion concentration in solution and ionic liquid content in resin, sorption isotherms, and sorption kinetic were investigated. The ion exchange mechanism involved in the binding of hexachloroplatinate species was supposed. Pt(IV) and Pd(IV) were recoved from HCl solutions using Amberlite XAD-7 impregnated with Cyphos IL-101 [41, 42]. Investigation of sorption isotherms showed that maximum sorption capacity increases with extractant loading and depends on HCl concentration. In the last several years, more research [43-45] has been reported on using ionic liquids and supported ionic liquid phase for recovery Pt(IV), heavy metals, and Pt group metals.

Promising results encourage further research in this field. Yet, an investigation of Pt(IV) sorption on the different IL impregnated solid carriers has not been reported so far. We report herein the use of trioctyl ammonium chloride ([N0888]Cl), methyltrioctylammonium chloride ([N1888]Cl), and tetraoctyl ammonium chloride ([N8888]Cl) ionic liquids as solvents or sorbents to recover Pt(IV) by both extraction and sorption methods. Three chloride based ionic liquids were chosen because i) they are available at moderate cost; ii) all ionic liquids and SILPs could be recovered by stripping with chloride anion containing eluent systems to transfer X_2PtCl_6 complex back to chloride ionic liquids again (chloride ions are exchanged with $PtCl_6^{2-}$ ion during the stripping to recover the ILs); and iii) sorbents prepared from these chloride ionic liquids are stable (chloride ions are not hydrolyzed in contact with water).

The subject of this work was to use three solid carriers such as silica gel (high polarity and hydrophilic), XDA-4 (unpolar and hydrophobic), and XAD-7 resins (moderate polar and hydrophilic) [46,47] of different chemical nature and different properties for preparing Pt(IV) sorbents (supported ionic liquid phase - SILPs) in order to find the influence of surface area, pore size, surface polarity, and hydrophilicity of solid carriers on Pt(IV) sorption performance.

To find the suitable condition for the sorption process, the influence of some important factors that dramatically affect process and the reusability of ionic liquids and SILPs was investigated.

EXPERIMENTAL

1. Materials

Hexachloroplatinic acid, ≥99.9% trace metals basis), amberlite XAD-7 and XAD-4 ion-exchange resins 99% were supplied as reagent grade products by Acros. Methyltrioctylammonium chloride 97% and tetraoctyl ammonium chloride were purchased from Sigma-Aldrich Company, USA. Trioctyl amine 99%, SiO_2-100 99.5%, and SiO_2-60 99% were purchased from Merck Schuchardt OHG Company, Germany. Thiourea 99.5%, H_2O_2 29-32%, acetone 99%, anhydrous NaOH 99.5%, diethyl ether 99%, ethanol 98%, $Na_2S_2O_3$·$5H_2O$ 98%, HCl 36-38%, and methanol were supplied by Guangdong Guanghua Company, China.

2. Synthesis of Trioctyl Ammonium Chloride

A mixture of equimolar amounts of trioctyl amine and 9 M HCl solution was stirred at 70-80 °C for 72 h. The ionic liquid was washed three times with diethyl ether to remove any unreacted material and then dried at 50 °C under vacuum (yield is 95%).

3. Liquid-liquid Extraction of Pt(IV) from Chloride Solution using ILs

Platinum in spent reforming catalyst of refinery was leached by using H_2O_2 in HCl 9 M solution [48]. Therefore, to simulate the platinum recovery process, a 9 M HCl solution containing H_2PtCl_6 (460 ppm of Pt(IV)) was used for extraction and sorption experiments.

All the Pt(IV) extraction experiments using ionic liquids were conducted in glass vials. The leaching liquor containing Pt(IV) and ionic liquid 15% solution in kerosene was added into the vials and heated to 40 °C. The volume ratio of leaching liquor to ionic liquid solution (A/O) was 1:1. The mixture was stirred for 30 min at 40 °C. After that the mixture was transferred to a separatory funnel and left still until the phase separation was completed. The aqueous layer was separated and analyzed for the Pt(IV) content in order to calculate the extraction yield.

The yield of Pt(IV) recovery in extraction and sorption experiments was determined by mass balance equation:

$$\text{Yield} = \frac{C_0 - C_{eq}}{C_0} 100\% \tag{1}$$

where yield is Pt(IV) recovery efficiency (%), C_0 is Pt(IV) concentration before extraction or sorption (mg Pt L^{-1}), and C_{eq} is the residual Pt(IV) concentration (mg Pt L^{-1}).

4. Impregnation of ILs on Solid Carriers

4-1. Solid Carrier Pre-treatment

SiO_2-60 and SiO_2-100 were dried in an oven at 100 °C for 5 hours. Amberlite XAD-4 and Amberlite XAD-7 exchange resins were pretreated to clean them by removing monomers, and NaCl and Na_2CO_3 salts those were used to inhibitor or delay bacterial growth during storage. 20 g of resin was soaked with 50 mL acetone in a 250 mL Erlenmeyer flask for 24 h, filtered under vacuum and then washed with de-mineralized water. After washing with an HNO_3 0.1 M solution for 24 h, the resins were rinsed with demineralized water until the pH of washing water was neutral. Finally, resins were soaked with acetone for 12 h and dried under vacuum at 50 °C.

4-2. Solid Carrier Impregnation

5 g of solid carrier was contacted with 25 mL of acetone for 24 h. The calculated amount of 0.5 M solution of ionic liquid in acetone was added into the carrier slurry and the mixture was stirred for 24 h. Acetone was removed by slow evaporation to get SILPs (sorbents). The ionic liquid loading was calculated by V_{IL}/V_{por} ratio (%) as follows:

$$\frac{V_{IL}}{V_{por}}(\%) = \frac{m_{IL}}{d_{IL} \times V_{por}} 100\% \qquad (2)$$

where: m_{IL} and d_{IL} are mass (g) and density (g mL^{-1}) of ionic liquid; V_{IL} is ionic liquid volume; V_{por} is pore volume of solid carrier.

The experimental procedure allowed the preparation of SILPs with V_{IL}/V_{por} ratios (IL loading) of 10%, 20%, and 30%. SILPs were stored in a dessicator for sorption experiments.

5. Characterization

Infrared (IR) spectrum of the prepared ionic liquid was measured using an FT-IR spectrometer (Infrared Bruker Tensor 27, Germany). The sample was measured using the method of a KBr pellet. ^{1}H NMR and ^{13}C-NMR were measured using FT-NMR Spectrometer (Bruker AM0) (at 500 MHz for proton at 125 MHz for ^{13}C) in CDCl$_3$. The Pt(IV) content in samples was measured by ICP-MS PE7300DV (Perkin Elmer). Textural properties of SILPs were investigated by NOVA 1000e Brunauer-Emmett-Teller (BET) instrument. The morphology images of SILPs were obtained from the scanning electron microscope (Hitachi-S4800).

6. Sorption of Pt(IV) using SILPs

The sorption experiments were performed by mixing the calculated amount of sorbents with the H$_2$PtCl$_6$ solution as described above for 48 h at 25 °C. The phase contact was operated on HY-2 Laboratory Shaker with an agitation speed of 150 movements min^{-1} at a constant room temperature. Pt(IV) remaining in aqueous phase was analyzed by inductively coupled plasma mass spectrometry. The amount of sorbent with different IL loading was varied to get the IL/Pt ratios in ranges of sorption experiments.

Experiments of influence of IL loading and sorption isotherms were plotted by mixing calculated amounts of SILP with fixed volumes (5 mL) of H$_2$PtCl$_6$ solutions so that the IL/Pt(IV) molar ratio varied from 1 to 14. At equilibrium (i.e., after 24 h of contact), the residual Pt(IV) concentration was measured and used to calculate the Pt(IV) sorption yield and capacity.

7. Recovery of Pt(IV)

In this work, Pt(IV) was recovered from loaded ionic liquids (or loaded SILPs) containing complex X$_2$PtCl$_6$ (X is cation of IL) after extraction (or sorption) using some stripping reagents (sodium thiosulfate, hydrazine, thiourea/HCl, and water) with different concentrations to find the suitable condition.

Loaded ILs (or loaded SILPs) were mixed with stripping reagent at 80 °C for 20 min. After cooling to room temperature the mixture was transferred to a separatory funnel and left still until the phase separation was completed. The aqueous layer was separated and analyzed for the Pt(IV) content in order to calculate the Pt recovery yield. The ionic liquid layer was dried under vacuum at 80 °C for 1 h.

$$Yield(\%)_{stripping} = \frac{m_{stripped\ Pt}}{m_{Pt\ loaded\ in\ organic\ phase\ (SILP)}} 100\% \qquad (3)$$

Before stripping with Na$_2$S$_2$O$_3$, loaded ILs (or loaded SILPs) was washed with de-mineralized water to remove any chloride ion that can release SO$_2$ because of the reaction of sodium thiosulfate in acid medium (reaction pathway 1).

$$Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + H_2O + S + SO_2 \uparrow \qquad (4)$$

The sorbent was then dried under vacuum at 80 °C.

RESULTS AND DISCUSSION

1. Characterization of Synthesized Ionic Liquids

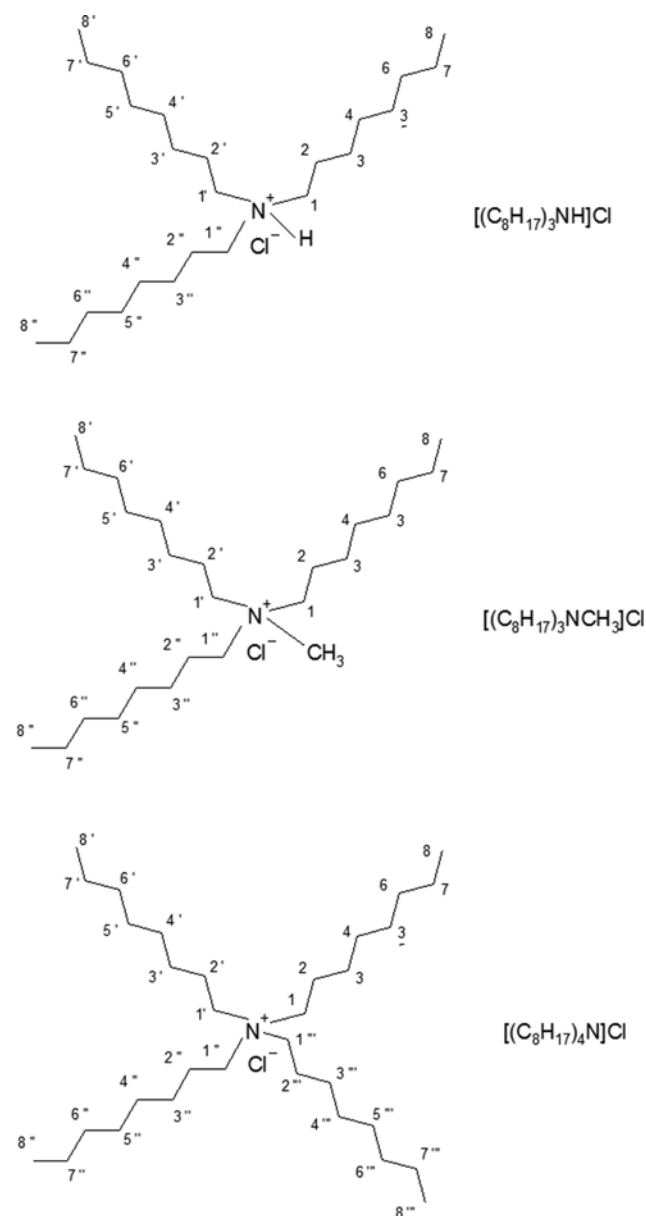The structure of three ionic liquids (N0888]Cl, [N1888]Cl, and

Fig. 1. Structure of three ionic liquids [(C$_8$H$_{17}$)$_3$NH]Cl ([N0888]Cl), [(C$_8$H$_{17}$)$_3$NCH$_3$]Cl ([N1888]Cl), and [(C$_8$H$_{17}$)$_4$N]Cl ([N8888]Cl).

Table 1. Platinum extraction yield of three ionic liquids ($V_{aqueous\ phase}$/$V_{Oil\ phase}$=1, 40 °C, 30 min)

Run	Ionic liquid	IL/Pt (mol)	Yield (%)
1	[N0888]Cl	37	98.23
2	[N1888]Cl	37	99.81
3	[N8888]Cl	37	97.12

[N8888]Cl) is given in Fig. 1. The synthesized ionic liquid [N0888]Cl was characterized by FT-IR, ^{1}H-NMR, and ^{13}C-NMR spectra.

^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, TMS): δ=11.94 (s, 1H; N**H**), 2.94 (m, 6H; (C^1**H$_2$**, C$^{1'}$**H$_2$**, C$^{1''}$**H$_2$**)), 1.76 (s, 6H; (C^2**H$_2$**, C$^{2'}$**H$_2$**, C$^{2''}$**H$_2$**)), 1.24-1.30 (m, 30H; (C^3**H$_2$**-C^7**H$_2$**, C$^{3'}$**H$_2$**-C$^{7'}$**H$_2$**, C$^{3''}$**H$_2$**-C$^{7''}$**H$_2$**)), 0.85 (t, j=5, 9H; (C^8**H$_3$**, C$^{8'}$**H$_3$**, C$^{8''}$**H$_3$**)).

^{13}C NMR (125 MHz, CDCl$_3$, 25 °C, TMS): 52.42 (s; (C^1, C$^{1'}$, C$^{1''}$)), 31.73 (s; (C^2, C$^{2'}$, C$^{2''}$)), 29.11 (s; 3 C); 29.05 (s; 3 C); 26.96 (s; 3 C); 23.24 (s; 3 C); 22.63 (s; 3 C); 14.10 (s; (C^8, C$^{8'}$, C$^{8''}$)).

IR (KBr): n=3,444 (N-H), 2,926 (C-H), 2,855 (C-H), 1,466 (C-N), 1,050 (C-C), 724 (C-Cl).

FT-IR and NMR of synthesized IL is in agreement with the literature data of [N0888]Cl [49].

2. Pt(IV) Extraction using ILs

Three ionic liquids were used as solvents for liquid-liquid extraction of Pt(IV) from chloride solution (inorganic phase) (Table 1). All of them showed their high ability in Pt(IV) recovery from chloride solution. The yields obtained higher than 97% were similar to results observed by extraction of Pt(IV) using Aliquat 336 [48]. This could be explained by the ion exchange between Cl$^-$ anion of IL in organic phase and PtCl$_6^{2-}$ anion in inorganic phase to form X$_2$PtCl$_6$ complex (X: cation of ionic liquid) which dissolves in IL/kerosene phase and leads to the extraction of Pt(IV) out of inorganic phase. Under similar conditions, [N1888]Cl led to a higher

Pt(IV) recovery than [N0888]Cl. The presence of the electron-donating group (methyl) in [N1888]Cl could make ion [N1888]$^+$ more stable and IL less viscous and, therefore, increased the access of [PtCl$_6$]$^{2-}$ ion to ammonium ion for exchanging. However, when increasing the alkyl chain length of the electron-donating group to octyl ([N8888]Cl), the Pt(IV) recovery decreased. This could be explained by a higher bulkiness and less hydrophilicity of [N8888]Cl than [N1888]Cl leading to the less efficient access to [PtCl$_6$]$^{2-}$ in the aqueous phase. In addition, the four electron-donating octyl groups of [N8888]Cl can decrease the positive charge density of nitrogen atom, leading to lower ionic exchange ability.

Only ionic liquids based on chloride anion were used in this work for extraction and sorption of Pt(IV) because of their availability and moderate cost. In addition, all ionic liquids and SILPs should be recovered by stripping with chloride anion containing eluent system to transfer X$_2$PtCl$_6$ complex back to chloride ionic liquids again. The length of alkyl groups in ILs is important to create their suitable hydrophilicity for extraction and sorption of Pt(IV).

In these experiments, the large amounts of ionic liquids used (high IL/Pt molar ratio) were necessary to get high Pt(IV) extraction yields, which was not very profitable. The impregnation of ionic liquids on solid carriers will therefore be an interesting and economical process to increase contact area between IL and aqueous phases and to heterogenize the process for easy handling on an industrial scale. So, the Pt(IV) sorption using different SILPs was further investigated in the next section.

3. Sorption of Pt(IV) on SILP Made from Different Solid Carriers

In this section [N1888]Cl ionic liquid was impregnated on four solid carriers that have different surface area, average pore diameter, and pore volume (Table 2) to form four sorbents for Pt(IV) sorption. Although the solid carriers having different characteris-

Table 2. Characteristics of different carriers and Pt sorption yields of sorbents prepared from different carriers and [N1888]Cl (T=25 °C; t=48 h, V_{IL}/V_{por} (IL loading)=50%; IL/Pt=37 : 1 (mol))

Solid carrier	Chemical nature	Average pore diameter (A°)	Surface area (m²g⁻¹)	Pore volume (cm³g⁻¹)	Pt sorption yield (%) on carriers	Pt sorption yield (%) on SILPs
SiO$_2$-100	Hydrophilic	105.5	307	0.9	5.5	99.5
SiO$_2$-60	Hydrophilic	60	510	0.79	4.7	99.8
XAD-4	Hydrophobic polyaromatic	90	725	1.14	3.5	96.3
XAD-7	Hydrophilic acrylic ester	90	450	1.14	5.8	98.5
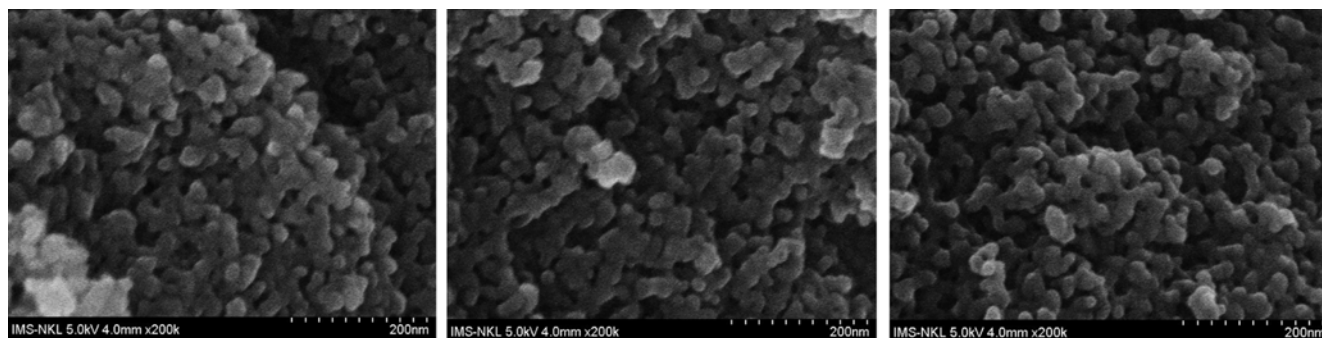
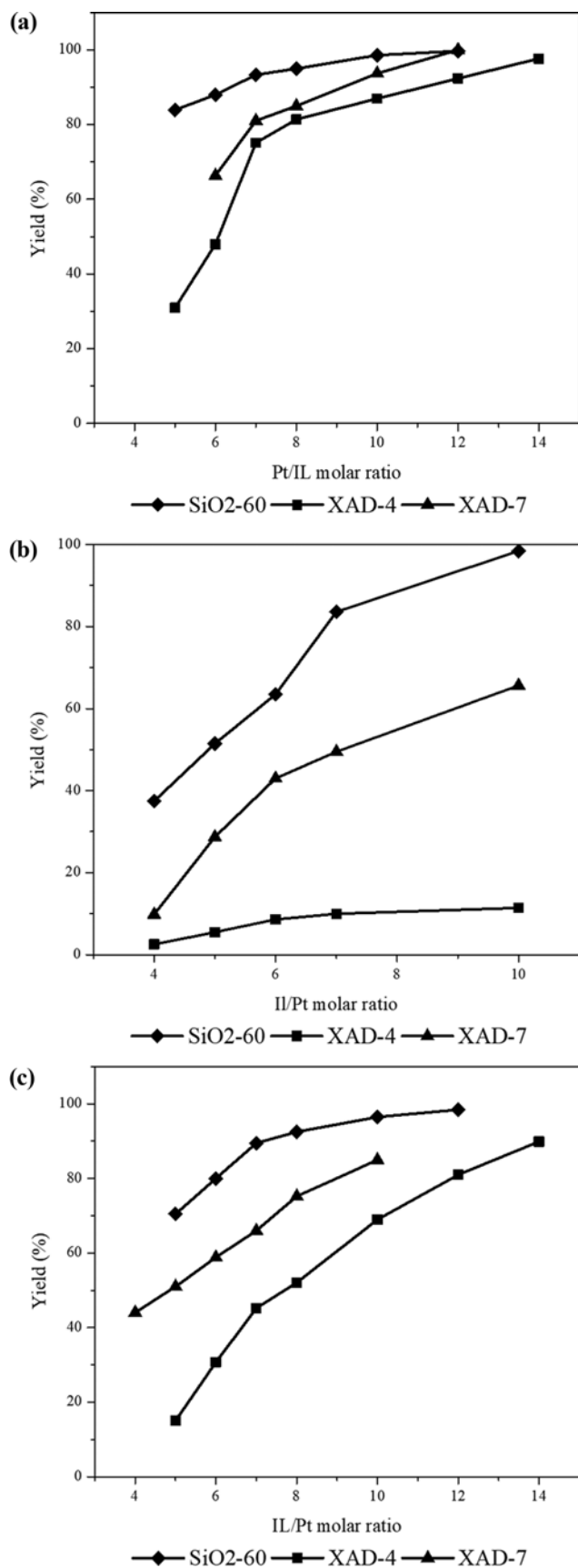**Fig. 2. SEM images of [N1888]Cl/SiO$_2$-60, [N1888]Cl/XAD-7, and [N1888]Cl/XAD-4 SILPs.**

Fig. 3. Platinum sorption of SILPs with: (a) [N1888]Cl, (b) [N0888]Cl, and (c) [N8888]Cl (IL loading 20%, 48 h and 25 °C).

tics, all SILPs led to high Pt(IV) sorption yield (approximately 95%) due to a very high molar ratio of IL/Pt(IV) (37 : 1) being used (Table 2). The very low Pt(IV) sorption yield (3-6%) of the four pure solid carriers confirmed that they were ILs, which were immobilized on solid carriers, being Pt(IV) sorption capacity of the four SILPs.

SEM analysis of [N1888]Cl/SiO₂, [N1888]Cl/XAD-7, and [N1888]Cl/XAD-4 SILPs showed that the ionic liquid molecules were distributed regularly on the surface of carriers (Fig. 2).

Some SiO₂-100 based sorbent particles had broken down during impregnating ionic liquid because of rather high particle diameters while sorbents based on SiO₂-60, XAD-7, and XAD-4 exchange resins remained stable. In addition, SiO₂-60, XAD-7, and XAD-4 exchange resins have rather high surface area and are commercially available; therefore, they were chosen for further sorption experiments with different ionic liquids, IL loading, and IL/Pt ratios.

SILPs prepared from silica gel SiO₂-60 and three ILs brought higher Pt(IV) recovery yields compared to those from ion exchange resins (Fig. 3). The Pt(IV) sorption of SILPs followed the order of solid carriers as follows: SiO₂-60>XAD-7 resin>XAD-4 resin. It is known that solid carrier with a higher surface area allows an easier contact between Pt(IV) and ionic liquid impregnated sorbents. The surface area of solid carriers follows the order XAD-4 resin> SiO₂-60>XAD-7 resin (Table 2). This shows that the Pt(IV) sorption is controlled not only by the surface area but also by the chemical nature of the carriers, such as polarity and hydrophilicity. Silica gel has high polarity and is hydrophilic, therefore can better adsorb the polar IL molecules. IL molecules can closely attach, cover themselves regularly, and remain stably on hydrophilic and polar surface of pores, while high surface area increases the phase contact between ionic liquids impregnated sorbents and H₂PtCl₆. These facilitate the Pt(IV) sorption of SILPs based on SiO₂-60. The hydrophobicity and low polarity of XAD-4 ionic exchange resin may reduce the IL stability in its pores and therefore decrease the Pt(IV) sorption.

4. Sorption of Pt(IV) on SILPs with Different ILs and IL/Pt Molar Ratios

The alkyl groups connected to N atom of ammonium ILs brought stability for ammonium ions [N0888]⁺, [N1888]⁺, and [N8888]⁺ and ion exchange capacity between ILs and H₂PtCl₆. As observed, in all extraction processes Pt(IV), under the same sorption conditions, [N1888]Cl led to a higher Pt(IV) recovery than [N0888]Cl (Fig. 4). This could be explained by the presence of the methyl group in [N1888]Cl that made its cation more stable and IL less viscous and, therefore, increased the ion exchange. Pt(IV) sorption using all SILPs based on [N1888]Cl increased rapidly when IL/Pt molar ratios went up to 7 and were higher than 85% with ratios over 7. The Pt(IV) sorption yield of [N1888]Cl/SiO₂-60 reached nearly 100% and remained stable at IL/Pt molar ratios from 10, while Pt(IV) sorption yield of [N0888]Cl/SiO₂-60 increased from 83.59% to 98.45%, that of [N0888]Cl/XAD-7 from 49.48% to 65.64%, and of [N0888]Cl/XAD-4 from 9.98% to 11.41% at IL/Pt molar ratios from 7 to 10.

Pt(IV) sorption of SILPs based on [N1888]Cl and [N8888]Cl was also compared in order to investigate the influence of the C chain length of the fourth alkyl group on nitrogen atom. [N1888]Cl
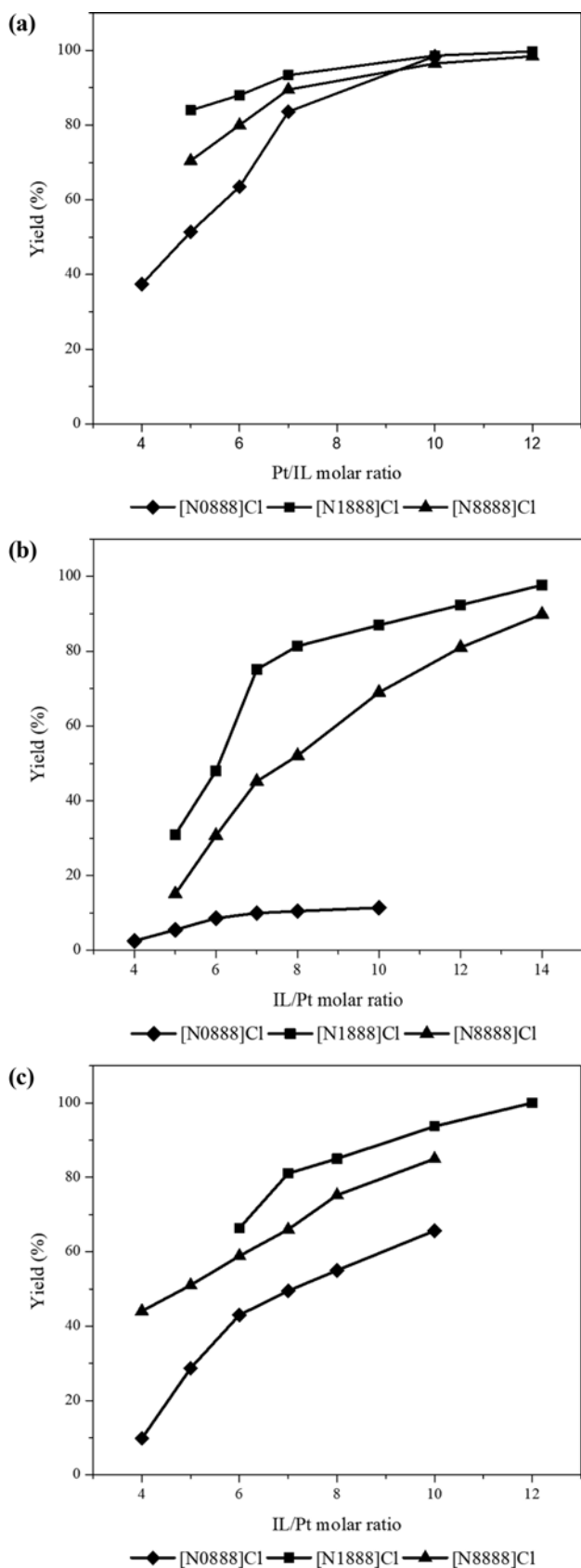
Fig. 4. Platinum sorption of SILPs with different ILs and IL/Pt molar ratios: (a) SiO₂-60, (b) XAD-4, and (c) XAD-7 (IL loading 20%, 48 h, and 25 °C).

Table 3. BET measurements of solid carriers and SILPs with different IL loading

Characteristic	SiO₂	SILP 10%	SILP 20%	SILP 30%
Surface area (m² g⁻¹)	510	385	279	190
Pore volume (cm³ g⁻¹)	0.8	0.62	0.49	0.29
Pore diameter (Å)	60	49	40	31

based SILPs had Pt(IV) recovery yield higher than [N8888]Cl based SILPs. At IL/Pt molar ratio of 5, Pt(IV) recovery yield of SILPs [N1888]Cl and [N8888]Cl based on SiO₂-60 was 83.97% and 70.48%, respectively. Pt(IV) recovery yield of SILPs [N1888]Cl/SiO₂-60 increased from 83.97% to 99.74% while yield of those of [N8888]Cl/SiO₂-60 increased from 70.48% to 97.70% with increasing IL/Pt ratio from 5 to 12. Similar results were observed with sorbents based on XAD-4 and XAD-4 resins under same sorption conditions. This may be because the presence of an octyl chain can hinder the access of hexachloroplatinate ions to ammonium ions.

5. Sorption Isotherms

The surface area, pore volume, and pore diameter of the SiO₂-60 decreased after immobilizing IL [M1888]Cl (Table 3).

The investigation of sorption isotherms was based on the sorption results of SILPs from SiO₂-60 and two ILs [N0888]Cl and [N1888]Cl, which gave higher Pt(IV) recovery.

The sorption isotherms are characterized, in most cases, by a Langmuir-type shape (sharp initial slope and appearance of a saturation plateau, i.e., asymptotic trend):

$$q = \frac{bq_m C_{eq}}{1+bC_{eq}} \tag{5a}$$

or

$$\frac{C_{eq}}{q} = \frac{1}{bq_m} + \frac{C_{eq}}{q_m} \tag{5b}$$

where q_m (mg Pt g⁻¹ IL or mg Pt g⁻¹ SILP or mmol Pt g⁻¹ SILP) is the maximum sorption capacity, b is the affinity coefficient (L mg⁻¹ Pt or L mmol⁻¹ Pt) and q is the sorption capacity (mg Pt g⁻¹ SILP or mmol Pt g⁻¹ SILP) in equilibrium with the residual concentration C_{eq} (mg Pt L⁻¹ or mmol Pt L⁻¹). It was determined by the mass balance equation, $q = V(C_0 - C_{eq})/m$, where V is the volume of solution (L) and m is the mass of SILP (or IL) (g). The results of sorption isotherms are shown in Fig. 5 and Table 5. The high reproducibility (higher than 99%) observed in almost cases showed that the sorption in this work was in agreement with the Langmuir isotherm equation. To gain an insight into Pt(IV) sorption, the maximum sorption capacity was expressed in three ways (mg Pt g⁻¹ IL or mg Pt g⁻¹ SILP or mmol Pt mmol⁻¹ IL). The first value was always higher than the second; the third was calculated from the first value and showed the conversion of IL to complex of IL and Pt (Table 4).

The results of Pt sorption isotherms showed that maximum Pt sorption capacity of SILPs with 20% IL loading was higher than that of SILPs with 10% or 30% IL loading. With the same amount of impregnated ionic liquid (IL/Pt molar ratio was kept constant) when IL loading was decreased the from 30% to 20%, the amount
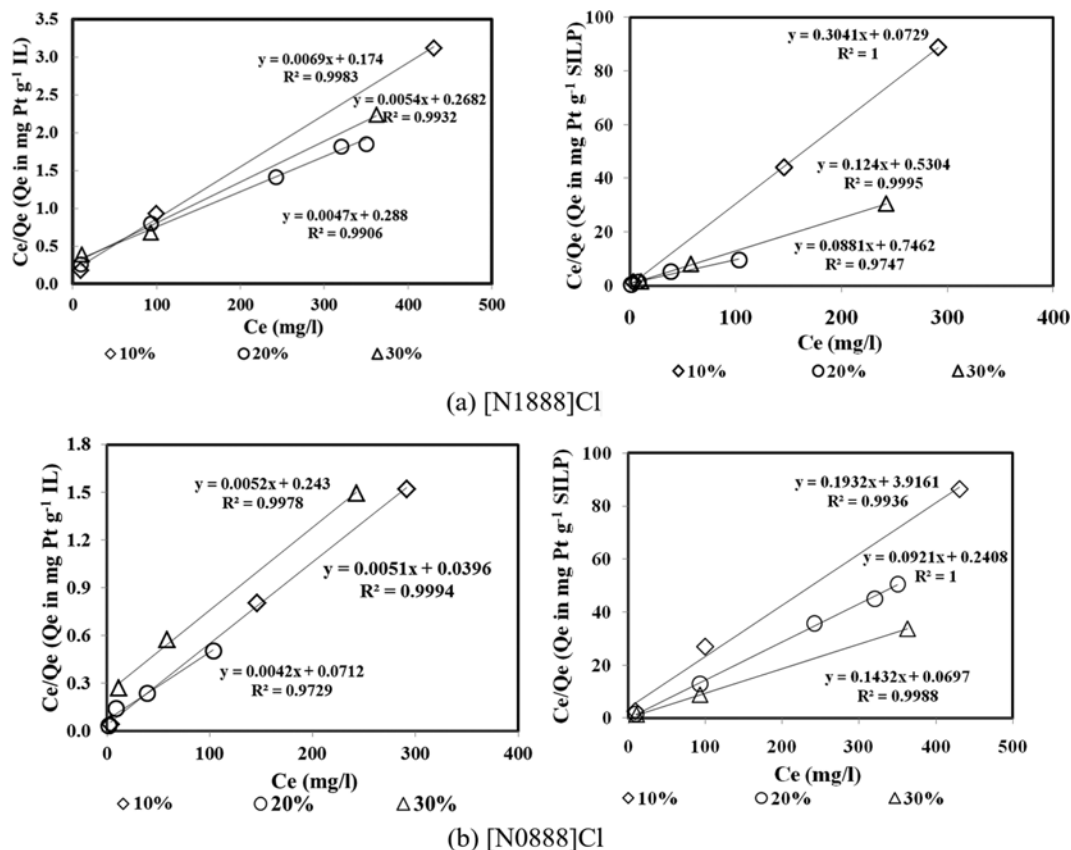
Fig. 5. Pt sorption isotherms using [N1888]Cl (a) and [N0888]Cl (b) with different IL loading (SiO$_2$-60 solid carrier, 48 h and 25 $^\circ$C).

Table 4. Parameters of Langmuir model for Pt sorption (SiO$_2$-60 solid carrier, 48 h and 25 $^\circ$C)

IL	IL loading	q_m (mg Pt g^{-1} IL) (From Fig. 6)	q_m (mg Pt g^{-1} SILP) (From Fig. 6)	q_m (mmol Pt mmol^{-1}IL)[*]	b (L mg^{-1} Pt)	R^2
[N1888]Cl	10%	195.48	3.29	0.402[*]	0.129	1
	20%	236.31	11.35	0.486[*]	0.059	0.9995
	30%	192.34	8.07	0.396[*]	0.021	0.9747
[N0880]Cl	10%	185.55	5.18	0.370[*]	0.017	0.9983
	20%	226.85	10.86	0.449[*]	0.013	0.9932
	30%	189.46	6.98	0.379[*]	0.014	0.9906

[*]Calculated from q_m (mg Pt g^{-1} IL)

of solid carrier increased, IL layer on the carrier surface became thinner and the contact between IL and Pt(IV) solution increased. Indeed, the maximum sorption capacity (mg Pt g^{-1} IL) of [N1888]Cl/SiO$_2$-60 with IL loading of 20% and 30% was 236.31 mg Pt g^{-1} IL and 192.34 mg Pt g^{-1} IL, respectively. However, when the amount of carrier increased, the maximum sorption capacity (mg Pt g^{-1} SILP) of [N1888]Cl/SiO$_2$-60 decreased, for instance, maximum sorption capacity of [N1888]Cl/SiO$_2$-60 with IL loading of 20% and 30% was 11.35 mg Pt g^{-1} SILP and 8.08 mg Pt g^{-1} SILP, respectively.

Further decreasing of IL loading to 10% by increasing amount of solid carrier did not bring any profit. This could be explained that a continuous and regular layer of IL on the solid carrier sur-

face was obtained with IL loading around 20%, a further increase in amount of solid carrier could lead to a decrease in Pt sorption.

The maximum Pt sorption capacity of [N1888]Cl/SiO$_2$-60 was about 0.4861 mmol Pt mmol^{-1} IL with IL loading of 20%. This Pt/IL ratio suggests that there is an ion exchange reaction with high conversion (higher than 97%) between IL and H$_2$PtCl$_6$ (having Pt/IL stoichiometric ratio of 0.5) as shown below (reaction pathway 2):

$$PtCl_6^{2-} + 2[(C_8H_{17})_3NCH_3]Cl \rightarrow [(C_8H_{17})_3NCH_3]_2PtCl_6 + 2Cl^- \quad (6)$$

Navarro et al. [32] used tetradecyl(trihexyl)phosphonium chloride impregnated XAD-7 for Pt sorption from (0.01 8 M) HCl solution and reported that the maximum sorption capacity was 74.6 mg Pt g^{-1} extractant impregnated resin (EIR) (256 mg Pt g^{-1}

Table 5. Platinum stripping from IL phase using different eluents (80 °C)

Run	Eluent	$V_{eluent}/V_{Pt(IV)\text{-}IL}$	Stripping efficiency (%)
1	$Na_2S_2O_3$ 0.5 M	1/1	1.24
2	Thiourea 0.5 M HCl 0.5 M	1/1	74.76
3	H_2O	1/1	3
4	$NH_2\text{-}NH_2$ 0.5 M	1/1	90.05

Table 6. Platinum stripping from IL phase under different conditions using thiourea/HCl system (80 °C)

Run	Eluent	$V_{eluent}/V_{Pt(IV)\text{-}IL}$	Stripping efficiency (%)
1	Thiourea 0.50 M HCl 0.5 M	1/1	74.76
2	Thiourea 0.75 M HCl 5 M	1/1	89.36
3	Thiourea 0.75 M HCl 5 M	2/1	91.87
4	Thiourea 2 M HCl 5 M	1/1	97.01

IL) with the IL content of 291 mg IL g^{-1} EIR. Vincent et al. [11] also immobilized that IL on biopolymer to form the capsules for Pt sorption. The results showed that equilibrium was very affected by the concentration of HCl and chloride ions, the maximum sorption capacity was 142 mg Pt g^{-1} for dry resin (i.e. 0.57 mmol Pt mmol^{-1} Cyphos) with the IL content of 291 mg IL g^{-1} EIR. While sorption capacity calculated in mg Pt g^{-1} IL of both previous studies was similar to those of this work; the numbers in mg Pt g^{-1} EIR or mg Pt g^{-1} capsules were higher those of this work. However, the sorption capacity in both cases decreased fast (down to nearly zero) when the HCl concentration increased from 0.01 M to 8 M and the higher IL loadings (equivalent to 40.23% and 65.61%) were used in both cases [11,32]. The sorbents used in this work showed high potential of recovery of Pt from 9 M HCl solution, which was obtained after leaching Pt from spent catalysts. In addition, the lower IL loading (20%) used in this work could help ILs to stay stable on the pore of solid and, therefore, easy to reuse as presented in the next section.

6. Metal Stripping and Desorption
6-1. Selection of Eluent

To transfer the extraction and sorption processes from laboratory to a larger scale, it would be necessary to strip the metal from the loaded ionic liquid phase or loaded SILPs and reuse ILs or SILPs. Pt(IV) stripping from a loaded ionic liquid system has been investigated using series of eluents such as sodium thiosulfate, hydrazine, thiourea/HCl, and water (Table 5).

The results show that sodium thiosulfate and water are not suitable eluents for Pt(IV) stripping. Platinum metal was stripped and precipitated with high efficiency 90% when using hydrazine as eluent. However, hydrazine is only suitable for Pt(IV) stripping from IL phase but not for Pt stripping from SILPs, because of precipitation of black platinum metal in the pores of SILPs which would make SILP recovery difficult. Using thiourea/HCl leads to rather high Pt(IV) stripping efficiency (74.76%). Some experiments were then conducted under different conditions using this eluent system (Table 6). Pt(IV) stripping from IL phase depends dramatically on the stripping conditions. Stripping efficiency increased from 74.76% to 89.36% with increasing the concentration of thiourea form 0.5 M to 0.75 M (runs 1 and 2). To further increase the stripping efficiency, the volume of the eluent solution was doubled; however, the efficiency only increased slightly from 89.36% to 91.87% (run 3). In addition, the increase in amount of eluent and in equipment volume made process become more complicated; therefore, in further experiments, the ratio of V_{eluent} to $V_{Pt(IV)\text{-}IL}$ was kept as 1.
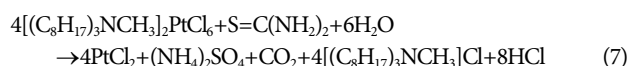
The increase in concentration of eluent agent $CS(NH_2)_2$ from 0.75 M to 2 M (thiourea 2 M and 5 M HCl) led to a higher stripping efficiency (97%) (Run 4). These results showed that concentration of eluent agent $CS(NH_2)_2$ governed the Pt(IV) stripping.

The driving force to extract Pt(IV) into the IL-phase is that the anion of $PtCl_6^{2-}$ in aqueous phase (chloride solution) combines with the cation of the involved IL to form $[(C_8H_{17})_3NCH_3]_2PtCl_6$ in the IL phase following the reaction pathway (2).

In the subsequent stripping and desorption of Pt(IV) or $PtCl_6^{2-}$ by using the eluent of thiourea 2 M+HCl 5 M aqueous solution, Pt(IV) was reduced to Pt(II) in the form of $PtCl_2$, which was transferred from the ionic liquid phase into water phase while $[(C_8H_{17})_3NCH_3]^+$ ion combined with Cl$^-$ ion and transferred back to original ionic liquid $[(C_8H_{17})_3NCH_3]Cl$ which remained in IL phase. During this process thiourea wass oxidized. The reaction pathways and the final products of this redox reaction depend on the reagents used and condition of the reaction mixtures. At a low pH in this work (HCl 5 M), thiourea was proposed to convert to ammonium sulfate (reaction pathway 3) [50]:

$$4[(C_8H_{17})_3NCH_3]_2PtCl_6+S=C(NH_2)_2+6H_2O$$
$$\rightarrow 4PtCl_2+(NH_4)_2SO_4+CO_2+4[(C_8H_{17})_3NCH_3]Cl+8HCl \qquad (7)$$

6-2. Recycling Capacity of Ionic Liquid

The solution of ionic liquid in kerosene recycled after stripping for Pt(IV) recovery was used again as solvent for Pt(IV) extraction. The recycling capacity of methyltrioctylammonium chloride was tested ten successive extraction and stripping cycles simultaneously. The yield of Pt(IV) extraction and recovery from stripping were calculated for each particular cycle. A negligible decrease in the extraction yields and recovery was observed up to ten cycles (Table 7).

6-3 Desorption and Reusability of SILPs

In the same way, the recycling capacity of SILP was also tested ten successive sorption and desorption cycles simultaneously. Studies on the recycling capacity of SILP for the sorption of Pt(IV) were carried out by first loading the SILP with an aqueous phase containing 460 ppm Pt(IV) and 9 M HCl. The loaded SILP was stripped with solution containing 5 M HCl and 2 M thiourea (5 mL eluent g^{-1} SILP) for the desorption of the metal. The recovery of each step was calculated from the amount of Pt(IV) that was introduced on the SILP in that particular cycle. The sorption and desorption yields of recycled SILP slightly changed in within ten cycles

Table 7. Recycling capacity of Aliquat 336 within 3 cycles ($V_{aqueous\ phase}/V_{oil\ phase}$=1 and 40 °C for extraction; $V_{eluent}/V_{Pt(IV)-IL}$=1, and 80 °C for stripping)

N°	Process	IL	Extraction yield (%)	Eluent	Stripping yield (%)
1	Extraction 1st	Fresh [N1888]Cl	99.81		
1′	Platinum tripping 1st			Thiourea 2 M HCl 5 M	97.01
2	Extraction 2nd	Recycled [N1888]Cl	99.34		
2′	Platinum tripping 2nd			Thiourea 2 M HCl 5 M	96.89
3	Extraction 3rd	Recycled [N1888]Cl	99.24		
3′	Platinum tripping 3rd			Thiourea 2 M HCl 5 M	97.64
10	Extraction 10th	Recycled [N1888]Cl	98.51		
10′	Platinum tripping 10th			Thiourea 2 M HCl 5 M	96.72

Table 8. Recycling capacity of SILP (N1888]Cl/SiO$_2$-60) ($V_{aqueous\ phase}/V_{oil\ phase}$=1 and 40 °C for sorption; IL loading 20%, $V_{eluent}/V_{Pt(IV)-IL}$=1, and 80 °C for stripping)

N°	Process	SILP[a]	Sorption yield (%)	Eluent	Desorption yield (%)
1	Sorption 1st	Fresh SILP	99.30		
1′	Desorption 1st			Thiourea 2 M HCl 5 M	98.04
2	Sorption 2nd	Recycled SILP	99.15		
2′	Desorption 2nd			Thiourea 2 M HCl 5 M	97.89
3	Sorption 3rd	Recycled SILP	99.04		
3′	Desorption 3rd			Thiourea 2 M HCl 5 M	97.81
10	Sorption 10th	Recycled SILP	98.06		
10′	Desorption 10th			Thiourea 2 M HCl 5 M	97.09

[a]Weight of fresh SILP=3.4190 g (3 g of SiO$_2$-60 and 0.4190 g of [N1888]Cl, IL loading 20%) and of SILP after the 10th desorption=3.4085 g.

(Table 8). These results showed the advantage of using SILPs as sorbent for Pt(IV) recovery from chloride solution.

The weights of dried SILPs were determined before the sorption and after desorption showed that there was a slight change in SILP weights after ten cycles, while only minor decrease in the sorption and desorption yields of recycled SILP was observed within ten cycles (Table 8). It can be seen that no ionic liquid leaching from SILPs was observed during ten successive sorption and desorption cycles. As discussed in Section 3.4.1, after platinum desorption $[(C_8H_{17})_3NCH_3]^+$ ion combines with Cl$^-$ ion and transfers back to original ionic liquid $[(C_8H_{17})_3NCH_3]Cl$ which remained in IL phase. The ammonium ionic liquid is insoluble in water and, therefore, stays stably in the pores of carriers.

CONCLUSION

This is an attempt of systematic sorption/desorption Pt(IV) using SILPs from different solid carriers and ammonium ionic liquids which have different number and length of alkyl groups. [N1888]Cl solution and SILPs from this ionic liquid showed better results among three ionic liquids. This can be due to [N1888]$^+$ being more stable than [N0888]$^+$ but less bulky than [N1888]$^+$], and [N1888]Cl is less viscous than [N0888]Cl. Among the three solid carriers studied, silica gel-60 showed higher ability for using as carriers for Pt(IV) recovery. In addition, silica gel has also the lowest price and is more stable during sorption process; therefore, it would be a promising solid carrier for preparing SILPs for Pt(IV)

recovery. The high sorption capacity, 236.31 mg Pt g^{-1} IL or 0.486 mmol Pt mmol^{-1} IL for [N1888]Cl]/SiO$_2$-60 with IL loading of 20% and 226.85 mg Pt g^{-1} IL or 0.449 mmol Pt mmol^{-1} IL for [N0888]Cl/SiO$_2$-60 with IL loading of 20%, shows the potential of using SILPs for Pt(IV) recovery from chloride solution. Ionic liquids and SILPs can be recovered and reused by stripping with thiourea 2 M/HCl 5 M solution. The recycled ionic liquids and SILPs can be reused ten cycles with only a slightly decrease in Pt(IV) recovery yield. Using SILPs could increase the Pt(IV) recovery while reducing the amount of required ionic liquid compared to extraction and ease of operation and recovery of sorbents.

ACKNOWLEDGEMENTS

ABBREVIATIONS

[N0888]Cl : trioctyl ammonium chloride
[N1888]Cl : methyltrioctylammonium chloride
[N8888]Cl : tetraoctyl ammonium chloride
FT-IR   : fourier transform infrared spectroscopy
IL   : ionic liquid
NMR   : nuclear magnetic resonance spectroscopy
SILP   : supported ionic liquid phase
XAD-4   : amberlite XAD-4 exchange resins
XAD-7   : amberlite XAD-7 exchange resins

SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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Supporting Information

Using solid carriers impregnated with ammonium ionic liquids for platinum(IV) recovery from chloride solutions

Thuy Thi Le Bui[*,†]**, Ha Thi Ngoc Uong**[**,***,****]**, Duy Khac Nguyen**[*]**,
Dung Thi Kim Hoang**[***,****]**, and Giang Vo-Thanh**[*****,†]

*Oil Refining and Petrochemistry Department, Hanoi University of Mining and Geology,
18-Vien, Duc Thang, Bac Tu Liem, Ha Noi, Viet Nam
**Chemistry Department, University of Medicine and Pharmacy, 227 Hong Bang, Ho Chi Minh City, Viet Nam
***Institute of Chemistry, Vietnam Academy of Sciences and Technology,
18-Hoang Quoc Viet, Nghia Đo, Cau Giay, Ha Noi, Viet Nam
****Institute of Chemical Technology, Vietnam Academy of Sciences and Technology,
1-Mac Dinh Chi street, Hochiminh City, Viet Nam
*****Institut de Chimie Moléculaire et des Matériaux d'Orsay, ICMMO, Université Paris-Saclay,
91405 Orsay Cedex, France

Fig. S1. IR spectrum of [N0888]Cl.
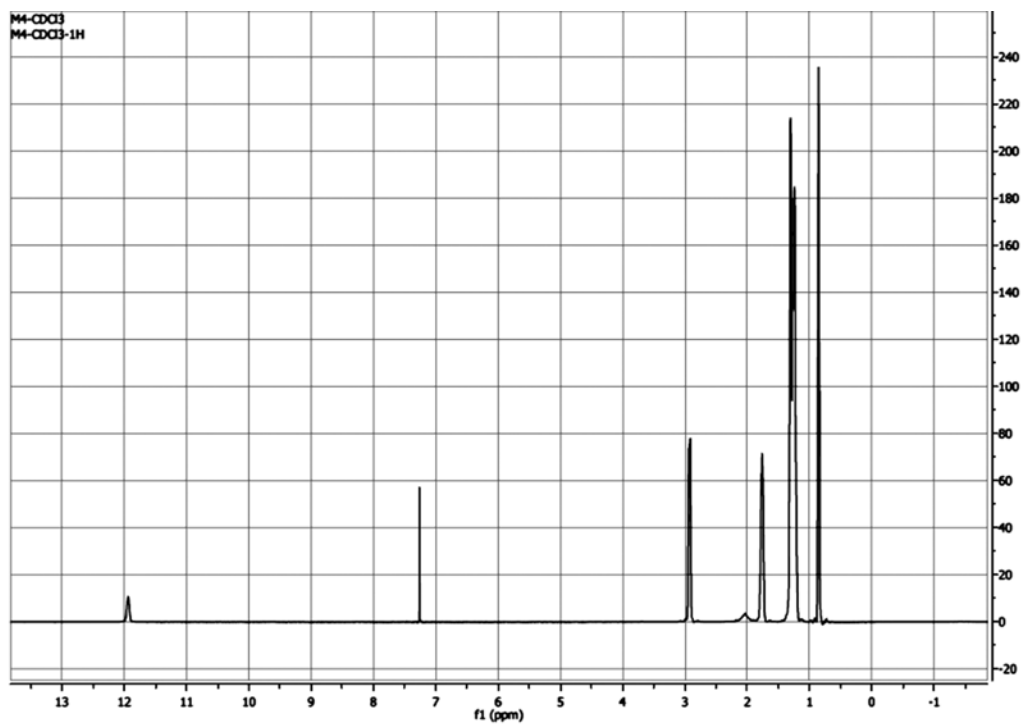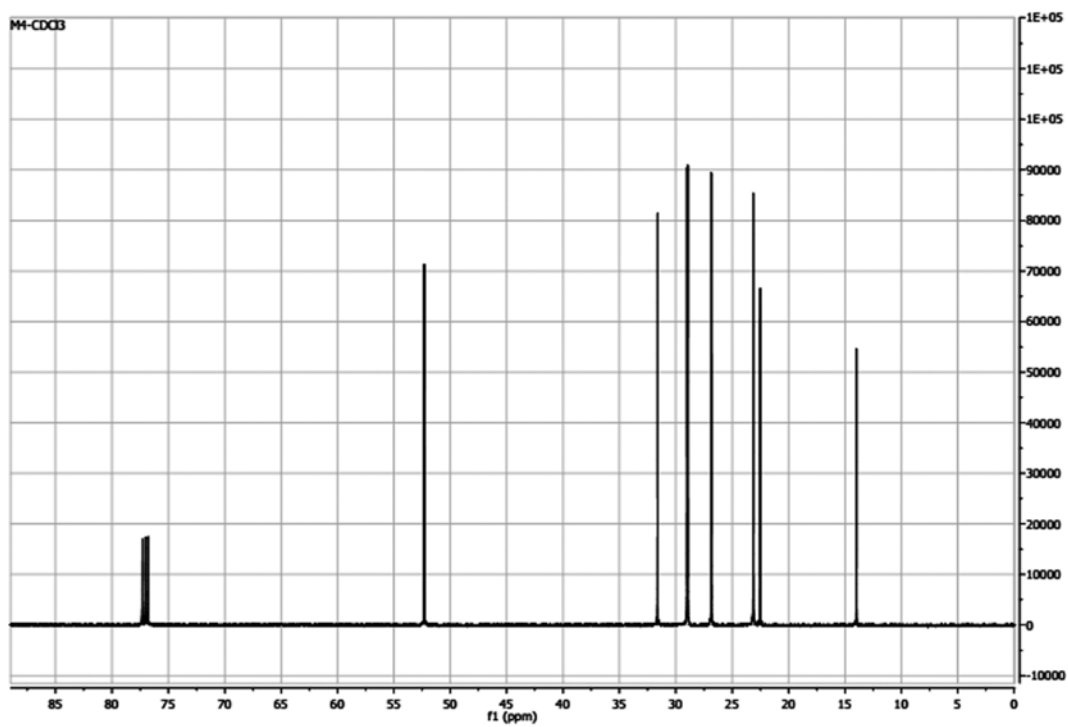
Fig. S2. (a) ^1H NMR and (b) NMR ^{13}C spectra of [N0888]Cl.