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Research Article

Silica Supported Ionic Liquids for the Efficient and Selective Recovery of Platinum and Palladium from Aqueous Media

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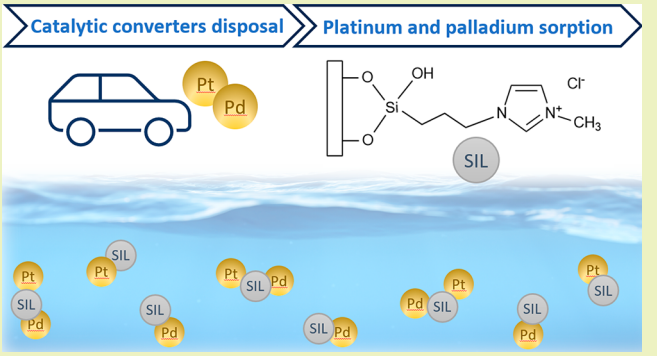
ABSTRACT: Platinum (Pt) and palladium (Pd) are considered critical elements due to their scarcity and high demand for important technologies, namely, in automotive catalytic converters. Therefore, sustainable technologies that are able to selectively extract such metals from secondary sources are extremely important. This work focuses on the preparation and evaluation of silica gel modified with ionic liquids (ILs) as alternative materials to recover Pt(IV) and Pd(II) species from aqueous media. The approach described here offers a way to reduce the amount of ILs employed in common liquid−liquid extraction methods for these metal species. The sorption equilibrium data obtained are well described by a Dubinin−Radushkevich isotherm model, with the SIL containing 1-methyl-3-propylimidazolium chloride having maximum equilibrium concentrations of 51.0 mg/g and 22.3 mg/g SIL for Pt and Pd, respectively. The gathered results pave the way for the use of materials modified with ILs in the recycling of obsolete automotive catalytic converters.



KEYWORDS: *platinum, palladium, supported ionic liquids, recovery, sorption*

INTRODUCTION

Waste containing critical elements and precious metals is of worldwide concern, which has increased during the last decades, in parallel with the increasing demand for technological goods by contemporary societies. Recycling of such waste has been an obvious strategy to mitigate negative environmental impacts, which considering the high content of critical valuable metals present also makes this approach an economical opportunity. For example, platinum (Pt) and palladium (Pd) are valuable metals found in obsolete automotive catalytic converters, whose recovery is of great interest due to their price and technological relevance, such as catalytic properties, considerable mechanical strength, resistance to corrosion at high temperatures and high melting point, and good ductility.[1] These two platinum group metals (PGMs) are used in the automotive industry for the fabrication of catalytic converters acting in the prevention or reduction of harmful chemical substances present in exhaust gases released by car engines. Thus, the continuously increasing demand of PGMs by the automotive industry, along with supplies largely determined by geopolitical factors, emphasizes the need to efficiently recover platinum and palladium from used automotive catalysts.

Nowadays, the leaching of PGMs from secondary sources and the subsequent separation of the metals from the resulting solutions are based on hydrometallurgical processes. These require volatile organic compounds and hazardous reagents, thus causing also environmental concerns.[2] In this context, the development of cost-efficient and ecofriendly techniques able to recover PGMs from secondary sources, such as spent catalysts, is an urgent requirement of a modern society striving for sustainable technologies. There has been great interest in the use of ionic liquids (ILs) in extraction and separation processes, since higher extraction and adsorption performances can be achieved with lower environmental impact, compared to conventional solvents.[3] ILs are molten salts with unique properties, namely, high ionic conductivity, high stability (thermal and chemical), and nonflammability. The combination of different cations and anions in an IL is an important chemical feature that allows for improving their performance by changing the respective physical and chemical properties.[4] The extraction of noble metals using ILs is mostly performed from acidic aqueous solutions, typically using hydrochloric acid. In this case, the metal species are mainly present as anionic complexes, which can be recovered by anion exchange with the IL.[5] Furthermore, the IL cations can coordinate to noble metal atoms, such Pt and Pd, via orbital overlapping with

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N-donor or P-donor sites.[6,7] Lastly, non-covalent interactions can occur between ILs and anionic complexes of noble metals, such as Pt and Pd chlorocomplexes.

Despite the potential of ILs in liquid−liquid extraction of metal species, there are also practical limitations displayed by some ILs, such as low diffusion coefficients, high viscosity, and difficulties in product purification and solvent recycling.[8] Supported ionic liquids (SILs) can be seen as an alternative approach to overcome such limitations while combining the advantages of common solid substrates, such as silica and organic polymers, with IL tuned properties. In addition, there is a decrease in the amount of required IL, as compared to conventional liquid−liquid separation, and, consequently, a reduction in the material's price. The use of sorbents based on IL modified silica-gel materials for the recovery of Pt and Pd species in solution has only been reported in a few studies.[2,7,9−12] For instance, Lanaridi et al.[2] reported the recovery of platinum group metals from a spent automotive catalyst using phosphonium-based ionic liquids. The authors prepared the SIL via physisorption of the ionic liquid on the silica support, and therefore, this material has low stability in the liquid phase with the possibility of leaching. Similarly, Bui et al.[9,10] prepared and applied solid supports impregnated with ammonium-, imidazolium-, and pyridinium-based ionic liquids for Pt(IV) recovery from chloride solutions. Konshina et al.[7] demonstrated the ion-exchange extraction of Pd(II) from chloride solutions using an imidazolium-based IL. Despite the high affinity of these materials for the removal of platinum and palladium, the authors used ILs with a long alkyl side chain, which may be more ecotoxic.[13] Despite their relevance, none of these studies have focused on the separation of platinum from palladium, and to the best of our knowledge, there are no reports on the use of SILs for such purposes.

In this work, a series of SILs have been prepared by covalent grafting of the IL cation to activated silica-gel surfaces. Screening studies have been performed with imidazolium- and ammonium-based cations of different alkyl side chain lengths aiming at tailoring their affinity to the target PGMs. In these studies, chloride was investigated as the counterion due to its more benign features when compared to common organic anions, as well as ease of materials regeneration. All synthesized SILs were chemically and morphologically characterized and further assessed as promising alternative sorbents for the recovery of Pt(IV) and Pd(II) from aqueous solutions by investigating the sorption kinetics and isotherms.

EXPERIMENTAL SECTION

Materials. Chemicals were supplied by commercial sources and used without further purification: (3-chloropropyl)trimethoxysilane (>98%, Acros Organics), ethanol (C_2H_5OH, 99.9%, Carlo Erba), hydrochloric acid (HCl 37%, Sigma-Aldrich), methanol (HPLC grade, Fisher Scientific), nitric acid (HNO_3, puriss. p.a., 65%, Merck), *N*-methylimidazole (99%, Acros Organics), *N*,*N*-dimethylbutylamine (99%, Aldrich), *N*,*N*-dimethyloctylamine (95%, Aldrich), palladium (Pd in 10% HCl, 1001 ± 7 μg/mL, Inorganic Ventures), platinum (Pt in 10% HCl, 999 ± 4 μg/mL, Inorganic Ventures), silica-gel particles (90 Å, 0.2−0.5 mm, Fluka), sodium hydroxide (NaOH, >98%, Pronolab), toluene (99.8%, Fisher Scientific), tributylamine (>98.5%, Sigma-Aldrich), triethylamine (HPLC grade, Carlo Erba), trihexylamine (96%, Aldrich), and trioctylamine (>98%, Fluka).

Synthesis of Silica Supported Ionic Liquids. The synthesis procedure, adapted from Qiu et al.[14] and described by Bernardo et al.,[15] started with the immersion of commercial silica gel (pore size: 90 Å) in hydrochloric acid for 24 h. This step allows one to enhance the silanol groups content on the particles surface. Then, the particles were rinsed with double distilled water and dried at 60 °C for 24 h. 5.0 g of the activated silica was suspended in 50 mL of dried toluene, and 5.0 mL of 3-chloropropyltrimethoxysilane was added. The suspension was refluxed under mechanical stirring and at 100 °C for 24 h. The chloropropyl silica obtained ([Si][C_3]Cl) was transferred to a vacuum glass filter and rinsed sequentially with 100 mL of toluene, 200 mL of ethanol−water mixture (1:1), 500 mL of double distilled water and 100 mL of methanol. Finally, the material was dried at 60 °C for 24 h. Afterward, 5.0 g of the [Si][C_3]Cl was suspended in 50 mL of dried toluene, and 5.0 mL of different reagents as the source of the cation (*N*-methylimidazole, *N*,*N*-dimethylbutylamine, *N*,*N*-dimethyloctylamine, tributylamine, triethylamine, trihexylamine or trioctylamine) were added, as represented in Scheme 1. The suspension was refluxed under mechanical stirring and at 110 °C for 24 h. The obtained materials, triethylammonium chloride ([Si][N_{3222}]Cl), tributylammonium chloride ([Si][N_{3444}]Cl), trihexylammonium chloride ([Si][N_{3666}]Cl), trioctylammonium chloride ([Si][N_{3888}]Cl), *N*,*N*-dimethylbutylammonium chloride ([Si][N_{3114}]Cl), *N*,*N*-dimethyloctylammonium chloride ([Si][N_{3118}]Cl) and 1-methyl-3-propylimidazolium chloride ([Si][C_3C_1Im]Cl), were transferred to a vacuum glass filter and rinsed sequentially with 100 mL of toluene, 350 mL of methanol, 300 mL of double distilled water and 150 mL of methanol. Finally, the materials were dried for 24 h at 60 °C. It is noteworthy that while different cation sources were employed, chloride was maintained as the counterion in all synthesized SILs.

Characterization Techniques. The chemical and physical characterization of modified silica particles were performed by using various techniques. Fourier transform infrared (FTIR) spectra (in the range 4000−350 cm^{-1}) were acquired using a Bruker Tensor 27 spectrophotometer, equipped with an attenuated total reflectance (ATR) accessory, after 256 scans with a resolution of 4 cm^{-1}. Solid-state ^{13}C nuclear magnetic resonance (NMR) spectra were recorded using a Bruker Avance III 400 MHz spectrometer operating at 9.7 T. The measurements were conducted on a 4 mm BL cross-polarization magic angle spinning (CPMAS) VTN probe at 100.6 MHz and room temperature, using the following parameters: recycle delay, 5 s; contact time, 3.5 ms; ν_R = 12 kHz. SPINAL-64 decoupling was applied during the data acquisition. Elemental analysis for the determination of carbon, hydrogen, and nitrogen contents (weight percentage) was performed using a Truspec Micro CHNS 630-200-200 elemental analyzer. Analysis parameters were as follows: sample amount of about 2 mg; combustion furnace temperature of 1075 °C; afterburner temperature of 850 °C. Regarding the detection method, infrared absorption was used to determine the amounts of carbon and hydrogen, while the amount of nitrogen was determined by thermal conductivity. The specific surface area of all samples was determined using an automated surface area analyzer (Quantachrome Autosorb IQ2) by means of nitrogen adsorption−desorption assays. The samples were degassed overnight at 100 °C prior to the measurements. Zeta potential measurements of the colloidal samples were performed by using a Zetasizer Nano ZS (Malvern Instruments). The pH of the colloid was varied between 2 and 10, using either NaOH or HNO_3 aqueous solutions. The temperature was kept at 25 °C, and three replicate measurements of zeta potential were performed for each sample.

Sorption Kinetics and Isotherms. The sorption kinetics and isotherms of Pt(IV) and Pd(II) on the SILs were determined using freshly prepared aqueous solutions by dilution of the standard commercial solution (1000 mg/L) in ultrapure water at pH 4. In this work, the pH was fixed with the primary objective of investigating the influence of the IL chemical structure on the materials sorption efficiency to infer the best IL chemical structures to adsorb Pd and Pt. The performance of different SILs for the sorption of Pt and Pd was preliminarily evaluated at pH 2 and pH 4. However, since the results obtained were better at pH 4, this was the pH selected for the study. For the sorption kinetics evaluation, a multielemental solution of platinum and palladium with a concentration of 1 mg/L was prepared, while for the sorption isotherms, concentrations of the elements

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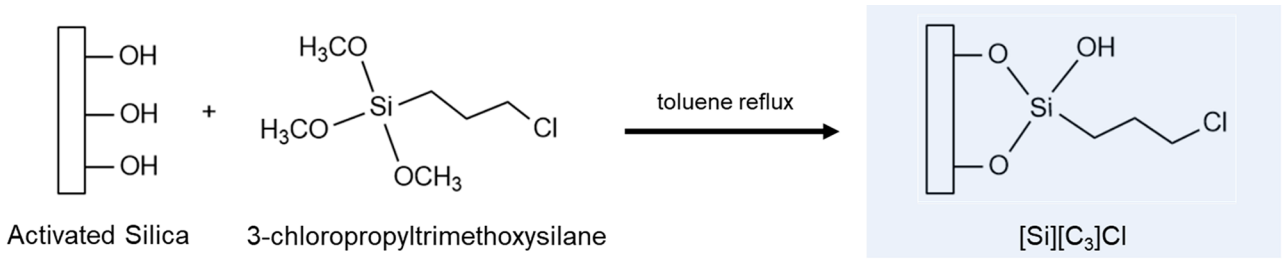
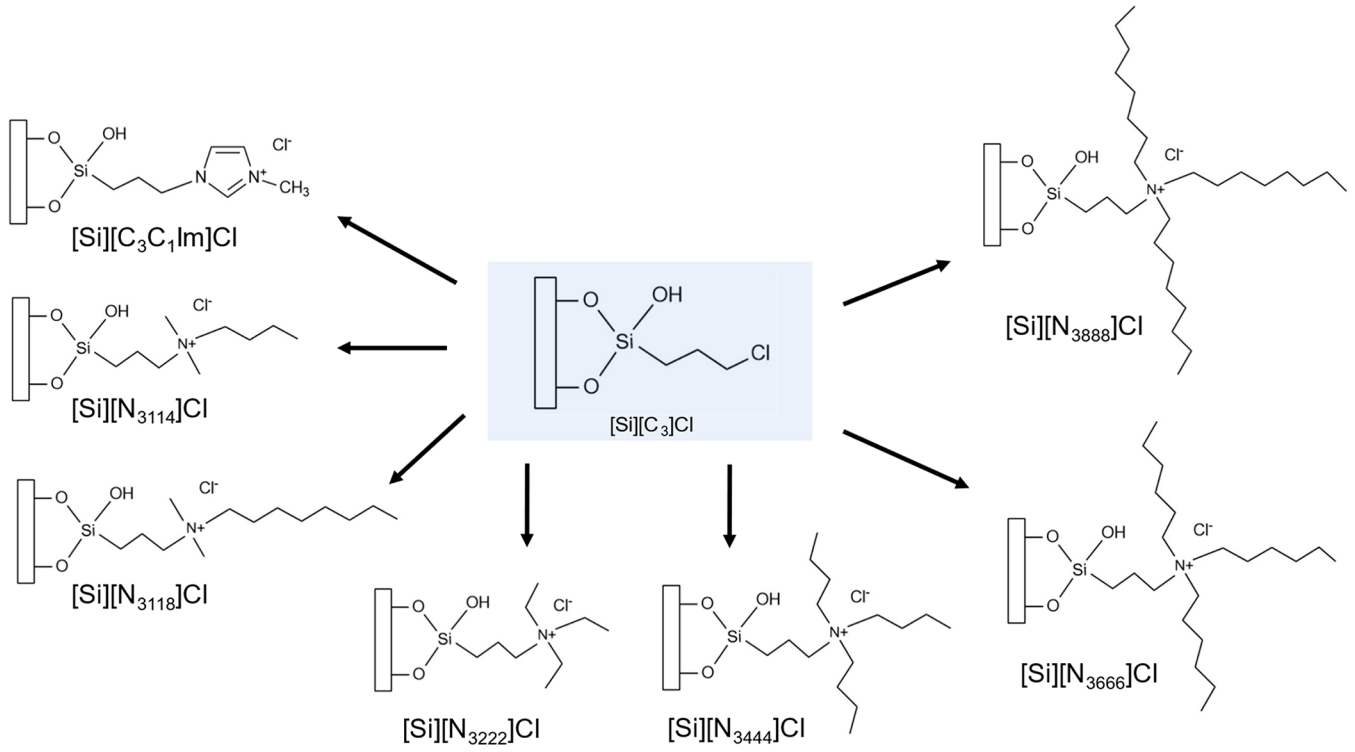
Scheme 1. Surface Functionalization of Silica Gel Leading to a Series of SILs, with the Indication of the Respective Abbreviations





ranging from 0.36 to 9.70 mg/L were used. In these experiments, 250 mg of SILs were dispersed in 1000 mL of PGEs aqueous solutions in Schott bottles and then placed in an orbital shaker at 250 rpm and 25 °C. Equilibration times ranging from 0 to 480 min were investigated for the sorption kinetics evaluation, while an equilibration time of 240 min was established for the sorption isotherm. After the assays, all samples were centrifuged at 5000 rpm for 5 min. The concentration of platinum and palladium in the aqueous phase was quantified by ICP-OES, performed on a Horiba Jobin Yvon Activa M spectrometer (radial configuration) equipped with a Burgener MiraMist nebulizer. Calibration curves were established using 5 standards with concentrations between 20 and 1000 μg/L, prepared by diluting Pt and Pd standard solutions into acidified water (aqua regia, 3% v/v HCl + 1% HNO_3 v/v). Calibration curves were considered valid only if they exhibited correlation coefficients above 0.999. The concentration of the lowest standard in the calibration curve (20 μg/L) was determined to be the limit of quantification. The coefficient of variation between sample replicates (at least three replicates were investigated) did not exceed 5%.

Selective Recovery of Platinum and Palladium from Solution. The study of selective recovery of platinum and palladium was performed using a multielemental solution of platinum and palladium with a concentration of 1 mg/L, in ultrapure water at pH 4. In this experiment, 250 mg of $[Si][N_{3222}]Cl$/L was added to the PGEs aqueous solution for 1 h. After this period of time, the SIL was separated from the solution by centrifugation, and 250 mg of $[Si][C_3C_1Im]Cl$/L was added to the PGEs aqueous solution for 1 h more. For comparative proposes, the recovery of the elements using only $[Si][C_3C_1Im]Cl$ was performed simultaneously.

RESULTS AND DISCUSSION

Surface Functionalization and Characterization of SILs. A series of SILs were prepared, as summarized in Scheme 1.

Activated silica gel was functionalized with selected IL cations, using in each case the chloropropyl silica material as the intermediate precursor (Scheme 1). The FTIR spectra of activated silica, $[Si][C_3]Cl$, $[Si][N_{3222}]Cl$, $[Si][N_{3444}]Cl$, $[Si][N_{3666}]Cl$, $[Si][N_{3888}]Cl$, $[Si][N_{3114}]Cl$, $[Si][N_{3118}]Cl$ and $[Si][C_3C_1Im]Cl$ were acquired to confirm the functionalization of silica with ILs, as shown in Figure 1. The absence of the band at 974 cm^{-1} in most of the samples, typically associated with the Si−OH bending vibration absorption,[15] suggests successful functionalization of silica. Note that the FTIR spectrum of sample $[Si][C_3C_1Im]Cl$ also presents a weak band at 1574 cm^{-1}, which is attributed to the imidazole ring vibration.

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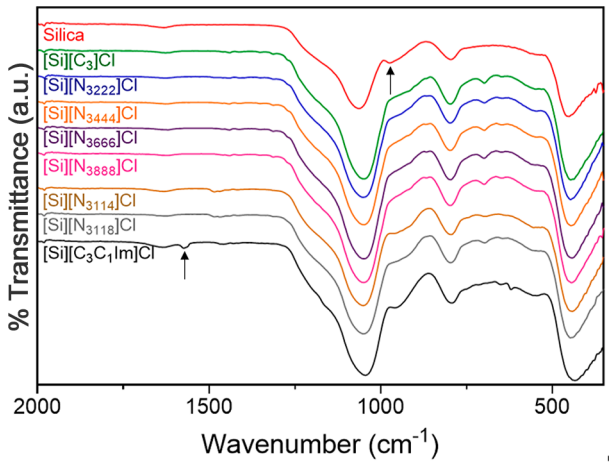

Figure 1. FTIR spectra of activated silica, [Si][C_3]Cl, [Si][N_{3222}]Cl, [Si][N_{3444}]Cl, [Si][N_{3666}]Cl, [Si][N_{3888}]Cl, [Si][N_{3114}]Cl, [Si]-[N_{3118}]Cl, and [Si][C_3C_1Im]Cl.

Solid-state ^{13}C NMR was used to confirm the successful synthesis of the seven SILs. The spectra are shown in Figure 2.

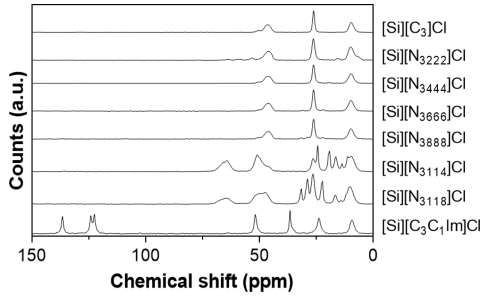

Figure 2. Solid-state ^{13}C NMR spectra of the intermediate sample and SILs.

First, the ^{13}C NMR spectrum of the intermediate sample shows peaks at 10, 26, and 47 ppm, corresponding to the carbons of the propyl alkyl chain. With a few exceptions, noted below, the ^{13}C NMR spectra of the different SILs obtained from the reaction of chloropropyl silica with different cations are in agreement with the respective functionalization.[15] Figure S1 (Supporting Information) shows the peaks' assignment with the respective carbon atom labeling. For the [Si][N_{3222}]Cl sample, the carbons of the propyl chain are shown at 10, 26, and 46 ppm, while the carbons of the ethyl chain are identified at 16 and 53 ppm. In the spectrum of [Si][N_{3114}]Cl, the peaks at 11, 24, and 66 ppm correspond to the carbons of the propyl chain, the peak at 51 ppm corresponds to the carbon of the methyl chain, and the peaks at 17, 19, 26, and 64 ppm correspond to the carbons of the butyl chain. In the spectrum of [Si][N_{3118}]Cl, the peaks at 10, 26, and 65 ppm correspond to the carbons of the propyl chain, the peak at 48 ppm corresponds to the carbon of the methyl chain, and the peaks at 17, 22, 29, 32, and 50 ppm correspond to the carbons of the octyl chain. For the [Si][C_3C_1Im]Cl sample, the carbons of the imidazolium ring are identified at 123−124 and 137 ppm, the peak at 37 ppm corresponds to the carbon of the methyl chain, and the carbons of the propyl chain are shown at 9, 24, and 52 ppm. The similarity between the spectrum of [Si][C_3]Cl and the spectra of [Si][N_{3444}]Cl, [Si][N_{3666}]Cl and [Si][N_{3888}]Cl can be explained by the low extent of functionalization in these materials. Figure S2 represents the ^{13}C NMR spectra of the [Si][C_3C_1Im]Cl sample before and after the sorption studies at pH 4, showing no alterations in the SIL structure by contact with acidic aqueous solutions.

Table 1 provides the results of elemental analysis of all of the samples, showing the carbon, hydrogen, and nitrogen contents

Table 1. Results of Elemental Analysis of Activated Silica, [Si][C_3]Cl, [Si][N_{3222}]Cl, [Si][N_{3444}]Cl, [Si][N_{3666}]Cl, [Si][N_{3888}]Cl, [Si][N_{3114}]Cl, [Si][N_{3118}]Cl and [Si][C_3C_1Im]Cl

Particles	%C	%H	%N	Bonding amount (mmol/g)
Activated silica	–	–	–	–
[Si][C_3]Cl	6.45	1.55	–	–
[Si][N_{3222}]Cl	7.46	1.99	0.36	0.26
[Si][N_{3444}]Cl	6.96	1.55	0.17	0.12
[Si][N_{3666}]Cl	7.05	1.24	0.13	0.09
[Si][N_{3888}]Cl	7.47	1.87	0.13	0.09
[Si][N_{3114}]Cl	8.92	2.52	1.00	0.71
[Si][N_{3118}]Cl	11.38	2.87	0.75	0.53
[Si][C_3C_1Im]Cl	9.02	2.37	2.96	1.05

in SILs. The carbon and nitrogen contents of SILs range from 6.967% to 11.387% and from 0.134% to 2.962%, respectively, being in line with silica-gel samples functionalized with ILs. Lastly, elemental analysis also confirms the low functionalization degree of [Si][N_{3444}]Cl, [Si][N_{3666}]Cl and [Si][N_{3888}]Cl samples, being in agreement with the ^{13}C NMR results discussed above.

The elemental analysis data were used to determine the amount of ILs bonded to the SILs. The bonding amount of IL in [Si][C_3C_1Im]Cl was calculated based on the percentage amount of nitrogen and considering that each molecule of methylimidazole has 2 nitrogen atoms; the bonding amount of other SILs was calculated by the percentage content of nitrogen and considering that each quaternary ammonium has 1 nitrogen atom. The number of IL functional groups in the SILs varies according to the type of IL cation used. The [Si][N_{3888}]Cl material has the lower amount of IL functional groups, followed by [Si][N_{3666}]Cl, [Si][N_{3444}]Cl, [Si][N_{3222}]-Cl, [Si][N_{3118}]Cl, [Si][N_{3114}]Cl, and [Si][C_3C_1Im]Cl, with values increasing from 0.09 to 1.05 mmol/g. These values are important to evaluate the performance of the materials for the sorption of platinum and palladium.

The specific surface areas of the functionalized and nonfunctionalized silica samples have been determined by nitrogen adsorption using the Brunauer−Emmett−Teller (BET) method (Table 2). The results show a lower specific

Table 2. BET Surface Area (S_{BET}), Porosity Volume (V_p) and Pore Diameter (D_p) of the Different SILs

Particles	S_{BET} (m^2/g)	V_p (cm^3/g)	D_p (nm)
Activated silica	466.37	0.7288	5.0633
[Si][C_3]Cl	345.41	0.3687	3.7962
[Si][N_{3222}]Cl	304.95	0.3464	3.7958
[Si][N_{3444}]Cl	259.01	0.3346	3.7978
[Si][N_{3666}]Cl	316.20	0.3436	3.7903
[Si][N_{3888}]Cl	320.10	0.3445	3.7924
[Si][N_{3114}]Cl	201.14	0.2914	3.7976
[Si][N_{3118}]Cl	224.80	0.3396	3.7931
[Si][C_3C_1Im]Cl	199.02	0.3318	3.7964

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surface area for the [Si][C_3]Cl sample, as compared to neat activated silica gel, but a superior value when compared with any of the derived SILs. The pore diameter of the silica is 5.0633 nm, which is the highest among all of the samples. All of the SILs have a pore diameter lower than that of the silica (approximately 3.8 nm), and the lowest pore diameter is 3.7903 nm, which belongs to the [Si][N_{3888}]Cl sample.

Zeta potential measurements were performed for all of the samples to appraise the surface charge of the functionalized and nonfunctionalized silica-based materials. Figure S4 contains the zeta potential data for the activated silica, [Si][C_3]Cl and all SILs as a function of pH. Accordingly, the point of zero charge (PZC) for each colloidal system was determined, as shown in Table 3. As expected by considering the type of surface functionalization performed on the silica-gel samples, all synthesized SILs exhibit higher PZC values compared to those of both [Si][C_3]Cl and activated silica, thus confirming the presence of a cation in SILs and the successful modification of the silica surface.

Table 3. PZC Values of Activated Silica, [Si][C_3]Cl, [Si][N_{3222}]Cl, [Si][N_{3444}]Cl, [Si][N_{3666}]Cl, [Si][N_{3888}]Cl, [Si][N_{3114}]Cl, [Si][N_{3118}]Cl and [Si][C_3C_1Im]Cl

Particles	PZC
Activated silica	3.9
[Si][C_3]Cl	4.3
[Si][N_{3222}]Cl	7.1
[Si][N_{3444}]Cl	5.1
[Si][N_{3666}]Cl	5.6
[Si][N_{3888}]Cl	5.5
[Si][N_{3114}]Cl	9.5
[Si][N_{3118}]Cl	9.4
[Si][C_3C_1Im]Cl	9.2

The SEM images of activated silica, intermediate material (chloropropyl silica) and the different SILs were not acquired since previous works have shown that no significant differences exist between the prepared SILs and the [Si][C_3]Cl.[15,16] Also, no significant morphological differences were observed among the SILs prepared.[15] However, they had a different morphology from the activated silica, which presented a more rough and less smooth or homogeneous surface, meaning that these differences are due to the thermal treatment of activated silica with toluene.[16]

Sorption Kinetics and Isotherms of Platinum and Palladium in SILs. The sorption kinetics of platinum and palladium in all SILs were determined to establish an optimal contact time for subsequent isotherm studies (Figure 3 and Tables S1−S7). Under the conditions assessed, in general, the equilibrium concentration of the sorbate in the sorbent reaches a plateau after 1 h. In the few cases that after 1 h of sorption still no plateau value was found, the additional time required to achieve the equilibrium did not justify the potential benefits of maximum platinum and palladium recovery from the solution. Notably, the highest equilibrium concentration of platinum in the sorbent was 3.74 mg/g with a sorption efficiency of 98%, achieved by using [Si][C_3C_1Im]Cl and [Si][N_{3118}]Cl; the highest equilibrium concentration of palladium in the sorbent was 3.43 mg/g with a sorption efficiency of 89%, achieved by using [Si][C_3C_1Im]Cl. The sorption of platinum and palladium at the conditions studied is highly fast (about 1 h), and the equilibrium concentration of PGEs in the sorbent increases in the following order of SILs: [Si][N_{3888}]Cl < [Si][N_{3666}]Cl < [Si][N_{3444}]Cl < [Si][N_{3222}]Cl < [Si][N_{3114}]Cl < [Si][N_{3118}]Cl < [Si][C_3C_1Im]Cl. Only for platinum are the performances of [Si][C_3C_1Im]Cl and [Si][N_{3118}]Cl similar.

As can be seen in Figure 3, SILs with groups based on *N*-methylimidazolium and asymmetric ammonium cations are the ones with the best performance for both platinum and palladium recovery. Also, the alkyl side chain length appears not to have a significant effect on sorption. Regarding SILs with symmetric ammonium-based ionic liquids, the sorption efficiency increases with the decrease of the alkyl side chain length. Thus, considering the affinity of SILs with Pt and Pd and the price of the amines used during the synthesis (*N*-methylimidazole is cheaper than *N*,*N*-dimethylbutylamine or *N*,*N*-dimethyloctylamine), [Si][C_3C_1Im]Cl is the most relevant SIL, being the only one considered in the following studies.

It should be remarked that the sorption behavior of activated silica gel was also evaluated under the same experimental conditions. Despite its higher specific surface area of ~466 m^2/g and larger pore size diameter, no sorption of platinum and palladium was found, even after prolonged exposure (up to 8 h).

To explore the sorption mechanisms of platinum and palladium in the prepared SILs, the experimental data were fitted to the pseudo-first-order, pseudo-second-order, and Elovich kinetic models. Tables 4 and 5 present the sorption

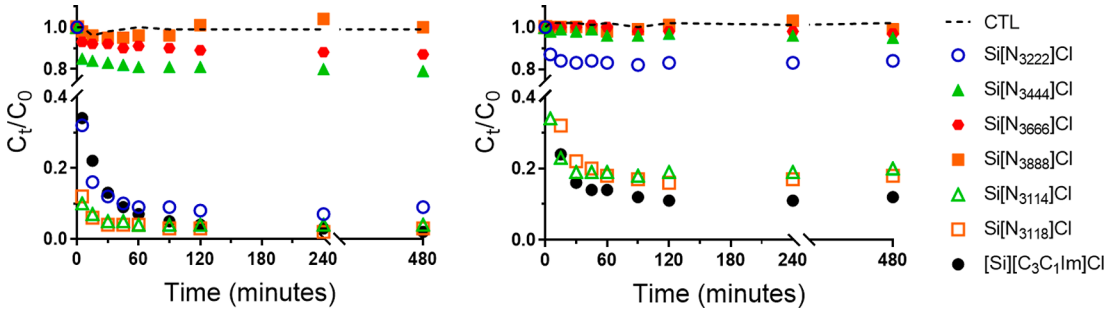

Figure 3. Sorption efficiency of seven SILs for platinum (on left) and palladium (on right): dashed line, control; open blue circle, [Si][N_{3222}]Cl; solid green triangle, [Si][N_{3444}]Cl; solid red hexagon, [Si][N_{3666}]Cl; solid orange square, [Si][N_{3888}]Cl; open green triangle, [Si][N_{3114}]Cl; open orange square, [Si][N_{3118}]Cl; and solid black circle, [Si][C_3C_1Im]Cl. Multielemental solution of 1 mg/L Pt and Pd, pH 4, 250 mg SIL/L, 0−480 min sorption. Most experimental points were repeated three times, and the coefficient of variation was inferior to 2%.

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kinetic parameters. Note that only materials with a sorption efficiency of at least 25% are considered.

Table 4. Parameters of the Pseudo-First-Order, Pseudo-Second-Order and Elovich Kinetic Models, Associated to the Sorption of Platinum

		Pseudo-first-order model		
	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_1 (min^{-1})	R^2
$[Si][N_{3222}]Cl$	3.47	3.379	0.267	0.9947
$[Si][N_{3114}]Cl$	3.80	3.769	0.559	0.9988
$[Si][N_{3118}]Cl$	3.74	3.701	0.476	0.9989
$[Si][C_3C_1Im]Cl$	3.74	3.540	0.224	0.9719
		Pseudo-second-order model		
	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_2 (min^{-1})	R^2
$[Si][N_{3222}]Cl$	3.47	3.488	0.157	0.9993
$[Si][N_{3114}]Cl$	3.80	3.800	0.677	0.9998
$[Si][N_{3118}]Cl$	3.74	3.743	0.471	0.9999
$[Si][C_3C_1Im]Cl$	3.74	3.707	0.101	0.9961
		Elovich model		
	$q_{e,exp}$ (mg/g)	β	α	R^2
$[Si][N_{3222}]Cl$	3.47	5.727	4.187×10^5	0.9779
$[Si][N_{3114}]Cl$	3.80	18.30	5.305×10^{26}	0.9988
$[Si][N_{3118}]Cl$	3.74	14.02	2.455×10^{19}	0.9969
$[Si][C_3C_1Im]Cl$	3.74	3.727	1471	0.9850

Table 5. Parameters of the Pseudo-First-Order, Pseudo-Second-Order and Elovich Kinetic Models, Associated to the Sorption of Palladium

		Pseudo-first-order model		
	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_1 (min^{-1})	R^2
$[Si][N_{3114}]Cl$	3.34	3.283	0.334	0.9976
$[Si][N_{3118}]Cl$	3.29	3.192	0.147	0.9907
$[Si][C_3C_1Im]Cl$	3.43	3.346	0.176	0.9919
		Pseudo-second-order model		
	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_2 (min^{-1})	R^2
$[Si][N_{3114}]Cl$	3.34	3.353	0.252	0.9982
$[Si][N_{3118}]Cl$	3.29	3.366	0.074	0.9964
$[Si][C_3C_1Im]Cl$	3.43	3.509	0.087	0.9985
		Elovich model		
	$q_{e,exp}$ (mg/g)	β	α	R^2
$[Si][N_{3114}]Cl$	3.34	9.190	1.240×10^{10}	0.9830
$[Si][N_{3118}]Cl$	3.29	3.486	162.3	0.9416
$[Si][C_3C_1Im]Cl$	3.43	3.751	660.2	0.9563

The pseudo-second-order model exhibits superior correlation coefficients (R^2) compared to the pseudo-first-order and Elovich models, indicating that the sorption mechanism is determined by strong chemical interactions at the liquid−solid interface of the sorbent.[17,18]

The Langmuir, Freundlich and Dubinin−Radushkevich models were used to fit the experimental data on the sorption isotherms using $[Si][C_3C_1Im]Cl$. To ensure that equilibrium was fully attained, the sorption isotherm studies were conducted for 240 min. Figure 4 shows the relationship between the equilibrium concentrations of platinum and palladium in the solid and liquid phases. More data are provided in the Supporting Information (Table S8).

The equilibrium sorption of both platinum and palladium onto SILs increases until an equilibrium concentration of PGEs

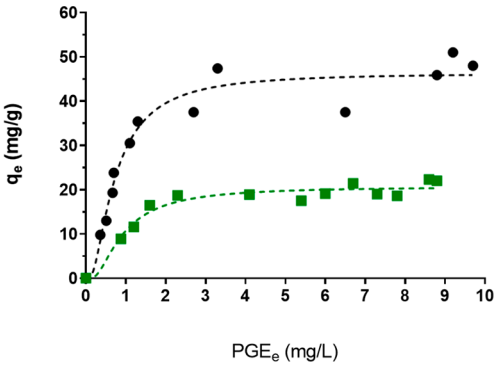

Figure 4. Sorption isotherms of platinum and palladium onto $[Si][C_3C_1Im]Cl$ at 25 °C: solid black circle, q_e Pt (mg/g) and Dubinin−Radushkevich fitting; and solid green square, q_e Pd (mg/g) and Dubinin−Radushkevich fitting. Monoelemental solutions of 1 mg/L Pt and Pd, pH 4, and 240 min sorption.

in solution is about 3.0 mg/L, where a plateau is reached. Beyond this point, no further increase in the sorption occurs. The sorption isotherm parameters obtained with the three models used are presented in Table 6. The sorption of PGEs

Table 6. Parameters of the Langmuir, Freundlich and Dubinin−Radushkevich Isotherm Models, Associated to the Sorption of Platinum and Palladium onto $[Si][C_3C_1Im]Cl$

	Langmuir model		
	q_{max} (mg/g)	K_L (L/mg)	R^2
Pt	52.76	1.022	0.9322
Pd	23.12	1.017	0.9316
	Freundlich model		
	K_F ($mg^{1-1/n}$ $L^{1/n}$/g)	n	R^2
Pt	25.34	3.324	0.8657
Pd	12.45	4.005	0.9076
	Dubinin−Radushkevich model		
	q_{max} (mg/g)	B (mol^2/kJ^2)	R^2
Pt	46.33	1.571×10^{-7}	0.9544
Pd	20.66	2.226×10^{-7}	0.9480

onto $[Si][C_3C_1Im]Cl$ is better described by the Dubinin−Radushkevich isotherm model ($R^2 \approx 0.95$), indicating that the sorption process occurs through the micropore volume filling, taking into account the energetic heterogeneity of the sorbent and the interactions between sorbed species.

A maximum equilibrium concentration of 51.0 mg of platinum and 22.3 mg of palladium were sorbed per gram of material ($[Si][C_3C_1Im]Cl$), as presented in Table S8.

Selective Recovery of Platinum and Palladium from Solution. For the recovery of platinum and palladium from an industrial effluent, it can be of interest to study the selective recovery of the elements. As shown in Figure 3 (and in Table S1), after 1 h of contact, the SIL $[Si][N_{3222}]Cl$ is capable to sorb 91% of the platinum in solution but only 17% of the palladium present. For the same time, $[Si][C_3C_1Im]Cl$ sorbs 93% of platinum and 86% of palladium. Thus, by combining 2 different SILs, namely, $[Si][N_{3222}]Cl$ and $[Si][C_3C_1Im]Cl$, it would be possible to selectively recover platinum and palladium from water, as depicted in Figure 5.

Selectivity is a crucial characteristic of the sorbents proposed to be used for platinum and palladium recovery from

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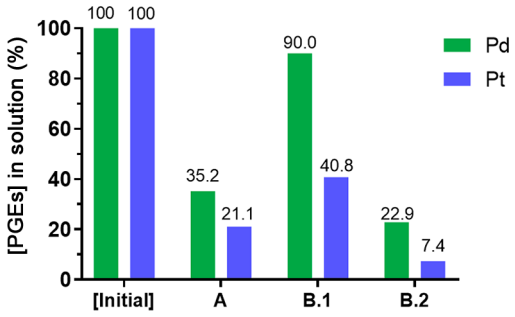

Figure 5. Concentration of platinum and palladium in solution (A) after the contact of the PGEs initial solution with [Si][C_3C_1Im]Cl, and (B) with a combination of 2 SILs ([Si][N_{3222}]Cl followed by [Si][C_3C_1Im]Cl, situations B.1 and B.2, respectively). The numbers over the bars correspond to the % of PGEs in solution.

secondary raw materials. Thus, by combination of two SILs with different cations, it would be possible to selectively recover these elements. Under the conditions studied, after the application of [Si][N_{3222}]Cl to a solution containing platinum and palladium, this material is able to remove almost 60% of the platinum present in the solution but only 10% of the palladium. The subsequent application of [Si][C_3C_1Im]Cl to the solution results in the recovery of more than 65% of the palladium present but also more than 30% of platinum. However, this can be optimized by applying [Si][N_{3222}]Cl, regenerating the material and applying it again. In this way, all the platinum would be recovered from the solution, while [Si][C_3C_1Im]Cl would recover only the palladium from the solution, which could be further preconcentrated and used by industries.

CONCLUSIONS

This work has established the efficacy of seven silica supported IL-based materials with the same anion as sorbents for the recovery of platinum and palladium from aqueous media. The sorption kinetics, best described by a pseudo-second-order model, revealed the formation of strong chemical bonds between the PEGs and the active sites on the sorbent surface. Notably, [Si][C_3C_1Im]Cl demonstrated superior performance, with its sorption data being well fitted by the Dubinin–Radushkevich model and achieving a maximum equilibrium concentration in the sorbent of 51.0 mg of platinum and 22.3 mg of palladium per g of SIL.

The key conclusion drawn from this work is that supported IL-modified silica materials present a viable and efficient solution for the separation and recovery of Pd(II) and Pt(IV). This finding holds significant implications for the recovery of high economic value chemical elements from aqueous matrixes, thereby offering a promising avenue for future research in the field and practical applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.3c06263.

Kinetic and isotherm models, results of equilibrium concentration of Pt and Pd after sorption with the different SILs synthesized, solid-state ^{13}C NMR spectra with peaks' assignment, solid-state ^{13}C NMR spectra of the [Si][C_3C_1Im]Cl sample (after and before sorption experiments), and graphs of zeta potential as a function of pH (PDF)

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Notes

The authors declare no competing financial interest.

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