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Amberlite XAD-7 impregnated with Cyphos IL-101 (tetraalkylphosphonium ionic liquid) for Pd(II) recovery from HCl solutions

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ABSTRACT

Cyphos IL-101 ionic liquid (IL; tetradecyl(trihexyl)phosphonium chloride) was immobilized in Amberlite XAD-7 for the preparation of an extractant impregnated resin (EIR) that was used for Pd(II) sorption from HCl solutions. Chloro-palladate anionic species are bound to the EIR by electrostatic/anion exchange mechanism between anionic species and phosphonium cation (IL). Maximum sorption capacity increases with extractant loading and depends on HCl concentration reaching values up to 71 mg Pd g^{-1} EIR for an EIR with 401 mg IL g^{-1} EIR, in 0.5 M HCl solutions. Uptake kinetics are controlled by the resistance to intraparticle diffusion (effective diffusivity varying in the range 1×10^{-11} to 20×10^{-11} m^2 min^{-1}) as confirmed by the limited impact of agitation speed (negligible resistance to film diffusion). IL loading is a key parameter since it controls the filling of resin porous network and consequently the mass transfer properties: diffusivity in the extractant phase is reduced compared to diffusivity in water. Increasing IL loading increases sorption capacity but induces supplementary limitations to intraparticle diffusion. Increasing temperature decreases IL viscosity, which, in turn, enhances diffusion in this extractant phase. Nitric acid and thiourea in hydrochloric acid solutions allows complete desorption of Pd(II) from loaded EIR. The resin can be recycled for at least five cycles maintaining high sorption and desorption efficiencies.

1. Introduction

The demand for precious metals, and especially platinum group metals (PGMs) is increasing with the development of catalytic processes for industry, automotive applications, fuel cells and so on. This growing demand and the cost of these metals have focused the interest of many research groups for recovering metals not only from primary sources (minerals) but also from secondary sources (waste materials such as used catalysts, electronic devices). Valorization of wastes is also part of the current politics on sustainable growth: in many countries a waste can only be disposed in landfill when it is proved that no other way to valorize it exists under economical constraints. Metals can be recovered from solid wastes by a series of unitary processes including grinding, gravimetric separation, magnetic separation, bio- or chemical leaching (solid to liquid transfer). When transferred in the liquid phase the metals can be recovered by several processes such as electrolytic processes, or solvent extraction [1–4]. However, these processes are generally designed for metal removal from concentrated solutions and alternative processes should be used for the treatment of dilute solutions (as a polishing treatment, for example). Sorption is frequently used for metal recovery from low-concentration solutions. A number of different sorbents have been tested including biosorbents (biomass, biopolymers) [5–10], and resins [11–19]. Biopolymers bearing amine groups such as chitosan have shown interesting properties for PGMs; however, the sorption efficiency is generally limited to medium acidity range (i.e., pH 2). Acidic leachates generated during the extraction of PGMs are generally much more acidic. This is necessary to modify the polymers to bring more specific reactive groups with broader range of active pH: phosphinic [20], sulfur [21], or imidazolium groups [15,16], for example.

Extractant impregnated resins (EIR) are alternative systems that combine the advantages of both resins and solvent extractants [22–26]. Indeed, solvent extraction is very efficient (fast and effective); however, its major drawback is the possible release (loss) of hazardous and expensive extractants (partially soluble in water). Resins offer possibilities for confining the extractant in a matrix preventing extractant loss, reducing economical constraints and environmental issues. A new class of extractants has been recently used for the preparation of EIRs: ionic liquids (ILs) offer interesting properties such as higher thermal stability, lower solubility in water and lower vapor pressure that make these extractants competitive against conventional materials for metal extraction [27]. Cyphos

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Table 1
Physical characteristics of Amberlite XAD-7 resin [24].

Parameter	Value
Particle size	20/60 mesh – 250–850 μm
Specific surface area	450 $m^2\,g^{-1}$
Resin porosity	0.55
Pore size (mean value)	85–90 Å
Pore volume	0.97–1.14 $cm^3\,g^{-1}$
Skeletal density	1.24 $g\,cm^{-3}$

IL-101 (tetradecyl(trihexyl)phosphonium chloride) is a member of the Cyphos ionic liquid family based on phosphonium cation (associated to different anions: mineral or organic compounds). It has been used for metal recovery in conventional liquid/liquid extraction processes [28,29]. Recently, these ILs have been also used for preparing new EIRs [30–36]. Two techniques have been developed for manufacturing these EIRs: (a) the conventional method consisting in the impregnation of the resin followed by solvent evaporation [30,32,34] and (b) the immobilization of the IL in biopolymer capsules [31,35,36].

The present study focuses on the sorption of Pd(II) from HCl solutions using an EIR prepared by the conventional method. Amberlite resins are supports commonly used for the preparation of EIR. They have been designed with different characteristics of porosity (pore volume and pore size) and with different surface characteristics (the most important being hydrophobicity that is controlled by the type of polymer (acrylic-ester or styrene-divinyl benzene polymers). In this study, Amberlite XAD-7 was used. This resin is a macroporous acrylic ester polymer, moderately polar (dipole moment: 1.8), with interesting textural properties such as high pore volume (1.14 $mL\,g^{-1}$), pore diameter (90 Å) and surface area (450 $m^2\,g^{-1}$). This resin impregnated with different extractants has showed greater efficiencies and faster extraction of metal ions that other hydrophobic macroporous styrene-divinyl benzene polymers such as Amberlite XAD-2 (dipole moment 0.3) [37].

This is part of a more extended research program consisting in the testing and comparison of the extraction of a series of metal ions using Cyphos IL-101 immobilized in different systems (i.e., Amberlite XAD-7 resin, but also alginate biopolymer capsules) [30–36,38–41]. The different systems allow identifying and explaining the impact of the mass transfer properties of the immobilization matrices and the effect of metal speciation on equilibrium and kinetic performance.

The effect of HCl concentration on sorption capacity is investigated, before determining the sorption isotherms for different IL loadings, and at different temperatures. In a second step uptake kinetics are carried out considering the influence of agitation speed, IL loading, temperature and metal concentration. In a third step, metal desorption and resin recycling are investigated.

2. Materials and methods

2.1. Materials

Amberlite XAD-7 was supplied by Sigma–Aldrich (Saint-Louis, U.S.A.). This is a polyacrylic acid ester type resin ($[CH_2{-}CH(COOR)]_n$). The physical characteristics of the resin are summarized in Table 1. Amberlite XAD-7 can be considered as a nonionic, moderately hydrophilic polymer. It is commercialized as a macroporous polymer, although it must be considered as a mesoporous material (pore diameter: 20–500 Å) according to IUPAC. The resin was conditioned by the supplier with NaCl and Na_2CO_3 to inhibit or delay bacterial growth. It was necessary to clean it to remove salts and monomeric material present on the resin. The resin was therefore put into contact with ketone for 24 h at 25 °C. After filtration under vacuum to remove excess ketone, the resin was rinsed with de-mineralized water, before being washed with nitric acid (0.1 M) for 24 h. The resin was filtered under vacuum and then rinsed with de-mineralized water to constant pH. Finally, the resin was put into contact with ketone for 12 h before being filtered under vacuum and dried in a roto-vapor at 50 °C. Cyphos IL-101 was kindly supplied by Cytec (Canada). This is a phosphonium salt (tetradecyl(trihexyl)phosphonium chloride, C.A.S. number: 258864-54-9, formula weight: 519.42 $g\,mol^{-1}$). It is a slightly viscous room temperature ionic liquid. It is less dense than water and colorless to pale yellow. It is immiscible with water although it is sparingly soluble in water and can dissolve up to 8% water. The chemical structure is $[R_3R'P]^+\,Cl^-$, where R = hexyl and R′ = tetradecyl. Other reagents (salts, acids, etc.) were analytical grade and supplied by KEM (Mexico). Standard metal solutions were supplied by Perkin Elmer (U.S.A.).

2.2. Resin impregnation

In the present work the extractant was immobilized on the resin by a physical technique. Different processes may be used for the physical impregnation of the resin including (i) the wet method, (ii) the dry method, (iii) the impregnation in the presence of a modifying agent, or (iv) the dynamic method [42]. Previous studies have shown that the dry method increases the stability of the extractant on the resin. The dry impregnation of the resin was actually performed by contact of 5 g of conditioned Amberlite XAD-7 with 25 mL of ketone for 24 h. Varying amounts of Cyphos IL-101 diluted in ketone (0.5 M) were added to resin slurry for 24 h, under agitation. The solvent was then slowly removed by evaporation in a roto-vapor. The amount of extractant immobilized on the resin ($q_{\text{Cyphos IL-101}}$) was quantified by the following procedure. A known amount of impregnated resin (250 mg) was mixed with methanol (3 mL) for 24 h to remove the extractant by dissolving. The washing treatment was carried out four times. The solvent was finally separated from the resin, which was dried at 50 °C for 24 h for complete evaporation of solvent. The mass difference ($M_{\text{Cyphos IL-101}}$) between impregnated ($M_{\text{XAD-7/Cyphos IL-101}}$) and washed resin ($M_{\text{XAD-7}}$) was used to calculate the amount of extractant immobilized on the EIR:

$$q_{\text{Cyphos IL-101}} = \frac{M_{\text{XAD-7/Cyphos IL-101}} - M_{\text{XAD-7}}}{M_{\text{XAD-7/Cyphos IL-101}}} \quad (1)$$

The experimental procedure allowed the preparation of EIR containing 59, 106, 152, 207, 291, 401, 498, and 586 mg IL g^{-1} EIR. Previous studies have shown that an excessive loading of IL in the EIR (around and above 600 mg IL g^{-1} EIR) resulted in a partial leakage of the IL: exudates were observed by optical microscope at the surface of the resin during metal sorption due to partial water and HCl co-extraction [30]. In addition, iridescence (typical of hydrocarbon release) was also observed at the surface of water. In the present study, the IL loading was maintained below 500 mg IL g^{-1} EIR for systematic sorption experiments (i.e., sorption isotherms and uptake kinetics) to prevent IL leakage. In a matter of fact, the observation of resin surface and water surface did not show any of these phenomena, indicating the stability of the IL in the porous network.

The drying of the resin at the end of the impregnation process may increase the hydrophobicity of the resin, which, in turn, hinders the intraparticle diffusion of metal ions inside the EIR. To minimize this effect the EIR particles were pre-hydrated at the target pH (or appropriate HCl concentration), prior to use in the kinetics studies.

2.3. Characterization

Element distribution (especially Pd and P, as the tracers of metal sorption and IL distribution, respectively) in the beads was