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Palladium Recovery from Dilute Effluents using Biopolymer-Immobilized Extractant

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Abstract: Cyanex 301-immobilized material (prepared by immobilization into an alginate matrix) was tested for Pd sorption in 1 M HCl solutions with a special attention to sorption isotherms and uptake kinetics. This immobilized extractant had great affinity for Pd, as shown by the initial slope of the sorption isotherms. Sorption capacities as high as 150 mg Pd g^{-1} were obtained in 1 M HCl solutions. However, kinetics was slow, compared to conventional resins. The main limiting step in the process is the diffusion of metal ions into the matrix. The influence of parameters such as HCl concentration, NaCl addition, presence of Pt (as a competitor metal) has been checked. It appeared that sorption performance of Cyanex 301-immobilized material was hardly influenced by the addition of NaCl and by HCl concentration (below 2.5 M). The resin was remarkably selective for Pd, versus Pt, especially at 1 M HCl concentration. Loaded resins can be desorbed using thiourea solutions.

Keywords: Cyanex 301, alginate, immobilization, palladium, isotherms, kinetics

INTRODUCTION

The increasing demand for precious metals for catalytic systems (automotive catalysts, chemical catalyst) has focused the interest of research community for the development of new materials and new processes for the recovery of

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platinum group metals (PGMs) from low grade ores or waste catalysts (1). In most cases their recovery is operated by pyro- (2) and hydro-metallurgy (3); and acidic leachates are frequently generated using concentrated hydrochloric solutions (4, 5). Resins and solvent extraction are commonly cited for the removal of PGMs from acidic solutions (6–8). A number of synthetic resins have been specially tailored for the sorption of Pd (9–13); materials of biological origin have been also used as based materials for the synthesis of derivatives with high sorption capacities (14–16). Biopolymers offer promising perspectives but their sorption capacities are frequently limited in very acidic solutions (15, 17–19). For example, chitosan derivatives obtained by chemical cross-linking (16) or grafting functional groups (17) have sorption capacities as high as 300–500 $\mathrm{mg\,Pd\,g^{-1}}$ at pH 2, but increasing the acidity of the solution (0.1–1 M HCl solutions, for example) drastically decreased sorption performance (below 50 $\mathrm{mg\,Pd\,g^{-1}}$). Solvent extraction systems developed for palladium recovery are generally less sensitive to acidity but the loss of extractant during the extraction process induces environmental risks and economic constraints (8, 20–23). To reduce the impact of extractant loss, a number of immobilization processes have been developed including impregnation procedures (12, 24), or encapsulation techniques (25–27). In most cases impregnation procedures consist in the impregnation of a porous support with the extractant dissolved in an appropriate solvent followed by evaporation of the solvent: the extractant remains immobilized in the porous network of the resin (28–30) or activated carbon (31). In the case of encapsulation processes the extractant is immobilized in the course of the preparation of the resin (25, 32, 33). The key parameters for the selection of the immobilization process are the stability of the extractant on the resin and the amount of extractant that can be immobilized. Recently, biopolymers have been used for the encapsulation of extractants for the binding of different metals (25–27, 32, 34–36).

Cyanex 301, 302, and 471X have been tested for recovery of palladium and platinum in conventional solvent extraction or supported systems (37–39); Mimura et al. (25) developed an original method for encapsulation of Cyanex 302 into alginate capsules for Pd recovery from acidic solutions. A derived procedure was used for the preparation of a series of immobilized–extractants. Preliminary tests have shown that best results were obtained with Cyanex 301 in terms of extractant stability (partial release of organic phase), binding capacities. Complementary experiments have thus been performed using Cyanex 301 as the active phase, investigating the effect of HCl concentration, addition of chloride ions on equilibrium. Sorption isotherms and uptake kinetics have been tested for different conditionings of the beads. The competitive sorption of Pd versus Pt was also tested from binary mixtures at different HCl concentrations. The desorption of saturated extractant-beads has been tested using concentrated HCl solutions and thiourea (at neutral pH and in acidic solutions).

EXPERIMENTAL SECTION

Reagents

Alginate was supplied by ACROS (Switzerland) under the form of sodium alginate. Gelatin was supplied by VWR Prolabo (France). Cyanex 301 (bis(2,4,4-trimethylpentyl)ditiophosphinic acid; assay: 75–80%, commercial data), Cyanex 302 (bis(2,4,4-trimethylpentyl)monotiophosphinic acid;; assay: 84%, commercial data) and Cyanex 471X (triisobutylphosphine sulfide; assay: 97%, commercial data) were kindly donated by Cytec (Cyanamid) (U.S.A.). The extractants were used as supplied without any purification step. Pd and Pt chloride salts ($PdCl_2$, and H_2PtCl_6) were supplied by Fluka (France). Other reagents were analytical grade supplied by Fluka (France).

Preparation of Biopolymer-Immobilized Extractant Beads

Ten grams of extractant were mixed with 10 g of a gelatin solution (20% w/w in water). The gelatin solution was prepared by dissolving solid gelatin in boiling water. The extractant was added dropwise into the gelatin solution with a gentle hand-made agitation using a spatula till obtaining a homogeneous and stable white emulsion. Three hundred eighty grams of alginate solution (1.5% w/w in water) were added to the extractant-gelatin mixture under agitation. The mixture was left to stand for 2 hours in order to remove bubbles and then the viscous solution was dropped into a $CaCl_2$ solution (0.5 M) through a thin nozzle (which diameter controls the size of resin beads). After 1 hour of ionotropic gellation the beads were rinsed 2 times with demineralized water. Some beads were used as prepared, other lots were submitted to complementary treatments involving drying at room temperature, or more sophisticated processes: impregnation of the beads with saccharose, drying at room temperature and re-hydration. This sequence of post-treatments has been used in order to check the possibility to increase the porosity of the beads and thus enhance diffusion properties. This process was successfully applied in the case of chitosan gel beads (16). The presence of saccharose during the drying step allowed maintaining the porous network of the beads and partially restores the initial properties of the materials, while a non-controlled drying induced an irreversible destruction of the porosity of the gel.

Characterization of Biopolymer-Immobilized Extractant Beads

For the determination of true concentrations of the extractants in the encapsulated beads, the beads were digested using concentrated HCl under heating (at boiling temperature). The degradation of the beads allowed after filtration and analysis of phosphorus content to determine the molar concentration of the extractant in the beads and to deduce the mass percentage of the extractant in the beads.

Sorption and Desorption Procedures

Palladium and platinum mother solutions were prepared by dissolving metal salts in concentrated solutions under heating. The mother solutions were 10 g Pd L^{-1} (in 1.1 M HCl solutions) and 2 g Pt L^{-1} (in 1.1 M HCl solutions) for palladium and platinum, respectively. The test solutions were prepared by dilution of mother solutions using appropriate acidic solutions (HCl solutions at the nominal concentration requested for experiments). The true concentrations (in terms of HCl concentration and chloride concentration) were calculated taking into account HCl concentration in mother solution, HCl concentration from dilution and chloride ions brought by the salt. Experiments in binary solutions (Pd-Pt) and in presence of base metals (at the concentration of 1 g metal L^{-1}) were performed using the same experimental procedure.

To prevent disruption of the extractant impregnated beads sorption isotherms were carried out using a reciprocal shaker, while kinetics were performed in batch systems with a flat impeller system. Using magnetic stirrer provoked a progressive degradation of the beads. Standard conditions for sorption isotherms corresponded to the contact for a minimum of 5 days of agitation of 30 mL of solution (at given metal concentrations in the range: 10–300 mg L^{-1}) with 20 mg of sorbent (dry weight). Flasks were maintained in agitation using a reciprocal shaker. After 5 days of agitation the solution was filtered and the filtrate was analyzed for the determination of residual metal concentration using inductively coupled plasma atomic emission spectrometry (ICP-AES) facilities (Jobin-Yvon 2000, Longjumeau, France). The mass balance equation was used for the determination of sorption capacities.

For kinetics, 250 mL of metal solution was agitated using a jar-test agitator at the rotation speed of 250 rpm. Samples were collected at fixed contact times, filtrated using 1.2 μm-pore size filter membranes, before being analyzed by ICP-AES.

Desorption was performed on reciprocal shaker by mixing overnight saturated resins with HCl (8 M), thiourea (0.1 M or 0.2 M in water and 0.1 or 0.2 M in 0.1 M HCl). Samples were filtrated and the residual concentration was determined by ICP-AES.

SEM-EDAX Analysis

Palladium distribution in the beads was investigated by Environmental Scanning Electron Microscopy (ESEM) Quanta FEG 200, equipped with an OXFORD Inca 350 Energy Dispersive X-ray microanalysis (EDX) system.

The system can be used to acquire qualitative or quantitative spot analyses and qualitative or quantitative X-ray elemental maps and line scans. This ESEM allows samples to be analyzed at pressures and humidity which approach normal laboratory conditions and avoids experimental artifact. More specifically, this is possible to analyze the samples at much higher pressure than with conventional SEM. Alternatively dry samples of free or saturated extractant-encapsulated beads were embedded in synthetic resin EPOTEK 301:4 parts glue and 1 part lubricant. After a drying step of 24 h at mild temperature, the embedded beads were cut and sections were polished with a series of abrasive GEOPOL disks of decreasing rain size (6/12, 2/6, and 0.5/3 μm). The sections were rinsed with water between each pair of abrasive disks after the polishing step. Finally the sections were polished with a fine tissue using a DP emulsion lubricant (DP lubricant) and diamond spray HQ (successive sizes 6, 3 and 1 μm). Finally, the sections were coated with carbon or gold by metallization (to increase sample conductivity).

RESULTS AND DISCUSSION

Preliminary Tests on Cyanex 301, Cyanex 302 and Cyanex 471X Extractants

Before investigating in detail the effect of experimental parameters on Pd sorption performance, preliminary experiments have been performed using a series of extractants, following the same immobilization procedure. Figure 1 shows the results of these preliminary tests performed in 1 M HCl solutions. This figure clearly shows that the sorption isotherms obtained with the beads prepared with Cyanex 301 are substantially better than those obtained with the other extractants. The beads can be classified in the following order:

$$\text{Cyanex 301} > \text{Cyanex 302} \gg \text{Cyanex 471X}$$

The isotherm curves can be modeled using the Langmuir equation:

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

where q and q_m are the sorption capacity and the maximum sorption capacity at saturation of the monolayer (mg Pd g^{-1}), respectively; b is the affinity coefficient (L mg^{-1}); C_{eq} is the residual metal concentration (mg L^{-1}).

For Cyanex 301 : $q_m = 144.5$ $b = 1.21$ (R^2 : 0.999)
For Cyanex 302 : $q_m = 125.6$ $b = 0.87$ (R^2 : 0.999)
For Cyanex 471X : $q_m = 70.0$ $b = 0.345$ (R^2 : 0.999)

Both the maximum sorption capacities and the affinity coefficients follow the cited ranking. The classification of the extractants can be explained by the

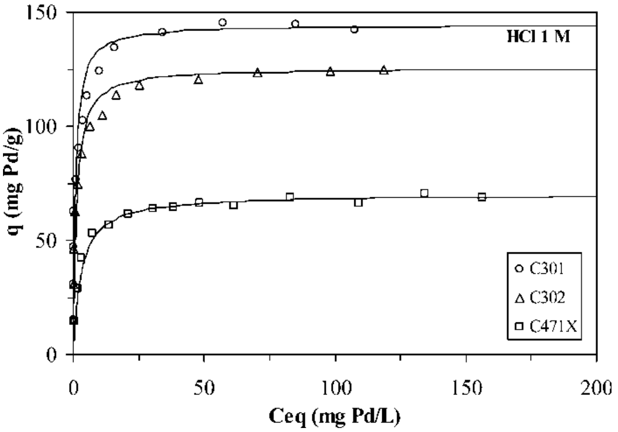

Figure 1. Comparison of Cyanex 301, Cyanex 302 and Cyanex 471X immobilized beads for Pd recovery in 1 M HCl solutions (experimental data: symbols, solid lines: modeling using the Langmuir equation).

differences in their functional groups: dithiophosphinic acid (for Cyanex 301), monophosphinic acid (for Cyanex 302) and phosphine sulfide (for Cyanex 471X); Dithiophosphinic groups having more affinity than monophosphinic groups and phosphine sulfide groups for interacting with palladium. This can be explained by the difference in the acidity of the extractants (pK_a (Cyanex 301): 2.61; pK_a (Cyanex 302): 5.63); and by the application of the Hard-Soft-Acid-Base (HSAB) principles (40). Cyanex 301 can be considered a soft acid having more affinity for a soft metal ion such as Pd^{2+}, compared to Cyanex 302 which is an intermediate soft acid.

It is also important to comment that Cyanex 471X was less stable on the beads than the other extractants: a partial release was observed at long contact time. For these reasons the experiments have been continued with Cyanex 301 immobilized material.

Characterization of Cyanex 301 Immobilized Beads

The size of standard immobilized beads was 450 μm ± 30 μm (dry beads). Figure 2 shows the SEM-EDAX analysis of Cyanex 301 immobilized beads. The distribution of Ca, S, P and Pd elements is shown on the cross-section of beads: it appears that each of the selected elements was homogeneously distributed along the cross-section. This clearly indicates that the extractant was distributed in the whole mass of the bead. Palladium was also present in the whole mass of the bead indicating that if a sufficient contact time is given to the system for saturating the sorbent palladium can access all the sorption sites present in the beads. The degradation of the extractant loaded beads using the digestion procedure allowed determining the

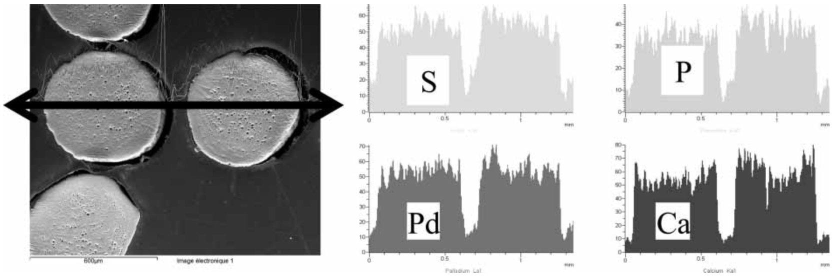

Figure 2. Cross-section of Cyanex 301-immobilized beads (SEM-EDAX) and distribution of selected elements along the section (marked by a double arrow on the SEM section).

actual proportion of Cyanex 301 inside the beads: the content of Cyanex 301 tended to 39% ± 2% (w/w on dry mass). This is a relatively high percentage compared to conventional impregnated resins.

The SEM microphotograph clearly shows that the texture of the bead was homogeneous; the procedure for the preparation of the beads significantly differed from that used by Mimura et al. (25), who obtained heterogeneous capsules with sections made of alginate gel and areas occupied by oil drops (resulting from emulsion formation).

Influence of HCl Concentration

Due to the strong acidity of leachates issued from the treatment of ores and waste catalysts it is important to consider the impact of changing the acidity of the solution on the efficiency of Pd extraction. Figure 3 shows the sorption isotherms obtained with solutions prepared at 0.1 M, 1 M and 2 M. The three curves are perfectly superimposed. This is confirmed by the parameters of the Langmuir equation for each experimental series:

$$\begin{array}{llll}\text{At } 0.1\text{ M}: & q_m = 142.7 & b = 1.02 & (R^2 : 0.999)\\ \text{At } 1\text{ M}: & q_m = 143.0 & b = 1.26 & (R^2 : 0.999)\\ \text{At } 2\text{ M}: & q_m = 143.1 & b = 1.50 & (R^2 : 0.999)\end{array}$$

The maximum sorption capacity was obviously independent of the acidity of the solution. The affinity coefficient slightly increased with the acidity of the solution. It is noteworthy observing that the series at 1 M HCl is a repetition of the series presented in the section comparing the behavior of Cyanex 301, Cyanex 302, and Cyanex 471X systems. The results are perfectly reproducible: the maximum sorption capacity varied by less than 1% and the affinity coefficient by less than 5%.

Simultaneously to the series 0.1 M, 1 M and 2 M, a sorption isotherm was also tested in 5 M HCl solutions. The results are not shown due to

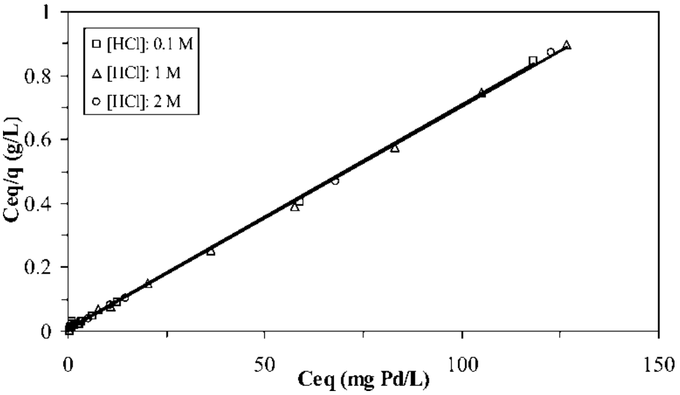

Figure 3. Influence of HCl concentration on Pd sorption isotherms using Cyanex 301 immobilized beads (experimental data: symbols, lines: modeling using the Langmuir equation).

the partial degradation of the sorbent, causing the release of a significant fraction of the extractant into the solution. This affects the meaning of experimental data. Figure 4 shows the impact of HCl concentration on sorption capacity and the distribution coefficient of Pd between liquid and solid phases ($K_d = q/C_{eq}$) for selected experimental conditions. In the range 0.1–2 M sorption capacity slightly decreased from 134 mg Pd g^{-1} to 120 mg Pd g^{-1}, while the distribution coefficient decreased from 7.5 L g^{-1} to 4.3 L g^{-1}. On the other hand, when HCl concentration increased to 5 M, both sorption capacity and distribution coefficient increased. This

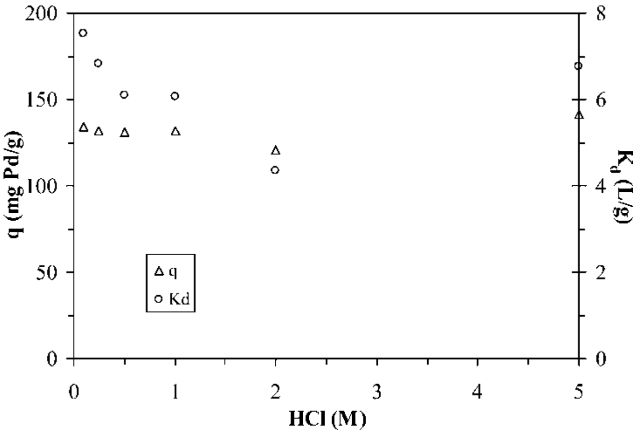

Figure 4. Influence of HCl concentration on Pd sorption capacity and distribution coefficient (K_d, L g^{-1}) (sorbent amount: 20 mg; Volume: 30 mL; Initial concentration, Co: 100 mg L^{-1}).

inversion of the trend can be explained by the degradation of the resin, the release of the extractant, which removed Pd by solvent extraction and not by sorption on the immobilized-extractant beads: at 5 M, sorption capacities were overestimated. The weak impact of HCl concentration confirms the binding mechanism of Pd on the extractant immobilized beads. The acidity of the solution is expected to play an important role in the case of ion exchange mechanisms and the slope of the plot of log K_d versus log [HCl] allows determining the number of protons to be exchanged during solute extraction. Mimura et al. (25) investigated the influence of nitric acid concentration on palladium recovery using Cyanex 302 encapsulated in alginate capsules. They found that the plot of log K_d versus log [HNO_3] was characterized by a slope close to -2 indicating that 2 moles of protons were exchanged for the uptake of 1 mole of Pd^{2+}. In nitric acid solutions, the absence of chloride ions does not allow the formation of chloropalladate species like in the present experimentation; additionally the difference in the extractant (monothiophosphinic acid instead of dithiophosphinic acid) makes the comparison of experimental data rather difficult. The distribution coefficient determined by Mimura et al. (25) was significantly decreased by increasing the pH: though it was comparable for 0.2–0.5 M HNO_3 concentrations around 6 L g^{-1} (against 6.2–6.8 L g^{-1} in the present study); for a 2.5 M concentration they found that the distribution coefficient decreased to 0.028 L g^{-1} (it exceeded 4 L g^{-1} at 2 M HCl concentration in the present study). While they obtained a slope close to -2 for the plots of log K_d versus log [HNO_3], in the present case the slope tended to -0.2.

In the case of mercury recovery from acidic chloride solutions solutions using Cyanex 301 and Cyanex 302, Francis and Reddy (40) observed a continuous decrease of the distribution coefficient when increasing HCl concentration (in the range 0.5–1 M): in logarithmic units the slope of the curve is close to -2. They correlated this decrease of the distribution coefficient to the formation of chloroanionic species of mercury with increasing the concentration of chloride (due to acid dissociation). Considering the impact of acidity at constant concentration of chloride, they observed that the distribution coefficient was independent of the acidity of the solution. They concluded that Cyanex 301 and Cyanex 302 did not behave as cation exchangers. They suggested that mercury was removed by the extractants by solvating effect, certainly due to the strong affinity of sulfur atoms of the extractants for the soft metal ions (Hg^{2+}).

Influence of Chloride Concentration

A series of sorption experiments was performed at 0.1 M HCl concentration with increasing concentrations of chloride (total concentration including chloride ions coming from metal salt, mother solution and dilution step).

Figure 5 reports the impact of this parameter on sorption capacity and distribution coefficient. In the concentration range 0.1–5 M chloride concentration did not change sorption capacity that remained close to 123 mg Pd g^{-1} (± 2 mg Pd g^{-1}), while the distribution coefficient K_d remained stable (around 6.4 L g^{-1}) between 0.1 and 1 M and progressively increased above 1 M (up to 10.7 L g^{-1}). The distribution of palladium species depends on Pd concentration, chloride concentration and pH [16, 41]. Increasing chloride excess versus palladium in acidic solution (pH below 2) leads to the predominance of chloro-anionic species (tri- and tetra-chloropalladate species). The weak effect of HCl concentration and chloride concentration may be explained by the predominance of anionic palladium species, which distribution was hardly affected by the variation of these parameters (in selected concentration range). The comparison of Figs. 4 and 5 shows that the sorption capacities were of the same order of magnitude in the range of concentration 0.1–2 M for HCl and Cl^-. Variations were less than 4% between the two series. This means that the acidity of the solution did not affect the binding capacity of the sorbent for Pd and that the amount of chloride (whatever its origin) was not a key parameter for the process: the speciation was not significantly changed and chloride ions did not compete for reaction on active sites. By analogy with the results of Francis and Reddy (40) on mercury extraction using Cyanex 301 and Cyanex 302 in HCl solutions, we can assume that binding of Pd occurred via binding on sulfur groups by solvating effect. The plot of X_m^2r against Z^2/r (where X_m is the Pauling's electronegativity, Z is the formal charge, and r is the radius of metal ion) shows that Hg^{2+} and Pd^{2+} are very close in terms of Nieboer and Richardson classification (42).

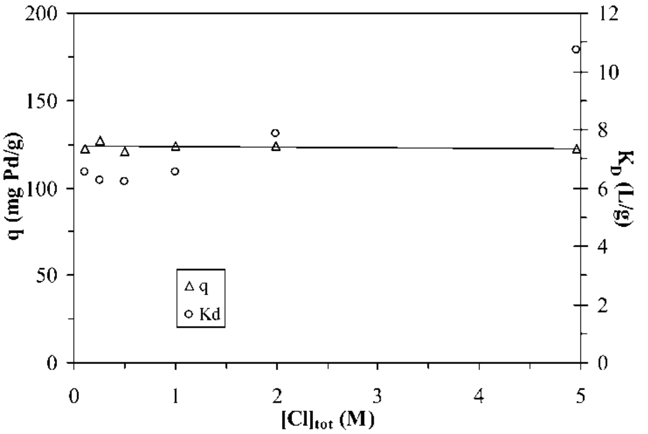

Figure 5. Influence of chloride concentration on Pd sorption capacity and distribution coefficient (K_d, L g^{-1}) (HCl: 0.1 M; sorbent amount: 20 mg; Volume: 30 mL; Initial concentration, Co: 100 mg L^{-1}).

Selectivity of Pd Uptake versus Pt and Base Metals

Mixed solutions have been prepared in order to check Pd binding in the presence of competitor ions such as Pt (separation between PGMs) and Cu, Ni, Zn (base metals present in the treatment of waste catalysts). In the case of Pd uptake in binary solutions with Pt the influence of HCl concentration was also tested varying the molar ratio between Pd and Pt (Figure 6). The selectivity coefficient, S, was calculated using the equation:

$$S = \frac{q(Pd)/q(Pt)}{C_{eq}(Pd)/C_{eq}(Pt)}$$

The selectivity of the sorbent for Pd clearly depended on the acidity of the solution and the initial molar ratio Pd/Pt. Regardless of the acidity of the solution when the molar excess of Pd (versus Pt) was large (i.e. close to 4) the selectivity coefficient increased up to 1500–2500. Surprisingly when the initial molar ratio Pd/Pt was close to 2 a pseudo minimum of the selectivity coefficient was observed. The selectivity was generally lower in 0.1 M HCl solutions and in 2 M HCl solutions it was slightly lower than in 1 M HCl solutions. In molar HCl solutions the selectivity for Pd recovery tended to reach a maximum, regardless of Pd/Pt molar ratio. It is important to observe that when palladium was in excess against platinum the selectivity coefficient was generally greater than 500. In the case of large excess of Pd (i.e. Pd/Pt close to 4), with the optimum HCl concentration (i.e. 1 M), the selectivity coefficient tended to 2400: this means that the sorbent has a much greater affinity for Pd than for Pt. Actually, preliminary tests performed on Pt uptake using similar experimental conditions have shown that in the 0.1–2 M HCl concentration range the sorption capacity varied

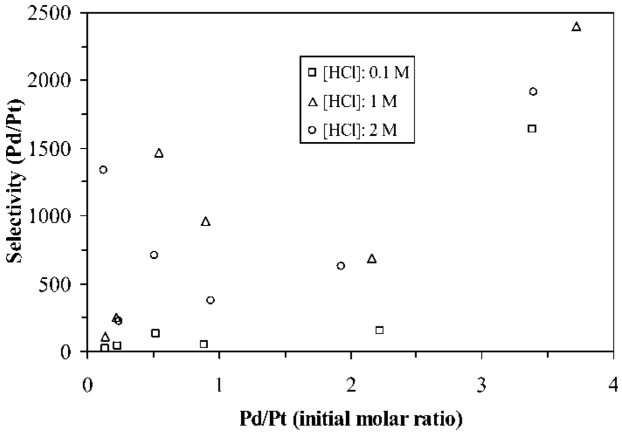

Figure 6. Influence of HCl concentration on the selectivity of Pd uptake from binary Pd/Pt solutions (sorbent amount: 20 mg; Volume: 30 mL).

between 18 and 25 mg Pt g^{-1} (sorbent amount 20 mg; solution volume: 30 mL; initial Pt concentration 100 mg L^{-1}): this means a sorption capacity close to 0.12 mmol Pt g^{-1} far from the levels reached with palladium (i.e. 1.3 mmol Pd g^{-1}, under comparable experimental conditions). This preliminary result on the greater affinity of the resin for Pd is confirmed by its preference for Pd in bi-component solutions: the molar ratio Pd/Pt at equilibrium on the resin exceeded 100. The influence of base metals (BMs) on Pd uptake from binary acidic solutions (1 M) has been tested using Cu, Ni and Zn chloride salts. Figure 7 (a) compares the sorption capacity of Pd in presence of increasing concentrations of competitor metals (in the range 0.1–5 g metal L^{-1}) to the value of sorption capacity of Pd (i.e. 130 mg Pd g^{-1} ± 3 mg Pd g^{-1}) in

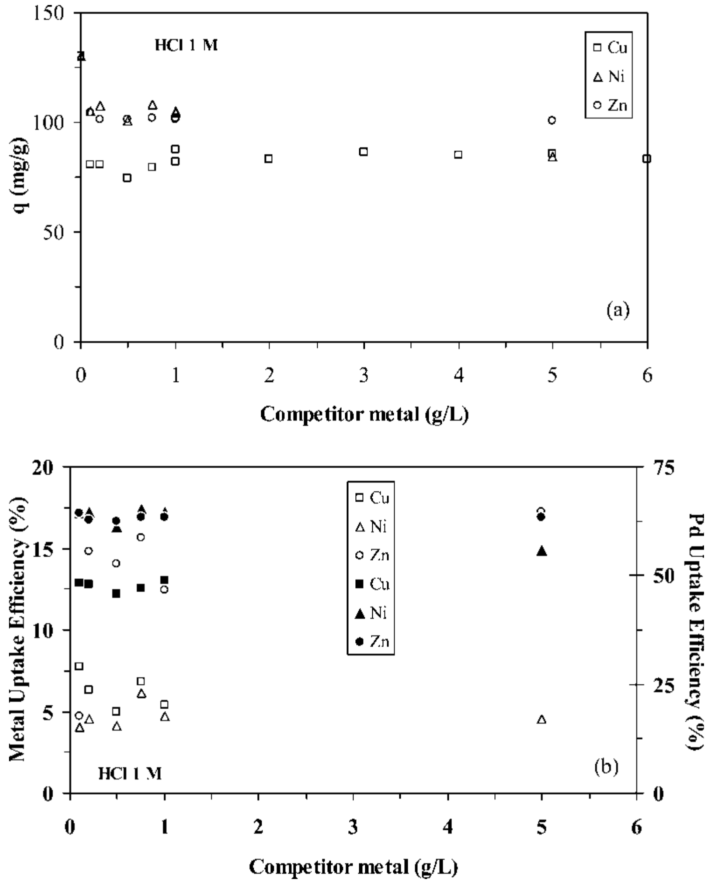

Figure 7. Influence of increasing concentrations of competitor metals (Cu, Ni, Zn) on (a) the uptake of Pd, and (b) the uptake efficiency for Pd and competitor metal in 0.1 M HCl solutions (closed symbols: Pd uptake; open symbols: competitor metal uptake; sorbent amount: 20 mg; Volume: 30 mL).

similar conditions (sorbent amount: 20 mg; volume of solution: 30 mL). The presence of competitor metal even at low concentration induced a decrease of Pd sorption capacity; however, the diminution of the sorption capacity was not controlled by the concentration of the metal. In the presence of copper the uptake capacity decreased from 130 mg Pd g^{-1} to 82 mg Pd g^{-1}. In the presence of nickel the decrease was less significant: in the range 0.1–1 g Ni L^{-1} the sorption capacity remained close to 105 mg Pd g^{-1}, but decreased to 85 mg Pd g^{-1} for 5 g Ni L^{-1} solutions. In the case of Zn, Pd sorption capacity was almost independent of Zn excess: the sorption capacity decreased to 102 mg Pd g^{-1} ($\pm$2 mg Pd g^{-1}). According to HSAB classification, Cu^{2+}, Ni^{2+} and Zn^{2+} are part of the borderline class (intermediary soft/hard acid metals) that might be less reactive with Cyanex 301 (soft base) than Pd^{2+} (soft acid); this can explain that Pd uptake was only slightly affected by the presence of these competitor ions. However, due to the large excess of competitor ions introduced (i.e. concentrations as high 1–5 g metal L^{-1}) a non negligible fraction of the competitor ions was removed from the solution. Figure 7 (b) compares the uptake efficiency for both Pd and the metal competitors. The binding of competitor ions remained between 4 and 8% for copper, between 4 and 6% for nickel and between 12 and 17% for zinc. The binding of Pd was around 47% in presence of copper and remained close to 63% in the presence of nickel and zinc. Despite a large excess of competitor metal the sorbent had a marked preference in terms of sorption efficiency against competitor metals. The sorption capacity for these competitor metals (calculated by the mass balance equation) increased with increasing the metal excess: up to 420 mg Cu g^{-1}, 370 mg Ni g^{-1} and 1400 mg Zn g^{-1} for copper, nickel and zinc respectively.

An additional effect of the binding of copper is related to the in-situ degradation of the extractant. Though this aspect has not been studied in these immobilized materials, it is known that Cyanex 301 and Cyanex 302 extractants are oxidized by small amounts of copper (or iron): the extractants being converted into Cyanex 272.

Kinetics of Pd Uptake—Influence of Beads Conditioning

Preliminary experiments have shown that 48 to 72 hours were generally necessary to reach the equilibrium. This long contact time indicates that the uptake of palladium is controlled, at least, by the diffusion properties of the resin. Similar kinetic restrictions have been observed in the case of chitosan gel beads (16). In this case, the drying of chitosan gel beads involved an irreversible destruction of the porous network that dramatically impacted sorption kinetics. To prevent the collapse of the porous structure a specific treatment was developed. The beads were saturated with sucrose prior to the drying step: the presence of sucrose in the porous network avoids the irreversible shrinking of the beads; after re-hydration they almost regained their initial volume and the diffusion performance was comparable to that of the original wet beads (16). For this reason a similar procedure was tested in the case of extractant immobilized beads. The kinetics of palladium sorption was tested in 1 M HCl solutions (sorbent dosage: 400 mg L^{-1}; initial Pd concentration: 30 mg Pd L^{-1}) with wet beads, dry beads, and beads impregnated with sucrose in both dry and wet state (Fig. 8). The figure shows that the resins treated with sucrose in the wet state were much less efficient than other conditionings: the increase of residual palladium concentration after a few hours of contact can be explained by the loss of stability of the extractant on the resin. A greater contact time was required in the case of dry beads compared to wet beads: this confirms that the resistance to

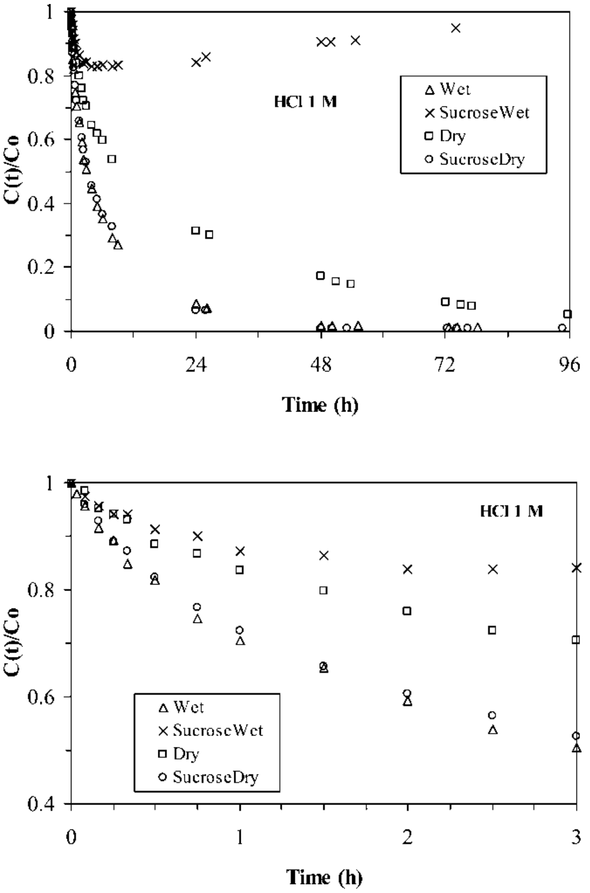

Figure 8. Influence of resin pre-treatment on Pd sorption kinetics (sorbent dosage: 400 mg L^{-1} dry weight; initial Pd concentration: 30 mg Pd L^{-1}).

intraparticle diffusion strongly contributed to the control of overall kinetics, especially in the case of dry beads. However, the bottom part of the figure shows that the differences were also significant in the early stage of sorption process: this early stage is usually controlled by the resistance to film mass transfer. The conditioning of the resins influenced both the external and intraparticle diffusion. On the other hand when the beads were impregnated with sucrose the kinetic profile was very close to that obtained with wet beads. The presence of sucrose maintained opened the porous structure of the resin. However, the impregnation with sucrose resulted in large weight increase of the resin: the volumetric sorption capacity was comparable but the mass sorption capacity was decreased if taking into account the total mass of the sorbent (including sucrose amount) and not the sole amount of resin.

Kinetics of Pd Uptake—Influence of Initial Pd Concentration

The influence of initial palladium concentration (in the range 10–30 mg Pd L^{-1}) on kinetic profiles was also carried out at the same sorbent dosage (i.e. 400 mg L^{-1} dry weight). This means that the sorbent was in large excess compared to the amount of metal to be sorbed and equilibrium concentration is expected to tend to 0. Figure 9 shows that the contact time required to reach equilibrium (actually the complete recovery of Pd) logically increased with initial Pd concentration. The extrapolated contact time required to remove more than 98% of Pd increased from 16 h to 24 h and 40 h for experiments performed with solutions containing 10 mg Pd L^{-1}, 20 mg Pd L^{-1}, and 30 mg Pd L^{-1}, respectively. The early stage of sorption process (i.e. first 15 min) appeared almost independent of initial metal concentration, while after 15 minutes of contact the kinetic profiles tended to separate. The excess of sorbent did not allow reaching the saturation of the sorbent under selected experimental conditions, for this reason it is difficult to evaluate the true contribution of intraparticle diffusion in the control of kinetic profile: the sorption of the solute occurred preferentially at the surface of the resin. This could explain that the concentration gradient between the outer and the inner layer of the resin was not sufficient to enhance mass transfer and improve sorption kinetics as it may occur in systems with less favorable sorbent/solute ratio.

Comparison of Sorption Isotherms for Dry and Wet Resins

The drying step involved a significant decrease in kinetic performance resulting in drastically increased contact times for reaching equilibrium. A comparison of sorption isotherms for resins in dry and wet states appeared necessary. Experiments were performed with beads produced in the same lot with identical content of both extractant and biopolymers: the comparison

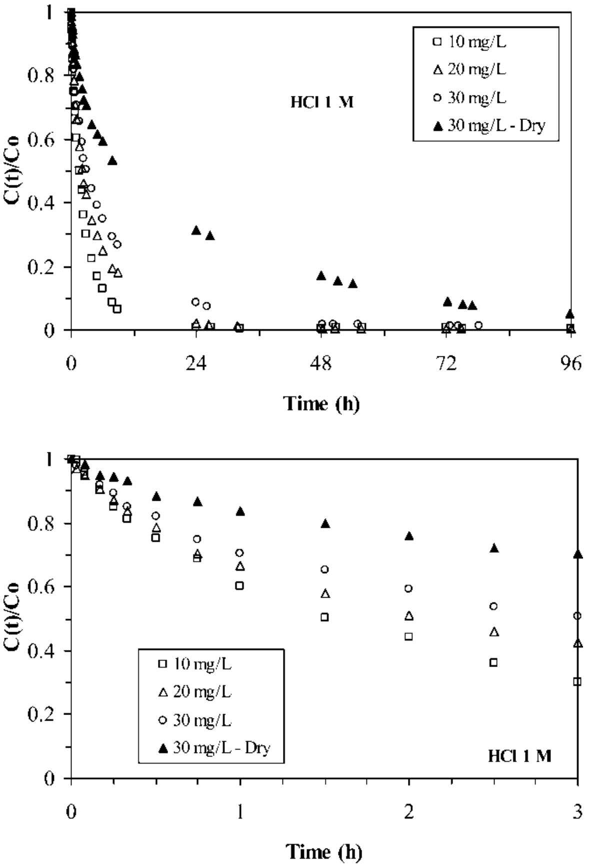

Figure 9. Influence of initial Pd concentration on Pd sorption kinetics (sorbent dosage: 400 mg L^{-1} dry weight; wet beads, except close symbols: dry beads).

was performed using the same number of beads to be sure to maintain same amount of resin for each set of experiments, and avoid problems in the reproducible weighing of wet beads (partial drying during the weighing step, interstitial water etc.). Figure 10 surprisingly shows that the sorption isotherm was significantly less favorable in the case of wet beads. The isotherm profiles remained quite similar corresponding to very favorable (almost irreversible) isotherm, characterized by very steep initial slope, followed by a saturation plateau. However, the maximum sorption capacity was significantly decreased by almost 30% using dry beads, while the affinity coefficient (b) was doubled.

$$\text{Wet state}: \quad q_m = 102.5 \quad b = 2.65 \quad (R^2 : 0.999)$$
$$\text{Dry state}: \quad q_m = 143.0 \quad b = 1.26 \quad (R^2 : 0.999)$$

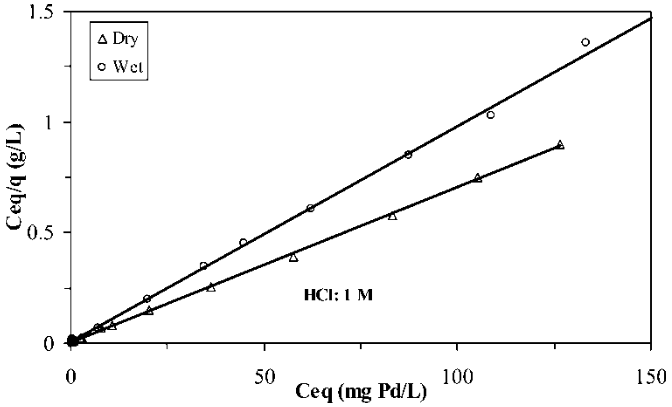

Figure 10. Influence of drying step on Pd sorption isotherm from 1 M HCl solutions (experimental data: symbols; solid lines: modeling using the Langmuir equation).

The presence of water surprisingly decreased the binding capacity of the material at large metal concentration. Indeed, at low initial metal concentration as seen in the case of kinetics (preceding sections) the wet beads were faster at binding palladium. At larger concentrations the positive impact of resin conditioning is lost in terms of equilibrium performance. No explanation was found for this behavior.

Desorption of Pd from Loaded Resins—Preliminary Results

In order to make the process cost-efficient it is necessary investigating the possibility to recover palladium from loaded material and re-use the resin for a number of cycles. This is a key point in the design of sorbent materials that is frequently less documented than sorption processes. Preliminary experiments have been performed with these biopolymer-immobilized extractants. The investigation of the effect of HCl concentration on sorption and resin stability had shown that the resins were not stable when acid concentration exceeded 2 M. For this reason the acid desorption is not applicable in the present case since it would require using concentrations of HCl as high as 5 to 8 M. Other eluting agents have been tested such as alkaline media (ammonia) but the method used for the immobilization of the extractants also resulted in poorly stable materials in these experimental conditions. For these reasons a complexing agent was preferred and thiourea was used for Pd desorption from saturated resins. Preliminary tests have been performed at concentrations of 0.1 M and 0.2 M, in presence or absence of HCl (0.1 M) using a elution volume / sorbent mass ratio of 1 : 2 (mL/g). The addition of HCl in the eluting solutions did not significantly change the desorption performance, that remained in the range 40–60%. Best desorption was observed with 0.2 M thiourea solutions: concentration in the eluate tended to 150 mg Pd L^{-1} for a desorption efficiency of 57%. Desorption should be optimized varying the volume/solid ratio, the number of successive desorption steps and checking the possibility to re-use the resin (determining the number of sorption/desorption cycles that can be performed).

CONCLUSION

Extractants such as as Cyanex 301 and Cyanex 302 can be efficiently immobilized in alginate by ionotropic gellation of extractant/sodium alginate mixture into a calcium chloride solution. Extractant contents as high as 40% (in dry weight) were obtained. The extractant immobilized resin has proved efficient for removing palladium from hydrochloric acid solutions. The sorption capacity and the distribution coefficient are almost independent of HCl concentration in the range 0.1–2 M. Unfortunately, the resins is not stable at higher HCl concentration, limiting the possibility to use HCl for desorption of palladium from loaded resins: thiourea (at concentration close to 0.2 M) can be used for palladium removal, though complementary studies (currently in progress) are required for process optimization. Sorption capacities close to 140 mg Pd g^{-1} where obtained with Cyanex 301: sorption capacities and distribution coefficient remained almost unaltered by strong additions of chloride ions (in 0.1 M HCl solutions). In binary solutions (Pd and Pt) the resins exhibit marked preference for Pd: Pt is poorly adsorbed on the resin (even in single component solutions), making the resins a promising material for the separation of Pd and Pt from mixed solutions, especially in 1 M HCl solutions. The presence of competitor cations (Cu^{2+}, Ni^{2+} and Zn^{2+}) decreases the adsorption of Pd (between 20 and 40%, under comparable experimental conditions) even at low competitor metal concentration (i.e. 100 mg metal L^{-1}); though increasing metal concentration does not decrease Pd sorption. Sorption kinetics are controlled by mass transfer resistance mechanisms: film diffusion and intraparticle mass transfer. The conditioning of resin beads (dry versus wet, drying in presence of sucrose) drastically affect the kinetics profiles. At low Pd concentration the wet resins beads are much faster than dry beads for Pd uptake; however, when increasing the concentration of the metal the presence of water in the beads strongly impacts sorption isotherms and stability of the beads: dry beads appear to be more appropriate.

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