Paper V

IMPREGNATED RESINS CONTAINING DI-(2-ETHYLHEXYL) THIOPHOSPHORIC ACID FOR THE EXTRACTION OF PALLADIUM(II). II. SELECTIVE PALLADIUM(II) RECOVERY FROM HYDROCHLORIC ACID SOLUTIONS

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ABSTRACT

The extraction of Pd(II) from HCl solutions by impregnated resins containing di-(2-ethylhexyl) thiophosphoric acid (DEHTPA or HL) on the Amberlite XAD2 polymeric support has been studied. Graphical and computer analysis with the program LETAGROP-DISTR demonstrated that the Pd(II) extraction can be explained by the formation of metal complexes in the resin phase of $PdL_2(HL)_2$ composition. DEHTPA/XAD2 resins extracted Pd(II) against other metals: Pt(IV), Rh(III), Cu(II), Fe(III) as well as Zn(II). The stripping of Pd(II) loaded on the organic phase and the lifetime of the resins were also investigated.

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INTRODUCTION

Palladium is included in the precious metal group. So-called precious metals have specific chemical and mechanical properties, and are widely applied in a variety of technological fields such as automotive catalyst converters, chemical catalysis and electronic industry. Therefore it is imperative to develop effective techniques for the separation and recovery of precious metals.

Precious metals have been traditionally recovered from low grade mineral ores, named primary sources. However, recently there is a growing interest in the recovery of precious metals from scrap and spent materials which constitute the secondary sources.

The processes for the recovery of precious metals comprise a great number of operations. Independently on the origin of the metals to be recovered, the final step in the extraction schemes consists in the separation and purification of the individual metals. Conventional routes for the extraction and separation of precious metals consisted of a series of precipitation steps which were generally rather inefficient in terms of degree of separation achieved. In the past years, the industries abandoned conventional precipitation procedures and have been using solvent extraction as one of the most suitable technologies in hydrometallurgy for the recovery of precious metals (1, 2). Although the good performance displayed by solvent extraction systems, they have still some drawbacks: lower ability for enrichment, solvent losses and difficulty in phase separation (3).

Since precious metals occur as minor components, a technology with high concentration efficiency as well as excellent selectivity is required for their recovery. In this sense, impregnated resins introduced in the 1970s by Warshawsky (4), Grinstead (5) and Kroebel and Meyer (6), are at the present well established as a technique which bridge the gap between solvent extraction and ion exchange resins, since they combine the properties of the organic phase in

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solvent extraction with the equipment and operation facilities of the ion exchange technique (7). Compared with solvent extraction, only few studies deal about the extraction of precious metals using impregnated resins.

Organophosphorous extractants have been extensively investigated and used for solvent extraction applications, however less is known about their analogues, where one or more oxygen atoms have been replaced by sulphur atoms. The presence of sulphur atoms is attractive because of the chemical characteristics they are expected to give to the molecules, properties which can be predicted by Pearson´s Hard and Soft Acids and Bases (HSAB) principle. Studies have unambiguously established that extractants containing sulphur, soft Lewis bases, are highly effective and selective for Pd(II), classified as soft Lewis acid (8-14).

In a previous work, Amberlite XAD2 impregnated resins containing di-(2-ethylhexyl) thiophosphoric acid (DEHTPA) were prepared and physico-chemically characterized (15). The aim of this paper, is better understand the reactions between the metal ions and thiophosphorous extractants immobilized into macroporous supports and use XAD2/DEHTPA resins for selective recovery of Pd(II) from HCl solutions as an alternative method to solvent extraction.

EXPERIMENTAL

Reagents and Solutions

Di-(2-ethylhexyl) thiophosphoric acid (DEHTPA or HL) was kindly supplied by Bayer and was purified through a procedure consisting in the formation of its potassium salt as described elsewhere obtaining a product with a purity of 96.9% (15).

Amberlite XAD2 with particle diameter between 0.3 and 0.9 mm, purchased from Rohm and Hass, was used as a macroporous polymer adsorbent.

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To remove impurities, the resin was kept in contact with a 50% methanol-water solution containing HCl 4 M for 12 hours, then the polymer was washed with water until chloride ion was not detected, and finally dried at 50°C.

Stock metal solutions were prepared by dissolving $PdCl_2$, $PtCl_4$, $RhCl_3.3H_2O$ (Johnson Matthey), $CuCl_2.2H_2O$, $ZnCl_2$ and $FeCl_3.6H_2O$ (Panreac) in hydrochloric acid.

All the other chemicals used in this work were of reagent grade.

Impregnation Procedure

Impregnated resins were prepared by using a dry impregnation method, mixing an appropriate amount of DEHTPA dissolved in acetone with 25g of dry XAD2 until total evaporation of the diluent was reached. Then the polymeric beads were washed several times with deionized water and dried at 50°C. The resins were characterized by means of potentiometric titrations and specific surface area measurements (15).

Metal Extraction

The metal extraction experiments were carried out in batch experiments at room temperature. Samples of 0.1 g of impregnated resin were shaken vigorously with 20 ml of metal aqueous phase during different periods of time depending on the purpose of the experiment. After phase separation, metal concentrations in the aqueous phase were determined by ICP (Spectroflame of Spectro Analytical Instruments).

Metal Stripping

Metal stripping tests were carried out in batch experiments at room temperature. First, 20 ml of Pd(II) solution was contacted with 0.1g of 1.27 mol/kg dry XAD2 resin. Then, immediately after separating the liquid from the resin phase, 10 ml of stripping reagent were added to the loaded resin and were

shaken vigorously for 24 hours if not otherwise stated. The metal concentrations after the extraction and stripping steps in the aqueous phase were determined by ICP. This experimental procedure was established on the basis of preliminary stripping experiments reported in a previous work (16).

RESULTS AND DISCUSSION

Extraction Kinetics of Pd(II) and Pt(IV)

The metal extraction percentage at different shaking times was calculated as follows:

$$E(\%) = 100 \frac{[M]_i - [M]_{aq}}{[M]_i} \qquad (1)$$

where $[M]_i$ and $[M]_{aq}$ in M, are the initial and equilibrium total metal concentration in the aqueous phase, respectively.

The extraction half time, $t_{1/2}$, was used to obtain a qualitative approach of the kinetics extraction and was defined as the time necessary to achieve 50% of the resin's final extraction.

Kinetics of Pd(II) extraction varying the DEHTPA concentration in the resin as well as the metal concentration are presented in Figure 1. The time needed to achieve the equilibrium, decreased when the ligand content in the polymeric bead was increased and when the initial Pd(II) concentration was reduced. It can well noticed by examining the extraction half times listed in Tables 1 and 2. This phenomena was also observed in previous works for the extraction of Pd(II) and Pt(IV) with XAD2/Alamine 336 resins. Assuming the diffusion inside the pores as the limiting rate step, since the chemical reaction is considered very fast and one can assume that the vigorous agitation used in the experiments destroyed the film diffusion, by increasing the metal concentration or reducing the extractant content

TABLE 1

Half time dependency on initial DEHTPA concentration in the resin ($[HL]_{i,org}$).
Experimental conditions: as in Figure 1 and initial Pd(II) concentration 4.7×10^{-4} M

$[HL]_{i,org}$ (mol/kg)	$t_{1/2}$ (h)
0.22	13.2
0.27	10.0
0.62	6.3
1.24	2.5

TABLE 2

Half time dependency on initial Pd(II) concentration.
Experimental conditions: as in Figure 1 and DEHTPA concentration
in the resin 1.24 mol/kg dry XAD2 resin

$[Pd]_i$ (M)	$t_{1/2}$ (h)
2.35×10^{-4}	1.8
4.7×10^{-4}	2.5

in the resin, the diffusion in the pores become slow reducing the overall metal extraction rate (16, 17).

Pt(IV) extraction kinetics is shown in Figure 2. As can be seen, platinum is poorly extracted and moreover the extraction is very slow in comparison with Pd(II). In the experimental conditions tested in this study, after 100 h the Pt(IV) extraction was only found to be around 7% and the kinetic equilibrium was still not attained. For these obvious practical reasons de Pt(IV) extraction equilibrium was not studied.

The very large difference on extraction rates between Pd(II) and Pt(IV) may allow to perform selective separation of Pd(II) from Pt(IV). In this sense, a solution containing 4.7×10^{-4} M of Pd(II) and Pt(IV) at 0.5 M HCl, was contacted with XAD2/DEHTPA resins at different shaking times in order to study the

possible separation of both metals on the basis of different extraction rates. Figure 3 illustrates the variation in the extraction rate of Pt(II) and Pt(IV); as could be expected from the previous single metal experiments, Pd(II) is extracted very fast in comparison with Pt(IV). After 16 hours, near 100% extraction of Pd(II) is attained whereas Pt(IV) extraction is almost negligible.

Extraction Equilibrium of Pd(II)

Figure 4 shows that the Pd(II) extraction percentage increases with increasing the extractant concentration on the resin and decreasing the HCl concentration. Approximately, when DEHTPA concentration was higher than 0.8 mol/kg dry XAD2 resin, in the experimental conditions used in this work, complete sorption of the metal on the resin was achieved.

The distribution ratio of Pd(II) between the resin phase containing DEHTPA and the aqueous phase can be obtained as:

$$D = \frac{[Pd]_{org}}{[Pd]_{aq}} = \frac{([Pd]_i - [Pd]_{aq})V}{[Pd]_{aq} m} \tag{2}$$

where $[Pd]_{org}$ and $[Pd]_{aq}$ are the total equilibrium Pd(II) concentrations in the resin and aqueous phase expressed in mol/kg dry impregnated resin and mol/l, respectively, $[Pd]_i$ is the initial Pd(II) concentration in mol/l, V is the volume in l of the aqueous phase and m the mass of dry impregnated resin, in kg.

Analysis of the experimental data obtained in the distribution equilibrium studies were evaluated using the computer program LETAGROP-DISTR (18). This program searches for the best equilibrium constant that minimizes the error squares sum, defined by:

$$U = \sum \left(\log D_{exp} - \log D_{calc} \right)^2 \tag{3}$$

where D_{exp} is the distribution coefficient determined experimentally and D_{calc} is the value calculated by the program. This program also calculates the standard deviation $\sigma(\log D)$ defined by:

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$$\sigma(logD) = \sqrt{\frac{U}{N_P}} \qquad (4)$$

where N_p is the number of experimental points.

Several models were investigated in order to fit the experimental results. The best fit of the data was found when the extraction of Pd(II) from HCl solutions with XAD2/DEHTPA was described through the following reaction:

$$PdCl_4^{-2}{}_{aq} + 4HL_{org} \Leftrightarrow PdL_2(HL)_{2\,org} + 4Cl^-{}_{aq} + 2H^+{}_{aq} \qquad (5)$$
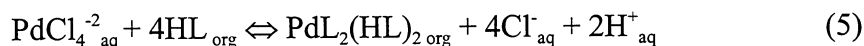
The stoichiometric equilibrium constant (K_{ex}) for the extraction reaction is:

$$K_{ex} = \frac{\left[PdL_2(HL)_2\right]_{org}\left[Cl^-\right]_{aq}^4\left[H^+\right]_{aq}^2}{\left[HL\right]_{org}^4\left[PdCl_4^{-2}\right]_{aq}} \qquad (6)$$

The equilibrium constants at different HCl concentrations were determined by means of the program LETAGROP-DISTR by treating the extraction data separately for each ionic strength. Stability constants for Pd(II) with Cl⁻ found in the literature (19) and the distribution, dimerization and acidity constants of the impregnated resins containing DEHTPA (15) were used in the calculations. The results are given in Table 3, and as it can be seen by increasing the HCl concentration the value of the equilibrium constant increases.

By combining adequately the definition of D and K_{ex}, the following equation is deduced:

$$logD = logK_{ex} + 4log[HL]_{org} - 4log[Cl^-]_{aq} - 2log[H^+]_{aq} \qquad (7)$$

In this way, for a specific ionic strength, plotting logD versus log[HL]$_{org}$, where [HL]$_{org}$ represents the free extractant concentration on the resin in the equilibrium, a straight line with slope 4 should be obtained. Good fit of the data can be noticed in Figure 5, where the values of free [HL]$_{org}$ were obtained by means of the program LETAGROP-DISTR.

On the other hand, liquid-liquid extraction studies demonstrated that DEHTPA dissolved in kerosene extracts Pd(II) by means of PdL$_2$ complexes (20).

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TABLE 3

Extraction constants for Pd(II) extraction by XAD2/DEHTPA resins
from hydrochloric acid solutions

[HCl](M)	log K_{ex}
0.5	5.5 ±0.4
3	9.1 ± 0.2
5	10.2 ±0.2

TABLE 4

Separation factors for Pd(II) respect to Cu(II) at different HCl concentrations.
Experimental conditions as in Figure 6

[HCl](M)	α(Pd/Cu)
0.5	0.79
1	11.6
3	85
5	425
7	4646

Pd(II) Extraction from Solutions containing Cu(II), Fe(III), Pt(IV), Rh(III) and Zn(II)

In this section, impregnated resins with a high concentration of DEHTPA, 1.24 kg/mol dry XAD2 resin, were used in order to favour Pd(II) extraction and reduce the shaking time.

Figure 6 exhibits the extraction of Pd(II) by XAD2/DEHTPA resins at different HCl concentrations from multimetal solutions containing some other precious metals: Pt(IV) and Rh(III) as well as some base metals: Cu(II), Fe(III) and Zn(II). Pd(II) was completely extracted from the multimetal solution, whereas the other metals, except Cu(II), in practice exhibited nil sorption. In the case of

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Cu(II), the extraction was very important at low HCl concentrations but was inhibited by increasing the acid concentration.

The separation factor of one metal (M1) respect another metal (M2) is defined as:

$$\alpha(M1 / M2) = \frac{[M1]_{org} / [M1]_{aq}}{[M2]_{org} / [M2]_{aq}} = \frac{D_{M1}}{D_{M2}} \tag{8}$$

Separation factors for Pd(II) respect Cu(II) are listed in Table 4. The separation factors of Pd(II) respect the other metals, are not shown due to the evident separation achieved in all the HCl concentrations range studied. The separation between Pd(II) and Cu(II) was almost complete at 7 M HCl, and since at these conditions all the other metals in the solution were also not extracted, this selective extraction of Pd(II) at high mineral acid concentration may result very interesting from an applied viewpoint in hydrometallurgical schemes of platinum group metals separation.

Metal Stripping

The palladium stripping percentage, S(%), was defined as the fraction of metal loaded in the resin which was re-extracted and was calculated as follows:

$$S(\%) = 100 \frac{V_s}{V_e} \frac{[Pd]_s}{\left([Pd]_i - [Pd]_{aq}\right)} \tag{9}$$

where V_s and V_e are the volumes of aqueous solutions used in the stripping and extraction steps respectively expressed in 1, $[Pd]_i$ and $[Pd]_{aq}$ are the initial and equilibrium palladium concentrations in the aqueous phases corresponding to the extraction step, and $[Pd]_s$ is the metal concentration in the aqueous phase after the metal elution, being all the concentrations expressed in M units.

HCl and thiourea (Tu) were tested as stripping reagents. For HCl re-extraction experiments, the acid concentration was varied from 0.5 to 10.2 M, and a nil stripping ratio was found in all cases though the data is not shown here.

However, as can be seen in Figure 7, when thiourea in 1 M HCl is used as stripping reagent around 100% of re-extraction is reached with a concentration factor of 2. It can be justified for the fact that thiourea which is a soft ligand can re-extract the Pd(II) from the organic phase as a water soluble complex.

Lifetime of XAD2/DEHTPA Resins

In this study, resin lifetime was tested by performing successive extraction-stripping experiments. Diluted metal solutions in comparison with previous experiments, 9.4×10^{-5} M Pd, were used for practical reasons in order to complete each extraction-stripping cycle in only 24 hours: 4 hours for extraction and 20 hours for stripping, avoiding the slow kinetics associated with high metal concentrations. The results obtained are listed in Table 5, and after 3 extraction-stripping cycles the resin was still offering an excellent performance. Consequently, it can be concluded that in the working conditions employed the loss of extractant from the resin phase to the aqueous phase did not affect the extraction. Taking into account that the experiments were conducted at 1 M HCl, the results obtained are in agreement with previous information indicating that DEHTPA losses were minimized at pH<4 (15).

TABLE 5
Life time tests for XAD2/DEHTPA resins.
Experimental conditions: mass of resin 0.1g, conc. 1.24 mol/kg dry XAD2 resin
Extraction: volume of aq. phase 20 ml, initial Pd(II) conc. 9.4×10^{-5} M (4 h)
Stripping: volume of aq. phase 10 ml, 0.05 M Tu at 1 M HCl (20 h)

Cycle	E(%)	S(%)
1st.	99.4	98.3
2nd.	99.9	99.8
3rd.	99.7	100.0

CONCLUSIONS

A straightforward, efficient and rapid method for the separation of Pd(II) and Pt(IV) using XAD2/DEHTPA resins is feasible on the basis of the much higher extraction kinetics and reactivity of Pd(II) over Pt(IV), since Pd(II) is a metal ion classified as soft Lewis acid which react with reagents containing sulphur atoms, soft Lewis bases. Pd(II) extraction proceeds through the formation of complexes $PdL_2(HL)_2$ and is enhanced when the HCl concentration is reduced or in the case that the extractant concentration on the resin is increased. Moreover, the selective extraction of Pd(II) from other precious and base metals can be achieved by means of XAD2/DEHTPA resins.

The elution of Pd(II) loaded on the impregnated resins can be attained with aqueous solutions of thiourea in 1 M HCl. The use of the resins in acidic media for several palladium extraction-stripping cycles is also demonstrated.

ACKNOWLEDGMENTS

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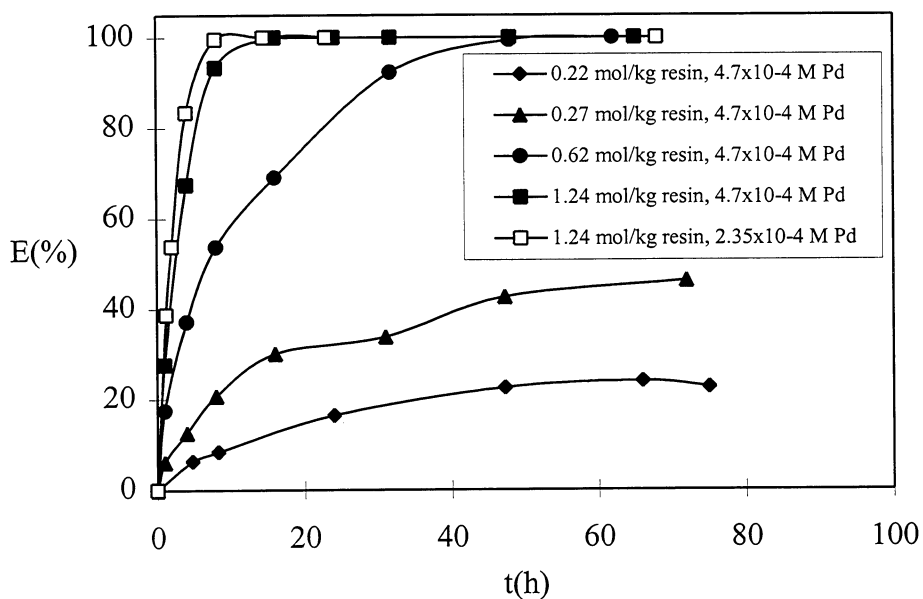
FIGURE 1. Effect of extractant content in the resin (expressed in mol/kg dry XAD2 resin) on extraction kinetics of Pd(II) by XAD2/DEHTPA resins. Experimental conditions: mass of resin 0.1g, volume of aqueous phase 20 ml, HCl 0.5 M and initial Pd(II) concentration 2.35×10^{-4} M or 4.7×10^{-4} M.
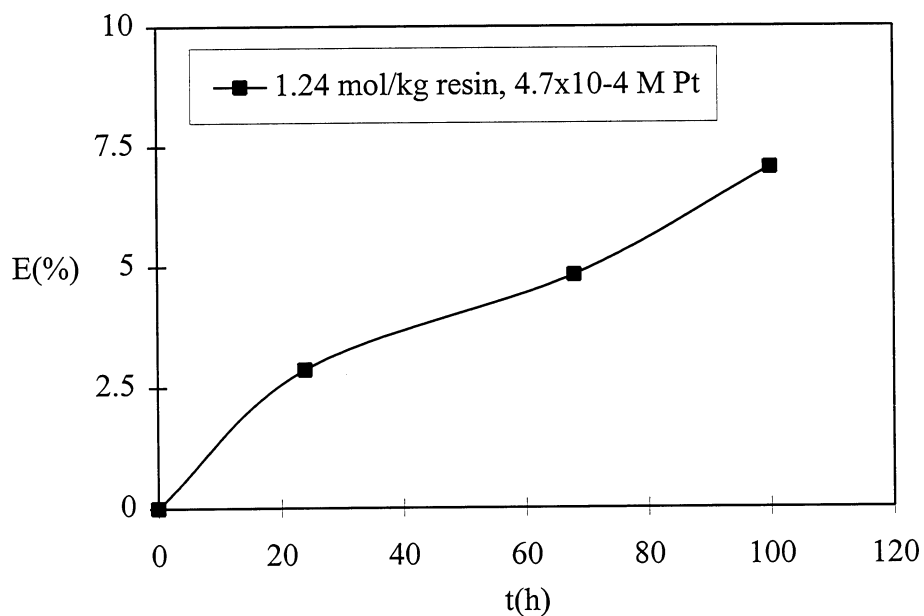
FIGURE 2. Extraction kinetics of Pt(IV) by XAD2/DEHTPA resins. Experimental conditions: mass of resin 0.1g, volume of aqueous phase 20 ml, DEHTPA concentration 1.24 mol/kg dry XAD2 resin, HCl 0.5 M and initial Pt(IV) concentration 4.7×10^{-4} M.
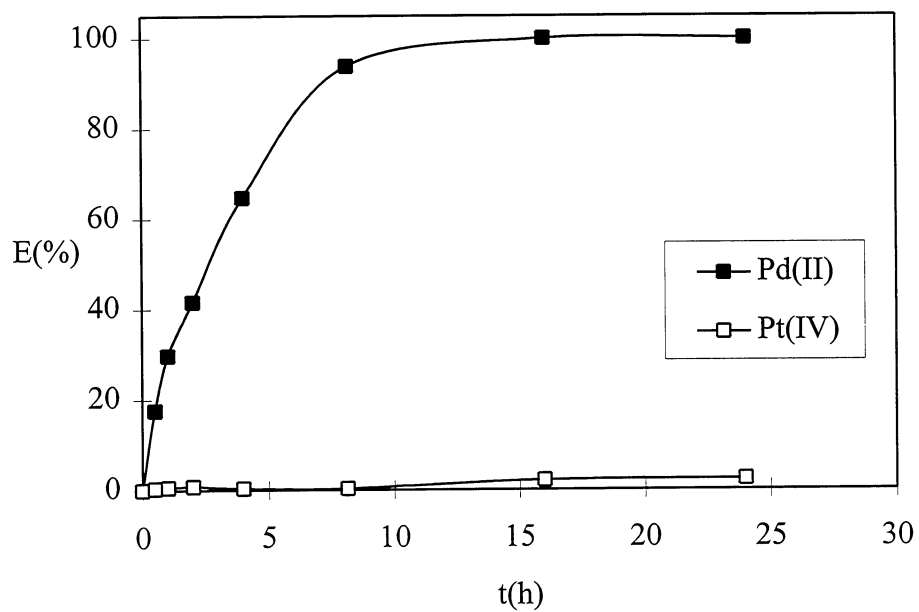
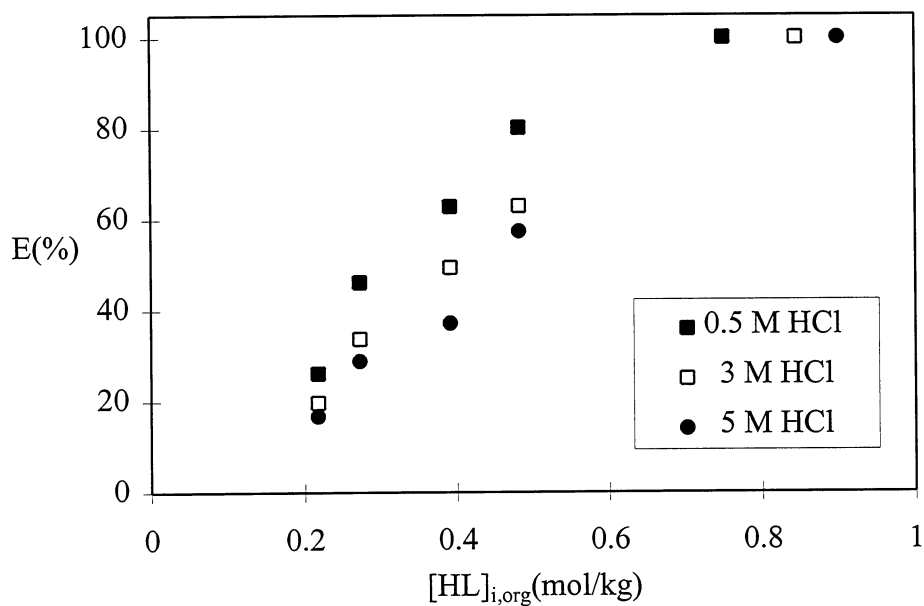FIGURE 3. Percent extraction of Pd(II) and Pt(IV) against contact time. Experimental conditions: mass of resin 0.1g, volume of aqueous phase 20 ml, DEHTPA concentration 1.24 mol/kg dry XAD2 resin, HCl 0.5 M and initial metal concentrations $[Pd]_i=[Pt]_i=4.7x10^{-4}$ M.

FIGURE 4. Effect of the initial HL concentration on the resin ($[HL]_{i,org}$, expressed in mol/kg dry XAD2 resin) on percent extraction of Pd(II) with XAD2/DEHTPA resins. Experimental conditions: mass of resin 0.1g, volume of aqueous phase 20 ml, initial Pd(II) concentration 4.7×10^{-4} M and shaking time 60 h.
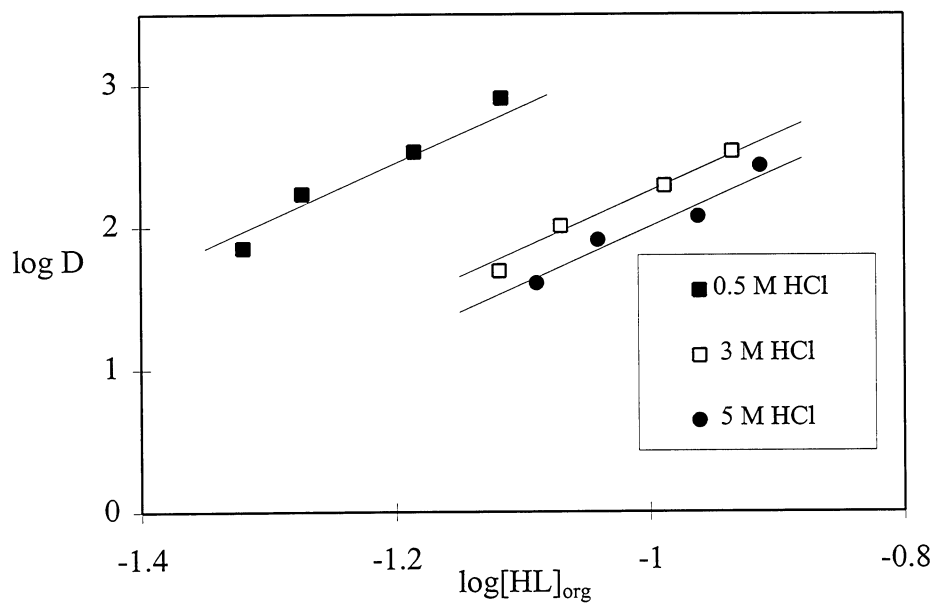
FIGURE 5. Effect of free HL concentration (expressed in mol/kg dry impregnated resin) on the distribution ratio of Pd(II). Solid lines were plotted taking into account slope 4. Experimental conditions: the same as those in Figure 4.
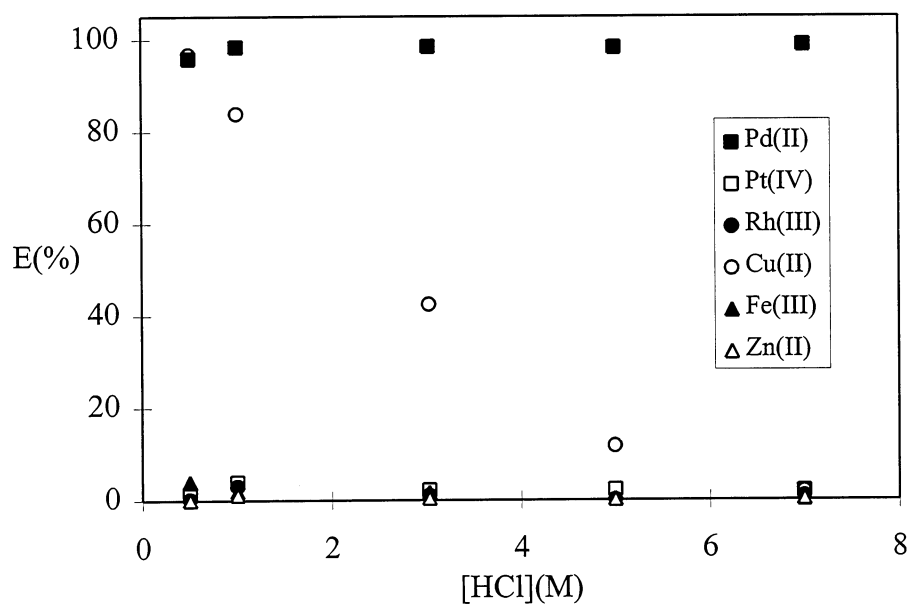
FIGURE 6. Effect of HCl concentration on percentage extraction of heavy metals. Experimental conditions: mass of resin 0.1g, volume of aqueous phase 20 ml, DEHTPA concentration 1.24 mol/kg dry XAD2 resin, initial Pd(II) concentration 4.7×10^{-4} M and shaking time 16 h.
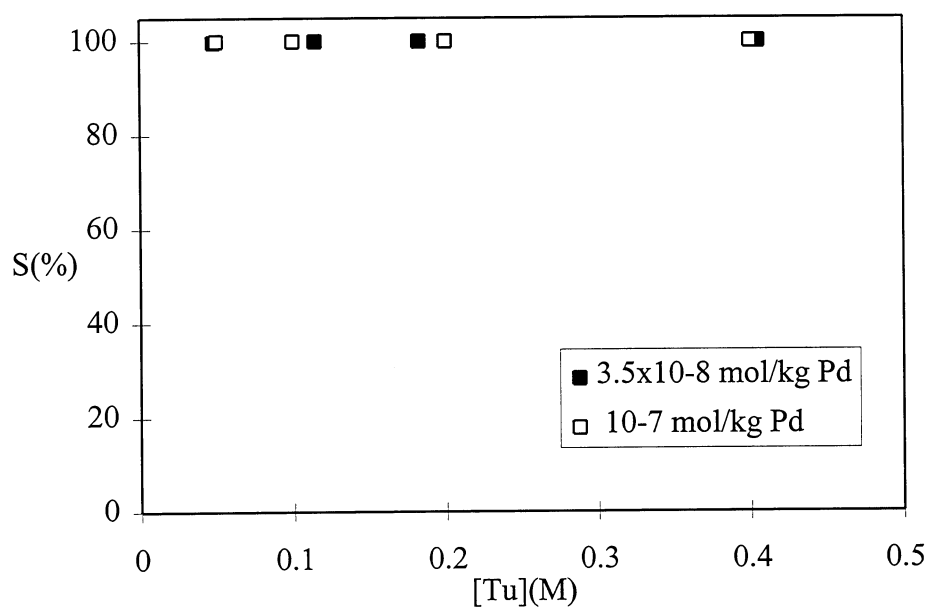
FIGURE 7. Effect of thiourea concentration in HCl 1 M medium on the percent stripping of Pd(II) loaded with XAD2/DEHTPA resins. Experimental conditions: mass of resin 0.1 g, volume of the stripping aqueous phase 10 ml, variable metal content in the resin (expressed in mol/kg dry impregnated resin) and stripping shaking time 24h.