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Surface Modification of Amberlite XAD-4 Resin with D_2EHPA by a Two-Step, Solvent–Nonsolvent Procedure and the Application on the Selective Separation of Lead and Copper Ions

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ABSTRACT

Di(2-ethylhexyl)phosphoric acid (D_2EHPA) has the tendency to adsorb at interfaces in an oriented fashion due to the amphiphilic structure. The study of the surface tension shows that the adsorption of D_2EHPA at interface can lower the surface tension of ethanol solution. The amount of adsorption is affected by the pH and ionic strength of the solution. Being a small surface-active molecule, a monolayer of D_2EHPA molecules can be immobilized on the surface of nonpolar Amberlite XAD-4

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resin by a two-step, organic solvent–nonorganic solvent process. The amount of immobilized D_2EHPA is as high as 1.02 (mol/kg of resin). The electron spectroscopy for chemical analysis (ESCA) results show that the immobilized D_2EHPA undergoes reorientation by further exposing the phosphoric acid group to the water phase. Since the hydrophobic alkyl chains of D_2EHPA physically entangle with the surface polymer chains of Amberlite XAD-4, the immobilized extractant has good stability on the resin surface. This D_2EHPA-modified Amberlite XAD-4 can be used for the separation of lead and copper ions as an ion-exchange resin. Ion-exchange isotherm experiments show that D_2EHPA-modified resin has higher Pb ion affinity than Cu ion. This new type of D_2EHPA-modified resin shows better Pb and Cu ions separation than analogous D_2EHPA-impregnated resin [extractant-impregnated resin (EIR)] and solvent extraction system. The selective separation results using series contacts of solution mixtures with resins further demonstrated the feasibility of using D_2EHPA-modified Amberlite XAD-4 resin for the separation of Pb/Cu mixed ion solution. After only six batches of contacts, the relative ion concentration of Cu ion increases from 50% to more than 99%, while the relative ion concentration of Pb ion decreases from 50% to less than 1%. The Cu recovery rate is more than 75%, comparing to 54% in the EIR system.

Key Words: Surface modification; Separation technology; Pb and Cu ions; Hydrometallurgy; D_2EHPA; Amberlite XAD-4 resin.

INTRODUCTION

The wastewater generated from the printed circuit board industry contains large amount of copper and some lead metal ions. In the course of recycling copper from the wastewater, the separation of toxic lead metal from copper is important from a resource recycling and an environment protection point of view. Resins with specific metal ion selectivity have been prepared for the separation of copper and lead metal ions. Among the numerous types of organic ion exchangers, chelating ion-exchange resins with ionogenic donor groups, such as oxygen, nitrogen, sulfur, or a combination of these elements in the same functional group, can form coordination bonds with Cu and Pb metal ions. Commercial chelating resins, such as Duolite ES-346, Amberlite IRC-718, and Dowex M-4195, have been used for selective extraction of Pb ions.[1–3] Resins containing amidoxime functional groups were synthesized for Pb preconcentration.[4,5] Amide and amino functional groups also have been synthesized.[6,7] Phosphonic acid functional groups were introduced into phenyl groups of a macroreticular poly(styrene-*co*-divinylbenzene)

matrix with higher Pb selectivity than Cu.[8] Functional polymers incorporating thiophosphoric acids were synthesized to prepare a covalent-type polymers, which show selectivity toward Cu, Cd, Ni, and Pb.[9] Phosphoric acid has also been attached to poly(glycidyl methacrylate-*co*-divinylbenzene) beads to prepare resins with large cation-exchange capacities.[10]

One way to prepare a resin with phosphoric acid functional groups is to directly attach di(2-ethylhexyl)phosphoric acid (D_2EHPA) molecules onto the surface of resin matrix. D_2EHPA is a phosphoric acid metal-ion extractant widely used for the separation of various kinds of metal ions by solvent extraction process.[11] D_2EHPA also has been impregnated into porous, nonpolar resin to prepare extractant-impregnated resin (as known as EIR) for the application in the separation process.[12–16] Both solvent extraction and EIR use D_2EHPA as a separation phase. Alternatively, in our previous study, D_2EHPA was chemically bonded to the surface of polar Amberlite 200 resin to prepare a resin with bifunctionality for the separation of V and Mo ions.[17] Despite the extensive publications on the extraction behavior of D_2EHPA, studies on the surface-active properties of D_2EHPA are relatively rare.[18] Since D_2EHPA has a hydrophilic phosphoric acid group and two hydrophobic alkyl chains, D_2EHPA exhibits a certain degree of surface-active property. This surface-active property can be used for the surface modification of nonfunctionalized resin beads, such as Amberltie XAD-4.

Polymer surface modification with small amphiphilic molecules provides an alternative way to prepare a resin with the desired surface properties.[19] Small amphiphilic molecules, such as surfactant and surface-active monomers, have also been chemically bounded to the surfaces of polymeric materials.[20–22] For linear polymer, surface modification can be achieved by physically blending the amphiphilic polymers with a polymer solution.[23] A more direct way for polymer surface modification is the adsorption of surface-active material by the entanglement of hydrophobic chains of the surface-active material with surface polymer chains of the matrix.[24–26] With suitable organic solvent treatment, surface-active D_2EHPA molecules will adsorb orderly at solvent-swelled polymer surface. Followed by nonorganic solvent treatment, the adsorbed amphiphilic molecules are stabilized on the surface of polymer. In our previous study, a layer of surface-active D_2EHPA was physically attached onto Amberlite XAD-4 resin to prepare a resin for the separation of Mo and V ions, using this organic solvent–nonorganic solvent process.[27]

In this study, the adsorption of surface-active D_2EHPA on the surface of porous Amberlite XAD-4 resin was further investigated. The amount of adsorbed D_2EHPA is influenced by many factors, including the concentration of D_2EHPA, the concentration of solvent, and the immersion in water (nonorganic solvent) environment. The surface of modified Amberlite XAD-4 was characterized by electron spectroscopy for chemical analysis (ESCA) and

observed by scanning electron microscopy (SEM). The selective extraction of Cu and Pb ions in aqueous solution were demonstrated for the application of this D_2EHPA-modified resin in metal-ion separation. Analogous EIRs were made by impregnation of D_2EHPA into Amberlite XAD-4 resin. Both D_2EHPA-modified and D_2EHPA-impregnated-type resins show selectivity toward Cu and Pb. Comparing the results of separation, D_2EHPA-modified resins are more effective and more selective than the D_2EHPA-impregnated type of resins.

MATERIALS AND METHODS

Reagents and Chemicals

D_2EHPA was provided by Daihachi Chemical Industry Co., Ltd. Japan, and used as received. Amberlite XAD-4, size 20–50 mesh, was supplied by Fluka, Germany. Sodium hydroxide (NaOH, pellets GR for analysis) and ethanol (C_2H_5OH, absolute ACS) were from Merck, Inc. Metal ion solutions of known concentration were prepared by dissolving appropriate amount of salt, such as lead nitrate (J.T. Baker) and copper nitrate (Fluka), in distilled and deionized water. The pH was controlled by the addition of dilute nitric acid and sodium hydroxide to control the pH at desired levels. The pH of nonaqueous ethanol/water solution was determined by titrations of acids and bases, using the glass electrode as an end-point detector.[28]

Surface Tension Measurement of D_2EHPA Solution

Since the properties related to surface-active species directly reflect on the interfacial tension, the surface-active property of D_2EHPA was characterized by measuring the surface tension of D_2EHPA solution using the Wilhelmy plate method (AEL-200, Shimazu, Japan). The effects of pH and ionic strength on the surface tension of D_2EHPA solution were investigated.

Two-Step, Organic Solvent–Nonorganic Solvent Process

Amberlite XAD-4 was first subjected to a cleaning pretreatment to remove the impurity in the resin. Amberlite XAD-4 was kept in contact with a 20% methanol–water solution containing 4-M HCl for 12 hr to eliminate impurities.[15] The specific surface area of Amberlite XAD-4 resin was determined by the Brunauer–Emmett–Teller (BET) method (Micrometritics ASAP 2010, US). Amberlite XAD-4 was then immersed in distilled and deionized

water for 12 hr to remove the residual methanol from the resin. D_2EHPA was physically immobilized on the surface of Amberlite XAD-4 by a two-step, organic solvent–nonorganic solvent process. At the first step, Amberlite XAD-4 resin was immersed five times in organic solution containing D_2EHPA for 2 hr to ensure the adsorption of D_2EHPA. At the second step, the resin was immersed in nonorganic solvent to remove the organic solvent from the Amberlite XAD-4. The amount of attached D_2EHPA was determined directly by NaOH titration. Due to the weak acidic nature of D_2EHPA, the equivalent point of titration was evaluated by using the Gran plot method, by which the equivalent titration volume was determined by using linear extrapolation of the titration data before or after the equivalent point.[29] The modified Amberlite XAD-4 resin was subjected to an ultrasonic bath (Ultrasonic Cleaner, 42 KHz, Cole-Parmer) to study the stability of immobilized D_2EHPA molecules. The chemical composition of the resin surface was characterized by ESCA (Sigma Probe, Thermo VG-Scientific). SEM was performed on S-2700, Hitachi, Japan. The resin was then dried for 24 hr to remove residual water. The prepared resin was then ready for metal-ion separation.

Metal Ions Extraction Isotherm

Liquid-liquid extraction isotherm experiments were carried out to investigate the extraction behavior of Pb and Cu ions by free D_2EHPA molecules. Different concentrations of D_2EHPA were prepared using kerosene as a diluent. The volume ratio of aqueous phase to organic phase was 1 : 1. After 30 min of vigorous mixing to achieve equilibrium, the aqueous phase was sampled and the metal ion concentrations in the aqueous solution were determined using an atomic adsorption spectrometer, Perkin Elmer AA 100.

Batch sorption isotherm experiments were carried out to investigate the sorptions of Pb and Cu ions by D_2EHPA-modified Amberlite XAD-4. Preexperiments showed that the equilibrium can be achieved within 30 min. A known amount of resin was immersed in metal ion solutions with different ion concentrations for 30 min at 298 K. The liquid phase was, then, sampled to determine the metal ion concentration using an atomic adsorption spectrometer, Perkin Elmer AA 100. FTIR study was performed on IR200 spectrometers, thermo electron spectroscopy, US.

Selective Separation of Metal Ions

Selective separation of Pb and Cu ions was conducted using a sequential contact of a mixed ions solution with D_2EHPA-modified Amberlite XAD-4.

Considering a series of contactors containing modified resin, a quantity of mixed ions solution was added to the first contactor (solid/liquid weight ratio equal to 1 : 5). After 30 min of mixing, the solution was decanted and added to the second contactor containing modified resin. The solid/liquid weight ratio was maintained at the same level by adjusting the amount of resin. The sequence was repeated for a series of six contacts. The solution was sampled and the metal ion concentrations were determined after each contact.

RESULTS AND DISCUSSION

Effects of Solvent on the Surface-Active Property of D_2EHPA

In the two-step, organic solvent–nonorganic solvent process, suitable organic solvent should be a solvent for both the D_2EHPA and hydrophobic Amberlite XAD-4 resin. Pure toluene [solubility parameter $\delta = 8.9$ $(cal/cm^3)^{1/2}$] and ethanol [$\delta = 10.0$ $(cal/cm^3)^{1/2}$][30] are organic solvents for both D_2EHPA and Amberlite XAD-4 [$\delta \approx 9.10$ $(cal/cm^3)^{1/2}$].[31] The surface-active properties of D_2EHPA in toluene and ethanol were first tested in this study. Experimental results showed that the surface tensions of pure ethanol and toluene decrease slightly by D_2EHPA, indicating that D_2EHPA does show some surface-active property in these two pure organic solvents. Nevertheless, to enhance the surface-active property of D_2EHPA to obtain an orderly adsorption of D_2EHPA molecules on polymer surface, more a polar ethanol/water solution was considered.

Figure 1 shows the surface tensions of ethanol/water (70/30) solution with respect to D_2EHPA concentration at pH 2 and 3. The surface tension of ethanol/water solution decreases with increasing D_2EHPA concentration. The decrease of surface tension in ethanol/water solution is more significant than those in pure ethanol and toluene solvents, indicating that the surface-active property of D_2EHPA is enhanced in ethanol/water (70/30) solution. Preexperimental results showed that D_2EHPA underwent proton dissociation in ethanol/water solution. Therefore, the surface-active property of D_2EHPA may also be affected by the pH of the solution. Since D_2EHPA is a weak acid with pK_a equal to 1.4,[11] Fig. 1 shows that the surface tension of ethanol/water solution at pH 3 is lower than that at pH 2. Apparently, the degree of acid dissociation influences the surface-active property of D_2EHPA. In addition, Fig. 1 shows that the surface tension of solution is affected by the addition of sodium chloride. Due to the dissociation of phosphoric acid, D_2EHPA in ethanol/water solution will act as an anionic surface-active material. The addition of sodium chloride electrolyte to a solution of ionic surface-active material causes an increase in the efficiency of adsorption, because of the decrease in repulsion between the

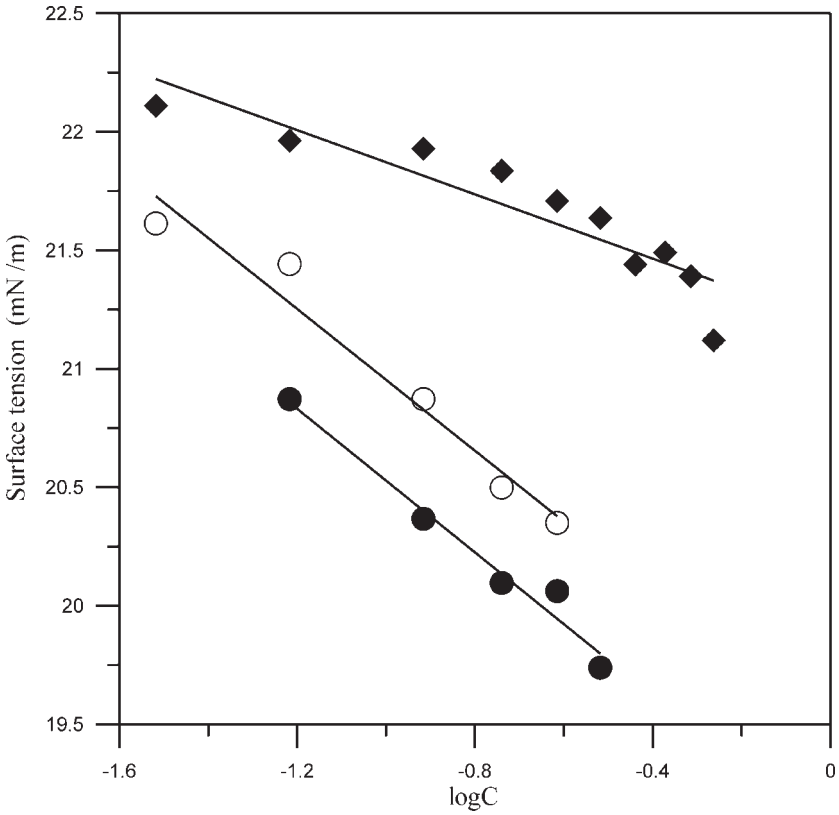

Figure 1. The effect of D_2EHPA concentration on the surface tension of ethanol/water solution (70/30); pH 2 (◆), pH 3 (○), pH 3, and 0.01 mol/dm^3 NaCl (●).

oriented ionic heads at the interface when the ionic strength of the solution is increased.[32] The results of surface tension experiments suggested that D_2EHPA should be adsorbed at the ethanol/water solution surface. The adsorbed D_2EHPA is in the form of monomer molecule and its dehydrogenated anion.[18] The surface concentrations of D_2EHPA (Γ_m) and the area per molecule at air/ethanol solution interface (A^s) are listed in Table 1.

Immobilization of D_2EHPA on Amberlite XAD-4 Resin

For a two-step, organic solvent–nonorganic solvent process, the swelling of the surface of resin by organic solvent and the followed elution of

Table 1. Surface concentration of D_2EHPA on ethanol/water solution (70/30) and the area per molecule at the interface.

Solution condition	Γ_m [D_2EHPA surface concentration (mol/cm^2)]	A^s [area per molecule ($Å^2$)]
pH 2.0	1.19×10^{-11}	1.40×10^3
pH 3.0	2.63×10^{-11}	6.32×10^2
pH 3.0 0.01 M NaCl	2.65×10^{-11}	6.27×10^2

Note: Γ_m was determined from Fig. 1 by $\Gamma_m = -(1/2.303RT)(\partial\gamma/(\partial \log C_{D_2EHPA}))_T$. A^s was calculated by $A^s = 10^{16}/(N\Gamma_m)$. γ, surface tension of solution (mN/m); $C_{D_2}EHPA$, concentration of D_2EHPA (mol/dm^3) in ethanol/water solution; and N, Avogadro's number.[32]

organic solvent by nonorganic solvent are crucial for the immobilization of D_2EHPA on Amberlite XAD-4. The effects of operation parameters on the adsorption of D_2EHPA and the stability of immobilized extractant were investigated.

Effect of Ethanol Concentration on the Swelling Volume of Amberlite XAD-4 Resin

It has been reported that by exposing to ethanol/water solution with a concentration higher than 30%, the surface of polystyrene will generate some loose surface polymer chains.[33] However, in ethanol/water (30/70) solution, experiment showed that the solubility of D_2EHPA was less than 3%, which is too low to achieve a sufficient amount of D_2EHPA adsorbed on polymer surface. Increase of ethanol concentration will increase both the solubility of D_2EHPA in ethanol/water solution and the swelling of Amberlite XAD-4 surface. Therefore, the effect of ethanol concentration on the swelling volume of Amberlite XAD-4 resin was investigated to determine the optimal ethanol concentration for the first step of organic solvent treatment. Figure 2 shows the effect of ethanol concentration on the swelling of resin volume. The resin volume is presented as the minimum tapped-down volume.[34] The results show that the resin volume increases about 30% as the ethanol concentration increased to 70%. However, for ethanol concentration higher than 70%, the resin volume starts to decrease. From SEM, it is clear that there is an apparent structure degradation of Amberlite XAD-4

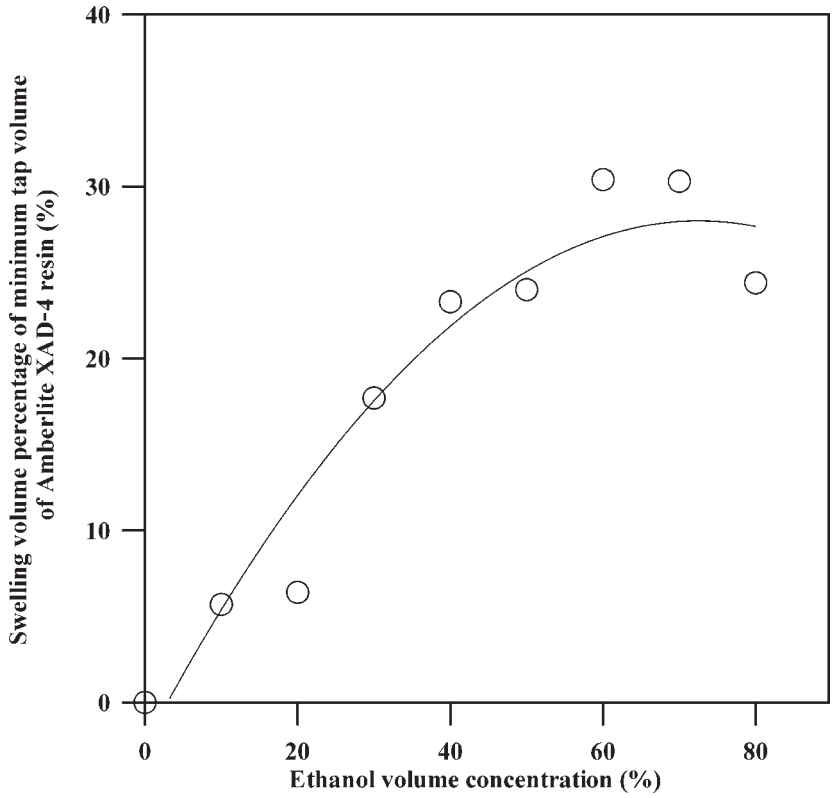

Figure 2. Effect of ethanol volume concentration on the swelling volume of Amberlite XAD-4 resin.

resin with an ethanol concentration higher than 70%, due to the high swelling pressure. In the experiment that followed, the ethanol solution was fixed at 70%, at which the swelling of resin is optimal.

Adsorption of D_2EHPA on Amberlite XAD-4 Resin

Figure 3 shows the adsorption of D_2EHPA on Amberlite XAD-4 by organic–nonorganic solvent process. The adsorption of D_2EHPA first increases almost linearly with increasing D_2EHPA concentration and then levels off as the concentration is higher than $0.25\,mol/dm^3$. The amount of maximum adsorption is about $1.02\,mol/kg$ of dried fresh Amberlite XAD-4 resin. As determined by the BET method, the surface area of Amberlite XAD-4 resin

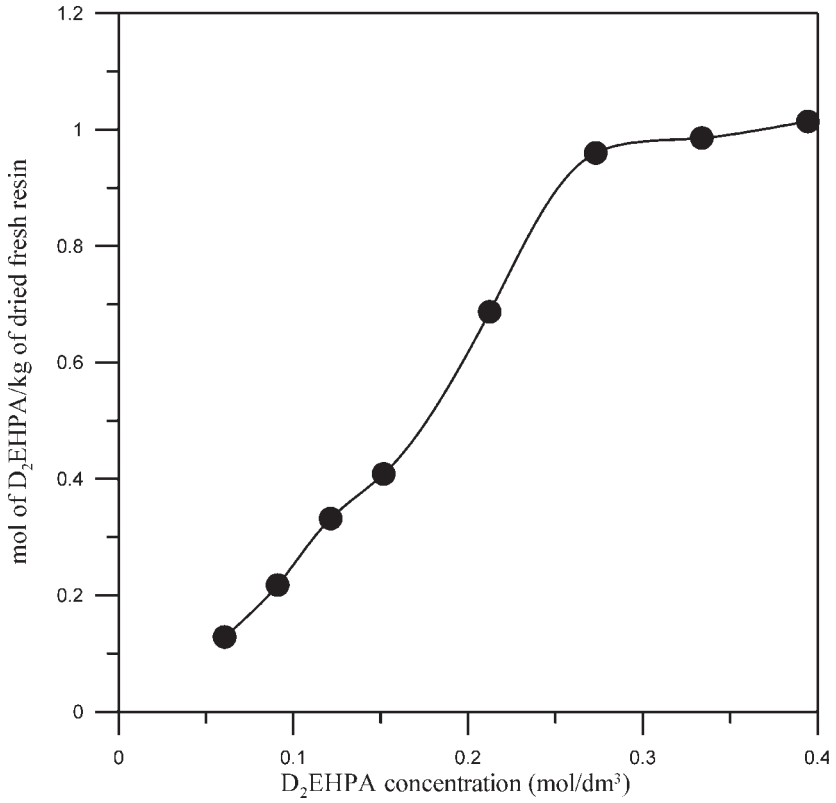

Figure 3. D_2EHPA adsorption on Amberlite XAD-4 resin.

is about $6.87 \times 10^5\,m^2/kg$ of resin. The maximum surface concentration of adsorbed D_2EHPA, therefore, is about $1.46 \times 10^{-6}\,mol/m^2$. It is interesting to note that the surface concentration of adsorbed D_2EHPA on Amberlite XAD-4 resin is close to surface concentration at water/benzene interface ($1.7 \times 10^{-6}\,mol/m^2$),[18] indicating that D_2EHPA may adsorb on the polymer surface as a monolayer.

In the two-step, organic solvent–nonorganic solvent process, the ethanol solvent was eluted from the swollen surface region by water, which is the nonorganic solvent in this study. The removal of ethanol will cause the swollen region on the polymer surface to become a solid state, resulting in physical entanglement of D_2EHPA with the surface molecule chains of Amberlite XAD-4. The amount of D_2EHPA removed during the second step of the process was also monitored. Experimental results indicated that after 15 hr

of rinsing in water, only approximately 2.3% of D_2EHPA was eluted. This is due to elution of nonadsorbed D_2EHPA in the ethanol solution. Figure 4 shows the SEM of modified resin. After the two-step immobilization of D_2EHPA, the matrix structure of the resin remains intact; the surface of D_2EHPA-modified resin is in the solid state.

The stability of immobilized D_2EHPA after two-step, organic solvent–nonorganic solvent process was compared with analogous D_2EHPA-impregnated resin (EIR) by immersing the modified resin in an ultrasonic bath for a different periods of time. The EIR resin was prepared according to the previous study.[35] The load of D_2EHPA in modified resin and EIR resin were 1.02 and 1.25 mol/kg of dried fresh resin. The results show that the two-step immobilized D_2EHPA has better stability than EIR (Table 2).

Effect of Water Environment on the Surface of Modified Amberlite XAD-4 Resin

Due to the surface-active characteristic of D_2EHPA, the immobilized D_2EHPA molecules will undergo molecules reorientation in a water environment. The surface property of D_2EHPA-immobilized Amberlite XAD-4 will

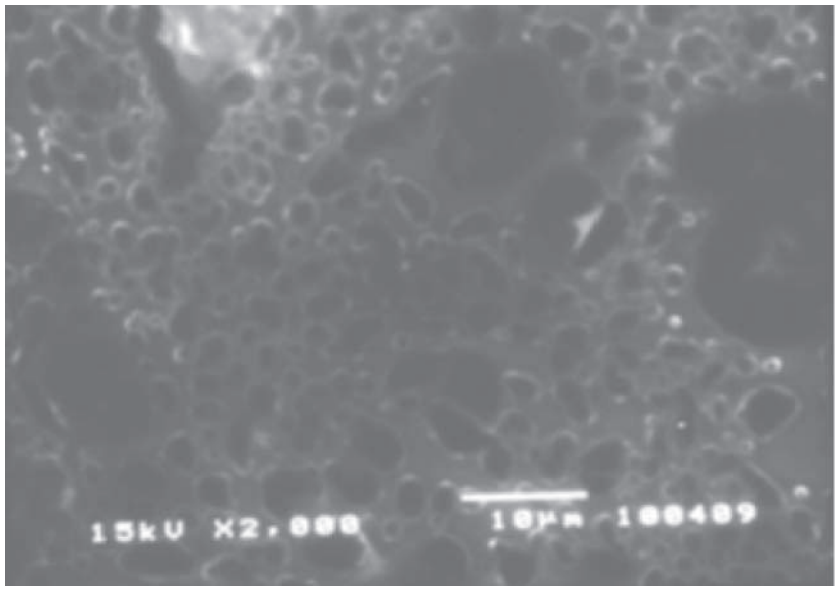

Figure 4. SEM of D_2EHPA-immobilized Amberlite XAD-4 after two-step, organic solvent–nonorganic solvent process.

Table 2. Stability of immobilized D_2EHPA on Amberlite XAD-4 prepared by organic solvent–nonorganic solvent process and EIR process.

Time of ultrasonic bath (min)	D_2EHPA-modified (%)	EIR (%)
5	0.75	1.50
10	0.75	1.50
15	0.75	1.50
20	1.00	1.50
30	1.00	2.00

change with immersion time in water. This effect was further demonstrated with ESCA analysis. Table 3 shows the results of ESCA for the surface of D_2EHPA-modified Amberlite XAD-4 after different periods of immersion time in water. For nonmodified Amberlite XAD-4, there was no phosphors element was detected. For D_2EHPA-modified Amberlite XAD 4, there was about 2.52% of phosphors element on the surface of Amberlite XAD-4 after 1 hr of immersion in water. After 24 hr of immersion in water, the phosphors element on the surface of D_2EHPA-modified Amberlite XAD-4 increased to 3.05%, indicating the reorientation and exposure of a phosphoric acid group due to the high polarity of a water environment. It is interesting to note that the atomic ratio of O/P is about 4.3, which is very close to the atomic ratio of the D_2EHPA molecule, indicating a monolayer adsorption of D_2EHPA on Amberlite XAD-4 resin. For an atomic ratio O/P higher than 4, it may be due to the incorporation of water during the preparation process.

Table 3. ESCA analysis of D_2EHPA-modified Amberlite XAD-4 before and after immersion in water.

Treatment condition	P (%)	O (%)	C (%)
Amberlite XAD-4	0	5.92	94.08
Immersed in water for 1 hr	2.52	15.45	82.03
Immersed in water for 24 hr	3.03	13.18	83.79

Adsorption of Pb and Cu Ions on D_2EHPA-Modified Amberlite XAD-4 Resin

Solvent extraction equilibrium experiments showed that D_2EHPA can extract Pb more preferentially than Cu (figure not shown). As a monobasic acid (HA), the D_2EHPA extraction of Cu and Pb ions and the distribution factors, $D_{Cu^{2+}}$ and $D_{Pb^{2+}}$, can be described as in Eqs. (1)–(4), based on the results of solvent extraction equilibrium.

$$Cu^{2+}_{(aq)} + 2(HA)_{2(org)} \Longleftrightarrow CuA_2(HA)_{2(org)} + 2H^{+}_{(aq)} \quad (1)$$

$$D_{Cu^{2+}} = \frac{[CuA_2(HA)_2]_{(org)}}{[Cu^{2+}]_{(aq)}} \quad (2)$$

$$Pb^{2+}_{(aq)} + 3(HA)_{2(org)} \Longleftrightarrow PbA_2(HA)_{4(org)} + 2H^{+}_{(aq)} \quad (3)$$

$$D_{Pb^{2+}} = \frac{[PbA_2(HA)_4]_{(org)}}{[Pb^{2+}]_{(aq)}} \quad (4)$$

Therefore, it is expected that the D_2EHPA-modified Amberlite XAD-4 resin can be used for the separation of Pb and Cu ions from aqueous solution. In contrast, D_2EHPA form dimers in the solvent extraction system, the D_2EHPA-modified Amberlite XAD-4 resin surface contains D_2EHPA monomeric molecule, which will separate Pb and Cu ions as an ion-exchange resin. The ion-exchange isotherm experiments of this new type of selective resin were investigated. The results were compared with the solvent extraction and analogous EIR.

Single Ion Solution

Figure 5 shows the molal selectivity coefficients [$K^{i}_{H} = (\bar{x}_H^{|z_i|}\, x_i^{|z_H|})/(\bar{x}_i^{|z_H|}\, x_H^{|z_i|})$] of the exchanges of Cu^{2+}/H^{+} and Pb^{2+}/H^{+} on D_2EHPA-modified Amberlite XAD-4 resin, where $\bar{x}_H$ is the equivalent ionic fraction of H^{+} in resin, $\bar{x}_i$ is the equivalent ionic fraction of counter ions (Cu^{2+} and Pb^{2+}) in resin, x_H is the equivalent ionic fraction of H^{+} in aqueous phase, and x_i is the equivalent ionic fraction of counter ions (Cu^{2+} or Pb^{2+}) in aqueous phase. The D_2EHPA-modified Amberlite XAD-4 has higher Pb ion selectivity than Cu ion. As expected from solvent extraction experiments, this selectivity is due to the phosphoric acid functional groups. Nevertheless, the interaction between metal ions and phosphoric acid groups will be different in ion-exchange and solvent extraction systems. The

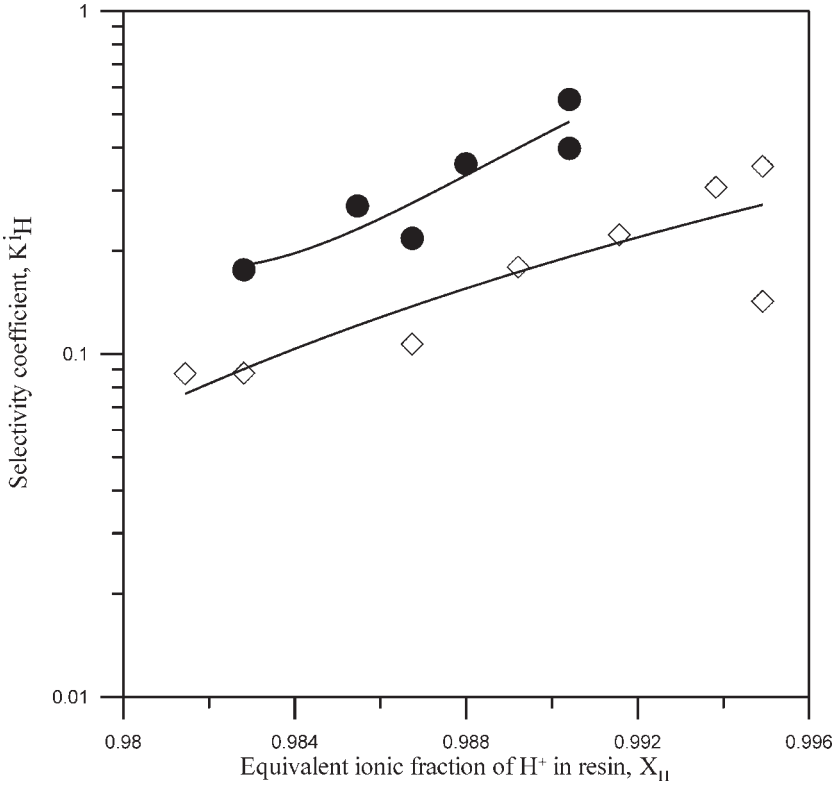

Figure 5. The selectivity coefficient of the exchanges Cu^{2+}/H^+ (◇) and Pb^{2+}/H^+ (●) on D_2EHPA-modified Amberlite XAD-4 resin.

ion-exchange isotherms of Cu and Pb single ion solutions on D_2EHPA-modified Amberlite XAD-4 resin were compared with the extraction equilibria of D_2EHPA in solvent extraction process. The solvent extractions were conducted under the conditions analogous to that in the ion-exchange isotherm experiments, in terms of similar metal ion to D_2EHPA molar ratios and metal ion concentrations. Figure 6 shows the ion-exchange isotherm and extraction equilibria of Cu and Pb single ion solutions. To compare the results of ion-exchange isotherm and extraction equilibria, $[\text{metal ion}]_{resin}/[D_2\ EHPA]_{resin}$ (or $[\text{metal ion}]_{org}/[D_2\text{-EHPA}]_{org}$) is plotted against $[\text{metal ion}]_{aqueous}$. The slope of the isotherm curve can therefore be regarded as the distribution factor normalized to the amount of D_2EHPA. For D_2EHPA-modified Amberlite XAD-4, the amounts of Pb and Cu ions extracted by per mole of D_2EHPA are higher than those in solvent extraction.

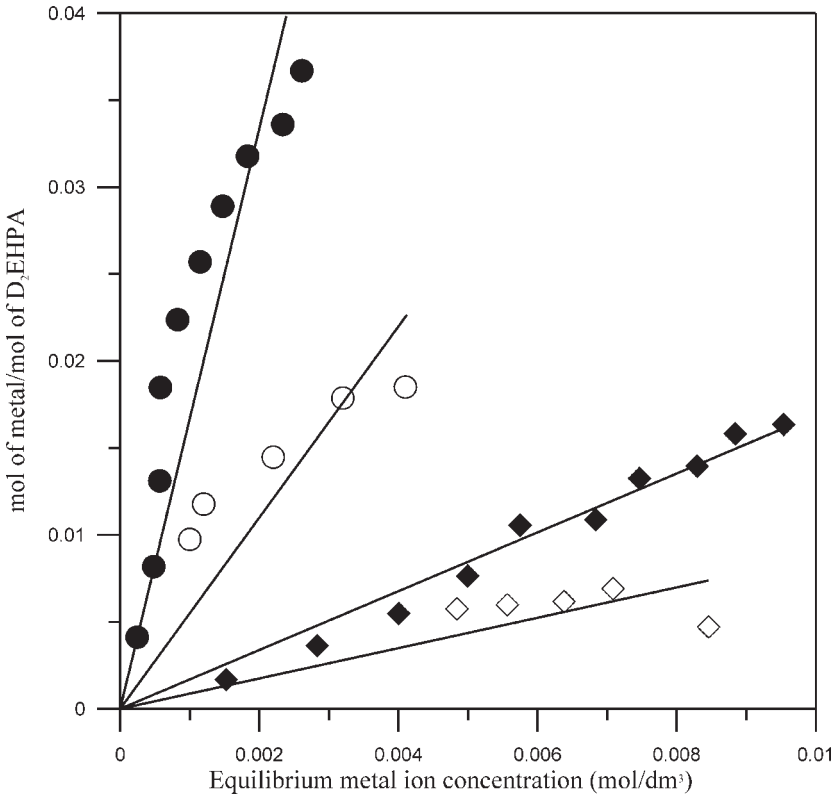

Figure 6. Ion-exchange isotherm and extraction equilibria of Cu and Pb single ion solution. Ion-exchange isotherm: Pb (●), Cu (◆). Solvent extraction equilibria: Pb (○), Cu (◇).

Since the immobilized D_2EHPA is in the monomeric form, the ion-exchange isotherm of Cu and Pb ions on D_2EHPA-modified resin can be described according to Eqs. (5) through (8).

$$Cu^{2+}_{(aq)} + 2HA_{(resin)} \Longleftrightarrow CuA_{2(resin)} + 2H^{+}_{(aq)} \tag{5}$$

$$D^{MR}_{Cu^{2+}} = \frac{[CuA_2]_{(resin)}}{[Cu^{2+}]_{(aq)}} \tag{6}$$

$$Pb^{2+}_{(aq)} + 2HA_{(resin)} \Longleftrightarrow PbA_{2(resin)} + 2H^{+}_{(aq)} \tag{7}$$

$$D^{MR}_{Pb^{2+}} = \frac{[PbA_2]_{(resin)}}{[Pb^{2+}]_{(aq)}} \tag{8}$$

where $D^{MR}_{Cu^{2+}}$ and $D^{MR}_{Pb^{2+}}$ are the distribution coefficients of metal ions on modified resin. The normalized distribution factors (slopes of isotherm curves) are summarized in Table 4. It is interesting to note that the Cu distribution factor of the ion-exchange isotherm is approximately two times of extraction equilibria (i.e., $D^{MR}_{Cu^{2+}}/D_{Cu^{2+}} = 1.94$). This may be because in solvent extraction, Cu ion interacts with D_2EHPA dimer, while in ion-exchanger, Cu ion interacts with D_2EHPA monomer [Eqs. (1) and (5)]. The Pb distribution factor of the ion-exchange isotherm is approximately 3.2 times the extraction equilibria [i.e., $D^{MR}_{Pb^{2+}}/D^{2+}_{Pb} = 3.2$].

To realize the interaction of metal ions with D_2EHPA-modified Amberlite XAD-4, the resin was subjected to FTIR study. Figure 7 shows the FTIR of resins after the adsorption of metal ions. For Pb adsorption, an intensive peak appeared at 3200–3400 nm, indicating the presence of −OH groups. This may be due to the formation of a Pb cluster in the resin. At higher concentration, Pb may form polymeric ion [$Pb_6O(OH)^{4+}_6$] with −OH bridges in crystalline salts.[36] This partly accounts for the higher Pb extraction in D_2EHPA-modified ion-exchange resin. Apparently, less amount of D_2EHPA is required for D_2EHPA-modified Amberlite XAD-4 resin than a conventional solvent extraction process. This is one of the advantages of using D_2EHPA-modified ion-exchange resin for Cu and Pb ion separation, since less amount of extractant is needed.

Mixed Ion Solution

To understand the separation of Cu and Pb ions by D_2EHPA-modified Amberlite XAD-4, ion-exchange equilibrium was carried out for Cu and Pb

Table 4. Distribution factors of isotherm equilibrium.

Isotherm equilibrium	Metal ion	Normalized distribution factor (D) (slope of equilibrium curve)
Single ion solution		
Solvent extraction	Pb	5.16
	Cu	0.87
D_2EHPA-modified	Pb	16.67
	Cu	1.69
Mixed solution		
Extractant impregnated resin	Pb	3.39
	Cu	0.84
D_2EHPA-modified	Pb	6.42
	Cu	0.33

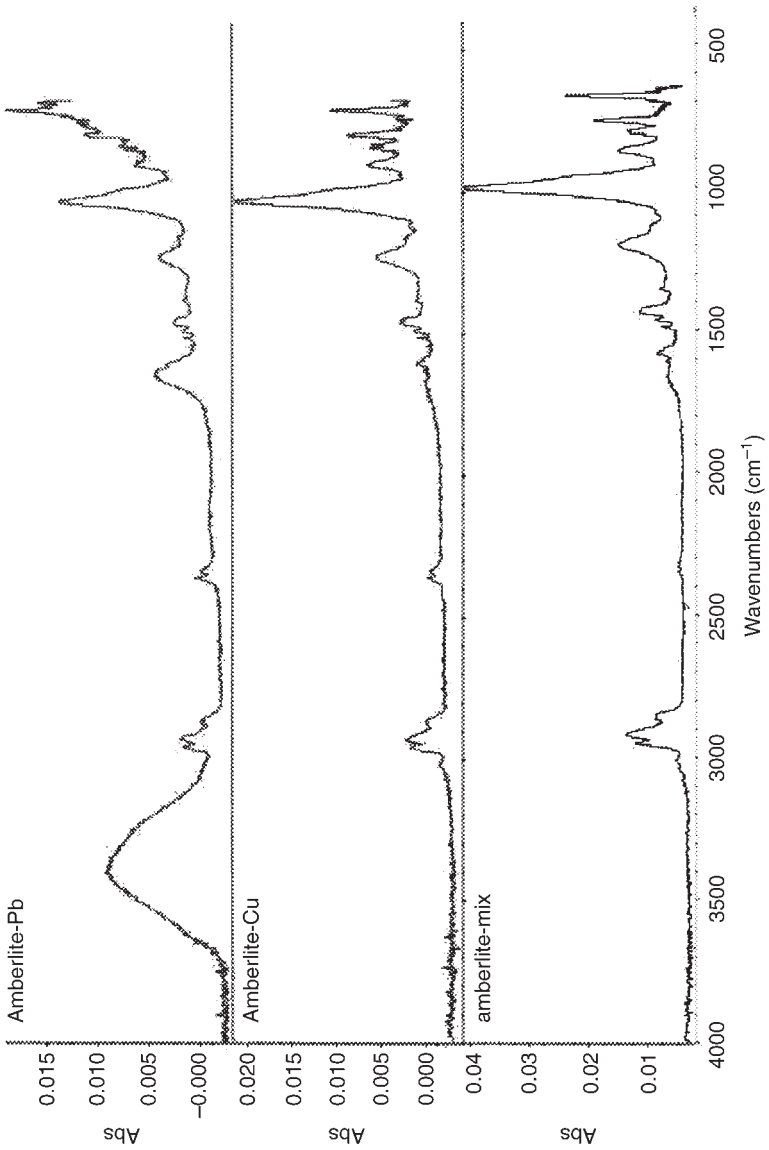

Figure 7. FTIR of D_2EHPA-immobilized Amberlite XAD-4 resins after the adsorption of metal ions.

mixed ions solution. This result is compared with the analogous D_2EHPA-impregnated Amberlite XAD-4 resin (EIR). Figure 8 shows the ion-exchange isotherm and extraction equilibria of Cu and Pb mixed ion solution, by plotting $[\text{metal ion}]_{\text{resin}}/[D_2\ \text{EHPA}]_{\text{resin}}$ vs $[\text{metal ion}]_{\text{aqueous}}$. Both adsorption isotherm and extraction equilibria show approximately linear correlations within the range of experiment. For D_2EHPA-modified Amberlite XAD-4 resin, the amounts of Pb ions extracted by per mole of D_2EHPA are higher than that by EIR. On the other hand, the amount of Cu ion extracted by D_2EHPA-modified resin is lower than that by EIR. The separation factor in the EIR system ($\alpha^{\text{EIR}}_{\text{Cu/Pb}}$) is about 4.04 and the separation factor in the D_2EHPA-modified ion-exchange system ($\alpha^{\text{MR}}_{\text{Cu/Pb}}$) is about 19.45. Comparing the ion-exchange system with single-ion (see Fig. 6) and mixed-ions solution (see Fig. 8), the Pb ion separation factor of mixed-ions solution is higher than that calculated from the distribution factors of metal ions in single-ion solution. This is due to the following two

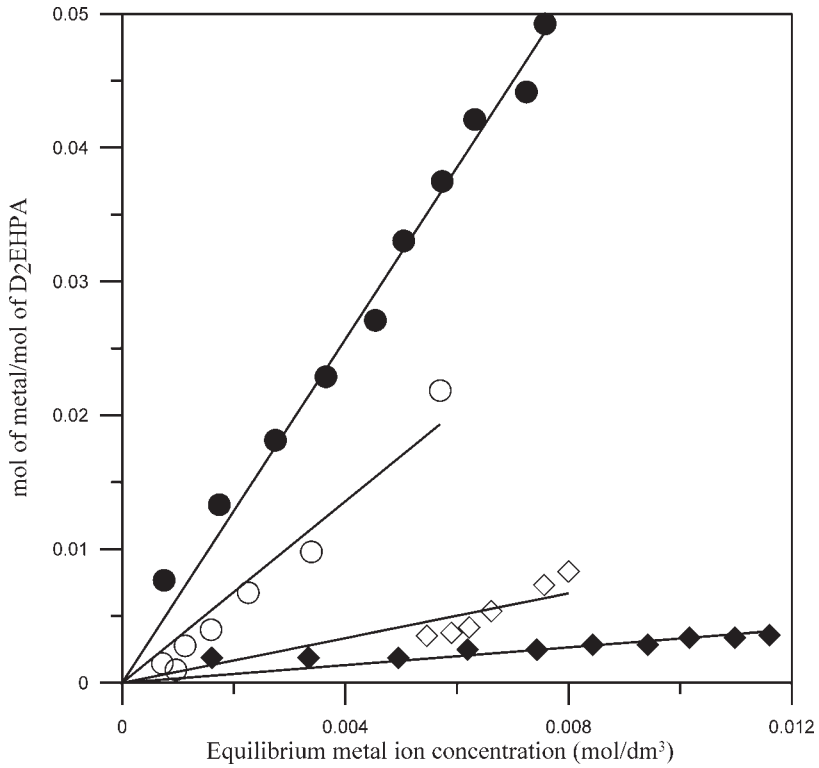

Figure 8. Ion-exchange isotherm and extraction isotherm of Cu and Pb mixed ion solution. Ion-exchange isotherm: Pb (●), Cu (◆). EIR extraction equilibria: Pb (○), Cu (◇).

reasons. First, the D_2EHPA-modified resin has a higher affinity toward Pb than Cu ion (as shown in Fig. 5). In addition, the Pb ion diffusion coefficient ($0.93\,m^2/s$) is higher than Cu ion diffusion coefficient ($0.72\,m^2/s$).[37] Consequently, Pb ion will diffuse into the resin faster than Cu ion and interact more preferentially with immobilized D_2EHPA. Both reasons account for the high separation factor of D_2EHPA-immobilized Amberlite XAD-4 resin.

Selective Separation of Pb and Cu Mixed-Ion Solution by Batch Process

The application of D_2EHPA-modified Amberlite XAD-4 resin on the separation of Pb and Cu mixed-ion solution was further demonstrated by a batch separation process to study the equilibrium front.[38] A mixed Pb/Cu solution was subjected to sequential contact with D_2EHPA-modified Amberlite XAD-4 resin at pH 2.0. Solid/liquid ratio was maintained at 1 : 5 in each contactor. The concentration of Pb and Cu ions in the liquid phase was measured after the adsorption equilibrium was established. Fig. 9 shows the batch separation of Pb and Cu ions in a mixed-ion solution with initial concentrations both equal to $0.01\,mol/dm^3$. After six batches of contacts, the relative ion concentration of Cu ion in aqueous phase increased from 50–99%, while the relative ion concentration of Pb ion decreased from 50% to 1%. The purified liquid phase contained Cu ion concentration as high as $0.0075\,mol/dm^3$. More than 75% of initial Cu metal ion is remained in the purified liquid. The dot lines in Fig. 9 represent the calculated curve $[\text{metal ion}]_{\text{aq, equilibrium}} = [\text{metal ion}]_{\text{aq, initial}}/(1 + aD^{\text{MR}}_{\text{metal}}$, where $D^{\text{MR}}_{\text{metal}}$ is the normalized distribution factor of metal ions in mixed-ion solution and a is the solid/liquid ratio predicted from the ion-exchange isotherm of mixed-ions solution (Table 4). Figure 9 also shows the separation of Pb and Cu ions using analogous EIR resin. After seven batches of contacts, the relative ion concentration of Cu ion in aqueous phase increased from 50% to 88.3%, while the relative ion concentration of Pb ion decreased from 50% to 11.7%. The liquid phase contained Cu ion concentration equal to $0.0054\,mol/dm^3$. Only 54% of initial Cu metal ion remained in the liquid phase. Apparently, the D_2EHPA-modified ion-exchange resin shows better separation results than EIR resin. These results of batch separation process provide important equilibrium information for understanding the performance of continuous column experiments.

SUMMARY

A new type of metal ion selective resin can be prepared by immobilizing D_2EHPA onto the surface of Amberlite XAD-4 resin employing an organic

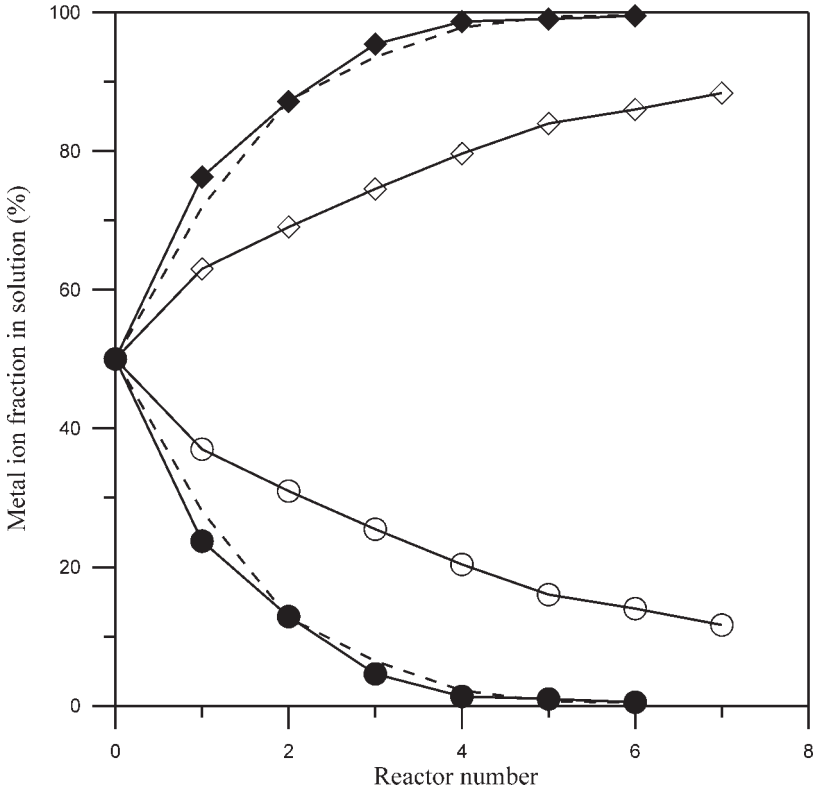

Figure 9. Batch separation of Pb and Cu ions in a mixed ion solution with initial concentrations both equal to 0.01 mol/dm^3. Ion-exchange: Pb (●), Cu (◆). EIR: Pb (○), Cu (◆). Dot lines: predicted from the distribution factor of mixed ions solution.

solvent–nonorganic solvent process. Due to its amphiphilic structure, D_2EHPA has the tendency to adsorb at interfaces in an oriented fashion. The adsorption of D_2EHPA can lower the surface tension of ethanol solution. The amount of adsorption is affected by the pH and ionic strength of the solution. The surface of Amberlite XAD-4 resin can be modified with surface-active D_2EHPA. The amount of immobilized D_2EHPA is as high as 1.02 mol/kg of Amberlite XAD-4 resin. Since the alkyl chains of extractant is physically entangled with the surface polymer chains of resin, the immobilized-D_2EHPA shows good stability. In a water environment, ESCA study showed that the immobilized D_2EHPA underwent molecule reorientation to expose the phosphoric acid group. The immobilized phosphoric acid polar groups changed the hydrophobic surface into a hydrophilic surface with specific metal ion selectivity.

Ion-exchange isotherm of single ion solution showed that D_2EHPA-modified Amberlite XAD-4 resin has higher Pb ion selectivity than Cu ion. For mixed ions solution, D_2EHPA-modified Amberlite XAD-4 resin showed a much higher separation factor than analogous EIR resin. The selective extraction results using a series contact of solution mixtures with resins further demonstrated the feasibility of using D_2EHPA-modified Amberlite XAD-4 resin for the separation of Pb/Cu mixed ion solution. After only six batches of contacts, the relative ion concentration of Cu ion increased from 50% to more than 99%, while the relative ion concentration of Pb ion decreased from 50% to less than 1%. The Cu recovery rate was more than 75%. For analogous EIR system, the relative ion concentration of Cu ion in aqueous phase increased from 50% to 88.3% after seven batches of separation, while the relative ion concentration of Pb ion decreased from 50% to 11.7%. Only 54% of the initial Cu metal ion remained in the liquid phase. Apparently, the D_2EHPA-modified ion-exchange resin showed a better separation result than EIR resin.

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REFERENCES

1. Ferreira, L.M.; Loureiro, J.M.; Rodrigues, A.E. Sorption of metals by an amidoxime chelating resin. Part I: equilibrium. Separ. Purif. Technol. **1998**, *33* (11), 1585–1604.
2. Malla, M.E.; Alvarez, M.B.; Batistoni, D.A. Evaluation of sorption and desorption characteristics of cadmium, lead and zinc on amberlite IRC-718 iminodiacetate chelating ion exchanger. Talanta **2002**, *57*, 277–287.
3. Diniz, C.V.; Doyle, F.M.; Ciminelli, V.S.T. Effect of pH on the adsorption of selected heavy metal ions from concentrated chloride solutions by the chelating resin Dowex M-4195. Separ. Sci. Technol. **2002**, *37*, 3169–3185.
4. Godjevargova, T.; Simeonova, A.; Dimov, A. Adsorption of lead and copper on modified polyacrylonitrile bead. J. Appl. Polym. Sci. **2001**, *79*, 283–288.
5. Rivas, B.L.; Maturana, H.A.; Villegas, S. Adsorption behavior of metal ions by amidoxime chelating resin. J. Appl. Polym. Sci. **2000**, *77*, 1994–1999.
6. Gong, B.; et al. Synthesis of spherical macroporous epoxy-dicyandiamide chelating resin and properties of concentration and separation of trace metal ions from samples. Talanta **2000**, *52*, 217–223.

7. Latha, A.G.; et al. Synthesis of a polyacrylamide chelating resin and applications in metal ion extractions. J. Appl. Polym. Sci. **1991**, *43* (6), 1159–1163.
8. Yamabe, K.; Ihara, T.; Jyo, A. Metal ion selectivity of macroreticular chelating cation exchange resins with phosphonic acid groups attached to phenyl groups of a styrene-divinylbenzene copolymer matrix. Separ. Sci. Technol. **2001**, *36* (15), 3511–3528.
9. Warshawsky, A.; et al. Synthesis of novel chelating resins containing dithiophosphoric functionality and comparison to analogous solvent impregnated resins. Separ. Sci. Technol. **2002**, *37* (4), 823–846.
10. Jyo, A.; et al. Preparation of phosphoric acid resins with large cation exchange capacities from macroreticular poly(glycidyl methacrylate-*co*-divinylbenzene) beads and their behavior in uptake of metal ions. J. Appl. Polym. Sci. **1997**, *63*, 1327–1334.
11. Sekine, T.; Hasegawa, Y. *Solvent Extraction Chemistry*; Marcel Dekker: New York, 1977.
12. Cortina, J.L.; et al. Solid–liquid extraction studies of Zn(II), Cu(II) and Cd(II) from chloride media with impregnated resins continining mixtures of organophosphorus compounds immobilized on to Amberlite XAD2. Hydrometallurgy **1995**, *37*, 301–322.
13. Cortina, J.L.; et al. Solid–liquid extraction studies of divalent metals with impregnated resins containing mixtures of organophosphorus extractants. React. Funct. Polym. **1997**, *32*, 221–229.
14. Juang, R.S.; Chen, M.L. Competitive sorption of metal ions from binary sulfate solutions with solvent-impregnated resins. React. Funct. Polym. **1997**, *34*, 93–102.
15. Juang, R.S.; Lee, S.H. Column separation of divalent metals from sulfate solutions using impregnated resins containing di(2-ehtylhexyl)phosphoric acid. React. Funct. Polym. **1996**, *29*, 175–183.
16. Warshawsky, A. Polystyrene impregnated with -diphenylglyoxime, a selective reagent for palladium. Talanta **1974**, *21* (6), 624–626.
17. Chen, J.H. Separation of Ni, Mo and V ions using D_2EHPA modified Amberlite 200 resin. 2002 TKJChE, Chinese Institute of Chemical Engineers: Taipei, 2002.
18. Kanki, T.; et al. Surface active species and their reaction schemes in extraction solution systems indentified from practical behaviors of interfacial tension. Separ. Purif. Technol. **2000**, *19*, 93–102.
19. Kato, K.; et al. Polymer surface with graft chains. Prog. Polym. Sci. **2003**, *28*, 209–259.
20. Lens, J.P.; et al. Introduction of sulfate groups on poly(ethylene) surface by argon plasma immobilization of sodium alkyl sulfates. Polymer **1998**, *39* (15), 3437–3444.

21. Nagai, K. Radical polymerization and potential applications of surface-active monomers. Trends Polym. Sci. **1996**, *4* (4), 122–127.
22. Linder, C.; Kedem, O. Asymmetric ion exchange mosaic membranes with unique selectivity. J. Membr. Sci. **2001**, *181*, 39–56.
23. Freij-Larsson, C.; Jannasch, P.; Wesslen, B. Polyurethane surfaces modified by amphiphilic polymers: effects on protein adsorption. Biomaterials **2000**, *21*, 307–315.
24. Chen, J.H.; Ruckenstein, E. Optimum immersion time in the surface modification of polymers by the two-liquid deposition of diblock copolymers. J. Colloid Interf. Sci. **1989**, *132*, 100–112.
25. Chen, J.H.; Ruckenstein, E. Surface modification by a two-phase deposition of surfactant. J. Colloid Interf. Sci. **1991**, *42*, 544–553.
26. Ruckenstein, E.; Chen, J.H. Effect of a surface active pyrrole on the conductivity of polypyrrole composities. J. Appl. Polym. Sci. **1991**, *47*, 1209–1218.
27. Chen, J.H.; Kao, Y.Y.; Lin, G.H. Selective separation of vanadium from molybdenum using D_2EHPA immobilized amberlite XAD-4 resin. Separ. Sci. Technol. **2003**, *38*, 3827–3852.
28. Butler, J.N. *Ionic Equilibrium: A Mathematical Approach*; Addison-Wesley Publishing: Reading, 1964.
29. de Levie, R. *Aqueous Acid–Base Equilibria and Titrations*; Oxford University Press: Oxford, 1999; 37–43.
30. Weast, R.C.; Astle, M.J.; Beyer, W.H. *CRC Handbook of Chemistry and Physics*, 68th Ed.; CRC Press, Inc.: Boca Raton, 1988.
31. Sperling, L.H. *Introduction to Physical Polymer Science*, 2nd Ed.; John Wiley & Sons, Inc.: New York, 1992; 66–71.
32. Rosen, M.J. *Surfactants and Interfacial Phenomena*; John Wiley & Sons: New York, 1989.
33. Galembeck, F.; et al. Latex coagulation induced by alcohol vapors: an unusual factor for colloidal instability. Colloid Surf. A. Physicochemi. Eng. Aspects. **2000**, *164*, 217–225.
34. Harland, C.E. *Ion Exchange: Theory and Practice*, 2nd Ed.; Cambridge, 1994.
35. Chen, J.H.; et al. The preparation of di(2-ethylhexyl)phosphoric acid modified amberlite 200 and its application in the separation of metal ions from sulfuric acid solution. React. Funct. Polym. **2003**, *56*, 175–188.
36. Cascales, C.; Rasines, I. Preparation and x-ray diffraction data for the new pyrochlores Pb_2(M0.33Sb1.67)O6.5 (M = Mg, Ni, Cu, or Zn). J. Chem. Soc. Dalton Trans. **1986**, 1247–1250.
37. Pickett, D. *Electrochemical Reactor Design*; Elsevier Scientific Publishing Company: Amsterdam, 1979.

38. Anderson, R.E. Ion-exchange separations. In *Handbook of Separation Techniques for Chemical Engineers*, 2nd Ed.; Schweitzer, P.A., Ed.; McGraw-Hill Book Company: New York, 1988.