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Adsorption of zinc (II), cadmium (II), and copper (II) with PTFE Selective Resin containing primary amine N1923 and Cyanex925

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Abstract−In the present study, a synergistic extraction mixture, primary amine N1923 (RNH_2) and Cyanex925 (B), was loaded on PTFE powder to prepare PTFE Selective Resin and was employed for the adsorption of zinc, cadmium, and copper from chloride medium. The effects of shaking time, resin amounts, concentration of metal ions, and experimental temperature on the distribution coefficients were determined. The stoichiometry of the adsorbed complexes was determined to be $MCl_2\cdot(1/2)RNH_2\cdot B$ with the Selective Resin. The equilibrium constants and thermodynamic quantities (ΔH, ΔG, and ΔS) were calculated. Furthermore, the Freundlich isotherm proved to be more suitable than the Langmuir isotherm to indicate the effect of concentration of M^{2+} on the adsorption with PTFE Selective Resin.

Key words: Adsorption, PTFE Selective Resin, Primary Amine N1923, Cyanex925

INTRODUCTION

Heavy metals, such as lead, zinc, cadmium, and copper, are major pollutants that can accumulate in the environment such as in the food chain, and thus may pose a significant danger to human health. Their removal from contaminated samples is of utmost importance. Many physicochemical methods have been proposed for this purpose, such as solvent extraction, adsorption, electro-chemical precipitation, ultrafiltration, and reverse osmosis. Among these methods, the technique of adsorption using viable adsorbents has attracted much attention. So far, many kinds of sorbents such as oxides [1-4], zeolites [5,6], tourmaline [7], minerals [8,9], biomaterials [10-17], carbon [18,19], CNTs [19,20], polytetrafluoroethylene (PTFE) [21,22], silica gel [23,24], ion-exchange resin [25-28], and extraction resin [29-32] have been used as materials for the adsorption of zinc, cadmium, and copper.

Extraction resins and extractant-impregnated resins have acquired great importance as a technique with interesting features for the recovery and chromatographic separation of metal ions because they combine the advantages of high selectivity and high efficiency. Kinds of extractants used in liquid-liquid extraction have been reported to be used for the preparation of extraction resins. A resin containing two extractants is called Selective Resin, which was first developed by Belfer et al. [33] It can combine the features of chromatographic separation and synergistic extraction, which have been regarded as effective for enhancing the extraction efficiency and selectivity of metal ions. After that, few reports have been given about Selective Resin except the adsorption of rare earths with Cyanex272-PC88A resin [34], scandium with D2EHPA-TBP resin [35], and thorium and uranium with TOPO-TBP resin [36].

PTFE is a well-known material that can apply a wide temperature range, high insulation, high lubricity with no poison. A few researchers have reported the application of PTFE as an adsorbent for the preconcentration of metal ions [21,32]. Some authors have employed a direct irradiation grafting method to prepare PTFE resins [22]. However, except for Duan et al.'s work [32], no other papers have been reported about the impregnation of extractants onto PTFE, to say nothing of the preparation and the application of Selective Resin based on this good material.

The object of this study was to prepare Selective Resins containing primary N1923 and Cyanex925 (hereafter abbreviated as C925) with PTFE as the support material and to study their ability to adsorb zinc, cadmium, and copper from aqueous solutions. Various operating parameters such as adsorption contact time, adsorbent dosage, metal concentrations, and experimental temperature on the adsorption capacity, were investigated. The equilibrium data obtained were analyzed in the light of the Freundlich and Langmuir isotherms.

EXPERIMENTAL

1. Reagents

Primary amine N1923 with a purity greater than 99% was supplied by Shanghai Institute of Organic Chemistry. C925 was supplied by Cytec Canada, Inc. The extractants were used as received.

PTFE powder of 100-mesh size was purchased from Nuo Ya Zhou Co. Ltd. (Beijing, China). The stock solutions of MCl_2 (M=zinc, cadmium, copper) were prepared with AR chemicals. The concentrations of M^{2+} were analyzed by titration with a standard solution of EDTA with xylenol orange as an indicator. All other reagents were of analytical reagent grade. All adsorption experiments were performed at constant ionic strength by adding NaCl (μ=0.3 mol·L^{-1}).

2. Apparatus

A pHS-3C digital pH meter made by Shanghai Rex Instruments Factory was used for pH measurements. Deionized water was prepared by the Milli-Q SP system (Millipore, Milford, MA, USA).

3. Methods

3-1. Synthesis of Selective Resin

PTFE powder was sequentially washed with deionized-distilled water (DDW), 1 mol·L^{-1} HCl, DDW, 1 mol·L^{-1} NaOH, DDW, and

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acetone, then dried in a vacuum oven at 50 °C for 48 h.

The pretreated PTFE powder, N1923-heptane and C925-heptane solutions were well mixed in a beaker and stirred for 3 h, then dried in a vacuum oven at 80 °C for 90 h. Heptane was completely removed by heating as the solvent. The obtained resin by this way contained N1923 and C925 contents of about 20% (w/w).

3-2. Batch Experiments

All the experiments of metal ions adsorption were carried out in a thermostated vessel by shaking PTFE Selective Resins containing N1923 and C925 and 5 mL aqueous solution of Zn^{2+}, Cd^{2+}, and Cu^{2+} in an equilibrium tube using a mechanical shaker. The experiments were conducted at 298±1 K except for the temperature experiments. After centrifugation, the metal concentration in the aqueous phase was determined by titration with an EDTA standard solution. The amount of metal ions adsorbed by the resin was determined by difference. The distribution ratio (D) and the amount of M^{2+} adsorbed by the resin (Q) were obtained as follows:

$$D=\frac{C_0-C}{C}\cdot\frac{V}{m}=\frac{Q}{C} \tag{1}$$

where C_0 and C denote the initial total concentration and the equilibrium concentration of metal ions in aqueous phase, respectively; m stands for the mass of dry resin; and V represents the volume of the aqueous phase.

RESULTS AND DISCUSSION

1. Influence of Shaking Time

To determine the time to reach equilibrium, the distribution coefficients of Zn^{2+}, Cd^{2+}, and Cu^{2+} on PTFE Selective Resins were studied as a function of time at constant pH values, concentration of M^{2+} and mass of resin. The shaking time varied in the range of 0-180 min. As seen in Fig. 1, 2 h was enough to reach equilibrium for all metal ions. Therefore, all the subsequent experiments of M^{2+} adsorption were conducted by shaking the resin phase and the aqueous phase together for 2 h.

2. Adsorption Stoichiometry

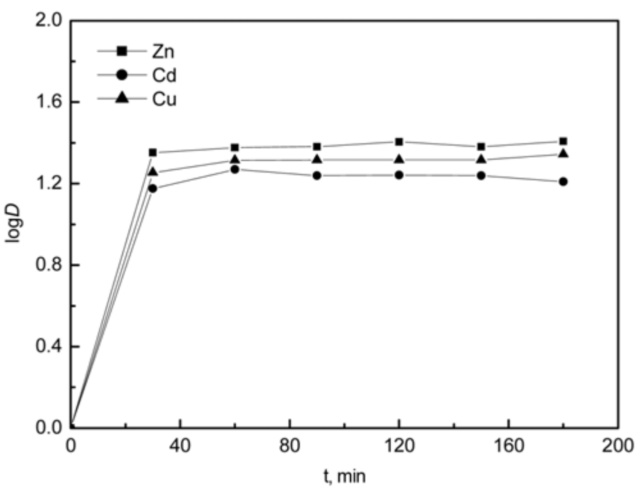

Fig. 1. Effect of time on the adsorption of M^{2+} with PTFE selective resin containing N1923 and C925: m_{resin}=0.02 g, [M^{2+}]=0.020 mol·L^{-1}, pH=2.70, μ=0.3 mol·L^{-1}.

The reaction of M^{2+} and neutral organophosphorus extractants (C925) can be described as the following [37]:

$$MCl_2+2B \rightleftharpoons MCl_2\cdot 2B \tag{2}$$

where "B" represents neutral organophosphorus extractants.

The extraction of Zn^{2+} and Cd^{2+} with N1923 from hydrochloric acid has been studied by Le et al. in detail. The reaction equations are [38,39]:

$$2RNH_2+ZnCl_2 \rightleftharpoons (RNH_2)_2ZnCl_2 \tag{3}$$

$$3RNH_2+CdCl_2 \rightleftharpoons (RNH_3)_3CdCl_2 \tag{4}$$

At high pH values, a solvation mechanism is followed:

$$(RNH_3Cl)_3+ZnCl_2 \rightleftharpoons (RNH_3)_3[ZnCl_5] \tag{5}$$

$$(RNH_3Cl)_3+CdCl_2 \rightleftharpoons (RNH_3^+)_3[CdCl_5^-] \tag{6}$$

However, there are no reports about the extraction of Cu^{2+} with N1923 from chloride medium. Zhang et al. studied the extraction of cupric acetate with N1923 and proposed the coordination mechanism [40]:

$$Cu^{2+}+2RNH_2+2CH_3COO^- \rightleftharpoons Cu(RNH_2)_2(CH_3COO)_2 \tag{7}$$

If the adsorption of M^{2+} with PTFE Selective Resin containing N1923 and C925 from chloride medium is described with a general reaction [41],

$$MCl_2+xRNH_{2(r)}+yB_{(r)} \rightleftharpoons MCl_2\cdot xRNH_2\cdot yB_{(r)} \tag{8}$$

where "r" denotes the resin phase, the stoichiometric equilibrium constant, K, can thus be described:

$$\log K=\log D-x\log[RNH_2]_{(r)}-y\log[B]_{(r)} \tag{9}$$

The total amount of M^{2+} adsorbed up to resin saturation is determined to be 67.98 mg Zn^{2+}/g·resin, 276.85 mg Cd^{2+}/g·resin, and 62.92 mg Cu^{2+}/g·resin, respectively [31]. According to the data of the content of N1923 and C925 in the resin and the total amount of M^{2+} adsorbed up to resin saturation, x and y for the three metal ions can be determined as about 0.5 and 1.0, respectively. Therefore, the sorption reactions of M^{2+} can be obtained as:

$$MCl_2+\frac{1}{2}RNH_{2(r)}+B_{(r)} \rightleftharpoons MCl_2\cdot\frac{1}{2}RNH_2\cdot B_{(r)} \tag{10}$$

In Eq. (10), the molar ratio of N1923 : C925 is 1 : 2, which is similar to the results in preliminary experiments. The mixtures of N1923 and C925 at different ratios were employed for the solvent extraction of Zn^{2+}, Cu^{2+}, and Cd^{2+}. The mixing system has evident synergistic effects on all the three metal ions, indicating that the distribution ratio reaches maximum at a N1923 : C925 ratio of about 1 : 2. The equilibrium constants for the species formed can be calculated according to Eq. (9) as: logK=4.74±0.04, 4.42±0.05, and 4.57±0.05 for Zn^{2+}, Cd^{2+}, and Cu^{2+}, respectively.

3. Influence of Resin Amount

Fig. 2 shows the effects of resin amount on the amount (Q) of Zn^{2+}, Cd^{2+}, and Cu^{2+} adsorbed with PTFE Selective Resin when the concentration of metal ions, acidity in aqueous phase and ionic strength are constant. It can be seen that the Q values decrease with an in-

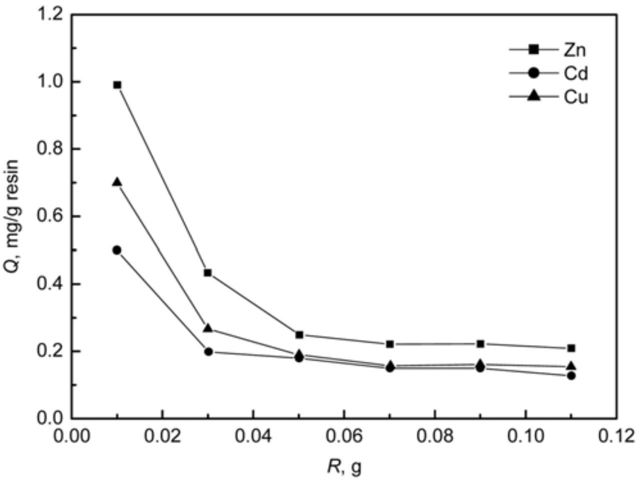

Fig. 2. Effect of resin amount on the adsorption of M^{2+} with PTFE Selective Resin containing N1923 and C925: $[M^{2+}]$=0.020 mol·L^{-1}, pH=2.70, μ=0.3 mol·L^{-1}.

crease of the mass of resin.

4. Influence of the Concentration of Metal Ions

The effect of concentration of M^{2+} on the sorption with PTFE Selective Resin is shown in Fig. 3. The Freundlich isothermal adsorption equation can be expressed as:

$$\log Q = \frac{1}{a} \cdot \log C + \log b \tag{11}$$

where 1/a and b stand for the Freundlich constants. 1/a and logb for M^{2+} are determined according to the slope and intercept values shown in Fig. 3. Eq. (11) can thus be rewritten as:

For Zn^{2+}: logQ=0.97logC+1.47 (R^2=0.9905) (12)

For Cd^{2+}: logQ=1.59logC+2.33 (R^2=0.9969) (13)

For Cu^{2+}: logQ=1.03logC+1.41 (R^2=0.9916) (14)

The sorption data were also fitted to the Langmuir isotherm model:

$$C_r = \frac{C_m AC}{1 + AC} \tag{15}$$

This equation can be rearranged to get the linear form:

$$\frac{1}{C_r} = \frac{1}{C_m AC} + \frac{1}{C_m} \tag{16}$$

where C_r is the equilibrium concentration of metal ions in the resin phase, C is the equilibrium concentration of metal ions in the aqueous phase, C_m is the monolayer sorption capacity, and A is a constant related to the energy of sorption. The fitted parameter values and values of the correlation coefficients are as follows:

For Zn^{2+}: $\frac{1}{C_r} = \frac{6.94}{C} + 67.79$ (R^2=0.9849) (17)

For Cd^{2+}: $\frac{1}{C_r} = \frac{31.86}{C} - 1215.60$ (R^2=0.9847) (18)

For Cu^{2+}: $\frac{1}{C_r} = \frac{10.95}{C} + 9.84$ (R^2=0.9860) (19)

It can be seen that the Langmuir isotherm is not as suitable as the Freundlich isotherm. The reason may be that the Langmuir model assumes that the surface of the sorbent can accommodate only a monolayer of the sorbate ions and no interaction between the sorbed species. The Freundlich isotherm model, on the other hand, does not have any restriction on the sorption capacity of the sorbent, and is more appropriate in situations where the sorption sites possess a heterogeneous nature.

5. Influence of Experimental Temperature

At fixed concentrations of M^{2+}, amounts of the resin, ion strength, and acidities in the aqueous phase, the amounts of M^{2+} adsorbed with PTFE Selective Resin containing N1923 and C925 (Q) were studied at different temperatures (20-60 °C). The logD vs. (1000/T) plots are shown in Fig. 4. The change of enthalpy of the reactions, ΔH, can be determined according to the following equation:

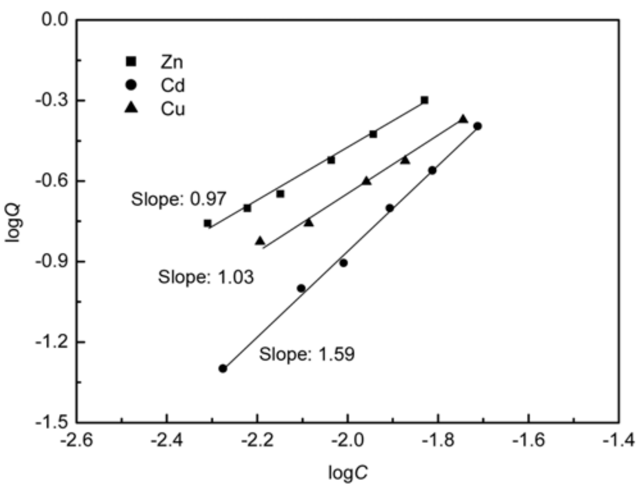

Fig. 3. Effect of M^{2+} concentration on the adsorption of M^{2+} with PTFE selective resin containing N1923 and C925: m_{resin}= 0.02 g, pH=2.70, μ=0.3 mol·L^{-1}.

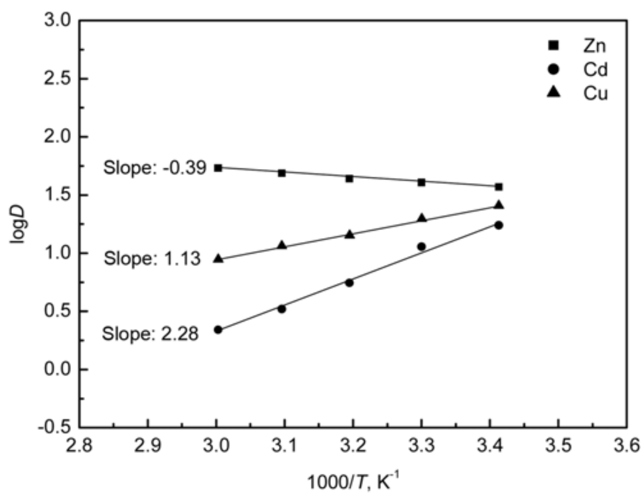

Fig. 4. Effect of experimental temperature on the adsorption of M^{2+} with PTFE selective resin containing N1923 and C925: m_{resin} =0.02 g, $[M^{2+}]$=0.020 mol·L^{-1}, pH=2.70, μ=0.3 mol·L^{-1}.

Table 1. Thermodynamic parameters for the adsorption of M^{2+} with PTFE Selective Resin containing N1923 and C925

M(II)	Zn	Cd	Cu
ΔH (kJ·mol^{-1})	7.49	−43.61	−21.62
ΔG (kJ·mol^{-1})	−27.05	−25.23	−26.08
ΔS (J·mol^{-1}·K^{-1})	115.86	−61.64	14.96

$$\frac{\Delta \log D}{\Delta \frac{1}{T}} = \frac{-\Delta H}{2.303R} \quad (20)$$

The change of Gibbs free energy, ΔG, and the change of entropy, ΔS of the system at 25 °C can be obtained, too.

$$\Delta G = -RT\ln K \quad (21)$$

$$\Delta G = \Delta H - T\Delta S \Rightarrow \Delta S = \frac{\Delta H - \Delta G}{T} \quad (22)$$

The values of ΔH, ΔG and ΔS are shown in Table 1, indicating that the adsorption process of Zn^{2+} with PTFE Selective Resin containing N1923 and C925 is an endothermic reaction, while those of Cd^{2+} and Cu^{2+} are exothermic ones.

CONCLUSIONS

Selective Resin containing N1923 and Cyanex925 based on PTFE material was synthesized and employed for the adsorption of zinc, cadmium, and copper from chloride medium. The stoichiometry of sorption was proposed and equilibrium constants of the adsorbed species were calculated. Freundlich and Langmuir isothermal adsorption equations were obtained. Thermodynamic quantities, i.e., ΔH, ΔG and ΔS, were also calculated for the system. The adsorption process of Zn^{2+} is an endothermic reaction, but the adsorption processes of Cd^{2+} and Cu^{2+} are exothermic reactions.

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