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REMOVAL OF CADMIUM FROM PHOSPHORIC ACID SOLUTION BY SOLVENT-IMPREGNATED RESINS

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ABSTRACT

Phosphoric acid, used in fertilizers is mostly produced by the wet process by making phosphate rocks react with H_2SO_4. Phosphate rocks contain a variety of heavy metals such as Cr, Cd, Cu, Mn, Ni, U, Zn. Production of phosphate fertilizer without eliminating these toxic heavy metals could cause soil or ground water contamination and surface water pollution.

Cadmium is definitely an undesirable element in fertilizers, although current fertilizer use presents no immediate danger. In this study, the removal of cadmium from phosphoric acid was studied by using solvent impregnated chelating resins.

Cyanex 302 (bis [2, 4, 4-trimethyl pentyl] mono thiophosphinic acid) has been used as an extractant for the preparation of solvent-impregnated resins (SIRs). The impregnation was performed by employing macroporous Diaion HP-10 and HP-1MG polymer matrices. The removal of Cd (II) from phosphoric acid solution has been studied as a function of impregnation ratio (g-Cyanex 302/ g-polymer adsorbent) and type of polymer matrix. Optimum conditions for batchwise extractions of Cd(II) from H_3PO_4 solution (40 %) were obtained.

1. INTRODUCTION

Phosphorous is an essential element for all living organisms. The phosphate industry supplies phosphate fertilizers to farmland areas throughout the world. Environmental problems such as calcium sulfate disposal, fluorine, cadmium, uranium and radon emissions are of primary importance (Hodge et al., 1994). The most important environmental concern is related to specific elements present in the composition of phosphate rock. These elements are found in small amounts in phosphate fertilizer as summarized in Table 1 (Bockman, 1990).

It was estimated that 75-80 % of the trace elements present in the rock become part of the phosphate fertilizer. With the exception of cadmium, the total input of heavy metal throughout fertilization was found to be small compared with that naturally present in the average soil. Phosphate rocks contain varying concentrations of cadmium depending on origin (Hodge et al., 1994).

Table 1. Contents of elements found in phosphate rock compared to a typical content in soil

Element	Average Content (mg/kg)		Element	Average Content (mg/kg)	
	rock [a]	soil[b]		rock [a]	Soil [b]
As	7	6	Mn	30	100
Cd	25	0.35	Hg	0.0	0.06
Cr	150	70	Mo	5	1.2
Co	2	8	Ni	35	50
Cu	30	30	Zn	100	90
Pb	6	35			

[a] The content in phosphate rock varies widely with origin and the type of rock.
[b] Median value.

Cadmium is a highly toxic element to human beings. According to the action program of the European Community, cadmium contents of industrial effluents should be lower than 0.2 for new plants or 0.3 mg/L for existing plants (EC, 1991). In the wet-process phosphoric acid production heavy metals such as Cd, U, Ni, Pb, Zn, V, Cr, Cu, Mn, Mo, Hg are redistributed between phosphoric acid and phosphogypsum. Therefore, the fertilizer industry needs to develop a suitable technology for Cd removal from wet-process phosphoric acid (Hodge et al., 1994; EC, 1991).

Several techniques for the removal of cadmium from phosphoric acid have been reported in the literature (Booker, 1988; Booker, 1989; Kabay et al., 1998). Most recently, an integrated process for the purification of wet-process phosphoric acid has been shown by Ortiz et al. (Ortiz et al., 1999).

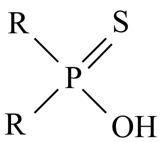
Solvent-impregnated resins (SIRs) have been developed as an emerging technological alternative for problems associated with metal separation (Muraviev et al., 1988; Strikovsky et al., 1996; Cortina et al., 1996). We have recently reported on the preparation of SIRs containing Cyanex-302 using Amberlite XAD-2, XAD-4, XAD-7 and XAD-8 as the polymeric support (Kabay et al., 1998). The resulting SIRs were investigated for their use in the batch and column extraction of Cd (II) and Cu (II) from phosphoric acid solution.

In this study, the preparation of SIRs has been performed by using two different polymer matrices. These are Diaion HP-10 based on poly(styrene-co-divinylbenzene) and highly polar methacrylic matrix HP-1MG. The active component of Cyanex-302 is bis [2,4,4-trimethylpentyl] monothiophosphinic acid. Optimum conditions for batchwise extraction of Cd from 40 % H_3PO_4 solution were studied.

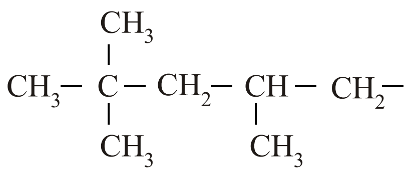
2. EXPERIMENTAL

2.1 Materials

The extractant Cyanex-302 was provided by Cytec Ltd (Canada). The active component of Cyanex-302 is bis [2,4,4- trimethylpentyl] monothiophosphinic acid and chemical structure of this extractant is shown below:



where

R: 

Typical properties of Cyanex-302 is given in Table 2.

Table 2. Properties of Cyanex 302

Appearance	:	Pale yellow
Odor	:	Faintly characteristics of hydrogen sulfide
Assay	:	84 % bis(2,4,4-trimethlpenthyl) monothiophosphinic acid
Specific gravity	:	0.93
Viscosity	:	195 cP
Pour point	:	-20 °C (Approximately)
Flash point (closed cup)	:	> 205 °F (>96 °C)
Auto ignition temperature	:	739 °F (393 °C)
Solubility in water:		3 mg/L at 50 °C

The characteristics of polymer adsorbents are summarized in Table 3. Diaion HP-10 is based on poly(styrene-co-diviniylbenzene) and has a relatively large surface area. Diaion HP-1MG has a highly polar methacrylic matrix.

Table 3. Properties of synthetic adsorbents HP-10 and HP-1MG

Properties			HP-10	HP-1MG
Moisture content (%)			55.5	63.0
Swelling (cm^3/g)			3.43	3.93
Specific surface area (m^2/g)			560	333
Pore volume		Hg	1.16	1.05
(cm^3/g)		N_2	0.92	1.18
Solvent swelling ratio	Toluene		-	1.04
	Methanol		-	1.05
	Acetone		-	1.06
	Isopropanol		-	1.05
	Butyl acetate		-	1.04
	Water		1.00	1.00
Specific gravity			1.01	1.07

2.2. Impregnation

1 g of dry polymer adsorbent was immersed into a 5 mL of absolute ethanol containing Cyanex-302 at different ratios (0.2, 0.5, 1.0, 2.0, 2.5, 3.0 g Cyanex-302/g-polymer adsorbent). The mixture was shaken at 30 °C for 24 h. The polymer adsorbent impregnated with Cyanex-302 was separated from the solution by filtration through a glass filter and washed with deionized water for several times, air-dried and dried under vacuo at room temperature.

2.3.Batch Sorptions

The tests were carried out with SIR prepared using various impregnation ratios. For this, 100 mg of SIR was contacted with 25 mL phosphoric acid solution (40%) containing 50 mg Cd(II)/L at 30 °C for 24 h.

3. RESULTS AND DISCUSSION

3.1. Batchwise Removal of Cd(II) from Phosphoric Acid Solution

SIRs were prepared using macroporous hydrophobic polymer adsorbent Diaion HP-10 based on styrene-divinylbenzene copolymer bead and hydrophilic methacrylic polymer matrix Diaion HP-1MG. The polymer adsorbents were impregnated by Cyanex-302 in absolute ethanol using various impregnation ratios (g-Cyanex-302/g-polymer adsorbent). The weight changes versus impregnation ratios were given in Figure 1 for the polymer adsorbents.

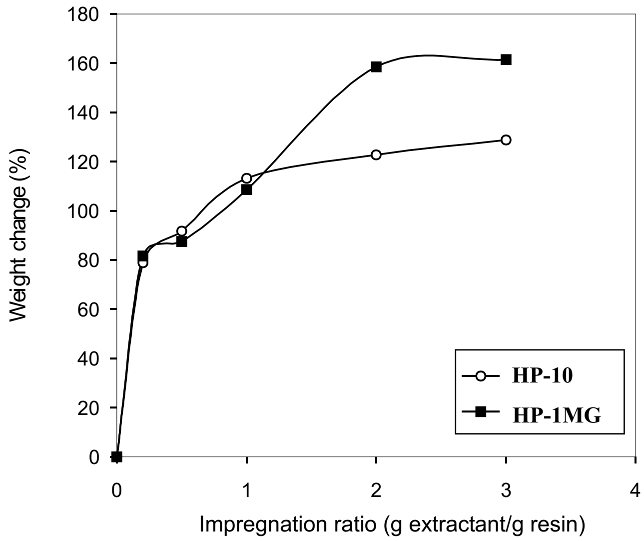


Figure 1. Weight change curves of HP-10 and HP-1MG impregnated with Cyanex-302

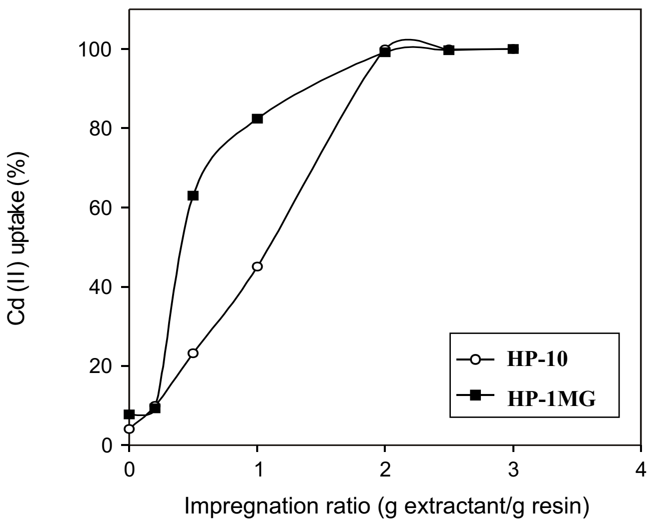


Figure 2. Effect of impregnation ratio on Cd (II) removal by HP-10 and HP-1MG impregnated with Cyanex-302

As shown in Figure 1, both Diaion HP-10 and HP-1MG reached a plateau at an impregnation ratio of 2 g Cyanex-302/g-polymer adsorbent. From these data, 2 g Cyanex-302/g-polymer adsorbent was recognised as the optimum impregnation ratio. Although the optimum impregnation ratios are the same for both resins, the amounts of Cyanex-302 sorbed by different polymer matrices are different as seen in Figure 1. The weight change in HP-1MG is greater than that in HP-10.

In order to see the effect of impregnation ratio on Cd (II) removal from 40% H_3PO_4 solution, a series of batch sorption tests were performed and the results were plotted in Figure 2. According to these results, impregnation ratio of 2 g Cyanex-302/g-polymer adsorbent was obtained as the optimum value for the quantitative removal of Cd (II) (99 %) from 40% H_3PO_4 solution. The reason for using 40% H_3PO_4 solution is that this concentration is close to the concentration of industrial grade wet-process phosphoric acid. Due to its hydrophilic character, the polymer adsorbent based on Diaion HP-1MG exhibited larger removal of Cd(II) than that of HP-10 with an impregnation ratio less than 2 g Cyanex 302/ g polymer adsorbent.

Another batch test was performed to find the optimum amount of SIR required for quantitative removal of cadmium from 40 % H_3PO_4 solution. As shown in Figure 3, 10 g of HP-1MG based resin and 20 g of HP-10 based resin are required for the removal of Cd with a percent uptake of 92 % and 91 %, respectively, from 1 L of H_3PO_4 solution (40 %).

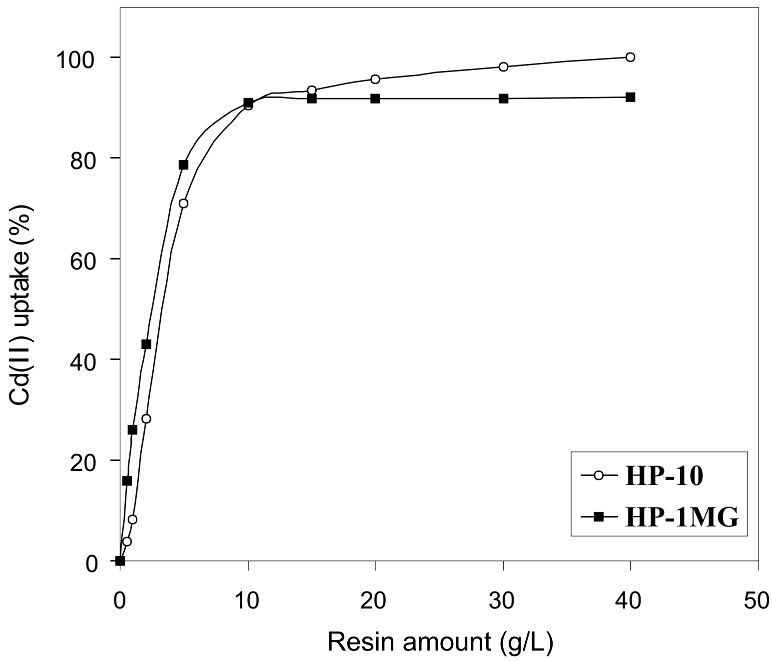


Figure 3. Effect of resin amount on Cd (II) removal by HP-10 and HP-1MG impregnated with Cyanex-302

4. CONCLUSIONS

SIRs containing Cyanex-302 have been prepared. The resulting chelating resins have been tested for the removal of Cd ions from H_3PO_4 solution. The resins exhibited a good performance for Cd removal from 40 % H_3PO_4 solution.

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