

# COLUMN SORPTION AND SEPARATION OF DIVALENT METALS BY A MACROMOLECULAR RESIN CONTAINING ORGANOPHOSPHORUS ACIDS

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## Introduction

In a previous work<sup>2)</sup>, we studied the sorption equilibrium and separation factor of divalent metal ions by two organophosphorus acid-impregnated sorbents with di-(2-ethylhexyl)phosphoric acid (D2EHPA) and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPNA) in a batch operation. The chemistry of the sorption was found to be expressible in terms of a simple ion-exchange mechanism, and the sorptibility of the sorbent to some transition metals is in the same sequence as the extractability of the organophosphorus acid extractants.

The present report discusses some problems about the continuous sorption and separation characteristics of divalent metal ions through a column packed with the organophosphorus acid-impregnated sorbents.

## 1. Experimental

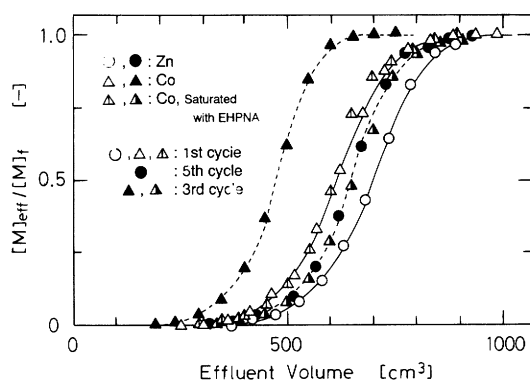
D2EHPA (Tokyo Kasei Co., Ltd.) and EHPNA (trade name: PC-88A, Daihachi Chemicals Ind. Co.,

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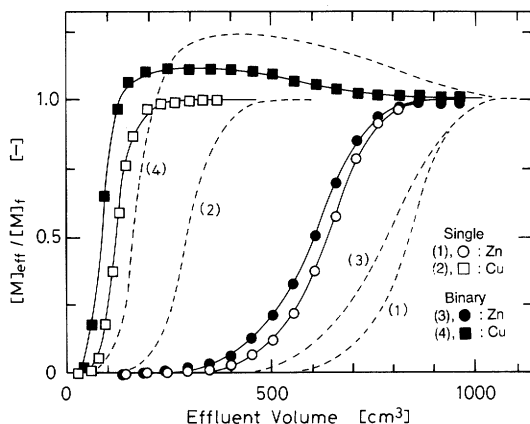
Ltd.) were used as active components without further purification. Amberlite XAD-2 (Organo Co., Ltd.), washed with acetone and water successively, vacuum-dried and fractionated in the particle size range of 500-710  $\mu\text{m}$ , was used as a resin matrix. An extractant-impregnated sorbent was prepared by the same method as described in the previous paper<sup>2)</sup>.

A glass column (I.D. 10 mm) packed with 2.0 g of the impregnated sorbent was used for determining breakthrough profiles and metal-separation characteristics. Bed height of the column was about 55 mm. Fresh sorbent was used for the determination of breakthrough curves except in a study of the degradation of the sorbent for its repeated use.

After the column had been conditioned with three solutions (0.5 M NaCl, 1.0 M HCl and blank solution), an aqueous feed solution was continuously introduced onto the top of the column at a constant flow rate. The effluent samples were collected at appropriate intervals, and the metal concentration was determined by atomic absorption spectroscopy.



**Fig. 1** Breakthrough behaviors for Zn(II) sorption with D2EHPA-impregnated sorbent and for Co(II) sorption with EHPNA-impregnated sorbent.  $F = 53 \text{ cm}^3/\text{hr}$ . Zn(II) system:  $[\text{D2EHPA}]_0 = 0.76 \text{ mol/kg}$ ,  $[\text{Zn}]_f = 5 \times 10^{-4} \text{ mol/dm}^3$  and pH 2.50. Co(II) system:  $[\text{EHPNA}]_0 = 0.77 \text{ mol/kg}$ ,  $[\text{Co}]_f = 2 \times 10^{-4} \text{ mol/dm}^3$  and pH 4.50 (0.02 mol/dm<sup>3</sup> acetic acid-acetate buffer).



**Fig. 2** Breakthrough curves for Zn(II) and/or Cu(II) sorption.  $[\text{D2EHPA}]_0 = 0.76 \text{ mol/kg}$ ,  $[\text{Zn}]_f = 5 \times 10^{-4} \text{ mol/dm}^3$ ,  $[\text{Cu}]_f = 5 \times 10^{-4} \text{ mol/dm}^3$  and  $F = 52 \text{ cm}^3/\text{hr}$ . All keys are for pH 2.50 and dashed lines for pH 3.00.

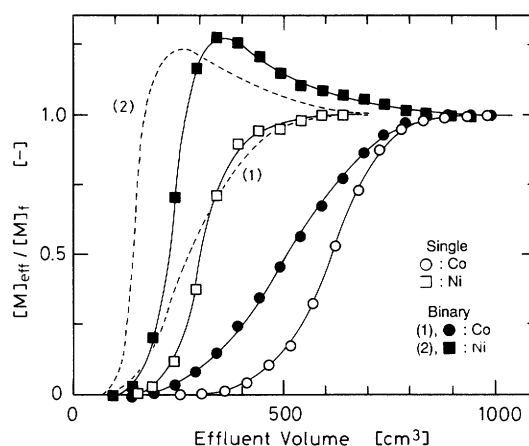
## 2. Results and Discussion

### 2.1 Sorption of single metal ion

Typical breakthrough curves obtained for Zn(II) sorption on the column packed with D2EHPA-impregnated sorbent are shown in **Fig. 1** together with those for Co(II) sorption with EHPNA-impregnated sorbent. From the curves, total sorption capacity (T.S.C.), defined as the total amount of metal sorbed until the effluent has the same composition as the influent, was determined to be 0.172 mol/kg for the Zn(II) sorption and 0.061 mol/kg for the Co(II) sorption.

The wash-out of the extractant from the sorbent, which causes a lowering of the sorption capacity, is crucial in the column operation. The closed symbol in **Fig. 1** represents the results obtained in a cyclic operation, by alternating the sorption and the desorption with 1 M HCl. For the Zn(II) sorption, the breakthrough curve in the 5th run does not differ much from that at the 1st one, whereby the decrease in the T.S.C. was only 7%.

For the Co(II) sorption, however, the capacity in



**Fig. 3** Breakthrough curves for Co(II) and/or Ni(II) sorption.  $[\text{EHPNA}]_0 = 0.77 \text{ mol/kg}$ ,  $[\text{Co}]_f = 2 \times 10^{-4} \text{ mol/dm}^3$ ,  $[\text{Ni}]_f = 2 \times 10^{-4} \text{ mol/dm}^3$  and  $F = 50 \text{ cm}^3/\text{hr}$ . All keys are for pH 4.50 and dashed lines for pH 4.20 (0.02 mol/dm<sup>3</sup> acetic acid-acetate buffer).

the 3rd run became much smaller than that in the 1st one. During the three sorption cycles, the total volume of influent passed through the column reached about 870 B.V., and then the sorbent lost its capacity by about 25% of the initial one. Such a significant loss of T.S.C. may be ascribed to an increase in solubility of the extractant in aqueous medium at the high pH 4.50 of acetic acid-acetate buffer, compared with pH 2.50 used for the Zn(II) sorption.

Here we attempted Co(II) sorption from an aqueous feed saturated with EHPNA. The results for the 1st and 3rd sorptions are also plotted in **Fig. 1**, indicating no decline in sorption capacity in the cyclic operation. Thus it is recommended to preequilibrate the influent with the extractant as a countermeasure to the wash-out.

### 2.2 Separation of Zn(II)/Cu(II) and Co(II)/Ni(II)

**Zn(II)/Cu(II) system** A previous work<sup>1)</sup> showed that complete separation of Cu(II) and Zn(II) can be attained from highly acidic media by use of TOA-impregnated sorbent in a column operation. With D2EHPA-impregnated sorbent, the breakthrough curves for Zn(II) and/or Cu(II) sorption at pH 2.50 are shown in **Fig. 2**. The breakthrough point for Cu(II) appeared much faster in comparison with Zn(II) sorption, and the effluent concentration rose rapidly owing to a low affinity of Cu(II) with D2EHPA-impregnated sorbent. Subsequently, the effluent could be obtained as a Cu(II) solution free from Zn(II) until 370 cm<sup>3</sup> of the binary feed solution flowed out. It should be noted that for the binary system the Cu(II) concentration in the effluent becomes higher than in the influent over the effluent-volume range of 140 to 900 cm<sup>3</sup>. Such an overshoot is attributable to the exchange of Cu(II) sorbed for an initial brief period of the operation with Zn(II) in the aqueous feed; it never appeared in the separation of Zn(II)/Cu(II) with TOA-impregnated sorbent<sup>1)</sup>.

The T.S.C. ratio for Zn(II) to the sum of Zn(II) and Cu(II) was found to be 0.95, which is nearly equal

to the result (0.98) calculated from the separation factor,  $([Zn]/[Zn])/([Cu]/[Cu]) = 55.2$ , obtained in a batch mode<sup>2)</sup>. In conclusion, the breakthrough volume is in reasonable agreement with the extent of sorption obtained in the batch mode. In Fig. 2 the breakthrough curves at pH 3.00 are shown with dashed lines.

**Co(II)/Ni(II) system** Figure 3 shows the breakthrough characteristics of an EHPNA-impregnated sorbent column for both single and binary systems at pH 4.50. For the binary system, Ni(II) first appeared in the effluent and was followed by Co(II); however, the breakthrough curves for the Co(II) and Ni(II) sorption were closer to each other. Thus the complete separation of Co(II) from Ni(II) cannot be achieved in the whole region under the present conditions. Nevertheless, the ratio of the T.S.C. for Co(II) to that for the two metals was 0.77, owing to the effect of displacement of Ni(II) by Co(II) in the sorbent. This value is a little smaller than the calculated value (0.87) from the separation factor (6.73) obtained in a batch mode<sup>2)</sup>. In Fig. 3 are also shown the breakthrough curves for the present binary system at pH 4.20.

From Fig. 3 we can conclude that effluent containing only Co(II) or Ni(II) as metal cation from the mixed aqueous feed is not obtained in the column operation, whereas a solution concentrating Co(II) preferentially is simply obtained as the eluate by desorbing the loaded metals from the sorbent bed with a mineral acid solution, e.g. 1.0 M HCl. Thus, when combining the column operation with conventional solvent extraction that is favorable to treatment of the concentrated metal solution, EHPNA-impregnated sorbent can possibly produce a purified metal solution.

## Conclusion

Sorption and separation of dilute metals on two organophosphorus acid-impregnated sorbents were examined in column operation, including degradation of the sorbents due to a cyclic sorption with desorption. The separation characteristics in a column mode were the same as in a batch mode previously investigated.

A preferential sorption of Zn(II) over Cu(II) from a dilute metal solution could be attained satisfactorily by use of D2EHPA-impregnated sorbent. For the separation of Co(II) from Ni(II) by EHPNA-impregnated sorbent, however, its selectivity is small; thus, a subsequent step such as solvent extraction should be employed. Furthermore, it was found that, although weaker acidic medium is liable to lead to more wash-out of the extractant from the sorbent, degradation can be prevented by preequilibrating the aqueous feed with the extractant.

## Nomenclature

$F$	= flow rate	[cm <sup>3</sup> /hr]
$M$	= metal species	
[ ]	= concentration in aqueous or sorbent phase	[mol/dm <sup>3</sup> ], [mol/kg]

## <Subscripts>

$eff$	= effluent
$f$	= feed
0	= initial

## <Superscripts>

—	= sorbent phase
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## Literature Cited

- 1) Akita, S. and H. Takeuchi: *J. Chem. Eng. Japan*, **23**, 439-443 (1990)
- 2) Akita, S. and H. Takeuchi: *J. Chem. Eng. Data*, **37**, 303-306 (1992)