

CITY UNIVERSITY OF HONG KONG

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**A Study of the Application of
Solvent Impregnated Solids for
Industrial Wastewater Treatment**
利用溶劑浸漬固體處理工業廢水之研究

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Abstract

Increasing awareness of the importance of environmental protection and resources conservation, together with more stringent wastewater discharge legislation, has generated a strong interest in developing efficient wastewater treatment processes for the recovery of resources. For the treatment of wastewater containing more than one metal ion, the current trend is to use highly selective methods to regenerate individual metals. A treatment method making use of solvent impregnated solids (SISs), has aroused a great deal of attention, but convincing evidence that the technique can effectively be applied in a column operation to remove metals to a low level to meet today's stringent environmental standards is scanty. This study aimed at a systematic investigation of the properties of SISs pertaining to their ability to extract and separate metals, based on which a process was designed to separately recover metals. The practicality of the process was demonstrated using SIS columns to treat a simulated rinsewater generated in Zn/Co alloy electroplating.

An SIS consists of an extractant impregnated onto a solid support. In this study, the extractants used were di-2-ethylhexyl-phosphoric acid (DEHPA); 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC-88A, Daihachi Chemical Industry Co. Ltd, Japan); bis(2,4,4,-trimethylpentyl) phosphinic acid (Cyanex 272, Cytec Canada); and bis(2,4,4,-trimethylpentyl) monothiophosphinic acid (Cyanex 302, Cytec Canada). The solid supports were Amberlite XAD-2 (Rohm and Haas), Amberlite XAD-7 (Rohm and Haas) and silica gel. SISs of various binary combinations of the extractants and supports were prepared. The extractant was first dissolved in a diluent to form the impregnation solution, which was shaken vigorously for sufficient time with the solid support to impregnate it with the extractant. The diluent was removed before the SIS was used in metal extraction experiments. n-hexane was in general used as the diluent.

From our study of the impregnation mechanism for XAD-7 with Cyanex 272 dissolved in n-hexane, the data suggest a model in which monolayer

adsorption of the extractant onto the wall of the pores of the support takes place at lower concentrations of Cyanex 272 in the impregnation solutions ($< 1 \text{ mol l}^{-1}$); at higher concentrations, other mechanisms such as multilayer adsorption and pore filling may also contribute to the impregnation.

The ability of the SISs to separate Zn and Co was tested in batch experiments in which Zn and Co were extracted from the simulated rinsewater adjusted to different pH's. Extraction by the SISs increased with pH as expected, since all the extractants were acids. The % extraction of Zn and Co when plotted against the equilibrium pH exhibited an "S" shape. From each "S"-shaped curve pertaining to the extraction of a metal by a particular SIS, a simple but useful parameter, pH_{50} (defined as the pH at which 50% of the metal ion is extracted) can be obtained. A metal ion with a low pH_{50} value is readily extracted at a low pH while a metal ion with a high pH_{50} value requires a high pH to effect the extraction. Thus, pH_{50} is a measure of how readily a metal ion can be extracted by a particular SIS. Furthermore, the larger the difference between the pH_{50} values of two metals (ΔpH_{50}), the better the two metals can be separated by the SIS. Using ΔpH_{50} as the criterion, we identified Cyanex 272 / XAD-7 to be the SIS which would provide the highest selectivity for Zn and Co ($\Delta\text{pH}_{50} = 2.36$) amongst all the SISs tested. A commercial Lewextrel resin (Lewatit OC 1026, DEHPA / XAD-2, Bayer A. G.) and a chelating ion exchange resin (Amberlite IRC-718, Rohm and Haas) were also studied for comparison. Both were much less effective; $\Delta\text{pH}_{50} = 1.72$ for Lewatit OC 1026, and $\Delta\text{pH}_{50} = 0.50$ for IRC-718.

The stoichiometry of the extracted species of Zn and Co with Cyanex 272 / XAD-7 was studied by the saturation loading method and was found to be ZnL_2 and CoL_2 , where L represents the deprotonated form of Cyanex 272. In other words, no Cyanex 272 molecules were coordinated to the central metal ions.

The rates of extraction of Zn with SISs were compared by measuring $t_{0.5}$ (time required to extract 50% Zn from the aqueous phase). The values of $t_{0.5}$ for nine SISs, which were binary combinations of DEHPA, Cyanex 272 and Cyanex 302 as the extractants with XAD-2, XAD-7 and silica as the solid supports, were found to be almost independent of the extractant, but very dependent on the

support in the following order: silica (1.78 – 2.32 min) < XAD-7 (2.05 – 3.88 min) << XAD-2 (10.3 – 14.1 min), i.e., the rates of extraction were highest for the silica SISs followed by those prepared from XAD-7 and XAD-2. The trend of the decreasing rate of extraction was attributed to the decrease of hydrophilicity from silica to XAD-7 and to XAD-2. In a separate set of experiments, it was found that treatment of Cyanex 272 / XAD-7 SISs with a surfactant (0.1 M sodium dodecyl sulfate) increased the extraction rate as a result of increased hydrophilicity of the SISs.

The Cyanex 272 / XAD-7 SISs with and without surfactant treatment were studied in shallow-bed experiments, where the extraction data were analyzed using a Homogeneous Particle Diffusion Model (HPDM). For both SISs, the rate of extraction was controlled by the rate of particle diffusion according to the HPDM analysis.

Extensive experiments were performed using columns packed with Cyanex 272 / XAD-7 SISs treated with sodium dodecyl sulfate to identify optimum conditions for extraction and stripping (regeneration). On the basis of the results, a flowsheet using two columns was designed. In the first column, Zn was extracted from the simulated rinsewater of Zn/Co at pH 4 buffered with potassium hydrogen phthalate. The pH of the product water was adjusted to 7 and was fed to the second column in which Co was extracted. The product water from the second column was the treated wastewater. The two columns were regenerated with 1 M HCl to recover the Zn and Co products.

The results were encouraging. In the treated wastewater, the concentrations of Zn and Co were < 0.05 ppm and < 0.1 ppm (both were below detection limits) fulfilling very stringent environmental requirements. In the Zn product, a concentration factor of 17 was achieved for Zn with respect to its original concentration in the simulated rinsewater. The impurity of Co was less than 0.01 %. In the Co product, a concentration factor of 71 was achieved for Co with respect to its original concentration in the simulated rinsewater. The impurity of Zn was less than 0.01 %.

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