CHEMISTRY LETTERS, pp. 1281-1284, 1988.

Selectivity Series in the Adsorption of Metal Ions on a Resin Prepared by Crosslinking Copper(II)-Complexed Chitosan

Katsutoshi INOUE, Yoshinari BABA, Kazuharu YOSHIZUKA,
Hiroyuki NOGUCHI, and Makoto YOSHIZAKI
Department of Applied Chemistry, Faculty of Science and Technology,
Saga University, Honjo-machi, Saga 840

The pH dependencies in the adsorption of various metal ions on a resin prepared by crosslinking copper(II)-complexed chitosan were investigated. Separations of gallium and indium from zinc, ferric iron and aluminum from zinc, and nickel from cobalt were possible with high selectivity by this resin. Some applications to hydrometallurgical processes are also proposed.

It is well known that chitin, a natural marine polymer, and chitosan, its deacetylated derivatives, can effectively adsorb not only various organics including polychlorinated biphenyls, proteins and nucleic acids but also metal ions.[1,2] Because of the excellent adsorption behaviors, chitosan has been employed as an effective coagulating agent in activated sludge plants and for recovering proteins from food processing factories. In addition, many works have been conducted on its application to chromatographic separations of metal ions. Although its excellent adsorption behaviors also suggests its feasible applications to separation, concentration and purification of metals in hydrometallurgy, only few data have been available as the fundamental information necessary for its hydrometallurgical application.[3)]

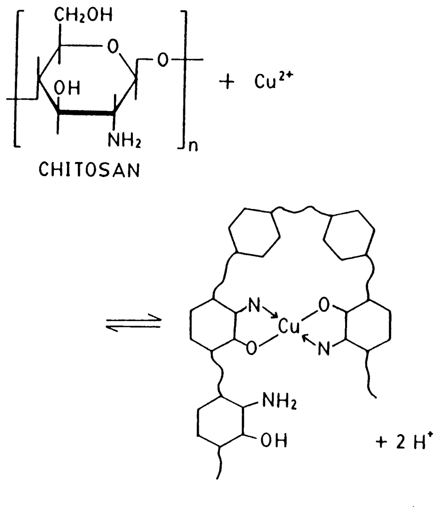

Fig. 1. Chelation of copper (II) ion with chitosan.

It is known that chitosan undergoes chelation with metal ions releasing hydrogen ions according to the reaction as shown in Fig. 1 as a typical example, that is, it behaves as a natural chelating polymer.[1)] This suggests that the adsorption of metal ions on chitosan is strongly dependent on pH in the aqueous solution. However, there have been no information on the pH dependency of the adsorption of metal ions on chitosan.

Chitosan as it is has some aqueous solubility in acidic media, that is, quite soluble in organic acids such as formic acid and acetic acid and sparingly soluble in dilute mineral acids. The latter property is one serious drawback from the practical viewpoint, especially from that of hydrometallurgy. In order to avoid the dissolution in the acidic aqueous solutions, crosslinking between polymer chains of chitosan has been proposed, which resulted in significant lowering of adsorptive activity. Recently, Ohga et al.4) proposed to prepare resins by crosslinking metal-complexed chitosans to overcome these disadvantages. In their method, central metal ions of the complexes are most likely to protect the amino group effective for the adsorption against the attack by the crosslinking agent and, at the same time, to preserve adsorption domains. This concept is similar to that proposed by Nishide et al.,5) who prepared crosslinked poly(4-vinylpyridine) resins with high selectivities to the metal ion which was used as a template.

In the present paper, the authors investigated the selectivity series in the adsorption of various metal ions on a resin prepared by crosslinking chitosan with copper(II) ion as a template by examining pH dependencies of the adsorption of metal ions to obtain fundamental information necessary for the hydrometallugical applications of chitosan.

Chitosan (Tokyo Kasei) was purified by gelation of its aqueous acetic acid solution with potassium hydroxide, lyophilized, and sufficiently dried in vacuo (<0.13 Pa). Other reagents were of reagent or higher grade and used without further purification. All aqueous solutions were prepared with distilled and deionized water. The resin was prepared by crosslinking copper(II)-complexed chitosan in the same manner proposed by Ohga et al.4)

About 50 mg of the resin sieved to 100 mesh size and 0.02 dm^3 of aqueous solution containing metal ion were shaken in a stoppered glass flask immersed in a thermostated water bath maintained at 30±0.1 °C for overnight to achieve equilibration. The aqueous solution contained 5 $mmol/dm^3$ metal ion and 1 mol/dm^3 ammonium nitrate to maintain constant ionic strength. Initial pH was adjusted by adding small amount of ammonia or nitric acid. Initial and equilibrium metal concentrations in the aqueous solutions were determined by titration with EDTA or by using a Nippon Jarrell-Ash model AA-782 atomic absorption spectrophotometer. The amount of adsorbed metal ion was calculated from the change in the metal concentration in the aqueous solution. The pH values at equilibrium were measured by using a TOA model HM-20E pH meter.

Figure 2 illustrates the relation between the equilibrium pH of the aqueous solution and the distribution ratio of metal ion (D) which is defined as the ratio of concentration of the metal ion on the resin (mol/kg) to that in the aqueous solution (mol/dm^3).

Compared with commercial chelating resins, especially with iminodiacetic acid type chelating resins, the order of adsorption of each metal ion on this resin nearly parallels that on the former resins. However, the adsorption with this resin takes place at much higher pH for all metal ions,6) which may be attributed to the large difference between the acid dissociation constant of the alcoholic hydroxyl group of glucosamine unit of chitosan and that of the iminodiacetic acid functional group of the former resin. It is noteworthy that this resin has higher selectivity than conventional commercial chelating resins, for example, to

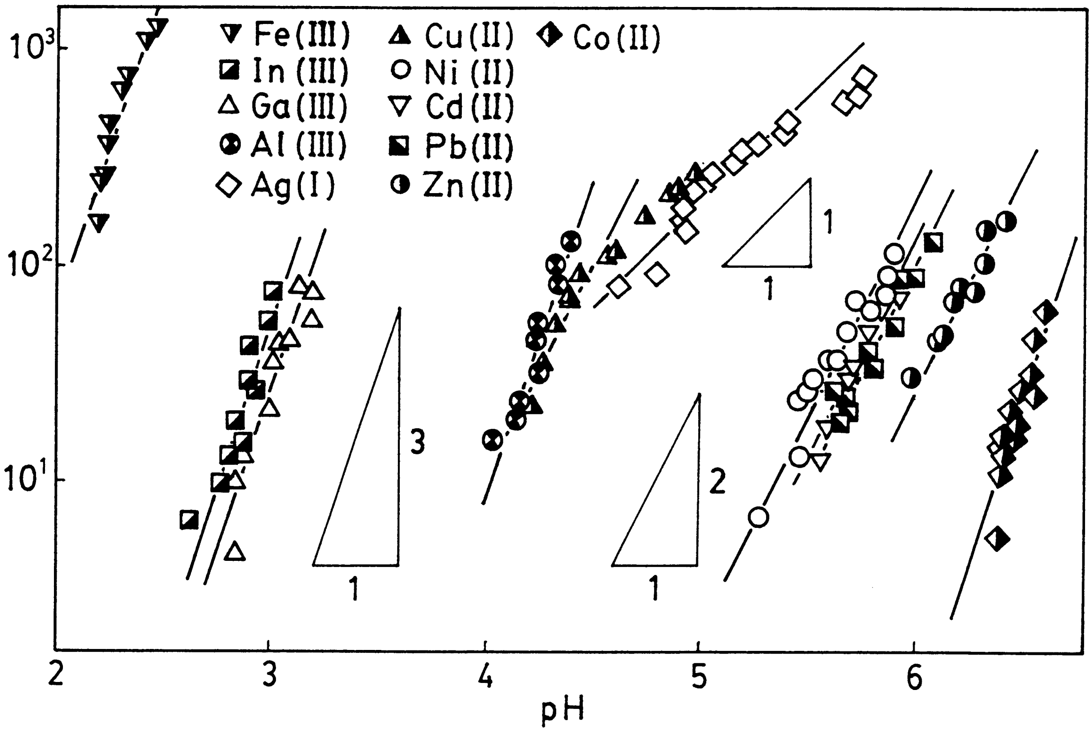

Fig. 2. Effect of pH on the distribution ratio in the adsorption of various metals on the chitosan resin.

copper(II) over nickel(II), to nickel(II) over cobalt(II), to iron(III) over copper(II) and so on,[6] as will be discussed later.

It is apparent also from Fig. 2 that the plots for trivalent metal ions, i.e., iron(III), indium(III), gallium(III), and aluminum(III), are lying on the straight lines with the slope of 3, those for divalent metal ions except for cobalt(II), i.e., copper(II), nickel(II), lead(II), cadmium(II), and zinc(II) on the straight lines with the slope of 2, and those for univalent metal ion, i.e., silver(I) on a straight line with the slope of 1. These results may indicate that n-valent metal ions are adsorbed on the resin as the metal-chelates with the composition of 1:n metal:glucosamine unit. On the other hand, the plots for cobalt(II) are lying on a straight line with the slope of 3, which suggests that divalent cobalt is oxidized to trivalent state during chelation, as observed in the solvent extraction with chelating extractant from aqueous ammoniacal solutions.[7]

Trivalent metal ions are selectively adsorbed over copper(II) ion. This result is against the expectation that copper(II) ion is selectively adsorbed over other metal ions since the ligand chain of chitosan is maintained in the best configuration to accept copper(II) ion, the template. This fact suggests that the copper(II) ion used as the template does not play the expected role, while it only behaves to protect the adsorptive sites from the attack by the crosslinking agent during the preparation of the resin.

From the results shown in Fig. 2, the following adsorption behaviors of this resin are also noticeable:

(1) Gallium(III) and indium(III) are adsorbed at much lower pH than zinc(II), which enables selective adsorption of small amount of gallium(III) and indium(III) in the presence of great amount of zinc(II).

(2) Iron(III) and aluminum(III) are adsorbed also at much lower pH than zinc(II), which enables effective separations of these two metals from zinc(II).

(3) In the adsorption of nickel(II) and cobalt(II), the difference between the pH values which provide the same value of the distribution ratio is as great as about 1 pH unit and, in addition, nickel(II) is selectively adsorbed over cobalt(II) in accordance with the so-called Irving-Williams series, which enables mutual separation of these metals with great efficiency.

These characteristic properties of this resin are expected to be applicable to the commercial separation and purification of metals as practically promising processes as follows: (1) the recovery of gallium and indium from zinc refinery by-product or zinc leach residue, (2) selective removal of iron and aluminum impurities in zinc plating bath of steel, and (3) highly effective separation of nickel from cobalt to produce high purity cobalt.

The authors are deeply indebted to Prof. K. Ohga of Oita Univ. for his instruction on the preparation of the resin.

References

1) K. Takemoto, Gendai Kagaku, 1981, (6), 57.
2) S. Hirano, Kagaku, 43, 155 (1988).
3) I. Blazquez, F. Vicente, and B. Gallo, J. Appl. Polym. Sci., 33, 2107 (1987).
4) K. Ohga, Y. Kurauchi, and H. Yanase, Bull. Chem. Soc. Jpn., 60, 444 (1987).
5) H. Nishide, J. Deguchi, and E. Tsuchida, Chem. Lett., 1976, 169.
6) S. Tomoshige, M. Hirai, and T. Shibata, Fusen, 29, 210 (1982).
7) P. Guesnet, J. L. Sabot, and D. Bauer, J. Inorg. Nucl. Chem., 42, 1459 (1980).

(Received April 27, 1988)