Selective Recovery of Metal Ions Based on Selective Sinking of Zeolite Modified with Octadecyl and Diethylenetriamine Groups

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Zeolite modified with octadecyl and diethylenetriamine groups (ZOD), which floats on surface of water, sinks into the water via the formation of metal–ligand complex, owing to the increase in hydrophilicity. The degree of the sinking depends on the metal ions coordinated, allowing selective recovery of ZOD particles loading high concentration of specific metal ion.

Selective recovery of target metal ion from aqueous solution has been one of the most important subjects in chemical industry. For this purpose, liquid–solid extraction, using insoluble inorganic materials (e.g., silica gel and zeolite) modified with organic functional groups, has been studied recently.[1–3] In these processes, it is important to modify the surface of the supporting material by suitable ligand groups that can coordinate the target metal ion selectively. However, high selectivity is achieved for limited metal ions owing to the limitation of the metal recognition ability of the ligand groups. One of the possible approaches for the improvement of the selectivity is to add a new function, which can help the target metal recognition, to the above materials.

We propose a zeolite modified with octadecyl and diethylenetriamine groups (ZOD), as the new material having additional metal recognition function, for selective recovery of metal ions. The ZOD was originally designed to just have a function that can float on surface of water owing to the hydrophobic octadecyl group,[4] in addition to metal-binding function by diethylenetriamine (DETA) group.[3] Astoundingly, the ZOD was found to change its float/sink behavior in aqueous solution via the formation of specific metal–DETA ligand complex, enabling the selective recovery of metal ion.

The ZOD was synthesized according to the procedures of literature[4,5] and as follows; a NaX zeolite (1 g, Tosoh Corp., average particle size: 5 μm)[6] was added into toluene (60 mL) and dispersed by ultrasonication. *n*-Octadecyltrichlorosilane (2 mL) was added to the mixture and stirred (12 h, 298 K). The resulting material (ZO: zeolite modified with octadecyl group)[6] was recovered by filtration, washed with acetone, and dried under vacuum (5 h, 333 K). This was then stirred with *N*-[3-(trimethoxysilyl)propyl]diethylenetriamine (2 mL) in toluene (60 mL) for 12 h at 383 K. The ZOD obtained[6] was washed with acetone and dried under vacuum at 333 K. By elemental analysis, the quantities of octadecyl and DETA groups on ZOD were estimated to be 0.24 and 1.70 mmol g^{-1}, respectively.

The metal separation experiments were performed by stirring an aqueous solution (10 mL) containing metal chloride with ZOD (0.05 g) for 10 min at 298 K.[7] When ZOD is stirred in a solution without containing metals, most of the ZOD floats on the surface of the solution. This is because of the surface coverage of hydrophobic octadecyl group on ZOD.[4] However, when ZOD is stirred in a solution containing Cu^{2+} (100 ppm), most of the ZOD sinks into the solution. By centrifugation of the resulting sample (5 min, 3000 rpm), the ZOD, dispersed in the solution, precipitates to the bottom of the flask. The mass percentage of the floated ZOD (ZOD^f) and precipitated ZOD (ZOD^p) is 83.1 and 16.9% in the absence of metal, while 9.4 and 90.6% in the presence of Cu^{2+}. In the latter case, the amounts of Cu^{2+} on ZOD^f and ZOD^p were estimated to be 4.0 and 41.3 μmol g^{-1}, respectively, indicating that Cu^{2+} amount on ZOD^p is 10 times higher than that on ZOD^f.

ESR spectra for Cu^{2+} on ZOD^f and ZOD^p are shown in Figure 1. As shown in Figure 1a, Cu^{2+} in aqueous solution shows isotropic signals at 2700–3200 G. In Figure 1b, of unmodified zeolite recovered following addition to Cu^{2+} solution, Cu^{2+} signals appear at higher magnetic field than those in Figure 1a. This is due to the adsorption of Cu^{2+} on the zeolite surface. Cu^{2+} signals on ZOD^f, as shown in Figure 1c, appear at the same position as those in Figure 1b. However, as shown in Figure 1d, Cu^{2+} signals on ZOD^p appear at different positions from those on ZOD^f in Figure 1c. The positions of the signals in Figure 1d agree with

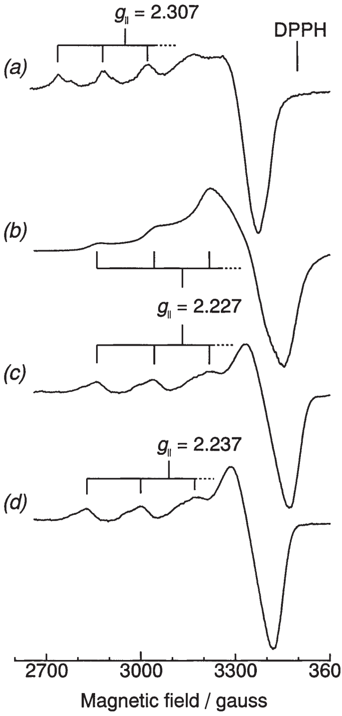

Figure 1. X-band ESR spectra (77 K) for (a) aqueous Cu^{2+} solution (pH 6), (b) unmodified zeolite recovered following addition to aqueous Cu^{2+} solution (pH^{eq} 6), (c) ZOD^f and (d) ZOD^p obtained following addition of ZOD to aqueous Cu^{2+} solution (pH^{eq} 6).

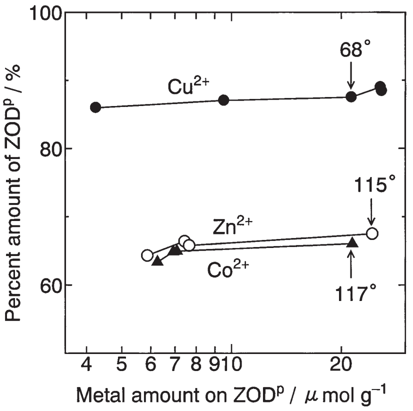

Figure 2. Relationship between the amount of metal loaded on ZOD^p and percent amount of the ZOD^p, when ZOD is added to aqueous solution, containing various concentration of Cu^{2+}, Zn^{2+}, or Co^{2+} ion (The values of contact angles for the surface of ZOD^p are shown in the figure).

those for aqueous Cu^{2+} solution in the presence of diethylenetriamine. The results suggest that most of Cu^{2+} on ZOD^f is adsorbed on the zeolite surface, while most of Cu^{2+} on ZOD^p is coordinated by DETA ligand on the zeolite surface. When a zeolite modified with octadecyl group (ZO) was added to Cu^{2+} solution, no increase in the amount of precipitated ZO particles was observed, indicating that Cu^{2+} adsorption on the zeolite surface does not affect the ZOD sinking. Contact angles of water for the surface of ZOD, ZOD^f, and ZOD^p were estimated to be 134°, 131°, and 47°, respectively,[8] indicating that the ZOD^p surface is significantly more hydrophilic. In aqueous solution, metal–DETA complex is coordinated by H_2O molecules to compensate the positive charge of the complex.[9] The H_2O coordination increases the hydrophilicity of the complex,[9] thus increasing the net hydrophilicity of the ZOD particle. This leads to the sinking of the ZOD particles loading the coordinated Cu^{2+} ion.

The ZOD, when added to a solution containing other metal ion (Zn^{2+} or Co^{2+}), also sinks into the solution. The relationship between the amount of the metal on ZOD^p and the percent amount of the ZOD^p, when ZOD was added to each solution containing various concentration of Cu^{2+}, Zn^{2+}, or Co^{2+}, is shown in Figure 2. The amount of the ZOD^p loading Cu^{2+} is clearly shown to be higher than that loading the same amount of Zn^{2+} or Co^{2+}. The contact angles for the surface of the ZOD^p loading relative metals, as indicated by arrows in Figure 2, lie in the order of $68° (Cu^{2+}) < 115° (Zn^{2+}) < 117° (Co^{2+})$. The order agrees with that of the amount of the ZOD^p. In aqueous solution, the coordinated H_2O molecules on metal–DETA complex are replaced incessantly by solvent H_2O molecules. The rate of the H_2O replacement depends on the numbers of d electron of the coordinated metal ion, and the complex of higher replacement rate is more hydrophilic.[10] The rate of the H_2O replacement is reported to lie in the order of the complex containing $Cu^{2+} > Zn^{2+} > Co^{2+}$ ions.[10] The hydrophilicity of the ZOD particles, loading the coordinated Cu^{2+}, is, therefore, higher than that loading other metals, such that the ZOD particles loading Cu^{2+} sink more easily. This suggests that the degree of the ZOD sinking depends on the coordinated metal ion, and this "selective sinking" function of the ZOD may be effective for selective recovery of metal ions.

Table 1. The amounts and mole ratios of metal ions on ZOD^f, ZOD^p, and ZD, when ZOD and ZD are added to aqueous solution (pH^{eq} 6) containing Cu^{2+}, Zn^{2+}, and Co^{2+} ions (each 10 ppm)[a]

	Amounts of metal ion / µmol g^{-1} (mole ratio / %)		
Metal ion	on ZOD^f	on ZOD^p	on ZD
Cu^{2+}	2.28 (51)	15.90 (80)	28.70 (50)
Zn^{2+}	1.18 (26)	2.66 (13)	15.8 (28)
Co^{2+}	1.00 (22)	1.24 (7)	12.7 (22)

[a] The percent amount of ZOD^p is 89.6%.

To test the effect of the unique function of ZOD on practical separation of metals, ZOD was added to a solution containing three metal ions, such as Cu^{2+}, Zn^{2+}, and Co^{2+} (each 10 ppm). The amount of the metals on ZOD^p and ZOD^f and the mole ratio of the metals are summarized in Table 1, where the data obtained, using a zeolite modified only with DETA ligand (ZD, the quantity of DETA group on ZD: 1.68 mmol g^{-1}),[3] is also shown for comparison. Using the ZD, the mole ratio of metals on ZD lies in the order of Cu^{2+} (50%) > Zn^{2+} (28%) > Co^{2+} (22%). The order agrees well with the stability constant of metal–DETA ligand complex.[11] Using ZOD, the Cu^{2+} ratio on ZOD^f is nearly the same as that on ZD, but the ratio on ZOD^p is increased up to 80%. This is because the ZOD particles, loading higher amount of coordinated Cu^{2+}, sink easily than those loading other metals. The selective sinking function of ZOD is, therefore, potential for the practical separation of metal ions from aqueous solution.

When the ZOD^p (0.01 g), recovered following the above separation procedure, was added to 1 mol L^{-1} HCl aqueous solution (10 mL) and stirred for 10 min at 298 K, the metals, both coordinated by DETA ligand and adsorbed on the zeolite surface, were removed completely. Elemental analysis of the resulting ZOD showed no composition changes as compared to the virgin ZOD and the resulting ZOD showed the same float/sink behavior in Cu^{2+} solution as that for the virgin ZOD. The reuse of the ZOD for further separation of metal ions showed the same high selectivity for Cu^{2+} as that obtained using the virgin ZOD, suggesting that the ZOD can be reused without the requirements of complicated regeneration step.

In conclusion, it was shown that the ZOD is effective for the selective recovery of metal ions from aqueous solution. This type of material, modified with hydrophobic group and chelating ligand group, is promising as a new material for separation of metals.

References and Notes

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6 (NaX zeolite) specific surface area: 409.3 m^2/g, average pore diameter: 0.863 nm, pore volume: 94.05×10^{-6} m^3/g; (ZO) 4.266 m^2/g, 0.524 nm, 0.980×10^{-6} m^3/g; (ZOD) 0.342 m^2/g, 0.379 nm, 0.079×10^{-6} m^3/g.
7 The pH of the solution at equilibrium (pH^{eq}) was adjusted to 6 using aqueous HCl or NaOH solution.
8 The contact angle measurements were carried out using a sessile drop technique on a pressed disk of the zeolite samples, which were prepared by compression at a pressure of 60 MPa.
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