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MICROCAPSULE FOR ADSORPTION AND RECOVERY OF CADMIUM(II) ION

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ABSTRACT

A chelate resin that adsorbed bathocuproinedisulfonate ion on an anion exchange resin was synthesized, and then polystyrene microcapsules containing the chelate resin were prepared by interfacial polymerization with W/O/W emulsions. The adsorption behavior of metallic ions such as Cu^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} ions into the microcapsules obtained then was examined at 25°C. The adsorption rate of the Cd^{2+} ion to the microcapsules was over 9 times more than that of the Cu^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} ions. None of the metallic complexes trapped in the microcapsules were affected by the outside environment such as pH, and the Cd^{2+} ion remained unaffected in the microcapsules even in a highly acidic solution.

Key Words: Cadmium ion; Microcapsule; Chelate resin; Adsorbent; Bathocuproinedisulfonic acid disodium salt

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INTRODUCTION

With advances in scientific technology, serious water pollution originating from the various chemical substances present in industrial wastewater has occurred. The toxic chemical substances have significant effects on the circulation of substances in environmental and biological mechanisms. In particular, water pollution due to metallic ions has caused various pollution-related diseases, e.g., ‘Itaiitai disease’ by Cd^{2+} ion and ‘Minamata disease’ from methyl mercury in Japan. Therefore, an advanced purification technology is needed for heavy metallic ions to maintain environmental standards. We have studied a microcapsule adsorbent for the selective removal and recovery of metallic ions.

A chelate resin can adsorb low concentrations of a targeted metallic ion present in industrial wastewaters (1–5). Therefore, it is possible to remove and recover specific metallic ions selectively from various wastewaters by using a chelate resin including appropriate ligands. Furthermore, capsulation of a chelate resin with a polymer material makes the recovery of the adsorbent simple because of the increase in particle size. In addition, the outside environment does not have any effect on the metallic ions adsorbed in the capsules. Thus, the metallic ions in the capsule do not elute out.

Microcapsules have very interesting characteristics, and the technology for the encapsulation of various functional materials and its application have been reported in the literature (6–11). The technology of microcapsulation has been used in various fields such as medicine, medical treatment, agriculture, foods, and the chemical industry (12–14). However, applications in the field of separation science for the recovery of chemical substances are few (15–17), and the recovery of the Cd^{2+} ion by microcapsules is not being examined in detail yet (18).

We prepared polystyrene microcapsules (12,18–20) containing a bathocuproinedisulfonate (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline disulfonate)–chelate resin, and reported the selective recovery of the Cu^{2+} ion (19). In this study, when the I^- ion was used as the pairing ion, it was found that the Cd^{2+} ion was adsorbed with a high selectivity. Therefore, the development of a microcapsule that incorporated a chelate resin to recover the Cd^{2+} ion, which is known as an endocrine disrupter, was carried out. By encapsulating the chelate resin, the facility of handling and retardation of elution of the chemical species that were adsorbed can be expected.

EXPERIMENTAL

Reagents

Bathocuproinedisulfonic acid disodium salt, which was used as the chelate agent, was supplied by Dojindo Lab. Co. (Kumamoto, Japan). Copper sulfate, cobalt sulfate, cadmium nitrate, zinc nitrate, nickel sulfate, ammonium acetate, hydrochloric acid, acetic acid, and sodium acetate were of analytical grade from the Wako Pure Chemical Ind. Co. (Osaka, Japan). Polystyrene, with an average molecular weight of 280,000, was of analytical grade from the Sowa Science Co. (Tokyo, Japan). Amberlite IRA-400 resin (Organo Co., Tokyo, Japan) with a diameter of 0.40–0.53 mm, a density of 1.11 g/cm^3, and a total exchange capacity of 3.7 meq/g, was used as the anion exchange resin. Gelatin was supplied from Yoneyama Chemical Industries Co. (Osaka, Japan) and used without purification.

Preparation of Microcapsules Incorporated Chelate Resin

Pretreatment of Anion Exchange Resin

Amberlite IRA-400 resin was powdered and then the resin, with a diameter from 0.074 to 0.149 mm was collected by sieving. The obtained anion exchange resin was washed sequentially with, 0.1 mol/L HCl solution, 0.1 mol/L NaOH solution, pure water, and acetone. The resin was then dried under a reduced pressure at 50°C.

Preparation of Chelate Resin

The bathocuproinedisulfonic acid disodium salt (0.0261 g) was dissolved in 25 mL of pure water. The solution was added to an Erlenmeyer flask (100 mL) containing 1.0 g of the prepared anion exchange resin. The suspension solution was shaken in a thermoshaker for 1 hr at 25°C. The resin was then washed with pure water, and dried under a reduced pressure at 50°C.

Preparation of Microcapsules

Polystyrene microcapsules with a chelate resin was prepared by an interfacial polymerization method with W/O/W emulsions as follows. A dichloromethane solution consisting of 10% polystyrene (20.0 g) and a 15% gelatin aqueous solution (5.0 g) including the chelate resin (0.5 g) was mixed and stirred using a magnetic stirrer for 10 min at room temperature (W/O emulsion solution). The gelatin was added to increase the viscosity of the aqueous solution including the chelate resin, resulting in a stable W/O emulsion. The W/O emulsion solution and a 2% gelatin aqueous solution were mixed and stirred using a magnetic stirrer for 2 hr at room temperature (W/O/W emulsion solution). The prepared microcapsules were spherical with a diameter of 200–300 μm, and the maximum adsorption amount of the Cd^{2+} ion into the microcapsule was 2.0×10^{-7} mol/g. Scanning electron microscopy revealed that the polystyrene microcapsule had a pore size of several μm.

Experiments for Adsorption Equilibrium

Adsorption equilibrium experiments for the microcapsules including a chelate resin were carried out using various metallic ions such as Ni^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+}, and Cu^{2+} ions, and then the adsorption characteristics of these metallic ions into the microcapsules were examined. Thirty mL of a 1.0×10^{-4} mol/L metallic ion solution, 10 mL of a 2.5×10^{-2} mol/L counter ion solution, and 10 mL of pure water were mixed, and then 2.0 g of the microcapsules was added into the mixture. The sample solution was shaken in a thermostated shaker for 10 min at 25°C. An aliquot (1 mL) of the sample solution was sampled at specific times, and the concentrations of the metallic ions in the sample solution were determined using an atomic absorption spectrophotometer. The adsorption rate of the metallic ion was calculated from a ratio of the adsorbed mol amount into the microcapsules to the initial mol amount in a solution.

Adsorption of Metallic Ion to Microcapsules

Figures 1 and 2 show the adsorption behavior of the metallic ion into the microcapsule and metal–bathocuproinedisulfonate complex on the chelate resin, respectively. The metallic ion permeates the pores of the polystyrene capsule membrane, and then diffuses into the microcapsule. The metallic ion in the

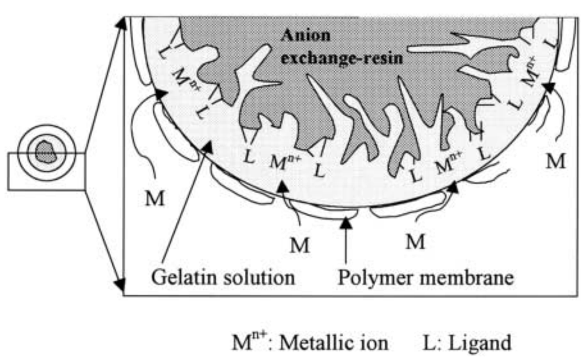

Figure 1. Microcapsule incorporated chelate resin.

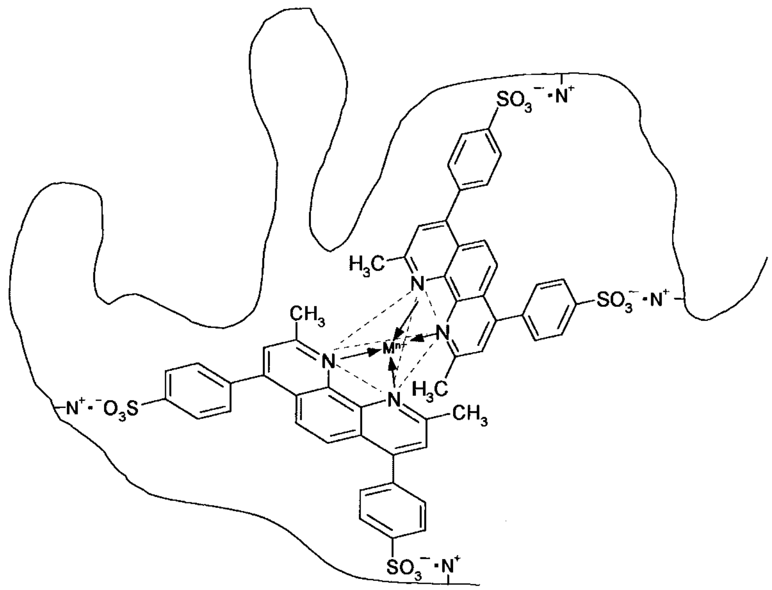

Figure 2. Metal–bathocuproinedisulfonate complex ion.

microcapsule produces coordinate bonds with the nitrogen atoms of the bathocuproinedisulfonate on the chelate resin and a chelate complex, consisting of 2 mol of chelate reagent and 1 mol of metallic ion (Cu^{+}), is formed. As a result, the metallic ion is trapped in the microcapsule.

RESULTS AND DISCUSSION

Effect of Counter Ion Species on Adsorption Behavior of Cd^{2+} Ion in the Microcapsules

The effect of pairing ion species was investigated for the adsorption behavior of the Cd^{2+} ion into the microcapsule. The initial concentrations of the metallic and counter ions (F^{-}, Br^{-}, Cl^{-}, I^{-}, NO_3^{-}, and ClO_4^{-}) were 1×10^{-4} and 2.5×10^{-2} mol/L, respectively, and 2.0 g of microcapsules was used in the adsorption equilibrium experiment.

Bathocuproine and bathocuproinedisulfonate are widely known selectively to form a chelate complex with the Cu^{+} ion and anion species such as Cl^{-} ion (19,21,22). Therefore, in a reduced circumstance, the adsorption experiments of some metallic ions into the microcapsule were carried out with coexisting

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different counter ions. As a result, the magnitude of the adsorption of the metallic ion into the microcapsule was in the order of F^-, Cl^-, Br^-, $ClO_4^- > NO_3^- \gg I^-$ for the Cu^+ ion, F^-, NO_3^-, $Br^- > Cl^- \gg I^-$, ClO_4^- for the Co^{2+}, and Ni^{2+} ions, F^-, Br^-, $Cl^- > NO_3^- \gg I^-$, ClO_4^- for the Zn^{2+} ion, and $I^- \gg Cl^- > Br^- \gg F^-$, ClO_4^-, NO_3^- for the Cd^{2+} ion. In addition, the adsorption rate of the Cu^+ ion was higher than other metallic ions on any other counter ions except the I^- ion. On the other hand, when the I^- ion was used as a counter ion, the magnitude of the adsorption rate of the metallic ions was in the order $Cd^{2+} > Cu^+ \gg Ni^{2+}$, Zn^{2+}, Co^{2+}, resulting in low selectivity of the Cu^+ ion. Furthermore, in a system without the addition of a reducing agent, the adsorption behavior of the Cd^{2+} ion was examined, and the changes in the adsorption rate of the Cd^{2+} ion vs. time for various pairing ion species at 25°C are shown in Fig. 3. We found that the adsorption capacity of the Cd^{2+} ion into the microcapsule is improved by the formation of an ion pair between the Cd^{2+}–bathocuproinedisulfonate complex ion and the I^- ion. The adsorption capacity of the Cu^{2+} ion is reduced because of the low reactivity between the Cu^{2+} ion and bathocuproinedisulfonate. The magnitude for the adsorption of the Cd^{2+} ion was in the order $I^- \gg Cl^- > Br^- \gg F^-$, ClO_4^-, NO_3^- ions. It is known that the Cd^{2+} and I^- ions are a soft acid and base, respectively. On the other hand, the Cl^- and Br^- ions are hard and middle bases, respectively. Therefore, the stability of the [Cd^{2+}

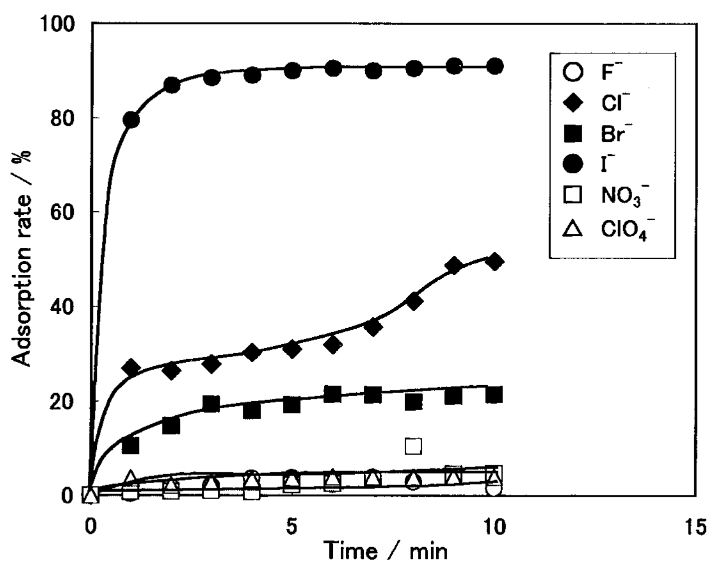

Figure 3. Relationship between adsorption rate of Cd^{2+} ion and counter ion for 2.0 g of microcapsule incorporated chelate resin.

(bathocuproinedisulfonate)$_2$ 2I^-] complex is higher than that of the [Cd^{2+} (bathocuproinedisulfonate)$_2$ 2Cl^- or 2Br^-] complexes, resulting in a high adsorption rate.

Effect of PH on Adsorption Behavior of Cd^{2+} Ion into Microcapsules

When a metallic ion and a ligand form a complex with coordination bonding, the pH has an effect on the rate of complex formation. Therefore, the effect of pH on the adsorption behavior of the Cd^{2+} ion was investigated. The initial concentrations of the metallic and I^- ions were 1×10^{-4} and 2.5×10^{-2} mol/L, respectively, and 2.0 g of microcapsules was used. The range of pH examined was 1.2–7.0. The adsorption behavior of the metallic ions into the microcapsule at pH 1.2 and 7.0 is shown in Figs. 4 and 5, respectively. In the pH range 1.2–7.0, the adsorption rate of Cd^{2+} ion was almost constant. The Cd^{2+} ion was adsorbed into the microcapsules with a selectivity over 9-times greater than that of the other metallic ions. Accordingly, even at high acidic intensity, it became clear that the Cd^{2+} ion is adsorbed into the capsule and retained without dissociation of the Cd^{2+} complex. It was considered that the high adsorption

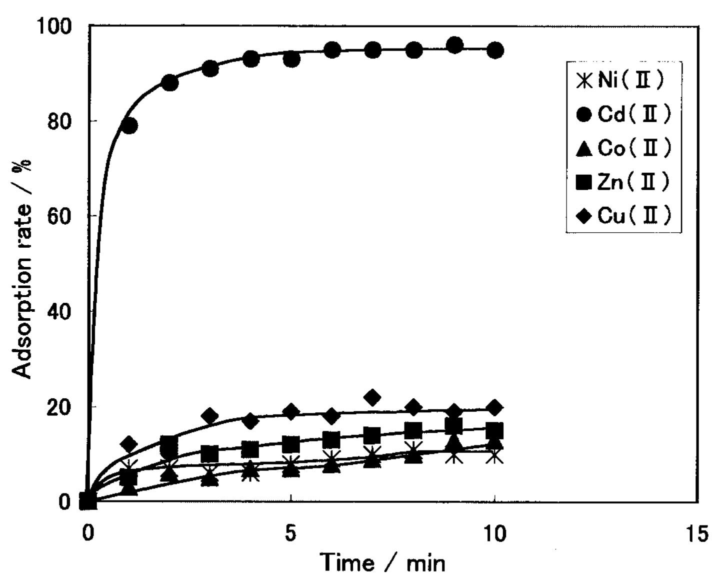

Figure 4. Adsorption behavior of metallic ions for microcapsule incorporated chelate resin at pH 1.2.

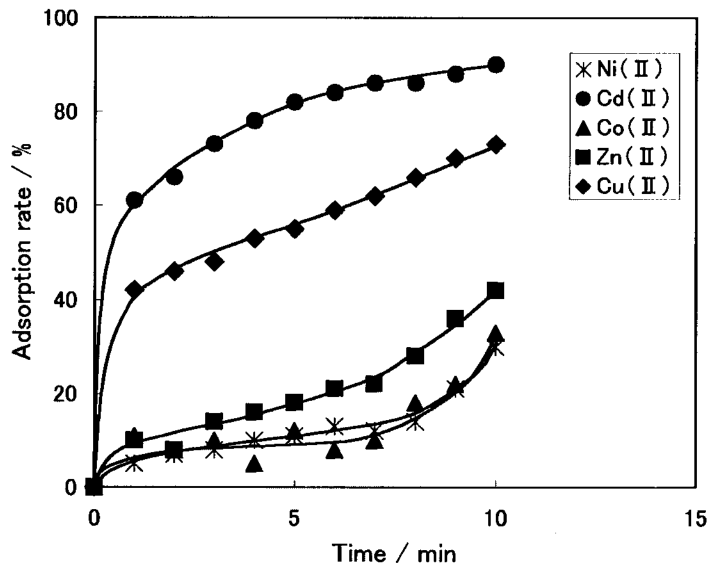

Figure 5. Adsorption behavior of metallic ions for microcapsule incorporated chelate resin at pH 7.0.

ability is caused by the high stability of the complex and the hydrophobic property of the Cd^{2+} complex.

Applications

Recovery of the Cd^{2+} ion in an environmental aqueous solution was carried out using the prepared microcapsule. A river water sample was taken and filtered with a 0.45 μm membrane filter. There were no Cd^{2+} ions in the sampled river water. Then, 1.0×10^{-4}, 1.0×10^{-5}, and 1.0×10^{-6} mol/L of Cd^{2+} ion sample solutions were prepared using the river water samples. The volumes of the sample solution, the 2.5×10^{-2} mol/L of I^- ion solution, and the added microcapsule in the sample solution were 40 cm^3, 10 cm^3 and 2.0 g, respectively.

The time course of the adsorption rates of the Cd^{2+} ion on the three kinds of concentration is shown in Fig. 6. All the Cd^{2+} ions in the sample solutions was adsorbed to the microcapsule at all concentrations, and were recovered with high efficiency without any effects on the coexisting substances such as other metallic ions, anion, and humic acid, which are generally included in environmental water. Therefore, as an adsorbent for the purification and the recovery of Cd^{2+} ions in various aqueous sample waters such as drinking water, industrial or

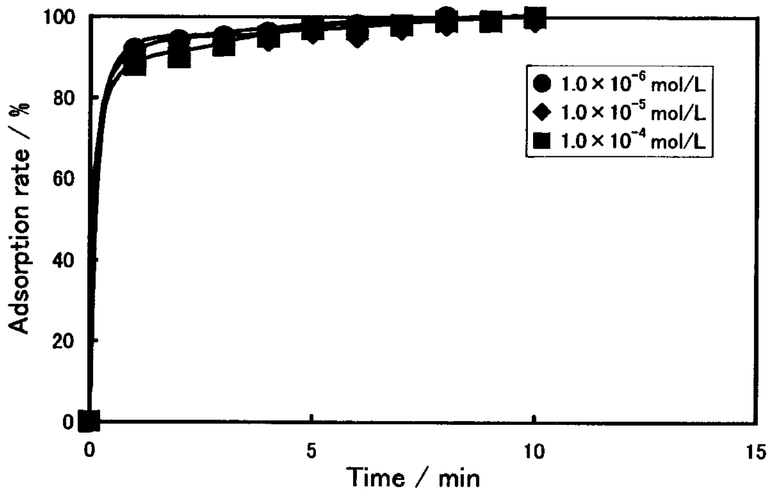

Figure 6. Adsorption behavior of metallic ions in river water samples for microcapsule incorporated chelate resin.

commercial wastewaters, and wastewater from a laboratory institution, it is considered that the microcapsules containing the bathocuproinedisulfonate–chelate resin can be utilized.

CONCLUSIONS

Microcapsule incorporated bathocuproinedisulfonate–chelate resin for efficient recovery of Cd^{2+} ions in an aqueous water sample was developed. In a pH range from 1.2 to 7, the adsorption rates of the Cd^{2+} ion was very high, and even in a high acidic solution the Cd^{2+} ion was trapped in the microcapsule with a selectivity over nine times greater than that of other metallic ions, and then the Cd^{2+}-complexes formed were retained in the microcapsules without dissociation. Furthermore, in Cd^{2+} ion samples that were prepared using a river water sample all the Cd^{2+} ions were recovered. Thus, one can look forward to the use of the microcapsule as an adsorbent for the recovery of Cd^{2+} ion in drinking waters, wastewaters, and environmental aqueous samples.

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