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# Preparation and Metal-Adsorption Properties of the Polymer-Coated Silica Gel Having Iminodiacetate Functional Group

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A new adsorbent containing an iminodiacetate group has been prepared by the surface modification of a polymer-coated silica gel. The obtained beads (SG-IDA) are porous and have a high specific surface area ($\approx 350\,m^2\,g^{-1}$). The adsorption properties of SG-IDA, including the adsorption capacities, equilibrium distribution coefficients ($K_d$) and adsorption rates, have been examined for divalent metal ions. The selectivity order of SG-IDA is Cu(II) > Pb(II) > Ni(II) > Zn(II) ≫ Ca(II) > Mg(II). The SG-IDA shows appreciably high $K_d$ values and rapid kinetics toward the adsorption of heavy metal ions. The concentration of 10 ppb level of metal ions [Cu(II), Zn(II), and Cd(II)] has been demonstrated using the SG-IDA column.

The application of solid adsorbents for the separation and concentration of trace metal ions has received recent attention owing to their operational conveniences.[1-3] Silica gel is one of the most widely used inorganic supports for a metal adsorbent because of its porous and hydrophilic nature. The nominal shrinking and swelling property is also of great advantage for use in the column stationary phase.[4] So far, numerous kinds of chelating reagents have been immobilized (adsorbed or chemically bound) onto silica-gel surface.[5,6] The use of sililation reagent is one of the most popular approaches for the modification of a silica-gel surface through chemical bonding.[6-11] However, commercially available sililation reagents having a chelating functional group are limited. Furthermore, the cleavage of a Si-O-Si bond formed by a coupling reaction tends to take place upon repeated use, leading to a lowering of the adsorption activity.[6]

We have proposed a convenient procedure for a surface modification which involves the adsorption of vinyl monomers over the surface of porous supports followed by the polymerization of the monomers.[12] The polymer network which covers a silica-gel surface can, subsequently, be functionalized with the desired reagents by the usual synthetic procedures. Preliminary results have been briefly reported.[13] This is a detailed paper in which we describe the preparation of the new adsorbent based on a polystyrene-coated silica gel having iminodiacetic acid (IDA) as the functional group. The adsorption properties of the adsorbent and its application to the column concentration of trace metal ions are reported.

## Experimental

**Reagents.** Silica-gel beads for chromatography shieved to 60—100 mesh were obtained from Nakarai Chemical Co., washed with water and then dried in vacuo. (Chloromethyl)styrene was purified by distillation prior to use. Diethyl iminodiacetate was prepared according to the usual procedure. The commercial chelating resin Dowex A-1 (60—100 mesh) was treated with 2 M (M=mol dm$^{-3}$) hydrochloric acid, washed thoroughly with water and then dried in vacuo. Other chemicals were reagent grade and used without further purification.

**Polymer-Coating of Silica-Gel Beads.** Silica-gel beads (100 g) were immersed in a DMF solution (60 cm$^3$) containing (chloromethyl)styrene (66 g), divinylbenzene (0.7 g) and $\alpha,\alpha'$-azobisisobutyronitrile (1 g) under cooling below 0 °C and then filtered. The beads were transferred to a glass autoclave and then heated at 80 °C for 5 h under a $N_2$ atmosphere. The product was washed with benzene in a Soxhlet extractor and dried. The polymer-coated silica-gel beads, thus formed, were functionalized with iminodiacetic acid through a reaction of the surface chloromethyl group with diethyl iminodiacetate in refluxed dioxane (48 h), followed by the hydrolysis of the ester moiety with 6 M hydrochloric acid. The hydrolysis of the ester moiety was monitored by the decrease in the IR intensity of the 1740 cm$^{-1}$ band. The IDA bound silica gel was washed successively with water, ethanol and diethyl ether and then dried in vacuo.

**Adsorption Capacity.** A batchwise technique was employed to determine the equilibrium adsorption capacity (amount of metal ion adsorbed on one gram of dry beads) with metal ions always being in excess over the ligand capacity.[14]

A 1 g portion of SG-IDA was added to ca. 80 cm$^3$ of a metal ion solution (0.02 M) of a certain pH; the suspension was stirred at room temperature overnight. Then, the mixture was transferred to a volumetric flask (100 cm$^3$) and finally diluted to the mark with water. The amount of metal ion that remained in the supernatant solution was determined using an atomic absorption spectrometer. The capacities of the adsorbent were calculated from the change in the observed metal concentration. The beads were then placed into a glass column and thoroughly washed with water. The adsorbed metal ions were liberated from the beads by elution with 2 M hydrochloric acid, and the metal ions in the eluent were analyzed. In most cases, a satisfactory material balance could be observed between the metal ions liberated from the beads and those remaining in the solution.

**Distribution Coefficient.** The equilibrium distribution coefficients of the metal ions were determined by a batchwise procedure.[14] Typically, dry SG-IDA beads (1 g) were immersed in 100 cm$^3$ of a 1 mM metal ion solution ($I$=0.05, $NaClO_4$). The pH from 3.0 to 5.0 was adjusted with an acetate buffer while that below 3.0 was adjusted with hydrochloric acid. After shaking for 3 d, the equilibrium pH was measured and the amount of metal ion remaining in

the supernatant solution were determined. The results are expressed as the distribution coefficient, $K_d$=(amount of metal adsorbed on 1 g of the beads)/(amount of metal remained in 1 $cm^3$ of the solution).

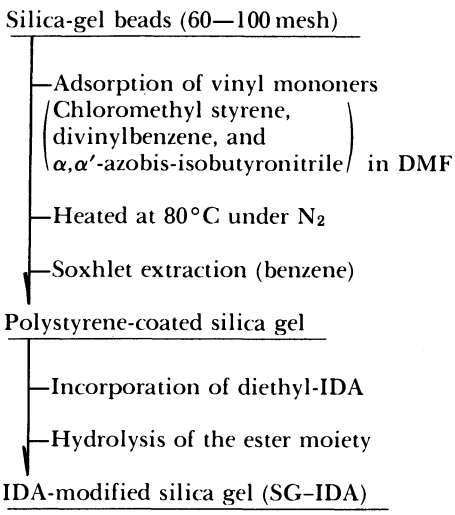
**Adsorption Rate.** The following batchwise procedure was employed: To a buffered metal ion solution (1 mM, 500 $cm^3$) at pH 4.5 was added 3 g of the SG-IDA beads ($H^+$ form). Small portions of the metal solution were withdrawn under stirring at appropriate intervals and analyzed with an atomic absorption spectrometer. Similar experiments were carried out by using Dowex A-1 ($H^+$ form), in which the IDA group is immobilized onto cross-linked polystyrene beads.

**Concentration of Metal Ions by the Column of SG-IDA.** A 5 $dm^3$ solution containing 10 ppb each of metal ions [Cu(II), Zn(II), and Cd(II)] at pH 4.5 was continuously passed through a column containing SG-IDA ($\phi$ 1.2×4 cm, 5 $cm^3$) at a constant flow rate that could be adjusted with a microtube-type pump. After the whole solution was fed to the column, the bed beads were washed with water in order to eliminate any free metal ions. Then, the adsorbed metal ions were eluted with 20 $cm^3$ of 2 M hydrochloric acid. The eluate was collected in a volumetric flask (50 $cm^3$) and finally diluted to the mark with water. The percentage recovery was calculated in terms of the ratio of the amount of metal ion recovered and that in the feed solution.

**Measurements.** The metal ion concentration was determined with a Shimadzu atomic absorption/flame photometer Model AA-610S. The IR spectra were measured using a KBr method with a Perkin-Elmer Model 599 spectrophotometer. A specific surface area was determined with an Yuasa Ionic MONOSORB; samples were treated for 30 min at 110 °C in the stream of a mixture gas consisting of 32% $N_2$ and 68% He prior to measurements. The polymer contents of the chemically modified silica gel were determined by a thermal gravimetric analysis using a Rigaku Thermoflex.

## Results and Discussion

**Preparation and Characterization of SG-IDA.** The silica-gel surface was coated with a (chloromethyl)-styrene-divinylbenzene copolymer through the adsorption and subsequent polymerization of the vinyl monomers. Polystyrene chains were partially cross-linked with divinylbenzene in order to avoid leaking of the polymer moiety upon contact with organic solvents. Unreacted monomers and oligomers were eliminated by Soxhlet extraction with benzene. The polymer-coated silica gel, thus formed, could successively be modified with a wide variety of functional groups. In the present study, diethyl iminodiacetate was introduced onto the polymer surface through a reaction of the ligand with the chloromethyl group (Scheme 1). This was confirmed by the characteristic IR bands at




Scheme 1. Procedures for polymer-coating of silica gel beads and subsequent functionalization with iminodiacetic acid.

around 1740 and 1640 $cm^{-1}$ due to (C=O) stretching vibrations of the carboxylic ester group. The band intensity at 1740 $cm^{-1}$ decreases upon the hydrolysis of the ester moiety, whereas that of 1640 $cm^{-1}$ increases. The obtained SG-IDA beads have a sufficient mechanical strength for use in the usual experimental procedures. Different from typical polymer chelating resins, the SG-IDA beads revealed minor volume changes upon adsorption and regeneration cycles. For example, the change in the volume of SG-IDA on interconversion between $H^+$ and $Na^+$ forms was only within 10%. However, the Dowex A-1, whose matrix is a gel-type polystyrene, showed an increase in volume by more than 60% with the change in ion forms from $H^+$ to $Na^+$. A large volume change must be unfavorable for uniform packing in a column system.

Table 1 shows the analytical data as well as the specific surface area of the functionalized silica gel along with the non-functionalized ones. A nitrogen analysis indicated that SG-IDA contains approximately 0.8 mmol of IDA per gram of the beads. Although SG-IDA is coated with a polymer, the specific surface area remains considerably high, i.e., 350 $m^2 g^{-1}$. This indicates that most of the pores with large diameters are not clogged with polymer, presumably because the inner surfaces of the pores are uniformly covered with a polymer network. The SG-IDA beads form colored complexes with Cu(II), Co(II), and Cr(VI) ions. The colors appeared to be homogeneously distributed over the beads when observed under an optical microscope.

Table 1. Numerical Data of the Chemically Modified Silica Gel

| Type of the modified silica | N/% | Polymer content/%[a] | Specific surface area[b]/$m^2 g^{-1}$ |
|---|---|---|---|
| Silica gel | — | — | 440 |
| Coated with poly[(chloromethyl)styrene] | 0.1 | 12.0 | 357 |
| Functionalized with IDA | 1.1 | 14.0 | 348 |

a) Weight percent of polymer determined by thermal gravimetric analysis. b) Obtained by B. E. T. method.

It has been pointed out that the specific surface area is closely related to the amount of polymer coated on silica gel.[15] When the polymer content exceeds about 15%, the specific surface area sharply decreases; in some cases, an aggregation of beads takes place.

The titration curve of SG-IDA with 0.1 M potassium hydroxide gave apparent inflection points at ca. pH 3.8 and 7.7 regions; this can be assigned to a dissociation of protons on the introduced IDA and surface silanol group, respectively, since non-functionalized silica-gel beads gave an inflection point at about pH 7.6.

**Equilibrium Adsorption Capacity.** The SG-IDA beads adsorb various kind of metal ions in a similar manner to that observed for polymer chelating resins having the IDA groups.[16,17] Profiles of the adsorption capacities vs. pH for several metal ions are given in Fig. 1. The maximum capacity of the SG-IDA lies in the range 0.3—0.4 mmol $g^{-1}$. The pH dependence of the curves is closely related to the stability of the metal complexes formed with the IDA group. Thus, a metal ion which forms a very stable complex with a functional group is retained to the beads at a much lower pH region. The adsorbed metal ions were released from SG-IDA upon a treatment of the beads with 2 M hydrochloric acid. The adsorption capacities for most of the metal ions examined were reproducible over several adsorption and regeneration cycles, with the exception of Fe(III). The capacity for Cu(II) was reproducible within a ±3% deviation for more than ten repeated cycles of use. Since Fe(III) is strongly retained to the beads, a quantitative recovery is difficult, even by treating with concd hydrochloric acid. In this case, a reduction of Fe(III) to Fe(II) with a 1 M $Na_2S_2O_4$ solution prior to acid leaching gave satisfactory results.

The SG-IDA beads are sufficiently durable in an acidic solution. For example, no obvious change in the Cu(II) capacity has been observed upon treating the beads in refluxed 3 M hydrochloric acid for 3 h. In a strongly alkaline media, on the contrary, a gradual dissolution of silica gel inevitably took place.

**Distribution Coefficient.** The distribution coefficient ($K_d$) for several metal ions was examined as a function of the pH; the results are given in Fig. 2. The slopes in the linear plots at a pH lower than 3.0 are approximately 2.0 for the adsorption of Cu(II), Pb(II), Ni(II), and Zn(II). This result indicates that the adsorption of these divalent metal ions at this pH region is accompanied by the release of two protons as given in the following formula, where $RH_2$ denotes the protonated form of SG-IDA:

$$RH_2 + M^{2+}(aq) \rightleftarrows RM + 2H^+$$

The log $K_d$ vs. pH profile clearly implies that the order of selectivity for SG-IDA is Cu(II)>Pb(II)>Ni(II) >Zn(II)>Cd(II)≫Ca(II)>Mg(II). The behavior of Pb(II) and Ni(II) is somewhat unusual in view of its stability constants of the IDA chelates where log $K_{ML}$ of the Ni(II) chelate is larger than that of the Pb(II) chelate. The shift in the position of the two ions is most likely to be due to the difference in the steric environment between the free and immobilized ligand. A similar change in the selectivity series has also been observed in IDA-type chelating resins with different types of polymer matrix.[16]

Appreciably high $K_d$ values (log $K_d$>4.0) were observed for the adsorption of Cu(II), Pb(II), Ni(II), Zn(II), and Cd(II), whereas those for alkaline earth metal ions are relatively low. The $K_d$ values for Mg(II) and Ca(II) are three to four orders of magnitude lower than those for other metal ions. Thus, interference from these alkaline earth metal ions by competed complexation must be less significant.

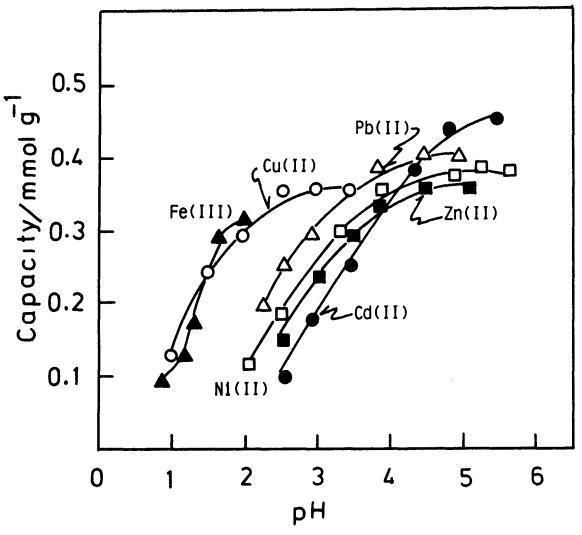



Fig. 1. Equilibrium adsorption capacity of the SG-IDA for Fe(III) (▲), Cu(II) (○), Pb(II) (△), Ni(II) (□), Zn(II) (■), Cd(II) (●).

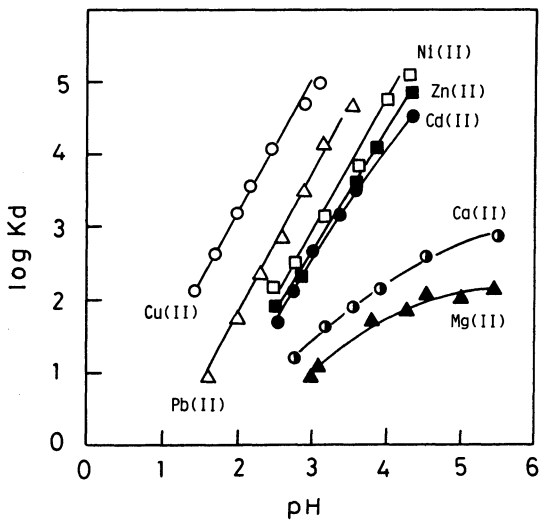



Fig. 2. Distribution coefficients of the SG-IDA for some metal ions as a function of pH. Cu(II) (○), Pb(II) (△), Ni(II) (□), Zn(II) (■), Cd(II) (●), Ca(II) (◑), Mg(II) (▲).

Table 2. Column Concentration of Trace Amount of Metal Ions[a)]

| Run | Foreign ion | % Recovered | | | Flow rate $SV/h^{-1}$ |
|---|---|---|---|---|---|
| | | Cu(II) | Zn(II) | Cd(II) | |
| 1 | — | 100 | 110 | 102 | 36 |
| 2 | — | 100 | 95 | 70 | 48 |
| 3[b)] | — | 107 | 108 | 105 | 50 |
| 4 | Ca(II), 1000 ppb | 100 | 108 | 100 | 36 |
| 5 | Mg(II), 1000 ppb | 100 | 110 | 98 | 36 |

a) Column bed: 5 $cm^3$ of SG-IDA feed metal: 10 ppb each (5000 $cm^3$), pH 4.5. b) The pH of feed solution was 5.5.

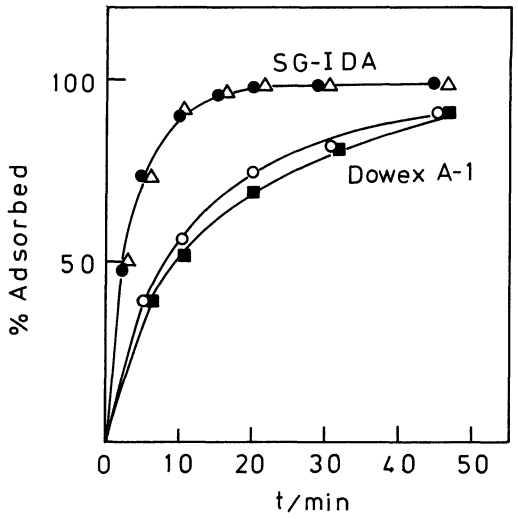



Fig. 3. Time-courses for the adsorption of metal ions with the SG-IDA and Dowex A-1. SG-IDA: Cu(II) (●); Ni(II) (△), Dowex A-1: Cu(II) (○); Ni(II) (■). Conditions: Adsorbent=3 g, $[M]_{feed}$= $1\times10^{-3}$ M (500 $cm^3$), pH of the feed solution=4.5.

**Adsorption Rate.** A rapid attainment of adsorption equilibrium is of fundamental importance for the concentration of metal ions from a practical point of view, particularly for the treatment of a large volume of a dilute solution. The time-courses for the adsorption of Cu(II) and Ni(II) were examined by monitoring the change in the metal concentration in the batch systems. Figure 3 shows the rate profiles using the SG-IDA along with those by Dowex A-1 (60—100 mesh). The SG-IDA adsorbed more than 95% of the metal ions within 15 min while the adsorption rate of the Dowex A-1 was relatively slow. The rapid kinetics of SG-IDA can be attributed to the porous structure of the beads which allows a facile diffusion of the metal ions inside the matrix. The hydrophilic nature of the surface due to the unshielded silanol groups may also contribute to the rapid adsorption.

**Column Concentration of Metal Ions.** Rapid kinetics and sufficiently high $K_d$ values of SG-IDA for the adsorption of heavy metal ions suggest the possibility of a fast concentration of trace metal ions in a column system.

A 5 $dm^3$ solution containing a 10 ppb level of Cu(II), Zn(II), and Cd(II) was continuously supplied onto the SG-IDA column; finally, the adsorbed metal ions were released from the column by elution with 2 M HCl. The percent recovery was then determined by the metal ratio in the eluate and in the feed solution. Typical results are given in Table 2. When the flow rate was controlled under 3 $cm^3 min^{-1}$, which corresponds to the space velocity ($SV$) of 36 $h^{-1}$ at the given experimental conditions, all the metal ions of interest were quantitatively recovered in a concentrated form. Copper(II) was quantitatively recovered, even at a higher flow ($SV$=48 $h^{-1}$), whereas the recovery of Zn(II) and Cd(II), which form less stable complexes with SG-IDA than Cu(II), decreased at this flow rate. At a much higher pH (=5.5), however, an improved result could be attained.

Interference from alkali and alkaline earth metal ions was not significant when they were present in concentrations of about hundred times that of the metal ions of interest.

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