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2-Mercaptoimidazole Covalently Bonded to a Silica Gel Surface for the Selective Separation of Mercury(II) from an Aqueous Solution

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2-Mercaptoimidazole Covalently Bonded to a Silica Gel Surface for the Selective Separation of Mercury(II) from an Aqueous Solution

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ABSTRACT

Silica gel with a specific surface area of 365 $m^2 \cdot g^{-1}$ and an average pore diameter of 60 Å was chemically modified with 2-mercaptoimidazole. The degree of functionalization of the covalently attached molecule, $(\equiv SiO)_3(CH_2)_3$—MI, where MI is the 2-mercaptoimidazole bound to the silica surface by a propyl group, was 0.58 $mmol \cdot g^{-1}$. In individual metal adsorption experiments from aqueous solutions by the batch procedure, the affinity order was $Hg^{II} \gg Cd^{II} > Cu^{II} \approx Zn^{II} \approx Pb^{II} > Mn^{II}$ at solution pHs between 4 and 7. Due to the high affinity by the sulfur atom, Hg^{II} is strongly bound to the functional groups. When solution containing a mixture of Hg^{II}, Cd^{II}, Cu^{II}, Zn^{II}, Pb^{II}, and Mn^{II} ions was passed through a column packed with the adsorbent, Hg^{II} was the only one whose adsorption and elution was not affected by the presence of other ions.

Key Words. Hg^{II} separation; 2-Mercaptoimidazole modified silica gel; 2-Mercaptoimidazole silica gel for Hg^{II} separation; Chemically modified silica gel; Hg^{II} selective adsorption

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INTRODUCTION

Most organofunctional groups attached on silica gel surfaces with the aim of adsorbing metal ions from aqueous and nonaqueous solutions invariably have nitrogen as the donor atom (1–5). A few organofunctional groups with sulfur as the donor atom in order to adsorb mainly heavier metal ions from solution have been immobilized on the silica gel surface (6–9). These materials have been prepared in order to obtain adsorbents having the following characteristics: good sorption capacity, chemical stability under the conditions of use, and, especially, high selectivity. Many applications in the field of chemical analyses have been found for materials having these characteristics (10–13). Covalently attached mercaptobenzimidazole molecules on a silica surface showed a particularly high chemical selectivity for Hg^{II} ions (13), and this property was used to prepare chemically modified electrodes based on carbon paste for use as an amperometric sensor (14). This molecule has also been attached on the surface of a silanized glassy carbon rod for a similar purpose (15).

In this work the preparation and use of 2-mercaptoimidazole covalently attached to a silica gel surface is described. The main interest in this molecule is related to its high chemically stability and selectivity toward Hg^{II} ion. The possibility of developing new chemical sensors based on this material led us to undertake this study.

EXPERIMENTAL

Preparation and Characterization

Silica gel (Merck) with a specific surface area, S_{BET}, of 365 $m^2 \cdot g^{-1}$, particle sizes between 0.05 and 0.2 mm, and an average pore diameter of 60 Å was used in the present work. Before derivatization, the silica was heated at 150°C under vacuum (10^{-3} torr) for 4 hours. About 50 g of the activated silica was immersed in 100 mL of dry xylene, 20 mL of 3-chloropropyl trimethoxysilane was added, and the mixture was stirred under nitrogen atmosphere for 24 hours at the reflux temperature. The resulting modified silica, 3-chloropropyl silica gel, was filtered under a nitrogen atmosphere and washed with xylene, ethanol, and ether. In the next step, 50 g of 3-chloropropyl silica gel, previously submitted to 10^{-3} torr at room temperature, was immersed in dimethylformamide (200 mL), and 0.08 mol of 2-mercaptoimidazole was added. The mixture was stirred for 40 hours at 110°C. The resulting product, 3-[2-mercaptoimidazole]propyl silica gel, was filtered and exhaustively washed with dimethylformamide, ethanol, and acetone. In order to eliminate traces of dimethylformamide, the resulting product was heated at 100°C under vacuum (10^{-3}

torr) for 8 hours. The quantity of mercaptoimidazole attached on the silica surface was determined by analyzing the amount of nitrogen by the Kjeldhal method.

S_{BET} was determined using a Micromeritics Flow Sorb 2300 from Micromeritics Instruments Corp.

The thermal stability of the 3-[2-mercaptoimidazole]propyl silica gel was measured using 10 mg of the sample with the temperature raised from 25 to 1000°C under a synthetic air atmosphere at a heating rate of $10°C \cdot min^{-1}$ using a V20B Dupont 9900 thermogravimetric analyzer.

Adsorption of the Metal Ions at Different pHs

The adsorption of the metal ions onto the modified silica gel surface was determined at 25.0 ± 0.2°C by the batch technique using several different buffered solutions (pH 1–2, buffer of KCl/HCl; pH 2–4, buffer of potassium hydrogenphthalate/HCl; pH 4–5.9, buffer of HOAc/NaOAc; pH 6–7, buffer of KH_2PO_4/KOH; pH 8–10, buffer of H_3BO_3/KCl/KOH; the concentration of the stock buffer agent of each component was 0.1 $mol \cdot L^{-1}$). To 50 mL of buffer solution containing 10^{-3} $mol \cdot L^{-1}$ of the metal ion, 0.1 g of the adsorbent was added and the mixture was shaken for 60 minutes. The solid was allowed to settle, and the metal was analyzed in the supernatant solution by atomic absorption spectroscopy. The quantity of the adsorbed metal, N_f, in each flask was determined by applying the equation

$$N_f = \frac{N_a - N_s}{m} \qquad (1)$$

where N_a is the initial number of moles of the metal in the solution phase, N_s is the number of moles in equilibrium with the solid phase, and m is the mass of the adsorbent.

In order to carry out this experiment, the following metal compound solutions were prepared: $MnCl_2$, $CuCl_2$, $ZnCl_2$, $CdCl_2$, $Hg(NO_3)_2$, and $Pb(NO_3)_2$.

Retention of Individual Metal Ions at Different pHs

The retention experiments were carried out using the batch technique. In the batch experiments, 0.1 g of the adsorbent was immersed in 50 mL of the metal ion solution of 10^{-3} $mol \cdot L^{-1}$ at different pHs in order to determine the optimum value at which 100% retention occurred. The mixtures were shaken for 60 minutes, the solids decanted, and the metals analyzed in the supernatant solutions. The retention values (in %) were calculated by applying the equation

$$\text{Retention} = \frac{N_a - N_s}{N_a} \times 100 \qquad (2)$$

Retention and Elution of Individual Metal Ion

The experiments were carried out using a glass column (20 cm height and 0.8 cm diameter) packed with 2 g of the material with a bed height of 10 cm. A solution with 5×10^{-6} mol of the metal ion at the optimum pH, as determined in a previous experiment, was passed through the column at a flow rate between 0.5 and 1.0 $\text{mL}\cdot\text{min}^{-1}$. Under these conditions, 100% retention of the metal ions was achieved. The column was washed with 10 mL of water, and then a solution of HCl was passed to elute the adsorbed metal. The volume of HCl was fixed at 25 mL, and the concentration of the acid was varied between 10^{-2} and 6.0×10^{-2} $\text{mol}\cdot\text{L}^{-1}$. In the case of Hg^{II}, the acid concentration was varied between 0.1 and 6.0 $\text{mol}\cdot\text{L}^{-1}$. The elution of the metal ion (in %) using HCl in various concentrations for each experimental point was calculated using the equation

$$\text{Elution} = \frac{N_e}{N_p} \times 100 \qquad (3)$$

where N_p is the number of moles of the metal passed through the column and N_e is the number of moles of the metal determined in the eluted solution.

Retention and Elution of a Mixture of Ions

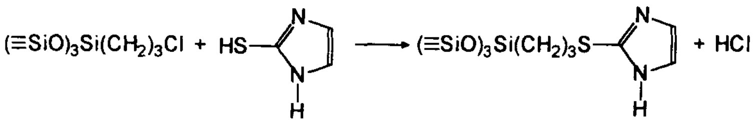
To study the retention and elution of a mixture of ions, solutions containing the above cited metal compounds were prepared under the following conditions: the concentrations of all metal ions were fixed at 10^{-4} $\text{mol}\cdot\text{L}^{-1}$ except one, whose concentration was 5.0×10^{-4} or 5.0×10^{-3} $\text{mol}\cdot\text{L}^{-1}$. For adsorption, 5 mL of the solution at pH 5 was passed through the column and the elution was done with 25 mL of 6 $\text{mol}\cdot\text{L}^{-1}$ HCl solution.

RESULTS AND DISCUSSION

Characteristics of the Material

The reactions which describe the preparations can be represented by the following equations:

$$3{\equiv}SiOH + (MeO)_3Si(CH_2)_3Cl \longrightarrow ({\equiv}SiO)_3Si(CH_2)_3Cl + 3MeOH$$



where ≡SiOH stands for silanol groups on the silica gel surface.

Bonding through the sulfur atom is assumed to occur as was observed in the case of the 2-mercaptobenzimidazole molecule (13). For the sake of brevity the product, 3-[2-mercaptoimidazole]propyl silica gel, will hereafter be denoted as SiMI. The chemical analyses and the specific surface areas for duplicate preparations are summarized in Table 1.

The results in Table 1 show that the preparation of the materials, denoted as SiMI(1) and SiMI(2), is very reproducible. The specific surface areas of the modified silica, compared to that of the native one, are practically the same. Assuming that the organofunctional groups uniformly cover the silica surface, the average surface density of the attached mercaptoimidazole is 0.93 molecules per 100 Å^2 with an average intermolecular distance of 11 Å.

The thermogravimetric (TG) curves showed that SiMI is very stable (Fig. 1), with no detectable loss of mass up to 200°C. This experiment is important because the temperature used in the present case to degas the material under vacuum was about 100°C. No loss of the adsorption capacity of the material was detected upon heating the sample at this temperature. The small loss of mass observed between room temperature and 100°C is due to physically adsorbed water. To ascertain this, the TGA curve was also obtained for SiO_2 (solid line in Fig. 1).

TABLE 1

Nitrogen Elemental Analyses and Specific Surface Areas

Preparations	N[a] (wt%)	N_0[b] ($mmol{\cdot}g^{-1}$)	S_{BET} ($m^2{\cdot}g^{-1}$)
SiO_2[c]	—	—	365 ± 15
SiMI (1)	1.60 ± 0.02	0.57	370 ± 15
SiMI (2)	1.66 ± 0.02	0.59	361 ± 15

[a] N is the quantity of nitrogen found by chemical analyses.

[b] N_0 is the corresponding quantity of attached organofunctional groups.

[c] Native silica used in the preparation.

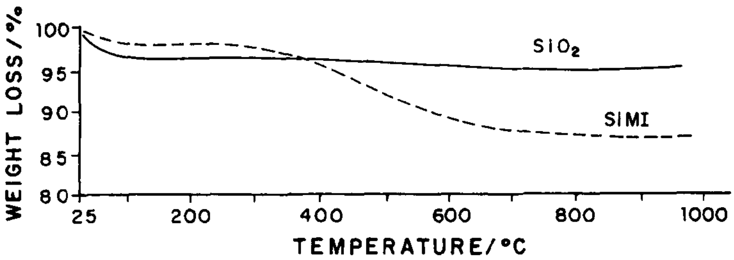


FIG. 1 Thermogravimetric analyses of ($\equiv$SiO)$_3$(CH$_2$)$_3$—MI and SiO$_2$. Heating rate of 10°C·min^{-1} under a synthetic air atmosphere.

Adsorption Dependence on Solution pH

Figure 2 shows the adsorption of the metal ions from aqueous solutions at 25°C and at different pHs. For Hg^{II} the adsorption achieved a constant value (saturation condition) at pH 4 with an adsorption capacity of 0.58

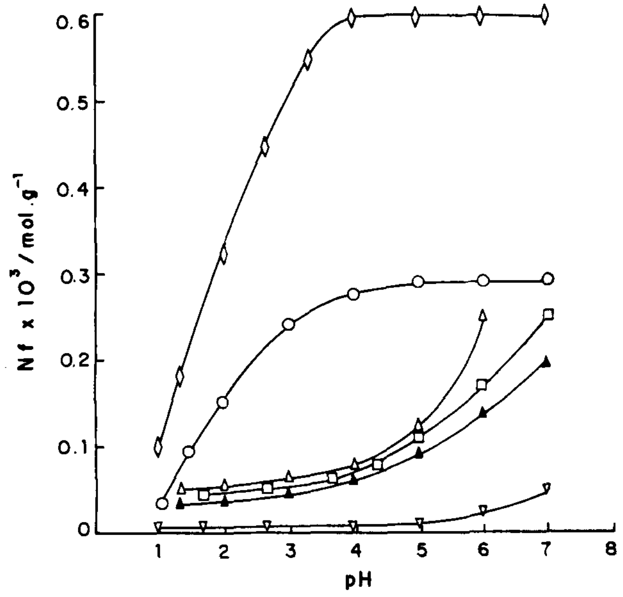


FIG. 2 Individual metal ion adsorptions on ($\equiv$SiO)$_3$(CH$_2$)$_3$—MI, by the batch technique, from aqueous solutions at different pH. (▽) Mn^{II}, (△) Cu^{II}, (□) Zn^{II}, (○) Cd^{II}, (◇) Hg^{II}, (▲) Pb^{II}.

mmol·g^{-1}. For Cd^{II} the saturation condition was achieved at pH 5 with an adsorption capacity of 0.28 mmol·g^{-1}. For the remaining ions, Cu^{II}, Zn^{II}, Pb^{II}, and Mn^{II}, the adsorption curves did not show a plateau such as was observed for Cd^{II} and Hg^{II}. The curve profiles observed for these ions are probably due to hydrolysis of the metal ions in the solution phase, which may occur above pH 5 (16), or by the adsorption of the metal ions by the unreacted free silanol groups which are ionized, i.e, $\equiv SiO^-$ (17).

Retention of Metal Ions at Different pHs Using the Batch Technique

In the batch procedure the quantity of the added individual metal ion, N_a, was 5 μmol and the mass of SiMI, m, was 0.1 g in order to keep the ratio $mN_0/N_a \approx 12$. Figure 3 shows the retention of the individual ions, calculated by applying Eq. (2), in various solution pHs. It can be observed that all Hg^{II} was retained by the solid phase at pH 4. At this solution pH, retention of the remaining ions was smaller, ≈ 40% for Cu^{II}, ≈ 20% for Zn^{II} and Cd^{II}, and less than 10% for Pb^{II}. Mn^{II} was not adsorbed at this pH. A 100% retention was observed for Cu^{II} and Pb^{II} at a pH near 4.5, for Cd^{II} at a pH near 7, and for Cd^{II} at a pH near 9. About 90% retention was observed for Mn^{II} at pH 9.5.

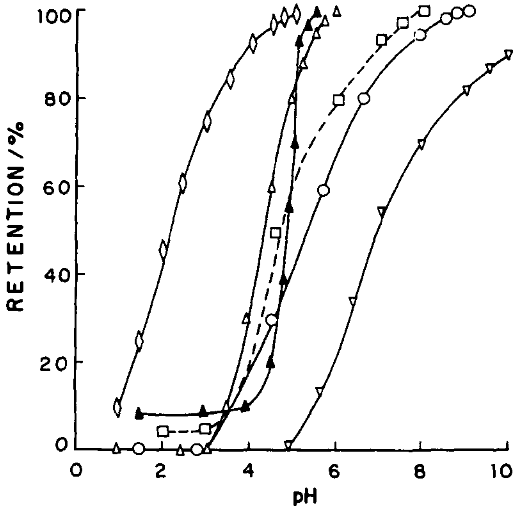


FIG. 3 Retention of metal ions on $(\equiv SiO)_3(CH_2)_3$—MI at different solution pH by the batch technique. (▽) Mn^{II}, (△) Cu^{II}, (□) Zn^{II}, (○) Cd^{II}, (◇) Hg^{II}, (▲) Pb^{II}.

Elution of the Individual Metal Ions from a Column

The column was loaded with the individual metal ion by passing 5 mL of a 10^{-3} mol·L^{-1} solution at pH 6 over 2 g of SiMI. The column was washed with bidistilled water and then with 25 mL of acid solutions between $[H^+] = 1 \times 10^{-3}$ and 6×10^{-2} mol·L^{-1}. Figure 4 shows the elution curves calculated using Eq. (3).

Mn^{II}, Cu^{II}, and Pb^{II} were completely eluted by passing an acid solution of $[H^+] = 2.5 \times 10^{-2}$ mol·L^{-1} through the column. For Zn^{II} and Cd^{II}, a slightly more concentrated acid, $[H^+] = 6 \times 10^{-2}$ mol·L^{-1}, was necessary to elute these ions. The Hg^{II} ion was not easily eluted from the column since it began to appear in the eluted solution only when an acid solution with a concentration of 1 mol·L^{-1} was used. Complete elution required 25 mL of 6 mol·L^{-1} acid solution. This strong adsorption of Hg^{II} by the mercaptoimidazole group attached to the silica surface is due to the normally high affinity shown by this metal for the sulfur atom. Since Hg^{II} and S atoms are a soft acid and a soft base, respectively, the result is in perfect accordance with Pearson's hard and soft acid–base concept (18).

The use of a such concentrated acid to elute Hg^{II} from the column led us to carry out experiments to determine the chemical stability of the attached organic group under this treatment. A sample of the SiMI mate-

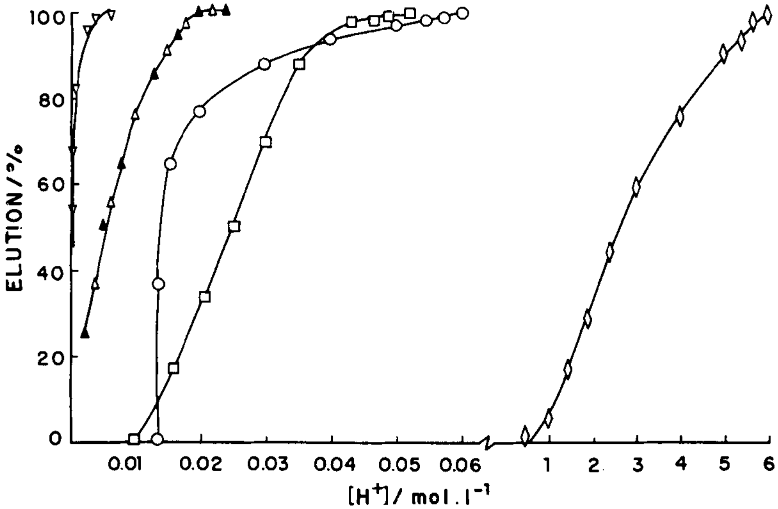


FIG. 4 Elution of adsorbed metal ion mixtures from a column packed with $(\equiv SiO)_3$-$(CH_2)_3$—MI by acid solutions. (▽) Mn^{II}, (△) Cu^{II}, (□) Zn^{II}, (○) Cd^{II}, (◇) Hg^{II}, (▲) Pb^{II}.

rial was immersed in 6 mol·L^{-1} HCl and allowed to stand for 24 hours. After this time the quantity of nitrogen was determined. No detectable decrease in nitrogen content of the sample was observed, and neither was a decrease of the adsorption capacity observed. In a second test of stability, the material in the column was submitted to 15 cycles of Hg^{II} adsorption–desorption operations. Even in this case, no significant loss of column efficiency was observed. A similar chemical stability has previously been observed for mercaptobenzimidazole attached to a silica gel surface through a propyl bridging group (13). Although the silica matrix can be attacked by alkali solution (pH above 7) with consequent breaking of the SiO—C bond, concentrated acid solutions did not affect this bond.

Elution of a Mixture of Metal Ions from a Column

The effects of mutual interactions between the ions in the process of elution from the column were studied, especially for situations where one ion was present at a higher concentration. For this experiment a series of solutions were prepared in which the metal ion concentrations were fixed at 0.1 × 10^{-3} mol·L^{-1} except for one which was fixed at 0.5 × 10^{-3} or 5 × 10^{-3} mol·L^{-1}. The results are presented in Table 2. It is observed that for Hg^{II} fixed at 0.5 × 10^{-3} mol·L^{-1} concentration, the recovery of the remaining ions was near 100% in every case. However,

TABLE 2
Elution of Mixture of Metal Ions Adsorbed in a Column Packed with SiMI

		Recovery (%)					
M^{II}	[M^{II}] × 10^3 (mol·L^{-1})	Mn^{II} [a]	Cu^{II} [a]	Zn^{II} [a]	Ca^{II} [a]	Pb^{II} [a]	Hg^{II} [a]
Mn^{II}	0.5	—	100	100	98	98	100
	5.0	—	80	74	70	67	100
Cu^{II}	0.5	71	—	100	100	100	100
	5.0	91	—	100	38	43	97
Zn^{II}	0.5	92	94	—	100	100	100
	5.0	45	55	—	39	45	100
Cd^{II}	0.5	100	100	100	—	100	100
	5.0	42	93	26	—	44	100
Pb^{II}	0.5	100	100	100	100	—	100
	5.0	34	50	45	39	—	98
Hg^{II}	0.5	89	98	98	97	96	—
	5.0	17	34	27	23	19	—

[a] [M^{II}] = 0.1 × 10^{-3} mol·L^{-1}.

when the Hg^{II} concentration was increased to 5.0×10^{-3} $mol \cdot L^{-1}$, interference became significant and the recovery of all ions was considerably reduced, i.e., between 17 and 34%. The interference of the other ions as their concentrations were changed from 0.5×10^{-3} and 5.0×10^{-3} $mol \cdot L^{-1}$ was much smaller than that of Hg^{II} under the same conditions. Table 2 also shows that Hg^{II} is the only ion whose elution was not affected by the presence of other ions, reaching 100% in every case within experimental error.

CONCLUSIONS

The present work indicated that 3-[2-mercaptoimidazole]propyl silica gel can be used to selectively separate Hg^{II} from a mixture of metals. The affinity order $Hg^{II} \gg Cd^{II} > Cu^{II} \approx Zn^{II} \approx Pb^{II} > Mn^{II}$ (Fig. 2) was observed at a solution pH of 4. The material is chemically very stable under acid treatment and potentially very useful as a packing material in separation or preconcentration columns where various cycles of adsorption/desorption operations are required. The material is also potentially useful to prepare new electrochemical sensor for Hg^{II} (14, 15).

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