

Preparation of Modified Silica for Heavy Metal Removal

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Abstract—2-hydroxy-5-nonyl-acetophenoneoxime, di-2,4,4-trimethylpentyl phosphinic acid, and a tertiary amine were bound on the silica surface after surface modification. The adsorption of the metal chelating agents appears to be due to physical attraction such as van der Waals interactions and not covalent bonding. Stability tests show that the adsorbents are stable under acidic conditions. Batch tests were conducted for heavy metal ion adsorption and elution. Heavy metal ions which were adsorbed to the surface of the adsorbents could be recovered by elution with 0.1 M HCl.

Key words: Metal Chelating Agents, Stability, Adsorption

INTRODUCTION

Ion-chelating agents can be immobilized on silica surfaces for purposes of the selective removal of heavy metals from aqueous solutions [Marshall et al., 1983; Alimarin et al., 1987; Fadeeva et al., 1989; Tikhomirova et al., 1991; Deorkar et al., 1997; Mahmoud et al., 1997]. The technique is the result of advances in the development of ion chelating agents for metal ion separation in hydrometallurgical industries [Ritcey, 1984].

Ion-chelating organic molecules are usually chemically bonded to silica surfaces via silanization procedures [Weetall, 1987]. However, a number of desirable ion-chelating agents do not contain a reactive functional group suitable for chemically bonding to the silanized inorganic surface. In this case, physical adsorption of organic chelating agents on the support is useful. Physical adsorption can be achieved through hydrophobic attraction such as van der Waals.

In this study, 2-hydroxy-5-nonyl-acetophenoneoxime (LIX 84), di-2,4,4-trimethylpentyl phosphinic acid (Cyanex 272) and a tertiary amine (Alamine 336) were immobilized on silica via surface silanization. In the case of LIX 84, the resulting modified silica has an affinity for aromatic compounds. As a result, the direct attachment of LIX 84 to silica was also attempted in order to examine the effect of silica surface silanization. In addition, in order to investigate the effect of the silane structure on stability, two different silane materials-DCDMS and CTPS-were used for the immobilization of LIX 84. The stabilities of the adsorbents under a variety of aqueous conditions were examined in order to investigate the effect of surface silanization. The adsorption capacities of these materials and the elution of heavy metal ions were also examined.

EXPERIMENTAL

1. Materials and Apparatus

Powdered silica (Aldrich Chemical Co.) was used as the sup-

Table 1. Properties of silica used as a support in this study

Properties	SP
Surface area (m ² /g)	300
Diameter (mm)	0.149-0.074
Average pore diameter (nm)	15.0
Pore volume (cm ³ /g)	1.15
Bulk density (g/ml)	0.34

data supplied by Aldrich Co.

port. The characteristics of the supports are listed in Table 1. LIX 84 (Henkel Co.), Cyanex 272 (Henkel Co.), and Alamine 336 (Henkel Co.) were used as chelating agents without further purification. Dichlorodimethyl silane (DCDMS, Aldrich Chemical Co.) and chlorotripropyl silane (CTPS, Aldrich Chemical Co.) were used for treatment of the silica supports. Cu(NO₃)₂·3H₂O (Junsei Chemical Co.) and Zn(NO₃)₂·6H₂O (Junsei Chemical Co.) were used to prepare metal ion solutions. pH 4 buffer solutions, which were prepared from 0.1 M C₈H₅KO₄ and 0.1 M HCl were used to maintain constant solution pH. All reagents were analytical grade.

The metal ion concentrations were determined by using an atomic absorption spectrometer (Perkin-Elmer, Model 3110). A CHN Corder (Yanaco, Model MT-2) was used for elemental analysis to determine the amount of bound organic molecules.

2. Preparation of Modified Silica

10 g of silica was dried at 110 °C in an oven for 3 h. The dried silica was refluxed for 16 h with 40 g of DCDMS and CTPS. Each silanized silica sample was dried in vacuum at 100 °C to remove HCl and unreacted silane. The impregnation method of each adsorbent is as follows, and the substrates which were prepared in this study are listed in Table 2.

2-1. DC-LIX, CT-LIX, and BS-LIX

10 g of silanized silica or unmodified silica was immersed in 3.2 mol 2-hydroxy-5-nonyl-acetophenoneoxime in kerosene in a flask. The flask was then shaken gently on a rotating shaker for 2 h. The impregnated silica was removed from the solution, dried at 130 °C under high vacuum, to remove the kerosene.

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Table 2. Modified silicas prepared

Notation	Explanation
S-DC	Silica modified with DCDMS
S-CT	Silica modified with CTPS
BS-LIX	Silica modified with LIX 84
DC-LIX	Silica impregnated with LIX 84 after treatment with DCDMS
CT-LIX	Silica impregnated with LIX 84 after treatment with CTPS
DC-CY	Silica impregnated with Cyanex 272 after treatment with DCDMS
DC-AL	Silica impregnated with Alamine 336 after treatment with DCDMS

2-2. DC-CY and DC-AL

10 g of silanized silica was immersed in 20 wt% of the metal chelating agent in toluene in a flask. The flask was then shaken gently by a rotating shaker for 2 h. The impregnated silica was removed from the solution and then dried at 100 °C to remove toluene.

3. Adsorption and Elution of Metal Ions

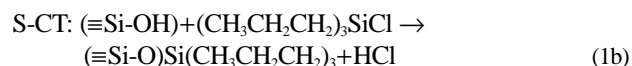
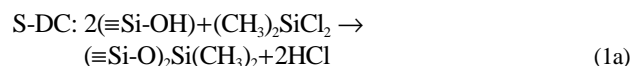
The stabilities of the functionalized silica surface under a variety of aqueous conditions were studied. The adsorbents were sequentially treated with two acidic aqueous solutions (0.1 M HCl and 1 M HCl), deionized water of pH 4.5, and 0.01 M NaOH aqueous solution, respectively over a period of 7 days. Next, 0.1 g of the treated and untreated samples were equilibrated with 25 ml of 5 mmol/L metal solutions (DC-LIX, CT-LIX: Cu; DC-

CY; Zn) at pH 4. For the case of DC-AL, zinc solutions in a 0.1 M HCl solution was used, since the Alamine 336 is capable of combining with metal ions in the presence of anions (Cl^- , SO_4^{2-} , etc.). The flasks were then placed on a shaker and rotated gently for 24 h.

RESULTS AND DISCUSSION

1. Immobilization of Metal Chelating Agents

The surfaces of the silica beads prepared are functionalized as follows [Shriver et al., 1994].



The LIX 84, Cyanex 272, and Alamine 336 do not contain functional groups which are capable of forming covalent bonds with the methyl groups on the silanized surface. However, the attachment of these chelating agents can be accomplished via hydrophobic attraction between the methyl groups on the silanized surface and the carbon chains of the chelating agents. This type of adsorption through van der Waals interactions or hydrophobic attractions has been suggested by a number of authors [Deorkar et al., 1997; Stumm, 1992; Unger, 1990; Valsaraj, 1992; Warshawsky, 1981; Wu et al., 1987]. The chelating agents used in this study would also be expected to bind with the hydrocarbon chains on the silanized surface by non-covalent bonding, such as van der Waals attraction.

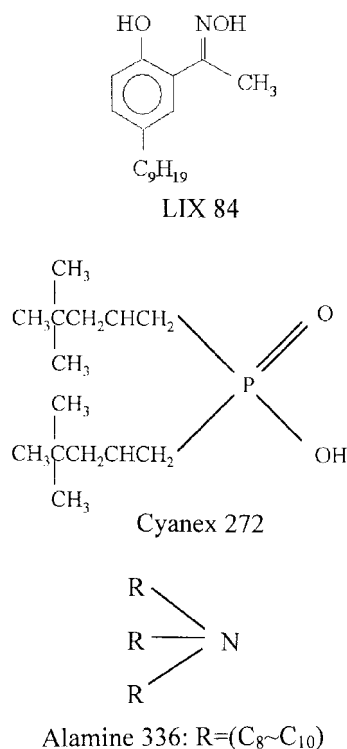
The carbon concentrations of the S-DC and S-CT were determined to be 6.33 and 13.6 mmol/g, respectively, from carbon analysis. The contents of the chelating agents in the adsorbents were also calculated from the results of carbon or nitrogen analysis, and the results are shown in Table 3(a).

2. Stability

Stability of an adsorbent is a critical issue for the case where attachment of the chelating agent is accomplished through physical attractions and not covalent bonding. The stabilities of the adsorbents under a variety of aqueous conditions were investigated. Table 3(b) shows the percentages of original chelating agent contents of the samples after treatment with various solutions. The order of stabilities for the LIX-immobilized adsorbents was found to be $\text{CT-LIX} > \text{DC-LIX} \gg \text{BS-LIX}$. These results indicate that LIX 84 is adsorbed more strongly on the silica surface through silanization, although the silica has an affinity for aromatics such as LIX 84. The higher stabilities of the CT-LIX over the DC-LIX could be due to the higher carbon concentration of the S-CT than that of the S-DC. For the case of DC-CY, the stabilities are relatively high at acidic conditions. However, when the DC-CY came into contact with an alkaline solution (0.01 M NaOH), a relatively significant loss of capacity was observed, as shown in Table 3(b). In the case of the DC-AL, the result showed that the DC-AL was relatively stable at acid concentrations below 1 M HCl.

3. Adsorption and Elution of Metal Ions

The LIX 84 and Cyanex 272 are acidic chelating agents and



Scheme 1. The chemical structure of LIX 84, Cyanex 272, and Alamine 336.

Table 3. Chelating agent content of the adsorbents, as determined by element analysis

(a) original chelating agent content

BS-LIX ^a	DC-LIX ^a	CT-LIX ^a	DC-CY ^b	DC-AL ^b
1.60	1.08	1.39	0.99	0.40

unit: mmol/g

^a determined from nitrogen content by CHN Corder.^b determined from carbon analysis by CHN Corder.

(b) stability

Treatment solution	Percentage of original chelating agent content				
	BS-LIX ^a	DC-LIX ^a	CT-LIX ^a	DC-CY ^b	DC-AL ^b
0.1 M HCl	92	95	97	100	100
1 M HCl	64	90	96	100	95
3 M HCl	-	-	-	-	83
Deionized water	80	96	98	100	-
0.01 M NaOH	71	93	98	75	-

treatment time: 7 days.

^a determined from nitrogen content by CHN Corder.^b determined from carbon analysis by CHN Corder.

the reaction scheme with divalent metal ions, M²⁺ is as follows [Ritcey, 1984].



Here, HR represents the chelating agent, and MR₂ is the metal-chelating agent complex. The above reaction is a reversible reaction wherein a cation and hydrogen ions are exchanged. Thus, the degree of extraction of metal ions depends on the pH of the aqueous solution.

The metal adsorption capacities of the DC-LIX, CT-LIX, and DC-CY are shown in Table 4(a). The copper adsorption capacity of the DC-LIX is similar to that of the CT-LIX while the chelating agent concentration of the DC-LIX is lower than that of the CT-LIX.

The results of the elution experiments for the three adsorbents are also listed in Table 3. The elution ratio is defined as the ratio of the amount eluted into the solution to that adsorbed initially in the adsorbent. For a 24 h elution operation, 85, 74, and 100% of elution ratios were obtained for the DC-LIX, CT-LIX, and DC-CY, respectively.

The stabilities of the DC-LIX, CT-LIX, and DC-CY were examined by measuring the metal adsorption capacities. Table 4(b) shows the percentages of the original capacities after treatment with various solutions. These results are consistent with the element analyses shown in Table 3(b). The adsorption capacity of the DC-AL for zinc ion was negligible in a 1 M HCl solution, although the amount of the Alamine 336 in the DC-AL was determined to be 0.40 mmol/g. This result indicates that the DC-AL should be used at HCl concentrations higher than 1 M to achieve an efficient removal of heavy metal ions. However, the stability of the DC-AL in the presence of 3 M HCl was poor. Therefore, it can be concluded that the DC-AL is not suitable for the efficient removal of zinc ions from aqueous solutions.

Table 4. Metal adsorption capacity, elution ratio, and stability, as determined from adsorption experiments

(a) metal adsorption capacity

Properties	DC-LIX	CT-LIX	DC-CY
Metal adsorption capacity (mmol/g)	0.314	0.330	0.284
Elution ratio (%)	85	74	100

metal solution: 25 ml of 5 mmol/L (pH=4), adsorbent: 0.1 g (LIX84: Cu, Cyanex 272: Zn), elution solution: 0.1 M HCl

(b) stabilities determined from metal adsorption experiments

Treatment solution	Percentage of original capacity		
	DC-LIX	CT-LIX	DC-CY
0.1 M HCl	100	100	92
1 M HCl	84	100	96
Deionized water	90	90	94
0.01 M NaOH	99	100	65

treatment time of stability test: 7 days. metal solution: 25 ml of 5 mmol/L (pH=4), adsorbent: 0.1 g (LIX84: Cu, Cyanex 272: Zn).

CONCLUSIONS

Three different metal chelating agents-LIX 84, Cyanex 272, Alamine 336-were impregnated on the surface of silica, after surface modification. The adsorption of the metal chelating agents appears to be due to physical attractions such as van der Waals forces and not covalent bonding. Stability tests show that the adsorbents are relatively stable under acidic conditions. The results of the metal adsorption experiments show that the adsorbents prepared are feasible for the extraction of heavy metal ions from aqueous solutions, except for DC-AL. Heavy metal ions which are adsorbed to the surface of the adsorbents could be recovered by eluting with an acidic solution. This permits the re-use of the adsorbents. The immobilization of other organic chelating agents on the silica surface by the methods developed herein, are expected to be successful in separating specific metal ions from aqueous streams.

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