Immobilization of Amino Functionalized Polyacrylamide on Silica Surface as Chelating Agent for Liquid Chromatography

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ABSTRACT

Amino functionalized polyacrylamide can be used as a polymeric chelating agent. In this work silica has been used as an inorganic support for organic polymer. Silica has been silylated with vinyltrichlorosilane, and then it is polymerized with acrylamide in the presence of benzoyl peroxide as an initiator. Polyacrylamide supported on silica has been transamidated with ethylenediamine to give poly(N-2-aminoethylacrylamide) immobilized on silica. This modified silica has been characterized with FT-IR, DSC, and elemental analysis and it is complexed with Cu(II), Co(II), Fe(III), Ni(II). Metal uptake capacity of this modified silica towards metal ions, especially Cu(II) cation, is several times greater than other silica-bound complexing agents such as silica modified 8-hydroxyquinoline and organic amines.

Key Words: silica, vinyltrichlorosilane, immobilization, modified silica, complexation

INTRODUCTION

Chemical modifications of silica have become important in several areas of industrial applications, for example, as catalyst supports [1, 2], immobilized enzymes [3, 4], chemically modified electrodes [5] and stationary phases in both gas and liquid chromatography [6, 7].

Industries whose processes involve systems of high ionic strength find trace metal analysis a difficult task. Determination of elements in such a matrix presents a severe problem for some standard methods.

The most stable materials are formed by reaction of organosilane compounds with surface hydroxy groups of silica, producing derivatives linked via a siloxane bond. These Si=O=Si—C linkages are stable in common organic solvents, water and acids, but they are destroyed by prolonged exposure to a strong base [8, 9].

Numerous reports have also been published describing the use of immobilized complexing agents for solvent clean-up purposes [10—12], and for preconcentrating trace metals and anions [13].

Hill [14] and Weetall [15—17] reported the preparation of 8-hydroxyquinoline substituted silica gel via azo coupling for the chelation chromatography of some metals. This was conducted through the silylation reaction of the silica surface with γ-aminopropyltriethoxysilane that is commercially available. The amino functional group is converted to the quinoline through a series of chemical
Immobilization of Amino Functionalized Polyacrylamide reactions.

Similarly, Hercules [18] reported the use of an immobilized dithiocarbamate for trace metal analysis. This was accomplished via silylation of a fiberglass matrix with silane containing an amino group which was easily converted to the dithiocarbamate.

Leyden and co-workers [19—22] have shown that silica-bound organic amine or diamine will quantitatively retain metal ions such as Hg(II), Cu(II), Zn(II) and Mn(II).

The major limitation of many silica-bound complexing agents which have been prepared previously, are their low metal uptake capacity.

Our primary interest in this field is the use of poly(N-2-aminoethylacrylamide), as an immobilized polymeric complexing agent on silica gel for liquid chromatography, with its metal uptake capacity greater than other silica-bound complexing agents such as silica substituted 8-hydroxyquinoline [14], organic amines and their dithiocarbamate derivatives [18—22].

Poly(N-2-aminoethylacrylamide) is a comb branched polymer with amino and amido groups as side-chain substitute of polyvinylic chain. The amino nitrogen is able to coordinate to the metal ions together with amido C=O group and form a seven membered ring as shown below [23]:

\[
\text{HN'C—Q Cu}^{2+}
\]

Mathew and co-workers reported the preparation and characterization of divinylbenzene cross-linked poly(N-2-aminoethylacrylamide) with various transition metal cations [24—27].

In this work, silica has been transamidated with ethylenediamine to produce silica substituted poly(N-2-amino-ethylacrylamide). Therefore, polymeric chains with pendant groups, which have capability of complexation with transition metal ions, attach to silica surface via the strong Si₈—O—Si—C linkages.

EXPERIMENTAL

Apparatus
FT-IR spectra of pellet samples (5—7 mg of modified silica without any binder such as KBr) were obtained with a Shimadzu model DR-8001 spectrophotometer. DSC thermograms were recorded on a Du Pont V40DB-2000. Elemental analysis of the modified silica gels were made with CHN-O-Rapid Heraeus analyzer. Atomic absorption measurements were carried out with a Shimadzu model AA-670 flame emission spectrophotometer.

Reagents
Silica gel (particle size<0.063 mm for column chromatography) was obtained from Fluka. All other chemicals were obtained from Merck.

Silica was dried under vacuum at 130 °C for 7 h before silylation. Toluene was dried over sodium. All other chemicals employed were of reagent grade and they were used without further purification.

Preparation of Vinyl-modified Silica
Dry silica (15 g) in 50 mL of sodium dried toluene and 25 mL of vinylchlorosilane were refluxed for 24 h. The vinyl-modified silica was then washed successively with toluene and methanol, and it was finally dried at 80 °C for 3 h in vacuum [6].

Vinyl Polymerization
Vinyl-modified silica (5 g) was placed in a round-bottomed flask. Dry DMF of 25 mL containing 2 g acrylamide was added and the mixture was well dispersed. It was then followed by addition of 25 mL dry DMF containing 0.2 g benzoyl peroxide.
The flask was cooled in liquid nitrogen bath, thawed three times and sealed. The mixture was heated with shaking for 4 h at 70 °C. The product was extracted using Soxhlet apparatus with 50/50 DMF-water for about 24 h (until the solution of the Soxhlet-extraction system was not cloudy when excess amount of the methanol was added). The white modified silica particles were then dried at 80 °C [6].

Transamidation of the Silica-modified Polyacrylamide

Preparation of Silica-bound Poly(N-2-aminoethylacrylamide)
Polyacrylamide-modified silica of 5 g was added in 30 mL of ethylenediamine. The mixture was stirred at 100 °C for 24 h. The product was then washed with water, extracted using Soxhlet apparatus with 50% methanol for about 24 h (tested with ninhydrin reagent), and dried at 80 °C [27].

Complexation of Metal Ions with Silica-bound Poly(N-2-aminoethylacrylamide)
The complexation of the silica-bound poly(N-2-aminoethylacrylamide) with Cu(II), Co(II), Ni(II), and Fe(III) cations were carried out at different pH.

To 100 mL solution of 0.005 M metal ions, at pH=2, 3, 4, 5 and neutral pH, 500 mg of the silica modified poly(N-2-aminoethylacrylamide) was added and stirred for 24 h at room temperature. The complexed modified silica particles were collected by filtration and washed with distilled water to remove uncomplexed metal ions. The rinsings were made up accurately to 200 mL and the metal concentration was determined by atomic absorption spectroscopy.

Recyclability of Complexed Modified Silica
Modified silica particles after complexation with metal ions were collected and stirred with 1 M H2SO4 for 1 h.

After acid-treatment, the white modified silica particles were stirred with 0.1 M sodium bicarbonate solution for 2 h, washed with water, dried at 80 °C and again subjected to complexation.

RESULTS AND DISCUSSION
Several methods have been reported for the surface grafting of organic polymers onto metal oxide surfaces such as silica by condensation
Immobilization of Amino Functionalized Polyacrylamide

Figure 1. DSC thermogram of vinyl-modified silica

[28, 29], ring opening [30], anionic [31], cationic [32–34] and free radical polymerizations [35–40].

The most stable materials are formed by reaction of organic silane compounds with the silanol groups present on silica surface, producing derivatives linked via a siloxane bond.

In this paper poly(N-2-aminoethylacrylamide) has been grafted onto silica surface according to Scheme I.

The first step of procedure is based on the reaction of vinyltrimchlorosilane with silica to produce reactive intermediate (vinyl-modified silica). The second step is the free radical polymerization of acrylamide with vinyl-modified silica in the presence of benzoyl peroxide as an initiator as shown in Scheme I. After completion of the polymerization, the product was extracted using Soxhlet apparatus with 50/50 DMF-water (for about 24 h) to remove surface adsorbed homopolymer until the extracted solution, on addition of the excess

Table 1. Elemental analysis results of the modified silica gels.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (%)</th>
<th>N (%)</th>
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<tbody>
<tr>
<td>S1</td>
<td>1.6</td>
<td>–</td>
</tr>
<tr>
<td>S2</td>
<td>7.9</td>
<td>2.3</td>
</tr>
<tr>
<td>S3</td>
<td>8.8</td>
<td>3.2</td>
</tr>
</tbody>
</table>

S1: silica modified vinyltrichlorosilane; S2: silica modified polyacrylamide; S3: silica modified poly(N-2-aminoethylacrylamide)

Figure 2. FT-IR spectra of silica (a) and polyacrylamide grafted silica (b).

Figure 3. FT-IR spectrum of the grafted polyacrylamide onto silica.
Maewori Y. et al.

Figure 4. DSC thermogram of polyacrylamide modified silica.

amount of methanol, did not turn cloudy.

The final step shown in Scheme I is the transamidation of the grafted polyacrylamide onto silica by ethylenediamine. This reaction is carried out in liquid ethylenediamine without any solvent. The white modified silica particles, after this reaction, was subjected to Soxhlet extraction with 50/50 methanol (for about 24 h) to remove unreacted ethylenediamine until the solution of the extraction system was free from ethylenediamine, as indicated by the absence of any blue colouration with ninhydrin reagent.

The attachment of vinyl groups on silica surface was detected by DSC thermogram of the vinyl-modified silica (Figure 1) and elemental analysis (Table 1). The elemental analysis results of the vinyl, polyacrylamide, and poly(N-2-aminoethylacrylamide) modified silica gels are summarized in Table 1. The increment in the extent of carbon and nitrogen of the modified silica gels confirm the reactions depicted as shown in Scheme I.

An exothermic sharp peak appeared at 340.06 °C that can be related to thermal decomposition of the vinyl group on silica (Figure 1).

Figure 2(a, b) shows the FT-IR spectra of silica and polyacrylamide grafted silica. In Figure 3 the FT-IR spectrum of the grafted polyacrylamide onto silica has been shown. This spectrum was obtained with digitally subtracting the absorbance contribution of silica from the spectrum of the polyacrylamide grafted silica. The absorption bands at 2950, 1663, 1617.6, 1456.5, 1415 cm\(^{-1}\) are related to C=O stretching vibration, amido N—H bending vibration, scissoring vibration of the methylene groups, and C—N stretching vibration, respectively.

The DSC thermogram of the polyacrylamide grafted silica (Figure 4) shows a broad exothermic peak at 370.24 °C which is related to thermal decomposition of the polyacrylamide chain.

Figure 5 shows the FT-IR spectrum of poly(N-2-aminoethylacrylamide) grafted silica which was obtained by transamidation reaction. The absorption band of the carbonyl group has appeared at 1665.8 cm\(^{-1}\), and the absorption band at 1545.2 cm\(^{-1}\) relates to amino N—H bending vibration.

The DSC thermogram of poly(N-2-aminoethylacrylamide) modified silica (Figure 6) shows two broad peaks at 371.02 °C and 496.76 °C which are related to thermal decomposition of unreacted polyacrylamide part and transamidated part of the
Table 2. The amount of vinyl groups, acrylamide grafted onto silica and percentage of transamidation reaction.

<table>
<thead>
<tr>
<th></th>
<th>Vinyl groups (mmol)/silica (g)</th>
<th>Acrylamide (mmol)/silica (g)</th>
<th>Percentage of transamidation reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.67*</td>
<td>1.64**</td>
<td>39.13**</td>
</tr>
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</table>

*Calculated from carbon extent; **Calculated from nitrogen extent.

The immobilization of amino functionalized polyacrylamide was studied. The amount of vinyl groups, acrylamide grafted onto silica and percentage of transamidation reaction that has been calculated from the extent of nitrogen:

Metal uptake capacity of the poly(N-2-aminoethylacrylamide) grafted silica towards Cu(II), Co(II), Ni(II), and Fe(III) cations at different pH has also been studied. Figures 7(a)–7(d) show the pH dependence of the metal uptake capacity of the poly(N-2-aminoethylacrylamide) modified silica towards Cu(II), Co(II), Ni(II), and Fe(III) cations.

Table 3 shows the maximum capacity of the poly(N-2-aminoethylacrylamide) modified silica towards metal ions. The pH values in Table 2 refer to the pH in which maximum capacity was observed.

As it is evident from data of Table 3, the Cu(II) uptake capacity of poly(N-2-aminoethylacrylamide) modified silica is 650 μmol/g of modified silica that is several times greater than 8-hydroxyquinoline and organic amines modified silica gels.

The complexation of poly(N-2-aminoethylacrylamide) grafted silica with transition metal ions can be observed visually. After treating with Cu(II), Co(II), Ni(II), and Fe(III) solutions, the modified silica produces blue, pinkish, green, and yellow complexes, respectively. The colours of the grafted polymeric chain, respectively.

Table 3. Maximum capacity of poly(N-2-aminoethylacrylamide) modified silica towards metal ions.

<table>
<thead>
<tr>
<th>Cation</th>
<th>Cu(II)</th>
<th>Co(II)</th>
<th>Ni(II)</th>
<th>Fe(III)</th>
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</thead>
<tbody>
<tr>
<td>pH=5.7</td>
<td>0.65</td>
<td>0.17</td>
<td>0.11</td>
<td>0.34</td>
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<tr>
<td>pH=6.1</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>pH=5</td>
<td></td>
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<td>pH=3</td>
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</table>
CONCLUSION

From the obtained results, it is concluded that the poly(N-2-aminoethylacrylamide) is chemically attached onto silica surface via Si—O—Si—C linkage. Because of stability of Si—O—Si—C linkage in common organic solvents, aqueous acidic and slightly basic media, our modified silica can be used as a stationary phase for solvent cleaning up purposes in liquid chromatography.

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REFERENCES