

Cu^{2+} & Pb^{2+} REMOVAL BY CHEMICALLY MODIFIED SILICA GEL WITH AMIDOXIME

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ABSTRACT

Chemically modified silica gel with amidoxime group was synthesized by silanization with 3-aminopropyltriethoxysilane (APTES) followed by an addition of acrylonitrile (AN) monomer to produce acrylonitrile modified silica (AN-SiO₂). The product undergoes amidoximation reaction after being treated with alkaline hydroxylamine hydrochloride solution to produce amidoxime modified silica (Ami-SiO₂). The final product was used as an adsorbent for copper(II) and lead(II) metal ions removal. All the structures of adsorbent and intermediate were characterized by FT-IR, SEM and elemental analysis to justify the presence of organic groups during and after modification. The optimum conditions for the removal of both metals at an initial concentration of 50 mg/L were 2 g/L of dose, pH6 and 2 hours of contact time. The removal of Cu^{2+} and Pb^{2+} by Ami-SiO₂ was substantially higher compared to its unmodified form. A significant binding property of metal ions by the adsorbent at the optimum conditions was observed and the maximum adsorption capacities for Cu^{2+} and Pb^{2+} were 24.88 mg/g and 23.87 mg/g, respectively. The sorption capacities of metal ions by Ami-SiO₂ were pH-dependent, and the selectivity of the adsorbent towards Cu^{2+} was higher compared to Pb^{2+} . The rate of exchange was rapid, which was $t_{1/2} < 10$ min for both of Cu^{2+} and Pb^{2+} .

Keywords: silica gel; silanization; acrylonitrile; amidoxime; adsorption.

1. INTRODUCTION

In recent years, many researchers have studied the treatment of heavy metals such as copper, lead, zinc and chromium in wastewater due to the regulation of effluent water in industry (Huang et al., 2008; Chang et al., 2008). These heavy metal ions could not only lead to direct and indirect health risk of human beings but also disserve the whole ecosystem, as a result the removal of those toxic substance from the wastewater has been becoming an urgent issue.

Heavy metals constitute the major class of inorganic pollutants that requires much attention to deal with, be it in wastewater or in solid waste treatment. This metal can be found as effluent of many industries, such as those of tanning, electroplating, paints, textiles, dyes, fertilizers,

and photography (Zhu, Liu & Chen, 2009) which can lead to autoimmunity, where a person's immune system attacks its own cells, and can arise due to exposure to some highly toxic metals such as mercury and lead (Barakat, 2011).

Several conventional techniques have been carried out for the removal of heavy metal ions from aqueous media including chemical precipitation, oxidation/reduction, electrochemical treatment, evaporative recovery, filtration, ion exchange and also membrane technology (Liang, Guo, Feng & Tian, 2010). However, adsorption process is recommended for the removal of low concentration heavy metal ions in wastewater where it requires a solid matrix adsorbent which able to bind with molecules by physical attractive forces, ion exchange and chemical binding (Demirbas, 2008).

Silica gel has gained attention as solid matrix for removal of metal ions due to its advantages such as nondeforming, good mechanical strength and heat stable (Demirbas, 2008). Besides, it also has the ability to undergo surface modification or coating with an impregnation medium or reagent (Mahmoud, Kenawy, Hafez & Lashein, 2010). Modification of silica gel surface can be done via two paths (Ngeontae, Aeungmaitrepirom, Tuntulani & Imyin, 2009), known as organic functionalization (Sarkar, Datta & Das, 2002), where organic molecule act as chelating ligand and inorganic functionalizations (Crippa et al., 2011), where inorganic compounds, usually metal oxides, anchored to the silica gel surface.

However, direct attachment of the chelating ligand to the silica gel surface is difficult due to inertness of the original surface of silica gel, therefore, it requires silylating agent which can reacts with the surface hydroxyl group and acts as precursors for further immobilization of organic ligands (Zhang et al., 2009).

The objective of this study was to synthesize chemically modified silica gel containing amidoxime functional group as an alternative sorbent. The amidoxime functional group was chosen due to its adsorption capacity and selectivity towards some metal ions (Ngeontae et al., 2009). The present investigation is focused on several parameters such as temperature, reaction time, volume of monomer and volume of silylating agent to obtain the optimum synthesis condition as well as to study the adsorption characteristic of Cu^{2+} and Pb^{2+} metal ions.

2. MATERIALS AND METHODS

2.1 Reagents

The sorbent was silica gel (Sigma-Aldrich) with average pore diameter 60Å (35-60 mesh). Toluene (System) was distilled and dried before use. 3-aminopropyltriethoxysilane (APTES) 99% (Sigma), cerium(IV) ammonium nitrate 99% (Sigma-Aldrich), methanol A.R (Merck) and hydroxylamine hydrochloride (Sigma) were used without any purification. Acrylonitrile (Sigma) was purified before use by passing through a column containing aluminum oxide.

2.2 Preparation of Acrylonitrile-Silica (AN-SiO₂)

The suspension of silica gel and APTES in toluene was stirred in reflux condition for 24 h under a nitrogen atmosphere. The collected material (AP-SiO₂) was then filtered out and washed with toluene and methanol before dried overnight in an oven. AP-SiO₂ (5.0g) was

then transferred into a new round bottom flask followed by addition of distilled water and acrylonitrile as well as 2.5×10^{-2} M ceric ammonium nitrate (CAN). The mixture was heated and refluxed for 4 h. The product was separated and washed three times with 50 mL distilled water and twice with 50 mL methanol. It was then dried in an oven for 24 hours at 120°C.

2.3 Preparation of Amidoxime-Silica (Ami-SiO₂)

hen, 10.0 g of AN-SiO₂ was transferred into a new 1 L round bottom flask. Next, 100 mL methanol and hydroxylamine hydrochloride solution (20.0 g, H₂NOH.HCl in 375 mL methanol + 125 mL distilled water, pH adjustment by NaOH to pH 7) were added into the flask. The mixture was heated as refluxed under nitrogen atmosphere for 4 h. The product was separated and washed three times with 100 mL methanol. Finally, the product was dried in an oven at 120°C and the product was notated as amidoxime-silica (Ami-SiO₂).

2.4 IR Analysis

Fourier transform infrared spectroscopy was used to identify the functional groups contained in various types of modified silica. About 0.001g of each of the sample was placed in the sample holder of the FTIR spectrometer (Perkin-Elmer 100). Pressure was exerted to the sample and the FTIR spectrometer analysis started. The data obtained consisted wavenumber ranged 4000-600cm⁻¹.

2.5 Scanning Electron Microscopy (SEM) Studies

A scanning electron microscope was employed to determine the size and surface morphology of the compounds. SEM images at 1000 magnifications were obtained for the various types of modified silica using EVO MA10 (London) scanning electron microscope. The samples were laid down on the sample holder and were sputter coated with gold.

2.6 Thermogravimetric (TG) Analysis

The TG analysis was carried out by using Perkin-Elmer TGA 6, USA. About 12.00 mg of the sample was weighed and placed in the sample holder of the TGA. Then the analysis was performed under a heating rate of 10 °C/min with a nitrogen flow rate of 50 mL/min. The temperature observed was in the range of 30-690 °C.

2.7 Batch Adsorption Studies

Batch technique was carried in order to measure the sorption capacity of the chemically modified silica gel with amidoxime by varying contact time and the pH of the solutions between pH 3.0 to pH 6.0. Copper and lead metals ion were used for the study and prepared from the standard solutions. Buffer solution used for this study was 0.1 mol/L acetate buffer solution and was adjusted to desirable pH using concentrated acetic acid.

3. RESULTS AND DISCUSSIONS

3.1 IR Analysis

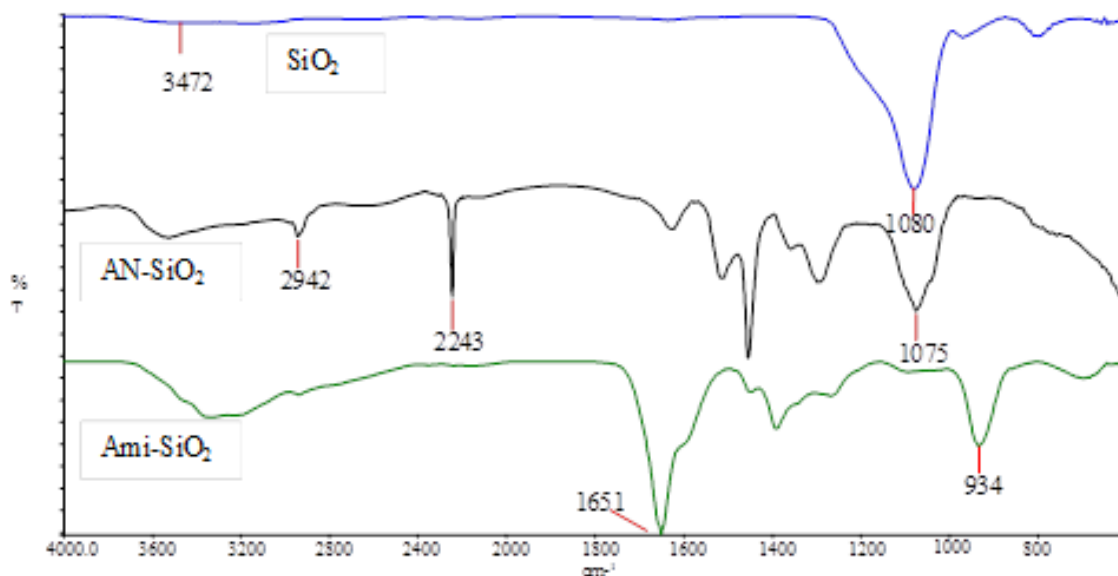


Figure 1: IR spectra for SiO₂, AN-SiO₂ and Ami-SiO₂.

Figure 1 presents the infrared spectra of three kinds of particles, silica gel, acrylonitrile-silica and also amidoxime-silica particles. The silanol group of the silica gel was found at 3472 cm⁻¹ while the siloxane group was found at 1080 cm⁻¹ and 805 cm⁻¹. Both of these groups were responsible as active site of the silica gel. For acrylonitrile-silica, two new bands were introduced at 2243 cm⁻¹ and 2942 cm⁻¹ which assigned to C≡N and -CH₂ groups, respectively and after conversion to amidoxime-silica, the C≡N band was disappeared and two new bands were found at 1651 cm⁻¹ and 934 cm⁻¹ which assigned to C-O and N-O groups, respectively (Budiman, Fransiska & Setiawan, 2009) indicated that amidoximation reaction has occurred.

3.2 Surface Morphology

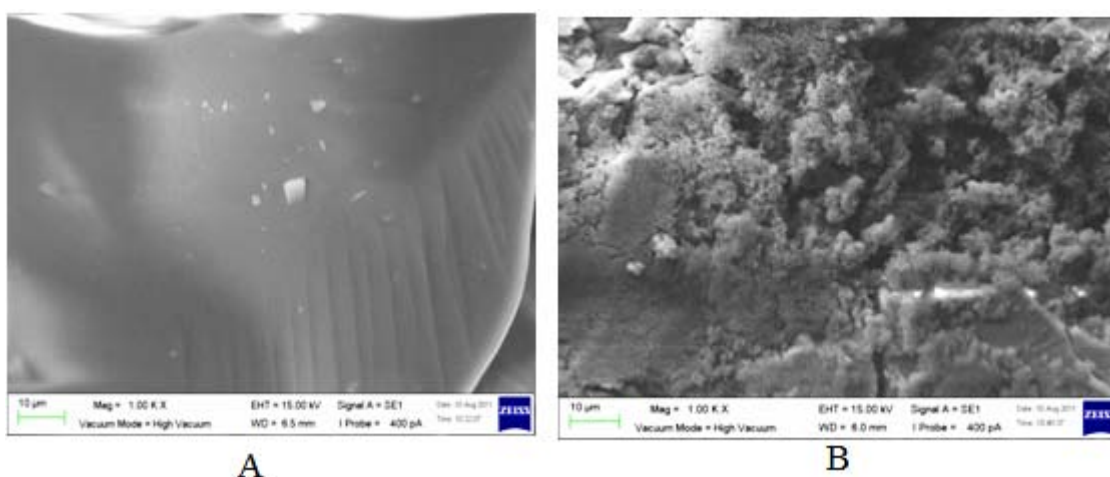


Figure 2: SEM images of A) activated silica gel and B) amidoxime-silica.

Figure 2 (A) and (B) presents the SEM images at 1000 magnifications of activated silica gel and amidoxime-silica, respectively. It can be found that before modification of the silica gel, the surface of activated silica was smooth, however, after the modification process, the

surface of amidoxime-silica was found rough and scraggy. This is mainly due to coating and filling up action by the acrylonitrile monomer (Das, Pandey, Athawale & Manchanda, 2009).

3.3 Electron Dispersive Spectroscopy (EDS) Analysis

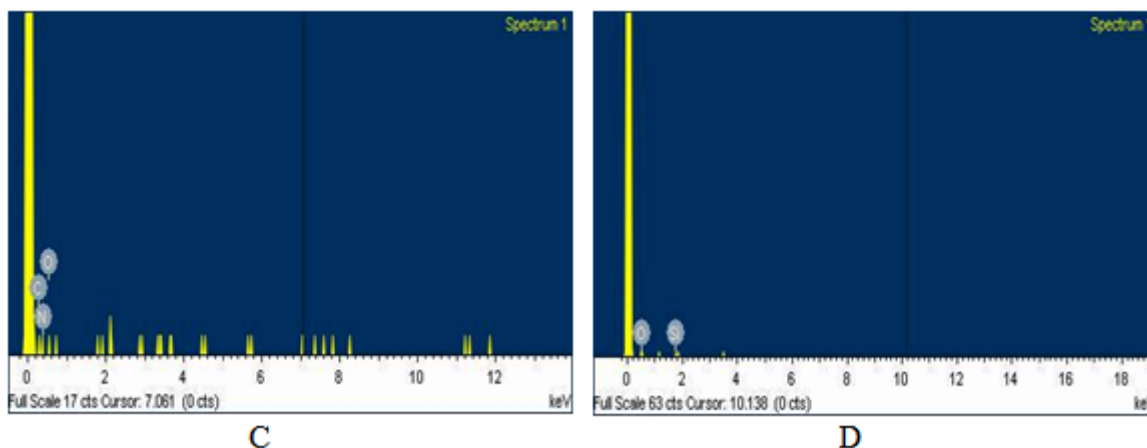


Figure 3: EDS spectrograms of C) activated silica gel and D) amidoxime-silica.

As can be seen in Figure 3, the EDS spectrogram of activated silica gel only showed Si and O peaks since silica gel contains only silicon and oxygen atoms as its building atoms. However, after the modification process was carried out and amidoxime silica was produced, it was observed that several atoms such as nitrogen and carbon peaks appeared on the spectrogram which provided the evidence that the modification process was successful since the nitrogen and carbon atoms were the main component in the structure of amidoxime silica.

3.4 Thermogravimetric Analysis

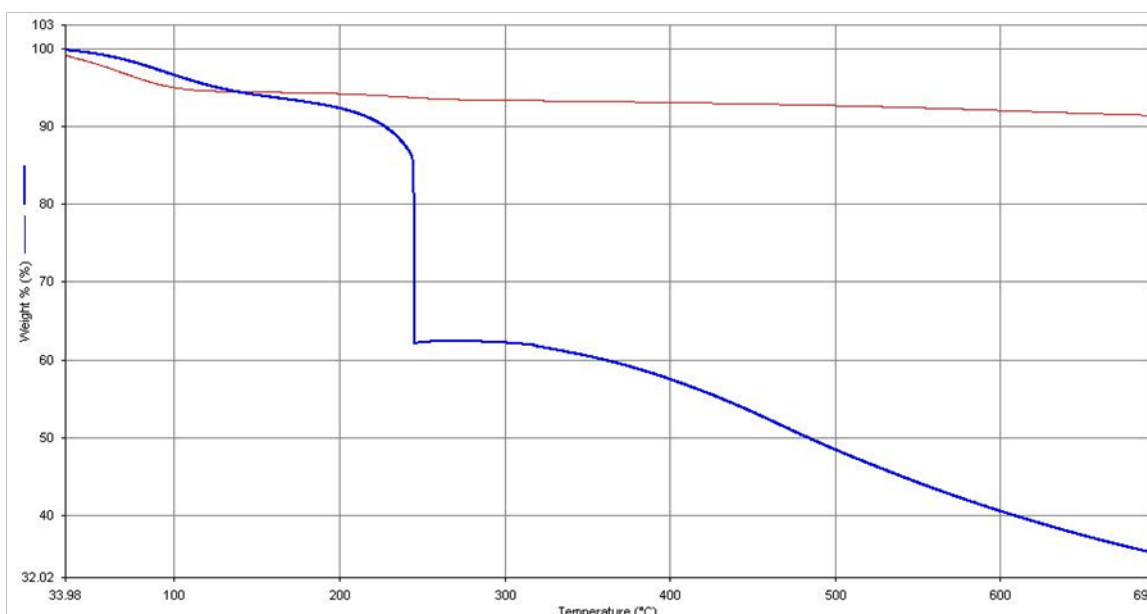


Figure 4: Thermograms of activated silica gel and amidoxime silica.

Based on Figure 4 above, the activated silica gel showed a first mass lost stage of 5.4% from 30°C to 110°C which was assigned to physically adsorbed water molecules. It was followed by 2% of weight loss from 200°C to 270°C which corresponding to condensation of the silanols which resulting in water loss to produce siloxane linkage (Kursunlu, Guler, Dumrul, Kocygıt & Hubbuk, 2009). The final weight remained was 91% as it approached the maximum temperature tested.

For amidoxime-silica thermogram, three stages of weight loss were found where the first stage showed 5% weight loss from 30°C to 120°C attributed to physically adsorbed water molecules. It was then followed by 23.5% and 25% weight loss from 244°C to 246°C and 360°C to 690°C, respectively, which was related to decomposition of amidoxime groups. The final weight of the sample was 35% at the maximum temperature tested.

3.5 Effect of pH

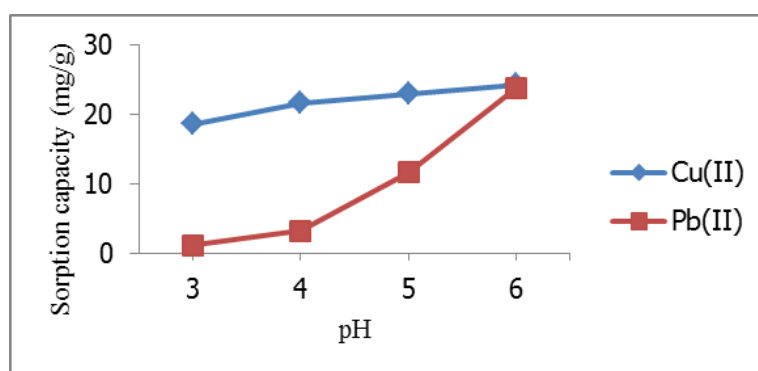


Figure 5: Effect of pH on the Cu²⁺ and Pb²⁺ sorption capacity.

As can be seen in Figure 5, after the sorbent was allowed to be in contact with the metal solution for two hours, it was observed that as pH < 6.0, the sorption capacity of amidoxime-silica towards metal ions were increased with an increasing pH value and reached its maximum value 24.88 mg/g and 23.87 mg/g at pH 6.0 for Cu²⁺ and Pb²⁺, respectively.

The chemically modified silica gel with amidoxime showed different adsorption abilities towards various metal ions though it has the identical functional group was due to the ionic structures of the metal ions tested where complexation between the metal ions and the active sites of the sorbent occurred while the stability of the complexes form were dependant on the structures of the valence electron orbits of the particular metal ions (Gao, Xu, Zou, Ji & Gan, 2010).

3.6 Effect of Contact Time

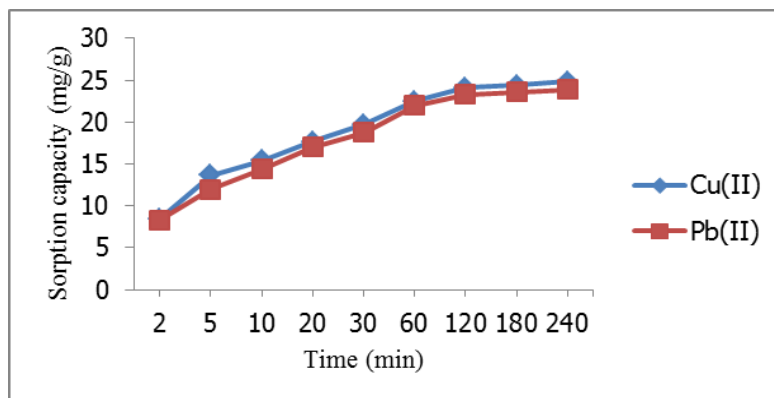


Figure 6: Effect of contact time on the Cu^{2+} and Pb^{2+} sorption capacity.

Based on Figure 6, it was shown that the adsorption of Cu^{2+} and Pb^{2+} were quite rapid at the initial stage and after that became slower with the passage of time and reached almost constant value around 120 min. Higher adsorption rate at the early stage can be related to the availability of the uncovered surface area, since the adsorption kinetics depends on the surface area of the adsorbent (Najafi, Rostamian & Rafati, 2011).

4. CONCLUSION

Immobilization of amidoxime functional group onto silica gel surface was carried out by series of processes starting with the preparation on aminopropyl-silica, followed by acrylonitrile-silica and then conversion of nitrile group to amidoxime. The optimum reaction conditions for preparation of amidoxime-silica were : 70°C for the reaction temperature, 4 h reaction time, 75% v/v methanol:water for the reaction medium and the ratio 2:1 for hydroxylamine hydrochloride with acrylonitrile-silica. The characterization of the modified silica gel by means of FTIR, SEM, EDS and TGA supported the evidences of immobilization of amidoxime group onto the silica gel surface. The modified silica gel also showed significant ability for Cu^{2+} and Pb^{2+} removal from aqueous media even so were pH-dependent. The rate of exchange was rapid, which was $t_{1/2} < 10$ min for both of Cu^{2+} and Pb^{2+} .

5. ACKNOWLEDGEMENTS

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