Adsorption of copper, nickel and chromium ions using silica aerogel synthesized by ambient-pressure drying and modified with EDTA

B Pornchuti, B Pongpattananurak, D Sutthiard and P Singtothong:

Chemical Engineering Department, Mahanakorn University of Technology, Bangkok, 10530, Thailand
Chemical Department, Mahanakorn University of Technology, Bangkok, 10530, Thailand
bawornpong@yahoo.com

Abstract. Adsorption of heavy metal ions was studied widely since it is one of the promising methods for treating wastewater. Silica aerogel was selected as an adsorbent in this study because it was easy to modify surface. Although most of aerogels were synthesized by supercritical drying, the silica aerogel in this work was dried at atmospheric pressure which safer. It was modified further with APTES (Aminopropyltriethoxysilane) and EDTA (Ethylenediaminetetraacetic acid) to increase adsorption capacity. The modified silica aerogels were used to adsorb copper, nickel and chromium ions from aqueous solution. It was found that efficiency of heavy metal removal in case of EDTA modified silica aerogel was better than those of APTES modified silica aerogel and unmodified adsorbent. The adsorption data agreed well with Langmuir isotherm model than Freundlich isotherm model. The maximum adsorption capacities of copper, nickel and chromium on EDTA modified silica aerogel were found to be 94.34, 84.75 and 169.49 mg/g, respectively.

1. Introduction
Copper, nickel and chromium ions are found in wastewater from electroplating industry. Firstly, copper ion is used to precoat because the quality of nickel coating on copper is better than coating on iron. Although, nickel and chromium coating can protect corrosion, chromium should be coated after nickel because of its brittleness.

Like other heavy metals, copper, nickel and chromium ions must be removed from wastewater due to their toxicities. There are several methods treating wastewater from electroplating process such as chemical precipitation, chemical coagulation and flocculation, ion exchange, adsorption, membrane filtration and electrochemical methods [1]. Chemical precipitation is not effective at low metal concentration and produces a large amount of hazardous sludge. Like chemical precipitation, chemical coagulation and flocculation also generates hazardous waste and uses a large amount of chemicals. Ion exchange has high operating cost and can remove only some metal ions. Membrane filtration is expensive and has fouling problem. Electrochemical methods need high electrical energy and high initial investment.

Adsorption is one of the promising methods. It is cheap and easy to use. Many adsorbents were developed for heavy metal removal. In this project, silica aerogel was selected because of its high surface area. Moreover, it is easy to modify the surface of silica aerogel. The procedure of silica aerogel synthesis can be divided into 3 steps: (a) sol-gel process (b) aging process and (c) drying. The critical step is the last one. Evaporation of liquid from the gel normally destroys the gel structure due to capillary stress. Therefore special method must be used to remove liquid from the pore. They are (a) supercritical drying (b) freeze drying and (c) ambient pressure drying with surface modification [2]. In this research the last method was selected because it is safer and cheaper.

Current research involving heavy metal treatment using silica aerogel may be divided into three groups (a) changing raw materials or synthesis method to reduce production cost (b) incorporation with other materials to increase surface area and (c) surface modification to increase affinity toward adsorbate.
Following researches were examples of group (a). Sodium silicate was used as precursor to prepare silica aerogel. The produced silica aerogel was modified further with mercaptopropyl trimethoxysilane. It was found that adsorption capacities for Cu (II), Cd (II) and Pb (II) ions were 90.1, 181.8 and 250.0 mg/g, respectively [3]. In 2018, Terzioglu et al. reduce production cost of silica aerogel synthesis by using wheat husk ash as silica source. Synthesized silica aerogel was used to remove Pb (II) ions and removal capacity was found to be 47.07 mg/g [4]. To reduce production cost, Wang et al. avoided surface modification and solvent exchange in 2016. The structure of silica aerogel was strengthened by crosslinking with disiocyanate to withstand surface tension of solvent. Monolithic silica aerogel has adsorption capacities of 118.73 mg/g for Pb (II), 57.03 mg/g for Cr (III) and 60.86 mg/g for Cd (II) ions [5].

For group (b), adsorption capacity of Cd (II) ions was improved by combining activated carbon and silica aerogel together as novel nanocomposite in 2013 [6]. While Wang et al. used silica aerogel as supporter of hydrozincite and carbonate-intercalated hydrotalcite in 2017. Consequently, adsorption capacity of Pb (II) ions was so high when comparing to other inorganic adsorbents [7].

For group (c), amino propyl triethoxysilane was used to modify surface of silica aerogel. It was found that the highest adsorption capacities of Pb (II) and Cd (II) ions were 45.45 mg/g and 35.71 mg/g, respectively [8]. In 2019, silica aerogel was modified with amine-mercapto groups (double functionalization) to capture a broader range of heavy metals. Each functional group preferred removing different cations [9].

Although, the adsorption capacities of metal ions were increased by assistance of amino functional groups, it was found that desorption of these ions was difficult. Mao et al. reported that adsorbent which was modified with EDTA can be reused [10]. Therefore, EDTA was chosen in this project to modify surface further.

2. Experimental

2.1 Chemicals

The chemicals used are tetraethyl orthosilicate (Sigma Aldrich), isopropanol (Merck), hydrochloric acid (Merck), cetyltrimethylammonium bromide (Sigma Aldrich), toluene (Merck), APTES (Sigma Aldrich), ethanol (Merck), EDTA (Sigma Aldrich), acetic acid (Merck), ammonium hydroxide solution (Merck) and methanol (Merck). All of them were used as received.

2.2 Preparation of silica aerogel

Silica aerogel was synthesized using adapted method of Aravind et al. [11]. Briefly, TEOS (Tetraethyl orthosilicate) 4.66 g was mixed with isopropanol 5.37 g and HCl solution 6.44g. When pH was adjusted to be 5, the aqua gel was formed and aged for 24 hours. Aged gel was then soaked in isopropanol, TEOS solution and 0.05%CTAB in isopropanol, respectively. The alcogel was dried at ambient condition to evaporate solvent as slow as possible.

2.3 Preparation of APTES modified silica aerogel

APTES modified silica aerogel was prepared by method of Parida and Rath [12]. Firstly, silica aerogel 2.0 g was mixed with toluene 60 mL. Then APTES 1.2 mL was dropped into the mixture. After the mixture was refluxed for 8 hours, APTES silica aerogel was washed with ethanol and distilled water, respectively. The adsorbent was dried 12 hours at room temperature.

2.4 Preparation of EDTA modified silica aerogel

EDTA modified silica aerogel was produced according to method of Repo et al. [13]. At first, APTES modified silica aerogel 2.0 g was mixed with EDTA anhydride 5.384 g and ethanol-acetic solution 42.0 mL. Then agitate the mixture for 3 hours. The resulted solid was washed with ammonium hydroxide solution, ethanol-acetic acid solution, distilled water and methanol, respectively. Finally, it was dried at 105°C for 6 hours.

2.5 Method
For all adsorption experiments, 100 mg of adsorbent was added into 100 mL of single metal solution. The mixture was shaken for 120 minutes. Then adsorbent was separated by vacuum filtration. The metal solution was measured by atomic absorption spectrophotometer. The equilibrium adsorption capacity was determined by equation (1).

\[ q_e = \frac{(C_i - C_e) V}{m} \]  

where \( q_e \) is the equilibrium adsorption capacity, \( C_i \) is the metal concentration before adsorption, \( C_e \) is the metal concentration at equilibrium, \( V \) is the volume of metal solution, \( m \) is the mass of adsorbent.

3. Results and discussion
From our last study, it was found that adsorption capacity was increased dramatically within 5 minutes and reached equilibrium within 20 minutes. Therefore, the effect of adsorption time was not presented in this paper.

3.1 Properties of adsorbents
During sol-gel process, precursor was hydrolyzed following by condensation. The three-dimensional structure was generated and the aqua gel was formed. Then aging process was used to reinforce the solid skeleton of the aqua gel. To dry the aged gel at atmospheric pressure without collapse of pore structure, the surface was modified to be hydrophobic. Without catalyst, it was believed that TEOS was reacted slowly and silica surface was covered with ethyl group. The pore solvent was exchange to hydrocarbon which has lower surface tension. Finally, the alcogel was dried as slow as possible at ambient pressure. The silica aerogel produced have BET surface area of 1,401.3 m\(^2\)/g and average pore size of 21.2 nm. When silica aerogel was modified further with APTES and EDTA, the appearance of silica aerogel was not changed after surface modification which can be seen in figure 1. The color of EDTA modified silica aerogel was changed after adsorption depending on type of metal solution used as demonstrated in figure 2. The color after adsorption of EDTA modified silica aerogel were blue, clear and yellow after adsorption of copper, nickel and chromium. They were easy to identify adsorbents after use except Ni adsorption. This may be caused by low adsorption capacity of nickel ion.

![Silica aerogel and EDTA modified silica aerogel](image)

Figure 1. The appearance of silica aerogel before and after surface modification.
3.2 Effect of surface modification
Modification of silica aerogel with APTES and EDTA can improve capability of capturing copper, nickel and chromium ions which can be seen in figure 3. Without surface modification, heavy metal ions may be interacted with hydroxyl group on the surface of silica aerogel. As mentioned earlier, APTES was used to coupling amino functional groups on solid surface. These amino groups helped clasp heavy metal ions and improved adsorption ability. EDTA was attached to solid surface by reacted with amino group prepared by APTES. One molecule of EDTA has four carboxylic groups and two amino groups. It was not surprising that adsorption capacity of EDTA modified silica aerogel higher than that of APTES modified silica aerogel.

3.3 Effect of initial metal concentration
Efficiency of heavy metal removal was illustrated as figure 4. It was found that removal efficiency was decreased when initial metal concentration was increased. Although adsorption capacity was increased with an increase of initial metal concentration, the correlation was not linear. Additionally, since the amount of adsorbent was fixed, the amount of heavy metal ions adsorbed was limited. As a result, the removal efficiency decreased with increasing of initial metal concentration.
3.4 Adsorption isotherm

Adsorption isotherm is important information in designing adsorption system. In this study, Langmuir isotherm model and Freundlich isotherm model were chosen due to its simplicity. The Langmuir model is as equation (2).

$$q_e = \frac{q_m K_L C_o}{1 + K_L C_e}$$  \hspace{1cm} (2)

where $q_m$ is the maximum equilibrium adsorption capacity, $K_L$ is the Langmuir constant. To obtain the parameters in the model, the linearized form of Langmuir model was used as equation (3).

$$\frac{1}{q_e} = \frac{1}{q_m K_L} \left(\frac{1}{C_e}\right) + \frac{1}{q_m}$$  \hspace{1cm} (3)

For Freundlich model, the equation is shown as equation (4)

$$q_e = K_F C_e^{1/n}$$  \hspace{1cm} (4)

where $K_F$ and $n$ are the Freundlich constants. Like Langmuir model, the linearized form of Freundlich model which demonstrated as equation (5) was used to obtain the parameters.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$  \hspace{1cm} (5)

The linearized form of Langmuir and Freundlich models were plotted as illustrated in figure 5 and 6, respectively. The Langmuir and Freundlich parameters were summarized in table 1. From parameters in table 1, Langmuir and Freundlich isotherm were generated as demonstrated in figure 7 and 8, respectively. It was important to note that the value of $R^2$ in parameter determining step did not show that the isotherm model used agreed well with experimental data or not. For example, in case of adsorption of nickel by silica aerogel, although the value of $R^2$ for Langmuir parameters calculation was low as 0.8527, the Langmuir isotherm agreed well with the experimental data as shown in figure 7. In addition, the use of $q_m$ must be careful, since it was just a parameter calculated for Langmuir model. For example, in case of adsorption of chromium by silica aerogel, the value of $q_m$ is so high as 158.73 mg/g. The Langmuir model predicted the highest value of adsorption capacity but it may occur at very high metal concentration which was out of experimental data range.

![Figure 4. Efficiency of heavy metal removal.](image-url)
Figure 5. Linearized form of Langmuir model.
Figure 6. Linearized form of Freundlich model.
Figure 7. Langmuir isotherm
Figure 8. Freundlich isotherm

Table 1. Langmuir and Freundlich parameters.

| Adsorbent : metal ion         | Langmuir parameters | Freundlich parameters |
|-------------------------------|---------------------|-----------------------|
|                               | $q_m$   | $K_L$  | $R^2$ | $K_F$  | $n$   | $R^2$ |
| EDTA modified : Cu            | 94.34   | 0.0211 | 0.9983 | 10.21 | 2.631 | 0.9559 |
| APTES modified : Cu           | 78.13   | 0.0143 | 0.9988 | 6.039 | 2.356 | 0.9655 |
| Silica aerogel : Cu           | 45.25   | 0.0124 | 0.9956 | 3.474 | 2.405 | 0.9527 |
| EDTA modified : Ni            | 84.75   | 0.00857| 0.9989 | 3.718 | 2.010 | 0.9808 |
| APTES modified : Ni           | 40.32   | 0.0114 | 0.9970 | 3.075 | 2.435 | 0.9962 |
| Silica aerogel : Ni           | 14.22   | 0.0225 | 0.8527 | 2.766 | 3.751 | 0.9231 |
| EDTA modified : Cr            | 169.49  | 0.0279 | 0.9997 | 16.16 | 2.347 | 0.9622 |
| APTES modified : Cr           | 135.14  | 0.0413 | 0.9982 | 19.23 | 2.805 | 0.9866 |
| Silica aerogel : Cr           | 158.73  | 0.000243| 0.9611 | 0.0642| 1.117 | 0.8200 |

From figure 7 and 8, the Langmuir and Freundlich isotherms were both agree well with experimental data but the Langmuir isotherm was more suitable. The maximum adsorption capacities of copper, nickel and chromium using EDTA modified silica aerogel were 94.34, 84.75 and 169.49 mg/g, respectively.
4. Conclusion
Adsorption of copper, nickel and chromium ions by EDTA modified silica aerogel was studied. It was found that surface modification with EDTA can improve adsorption capacities of metal ions. The removal efficiency decreased when initial metal concentration increased. The adsorption loading of chromium ion was higher than that of copper and nickel, respectively. Both Langmuir and Freundlich isotherms were agree well the experimental data.

5. References
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