

Performance of silica aerogels modified with amino functional groups in Pb(II) and Cd(II) removal from aqueous solutions

Hossein Faghihian¹, Heshmatollah Nourmoradi², Maryam Shokouhi^{3*}

¹Islamic Azad University, Department of Chemistry, Shahreza Branch, Professor of Analytical Chemistry, Isfahan, Iran.

²Ilam University of Medical Sciences, Department of Environmental Health Engineering, School of Health, Ilam, Iran.

³Islamic Azad University, MSc of Analytical Chemistry, Department of Chemistry, Shahreza Branch, Isfahan, Iran.

*Corresponding author: e-mail: m.shokouhi89@gmail.com

The adsorption behavior of Pb(II) and Cd(II) ions in aqueous solutions on silica aerogels modified with amino propyl triethoxysilane was investigated as a function of pH, contact time, adsorbate concentration and adsorbent dose. It was found that maximum adsorption of Pb(II) and Cd(II) ions occurs at pH 6.0 and pH 8.0, respectively. The optimum contact time to obtain equilibrium adsorption with the modified silica aerogel was experimentally found to be around 48h. Adsorption isotherms clearly indicated that the adsorption behavior of metals ions on the modified silica aerogels is fitted well with both the Langmuir and Freundlich isotherms. The maximum adsorption capacities of Pb(II) and Cd(II) on modified silica aerogel were found to be 45.45mg/g and 35.71mg/g, respectively. The results indicated that silica aerogels modified with amino functional groups can be used as an efficient adsorbent in the removal of metal ions such as Pb(II) and Cd(II) from aqueous solutions.

Keywords: silica aerogel, amino groups, adsorption, isotherm, Pb(II), Cd(II)

INTRODUCTION

Rapid development of industries such as metal electroplating, steel industries, mining operations, fertilizer industries, tanneries, batteries, ceramic industries, paper industries, painting operations and pesticides leads to the discharge of wastewaters containing heavy metals into the environment, particularly in developing countries¹⁻². The pollution of waters by toxic heavy metals is considered as a major threat. This is due to their high toxicity, non-biodegradability as well as long biological half-lives. Heavy metals can accumulate in food chain and endanger the aquatic organisms, plants, animals and human health³⁻⁶. Cadmium ions cause renal disease⁷, lung fibrosis, dyspnea, weight loss⁸ and Itai Itai disease⁹. Lead ions damage to the central nervous system⁷, cause problems in the synthesis of hemoglobin, have adverse effects on the gastrointestinal tract, kidney, liver and also lead to a weakness of muscles and joints¹⁰⁻¹¹. Based on the World Health Organization (WHO) guidelines, the maximum allowed concentration of lead and cadmium ions in drinking water is 0.01 and 0.003 mg/L, respectively⁷. Due to the environmental and health risks created by Lead and Cadmium, the removal of these heavy metals from water and wastewater is essential. In this regard, several methods including chemical precipitation, ion exchange, electrochemical treatment, membrane separation, solvent extraction and adsorption have been applied¹²⁻¹³. The adsorption method has been shown to be effective in the removal of heavy metals from aqueous solution⁸. The major factors affecting the adsorption process consist of pore size, pore distribution, surface area and surface chemistry of the adsorbent. As shown in Table 1, different adsorbents have been applied for the adsorption of lead and cadmium from aqueous solutions^{1,9-10,14-18}. Silica aerogels having high porous structure (up to 99%), high specific surface area (500–1000 m²/g) and low density (as low as 5 kg/m³) show high adsorption capacities which are similar or even higher than the traditionally used adsorbents¹⁹. Modification of silica aerogel

Table 1. Materials for adsorption of Pb(II) and Cd(II)

Adsorbent	q _e (mg/g)		References
	Pb	Cd	
Mustard husk	30.48	42.85	14
Calcitic limestone	40	1.3	1
Agave sisalana (sisal fiber)	1.34	1.85	15
Ethylenediamine functionalized SBA-15	0.36	0.1	10
Limestone	0.0128	0.0155	16
Chitosans	30.5	–	17
Soybean	–	0.4	9
Raw kaolin	4.73	–	18

with organic functional groups increased the adsorption capacity of heavy metals. Standeker et al. reported that silica aerogels modified with mercapto functional groups show very high adsorption potential in removing Cu(II) and Hg(II) ions from aqueous solution. It could adsorb more than 99.0% of these metals in the pH ranges of 4–6²⁰. The main objective of this study was to investigate the performance of silica aerogels modified with amino Propyl Triethoxysilane (amino functional groups) in the removal of Pb(II) and Cd(II) from aqueous solutions.

EXPERIMENTAL

Chemicals and reagents

All chemicals including tetraethoxysilane (TEOS), 3-aminopropyl triethoxysilane (APTES), isopropanol, hexane, Cd(NO₃)₂·4H₂O, Pb(NO₃)₂, HCl, NaOH were purchased from Merck Company. The stock solutions of Cd (II) and Pb(II) (1000 mg/L) were prepared by dissolving stoichiometric quantities of their nitrate salts (analytical grade) in distilled water. These stock solutions were further diluted with distilled water to achieve desired concentration as working solutions.

Adsorbent: Preparation and Modification

Tetraethoxysilane (TEOS) was utilized as the main

substance for the synthesis of silica aerogel. TEOS was mixed with isopropanol and 0.001 M hydrochloric acid to achieve a molar ratio of 1:4:16:21 and a homogeneous mixture was attained by stirring. Then, this sol was transferred to a beaker and incubated for 24 h at 36°C to make gel. For aging, the alcogel was transferred to a 1:1 mixture of isopropanol and water and was left for 24 h at 50°C. In order to prevent the reverse reaction during the surface modification process, the isopropanol in the alcogel was replaced with a nonpolar solvent such as hexane through maintaining in hexane for 48 h at 36°C²². The surface modification was then accomplished by immersing the alcogel in a hexane solution containing 3-aminopropyl triethoxysilane (APTES). The molar ratio of TEOS/APTES in the solution was 2:1. silica aerogel was dried in an oven at 36°C for 24 h and then at 56°C for 48 h. The aerogel sample was cooled at room temperature, grinded by mortar and pestle and characterized by various techniques.

Analysis and Characterization

The surface modification of silica aerogel was corroborated by infrared spectroscopy using Nicolet IR spectrophotometer (Model: Impact-400 D). The morphology of nano-porous silica aerogel was assigned by scanning electron microscopy (SEM) (Model: Philips XL-30). The thermal stability of the silica aerogel was studied by thermogravimetric analysis (TGA) using Setaram Labsys. The surface area of the adsorbent was determined by a single-point N₂ gas adsorption method using a model Quanta Chrome Instrument Mono Sorb device. The concentration of the metal ion in the solutions was determined with a Perkin-Elmer atomic absorption spectrometer (AAS) (Model AAAnalyst300). A pH-meter (Jenway 3010) and rotary shaker (Nuve ST 400) were used for pH measurement and shaking the samples, respectively.

Adsorption experiments

Initially, the adsorption experiments through the unmodified adsorbent showed that the removal efficiency of Pb(II) and Cd(II) was found to be 25.6% and 14.2%, respectively. Therefore the modified adsorbent because of the higher removal efficiency was used for rest of the experiments. Batch adsorption experiments were conducted to study the effect of parameters such as pH, contact time, metal concentration and adsorbent dose on the removal of Pb(II) and Cd(II) from aqueous solutions by silica aerogel modified with amino functional groups. All the adsorption experiments were carried out at room temperature (25°C) with 50 mL of metal ions solution in a 150 mL conical flask and shaking by rotary shaker at 200 rpm for 48 h. After agitation, the suspensions were centrifuged at 2500 rpm for 10 min and the clear supernatant was analyzed for the metal ions by atomic absorption spectrometer. The removal efficiency (%) of tested metals was calculated through the equation (1):

$$\text{removal efficiency (\%)} = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

Where; C_o is the initial metal ion concentration in the solution (mg/L) and C_e is the final equilibrium concentration in the solution at equilibrium time (mg/L).

Effect of pH and contact time

Evaluation of the effect of pH on the adsorption was conducted using 50 mL of a solution containing 0.5 g adsorbent and 400 mg/L metal ion at various pH values ranged from 2 to 12. HCl (0.1 M) or NaOH (0.1 M) was used for adjustment of solution pH the desired value. The experiments were carried out with the fixed optimum pH and varying contact times (1, 3, 5, 25, 48 h) to assess the influence of contact time on metal removal efficiencies. The effects of pH and contact time on the adsorption were determined by using a rotary shaker at 25°C for 48h. The suspensions then were centrifuged and the metal content of the clear supernatants were analyzed using AAS.

Effect of initial concentration of heavy metals and adsorbent dose

The effect of initial concentration of heavy metals was evaluated using different Pb(II) and Cd(II) concentrations (50, 100, 200, 300, 400, 500 mg/L) in 50 mL solution containing 0.5 g adsorbent at the optimum pH and 25°C for 48 h (equilibrium time). After agitation the suspensions were centrifuged and the metal contents were measured by AAS.

The effect of adsorbent concentration was evaluated by different doses (0.05, 0.2, 0.4, 0.8, 1.6 g) in 50 mL of heavy metal solutions with a fixed concentration of each Pb(II) and Cd(II) (400 mg/L), the equilibrium time (48 h) and the optimum pH values at 25°C. After agitation, the suspensions were centrifuged and the metal contents measured by AAS.

Adsorption isotherm

To assess the sorption capacity of the adsorbent, isotherm experiments were carried out by adding 0.5 g adsorbent into 50 mL of various concentrations of each Pb(II) and Cd(II) solution (50, 100, 200, 300, 400 and 500 mg/L) at room temperature (25°C). The suspensions were shaken by rotary shaker (200 rpm) for 48h and the suspensions were then centrifuged (2500 rpm for 10 min) and analyzed using AAS. The metal adsorption capacity of the adsorbent was calculated via the equation (2):

$$q_e = \frac{(C_o - C_e)V}{m} \quad (2)$$

Where q_e is the capacity of adsorbent for the heavy metal (mg/g), C_o is the initial concentration of heavy metal (mg/L), C_e is the equilibrium heavy metal concentration in solution (mg/L), m is the mass of adsorbent (g) and V is the volume of the solution (L).

RESULTS AND DISCUSSION

Characterization of the adsorbent

The spectra of FT-IR analysis of the silica aerogel before and after modification are shown in Fig. 1. In both of the adsorbents, the strong peak near 1080 cm⁻¹ and the weak peak near 800 cm⁻¹ were related to the asymmetric and symmetric bending of Si—O—Si bonds, respectively. The strong peak near 470 cm⁻¹ was also attributed to the bending of the O—Si—O bonds. In the spectra of the unmodified aerogel, the wide peak at 3426 cm⁻¹ correspond to the hydroxyl groups adsorbed on the surface

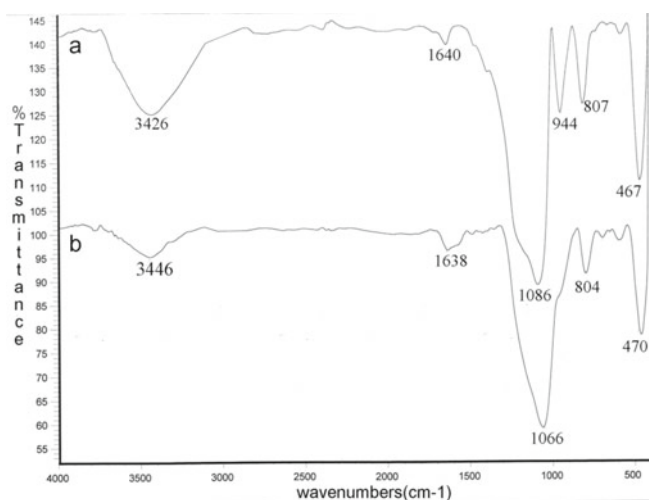


Figure 1. FT-IR spectra of the modified silica aerogel (a) before modification (b) after modification

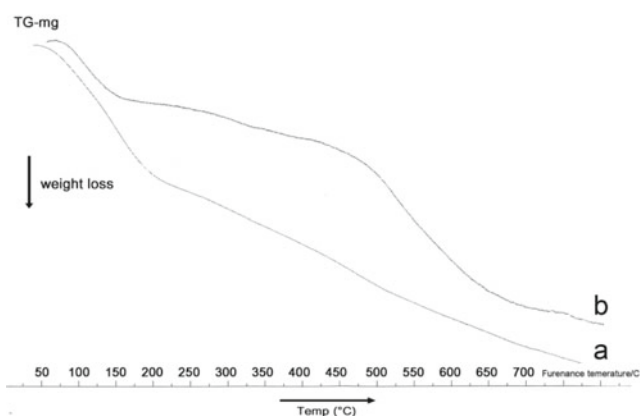


Figure 2. TGA of silica aerogels (a) before modification (b) after modification

and the peaks at 1640 cm^{-1} and 944 cm^{-1} correspond to the bending of the H–O–H bonds and the stretching of the Si–OH bonds, respectively^{23–24}. In the spectra of the modified silica aerogel, stretching vibration of N–H appeared at 3446 cm^{-1} that overlaps with a wide peak at 3426 cm^{-1} correspond to the hydroxyl groups.

Fig. 2 (a) and (b) show the TGA curves of silica aerogel before and after modification, respectively. In Fig. 2 (a) evaporation of trapped H_2O and alcoholic groups that produced from the condensation reaction of Si–OH and Si(OC_2H_5) groups cause rapid weight loss from 55°C up to 175°C . Beyond this point, the sample shows uniform thermal behavior. In Fig. 2 (b) increase in temperature after 460°C causes sudden weight loss corresponding to the thermal decomposition of NH_2 that stand on the surface of the silica aerogel.

The morphology of the modified silica aerogels before and after modification has been studied by scanning electron microscopy (SEM). The SEM images in Fig. 3 show that the particles and pore size in the modified silica aerogel (3b) were much uniform than those in the unmodified silica aerogel (3a). In other words, the modified silica aerogel has heterogeneous particles size with some agglomerated particles. Also particles and pore sizes in the modified silica aerogel are bigger than these of the unmodified silica aerogel. N_2 adsorption data show that the BET surface areas of the silica aerogel before and after modification are $940\pm 23\text{ m}^2/\text{g}$

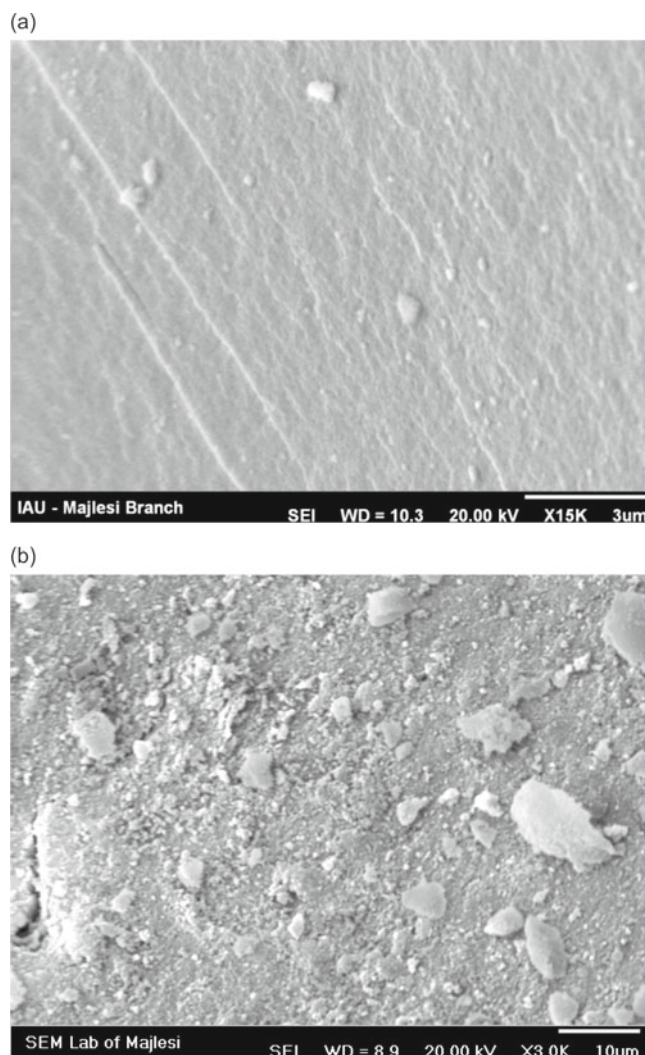


Figure 3. SEM microstructures for silica aerogel (a) before modification (b) after modification and $240\pm 7\text{ m}^2/\text{g}$, respectively. Substantial reduction in the specific surface area after modification is observed, which could be attributed to the insertion of NH_2 in the pore structure of the silica aerogel²⁵.

EFFECT OF PH

The pH of a solution is an important factor governing the adsorption process. It affects the surface charge of the adsorbent and the ionization process²⁶. The results of Pb(II) and Cd(II) ions adsorbed by modified silica aerogel at different pH are shown in Fig. 4. It was found that the maximum adsorption of Pb occurred at pH 6.0 and Cd(II) at pH 8.0 with a removal efficiencies of 99.60%, and 75.01%, respectively. For the pH values higher and lower than the optimum, the metal ions removal efficiency was decreased. At lower pH, the decrease in the removal efficiency may be related to the increased competition between hydrogen ions and metal ions to protonate the amino groups of modified silica aerogel. In addition, an increase in the positive surface charge at lower pH leads to an increase in the electrostatic repulsion between the surface and metal ions¹⁰. The main reactions that occur at the solid-solution interface may be exhibited by the equations (a)–(d)²⁷.



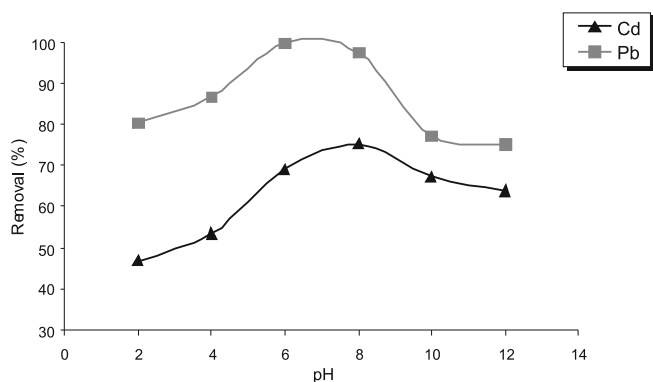


Figure 4. The effect of pH on the adsorption of metal ions onto the modified silica aerogel (The initial metal ions concentration=400 mg/L, Adsorbent dose=0.5 g and Contact time=48h)



Eq. (a) represents the protonation of the amino groups of modified silica aerogel in solution that occurs at low pH. Eq. (b) shows the formation of surface complexes of metal ions and amino groups. As discussed above, the competition between hydrogen and metal ions at low pH leads to fewer adsorptions of metal ions because the adsorption of H^+ results in the protonation of NH_2 to form NH_3^+ . Eq. (c) indicates the adsorption of hydroxyl ions by amino groups at high pH which leads to the reduction of metal ions adsorption. At higher pH, the adsorption of metal ions via electrostatic attraction as displayed in Eq. (d) might increase²⁷. Therefore, pH 6.0 and 8.0 were selected as optimums for Pb(II) and Cd(II) adsorption experiments, respectively. According to an adsorption study with mustard husk, the maximum removal efficiency for Pb(II) was occurred at pH 6 (97%) and for Cd(II) was observed at pH 4 (70%)¹⁴.

Effect of contact time

Fig. 5 shows the effect of various contact times (1–48h) on the metal ions removal efficiency by the modified silica aerogel at optimum pH. The removal percentages of both cations are increased with increasing the contact time until equilibrium is achieved. The optimum contact time was experimentally found to be about 24h and no significant changes were observed after this time. The removal percentage for Pb(II) and Cd(II) ions by modified silica aerogel up to 24h contact time were 98.95% and 74.83%, respectively. However, the 48h contact time for adsorption equilibrium of the samples was used for all subsequent experiments. In the study for the removal of Pb(II) and Cd(II) by mustard husk, the equilibrium contact time was selected 72h¹⁴.

Effect of initial concentration of heavy metals

The initial concentration of metal ions is a main factor for effective adsorption. The removal percentages of the heavy metals at different concentrations by modified silica aerogel are shown in Fig. 6. With increasing the initial heavy metal concentration, the removal percentage was decreased. For the initial Pb(II) and Cd(II) concentration ranges of 50–200 mg/L and 50–100 mg/L, respectively, their removal is nearly 100%. At lower concentrations, more adsorption sites are available for adsorption of the heavy metals ions. Thus, at lower concentrations the

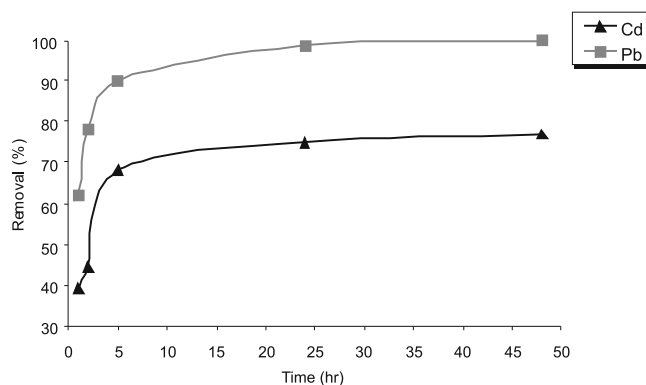


Figure 5. The effect of contact time on the adsorption of metal ions onto the modified silica aerogel (The initial metal ions concentration=400 mg/L, Adsorbent dose=0.5 g, pH= 6 for Pb; 8 for Cd)

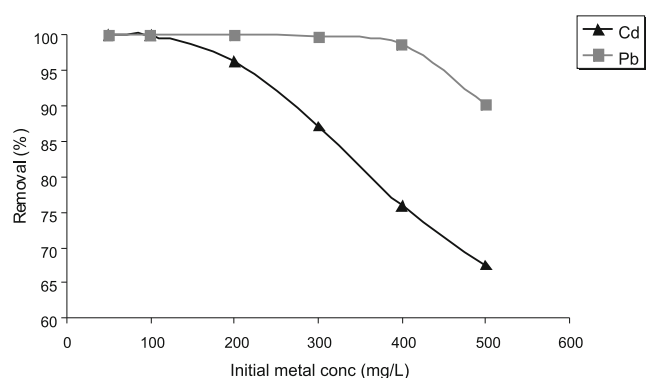


Figure 6. The effect of initial metal concentration on the adsorption of metal ions onto the modified silica aerogel (Contact time= 48h, Adsorbent dose=0.5 g, pH= 6 for Pb; 8 for Cd)

amount of adsorption was independent on the numbers of adsorption sites. However, at higher concentrations the adsorption sites are relatively insufficient²⁸. When the initial metal ion concentrations were increased up to 500 mg/L, the removal percentages were decreased to 90.13% for Pb(II) and 67.51% for Cd(II). This finding demonstrated that the Pb ions were removed better than Cd ions. This could be related to the differences of hydrated diameter and hydration energy between Pb and Cd cations. The hydrated diameter of Pb cation (5.2 Å) is smaller than that of Cd cation (5.5 Å). Pb and Cd cations in average have 6.1 and 7.6 water molecules in their hydration layers, respectively. The hydrated diameter of Pb cation (5.2 Å) is smaller than that of Cd cation (5.5 Å). Pb and Cd cations in average have 6.1 and 7.6 water molecules in their hydration layers, respectively. The hydration energies of Pb and Cd are -1425 kJ/mol and -1755 kJ/mol, respectively²⁹. Thus, the cadmium loses its hydration layer harder than lead due to its higher hydration energy level³⁰.

Effect of adsorbent dose

The removal percentage of the heavy metals at different adsorbent doses (0.05–1.6 g) is presented in Fig. 7. The removal efficiency increases with an increase in the adsorbent dose. By increasing the adsorbent dose from 0.05 g to 1.6 g, the removal percentage of Pb(II) and Cd(II) increase from 88.03% to 100% and from 37.78% to 90.98%, respectively. This is due to the availability of more adsorption sites on the surface of adsorbent to react with metal ions.

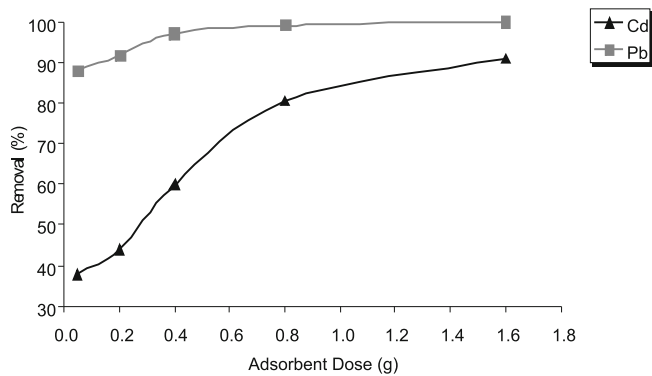


Figure 7. The effect of adsorbent dose on the adsorption of metal ions onto the modified silica aerogel (The initial metal ions concentration=400 mg/L, Contact time= 48h, pH= 6 for Pb; 8 for Cd)

Adsorption isotherm

Adsorption isotherms are the important information of designing any sorption system. The adsorption isotherms were studied by adding 0.5 g adsorbent into 50 mL solution containing various concentration of each Pb(II) and Cd(II) (50, 100, 200, 300, 400 and 500 mg/L) at room temperature (25°C). The adsorption data were analyzed by Langmuir, Freundlich and Dubinin- Radushkevich (D-R) isotherm models. The Langmuir isotherm can be shown by the equation (3):

$$q_e = \frac{Q_m b C_e}{1 + b C_e} \quad (3)$$

Where q_e (mg/g) is the amount of metal ion adsorbed per unit mass of adsorbent at equilibrium state, C_e (mg/L) is the equilibrium concentration of metal ion, b (L/mg) is the equilibrium constant and Q_m (mg/g) is the maximum amount of metal ion adsorbed. The linearized equation of Langmuir is represented by the following equation³¹:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{b Q_m} \quad (4)$$

The linear plot of C_e/q_e versus C_e enables determination of Q_m and b from the intercept and slope, respectively³¹. The Langmuir isotherm could be expressed by dimension constant called equilibrium parameter, R_L ³².

$$R_L = \frac{1}{1 + b C_o} \quad (5)$$

Where, C_o (mg/L) is the initial metal ion concentration. The value of R_L shows the type of isotherm to be favorable ($0 < R_L < 1$), irreversible ($R_L = 0$), unfavorable ($R_L > 1$) and linear ($R_L = 1$). The Freundlich isotherm was also used to model the observed phenomena as given in the equation (6)³¹:

$$q_e = K_f C_e^{1/n} \quad (6)$$

Where q_e is the same as above and n , K_f (L/g) are constants. Freundlich isotherm may be linearized via a logarithmic plot as in the following equation (7):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (7)$$

The values of K_f and $1/n$ are determined from the intercept and slope of linear plot of $\log q_e$ against $\log C_e$, respectively.

The Dubinin-Radushkevich (D-R) specifies the nature of adsorption processes as chemical or physical

D-R isotherm equation may be linearized as follows³¹:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (8)$$

Where q_m (mg/g) is the theoretical saturation sorption capacity based on D-R isotherm, β (kJ/mol) is related to mean adsorption energy and ε (Polanyi Potential) is equal to $RT \ln(1+1/C_e)$. R (kJ/mol.K) is universal gas constant and T (K) is temperature. When $\ln q_e$ plotted versus ε^2 , the q_m and β are attained from the intercept and slope, respectively. E (kJ/mol) is the average of energy adsorption that is obtained by the equation (9)³³:

$$E = \frac{1}{\sqrt{2\beta}} \quad (9)$$

The value of E indicates the type of adsorption process to be physical ($E < 8$ kJ/mol), chemical ion exchange (E value 8–16 kJ/mol) and chemical adsorption ($E > 16$ kJ/mol)³³.

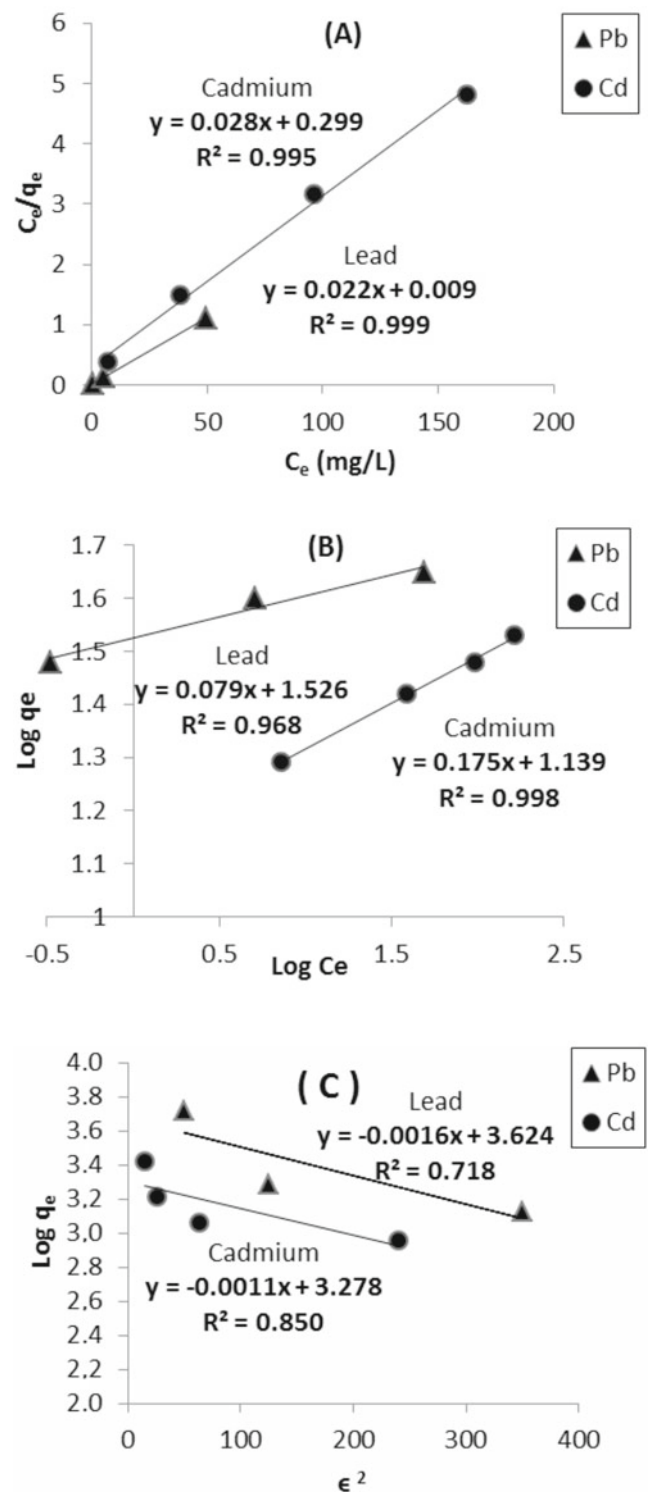


Figure 8. (a) Langmuir, (b) Freundlich and (c) D-R isotherm model

Table 2. Langmuir, Freundlich and D-R isotherm parameters for adsorption of Pb(II) and Cd(II) by the modified silica aerogel

Metal ion	Langmuir isotherm				Freundlich isotherm			D-R isotherm		
	Q _m (mg/g)	b(L/mg)	R ²	R _L	K _f	n	R ²	q _m (mg/g)	E (kJ/mol)	R ²
Pb(II)	45.45	2.44	0.999	0.001	33.57	12.65	0.968	37.51	17.68	0.718
Cd(II)	35.71	0.09	0.995	0.02	13.77	5.71	0.998	26.54	21.32	0.850

The obtained isotherm values are shown in fig. 8 and summarized in Table. 2. The adsorption isotherms clearly showed that the adsorption behavior of the metal ions on the silica aerogel modified with amino functional groups is in concordance with the isotherms of Langmuir and Freundlich. The *E* values higher than 16 showed that the mechanisms of adsorption for both the metal ions are chemical. The maximum adsorption capacity for Pb(II) and Cd(II) on modified silica aerogel were found to be 45.45 mg/g and 35.71 mg/g, respectively.

CONCLUSIONS

The results of the present study showed that silica aerogels modified with amino functional groups can be used as an efficient adsorbent in metal ions removal such as Pb(II) and Cd(II) from aqueous solutions. As seen from table 1, the adsorption capacity (mg/g) of the modified silica aerogel in the removal of Pb(II) and Cd(II) is higher than most of the adsorbents but economical analysis must be considered. The reduction of silica aerogel specific surface area after modification is due to the insertion of NH₂ in the pores surface of the silica aerogel.

D-R isotherm showed that chemical adsorption was the main mechanism for the removal of the metal ions. The adsorption was higher at pH 6.0 and 8.0 for Pb(II) and Cd(II) ions, respectively. The removal percentage of Pb(II) ions from aqueous solutions by silica aerogels modified with amino functional groups is higher than that Cd(II) ions.

LITERATURE CITED

- Rangel-Porras, G., García-Magno, J. & González-Muñoz, M. (2010). Lead and cadmium immobilization on calcitic limestone materials. *Desalination*. 262(1-3), 1-10. DOI:10.1016/j.desal.2010.04.043.
- Fu, F. & Wang, Q. (2010). Removal of heavy metal ions from wastewaters: A review. *J. Environ. Manage.* 92(3), 407-418. DOI:10.1016/j.jenvman.2010.11.011.
- Murugesan, A., Ravikumar, L. Sathyasel Vabala, V. Senthilkumar, P. Vidhyadevi, T. Kirupha, S.D. Kalaivani, S. Krithiga, S. & Sivanesan, S. (2011). Removal of Pb (II), Cu (II) and Cd (II) ions from aqueous solution using polyazomethineamides: Equilibrium and kinetic approach. *Desalination*. 271(1-3), 199-208. DOI:10.1016/j.desal.2010.12.029.
- Viti, C., Pace, A. & Giovannetti, L. (2003). Characterization of Cr (VI)-resistant bacteria isolated from chromium-contaminated soil by tannery activity. *Curr. Microbiol.* 46(1), 1-5. DOI: 10.1007/s00284-002-3800-z.
- Wong, K., Lee, C. Low, K. & Haron, M. (2003). Removal of Cu and Pb by tartaric acid modified rice husk from aqueous solutions. *Chemosphere*. 50(1), 23-8. DOI:10.1016/S0045-6535(02)00598-2.
- Arora, M., Kiran, B. Rani, S. Rani, A. Kaur, B. & Mittal, N. (2008). Heavy metal accumulation in vegetables irrigated with water from different sources. *Food Chem.* 111(4), 811-5. DOI:10.1016/j.foodchem.2008.04.049.

- World Health Organization. (2004). Guidelines for drinking-water quality, World Health Organization, Distribution and Sales Geneva 27 CH-1211 Switzerland. from <http://library.nu/>. ISBN 92 4 154696 4.

- Sud, D., Mahajan, G. & Kaur, M. (2008). Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions-A review. *Bioresour. Technol.* 99(14), 6017-27. DOI:10.1016/j.biortech.2007.11.064.

- Kawasaki, N., Tominaga, H. Ogata, F. & Kakehi, K. (2010). Removal of cadmium and copper by vegetable biomass treated with hydrochloric acid. *Chem. Eng. J.* 157(1), 249-53. DOI:10.1016/j.cej.2009.11.028.

- Hajiaghababaei, L., Badiei, A. Ganjali, M.R. Heydari, S. Khaniani, Y. & Ziarani, G.M. (2011). Highly efficient removal and preconcentration of lead and cadmium cations from water and wastewater samples using ethylenediamine functionalized SBA-15. *Desalination*. 266(1-3), 182-7. DOI:10.1016/j.desal.2010.08.024.

- Naseem, R. & Tahir, S. (2001). Removal of Pb (II) from aqueous/acidic solutions by using bentonite as an adsorbent. *Water Res.* 35(16), 3982-6. DOI:10.1016/S0043-1354(01)00130-0.

- Mahmoud, M.E., Osman, M.M. Hafez, O.F. Hegazi, A.H. & Elmelehy, E. (2010). Removal and preconcentration of lead (II) and other heavy metals from water by alumina adsorbents developed by surface-adsorbed-dithizone. *Desalination*. 251(1-3), 123-30. DOI:10.1016/j.desal.2009.08.008.

- Srivastava, N. & Majumder, C. (2008). Novel biofiltration methods for the treatment of heavy metals from industrial wastewater. *J. Hazard. Mater.* 151(1), 1-8. DOI:10.1016/j.jhazmat.2007.09.101.

- Meena, A.K., Kadirvelu, K. Mishra, G.K. Rajagopal, C. & Nagar, P.N. (2008). Adsorption of Pb(II) and Cd(II) metal ions from aqueous solutions by mustard husk. *J. Hazard. Mater.* 150(3), 619-625. doi:10.1016/j.jhazmat.2007.05.011.

- Walter, N.L. dos Santos, Dannuza Dias Cavalcante, Erik Galvão Paranhos da Silva, Cesário Francisco das Virgens, Fabio de Souza Dias. (2011). Biosorption of Pb(II) and Cd(II) ions by Agave sisalana (sisal fiber). *Microchem. J.* 97(2), 269-273. doi:10.1016/j.microc.2010.09.014.

- Aziz, HA., Adlan, MN. & Ariffin, KS. (2008). Heavy metals (Cd, Pb, Zn, Ni, Cu and Cr(III)) removal from water in Malaysia: post treatment by high quality limestone. *Bioresour. Technol.* 99(6), 1578-1583. doi: 10.1016/j.biortech.2007.04.007.

- Chia-Yun Chen, Cheng-Yu Yang, Arh-Hwang Chen. (2011). Biosorption of Cu(II), Zn(II), Ni(II) and Pb(II) ions by cross-linked metal-imprinted chitosans with epichlorohydrin. *J. Environ. Manage.* 92(3), 796-802. doi:10.1016/j.jenvman.2010.10.029.

- Ming-qin Jiang, Qing-ping Wang, Xiao-ying Jin, Zu-liang Chen. (2009). Removal of Pb(II) from aqueous solution using modified and unmodified kaolinite clay. *J. Hazard. Mater.* 170(1), 332-9. doi:10.1016/j.jhazmat.2009.04.092.

- Standeker, S., Novak, Z. & Knez, Z. (2009). Removal of BTEX vapours from waste gas streams using silica aerogels of different hydrophobicity. *J. Hazard. Mater.* 165(1-3), 1114-8. DOI:10.1016/j.jhazmat.2008.10.123.

- Standeker, S., Veronovski, A. Novak, Z. & Knez, Z. (2010). Silica aerogels modified with mercapto functional groups used for Cu (II) and Hg (II) removal from aqueous solutions. *Desalination*. 269, 223-230. DOI:10.1016/j.desal.2010.10.064.

- Rajesh Kumar, S., Krishna Pillai, P. & Warriar, K. (1998). Synthesis of high surface area silica by solvent exchange in alkoxy

derived silica gels. *Polyhedron*. 17(10), 1699–703. DOI:10.1016/S0277-5387(97)00446-4.

22. Schwarz, W., Ebert, V. Geerds, H. Jungmann, K. Klirches, S. Koppe, S. Maas, F. Mundinger, H.J. Zu Putlitz, G. & Rosenkranz, J. (1992). Thermal muonium in vacuo from silica aerogels. *J Non-Cryst. Solids*. 145, 244–9. DOI:10.1016/S0022-3093(05)80465-X.

23. Reynolds, J.G., Coronado, P.R. & Hurbesh, L.W. (2001). Hydrophobic aerogels for oil-spill clean up-synthesis and characterization. *J. Non-Cryst. Solids*. 292(1–3), 127–37. DOI:10.1016/S0022-3093(01)00882-1.

24. Anappara, A.A., Rajeshkumar, S. Mukundan, P. Warriar, P. Ghosh, S. & Warriar, K. (2004). Impedance spectroscopic studies of sol-gel derived subcritically dried silica aerogels. *Acta Mater*. 52(2), 369–75. DOI:10.1016/j.actamat.2003.09.035.

25. Ngeontae, W., Aeungmaitrepirom, W. & Tuntulani, T. (2007). Chemically modified silica gel with aminothioamido-anthraquinone for solid phase extraction and preconcentration of Pb (II), Cu (II), Ni (II), Co (II) and Cd (II). *Talanta*. 71(3), 1075–82. DOI: 10.1016/j.talanta.2006.05.094.

26. Aksu, Z. (2005). Application of biosorption for the removal of organic pollutants: a review. *Process Biochem*. 40(3–4), 997–1026. DOI: 10.1016/j.procbio.2004.04.008.

27. Banerjee, S.S. & Chen, D.H. (2007). Fast removal of copper ions by gum arabic modified magnetic nano-adsorbent. *J. Hazard. Mater*. 147(3), 792–9. DOI:10.1016/j.jhazmat.2007.01.079.

28. Meena, A.K., Mishra, G. Rai, P. Rajagopal, C. & Nagar, P. (2005). Removal of heavy metal ions from aqueous solutions using carbon aerogel as an adsorbent. *J. Hazard. Mater*. 122(1–2), 161–70. DOI:10.1016/j.jhazmat.2005.03.024.

29. Marcus, Y. (1991). Thermodynamics of solvation of ions. Part 5.-Gibbs free energy of hydration at 298-15 K. *J Chem Soc Faraday Trans*. 87(18), 2995–9. DOI: 10.1039/FT9918702995.

30. Inglezakis, V.J., Loizidou, M.D. & Grigoropoulou, H.P. (2003). Ion exchange of Pb²⁺, Cu²⁺, Fe³⁺, and Cr³⁺ on natural clinoptilolite: selectivity determination and influence of acidity on metal uptake. *J. Colloid Interface Sci*. 261(1), 49–54. DOI:10.1016/S0021-9797(02)00244-8.

31. Aydin, Y. A. & Aksoy, N.D. (2009). Adsorption of chromium on chitosan: Optimization, kinetics and thermodynamics. *Chem. Eng. J*. 151(1–3), 188–94. DOI:10.1016/j.cej.2009.02.010.

32. Rojas, G., Silva, J. Flores, J.A. Rodriguez, A. Ly, M. & Maldonado, H. (2005). Adsorption of chromium onto cross-linked chitosan. *Sep. Purif. Technol*. 44(1), 31–36. DOI:10.1016/j.seppur.2004.11.013.

33. Uluozlu, O.D., Sari, A. Tuzen, M. & Soylak, M. (2008). Biosorption of Pb (II) and Cr (III) from aqueous solution by lichen (*Parmelina tiliaceae*) biomass. *Bioresour. Technol*. 99(8), 2972–80. DOI:10.1016/j.biortech.2007.06.052.