

## **Removal of Cadmium Using a Novel Nano Composite, Silica Aerogel, Activated Carbon**

M. H. Givianrad\*, M. Saber-Tehrani, P. Aberoomand-Azar and M. Hosseini Sabzevari

Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Ira

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### **ABSTRACT**

A novel composite adsorbent, Silica aerogel activated carbon was synthesized by sol-gel process at ambient pressure drying method. The composite was characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and Nitrogen adsorption / desorption isotherms (BET).

In the present study, the mentioned adsorbent was used moderately for removal of cadmium ions from aqueous solutions and was compared with two other adsorbents of cadmium, activated carbon and silica aerogel. The experiments of Cd adsorption by adsorbents were performed at different initial ion concentration, pH of the solution, adsorption temperature, adsorbent dosage and contact time. Moreover, the optimum pH for the adsorption was found to be 6.0 with corresponding adsorbent dosage level of 0.1 g at 60°C temperature. Subsequently, the equilibrium was achieved for Cd with 120 minutes of contact time.

Consequently, the results show that using this composite adsorbent could remove more than 60% of Cd under optimum experimental conditions. Langmuir and Freundlich isotherm model was applied to analyze the data, which the adsorption equilibrium data were correlated well with the Freundlich isotherm model and equilibrium adsorption capacity ( $q_e$ ) was found to be 0.384mg/g in the 3mg/L solution of cadmium.

**Keywords:** Cadmium; Cd adsorption; Silica aerogel activated carbon; Heavy metal; Adsorption Isotherms

### **INTRODUCTION**

Heavy metal pollution is a common environmental problem facing many places worldwide with the rapid development of economies and industries [1].

The increasing presence of cadmium in the environment is mainly due to its use in phosphate fertilizer, stabilizers, alloys, ceramics, pigments, battery and electroplating plants [2].

Cadmium is a naturally occurring metal and known as an extremely toxic in any of its different chemical forms as chloride, sulfate, sulfide, carbonate, oxide, and others [3].

Human toxicity with cadmium is usually related to smoking, refined foods, water pipes, coffee and tea, coal burning, and shellfish. High

percent of accumulated cadmium is deposited and retained in the kidney and liver based on its strong ability to replace the essential mineral zinc in these organs of human body [4]. Cd can cause serious damage to the liver and kidneys such as emphysema, bone disorders, cancer [5], hypertension and testicular atrophy; it combines with sulfhydryl group in protein and restrains the activity of enzymes [6].

Various materials have been reported to remove cadmium from waste waters, natural soils [7] minerals [8], tailing wastes and biomasses [9], waste Fe (III) / Cr (III) hydroxide [10] red mud and fly ash [11], spent grain [12] silica gel and alumina, processed solid residue of oil mill products, tea-industry waste [13], rice husk ash [14] calcite, hydroxyapatite [15],

\* Corresponding author: givianradh@yahoo.com

nanocrystallite hydroxyapatite [11], amino modified starch [16] olive leaves [17], activated carbon [18], new adsorbents with locally available, high adsorption capacity and economic materials are still needed.

In adsorption processes, adsorbents with high specific surface areas are needed. Small pores, such as micropores and mesopores, result in large specific surface area responsible for adsorption. Pore size, pore distribution and surface area, as well as pore surface chemistry, are the major factors in the adsorption process [19]. Silica aerogels meet these conditions because they are extremely porous (up to 99%) nanostructured materials, showing large specific surface areas (up to  $1000\text{m}^2/\text{g}$ ), an extraordinarily large surface-to-volume rating and low densities ( $0.003\text{--}0.35\text{g}/\text{cm}^3$ ) [20]. Silica aerogels are prepared with sol-gel processing.

The large surface area of activated carbon enables it to efficiently adsorb many kinds of pollutants but activated carbon does not have sufficient functional groups to adsorb heavy metals economically. To overcome this limitation many methods of modifying the activated carbon surface have been introduced using chemical / physical treatment [21].

In the present study, we have prepared a novel nanocomposite silica aerogel activated carbon with sol-gel process at ambient pressure drying method. The adsorbent was characterized by Fourier transform infrared spectrum (FT-IR), Scanning electron microscopy (SEM), Differential scanning calorimetric (DSC) and Nitrogen adsorption / desorption isotherms (BET) on the other hand, we have prepared a novel adsorbent with combining two separate adsorbents and this new adsorbent was used for removal of cadmium from aqueous solutions. Adsorption isotherms on the adsorption of Cd (II) were studied in a batch system. The effects of the cadmium ions concentration, temperature, pH and adsorbent dosage were studied to determine the optimal adsorption conditions.

## EXPERIMENTAL

### Reagents and apparatus

All reagents used in the present study were of analytical grade obtained from Merck and

Aldrich. Tetramethylortho silicate (TMOS-Aldrich), Methyltrimethoxy silane (MTMS-Aldrich), Methanol (MEOH-Merck) 25% wt,  $\text{NH}_4\text{F}$  and the activated carbon used in this study was obtained from Merck too. Deionized water of high purity (from a Millipore ultra-pure water system) was used.

The calibration curve was established using the standard solutions prepared in  $1\text{M HNO}_3$  by dilution from  $1000\text{mg}/\text{L}$  stock solutions (Merck) for pH adjustment (1-7), boric acid, citric acid and sodium phosphate were used.

Concentration of the metal ion solutions was performed by using Varian model spectra AA-240 (Mulgrara, Victoria, Australia). The pH-measurements of metal ion and buffer solutions were carried out by an Orion 420.

### Preparation of Adsorbent

Silica gels doped with methyl groups were synthesized by mixing TMOS, MTMS, Methanol,  $\text{NH}_4\text{F}$  and water. In order to get the best quality aerogels in terms of low density and good hydrophobicity, the molar ratio of TMOS: MTMS: Methanol:  $\text{NH}_4\text{F}$  was 1: 0.31: 33: 3.6 respectively. Silica wet gel was prepared with TMOS as starting material. The TMOS was diluted with Methanol, and then MTMS and  $\text{NH}_4\text{F}$  solution were added to mixture. During the adding of the materials, the mixture was stirring for 30 minutes. The next step was the homogenization of the mixture by homogenizer with 20000 rpm, which during the homogenization; activated carbon was added to mixture. The obtained silica-carbon sol was poured into a glass beaker where the sol was aged into hydrogel within about 10 minutes. After gelation, the gel was left for one day. The hydrogel were immersed into Methanol and aged for 24 hours at room temperature in order to strength its network. Before drying the alcogel, three different methods were used to find the best one.

1. Alcogel was placed in an ordinary Microwave oven with 200 watts of emitting power for 20 seconds and was called sample A.
2. Alcogel was left to remain for 5 days at room temperature and was called sample B.
3. Alcogel was put in the Vacuum desiccators for 48 hours and was called sample C.

Finally, the aged wet gels were dried at 40°C (1 hour), 60°C (1 hour), 80°C (1 hour), 100°C (1 hour), 120°C (1 hour), 150°C (2 hours), and 200°C (1 hour) in an oven. To protect gel from temperature shock and shrinkage, temperature was decreased slowly to the environment temperature.

### Adsorbent characterization

- The infrared spectroscopy measurements were performed (FT-IR, Perkin-Elmer, Spectrum 100) to identify the Vibration frequency in the functional groups of the materials.
- The microstructure and morphology of the materials were observed with scanning electron microscopy (SEM-EDX, XL30 and Philips Nether land).
- Surface area and porosity were defined by Nitrogen adsorption / desorption isotherms of the materials, by a porosimeter, surface analyzer (BET).
- The thermal behavior of the nanocomposite was examined using differential scanning calorimetric (DSC – setsys 24, SETARAM).

### Adsorption experiments

The adsorption of cadmium by the adsorbents was studied by batch technique. The batch mode adsorption was selected due to its simplicity. Cadmium solution (3mg/L was added to 0.1 g of adsorbents. pH of the solution was adjusted to 6.0 using a buffer. The time of mixing was 2 hours and experiments were done at room temperature. After a period of agitation, the suspensions were centrifuged at 8000rpm for 15 minutes. Then the supernatant was collected and analyzed for cadmium concentration by flame atomic adsorption spectrometry.

The effects of several parameters, such as contact time, pH, amount of adsorbent and temperature on the adsorption were also studied. The results of these studies were used to obtain the optimum conditions for adsorption capacity measurements.

The percent of adsorbate removal was calculated using Eq. (1).

$$E(\%) = (C_0 - C_e) \times 100 / C_0 \quad (1)$$

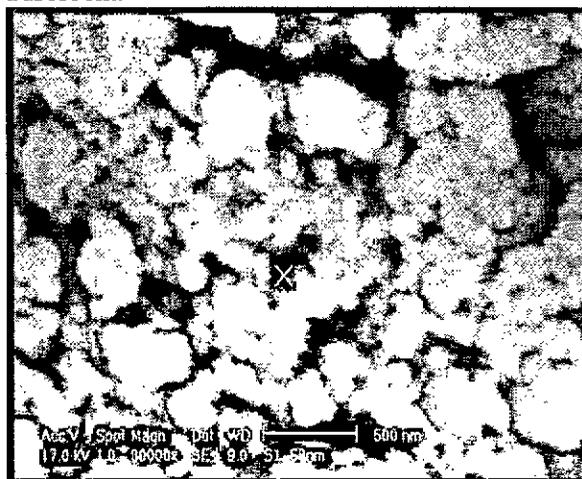
Where E is cadmium ion removal,  $C_0$  initial cadmium concentration and  $C_e$  final equilibrium.

Adsorption isotherms were obtained by mixing 0.1g of adsorbents in a series of flasks containing 20ml of different initial metal ion concentrations for 2 hours. The initial pH was adjusted to 6.0 for Cd (II) ions.

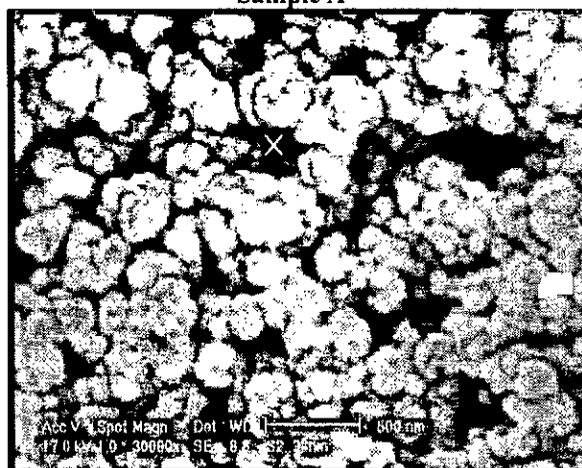
## RESULTS AND DISCUSSION

### Microstructure of nanocomposite

Fig. 1 shows the SEM morphology of the three samples. Sample (A) exhibits a porous network structure. The sizes of particles were 58nm. Sample (B) exhibits a porous network structure such as sample (A); but particles are smaller than sample (A) and are about 38nm. The network structure of sample (C) was not porous enough to be used as an adsorbent. It is obvious that sample (B) has the best network structure for our study, so samples (A) and (C) were not used and we suggest method number two as the proper method for making this kind of adsorbent.



Sample A



Sample B



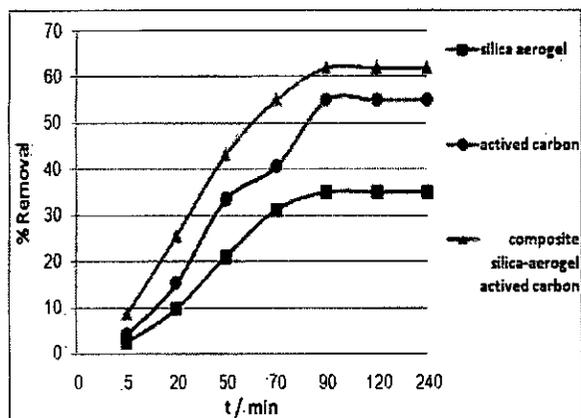


Fig.4. Effect of contact time of Cd (II) ions adsorption on adsorbents, conditions: 20ml of 3mg/ L of cadmium ions, pH 6.0 and 0.1g adsorbent.

### Effect of the amount of adsorbent

To investigate the effect of the various adsorbents dosage on the adsorption, several amounts of adsorbents were tested where masses between 0.02 and 0.5g were used per experiment. The tests were carried out at room temperature and at pH 6.0. The samples were stirred for 120 minutes, centrifuged and then, the supernatant was analyzed by AAS. The results are shown in Fig. 5. The removal percentage of cadmium increased by increasing amount of adsorbent from 0.02-0.10g and fixed at greater amount. The adsorption reached maximum percentage with using 0.10g of adsorbents.

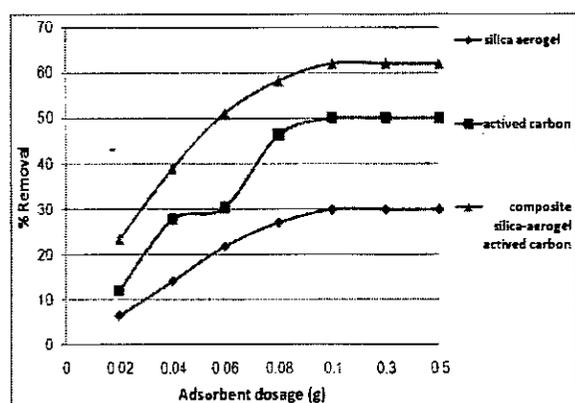


Fig.5. Removal percentages of cadmium ions at different amounts of adsorbent, conditions: 20ml of 3mg/L of cadmium ions, pH 6.0 and agitation time of 120 minutes.

### Adsorption isotherms

The relationship between the amount of a substance adsorbed per unit mass of adsorbent at constant temperature and its concentration in the

equilibrium solution is called the adsorption isotherm. The more common models used to investigate the adsorption isotherm are Langmuir and Freundlich equations [22, 23]. The experimental results of this study were fitted with these two models. The equilibrium adsorption capacity of adsorbent was calculated by the following equation (2).

$$q_e = V(C_0 - C_e) / W \quad (2)$$

Where  $q_e$  is the equilibrium adsorption capacity of adsorbent in mg metal/g adsorbent,  $C_0$  is the initial concentration of the metal ions in mg/L,  $C_e$  is the equilibrium concentration of metal ions in mg/L,  $V$  is the volume of metal ions solution in L, and  $W$  is the weight of the adsorbent in g. The equilibrium adsorption of cadmium ion solutions by nanocomposite was measured (20 ml of 0.25 – 4mg/L Solutions) after equilibrium time.

### Langmuir model

The most widely used Langmuir equation, which is valid for monolayer sorption on a surface with finite number of identical sites, is given by Eq. (3).

$$q_{max} = (q_{max} K_L C_e) / (1 + K_L C_e) \quad (3)$$

Where  $q_{max}$  is the monolayer capacity of the adsorbent (mg/L) and  $K_L$  is the Langmuir equilibrium constant (L/mg). By using the linear form of this isotherm, the plot of  $C_e/q_e$  versus  $C_e$  gives a line with a slope of  $1/q_{max}$  and an intercept of  $1/K_L q_{max}$ . The results showed that the cadmium uptake would not follow the Langmuir adsorption isotherm, since the correlation coefficient is 0.5390.

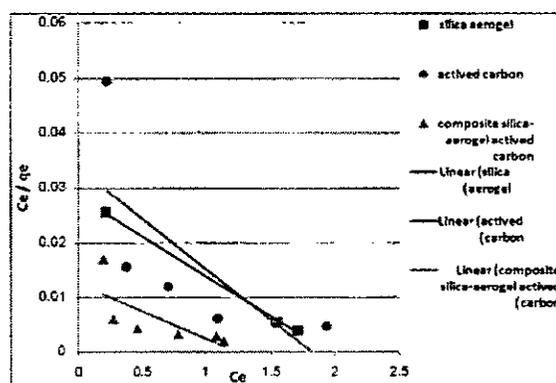


Fig.6. Langmuir adsorption isotherm for cadmium by adsorbents, conditions: 20ml of 3mg/L of cadmium ions, pH 6.0, 0.1g adsorbent and agitation time of 120 minutes.

### Freundlich model

Freundlich equation is derived to model the multilayer adsorption and for the adsorption on heterogeneous surface. The empirical equation used to describe the Freundlich isotherm is given by Eq. (4).

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

Where  $q_e$  (mg/L) is the amount adsorbed at the equilibrium concentration  $C_e$  (mg/L).  $K_F$  is the Freundlich constant (L/g) which represents the strength of the adsorptive bond,  $n$  is the heterogeneity factor, which represents the bond distribution. According to this equation, the plot of the  $\log q_e$  versus  $\log C_e$  gives a straight line and  $K_F$  and  $n$  values can be calculated from the intercept and slope of the straight line, respectively. The results showed that cadmium uptake by nanocomposite would follow Freundlich adsorption isotherm, because the correlation coefficient is 0.9688. Equilibrium adsorption capacity ( $q_e$ ) was found to be 0.384 mg/g in the 3mg/L solution of cadmium.

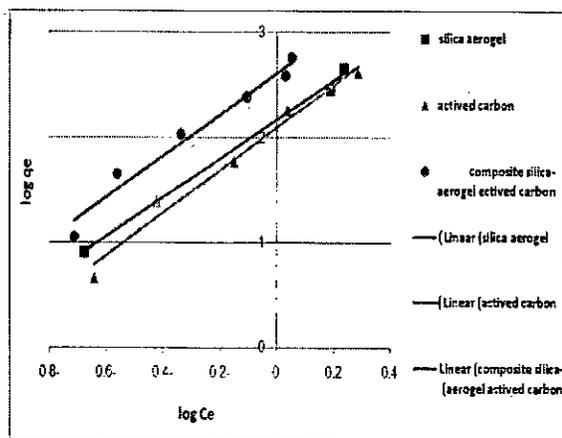


Fig.7. Freundlich adsorption isotherm for cadmium by adsorbents, conditions: 20ml of 3mg/L of cadmium ions, pH 6.0, 0.1g adsorbent and agitation time of 120 minutes.

### Effect of temperature on adsorption

In order to evaluate the influence of temperature on adsorption of cadmium, the experiments were carried out with the temperature range of 20–60°C. For this purpose, 0.1g of each three adsorbents we added to 3 mg/L of cadmium solutions with pH 6.0 and the samples were stirred for 120 minutes. After centrifuging at 8000rpm, it was found that the cadmium uptake increased with increasing of temperature.

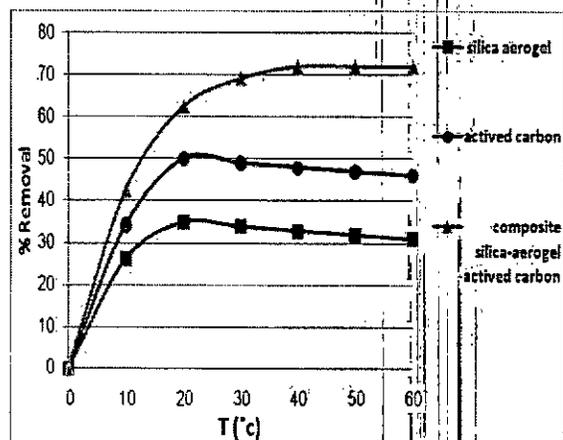


Fig.8. Effect of temperature on adsorption of cadmium ions, conditions: 20ml of 3mg/L of cadmium ions, pH 6.0, 0.1g adsorbent and agitation time of 120 minutes.

### Desorption experiments

In this study, desorption experiments were accomplished for each run. First, nanocomposite was washed by deionized water and dried at 50°C in Oven, and then it was washed by nitric acid. The results revealed that the nanocomposite was remained active, after three runs, and uptake percentage decreased from 64.23 to 36.08 %.

### CONCLUSION

The results of this study show that the nanocomposite silica aerogel activated carbon could be successfully used for removal of cadmium from aqueous solutions. Optimum conditions of adsorption were determined and the most efficient condition for cadmium removal was achieved at pH=6.0. Increasing the concentration of cadmium showed an increase of the uptake capacity of the composite. The Freundlich isotherm model was recognized more suitable than Langmuir isotherm to fit the obtained equilibrium. Furthermore, the adsorption process was realized more favorable at high temperatures (60°C). Desorption experiments showed that even after three adsorption-desorption of cycles the composite could be reused without significant losses of its initial properties. The adsorption capacity of the nanocomposite is higher than silica aerogel and activated carbon, since the results showed that using this nanocomposite adsorbent, activated carbon, and silica aerogel could remove more

than 60, 50, and 30% of Cd under optimum experimental conditions, respectively.

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