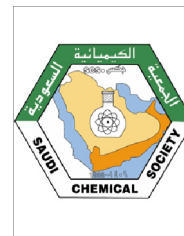




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ORIGINAL ARTICLE

Preparation and characterization of nanocomposite, silica aerogel, activated carbon and its adsorption properties for Cd (II) ions from aqueous solution

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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 the 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 concentrations, 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 the corresponding adsorbent dosage level of 0.1 g at 60 °C temperature. Subsequently, the equilibrium was achieved for Cd with 120 min of contact time.

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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, in which the adsorption equilibrium data were correlated well with the Freundlich isotherm model and the equilibrium adsorption capacity (q_e) was found to be 0.384 mg/g in the 3 mg/L solution of cadmium.

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1. Introduction

Heavy metal pollution is a common environmental problem facing many places worldwide with the rapid development of economies and industries (Suzuki et al., 1997).

Numerous metals such as mercury, lead, cadmium, etc. are known to be highly toxic. Cadmium like other heavy metals can be introduced into surface waters in amounts significant to human health by industrial effluents (Hammer, 1996).

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 (Poon, 1986; Volesky, 1990; Wase and Forster, 1997).

Cadmium is a naturally occurring metal and is known to be extremely toxic in any of its different chemical forms such as chloride, sulfate, sulfide, carbonate, oxide, and others (Mahmoud and Haggag, 2011).

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 the human body (Amoyaw et al., 2009). Cd can cause serious damage to the liver and kidneys such as emphysema, bone disorders, cancer (Ramos et al., 1997; Hajiaghababaei et al., 2010), hypertension and testicular atrophy; it combines with the sulfhydryl group in protein and restrains the activity of enzymes (Chen et al., 2008).

The methods used to remove heavy metal ions are chemical precipitation, ion exchange mechanism (Rengaraj et al., 2002; Zhao et al., 2002; Peric et al., 2004), complexation using natural and synthetic reagents (Vermeer et al., 1999; Brown et al., 1999; Saitoh et al., 2003), reverse osmosis, electro dialysis, electro chemical reduction membrane processes, adsorption layer-by-layer chemical deposition technique (Mobasherpour et al., 2011), etc. adsorption process is the most frequently applied method in industries (Rengaraj et al., 2002).

Various materials have been reported to remove cadmium from waste waters, natural soils (Serrano et al., 2005; Shaheen, 2009) minerals (Asci et al., 2007; Wang et al., 2009), tailing wastes and biomasses (Goel et al., 2006; Ozer and Pirincci, 2006; El-Shafey, 2007; Shin et al., 2007), waste Fe (III)/Cr (III) hydroxide (Namasivayam and Ranganathan, 1995) red mud and fly ash (Mobasherpour et al., 2011), spent grain (Low et al., 2000) silica gel and alumina (El-Shafey, 2007), processed solid residue of oil mill products (Shaheen, 2009), tea-industry waste (Butterman and Castaldi, 2007), rice husk ash (Li et al., 2009) calcite, hydroxyapatite (Shen and Gu, 2009), nanocrystallite hydroxyapatite (Mobasherpour et al., 2011), amino modified starch (Xie et al., 2011) olive leaves (Hamdaoui, 2009), activated carbon (Mu and Tang, 2002; Youssef et al., 2004; Kannan and Rengasamy, 2005; Ahn et al., 2009), 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 a 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 (Yang, 2003). Silica aerogels meet these conditions because they are extremely porous (up to 99%) nanostructured materials, showing large specific surface areas (up to 1000 m²/g), an extraordinarily large surface-to-volume rating and low densities (0.003–0.35 g/cm³) (Kistlers, 1931). Silica aerogels are prepared with sol-gel processing.

The large surface area of activated carbon enables it to efficiently adsorb many kinds of pollutants (McKay et al., 1985, 1986) 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 (Ahn et al., 2009).

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 by combining two separate adsorbents and this new adsorbent was used for the 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.

2. Materials and methods

2.1. Materials

All the 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, NH₄F 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 M HNO₃ by dilution from 1000 mg/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 determined by using the Varian model spectra AA-240 (Mulgrara, Victoria,

Australia). The pH-measurements of the metal ion and buffer solutions were carried out by an Orion 420.

2.2. Preparation of adsorbent

Silica gels doped with methyl groups were synthesized by mixing TMOS, MTMS, Methanol, NH_4F 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: NH_4F was 1:0.31:33:3.6, respectively. Silica wet gel was prepared with TMOS as the starting material. The TMOS was diluted with Methanol, and then MTMS and NH_4F solution were added to the mixture. During the adding of the materials, the mixture was stirred for 30 min. The next step was the homogenization of the mixture by a homogenizer at 20000 rpm and during the homogenization, activated carbon was added to the mixture. The obtained silica-carbon sol was poured into a glass beaker where the sol was aged into hydrogel within about 10 min. After gelation, the gel was left for one day. The hydrogel were immersed into Methanol and aged for 24 h at room temperature in order to strengthen 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 W of emitting power for 20 s 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 h and was called sample C.

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

2.3. 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).

2.4. Adsorption experiments

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

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

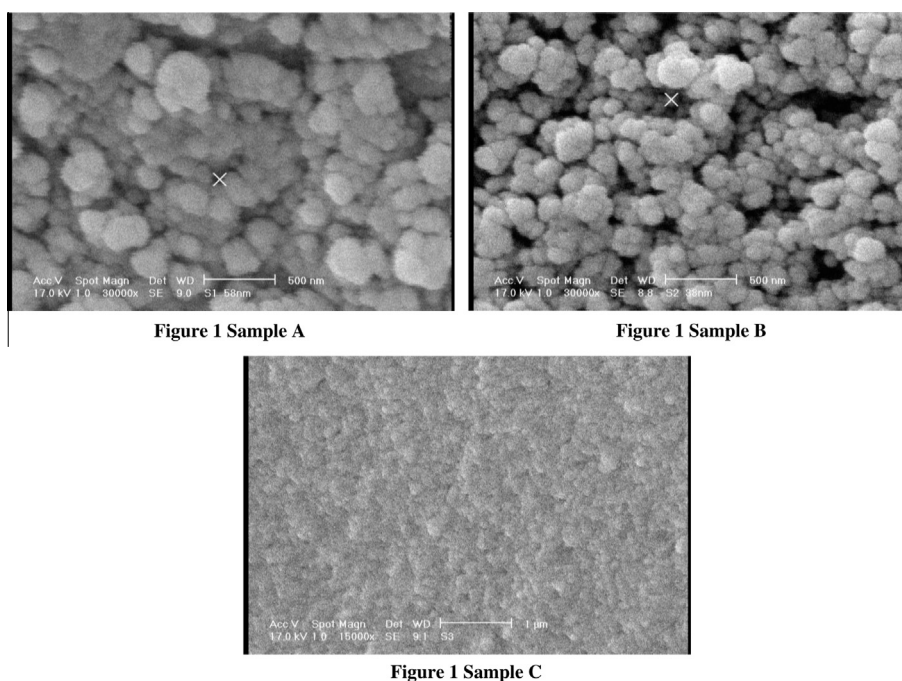


Figure 1 SEM of samples A, B, and C.

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

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

3. Results and discussions

3.1. Properties of nanocomposite silica aerogel activated carbon

3.1.1. 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 58 nm. Sample (B) exhibits a porous network structure such as sample (A); but the particles are smaller than sample (A) and are about 38 nm. 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.

3.1.2. BET specific surface measurement

Specific surface area of sample (B) is $916.4204 \text{ m}^2/\text{g}$ and total surface area is 8.7060 m^2 that were determined by nitrogen physisorption at 24.85°C .

3.1.3. Infrared spectrum of the nanocomposite

The FTIR investigation of the nanocomposite is shown in Fig. 2. On FTIR spectrum of sample B peaks around 2900 and 1460 cm^{-1} , which are due to C - H bonds are also observed and only the small peaks at around 3500 and 1630 cm^{-1} are the evidence of O-H bondings. The peaks at

around 1100 , 800 and 470 cm^{-1} are due to asymmetric, symmetric and the bending modes of SiO_2 , respectively.

3.1.4. Thermal analysis of nanocomposite

There is very little weight loss up to a temperature of 300°C . A further increase of temperature causes weight loss along with exothermic peaks corresponding to the oxidation of surface organic (CH_3) groups. This is the reason why samples become hydrophilic after heating above a temperature of around 300°C .

3.2. Effect of pH

The pH of the solution plays an important role in the whole adsorption process and particularly on the adsorption capacity as the sorbent surface creates positive or negative charge on its surface depending on the solution pH.

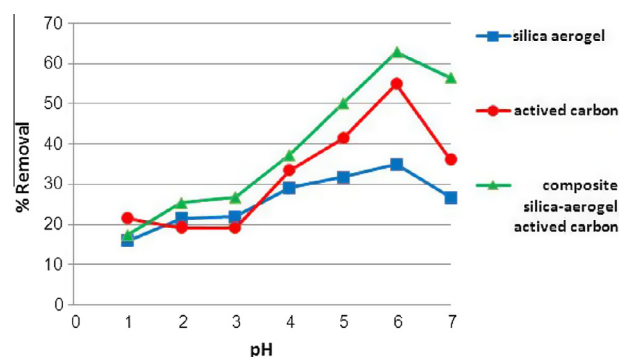


Figure 3 Effect of pH on adsorption of cadmium ions on the adsorbents, conditions: 0.1 g adsorbent, 20 ml of 3 mg/L of cadmium ions, agitation time of 24 h.

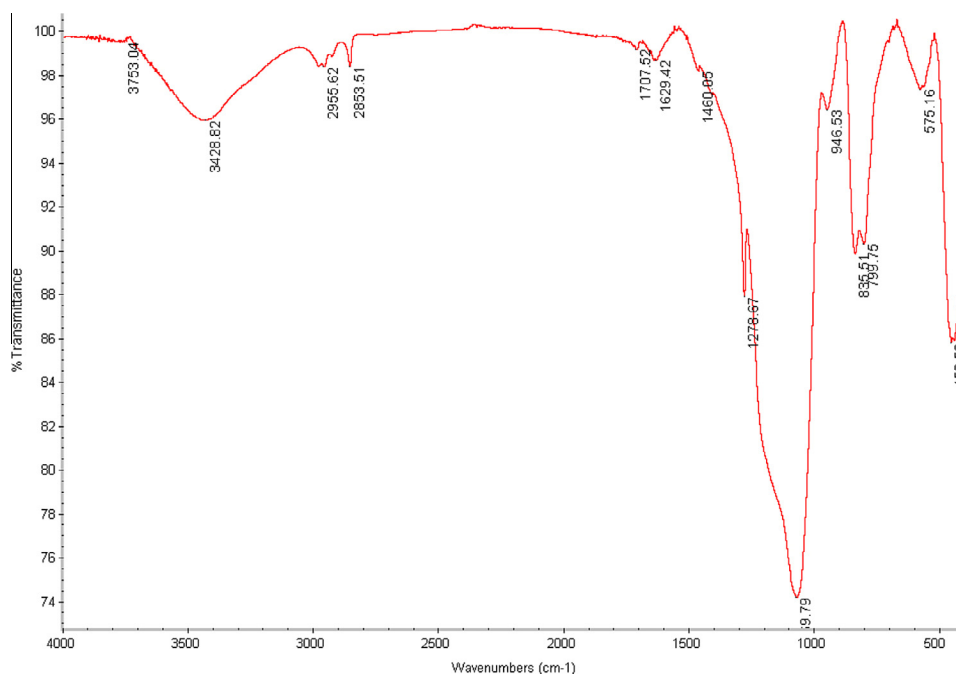


Figure 2 FT-IR Spectrum of the Nanocomposite

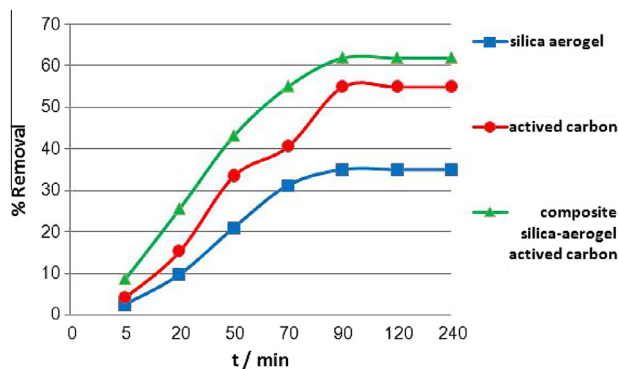


Figure 4 Effect of contact time of Cd (II) ions adsorption on adsorbents, conditions: 20 ml of 3 mg/L of cadmium ions, pH 6.0 and 0.1 g adsorbent.

In order to evaluate the influence of pH on sorption of cadmium, the experiments were carried out with the pH range of (1–7), which are shown in Fig. 3.

For this purpose, 0.1 g of adsorbents was added to 3 mg/L cadmium solutions where the pH was adjusted using boric acid, citric acid and sodium phosphate. These samples were stirred for 24 h at 175 rpm. Then the samples were centrifuged at 8000 rpm for 15 min at room temperature. Removal of Cd (II) increases with increasing pH and a maximum value was found at pH 6.0.

In acid medium, the competition between ion metals and protons causes the weak adsorption and in basic medium, precipitation of metal cations occurs because of the forming of hydroxides metals.

Therefore, in this study, all adsorption experiments are conducted at pH 6.0 in order to prevent precipitation and maximize cadmium sorption onto the adsorbents.

3.3. Effect of contact time

Adsorption reactions for adsorbents were carried out using 20 ml solution containing 3 mg/L of cadmium and 0.1 g of adsorbent at room temperature with pH adjusted to 6.0. Fig. 4 shows cadmium uptake capacity at different time intervals, 5 min until 240 min.

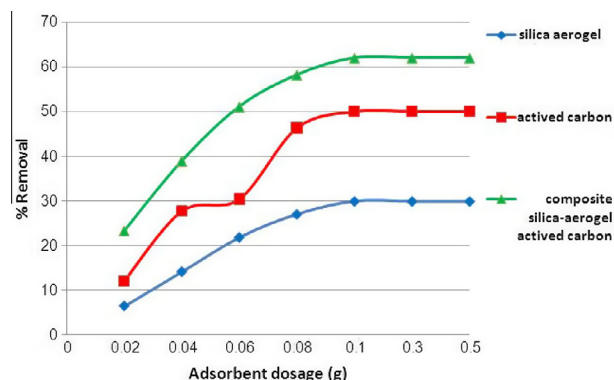


Figure 5 Removal percentages of cadmium ions at different amounts of adsorbent, conditions: 20 ml of 3 mg/L of cadmium ions, pH 6.0 and agitation time of 120 min.

The results of analysis show that after around 90 min the adsorbents removed 60% of cadmium from the solution. Therefore, the optimum value was considered to be 90 min, but to guarantee the maximum adsorption and a complete equilibrium condition, the subsequent experiments were performed with 120 min of contact time.

3.4. 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 0.5 g were used per experiment. The tests were carried out at room temperature and at pH 6.0. The samples were stirred for 120 min, centrifuged and then, the supernatant was analyzed by AAS. The results are shown in Fig. 5. The removal percentage of cadmium increased by increasing the amount of adsorbent from 0.02 to 0.10 g and fixed at greater amount. The adsorption reached maximum percentage with using 0.10 g of adsorbents.

3.5. Effect of initial Cd concentration

The cadmium adsorption capacity of the adsorbents has been studied as a function of the initial concentration. The cadmium ion concentrations were between 0.25 and 4 mg/L the pH of the solutions was adjusted to 6.0, the experiments were performed at room temperature, and the cadmium concentration was measured after 2 h of contact. It was found that an increase in cadmium concentration leads to an increase in adsorption capacity of cadmium by adsorbents.

This increase in adsorption capacity with relation to the Cd (II) ion concentration could be explained with the high driving force for mass transfer.

3.6. 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 (Langmuir, 1918; Freundlich and Heller, 1939). The experimental results of this study were fitted with these two models. The equilibrium adsorption capacity of the adsorbent was calculated by the following Eq. (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 0.25–4 mg/L Solutions) after equilibrium time.

3.6.1. 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).

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

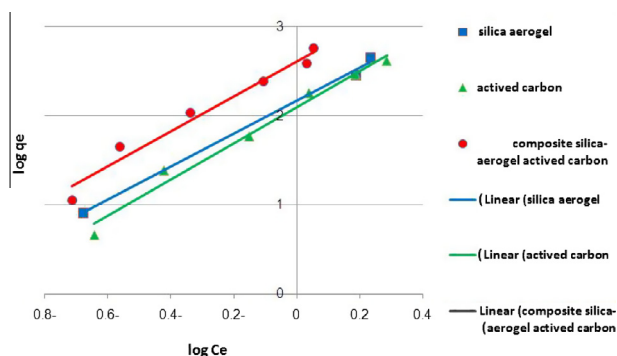


Figure 6 Freundlich adsorption isotherm for cadmium by adsorbents, conditions: 20 ml of 3 mg/L of cadmium ions, pH 6.0, 0.1 g adsorbent and agitation time of 120 min.

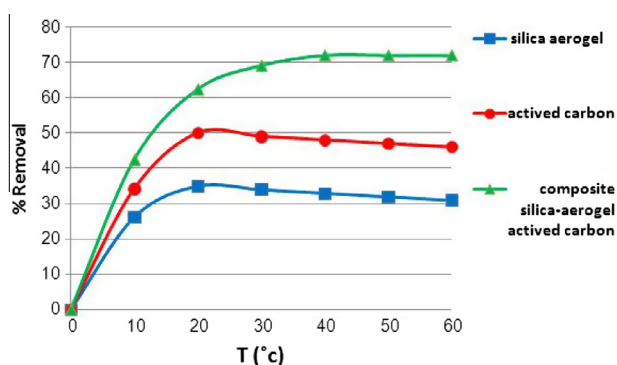


Figure 7 Effect of temperature on adsorption of cadmium ions, conditions: 20 ml of 3 mg/L of cadmium ions, pH 6.0, 0.1 g adsorbent and agitation time of 120 min.

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.

3.6.2. 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 correla-

tion coefficient is 0.9688, which is shown in Fig. 6. Equilibrium adsorption capacity (q_e) was found to be 0.384 mg/g in the 3 mg/L solution of cadmium.

3.7. 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, 0.1 g of each of the three adsorbents were added to 3 mg/L of cadmium solutions with pH 6.0 and the samples were stirred for 120 min. After centrifuging at 8000 rpm, it was found that the cadmium uptake increased with increasing of temperature, which is shown in Fig. 7.

3.8. 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 remained active, after three runs, and uptake percentage decreased from 64.23% to 36.08 %.

4. Conclusions

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 chosen because there were considerable differences between the coefficients of determination (R^2) of these two isotherms (0.9688 versus 0.5390); subsequently the Freundlich isotherm model was chosen from the statistical point of view. On the other hand, the good results were achieved in low concentration of cadmium with Freundlich isotherm than the Langmuir isotherm from the analytical point of view. The Freundlich isotherm model was recognized as more suitable than the Langmuir isotherm to fit the obtained equilibrium. Furthermore, the adsorption process was realized as more favorable at high temperatures (60 °C). Desorption experiments showed that even after three adsorption-desorption 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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