

Preparation of Nanoporous Silica Aerogel from Wheat Husk Ash by Ambient Pressure Drying Process for the Adsorptive Removal of Lead from Aqueous Solution

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Abstract

Hydrophilic nanoporous silica aerogels were synthesized from a low-cost wheat husk silica precursor via ambient pressure drying method for the first time. The prepared aerogels were characterized by using Fourier transform infrared spectra (FTIR), nitrogen adsorption/desorption measurement and scanning electron microscopy- energy dispersive X-ray (SEM-EDX) techniques. The aerogels were used in adsorption of lead (II) ions from aqueous solutions under various conditions such as pH, the adsorbent dosage, the initial lead (II) concentration and the contact time. The optimum adsorption efficiency (99%) was obtained in a pH of 5.5, adsorbent dosage of 4 g L⁻¹, initial lead concentration of 50 mg mL⁻¹ and contact time of 30 minutes. The adsorption data was well described by Langmuir isotherm and pseudo-second-order kinetic model. These results show that low-cost silica aerogel prepared from an agricultural waste can be used as an effective sorbent for lead (II) ions removal.

Keywords Adsorption; Biomass waste; Biosilica; Lead; Silica aerogel; Wheat husk

Introduction

Lead has a widespread application in several industries due to its low melting point, high malleability, softness, and corrosion resistance. This resulted in the existing of free lead in wastewater streams. Lead contamination in water has been a seriously concerned matter all around the world since it induces various health problems, such as anemia, chills, diarrhea, headache, and also affects the central nervous and reproductive systems [1,2]. Therefore, the elimination of lead from water has significance for the prevention of diseases. Several techniques including electrochemical coagulation, electrochemical precipitation, floatation, ion exchange and solvent extraction have been investigated for removal of lead [3]. Among the physicochemical techniques, adsorption is the simplest and cheapest practicable alternative which has been extensively utilized in the treatment of contaminated waters [4,5].

The development of nanoporous advanced materials is an important issue due to the demand for the development of more effective sorbent with fast adsorption rate and high adsorption capacity [6,7]. Carbon based adsorbents such as activated carbon and graphite, and inorganic materials such as clays, silica and zeolites are mostly used as water purification agents. Moreover, the evaluation of silica aerogels as a sorbent for removal of various pollutants has an intensified interest in the last decade because of their unique physicochemical features such as adjustable surface chemistry, high surface area, high porosity and nano-sized pores [8,9].

Traditional production of silica aerogels comprises pricey precursors such as silicon alkoxides (e.g. tetramethoxysilane and tetraethoxysilane) and supercritical drying [10]. The high production

cost is the main drawback of the large-scale commercialization of aerogels. Therefore, the improvement of ambient drying route [11] and the evaluation of low-cost raw materials such as water-glass [12] and agricultural wastes [13, 14] is an ongoing task. Wheat husk which is generally assumed as a waste product of wheat milling contains amorphous silica [15]. A significant amount of wheat husk ash is created in cogeneration plants which resulted in a disposal problem due to having no convenient treatment procedure. Wheat husk ash can be evaluated as a cheap practical source for the synthesis of silica-based materials [16-18].

This study investigates the probability of silica aerogel prepared using a new biosilica source (wheat husk) as an adsorbent to remove lead (II) ions from aqueous solutions. Batch experiments were carried out to determine the effect of several parameters such as pH, adsorbent dosage, initial lead (II) concentration and contact time on the adsorption of metal ions onto silica aerogel. The adsorption equilibrium data was evaluated by Langmuir, Freundlich and Dubinin-Radushkevich isotherm models.

Materials and Methods

Materials

The wheat husk samples were obtained from Doruk Marmara Flour Factory in Tekirdağ (Turkey). The sodium hydroxide (NaOH), hydrochloric acid (HCl) and lead (II) nitrate (Pb(NO₃)₂) were purchased from Sigma-Aldrich (Steinheim, Germany). Tetraethoxysilane (TEOS) and n-heptane were purchased from Merck (Darmstadt, Germany). Deionized water was used to prepare all the solutions.

Preparation of silica aerogel

The sodium silicate solution was prepared from acid leached wheat husk according to the method of Terzioglu et al. [18]. Silica aquagel was prepared by adjusting the pH of the sodium silicate solution to 6 by the addition of hydrochloric acid. The aquagel was aged for 1 day at room temperature. After ageing, the gel was washed three times with distilled water to remove sodium salt (NaCl). A solution of ethanol in water (80%, v/v) was used to replace the pore water of gel by ageing for 1 day at room temperature. The ageing was proceeded with 70% (v/v) TEOS in ethanol solution for 17 hours at room temperature and 4 hours at 70°C. The n-heptane was used to remove TEOS-ethanol solution present in the gels and the gel was aged for 1 day at room temperature. The ageing step was repeated twice with fresh n-heptane. Finally, the prepared gels were centrifuged (5 minutes, 4800 rpm) and dried at 60°C, 70°C and 80°C with 6 hour intervals in air dryer (Elektromag M420P, Turkey).

Characterization of silica aerogel derived from wheat husk

The surface area, pore size, micropore volume, mesopore volume and single point total pore volume of the silica aerogels were analyzed using a Specific Surface Area and Pore Size Distribution Analyzer (Micromeritics, TriStar II 3020) at 77 K. The Brunauer-Emmett-Teller (BET) method was used to estimate the specific surface area of aerogels. Pore size and pore volume was calculated using Barrett-Joyner-Halenda (BJH) method. The chemical structure of initial and lead adsorbed aerogels was characterized by FT-IR (Shimadzu IR Prestige 21, Kyoto, Japan) instrument in the wave number range of 650 to 4000 cm^{-1} . The morphology of the aerogels before and after adsorption was determined with a JEOL JSM-7600 F scanning electron microscope (SEM).

Adsorption of lead (II) ions

The batch adsorption experiments were carried out in a 100 mL stoppered conical flasks containing 25 mL of lead (II) solution with desired concentration. The desired concentration of lead(II) solution was prepared by diluting the stock solution (250 mg L^{-1}) which was obtained by dissolving $\text{Pb}(\text{NO}_3)_2$ (Sigma-Aldrich) in distilled water. The pH of the suspension was adjusted by adding dilute NaOH or HCl

solution. The suspensions were then shaken at 160 rpm in a water bath shaker (Memmert WBN 7–45) at 25°C for 60 minutes. All adsorption experiments were conducted at various pHs (2–6), adsorbent dosages (0.025–0.125 grams), initial lead concentrations (50–87.5 mg L^{-1}). The effect of contact time was determined at various time intervals (10–90 minutes). The final concentration of lead(II) ions in the solution were analyzed using an Atomic Absorption Spectrometer (Agilent 240FS AA Fast Sequential) with an air-acetylene flame (2.00/13.50 L min^{-1}) and a hollow cathode lamp at 217 nm. The adsorption amount of lead (II) adsorbed by silica aerogel (q , mg g^{-1}) was calculated according to the following equation:

$$q = \frac{(C_0 - C_e)}{W} \times V$$

Where q is the adsorption capacity at equilibrium (mg g^{-1}), V is the volume of the solution (L), W is the weight of adsorbent (g), C_0 and C_e are the initial and final concentration of lead (II) (mg L^{-1}), respectively. All experiments were conducted for three times, and arithmetic averaged results were presented.

The lead (II) removal efficiency was calculated as follows:

$$\text{Removal (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100$$

Results and Discussion

Characterization of adsorbent

The BET surface area and the micropore surface area for the aerogel were measured to be 328.88 and 24.61 $\text{m}^2 \text{g}^{-1}$, respectively. Total pore volume and micropore volume of aerogel were found to be 0.968 and 0.010 $\text{cm}^3 \text{g}^{-1}$, respectively. According to the ISO/TS 80004-1:2010 from the International Organization for Standardization, the prepared aerogels were nanoporous materials due to the average pore diameter results (10.12 nm). Nayak and Bera [19], synthesized silica aerogel from rice husk in the presence of nitric acid at pH 6 using ambient pressure drying method. The surface area (273 $\text{m}^2 \text{g}^{-1}$) of rice husk silica aerogel was found to be lower than the surface area of aerogel (328.88 $\text{m}^2 \text{g}^{-1}$) obtained in this study (Table 1).

Property	Silica Aerogel
BET surface area ($\text{m}^2 \text{g}^{-1}$)	328.88
Micro pore surface area ($\text{m}^2 \text{g}^{-1}$)	24.61
Total pore volume ($\text{cm}^3 \text{g}^{-1}$)	0.968
Micro pore volume ($\text{cm}^3 \text{g}^{-1}$)	0.010
Average pore diameter (nm)	10.12

Table 1: The textural properties of wheat husk silica-based aerogel.

The SEM micrographs of aerogel before and after lead (II) ions adsorption are presented in Figure 1. The surface of aerogel was rough (Figure 1). It is already reported that this phenomenon promotes the heavy metal adsorption [20,21]. It is clear from the SEM images that the surface morphology of lead (II) ions adsorbed aerogel was different from the surface of initial aerogel. Moreover, the EDX results

confirmed that the Pb^{2+} ions were adsorbed onto the surface of adsorbent (Figure 1).

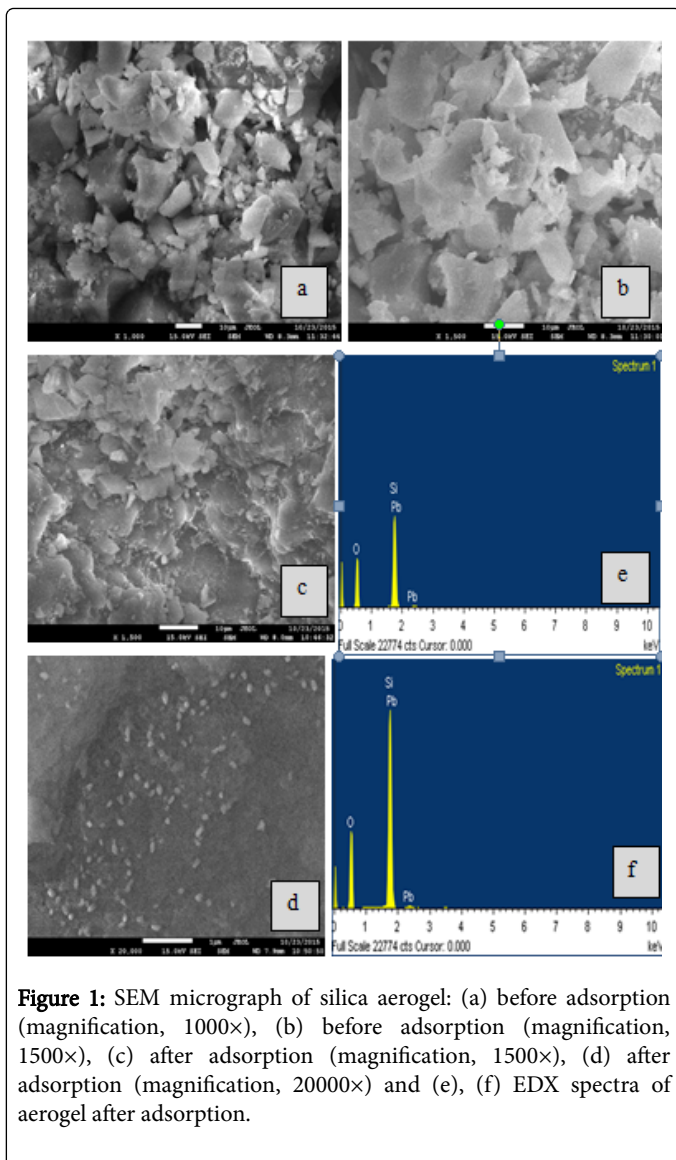


Figure 1: SEM micrograph of silica aerogel: (a) before adsorption (magnification, 1000 \times), (b) before adsorption (magnification, 1500 \times), (c) after adsorption (magnification, 1500 \times), (d) after adsorption (magnification, 20000 \times) and (e), (f) EDX spectra of aerogel after adsorption.

The FT-IR spectra of aerogel before and after lead (II) ions adsorption are shown in Figure 2. The characteristic peaks of Si-OH stretching mode (945 cm^{-1}), Si-O-Si asymmetric bond stretching (1059 cm^{-1}), Si-O-Si symmetric bond stretching (796 cm^{-1}) vibrations were observed for silica aerogel. The small absorption peaks at 2926 and 2858 cm^{-1} assigned to $-\text{OC}_2\text{H}_5$ terminal group [19]. Additionally, the band at 3417 cm^{-1} and 1632 cm^{-1} represented the -OH stretching vibrations.

he FT-IR spectrum of aerogel after lead (II) adsorption (Figure 2a, 2b) showed that the intensity of Si-O-Si group at 1059 cm^{-1} decreased which indicated that this group had a significant role in the lead (II) binding. After adsorption, the absorption peak at 1632 cm^{-1} of aerogel was slightly shifted to higher wave number of 1643 cm^{-1} , while the peaks at 3417 cm^{-1} and 2858 cm^{-1} of aerogel were slightly shifted to lower wave number of 3354 cm^{-1} and 2854 cm^{-1} , respectively. he shift and decrease in intensity of peaks belong to functional groups of -OH and $-\text{OC}_2\text{H}_5$ also evidence of complexation of the groups with lead (II) ions.

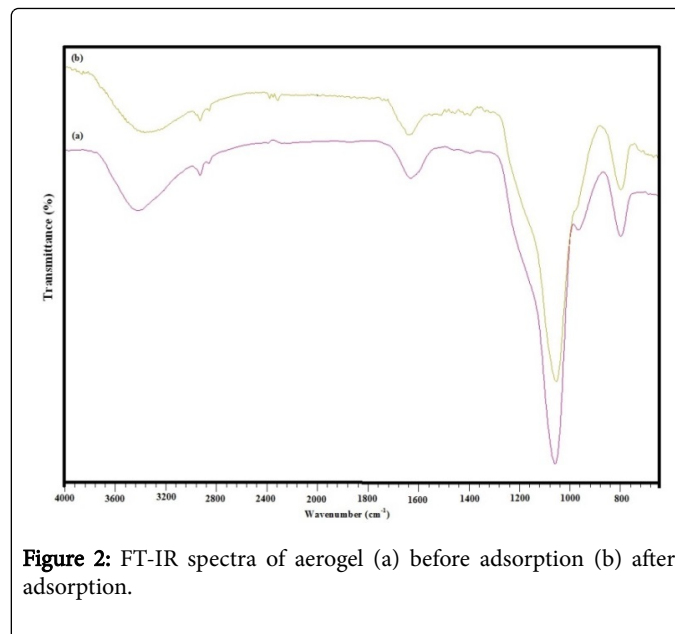


Figure 2: FT-IR spectra of aerogel (a) before adsorption (b) after adsorption.

Effect of pH

The pH of the aqueous solution is a significant parameter controlling the uptake of heavy metals on the adsorbents. The effect of pH on the percentage removal of lead by silica aerogel is shown in Figure 3. As expected, the adsorption increased with the increment of pH from 2 to 6. The maximum removal efficiency was found to be 99% at pH 5.5. At low acidic conditions such as pH 2, lead (II) ions cannot reach the adsorption sites because the surface of silica aerogel may completely covered with H^+ ions [22]. Therefore, an electrostatic repulsion actualized between the lead (II) ions and the positively charged surface edge groups of aerogel. At alkaline conditions, lead precipitation occurred and adsorbent was disturbed with aggregation of lead ions [23]. Thus, further studies were executed with the optimal pH value 5.5.

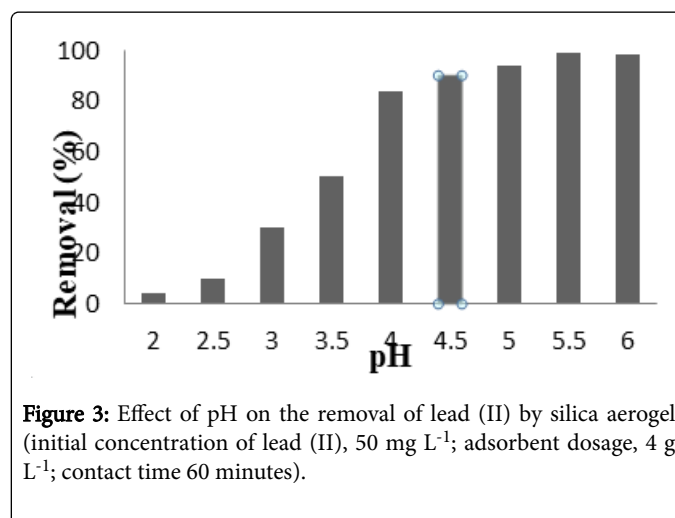


Figure 3: Effect of pH on the removal of lead (II) by silica aerogel (initial concentration of lead (II), 50 mg L^{-1} ; adsorbent dosage, 4 g L^{-1} ; contact time 60 minutes).

Effect of adsorbent dosage

The ratio of adsorbent and the aqueous solution was clearly an important parameter affecting the adsorption efficiency. The results for

the percentage removal of lead (II) with respect to adsorbent dosage are given in Figure 4. It was observed that the removal efficiency was increased with increasing adsorbent dose. The removal efficiency was increased from 60 to 99% with the increment of adsorbent dose from 0.025 to 0.1 mg. The percentage adsorption reached maximums when the experiments carried out using 0.1 mg adsorbent. Further increment of the adsorbent dose did not affect the removal efficiency. The enhanced removal efficiency with increased adsorbent dose is related to the greater availability of surface area or vacant exchangeable sites [24,25], however, high adsorbent dosages are ineffective when the adsorption reaches equilibrium [26].

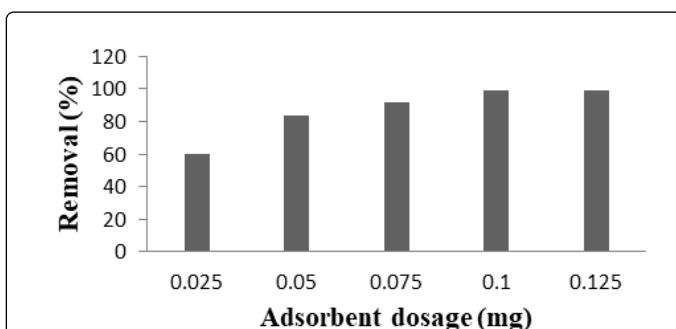


Figure 4: Effect of pH on the removal of lead (II) by silica aerogel (initial concentration of lead (II), 50 mg L⁻¹; contact time 60 minutes; pH value 5.5).

Effect of initial lead (II) concentration

The initial heavy metal concentration is one of the most important variables on adsorption process. Therefore, the removal of lead (II) ions as a function of initial metal concentrations was also investigated at room temperature. The effect of initial lead (II) concentration on removal efficiencies is shown in Figure 5. From the results, it is revealed that the percentage of metal removal was decreased, within the increase of initial lead (II) concentration. This could be explained by the high ratio of the surface active sites to the whole metal ions in the solution at low ion concentrations which provides the interaction of majority of metal ions with the adsorbent [27].

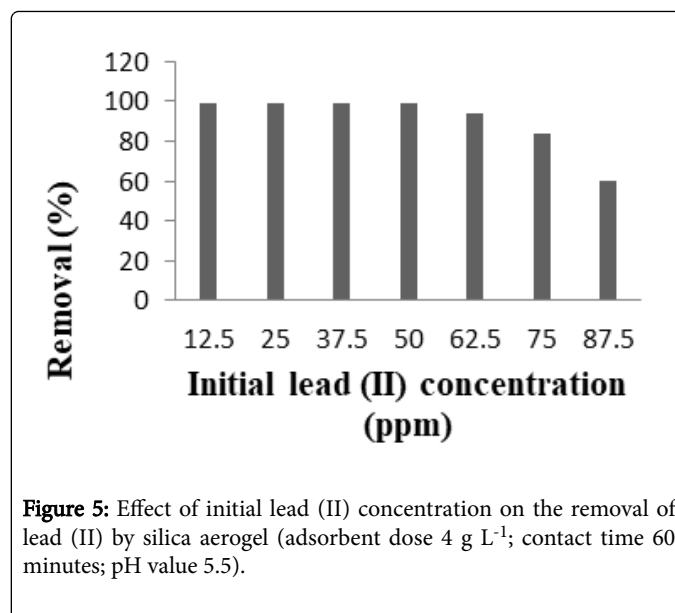


Figure 5: Effect of initial lead (II) concentration on the removal of lead (II) by silica aerogel (adsorbent dose 4 g L⁻¹; contact time 60 minutes; pH value 5.5).

Effect of contact time

It is important to determine the suitable contact time to optimize adsorption process. It was found that the aerogel removed 94.14% of lead (II) in the first 10 minutes of reaction time. The adsorption reached equilibrium at 60 minutes with a 99% lead (II) adsorption (Figure 6) then attained a constant value. The results indicate that the lead (II) removal increased initially as the contact time increased and then and no marked alterations were monitored for higher contact times. Similar results were proposed in the earlier studies for the removal of many heavy metals on various adsorbents [28-30].

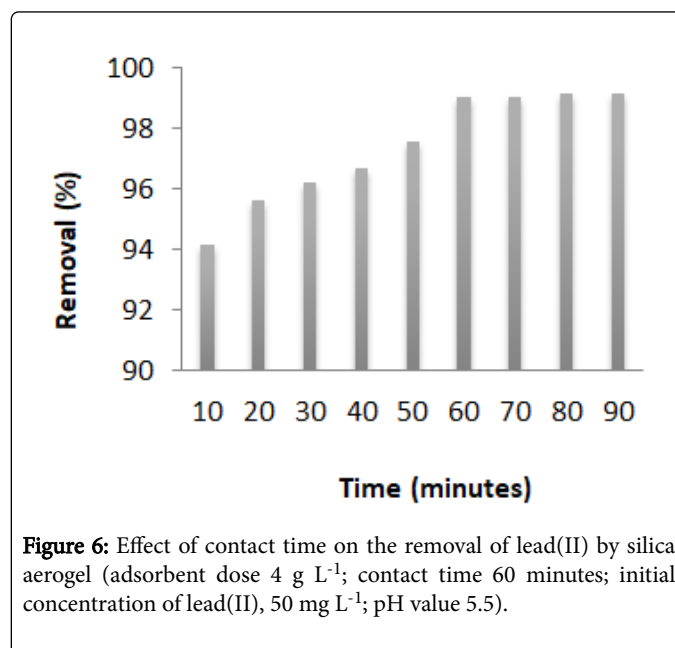


Figure 6: Effect of contact time on the removal of lead(II) by silica aerogel (adsorbent dose 4 g L⁻¹; contact time 60 minutes; initial concentration of lead(II), 50 mg L⁻¹; pH value 5.5).

Determination of adsorption isotherms

Three isotherm models were applied to evaluate the appropriate correlation of adsorption data namely, Langmuir, Freundlich and

Dubinin-Radushkevich adsorption isotherm equations. The parameters and correlation coefficients of isotherm models. It is apparent that the correlation coefficient of the Langmuir isotherm is higher than that of the Freundlich and Dubinin-Radushkevich isotherm. Accordingly, it demonstrates that Langmuir equation could well explicate the removal of lead (II) ions by silica aerogel. The better fit of lead (II) adsorption data with the Langmuir isotherm was reported earlier by Pouretedal and Kazemi [31]. Moreover, the RL value was found to be 0.060 for the initial lead (II) concentration value of 50 mg L⁻¹. The RL value ($0 < RL < 1$) indicating that the type of isotherm was very favorable [32].

When the result of Freundlich characteristic constant (n) for the adsorption system was evaluated, it was determined that the sorption of lead (II) ions onto silica aerogel was physical because the n value (2.55) was between 1 and 10 [33]. The $1/n$ value was lower than 1 indicating that the adsorption intensity of lead (II) onto silica aerogel was favourable at higher concentrations [34]. Moreover, the KF was found to be 109.110 L g⁻¹.

In the Dubinin-Radushkevich isotherm the q_m and β was found to be 1.59 mmol g⁻¹ and $6.00 \cdot 10^{-9}$ mol² J⁻², respectively.

The sorption energy can be calculated using the following equation:

$$E = \frac{1}{\sqrt{-2\beta}}$$

The mean free energy of sorption, E was 0.280 kJ mol⁻¹ which was lower than 8 kJ mol⁻¹ showing the physical nature of adsorption process [33]. The E had a positive value suggesting that the sorption process is endothermic and also it was pointing that the sorption process is more convenient at high solution temperatures [34] (Figure 7). It can be proposed that sorption of lead (II) on silica aerogel was a physisorption process due to sorption energy was less than

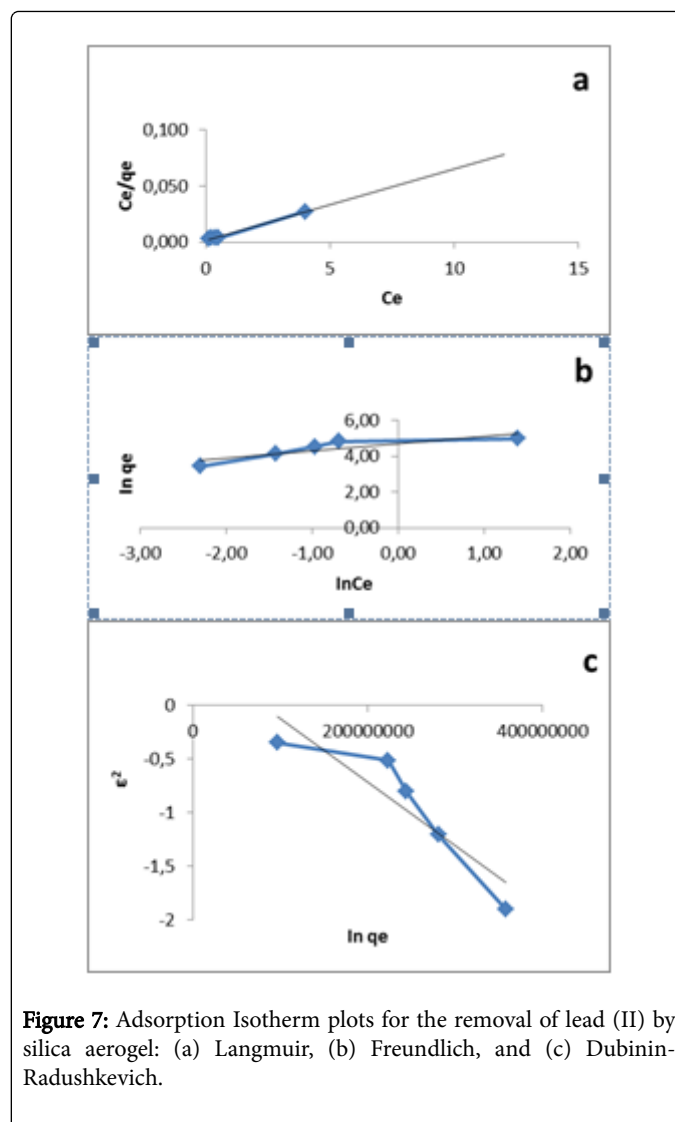


Figure 7: Adsorption Isotherm plots for the removal of lead (II) by silica aerogel: (a) Langmuir, (b) Freundlich, and (c) Dubinin-Radushkevich.

Conclusions

Nanoporous silica aerogel has been successfully prepared from wheat husk silica by ambient pressure drying method. The aerogel appears to be a suitable agent for the elimination of a heavy metal cation (Pb^{2+}) from aqueous solutions. The potent parameters were examined for the removal of lead (II) by silica aerogel. It showed an excellent removal capacity toward lead (II) ions (47.07 mg g^{-1}) in a short time (10 minutes). Using equilibrium data of lead sorption on silica aerogel, the adsorption process better fitted to the Langmuir as compared to the Freundlich and Dubinin-Radushkevich isotherm models. Based on the results, wheat husk silica can be utilized to produce advanced adsorbents such as silica aerogel. Moreover, silica aerogel may also be a promising adsorbent for other toxic metals. In conclusion, this work would bring a new pathway for evaluation of an agricultural waste as well as fulfill the heavy metal polluted water.

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