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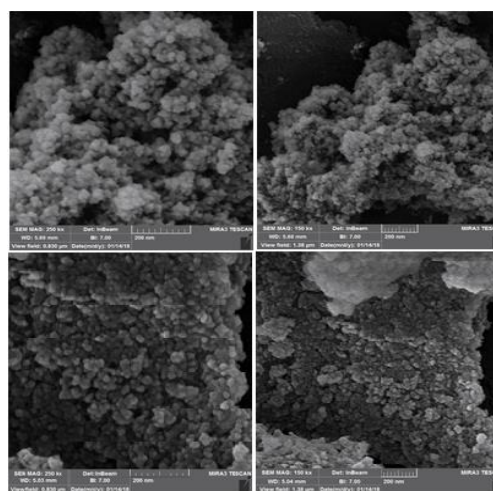
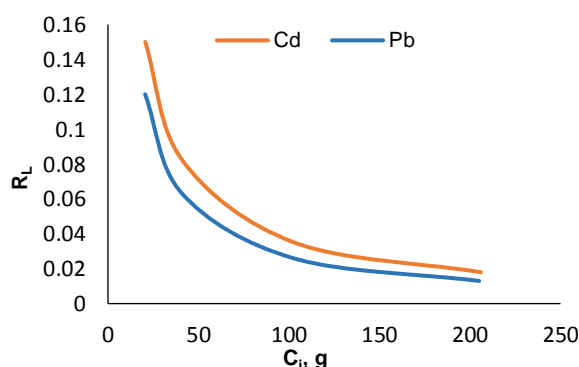
## Removal of heavy metals from synthetic wastewater using silica aerogel-activated carbon composite by adsorption method

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### GRAPHICAL ABSTRACT



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### ABSTRACT

In this study, removal of heavy metals from synthetic wastewater has been investigated using silica aerogel-activated carbon composite. The synthesized adsorbent was characterized by FE-SEM, FTIR and BET techniques. The effect of amine functional groups embedded on the surface of silica aerogel-activated carbon 0.5 wt. % composite, optimal initial pH of removal of ions, impact of initial concentration of the solution containing heavy metal ions, adsorbent amount and contact time on removal percentage of ions were investigated. The results showed the optimal pH of 8, optimal adsorbent amount of 0.3 g for the removal of cadmium ion and 0.06 g for the removal of lead ion and optimal contact time of 80 min for cadmium and 60 min for lead ions. Adsorption data were investigated using Langmuir and Freundlich isotherms and maximum adsorption capability for cadmium and lead was obtained at 38.16 and 175.44 mg/g adsorbent, respectively.

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### 1. Introduction

The substances existing within industrial wastewater have resulted in many harmful environmental effects, and they threaten the health of humans and animals. The common methods for removal of contaminants from water are divided into three categories of physical, chemical and biological methods. Among these methods, physical adsorption is applicable as a high efficiency and reversible method for recovery of the adsorbent (Ahmadpour et al. 2016; Karnib et al. 2014). The aerogels are nano-structured, porous materials with a three-dimensional network that can be obtained by removing liquid from the wet-gel without any significant volume drop. These materials have

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unique properties, including high surface area, low thermal conductivity, high porosity, low density, low sound speed, high transparency etc. According to these properties they can be used in a wide variety of applications such as supercapacitors, batteries, catalyst supports, sound and thermal insulation and most importantly as adsorbents and so on (Soleimani Dorcheh and Abbasi. 2008).

The reasons for using adsorption method includes the large variety in the types of contaminants can be removed, fast reaction kinetics, high removal capability even at low concentrations, low operating cost, selectivity depending on the type of adsorbent, capability of adsorbent recovery, high capability of binding metals with adsorbents, etc. (Chanani et al. 2015; Roque-Malherbe. 2018). As it was mentioned

earlier, silica aerogel is used as an adsorbent because of its unique properties such as high specific surface area. The adsorption process was first introduced by Scheele and Fontana in 1773 and 1777, respectively by studying the absorption of the gases using charcoal and clay. Modern application of adsorption is related to the observations of Lowitz, who used charcoal for decolorization of tartaric acid solutions as a result in adsorption of organic impurities (Karnib et al. 2014). Systematic studies of adsorption initiated by works of De Saussure. He concluded that various gases are adsorbed by porous materials (marine foam, cork, charcoal and asbestos). He discovered the exothermic nature of adsorption processes and was the first one who paid attention to the generality of adsorption (Dąbrowski. 2001). Practical application of the adsorption processes mainly relies on the selective adsorption of individual components from their mixtures. Selective adsorption was discovered by Tswett in 1903. He used this phenomenon to separate chlorophyll and other herbal pigments by silica materials (Dąbrowski. 2001). Amirkhani et al. (2010) synthesized silica aerogel composite with multiwall carbon nanotubes (MWCNT) to adsorb organic contaminants with sodium silicate precursor using ion-exchange resins and drying in ambient pressure. They showed that specific surface area of composites aerogels was increased in comparison to the pure silica aerogels (Bargozin et al., 2010). Furthermore, Štandeker et al. (2010) synthesized the mercapto-functionalized silica aerogel using tetramethylorthosilicate precursor and the mercaptopropyltrimethoxysilane surface modifier. At MPTMS / TMOS molar ratio of 0.5, the specific surface area was 518 m<sup>2</sup>/g, and the adsorbent was used to remove heavy metal ions such as mercury and copper, with a maximum absorption capacity of 181.81 mg and 51.02 mg for mercury ion and copper ion, respectively (Štandeker et al., 2011). Givianrad et al. (2011) synthesized silica aerogel-activated carbon composite using tetramethyl orthosilicate precursor, methyltrimethoxysilane (MTMS) surface modifier and rinsing with solvent method and drying in ambient pressure. The adsorption capacity reported in their work for adsorbing cadmium heavy metal from initial solution having 3 mg/L cadmium was 0.384 mg/g adsorbent (Givianrad et al. 2013). Continuing the researches, Khanahmadzadeh et al. (2012), synthesized silica aerogel-activated carbon composite using tetramethyl orthosilicate precursor and the mercaptopropyltrimethoxysilane surface modifier, and applied that for removal of phenol from aqueous solution. The specific surface area of composites was 916 m<sup>2</sup>/g and the phenol removal of 98 % was obtained under the experimental conditions of pH=2, the initial concentration of phenol equal to 5 mg/L, contact time of 1 h, adsorbent concentration of 0.1 g and temperature of 20 °C (Khanahmadzadeh et al. 2012). Faghihian et al. (2012) synthesized silica aerogel functionalized by amine groups using tetraethoxysilane as precursor and aminopropyltriethoxysilane as modifier. The maximum adsorption capacity of 45.45 and 35.71 mg/g was obtained for lead and cadmium ions, respectively. They also concluded that removal of lead ions was better than cadmium (Faghihian et al. 2012). Mohammadi (2015) studied synthesis and investigated the properties and amount of benzene and ethyl benzene adsorbed by silica aerogel and silica aerogel-activated carbon composite. In order to recover the silica and silica aerogel-activated carbon composites adsorbents, the solvent thermal extraction method was performed which after 15 times performing the adsorption/desorption cycle, the initial adsorption capacity was reached (Mohammadi and Moghaddas. 2015). Pour Etedal and Kazemi (2012) synthesized functionalized silica aerogel with mercapto functional groups using sodium silicate precursor and mercapto propyl trimethoxy silane surface modifier. This adsorbent has been used for removal of copper, cadmium and lead ions with maximum adsorption capacity of 83.3, 200 and 250 mg/g adsorbent, respectively (Pouretedal and Kazemi. 2012). Tadayyon et al. (2012) synthesized silica aerogel-activated carbon composite using tetra methyl ortho silicate precursor and methyl trimethoxy silane surface modifier. According to the results he obtained, silica aerogel-activated carbon composite shows higher maximum adsorption capacity compared to activated carbon and silica aerogel (Tadayyon et al. 2012). The removal of heavy metal ions of cadmium and chromium from aqueous solution was studied by Naghizadeh (2015) comparing activated carbon and multiwall carbon. The obtained adsorption capacities of activated carbon for removal of cadmium ion and chromium ion were 2.8 and 2.4 mg/g, respectively, and the adsorption capacities of 4.5 and 3.1 mg/g was achieved for multiwall carbon for removal of these ions, respectively (Naghizadeh. 2015). Huang et al. (2016) synthesized silica aerogel using sodium silicate precursor and ion-exchange resins and functionalized it with amine functional groups, and then used it for

adsorption of cadmium heavy metal. The maximum adsorption capacity obtained from Langmuir isotherm was 407.04 mg/g adsorbent (Huang et al. 2016). Chen et al. (2017), modified the surface of activated carbon using ammonium persulfate and removed cadmium ion from water with maximum adsorption capacity of 67.57 mg/g adsorbent (Chen et al. 2017).

This study aims at the removal of heavy metals from synthetic wastewater using silica aerogel-activated carbon by adsorption method. The silica aerogel-composite possessing the favorable properties of silica aerogels are functionalized by amine groups and the effects of different parameters on the removal percentage are determined.

## 2. Materials and methods

### 2.1. Materials

The chemicals used for synthesis of silica aerogel-activated carbon composite included water-glass as starting material with formula of Na<sub>2</sub>SiO<sub>3</sub> (1.35 g/ml), Trimethylchlorosilane (TMCS), isopropyl alcohol (IPA), Tartaric acid, n-Hexane, 3-aminopropyl trimethoxysilane, nitric acid (HNO<sub>3</sub>) and activated carbon which were all acquired from Merck Company, Germany. The synthetic wastewater used in the study was prepared using cadmium nitrate (Cd(NO<sub>3</sub>)<sub>2</sub> .4H<sub>2</sub>O, 308.48 g/mol), and lead nitrate (Pb(NO<sub>3</sub>)<sub>2</sub>, 331.21g/mol) purchased from Merck Company, Germany.

### 2.2. Synthesis of silica aerogel

Sodium silicate was slightly diluted by addition of deionized water with volume ratio of 1:4, then, the activated carbon with the desired weight percentage was added to the solution which was then placed under the ultrasonic apparatus probe with power of 75 watts for half an hour, in order to prevent sedimentation and better homogenization. Afterwards, a 3.6 normal tartaric acid solution was added to the solution of sodium silicate and carbon and until initiation of the nucleation process, it was placed on a magnetic stirrer during the mixing process which changed the color and viscosity of the initial solution. Finally, the solution was transferred to closed Teflon containers to give the required time to form the gel.

### 2.3. Aging

As mentioned, the prepared gel was placed inside a closed batch Teflon reactor –completely sealed and impenetrable- for 3 hours at a temperature of 50 °C to complete the aging stage.

### 2.4. Surface modification and drying stage

Surface modification solution (TMCS) (Nah et al., 2018) and normal hexane solvent were prepared with the volume ratio of 1 to 5, and it was poured onto the gel after solvent evacuation and remained at temperature of 50 °C for 24 hours. At this stage, the resulting gel sample had hydrophobic properties and its specific surface area increased. This also had a significant impact on the gel properties and specifications, including porosity and density. After 24 hours and completion of the surface modification process, it was dried. For this purpose, after discharging the surface modifier solution from the reactor the sample was placed in the ambient temperature for 24 hours to allow the initial release of water, alcohol, surface modifier and the solvent remaining in the sample. Because the temperature should gradually increase to prevent thermal shock, the sample was placed at temperature of 50 °C for 2 hours, at 70 °C for 1 hour, at 90 °C for 1 hour and at 120 °C for 1 hour. In this way, the silica aerogel-activated carbon mineral composite was obtained.

### 2.5. Amination stage

Insemination method is applied for embedding amine groups on the surface of silica aerogel-activated carbon composite. A mixture containing certain amounts of 3-amino propyl trimethoxy silane (Begag et al. 2018) and 4 mL normal hexane was added to 0.08 g of the synthesized silica aerogel-activated carbon sample, and they were placed at 50 °C for 24 hours. Then the solution was discharged onto the composite, and the gel was placed at ambient temperature for 24 h, at 50 °C for 2 h, 70 °C for 1 h, 90 °C for 1 h and 120 °C for 1 h in order to complete the drying process.

## 2.6. Preparation of artificial wastewater containing heavy metals

In order to reduce experimental error, for preparing the mother solution, 1000 mg of intended heavy metal salts were weighed carefully and diluted with deionized water in a 1000 mL volumetric flask. From sequential dilution of the mother solution, the solutions with the desired concentration were prepared. Ammonia and nitric acid were used in order to adjust pH using the pen type pH-meter.

## 2.7. Characterization methods

The synthesized silica aerogels were characterized by different methods. The specific surface areas of samples were measured by BET analysis (Brunauer–Emmett–Teller, model CHEMBET-3000, Quantichrome Instruments, USA). To determine the functional groups on the surface of the amine silica aerogel-activated carbon samples, FTIR analysis (Fourier-Transform Infrared Spectroscopy, Mode Tensor 27, Bruker, USA) was applied and the microstructural properties of the samples was investigated by analysis of field emission scanning electron microscopy (FE-SEM; TESCAN, MIRA3, Czech Republic).

## 3. Results and discussion

### 3.1. BET analysis

In order to investigate the impact of the amount of activated carbon, different weights of activated carbon were added to three silica aerogel samples having equal weights. BET analysis was used for estimation and relative comparison of the specific surface areas of samples. As it can be seen in Table 1, the sample containing 0.5 wt. % activated carbon has the most specific surface area which is considered the best carbon amount. By increasing the amount of activated carbon up to the optimal amount, the specific surface area increases, but increasing the amount of activated carbon more than the optimal amount the specific surface area decreases. That could happen because increasing the carbon percentage more than the optimal amount leads to the arrival of

carbon particles in the silica structure, and it prevents better formation of the network and the pores of the silica structure.

### 3.2. FTIR analysis

Fig. 1 indicates the FTIR diagram of functionalized aerogels with different amounts of 3-aminopropyl trimethoxysilane. According to the initial information about the structure of the precursor, the peaks obtained from the analysis were investigated. The peak observed at 869 and 1200  $\text{cm}^{-1}$  wavelength indicates the existence of the Si-CH<sub>3</sub> functional group caused by surface modification. Peaks existing in 1089 and 469  $\text{cm}^{-1}$  wave number are related to O-Si-O bands and the difference in intensity of peaks can be due to arrival of activated carbon in the network, which causes disorder in the structure and prevents better formation of O-Si-O bands. The peak observed at 812  $\text{cm}^{-1}$  is related to Si-O-Si band as well. In this Fig., the vibrating bands in the 2900-2950  $\text{cm}^{-1}$  region are related to -CH<sub>3</sub> end groups. Vibrating bands existing within 1500-1550  $\text{cm}^{-1}$  and 3460-3500  $\text{cm}^{-1}$  regions imply the presence of -NH<sub>2</sub> groups, and due to existing amine groups, the difference in peak intensities are more in samples 2, 3 and 4, respectively (Faghian et al. 2012).

### 3.3. FE-SEM analysis

Fig. 2 illustrates the images of the composite without amine and the composite having 0.2 mL APTMS. As it can be seen in Figure 2, addition of the amine to the silica aerogel-activated carbon composite by insemination method, makes some parts of the pore spaces be occupied by amine groups and as a consequence the porosity decreases. The decrease in porosity causes the decrease in specific surface area which is proved by BET analysis. As the results of the last three analysis show, the sample of the composite with 0.5 wt.% carbon functionalized with 0.2 mL APTMS has been chosen as a best adsorbent, that has the most specific surface area which is considered the best carbon amount and functional groups on the surface of the amine silica aerogel-activated carbon.

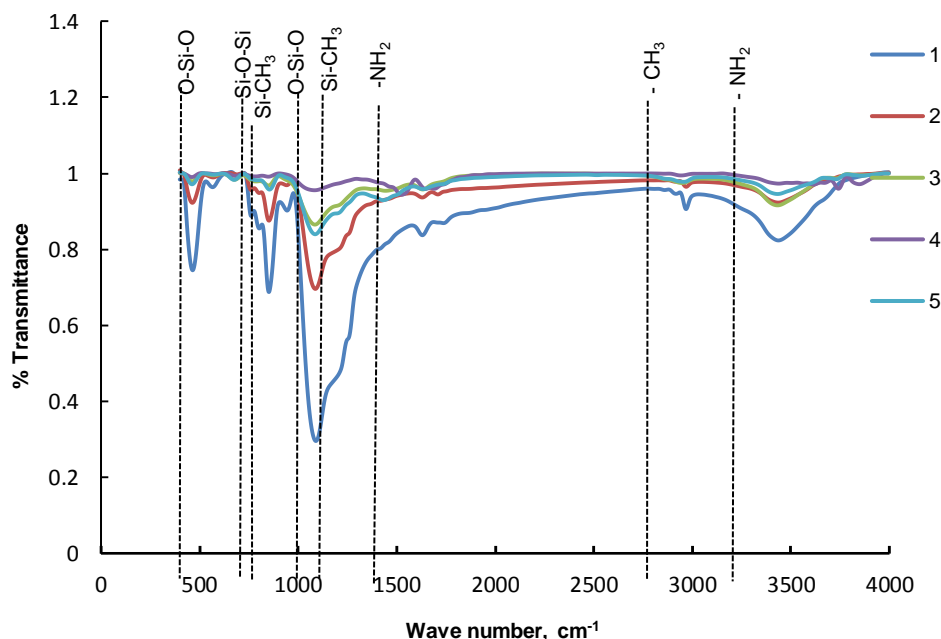


Fig. 1. FTIR diagram of samples, 1) pure silica aerogel, 2) composite with 0.5 wt.% carbon without amine, 3) composite with 0.5 wt.% carbon with 0.2 mL APTMS, 4) composite with 0.5 wt.% carbon with 0.25 mL APTMS, 5) composite with 0.5 wt.% carbon with 0.3 mL APTMS.

## 3.4. The impact of different parameters on adsorption rate

### 3.4.1. Impact of amination extent on removal percentage of cadmium and lead metal ions

For investigating the impact of amine groups on removal percentage of metal ions, a solution with a concentration of 100 mg/L of cadmium and lead heavy metal ions were prepared. 0.2 g of functionalized silica aerogel-activated carbon composite with different amounts of 3-amino propyl trimethoxysilane, were added to each solution, and they were constantly stirred for 45 minutes at 500 rpm. The results of this experiment are provided in Fig. 3. As seen in the Fig., the most removal of metal ions was obtained using 0.2 mL amine.

However, the lower adsorption capacity of the adsorbents with more amine groups which were expected to have more adsorption can be attributed to the increase in the density of the sample due to accumulation and aggregation of the inseminated material in the pores.

### 3.4.2. Impact of the initial pH of the solution on adsorption of the lead and cadmium

The initial pH of the solution is one of the affecting factors on the adsorption rate of the adsorbent. To study the effect of pH, a solution with a concentration of 100 mg/L and volume of 100 mL was prepared for each of cadmium and lead heavy metals. To each solution, 0.2 g

adsorbent functionalized by amine was added and by adding ammonia and nitric acid to the solutions, pHs of 5, 6, 7, 8 were investigated. The samples were tested for 45 minutes at 500 rpm. The obtained results for pH impact are indicated in Figure 4. In fact, the reason of difference in adsorption capacities with pH variation can be explained as follows; At lower pHs, the amine groups on the composite surface which are chelated with metal ion, are protonated, and they lose their capability to complex the metal ion. In other words, by increasing pH, the competition between H<sup>+</sup> and metal ions on the amine groups over the adsorbent surface decrease. But at higher pHs than the optimal pH, we face reduction in adsorption rate that can be due to OH<sup>-</sup> ions and sediment formation as metal hydroxide.

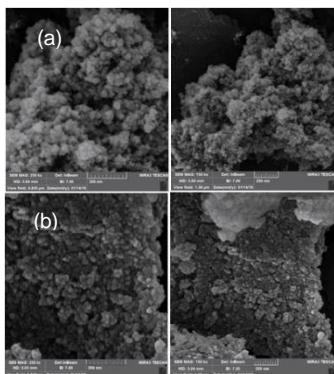


Fig. 2. (a) Composite with 0.5 wt.% carbon non-functionalized with amine, (b) Composite with 0.5 wt.% carbon functionalized with 0.2 mL APTMS.

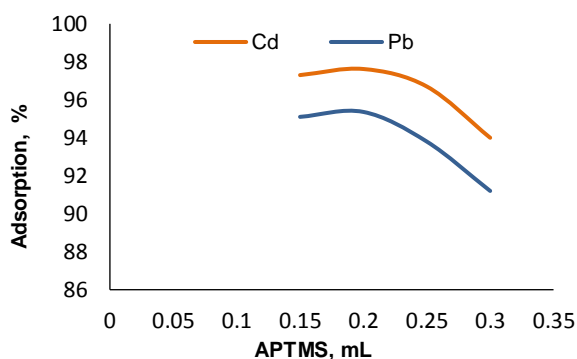


Fig. 3. Diagram of Amination extent impacts on the removal percentage of cadmium and lead metal ions.

**3.4.3. The impact of the adsorbent amount on adsorption rates of cadmium and lead ions**

For investigating the impact of adsorbent amount, a solution with a concentration of 100 mg/L with volume of 100 mL and pH of 8 was prepared for each heavy metal. Four adsorbent weights of 0.1, 0.2, 0.3 and 0.4 g to cadmium solution and four weight amounts of 0.02, 0.04, 0.06 and 0.08 g adsorbent functionalized with 0.2 amine was added to the lead solution, respectively (It's worth mentioning that in case of lead ion, the amounts higher than 0.1 g for adsorbent lead to the almost 100 % adsorption percentage, so lower amounts were applied for this metal). The solutions were stirred for 1.5 h at 500 rpm. The amount of adsorbent has a significant effect on the reduction of the equilibrium concentration of metal ions.

**3.4.4. The impact of the adsorbent contact time on adsorption rate of cadmium and lead ions**

In order to investigate the impact of contact time on adsorption rate, for each of cadmium and lead heavy metals, a solution with a concentration of 100 mg/L, volume of 100 mL and pH equal to 8 was prepared. According to the results of experiments carried out on the previous step, the amounts of adsorbent for cadmium and lead ions were considered to be 0.3 g and 0.06 g, respectively. They were added to the solutions. The solution containing cadmium were stirred for 20, 40, 60, 80 and 100 minutes and the solution containing lead were stirred for 11, 20, 30, 40, 50, 60 and 70 min at 500 rpm.

**3.4.5. The impact of the initial concentration on adsorption rate**

In order to study the impact of initial concentrations of cadmium and lead ions on adsorption rate, four solutions with concentrations of 20.6, 41.2, 103 and 206 mg/L were prepared for cadmium ion and four solutions with concentrations of 20.5, 41, 102.5 and 205 mg/L were prepared for lead ion by dilution of the mother solution with a pH of 8. For each solution, the optimal adsorbent amount and equilibrium time of 0.3 g and 80 minutes for cadmium and 0.06 g and 60 minutes for lead was used. Then the solution was stirred at 500 rpm.

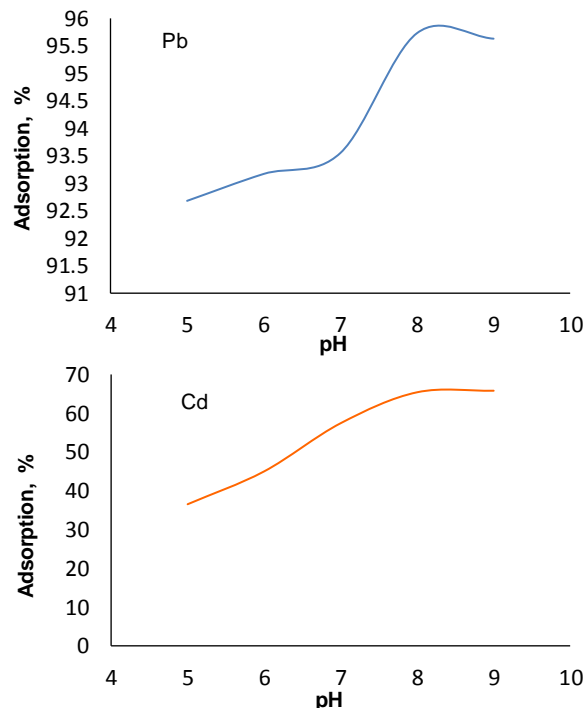


Fig. 4. The impact of the initial pH of the solution on adsorption of the lead and cadmium ions.

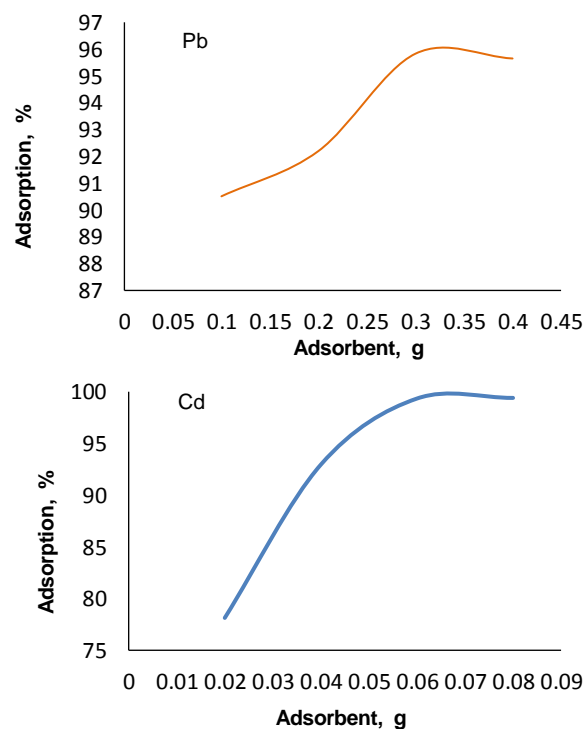


Fig. 5. The impact of adsorbent amount on adsorption rates of cadmium and lead ions.

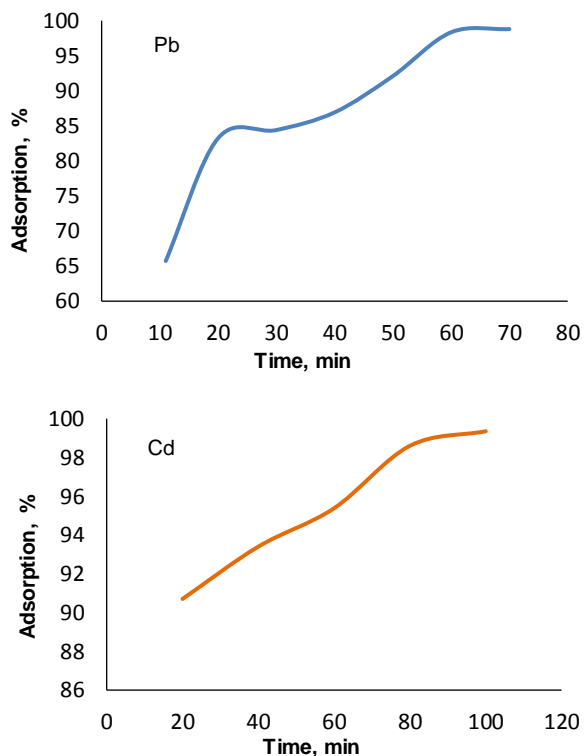


Fig. 6. The impact of the adsorbent contact time on adsorption rate of cadmium and lead ions.

As it can be seen, increasing the initial concentration of both ions causes a decrease in removal percentage. This is because the number of competing ions over reaction with amine groups on the adsorbent surface increases and consequently the active sites of adsorbent become saturated.

3.5. Adsorption isotherms

In order to investigate the impact of adsorption isotherms, for each of cadmium and lead heavy metals, four solutions with different concentrations and equal volumes of 100 ml were prepared. To the solutions containing cadmium and lead 0.3 g and 0.06 g adsorbent, respectively were added and cadmium solutions for 80 minutes and lead solutions for 60 min are stirred at 500 rpm.

3.5.1. Freundlich isotherm

The Freundlich isotherm equation, in the form of  $q_e = k_F C_e^{1/n}$ , was derived by treating the model with the ensemble theory in statistical mechanics as a theoretical tool, the model being set up for the adsorption system with emphasis on two factors, namely the lateral interaction between the adsorbed molecules and the energetic surface heterogeneity (Yang, 1998). A non-linear form of Freundlich isotherm is as follows:

$$q_F = K_F C_e^{1/n} \tag{1}$$

where,  $K_F$  is the constant of Freundlich isotherm (mg/g) and  $n$  is the adsorption intensity. The linear form of this equation can be written as follows:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \tag{2}$$

By plotting the changes of  $\ln(q_e)$  versus  $\ln(C_e)$ , the constants of  $n$  and  $K_F$  can be obtained from the slope and intercept of the graph. As can be seen in Table 2, the amount of “ $n$ ” for adsorption data on both metals is a number between 1 and 10 which indicates that the adsorption process is desirable.

3.5.2. Langmuir isotherm

The adsorption equilibrium model used in this study is the well-known Langmuir equation, which is obtained by combining the adsorption and desorption rate equations (Chiron et al., 2003).

$$\frac{d\theta_t}{dt} = k_{ads} C_t N(1-\theta_t) - k_d N \theta_t \tag{3}$$

where,  $N$  is the maximum number of adsorption sites occupied by the metal and  $\theta_t$ ; the dimensionless surface coverage ratio ( $\theta_t = \frac{q_t}{q_m}$ ). The mathematical expression of the Langmuir isotherm when the sorption process reaches equilibrium is as follows:

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \tag{4}$$

where,  $q_e$  is the adsorption capacity of the adsorbent in equilibrium (mg/g),  $q_m$  is the maximum adsorption (mg/g),  $K_L$  is the constant of the Langmuir isotherm (L/mg), and  $C_e$  is the equilibrium concentration of adsorbate. The linear form of the isotherm is as follows:

$$\frac{1}{q_e} = \frac{1}{k_L q_m C_e} + \frac{1}{q_m} \tag{5}$$

These results show that the Langmuir model well describes the adsorption of Cd and Pb for both adsorbents. The isotherms calculated according to the Langmuir isotherm are shown in Fig. 9. The generated curves confirm the model fits the experimental data well.

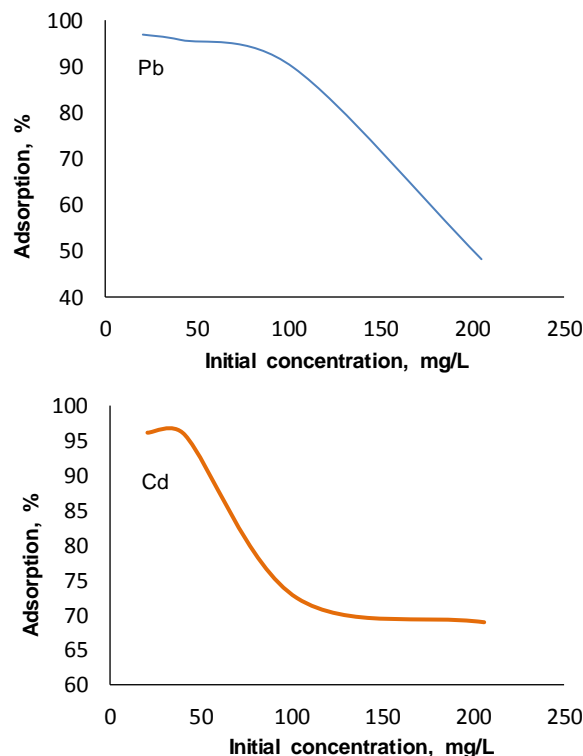


Fig. 7. The impact of the initial concentration of cadmium and lead on adsorption rate.

Table 1. Constants of Freundlich isotherm obtained from the empirical data for adsorption of cadmium and lead ions by silica aerogel-activated carbon composite functionalized with amine groups.

Metal ion	$\ln q_e = \ln K_F + (1/n) \ln C_e$	$K_F$ , mg/g	$n$	$R^2$
Cadmium	$\ln q_e = 2.1296 + 0.3853 \ln C_e$	8.41	2.59	0.9355
Lead	$\ln q_e = 3.9034 + 0.3089 \ln C_e$	49.57	3.24	0.827

Table 2. Constants of the Langmuir isotherm obtained from the empirical data for adsorption of cadmium and lead ions by silica aerogel-activated carbon composite functionalized with amine groups.

Metal ion	$1/q_e = (1/k_L q_m C_e) + (1/q_m)$	$K_L$ , L/mg	$q_{max}$ , mg/g	$R^2$
Cadmium	$1/q_e = (0.0979 / C_e) + 0.0262$	0.27	38.16	0.9789
Lead	$1/q_e = (0.0158 / C_e) + 0.0057$	0.36	175.44	0.9978

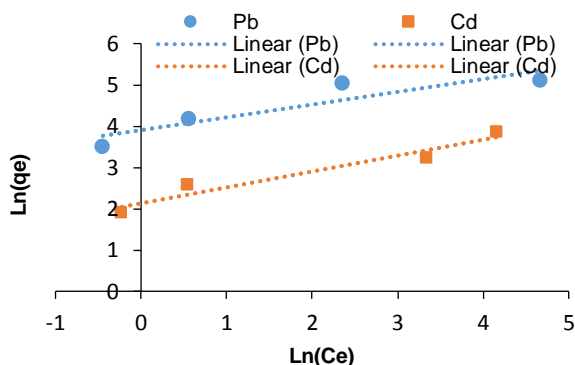


Fig. 8. Diagram of the Freundlich isotherm.

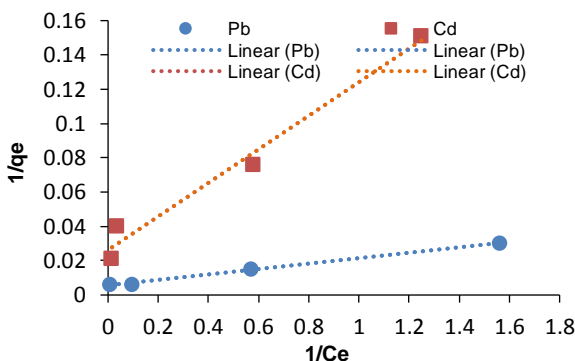


Fig. 9. Diagram of the Langmuir isotherm.

3.5.3. Separation factor

The main specification of the Langmuir isotherm is generally described by a dimensionless constant called separation factor,  $R_L$ :

$$R_L = \frac{1}{1 + K_L C_i} \tag{6}$$

where,  $K_L$  is the constant of the Langmuir isotherm (L/mg) and  $C_i$  is the initial concentration of adsorbate (mg/L).  $R_L$  values indicate the adsorption is unfavourable if  $R_L > 1$ , linear if  $R_L = 1$ , favourable if  $0 < R_L < 1$  and irreversible if  $R_L = 0$ . The comparison between the amounts of the correlation coefficient of Freundlich and Langmuir isotherms indicates that the adsorption data for cadmium and lead ions comply with Langmuir isotherm (Dada et al. 2012).

3.6. Study of adsorption kinetics

In order to investigate the adsorption kinetics, solutions with concentrations of 41.2 and 41 mg/L and equal volumes of 100 mL were prepared for each of cadmium and lead heavy metals, respectively. To the solutions containing cadmium, 0.3 g and to the solutions containing lead 0.06 g adsorbent were added, and they were stirred for different times at 500 rpm.

3.6.1. Pseudo first order kinetics

A simple kinetic model that describes the process of adsorption is the pseudo-first-order equation (Chiron et al. 2003). The linear form of pseudo first order rate equation is as follows:

$$\log(q - q_t) = \log(q_e) - \frac{k_1}{2.303} t \tag{7}$$

In this equation,  $q$  is the adsorption capacity at equilibrium (mg/g) and  $q_t$  is the adsorption capacity at time  $t$ . By plotting the  $\log(q - q_t)$  vs.  $t$ , the amount of  $q_e$  (maximum adsorption capacity) and  $k_1$  (pseudo rate constant) (1/min) are obtained (Wu and Yu. 2007). As seen in Table 4,  $R^2$  is more than 0.9 for cadmium and lead, but the  $q_e$  obtained from the model has a significant difference with empirical  $q_e$ . Accordingly, this model is not an appropriate model for empirical data.

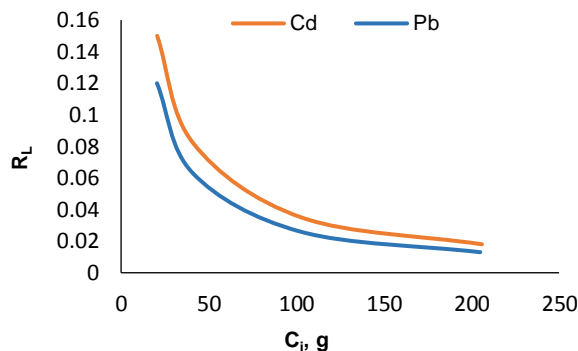


Fig. 10. Diagram of the separation factor.

Table 3. The parameters of pseudo first order kinetics for cadmium and lead ions.

Ion	$k_1$ , 1/min	$q_e$ empirical	$q_e$ model	$R^2$
Cadmium	0.02256	13.54	1.73	0.9990
Lead	0.03661	67.13	28.2	0.9026

3.6.2. Pseudo second order kinetics

Another simple kinetic model, cited by Hamadi et al. (2001), is the pseudo-second-order adsorption:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{9}$$

By plotting the variations of  $t/q_t$  vs.  $t$ , constants, maximum adsorption capacity and pseudo second order rate constant,  $k_2$  (g/mg.min) are obtained (Bayramoglu et al., 2009).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{9}$$

As seen in the Table 5,  $R^2$  is more than 0.9 for cadmium and lead and the obtained  $q_e$  from the model is almost equal to empirical  $q_e$ . Therefore, this model is an appropriate model for empirical data. During the analysis of the discontinuous adsorption of synthetic effluent, adsorption data are analyzed with Langmuir and Freundlich isotherms, and the maximum adsorption capacities of Cadmium and Lead were obtained 38.16 and 175.44 mg/g, respectively. The results are acceptable compared to other studies (Ebisike et al. 2019; Faghian et al. 2012; Guo et al. 2018).

Table 4. The parameters of pseudo second order kinetics for cadmium and lead ions.

Ion	$k_2$ , g/mg.min	$q_e$ empirical	$q_e$ model	$R^2$
Cadmium	0.0432	13.54	13.46	0.9999
Lead	0.0027	67.13	68.96	0.9967

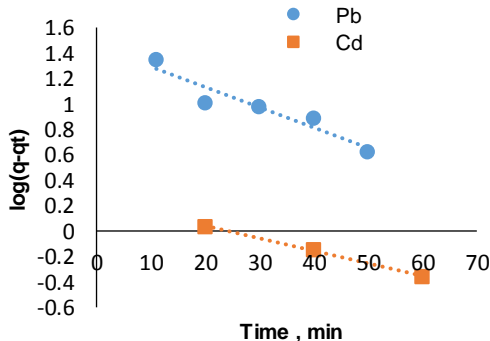


Fig. 11. Diagram of the pseudo first order kinetics.

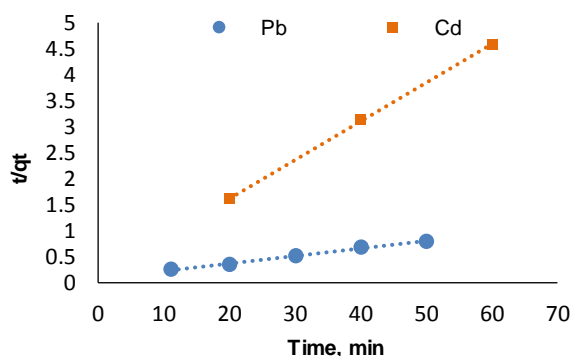


Fig. 12. Diagram of the pseudo second order kinetics.

#### 4. Conclusions

In this study, silica aerogel and silica aerogel-activated carbon composite were synthesized by ambient pressure drying method using water glass as precursor. The hydrophobicity of the samples increases by TMCS which is a surface modifying agent and hydrophilic OH groups are replaced by hydrophobic  $\text{CH}_3$  groups. Also, amine groups are coated on the composite using APTMS surface modifier. Silica aerogel-activated carbon composite with 0.5 wt. % activated carbon exhibited the highest specific surface of  $698.63 \text{ m}^2/\text{g}$ . According to BET, FTIR and FE-SEM analysis, silica aerogel-activated carbon composite with 0.5 wt. % activated carbon and 0.2 mL of APTMS surface modifier is selected as optimal adsorbent. From the Langmuir isotherm, the maximum adsorption capacity for Cd and Pb is 38.16 and 175.44 mg/g, respectively.

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#### References

- Ahmadpour A., Zabihi M., Bastami T.R., Tahmasbi M., Ayati A., Rapid removal of mercury ion (II) from aqueous solution by chemically activated eggplant hull adsorbent, *Journal of Applied Research in Water and Wastewater* 6 (2016) 236–240.
- Bargozin H., Amirkhani L., Moghaddas J., Ahadian M., Synthesis and application of silica aerogel-MWCNT nanocomposites for adsorption of organic pollutants, *Scientia Iranica* 17 (2010) 122-132.
- Bayramoglu G., Gursel I., Tunali Y., Arica M.Y., Biosorption of phenol and 2-chlorophenol by *Funalia trogii* pellets, *Bioresource Technology* 100 (2009) 2685-2691.
- Begag R., Rhine W.E., Dong W., Aerogel sorbents, <https://patents.google.com/patent/US9931612B2/en>; (2018).
- Eisapour Chanani M., Bahramifar N., Younesi H., Synthesis of  $\text{Fe}_3\text{O}_4$ @silica core-shell particles and their application for removal of copper ions from water, *Journal of Applied Research in Water and Wastewater* 4 (2015) 176-182.
- Chen A., Xin X., Xu J., Bian Y., Bian Z., Cadmium ion adsorption by amine-modified activated carbon, *Water Science and Technology* 75 (2017) 1675-1683.
- Chiron N., Guilet R., Deydier E., Adsorption of Cu (II) and Pb (II) onto a grafted silica: isotherms and kinetic models, *Water Research* 37 (2003) 3079-3086.
- Dąbrowski A., Adsorption — from theory to practice, *Advances in Colloid and Interface Science* 93 (2001) 135-224.
- Dada A., Olalekan A., Olatunya A., Dada O., Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of  $\text{Zn}^{2+}$  onto phosphoric acid modified rice husk, *IOSR Journal of Applied Chemistry (IOSR-JAC)* 3 (2012) 38-45.
- Ebisike K., Okoronkwo A.E., Alaneme K.K., Adsorption of Cd (II) on chitosan–silica hybrid aerogel from aqueous solution, *Environmental Technology & Innovation* 14 (2019) 3-20.
- Faghihian H., Nourmoradi H., Shokouhi M., Performance of silica aerogels modified with amino functional groups in PB (II) and CD (II) removal from aqueous solutions, *Polish Journal of Chemical Technology* 14 (2012) 50-56.
- Fariba T., Mina H., Shiva M., Nanocomposite silica aerogel activated carbon: preparation, characterization and application to remove lead (ii) from aqueous solutions, *Journal of the Chinese Chemical Society* 59 (2012) 1578-1583.
- Givianrad M.H., Rabani M., Saber-Tehrani M., Aberoomand-Azar P., Hosseini Sabzevari M., Preparation and characterization of nanocomposite, silica aerogel, activated carbon and its adsorption properties for Cd (II) ions from aqueous solution, *Journal of Saudi Chemical Society* 17 (2013) 329-335.
- Guo S., Dan Z., Duan N., Chen G., Gao W., Zhao W., Zn (II), Pb (II), and Cd (II) adsorption from aqueous solution by magnetic silica gel: preparation, characterization, and adsorption, *Environmental Science and Pollution Research* 25 (2018) 30938-30948.
- Hamadi N.K., Chen X. D., Farid M.M., Lu M.G., Adsorption kinetics for the removal of chromium (VI) from aqueous solution by adsorbents derived from used tyres and sawdust, *Chemical Engineering Journal* 84 (2001) 95-105.
- Huang, Y.-D., Gao, X.-D., Gu, Z.-Y., & Li, X.-M., Amino-terminated  $\text{SiO}_2$  aerogel towards highly-effective lead (II) adsorbent via the ambient drying process, *Journal of Non-Crystalline Solids* 443 (2016) 39-46.
- Karnib M., Kabbani A., Holail H., Olama Z., Heavy metals removal using activated carbon, silica and silica activated carbon composite, *Energy Procedia* 50 (2014) 113-120.
- Khanahmadzadeh S., Khorshidi N., Rabbani M., Khezri B., Removal of phenol in aqueous solutions by silica aerogel-activated carbon nano composite, *Journal of Applied Environmental and Biological Sciences* 2 (2012) 281-286.
- Mohammadi A., and Moghaddas J., Synthesis, adsorption and regeneration of nanoporous silica aerogel and silica aerogel-activated carbon composites, *Chemical Engineering Research and Design* 94 (2015) 475-484.
- Naghizadeh A., Comparison between activated carbon and multiwall carbon nanotubes in the removal of cadmium (II) and chromium (VI) from water solutions, *Journal of Water Supply: Research and Technology-Aqua* 64 (2015) 64-73.
- Nah H.-Y., Parale V. G., Lee K.-Y., Choi H., Kim T., Lim C.-H., Park H.-H., Silylation of sodium silicate-based silica aerogel using trimethylethoxysilane as alternative surface modification agent, *Journal of Sol-Gel Science and Technology* 87 (2018) 319-330.
- Pouretedal H., and Kazemi M., Characterization of modified silica aerogel using sodium silicate precursor and its application as adsorbent of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$  ions, *International Journal of Industrial Chemistry* 3 (2012) 3-20.
- Roque-Malherbe R.M., Adsorption and diffusion in nanoporous materials: CRC press, Taylor & Francis Group; (2018).
- Soleimani Dorcheh A., and Abbasi M.H., Silica aerogel; synthesis, properties and characterization, *Journal of Materials Processing Technology* 199 (2008) 10-26.
- Štandeker S., Veronovski A., Novak Z., Knez Ž., Silica aerogels modified with mercapto functional groups used for Cu (II) and Hg (II) removal from aqueous solutions, *Desalination* 269 (2011) 223-230.
- Wu J., and Yu H.-Q., Biosorption of 2, 4-dichlorophenol by immobilized white-rot fungus *Phanerochaete chrysosporium* from aqueous solutions, *Bioresource Technology* 98 (2007) 253-259.
- Yang C.h., Statistical mechanical study on the Freundlich isotherm equation, *Journal of Colloid and Interface Science* 208 (1998) 379-387.