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Absorption of heavy metals using resorcinol formaldehyde aerogel modified with amine groups

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ABSTRACT

Resorcinol–formaldehyde (RF) aerogels modified with amine groups were used to remove heavy metal ions from aqueous solutions. RF aerogel was synthetized under subcritical conditions and then was modified by 3-aminopropyl trimethoxysilane. The ability of modified RF aerogels to remove Pb(II), Hg(II), and Cd(II) ions from aqueous solution was investigated using batch-adsorption technique with respect to the changes in pH, contact time, sorbent concentration, initial metal concentration, and temperature. The maximum adsorption capacity of metal ions Pb(II), Hg(II), and Cd(II), was found to happen at pH 6, 6, and 5, respectively, after about one hour. The experimental findings showed that the ions' adsorption on the surface of the aerogel was endothermic. Adsorption isotherms indicated that the adsorption behavior of modified aerogel could fit in both Langmuir and Freundlich models. The outcomes of this study also showed that amine-modified RF aerogels can be used as an effective sorbent for the removal of heavy metal ions Pb(II), Hg(II), and Cd(II) from aqueous solutions.

Keywords: Resorcinol–formaldehyde aerogels; Absorption; Heavy metals; 3-aminopropyl trimethoxysilane

1. Introduction

With the proliferation of the use of heavy metals in industrial settings throughout recent decades, the predicament of the pollution of surface and underground water supplies by heavy metals, specifically in developing countries, has reached a level of international concern. Despite the fact that many of these heavy metals are paramount to the proper physiological function of organisms, a great deal of these metals can act as toxins in the environment and disturb the natural flow of the organisms within these environments.

Among the most commonly used metals within industries, which exerts cumulative effects over time, is lead. This metal is used in a variety of commodities such as storage batteries, insecticides, as well as ointments and medicinal concoctions [1]. Accumulation of this metal within water supplies can lead to many health problems such as damage to the kidneys and liver, disturbances in the production of hemoglobin, mental retardation, complication during pregnancy, weakening of muscles and joints, and gastrointestinal damage [2,3].

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Furthermore, a chief source of pollution in industries such as electroplating, pigmentation, silver–cadmium batteries [1], smelting, stabilizers, phosphate fertilizers, mining, and alloys are from cadmium [4,5]. Cadmium acts as a stimulant in the respiratory system and prolonged exposure to this element can cause anemia, damage to the liver and kidneys, emphysema, bone disorders, lung fibrosis, weight loss [6], itai-itai disease [7], cancer [3,8], hypertension, and testicular atrophy. Cadmium, when mixed with chemical groups containing sulfide, can disturb the action of certain enzymes [9].

Mercury is also one of the most toxic heavy metals in the environment and can accumulate within the human body. Examples of the main sources of mercury pollution within the environment are chlor-alkali, paints, paper & pulp, oil refining [10], thermometers, fertilizers, fluorescent light tubes and high intensity street lamps, cosmetics, and pharmaceutical products [11]. Health effects of mercury poisoning mainly involve the nervous system (teratogenic) which can manifest as mental retardation in infants, cerebral palsy, and convulsions. Other effects include defects causing chromosomal breaking and interference with cell division [12,13]. Other problems are caused by the fact that mercury is not metabolized within the human body and has a long half-life. Filtering this toxic metal from within industrial waste is critical to the maintenance of a healthy water supply and the continued preservation of the environment [14].

A variety of methods exist for the filtration of heavy metals from water supplies such as precipitation, ion exchange, reverse osmosis, flocculation [15,16], electrochemical and biological operations, complexation/sequestration [17,18], membrane filters, and solvent extraction [19,20]. However, when the concentration of the heavy metals is very low, these methods do not suffice and it is necessary to use absorbent. Their ability to recycle and their higher efficiency compared to other methods are some of the benefits of using absorbents.

There are a number of materials which can be used as absorbents such as lignocellulosic materials, wheat bran, peanut shell, moss peat, fly ash, bagasse, tree fern, gram husk, saw dust, coir, rice husk, and manure are the examples [21–27].

These materials have been found to possess good adsorption capabilities mainly given to the fact that they contain cellulose materials similar to cellulose such as tannin, lignin, and pectin, which contain polyphenols and aliphatic hydroxyl and carboxylic groups [28–30]. The main drawback of using the said materials is their lack of resistance to abrasion force while in batch or column applications and leaching of some organics (water extractives) during adsorption.

The process of adsorption requires an absorbent with a high surface area. Small pores such as micropores and mesopores can cause an absorbent to acquire a higher surface area which can greatly aid in the process. Pore sizes, pore size distribution, surface area, and chemical composition are important factors in the adsorption process [31,32]. Many different types of both organic and inorganic aerogels are produced in recent years [33–36]. Resorcinol–formaldehyde (RF) aerogels are among the organic aerogels which are highly porous (>90%) and they provide a large surface area and a very low density as well as giving the user the ability to modify their chemical structure by mixing with organic compounds. These great deals of properties make RF aerogels excellent materials for adsorption applications. The purpose of this research was to investigate the feasibility of using RF aerogels modified with amine groups to adsorb heavy metals (lead, mercury, and cadmium) and providing adsorption capacity data. The adsorption of heavy metals from aqueous solutions is dependent on pH, contact time, initial concentration of heavy metal, dose of the absorbent, and temperature. Therefore, in this study, at first the adsorption optimum conditions were found and then the adsorption isotherms were measured and the results were fitted to the Freundlich and Langmuir isotherm models.

2. Experimental

2.1. Materials

RF aerogels modified with amine group were prepared using the sol–gel method by poly-condensation of resorcinol with formaldehyde (37 wt% in aqueous solution). 3-aminopropyl trimethoxysilane (APTES) was used as the amine modifier, magnesium sulfate heptahydrate (Merck grade) was the reaction catalyst, and the solvent was deionized distilled water. Lead, cadmium, and mercury nitrate salts (Merck analyze grade) were dissolved in distilled water to produce 1,000 ppm heavy metal solutions. The pH of the solution was controlled using the buffers disodium dihydrogen, sodium hydroxide/acetic acid, and phosphate/potassium dihydrogen phosphate. Sodium chloride was used for the desorption process and deionized distilled water was used as the solvent throughout all the steps.

2.2. Adsorbent preparation

The modified RF aerogel samples were synthesized by poly-condensation of resorcinol and formaldehyde, using magnesium sulfate heptahydrate as the catalyst and APTES as the amine modifying agent. Distilled water was used as the diluting agent. Table 1 shows the amount of chemicals used to prepare each sample. As can be seen in the table, five samples have been synthetized with different amounts of APTES as the modifier. The samples are named as RF-A followed by a number that represents the molar ratio of the APTES to R, as percentage, used to modify RF aerogels. For instance, RF-A2.5% presents the RF sample modified with 2.5% of APTES.

The components were mixed at room temperature to acquire a dilute and homogenous solution. The solution was stored in an airtight glass container to prevent the vaporization of the solvent. This solution was kept for 24 h at room temperature and 72 h at 40˚C to produce a hydrogel. The hydrogel was cured by storing it for 2 d at room temperature, 2 d at a temperature of 40˚C, and finally for 3 d at a temperature of 80˚C. During the curing process, the color of the samples changed from transparent to a light red and finally to a dark red.

Upon removal from their container, the gels were placed in a 5% acetic acid solution to increase the cross-link density through further condensation of the hydroxymethyl groups. The synthesized RF hydrogels were then dried using the sub-critical method. The RF hydrogels were taken from the glass containers and immersed in acetone for 3 d in order to exchange the water with acetone. The acetone was replaced with fresh acetone on a daily basis. The final wet hydrogel samples were then dried for 3 d at a temperature of 50˚C and ambient pressure. The chemical modification of RF with APTES is discussed later in FTIR analysis section.

2.3. Characterization of the adsorbent

The characteristics of the aerogel adsorbents were elucidated using the standard procedures. The organic and inorganic bonds forming the aerogel structure were studied using the Fourier transform infrared spectra (FTIR) (Brucker model). The thermal stability of the aerogels was observed using the thermal gravimetric analysis measurements. The morphology of the samples was studied using a scanning electron microscope (SEM) (model: Philips XL-3). The nitrogen adsorption data were obtained using an ASAP2000 sorption instrument. BET tests were carried out over a relative pressure range of 0.1–0.26 to measure the specific surface areas of the aerogel (S_{BET}). Pore size distribution was estimated using the BJH model applied to the adsorption branch of the isotherm.

2.4. Adsorption experiment

In this study, adsorption of metal ions Hg(II), Cd(II), and Pb(II) onto the surface of the RF aerogel was observed using the batch technique. The aerogels were produced with varying percentages of APTES according to Table 1. Then, 1–5 g/l of the modified RF was mixed with 50 ml solution including 100 ppm of cadmium ion at room temperature and pH of 5 in different experiments. Then, the mixture was mixed for 2 h in order for adsorption to take place. In the next step, suspension was centrifuged at a speed of 2,500 rpm for a period of 10 min in order to separate the solid particles. The concentration of the metal ion within the solution was measured using atomic adsorption spectroscopy. The experiments showed that the highest adsorption of the metal ions is achieved by the sample RF-A10%. This will be discussed later. Sample RF-A10% was taken as the basis for the experiments and the rest of the tests were continued using that. In continuation of the experiments, the effects of initial heavy metal concentration, contact time, adsorbent dose, solution pH, and temperature on the adsorption of metal ions Hg(II), Cd(II), and Pb (II) by the prepared aerogel were studied.

The percentage of adsorbed material can be obtained using Eq. (1):

$$R\,(\text{Removal efficiency}\,\%) = (C_0 - C_e) \times 100/C_0 \qquad (1)$$

Table 1
Formulation of different RF aerogels modified with amino groups, R: Resorcinol, W: Water, F: Formaldehyde

Sample (%)	R/W (mole ratio)	R/F (mole ratio)	APTES/R (mole ratio)	R/Catalyst (mole ratio)
RF-A0	0.037	0.5	0	600
RF-A2.5	0.037	0.5	0.025	600
RF-A5	0.037	0.5	0.05	600
RF-A10	0.037	0.5	0.1	600
RF-A20	0.037	0.5	0.2	600

where R is the removal efficiency percentage, C_0 is the initial concentration of the heavy metal (mg/l), and C_e the final concentration of the heavy metal solution (mg/l).

The isothermal adsorption process can explain the interaction between the adsorbent and adsorber and can also be used to optimize the adsorption conditions. By comparing the experimental results with the theoretical models, the surface adsorption rate can be optimized as well. In order to study the adsorbent isotherms, 1 g/l of the adsorbent was mixed with the heavy metal solution with varying concentrations of 20, 100, 200, 300, 400, and 500 ppm of the ions Hg(II), Cd(II), and Pb(II), at the temperature of 35 and 25°C and adsorption took place for a period of 2 h. The adsorption capacity of the adsorbent was calculated using Eq. (2):

$$q = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where q is the capacity of the adsorbent for the heavy metal ions (mg/l), m is the mass of the adsorbent (g), and V is the volume of the solution (l). The results were then fitted to the Freundlich and Langmuir isotherm models.

2.5. Desorption experiments

The adsorption and desorption experiments were carried out repeatedly for five total trials. The desorption of the ion Cd^{2+} from the RF aerogel was carried out using a solution of 0.5 M HNO_3/0.1 M HCl with an equal volume proportion and for a period of 4 h.

3. Results and discussion

3.1. Adsorbent characterization

3.1.1. FTIR analysis

In Fig. 1, a FTIR comparison between the RF aerogel modified with amine and a non-modified aerogel can be observed. In both cases, the points corresponding to the wavelengths 1,089 and 1,217 cm^{-1} represent C–O–C, a dimethyl ether bond which exists between the two resorcinol molecules. The wavelengths 2,928 and 1,474 cm^{-1} correspond to the C–H stretching and scissor vibrations. The wavelength 1,613 cm^{-1} represents aromatic ring stretching vibration and the wavelengths 1,363 and 3,242 cm^{-1} can be attributed to O–H stretching vibration. The wavelength 1,698 cm^{-1} represents a carbonyl bond stretching vibration and the wavelength 3,844 cm^{-1} can be observed in the modified sample but is absent in the non-modified sample.

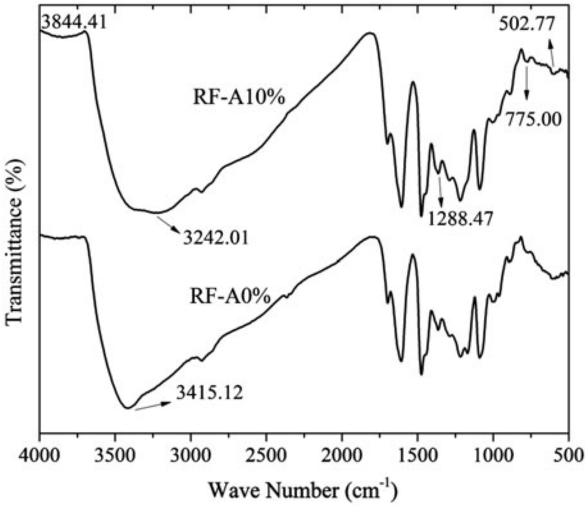

Fig. 1. FTIR absorption spectra of modified and unmodified RF aerogel.

3.1.2. Thermal analysis

Fig. 2 shows the thermal breakdown of the modified and non-modified aerogels. In this Figure, the drop in weight of the aerogel, which starts at lower temperatures, can be attributed to the departure of smaller molecules as well as adsorbed molecules of water within the structure of the aerogel. However, the drop in weight slows down at a temperature of 100° and again picks up at a temperature of 400°. At a temperature of 700°, approximately 58% of the aerogel

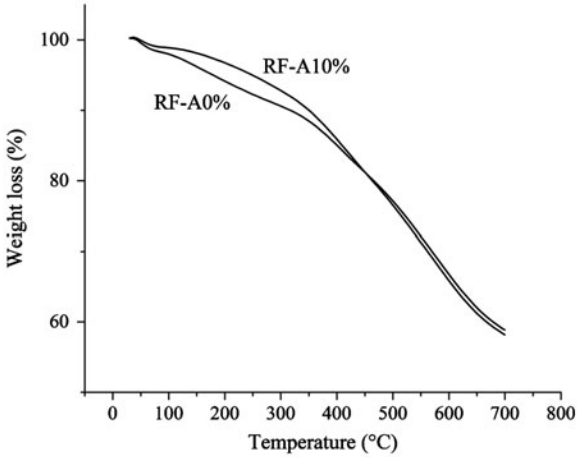

Fig. 2. Thermal stability of RF aerogels after and before amine modification.

is what remains of the original sample. The modified and non-modified aerogels do not show a significant difference in their behavior towards thermal breakdown.

3.1.3. Texture properties

The specific surface area, total pore volume, and pore diameter can be observed in Table 2. These results show that, with an increasing amount of APTES, a decrease in surface area can be observed. A comparison between the isothermal adsorption and desorption of the samples with varying APTES levels can be seen in Fig. 3.

3.1.4. Morphology

The morphology of the samples, before and after modification, were observed using SEM. Fig. 4 shows that modification of RF aerogel by APTES leads to an increase in particle size, and by considering data in Table 2, the surface area decreases.

3.2. Removal of heavy metal ions from water solutions

3.2.1. Effect of modification of RF aerogel adsorbent

RF aerogels were modified by different amount of APTES during aerogel synthesis. Fig. 5 shows that an increasing level of the amine group correlates to an increase in the elimination of heavy metals but drops off at a certain point. An increase in the APTES/*R* ratio, from one perspective increases the level of amination which improves the heavy metal elimination, and from another perspective causes a decrease in the surface area which leads to a decrease in the heavy metal elimination rate.

3.2.2. Effect of contact time

Fig. 6 shows the effects of various contact times (1–24 h) on the percentage of heavy metal elimination caused by the RF aerogel modified with an amino functional group at a pH 5. This figure shows that the percentage of elimination increases with a longer contact time. The results of this figure also show that the initial rate of elimination had the highest pace to the point that within the first hour, the amounts of the Cd, Pb, and Hg ions which were eliminated were respectively 73, 80, and 86%. This can be attributed to the existence of a large amount of active sites on the surface of the sample which are quickly occupied by the heavy metals within the initial moments of contact and cause the rate of heavy metal elimination to drop quickly to the point that the rate of elimination of Hg(II) after 6 h, and Cd(II) and Pb(II) after 12 h, has dropped to zero.

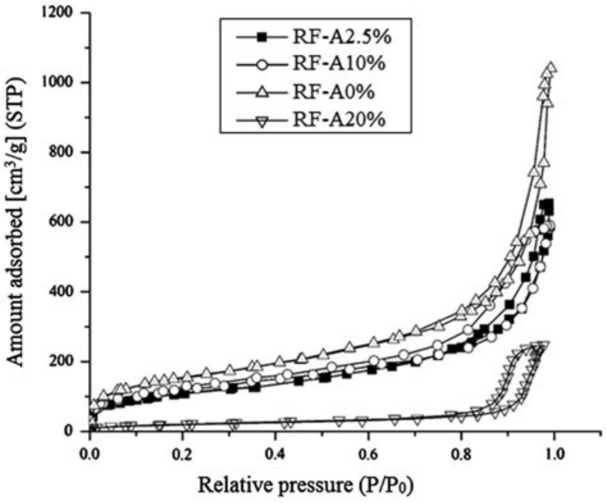

Fig. 3. Adsorption–desorption isotherms of nitrogen by modified and unmodified RF aerogels.

3.2.3. Effect of pH

The pH of the solution is an important governing factor in the process of adsorption. It affects the surface charge of the particles undergoing the adsorption

Table 2
Texture properties of the RF aerogels doped with amino groups

Samples (%)	APTES/*R* (mole ratio)	Surface area (m^2/g)	Average pore size (nm)
RF-A0	0	312	21.6
RF-A2.5	0.025	170.7	18.6
RF-A5	0.05	149.1	13.9
RF-A10	0.1	120.8	17.9
RF-A20	0.2	84.2	15.4

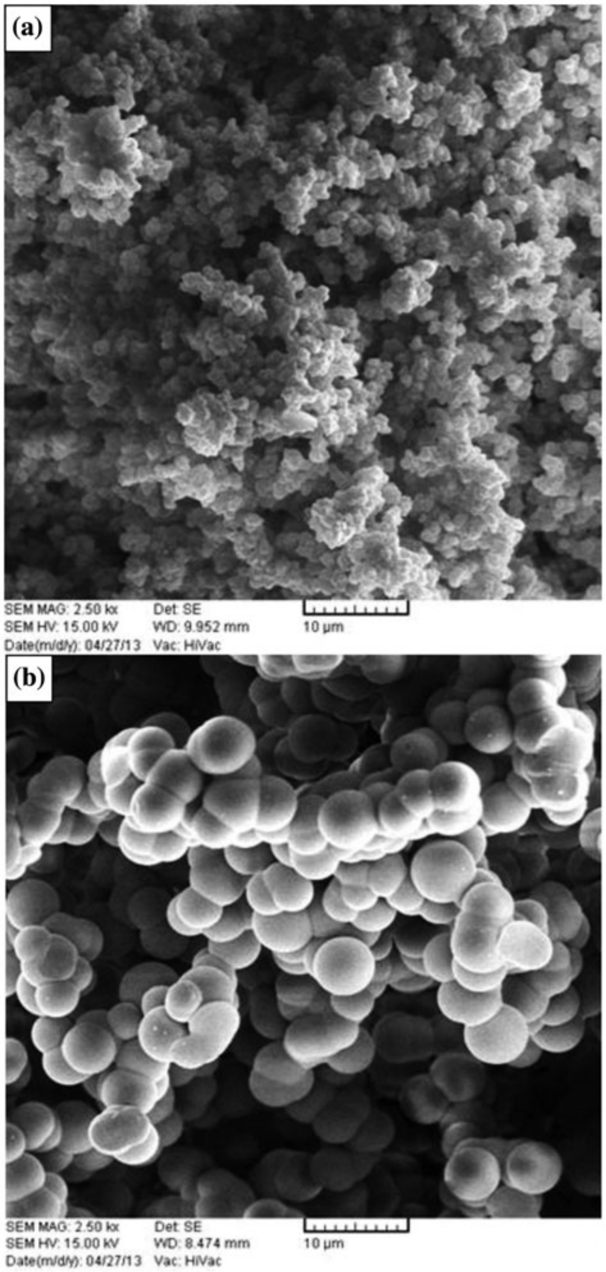

Fig. 4. SEM microstructure of RF aerogel (a) before modification and (b) after modification.

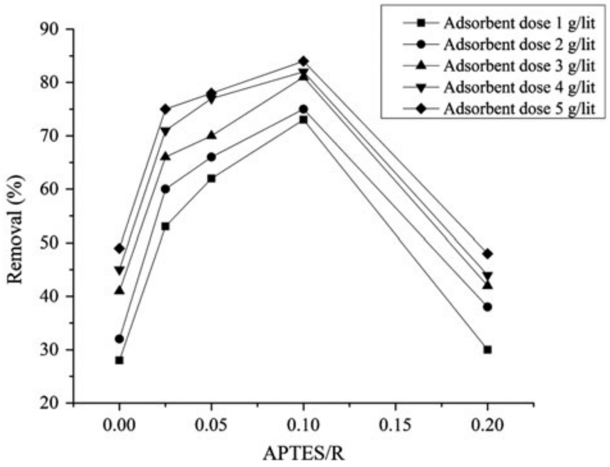

Fig. 5. Effect of quantity of APTES in RF modified aerogel on the removal of Cd ions from aqueous solution.

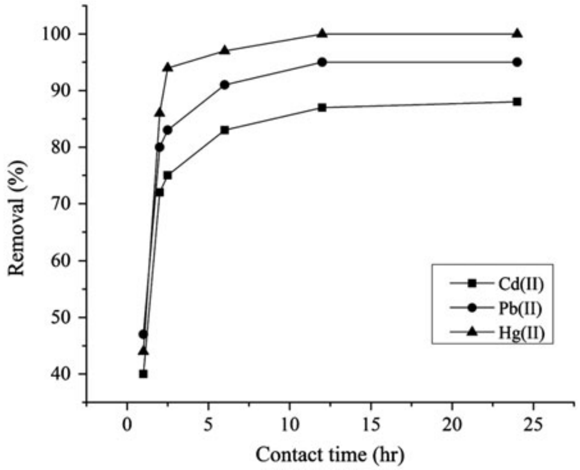

Fig. 6. Effect of contact time on removal of metal ions by RF aerogel modified with amino functional groups.

and ionization process. The results of pH effect on adsorption are presented in Fig. 7.

These results show that the mechanism which governs the adsorption of metal ions corresponds to the mechanism of ion exchange. The optimum pH for the elimination of cadmium, lead, and mercury is 5, 6, and 6, respectively. When the pH increases in the interval of 2–7, the rate of heavy metal ion elimination increases as well. Overall, it can be said that the following reactions occur on the surface of the amine modified aerogel:

$$\mathrm{NH_2 + H^+ \rightarrow NH_3^+}$$

$$\mathrm{NH_2 + M^{2+} \rightarrow NH_2M^{2+}}$$

$$\mathrm{NH_2 + OH^- \rightarrow NH_2OH^-}$$

$$\begin{aligned}&\mathrm{NH_2OH^- + M^{2+}(or\,MOH^-)}\\&\quad\mathrm{\rightarrow NH_2OH^-M^{2+}(or - NH_2OH^-\,MOH^+)}\end{aligned}$$

The first reaction shows the adsorption of protons onto the amine group of the aerogel. The second reaction shows the formation of a complex between

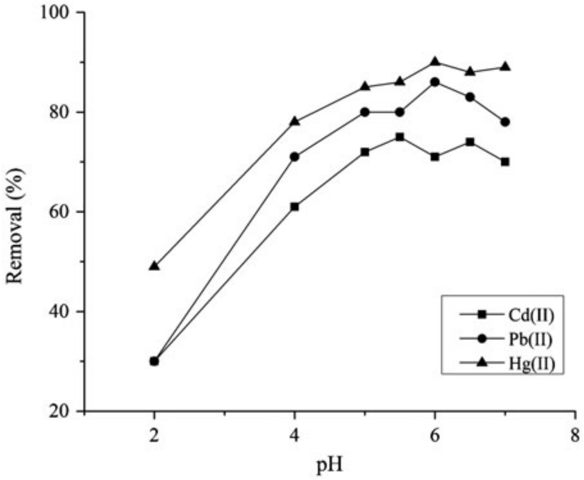

Fig. 7. Effect of PH on removal of Pb, Cd, and Hg ions by resorcinol formaldehyde aerogel modified with amino groups.

the amine group and the heavy metal ions. At a lower pH, the first and second reaction are at odds with each other due to the high concentration of H^+; therefore, the removal efficiency decreases at lower pHs. The third reaction shows the adsorption of hydroxyl ions by the amine groups which causes the rate of the adsorption to reach a maximum at higher pHs. The fourth reaction can occur for certain metal ions at higher pHs which aids the removal of the metal ions, specifically mercury, and the elimination rate again increases when the pH reaches 7.

A comparison of the effect of pH on removal efficiency between activated carbon and RF aerogel modified with amine groups considering Gonzalez et al. [37] work is presented in Table 3. It can be concluded that removal efficiency increases by increasing pH while using activated carbon, but there is a maximum point at pH 6, while using RF aerogel modified with amine.

3.2.4. Effect of adsorbent dose

The samples of aerogels and the metal ion solutions were prepared at interval of 0.5–5 g/l of absorbent at initial concentration of 100 mg/l of metal ions, at pH 5, and at two different temperatures of 25 and 35˚C. The results of the elimination of the ions Hg(II), Cd(II), and Pb(II) by the RF aerogel modified with amino functional group can be seen in Fig. 8. It can be observed that the percentage of elimination increases with the increasing dose of adsorbent due to the presence of more active sites. The removal of the ions mercury and lead at a concentration of 3 g/l and an adsorbent concentration of 5 g/l goes to 100% completion and no ions were observed in the solution.

3.2.5. Effect of initial heavy metal concentration

The effects of various initial concentrations of the heavy metal ion solutions of Hg(II), Cd(II), and Pb(II), at the temperatures of 25 and 35˚C, and at pH 5, were studied. Figs. 9–11 show that the elimination of the cadmium, lead and mercury ions increase with a higher initial concentration. The elimination of all the ions increases when the temperature increases due to the fact that the adsorption of the ions by the RF aerogel modified with an amino functional group is endothermic as described later in Section 3.3.

3.3. Adsorption isotherm

3.3.1. Langmuir isotherm

The Langmuir surface adsorption isothermal model supposes that a single layer of the target molecule is adsorbed onto the surface of the adsorbent which means that the energy and enthalpy of adsorption are equal. In order to use the Langmuir formula, the linear Eqs. (3) and (4) can be used.

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{C_e}\frac{1}{k_l q_m} \tag{3}$$

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

where in q_e represents the mass of the adsorbed material based on the mass of the adsorbent (mg/g), q_m being the Langmuir constant which represents the maximum capacity of adsorption (mg/g), and k_l being the Langmuir constant which gives the adsorption energy (1/mg). Using the Langmuir constants, the parameter R_l can be calculated which represents the practicality of the adsorbent. R_l can be calculated using Eq. (5):

$$R_l = 1/(1 + k_l C_0) \tag{5}$$

3.3.2. Freundlich isotherm

The Freundlich model shows the non-homogeneity of the energy level of the adsorbent and that the

Table 3
Comparison of effect of pH on removal efficiency between activated carbon and RF aerogel modified with amine

RF aerogel modified with amine			Activated carbon		
pH	Removal efficiency of Cd(II) (%)	Removal efficiency of Hg(II) (%)	pH	Removal efficiency of Cd(II) (%)	Removal efficiency of Hg(II) (%)
4	60	79	4	68	85
5	72	83	5	70	84
6	70	91	6	73	82
7	69	89	7	78	79

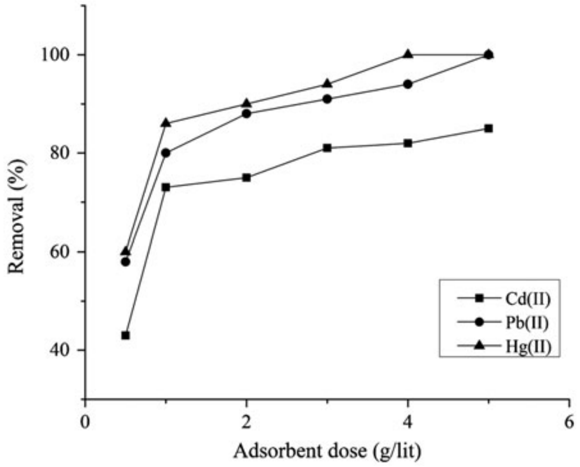

Fig. 8. Effect of adsorbent dose of RF aerogel modified with amino functional group on removal of Cd(II), Pb(II), and Hg(II) ions.

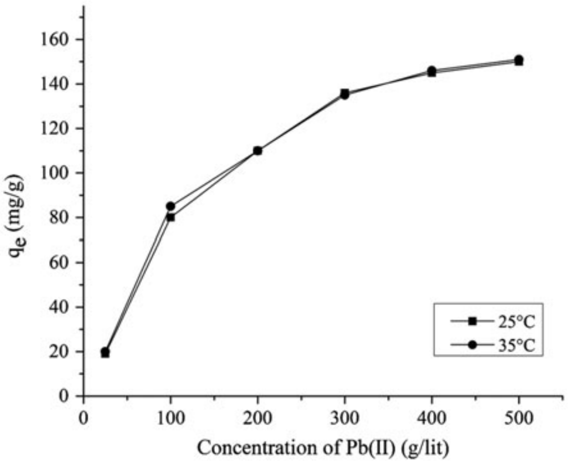

Fig. 10. Effect of initial concentration Pb(II) ion on capacity of adsorption.

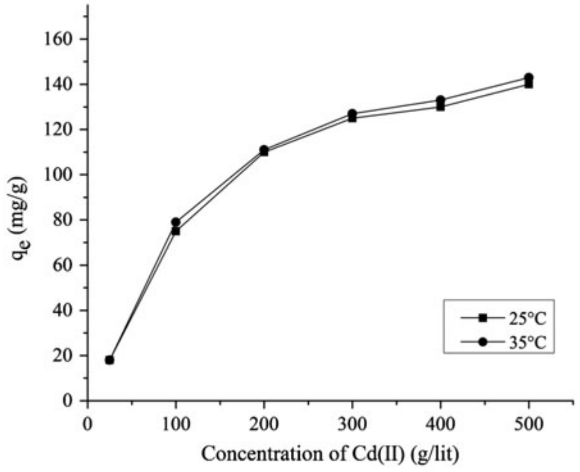

Fig. 9. Effect of initial concentration of Cd(II) ion on adsorption capacity.

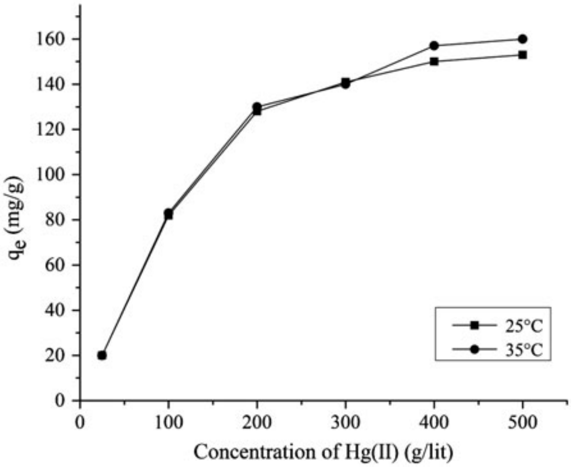

Fig. 11. Effect of initial concentration Hg(II) ion on capacity of adsorption.

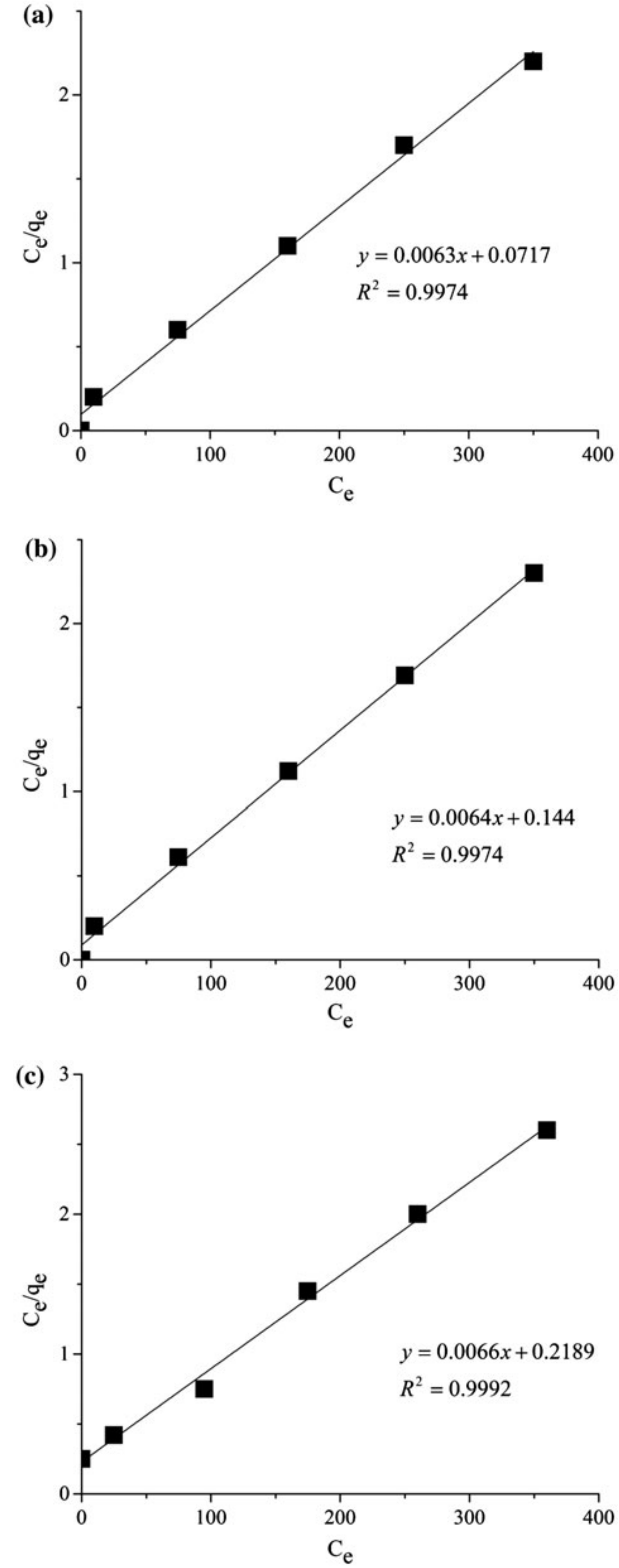

Fig. 12. Langmuir isotherm for adsorption of (a) Hg (b) Pb and (c) Cd ions.

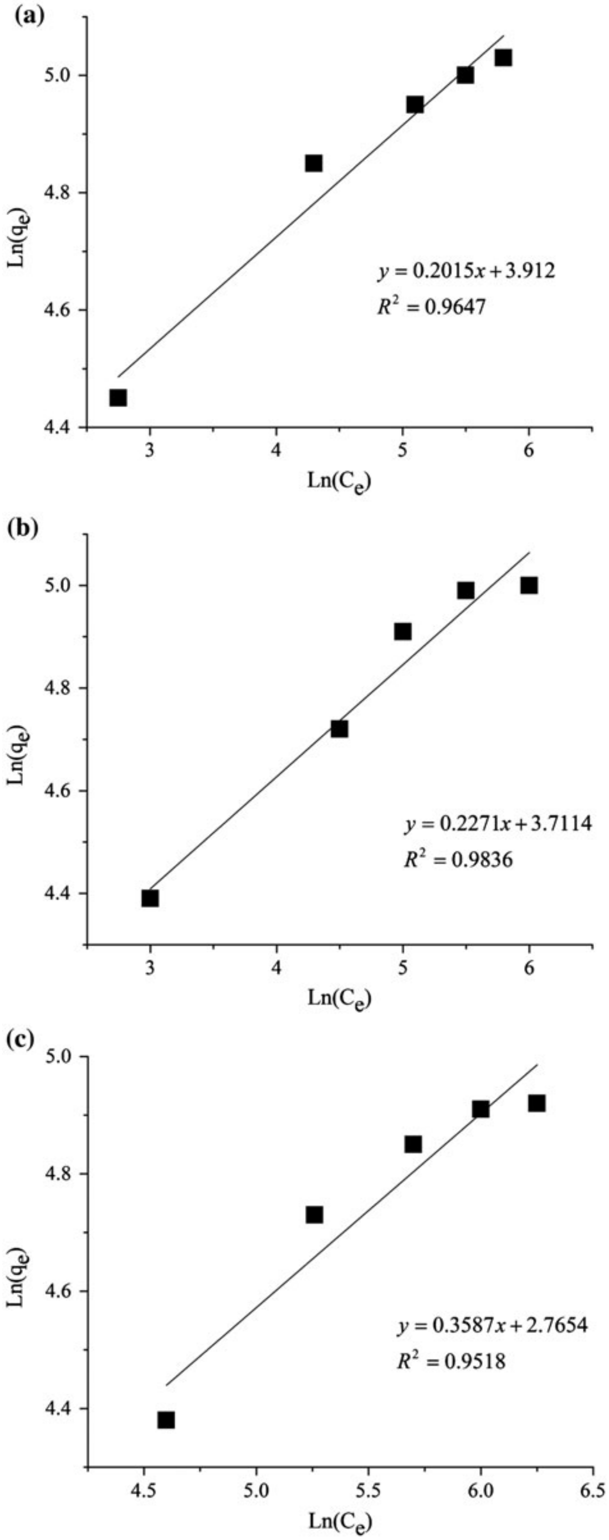

Fig. 13. Freundlich isotherms for adsorption of (a) Hg (b) Pb and (c) Cd ions.

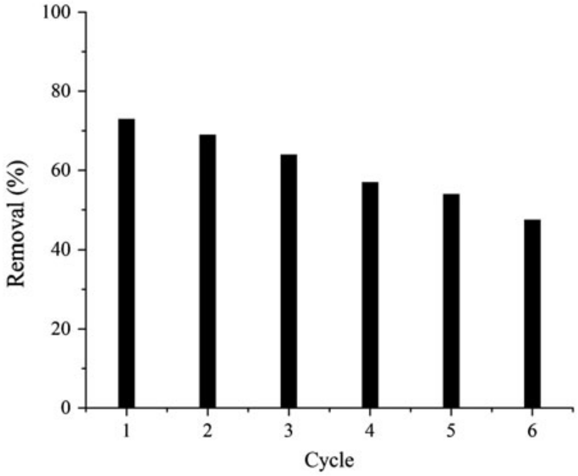

Fig. 14. Sorption–desorption cycles for Cd(II) ion.

adsorption energy decreases with an increasing adsorption rate. The Freundlich model uses Eq. (6):

$$q_e = k_f C_e^{1/n} \tag{6}$$

where in q_e represents the mass of the adsorbed material based on the mass of the adsorbent (mg/g), C_e represents the concentration of the heavy metal solution after adsorption, k_f being the Freundlich constant, and $1/n$ being the Freundlich intensity parameter. The Freundlich constants can be calculated by plotting the graph of log (q_e) against log (C_e).

The amounts obtained from the Freundlich and Langmuir isotherm formulas, shown in Figs. 12 and 13, show that adsorption increases with an increasing equilibrium concentration of the particles being adsorbed. It can also be seen from Figs. 12 and 13 that the process of adsorption corresponds to the Freundlich and Langmuir isotherm models.

3.4. Reclamation of the adsorbent

Fig. 14 shows that the adsorption capacity of the resorcinol formaldehyde aerogel decreases by only 25% after six trials of use which means that this adsorbent can be used repeatedly without a stark drop in its capabilities of adsorbing heavy metals.

Finally, different maximum adsorption capacities of activated carbon from different studies and maximum adsorption capacity of RF aerogel modified with amine, developed in this study, are compared in Table 4.

4. Conclusion

In this study, RF aerogel is modified with APTES which provides amino functional groups on the surface of the aerogel. The modified aerogel is used to absorb the heavy metal ions cadmium, lead, and mercury from within an aqueous solution. This study shows that the surface area of the aerogels decreases with an increasing level of amino groups while the cluster sizes increase. It is also indicated that the aerogel made of a molar ratio of APTES to resorcinol equal 0.1 provides the highest level of absorption of the metal ions. The optimum pH for the adsorption of cadmium was shown to be 5 and for the ions lead and mercury, 6. The time it takes for the heavy metal solutions to reach equilibrium was 12 h. The equilibrium isotherms can be fitted to both the Freundlich and Langmuir isotherm models and are shown to correspond well with the theoretical values which are calculated.

Table 4
Comparison of maximum adsorption capacities (q_m) between activated carbon and RF aerogel modified with amine

Metallic ion	Precursors	q_m (mg/g) of activated carbon (Refs.)	q_m (mg/g) of RF aerogel modified with amine (this study)
Cd(II)	Nut shell	104.17 [38]	151.52
	Sulfurized nut shell	142.86 [38]	
	Bambusa vulgaris striata	239.45 [37]	
Hg(II)	Pistachio-nut/licorice residues	147.10 [39]	158.73
	Walnut shell	151.50 [39]	
	Bambusa vulgaris striata	248.05 [37]	
Pb(II)	Black gram husk	50.20 [23]	156.25
	Alumina developed by surface-adsorbed-dithizone	180.00 [19]	

List of Symbols

R — removal efficiency percentage
C_0 — initial concentration of the heavy metal (mg/l)
C_e — final concentration of the heavy metal solution (mg/l)
q — capacity of the adsorbent for the heavy metal ions (mg/l)
m — mass of the adsorbent (g)
V — volume of the solution (l)
q_e — mass of the adsorbed material based on the mass of the adsorbent (mg/g)
q_m — Langmuir constant which represents the maximum capacity of adsorption (mg/g)
k_l — Langmuir constant which gives the adsorption energy (1/mg)
R_l — practicality of the adsorbent
k_f — Freundlich constant
$1/n$ — Freundlich intensity parameter

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