The effective removal of heavy metals from water by activated carbon adsorbents of *Albizia lebbeck* and *Melia azedarach* seed shells

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Abstract: The removal of toxic metals like lead (Pb) and cadmium (Cd) is very urgent keeping their hazardous effects in view. In this work, seeds of *Albizia lebbeck* and *Melia azedarach* trees were converted into activated carbon adsorbents and applied for the adsorptive removal of Pb and Cd metals from an aqueous solution. The as prepared adsorbents were characterised by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The removal efficiencies of both metals were strongly dependent on their initial concentration, contact time, pH, temperature and the quantity of adsorbents. 0.2 g of both adsorbents removed respectively 75 and 62% Pb and 77 and 66% Cd from from 100 ml of a 40 mg/l concentrated solution in 120 min at pH 5 and a temperature of 20°C. Both the Freundlich and Langmuir isotherms were well fitted to the experimental data. We believe that this work will provide a convenient way to synthesise low cost activated carbon adsorbents for the remediation of highly toxic metals from wastewater to safeguard our environment for future generations.

Keywords: cadmium; hazardous effect; lead; pH; temperature

The modernisation and rapid development of society has resulted in the release of many objectionable pollutants into the environment (Zada *et al.* 2018). Among them, the introduction of heavy metals via both natural and anthropogenic sources has caused tremendous melancholies in the scientific society during the last few decades as these are easily adsorbed on the surface of cell membranes to cause many incurable diseases in both human beings and aquatic flora and fauna. Heavy metals such as lead (Pb) and cadmium (Cd) are widespread in the environment and are extremely hazardous (Jamali *et al.* 2106; Demey *et al.* 2018). These metals slowly accumulate in the human nervous system when exposed to contaminated water and air sources and cause fatal diseases even at very low concentrations. According to the guidelines issued by the World Health Organization (WHO), the desired limit of the concentrations of Pb and Cd are 0.01 and 0.003 mg/l, respectively. Therefore, their disposal is extremely vital before their concentration rises above the acceptable levels (Shi *et al.* 2016; Cen *et al.* 2017; Xu *et al.* 2018).

A number of chemical and physical methods have been applied successfully to reduce the concentration of heavy metals in waste water effluent before they are released to the external environment (Gupta &

Nayak 2012). These include chemical precipitation (Rock & Stevens 1975; Cao *et al.* 1999; Maurer & Boller 1999), coagulation, membrane technology (Yang *et al.* 2003) and photocatalysis that are mainly applied for organic contaminants degradation (Budinova *et al.* 2009; Ali *et al.* 2018; Wang *et al.* 2018a) and adsorption. Although these methods have shown good results, they have low efficiencies, have high operational costs, do not completely remove the heavy metals and produce secondary pollutants (Wang *et al.* 2018b). It is, therefore, extremely important to develop cheap, cost effective and efficient methods to treat heavy metals to safeguard our future generations.

Adsorption is considered one of the most effective and low-cost methods to eradicate heavy metals from water (Demey *et al.* 2018). It is an environmentally friendly technique with flexibility in design and operation. The process of adsorption is reversible and the adsorbents can be regenerated through desorption of the adsorbed species. Meanwhile, different types of biological, agricultural and industrial materials and mineral oxides have been applied with high efficiency for the removal of heavy metals (Chammui *et al.* 2014; Saleh *et al.* 2016).

Both adsorption and photocatalysis have been used for the removal of toxic pollutants from wastewater. However, adsorption is more preferable than photocatalysis as it is more economical and requires less labuor than photocatalysis. Adsorption takes place even in the dark while photocatalysis needs the presence of suitable solar photons and only takes place during the day time. Adsorption produces no secondary and tertiary pollutants while photocatalysis is involved in the production of secondary and tertiary pollutants, some of which cannot be degraded under the stipulated conditions. The adsorbents are easily generated and separated from the mixture (Ali *et al.* 2019). A number of natural and synthetic adsorbents belonging to different sources have been applied for the adsorption of different metals from wastewater effluents. However, they do not fulfil the requirements of low cost and high efficiency especially for the removal of toxic substances. Therefore, preparation of highly efficient materials with a wide range of applicability, easy reversibility and low cost for the adsorption of a wide range of heavy metals is extremely important.

Over the last few decades, activated carbon have been extensively applied as a potent adsorbent for the expulsion of poisonous metals from wastewater due to the tunable surface chemistry and well-developed permeable structure with a high specific surface area. The selection of carbon as an adsorbent is, therefore, extremely significant as heavy metals are removed through complexation or by electrostatic attraction between the metal ions and different oxygen carrying functional groups present on the surface of the activated carbon adsorbents (Mahaninia *et al.* 2015; Vytopilová *et al.* 2015; Burakov *et al.* 2018; Huang *et al.* 2018).

The major aim of this work is to prepare low cost activated carbon adsorbents with high adsorption efficiency towards Pb and Cd ions using the seed shells of *Albizia lebbeck* and *Melia azedarach* plants as carbon precursors. The efficiency of the prepared adsorbents was checked by taking the initial metal concentration, adsorbent dosage, pH, contact time and temperature into account. The obtained results show that the prepared low-cost adsorbents could be applied for the effective removal of heavy metals for environmental remediation.

MATERIAL AND METHODS

Preparation of adsorbent (activated carbon). Seed shells of *Albizia lebbeck* and *Melia azedarach* plants were collected from the Karak District of Khyber Pakhtunkhwa, Pakistan, washed with distilled water to remove dust particles and then dried at 100°C for 24 h. The dried materials were then crushed and grounded into small particles and again washed several times with deionised water to remove any traces of any absorbed salts. After drying in an oven at 100°C, the grounded materials were treated with HCl (85%) and placed in a muffle furnace at 550°C for 4 h with 10°C/min rise in temperature. The furnace was cooled to room temperature under vacuum and the obtained products were washed with deionised water until the pH of the filtrate reached 7. The samples were then dried at 100°C and ground to a particle size of a 100 μ mesh to obtain a fine powder of the activated carbon. The as prepared activated carbon adsorbents were stored in desiccators for further use.

Characterisation techniques. The surface morphology of the prepared adsorbents was studied with the help of a scanning electron microscope (JEOL-JSM-5910, JEOL Ltd., Japan). Fourier transform infrared (FTIR) analysis was carried out to find the functional groups present on the surface of the adsorbents using a FTIR spectroscope (AA670 Mattson 5000 FT-IR spectrophotometer, Shimadzu, Japan). The spectra were recorded from 4000 to 500 cm^{-1}.

Adsorption experiments. 100 ml aqueous solutions of both Pb and Cd ions (10, 20, 30, 40 and 50 mg/l) were prepared and their pH values were adjusted by adding a 0.1 N HCl/NaOH solution. The adsorption experiments were carried out in Erlenmeyer flasks containing metal solution at the given initial concentrations. The mixture of the metal solution and adsorbent was kept under constant stirring in the dark in order to avoid any photochemical reduction (if possible, under the given conditions) of the metal ions taking place on the surface of the activated carbon. After 120 min, the mixture was filtered and the filtrate was analysed for the detection of Pb and Cd metals by an atomic absorption spectrophotometer. A number of experimental parameters such as the metal ion concentration (10–50 mg/l), adsorbent dose (0.1–0.5 g/50 ml), pH (2–7), temperature (20–70°C) and time of contact were checked to evaluate the optimum conditions for the maximum adsorption of both the Pb and Cd metals from the 100 ml aqueous solution over the applied adsorbents.

RESULT AND DISCUSSION

Structural characterisation of the adsorbents. The scanning electron microscopic images of both adsorbents were taken with the help of a JEOL-JSM-5910 (Japan) at a centralised resource laboratory, at the University of Peshawar and the images are shown in Figure 1. It is clear that both adsorbents show fairly smooth surfaces for the adsorption of the

metal ions. However, the adsorbent obtained from the *Melia azedarach* seed shells show an irregular particle distribution when compared to that obtained from the *Albizia lebbeck* seed shells.

The active functional groups responsible for the adsorption of the metal ions on the surface of the prepared adsorbents were identified by FTIR spectroscopy (Shimadzu model AA670 Mattson 5000 FT-IR spectrophotometer) and the spectra were collected in the range from 4000 to 400 cm^{-1}. It is clear from Figure 1c and d that the absorption peaks observed between 3705 and 3630 cm^{-1} indicate the presence of OH groups due to the alcoholic or phenolic functional groups. The peaks observed between 2922 and 2800 cm^{-1} show the presence of carboxylic acid groups. Similarly, the peaks observed in the range of 1743 cm^{-1} show the presence of N-H due to the amine functional group. The peak at 1457 cm^{-1} is related to the O-H group of the carboxylic acid. The investigation of these functional groups is very important, as the heavy metals are removed through complexation or by electrostatic attraction between the metal ions and various surface oxygen-containing functional groups carried by the activated carbons.

The effect of the initial concentration of the metal ions. The initial concentration of metals has a vast effect on the adsorption capacity of the adsorbents. In order to determine it, adsorption experiments were conducted in the presence of the different initial concentrations (10, 20, 30, 40 and 50 mg/l) of both the Pb and Cd ions at a pH value of 5 and the results are
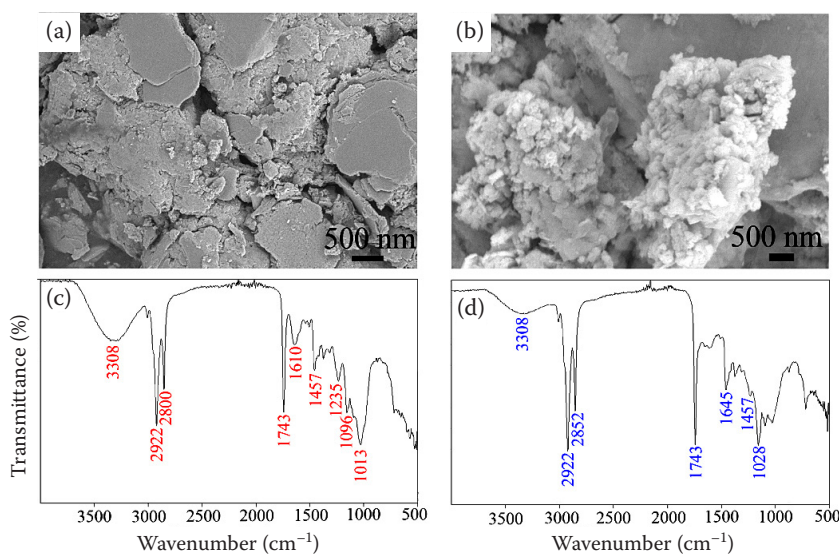

Figure 1. The scanning electron microscopy (SEM) images of the as prepared activated carbon of *Albizia lebbeck* (a) and *Melia azedarach* (b) seed shells and the Fourier transform infrared (FTIR) spectra of activated carbon of the *Albizia lebbeck* (c) and *Melia azedarach* (d) seed shells
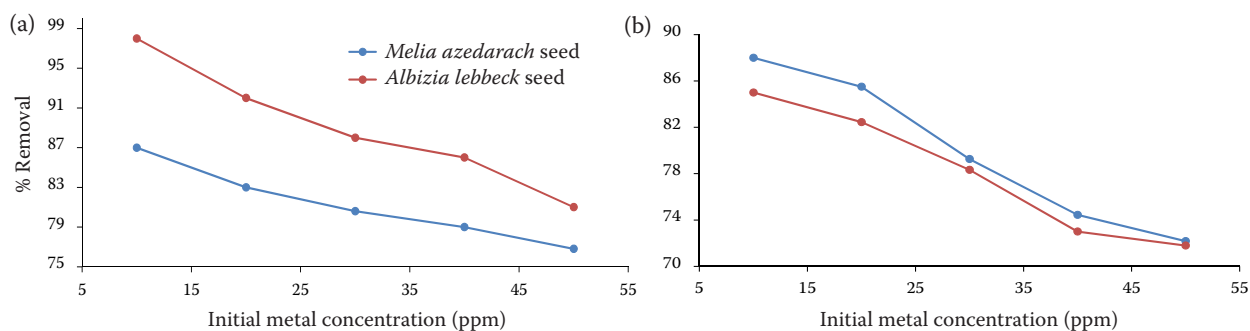
Figure 2. The effect of the different initial metal concentrations on the adsorption of Pb (a) and Cd (b) over the activated carbon prepared from the *Albizia lebbeck* and *Melia azedarach* seed shells

shown in Figure 2. It is clear that the adsorption rate of both metals increased when their concentration was increased up to 40 mg/l. This is because as the concentration of the metal ions increases, they are frequently in contact with active sites on the surface of the adsorbents and are removed as adsorbed ions. However, a further increase in the concentration of the metal ions (50 mg/l) decreases the rate of adsorption of both metals. This is because, at lower concentration, the number of metal ions is low when compared to the available adsorbent active sites, therefore, adsorption is more frequent. When the metal ion concentration is increased, more ions are crowded on the surface of the adsorbents and the active sites are quickly occupied by them. Thus, equilibrium between the adsorbed and spectator ions is established which decreases the rate of adsorption. More interestingly, the adoption activity of the *Albizia lebbeck* seeds is higher towards both Pb and Cd when the compared to *Melia azedarach* seeds due to their more porous structure as mentioned in the scanning electron microscopy (SEM) study.

The effect of the adsorbent dosage. In this work, different dosages of both adsorbents (0.1, 0.2, 0.3, 0.4 and 0.5 g) were used under an identical pH condition (pH = 5), a metal ion concentration (40 mg/l) and

contact time (120 min). It is clear from Figure 3 that as the amount of adsorbent is increased, the percent removal of both the Pb and Cd metals also increased. This is because as the mount of adsorbent is increased, the number of available adsorptions sites increased which directly increases the rate of adsorption. Also, it is clear that the adsorbent made from the *Albizia lebbeck* seeds is more pronounced than the adsorbent made from the *Melia azedarach* seeds.

The effect of the pH. In order to study the effect of the pH of the adsorption of Pb and Cd, the process of adsorption was carried out at different pH values (2, 3, 4, 5, 6 and 7) under the identical initial metal concentration conditions (40 mg/l), constant adsorbent dosage and constant contact time (120 min). It is clear from Figure 4 that as pH value is increased, the adsorption of both metal ions in the presence of both adsorbents increased and the maximum adsorption is achieved for both Pb and Cd at a pH value of 5. Naturally, at a low pH, the positively charged H^+ ions are high and they preferentially bind to the adsorbents by electrostatic adsorption as both H^+ and oxygen (in the functional groups of the adsorbents already mentioned in the FTIR study) have a strong affinity for each other to occupy the
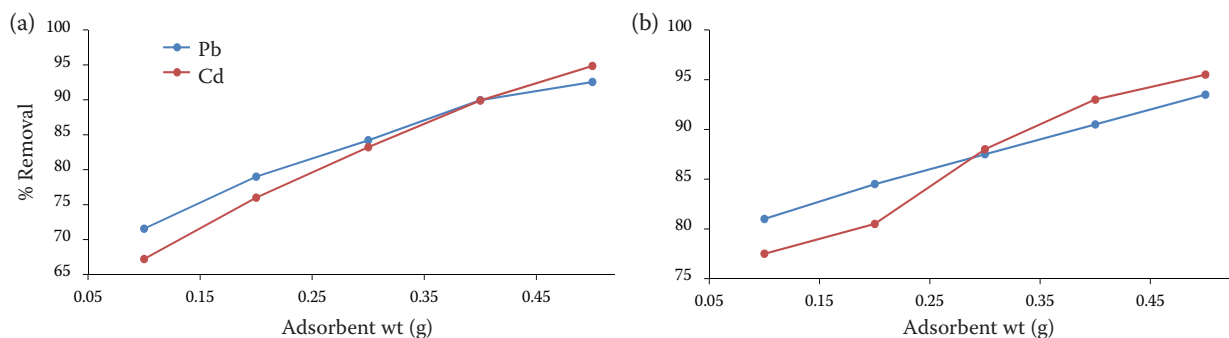

Figure 3. The effect of the adsorbent dosage on the removal of Pb and Cd over the adsorbent obtained from the *Albizia lebbeck* (a) and *Melia azedarach* (b) plant
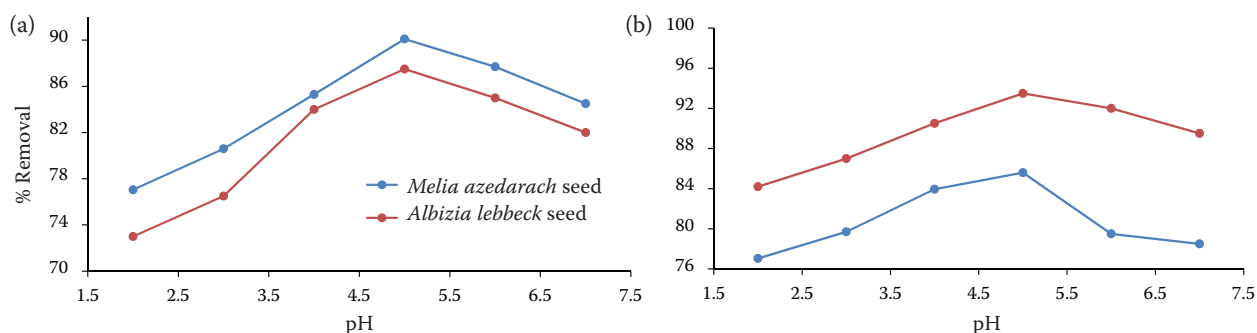
Figure 4. The effect of the different pH values on the adsorption of Pb (a) and Cd (b)

binding sites. When the pH value is increased, the number of H$^+$ ions decrease and the surface of the adsorbents is negatively charged, therefore, both metal ions get the opportunity to be adsorbed and, thus, the removal efficiency increases. Interestingly, when the pH value is increased beyond 5, the rate of adsorption decreases for both metal ions. This is because, at a high pH value, there are more hydroxyl ions (OH$^-$) in the solution which react with the Pb and Cd ions to form their insoluble hydroxides (HUANG *et al.* 2017). Thus, precipitation takes place which reduces the rate of adsorption.

The effect of the contact time. Adsorption of both Pb and Cd was studied under a variable contact time (30, 60, 90, 120 and 150 min) in the dark using the optimised amount of 0.2 g adsorbents and metal ion concentration (40 mg/l) at the given pH value of 5. It is clear from Figure 5 that as the contact time increases, the percent removal of both metal ions increases and the maximum adsorption is achieved at 120 min in the presence of both adsorbents. It means that after shaking both adsorbents for 120 min, the saturation point is reached and equilibrium is established between the adsorbed metal ions and the metal ions in the solution. Beyond 120 min, there is no change in the adsorption efficiencies of both adsorbents.

Furthermore, the *Albizia lebbeck* seeds show a higher adsorption efficiency for both metal ions than the *Melia azedarach* seeds under the identical conditions.

The effect of the temperature. The temperature has strong effects on the intermolecular forces between the adsorbate and adsorbent particles. At low temperature, the kinetic energy of the particles is low and the intermolecular attractive forces are strong, therefore, the adsorbate molecules are easily and strongly attracted to the surface of the adsorbent resulting in the more pronounced adsorption. As the temperature increases, the kinetic energy of both the adsorbate and adsorbent particles increases and the intermolecular interaction between them decreases. As a result, the adsorbate molecules are gradually desorbed from the surface of the adsorbent to decrease the rate of adsorption. As can be seen from Figure 6, the rate of adsorption of both Pb and Cd decreases as the temperature increases in the case of both adsorbents. Clearly, the rate of adsorption of both Pb and Cd is high at 20°C and decreases as the temperature increases. Interestingly, the rate of adsorption of the *Melia azedarach* adsorbent is higher than the *Albizia lebbeck* for both Pb and Cd which is explained on the basis of the nature of the interacting particles as the strength of the intermo-
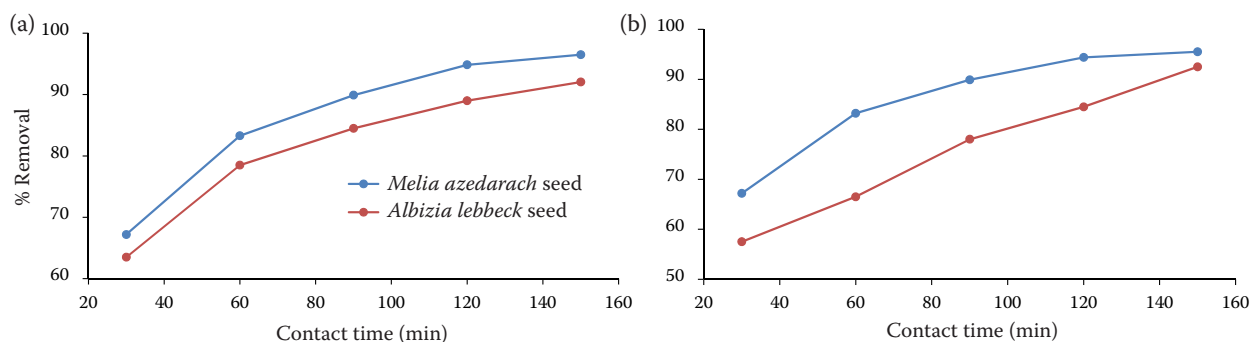

Figure 5. The effect of the contact time on the adsorption of Pb (a) and Cd (b)
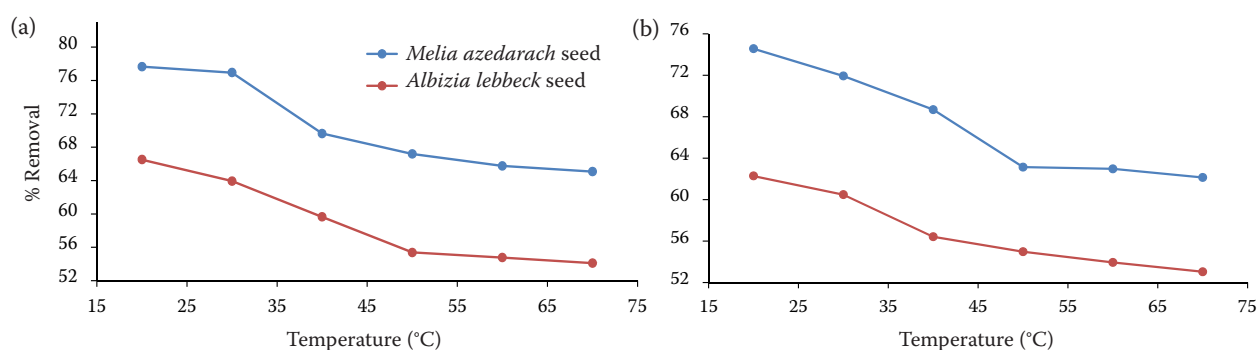
Figure 6. The effect of the temperature on the adsorption of Pb (a) Cd and (b)

lecular forces are strongly dependent on the nature of the adsorbate and adsorbent molecules.

Adsorption isotherms. The adsorption isotherms for both Pb and Cd are shown in Figures 7 and 8 as a function of the metal ion concentrations at room temperature. The obtained results were tested with the Langmuir and Freundlich equations. As the linear Langmuir equation is:

$$C_e/q_e = 1/q_m K_L + C_e/q_m$$

where:
C_e – the metal concentration
q_e – the amount of adsorbate
q_m – the highest monolayer capability
K_L – constant

Similarly, Freundlich's equation is:

$$\log q_e = \log K_f + 1/n \log C_e$$

where:
K_f – constant
n – the intensity of the adsorption

It is clear from Figures 7 and 8 that the values of q_e or $\log q_e$ linearly increase with C_e or $\log C_e$ indicating the usefulness of both models. The values of K_L and q_m in the Langmuir equation were calculated from the slopes and intercept of the linear graph and are shown in Table 1. Similarly, the values of K_f and n in the Freundlich equation were calculated from the slopes and intercept of the linear graph in Figure 8 and are shown in Table 2. The values of n obtained from the Freundlich model show that adsorptions of both Pb and Cd are favourable under the given conditions. It is clear that both plots in both Figures 7 and 8 are linear and the values of the correlation coefficients (R^2) obtained show that the adsorption of Pb and Cd on both adsorbents are well described
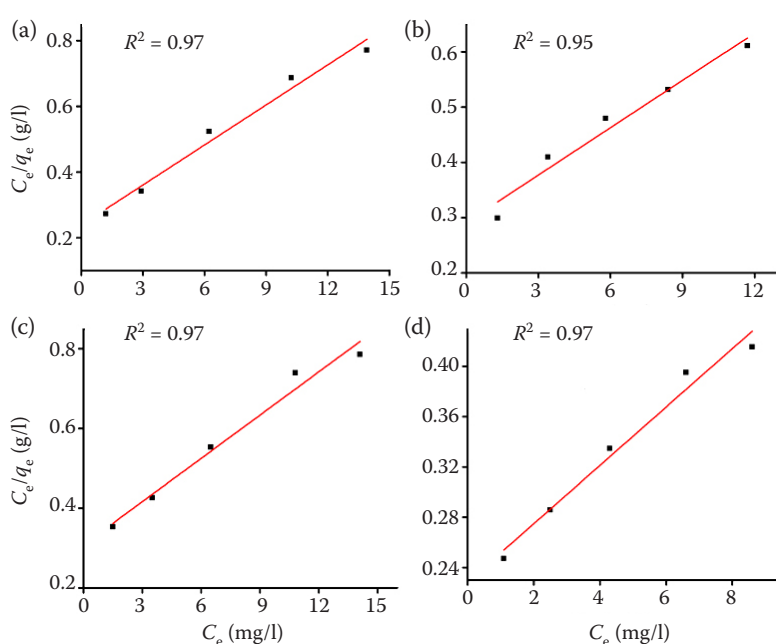

Figure 7. The Langmuir isotherms for the adsorption of Cd (a) and Pb (b) over the *Albizia lebbeck* seed shells and Cd (c) and Pb (d) over the *Melia azedarach* seed shells

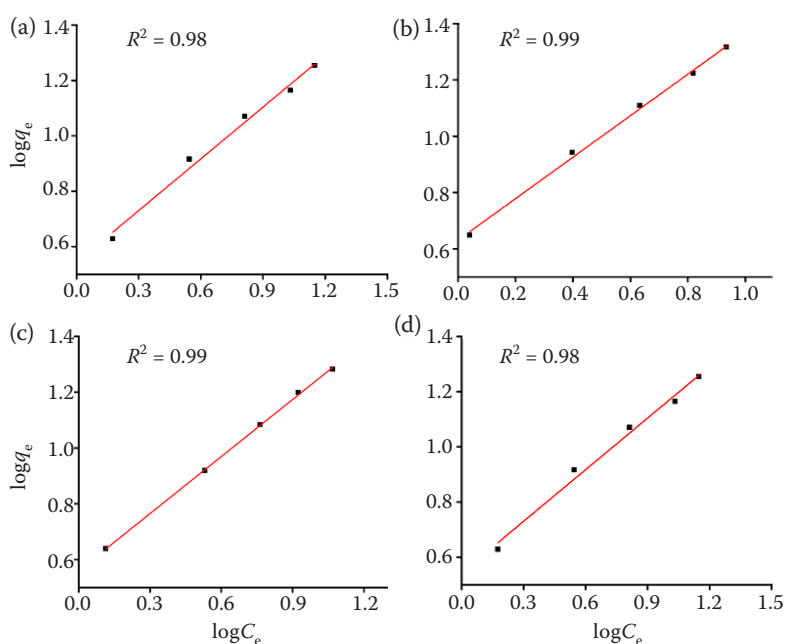C_e – the metal concentration; q_e – the amount of adsorbate

Figure 8. The Freundlich isotherms for the adsorption of Cd (a) and Pb (b) over the *Albizia lebbeck* seed shells and Cd (c) and Pb (d) over the *Melia azedarach* seed shells

C_e – the metal concentration; q_e – the amount of adsorbate

Table 1. The Langmuir constant for the adsorption of Cd and Pb by the *Albizia lebbeck* and *Melia azedarach* seed shells

Adsorbents	Cd			Pb		
	q_m	K_L	R^2	q_m	K_L	R^2
Albizia lebbeck	3.25	0.117	0.97	4.38	0.10	0.95
Melia azedarach	4.20	0.168	0.97	3.43	0.096	0.97

q_m – the highest monolayer capability; K_L – constant

Table 2. The Freundlich constant for the adsorption of Cd and Pb by the *Albizia lebbeck* seed shells and *Melia azedarach* seed shells

Adsorbents	Cd			Pb		
	K_f	n	R^2	K_f	n	R^2
Albizia lebbeck	0.20	1.79	0.98	0.20	1.35	0.99
Melia azedarach	0.64	2.14	0.99	0.251	1.46	0.98

K_f – constant; n – the intensity of adsorption

by the Langmuir and Freundlich models. The results show that the prepared adsorbents from both plants are extremely active in the adsorption of both Pb and Cd from an aqueous solution.

CONCLUSION

Activated carbon adsorbents were prepared from *Albizia lebbeck* and *Melia azedarach* seeds and applied for the adsorption of lead and cadmium metals from wastewater by changing some basic parameters. The studies showed that activated carbon can be consid-

ered an effective, easily available, low cost and natural adsorbent for removing Pb and Cd from contaminant wastewater. The removal efficiencies of both metals were strongly dependent on their initial concentration, contact time, pH and amount of adsorbent. Interestingly, the *Albizia lebbeck* seeds were more superior to the *Melia azedarach* seeds. 0.2 g adsorbent each of *Albizia lebbeck* and *Melia azedarach* removed 75 and 62% Pb and 77 and 66% Cd from 100 ml of a 40 mg/l concentrated solution at 120 min at pH 5, respectively. The Freundlich isotherm and Langmuir isotherm were well fitted to the experimental data. We believe that this work will provide a convenient way to synthesise low cost activated carbon adsorbents for the removal of highly toxic metals from wastewater to safeguard our environment for future generations.

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