Adsorption of Pb(II) by activated carbon prepared from Melia azedarach fruit: Equilibrium and thermodynamics

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Abstract

In this work, a low-cost activated carbon as well as non-hazardous material, with high adsorption capacity, was prepared from *Melia azedarach* fruit (MF) by ZnCl2 activation for the removal of Pb(II) toxic metal from aqueous solutions. The microstructure of the activated carbon was observed by Scanning Electron Microscopy (SEM). Batch experiments have been performed as a function of pH, contact time, dose of sorbent, initial Pb(II) concentration, temperature and strength ionic. It was found that the adsorption process was very quick and the equilibrium attained within 10 min. The maximum adsorption capacity for Pb(II) using Langmuir isotherm was 111.11 mg g-1. Thermodynamic study indicated that the Pb(II) adsorption was feasible, spontaneous, and endothermic. The results show that the produced activated carbon from *Melia azedarach* fruit is an efficient and cost-effective adsorbent for removing Pb(II).

Keywords: Chemically prepared activated carbon; lead; *Melia azedarach* fruit; removal.

Introduction

Lead is an important compound used as an intermediate in processing industries such as plating, paint and dyes, glass operations, and lead batteries [1,2]. However, the presence of lead in environment, even at a very low level, would be harmful to aquatic life and human health in terms of its toxicological, potential carcinogenic and neurotoxical effects [3]. The permissible limit of lead in drinking water and surface water intended for drinking, as set by EU, USEPA and WHO, are 0.010, 0.015 and 0.010 mg L-1, respectively [4,5]. There are many methods for removing lead from wastewaters, including chemical precipitation [6], electrolysis [7], adsorption [8,9], ion exchange [10], reverse osmosis and membrane separation [11]. However, these techniques are almost expensive. Among of the mentioned methods, adsorption has been proven to be one of the most effective and simplest techniques [12]. Activated carbon is an adsorbent that was used widely in wastewater treatments [13]. It has high porosity, large internal surface area, and relatively good mechanical strength. Despite its widespread application in industry, activated carbon remains an expensive

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material. So, it is necessary to develop low-cost effective carbons that can be used to water pollution control. A wide variety of low-cost materials have been applied to remove heavy metals from aqueous solutions, including Enteromorpha prolifera [14], Polygonum orientale Linn [13], hazelnut husks [15], palm shells [16], spartina alterniflora [17], marine green algae [18], bamboo [19], hazelnut shell [20], arachis hypogea shell powder and Eucalyptus cameldulensis saw dust [21], rice bran [22], Portulaca plant [23], Bacillus gibsonii waste biomass[24], Lemna minor [25] and rubber tire [26].

Melia azedarach (MF) is a plant that is widely distributed in streets and parks of Iran for its shadow. Its fruits are waste and toxic for human. No investigations, however, have been carried out to adsorb Pb(II) ions by using *Melia azedarach* fruit-activated carbon (MFAC). Consequently, this paper aims to examine the application potential of developing an effective low-cost adsorbent from MF by ZnCl2 activation and to investigate its ability to treat wastewater that contains toxic lead. The properties of MFAC are investigated through SEM analysis. The adsorption performances (i.e., pH, contact time, dose of sorbent, temperature, and ionic strength) of MFAC are studied. The adsorption isotherms and probable mechanism have also been explained.

Experimental

Materials and reagent

All reagents were of analytical grade. Deionized and distilled water was used in all experiments. The stock solution 1000.0 µg mL^{-1} of Pb (II) was prepared by dissolving an appropriate amount of Pb(NO$_3$)$_2$, (99.99%, Merck, Darmstad, Germany), in distilled water and diluting to 100.0 mL. The standard working solutions were diluted daily prior to use. NaCl and Na$_2$SO$_4$ 99% obtained from Merck were used for ionic strength examination.

Instruments

A SensAA GBC (Dandenong, Australia) atomic absorption spectrometer was used for measurement of lead in air-acetylene flame. A mechanical shaker KS 130 basic (Deutschland, Germany) having speed control and timer was used for batch experiments. A Metrohm pH meter (Herisau, Switzerland) was employed for pH measurements.

Preparation of MFAC

The *Melia azedarach* fruits were obtained from Kerman province in Iran. They were washed with distilled water to remove all foreign materials and sun dried until all the moisture was evaporated. Then, the fruits were ground to a fine powder using a laboratory mill, and sieved to a uniform particle size (40 - 70 mesh) prior to the activation process. The obtained powder was mixed with a ZnCl$_2$ solution at a ratio of 1:2 (g MF/g ZnCl$_2$) and allowed to soak for 24 h at ambient temperature. The excess ZnCl$_2$ solution was then decanted and treated *Melia azedarach* fruit with ZnCl$_2$ was dried in an oven for 24 h at 100 °C. The residue was then placed in a muffle furnace, at 500 °C for 2 h. The obtained activated carbon (MFAC) was cooled to room temperature and washed several times with deionized water. Wash waters were tested with silver nitrate solutions for the detection of chloride ions. Then activated carbon was dried

at 110 °C and sieved to obtain the desired particle size (40 – 70 mesh).

Characterization of the prepared adsorbent

The microstructure of the MFAC was observed by Scanning Electron Microscopy (SEM) (Cam Scan MV2300) and is shown in Figure 1. Scanning electron micrographs were recorded without sample coating with 500 and 1000x magnification. These figures show that the adsorbent had a coarse porous surface with irregular pores, indicating relatively high surface areas.
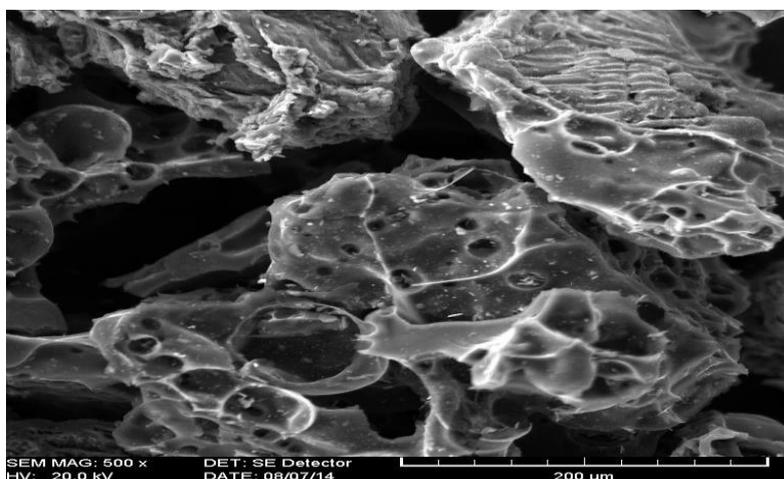
(a)
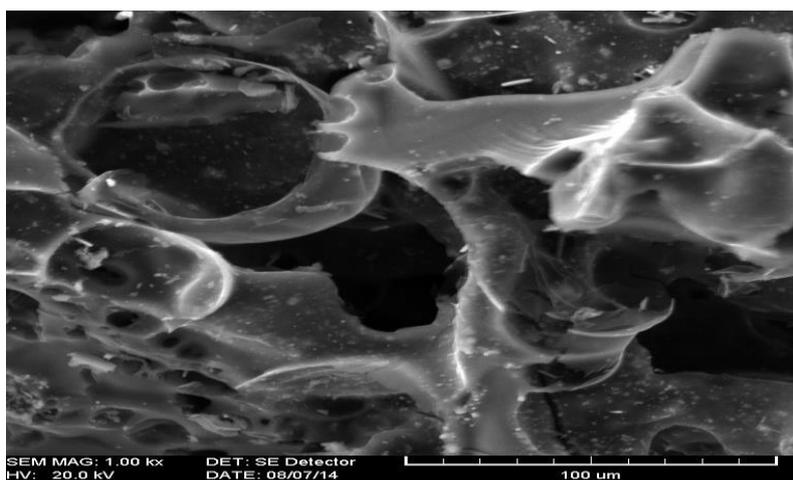
(b)

Figure 1. SEM images of MFAC (a) magnification: 500x and (b) magnification: 1000x

Chemical characterization was studied by Fourier transform infrared (FTIR) spectroscopy, also, in order to identify the functional groups at the surface of the MFAC. FTIR spectrum was recorded (Figure 2) with a Brucker Tensor 27 spectrometer (Deutschland, Germany), from 400 to 4000 cm^{-1}, using the KBr wafer technique. The bands at about 3400 and 1000-1220 cm^{-1} are attributed to ν(O–H) vibrations in the hydroxyl and phenolic groups. The location of the

bands for hydrogen-bonded OH groups are usually in the range of 3200–3650 cm^{-1} for alcohols and phenols. Two bands at about 1200 and 1700 cm^{-1} are attributed to the carboxylate group.
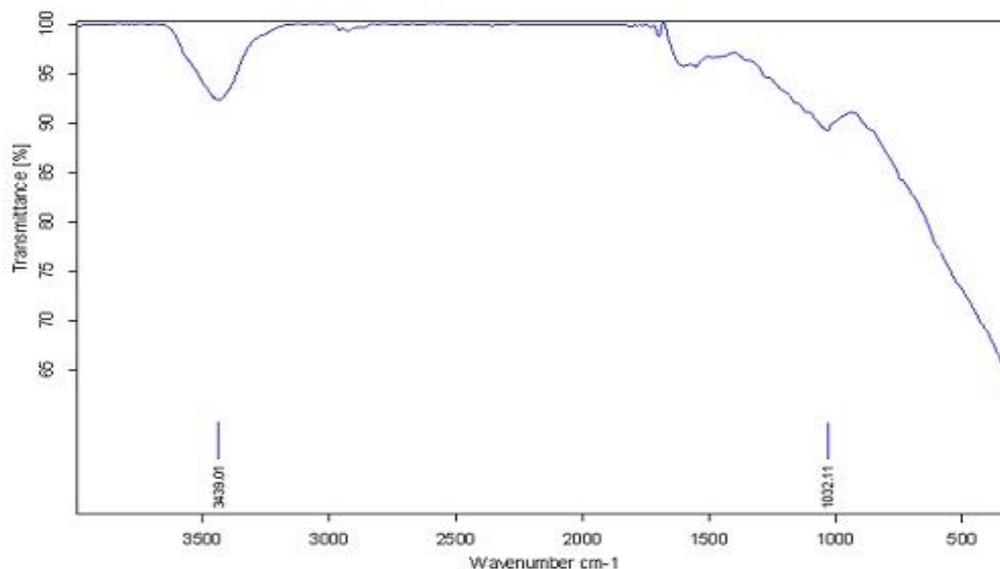
Figure 2. Fourier transforms infrared spectrum of MFAC

Adsorption experiments

Batch adsorption experiments were carried out by shaking 0.3 g of the adsorbent (MFAC) with 50 mL of the aqueous solutions 30 µg mL^{-1} of Pb(II) ions in 125 mL stoppered pyrex glass flask, at a fixed temperature. The initial pH of the solutions was adjusted with diluted HNO$_3$ or NaOH 0.1 M solution and the shaking speed was 400 rpm for 10 min. At the end of the adsorption period, the mixtures were filtered out and analyzed for its metal ion concentration using flame atomic adsorption spectrometer. The amount of Pb(II) ions adsorbed was obtained from the following equation:

$$q_e = V (C_0 - C_e) / M \qquad (1)$$

The equilibrium adsorption capacity (qe) of the adsorbent can be defined as the equilibrium amount in (mg) of MFAC adsorbed per unit mass (gram) of adsorbent, and Co and Ce represent the Lead concentrations before and after equilibrium (mg/L)

respectively, V is the volume of the lead solution (L) and M is the mass of the adsorbent used in the reaction mixture (g).

The removal percent was calculated as follow:

$$R\% = (C_0 - C_e) \times 100 / C_0 \qquad (2)$$

Results and discussion

Generally, two different processes of physical and chemical activations were used to prepare activated carbon. Physical activation is to carbonize raw materials at high temperatures in an inert atmosphere followed by oxidation treatment with steam, air, or CO$_2$. Chemical activation involves impregnation of the raw materials with dehydrating chemical agents including phosphoric acid, sulfuric acid, KOH, NaOH, and ZnCl$_2$. The impregnation with ZnCl$_2$ plays an important role in increasing carbonization ability of the precursors and acquiring a desired pore structure of activated carbon [14]. In this work a low-cost carbon active was prepared and activated by ZnCl$_2$ and

then adsorption properties of this sorbent was investigated.

Effect of the sample pH

The pH of aqueous solution is an important factor, because it influences the metal speciation solutions and surface properties of the adsorbent, and hence can affect the extent of adsorption. Thus, the adsorption behavior of Pb(II) onto MFAC was investigated over a pH range of 2.2-7.4 at room temperature (Figure 3). Higher pH values were not examined because lead hydroxide could be formed.

It was observed that the percentage of Pb(II) adsorption on MFAC increased with increasing pH. The maximum removal was occurred at initial pH about 7.4. The decrease in the adsorption at low pH values could be attributed to the increase in competition between protons and Pb(II) ions for the adsorption sites. With increasing pH, the negative charge on the surfaces of carbon increased since the oxygen-containing functional groups became more and more deprotonated, which enhances the adsorption of the positively charged Pb(II) ions through electrostatic force of attraction. To avoid precipitation of Pb(II) ions, the experiments were not carried out at pH>8.

Effect of contact time

Figure 4 shows the effect of contact time on the adsorbed amount of Pb(II) by MFAC from a solution with an initial Pb(II) concentration of 30 mg L^{-1} at room temperature. The adsorption rate was very fast initially; about 83.5% of total Pb(II) was removed within 2 min. However, the rate of adsorption becomes almost constant 10 min. Thus, 10 min was selected as equilibration time, which was sufficient for the removal of Pb(II) by this adsorbent.
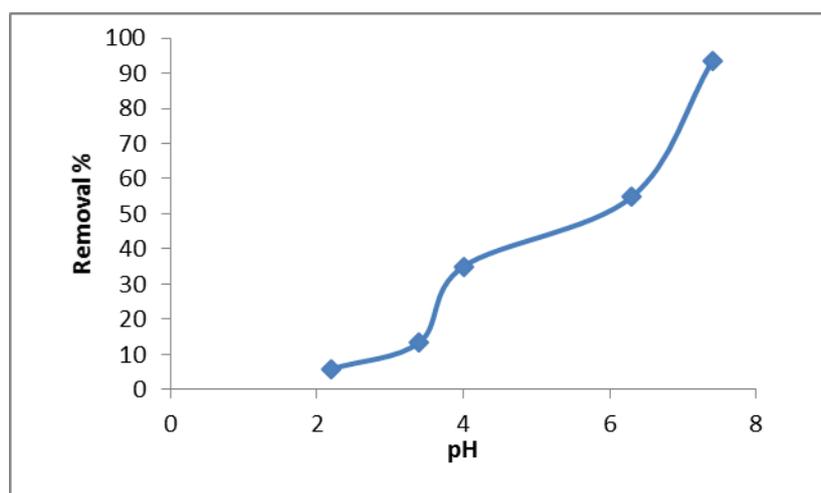
Figure 3. The effect of pH on removal of lead (adsorbent: 0.3 g, C_0: 30 µg mL^{-1}, T: 301 K, time: 10 min)
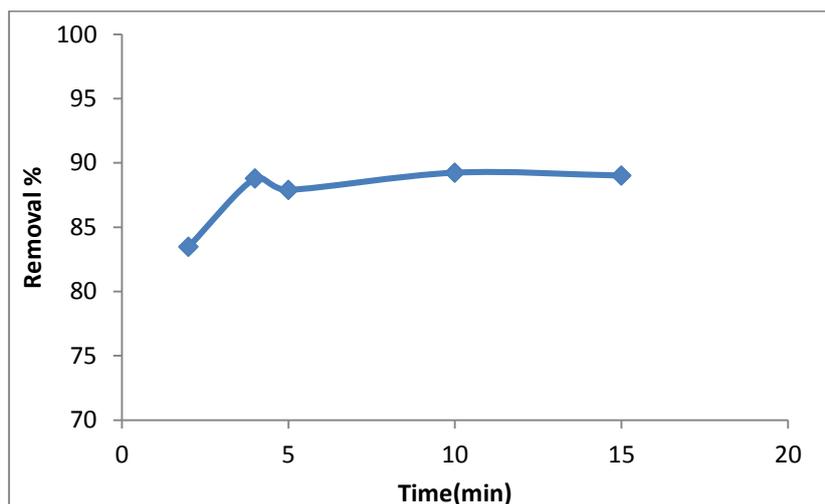
Figure 4. The effect of contact time on the sorption of lead (pH=7.4, C_0: 30 µg mL^{-1}, T: 301 K, adsorbent: 0.3 g)

Effect of adsorbent dosage

The amount of adsorbent is an important parameter, because this factor determines capacity of an adsorbent. The influence of adsorbent dosage on Pb^{2+} sorption was studied by varying the amount of adsorbent. Figure 5 shows that the percentage removal of lead increased from 72.35% to 93.47% with increase of adsorbent dosage from 0.02 to 0.4 g. As adsorbent dose increase, the number of adsorbent particles also increases, that makes the greater availability of exchangeable sites for adsorption. There was no significant increase in removal, at amount of more than 0.3 g of the adsorbent. Therefore, 0.3 g of adsorbent was selected for after-steps.

Effect of initial concentration and adsorption isotherms

The effect of Pb(II) concentration on the sorption by MFAC was investigated with varying the lead solution concentrations. With increasing concentration of the solution, qe increased, while R% decreased. At low initial concentration, the surface area and the availability of adsorption sites were high, and the Pb(II) ions were easily adsorbed and removed. At high initial concentration, the total available sites are limited, resulting in a decrease in removal of the Pb(II) ions. The increased qe at high concentration can be attributed to the enhanced driving force.
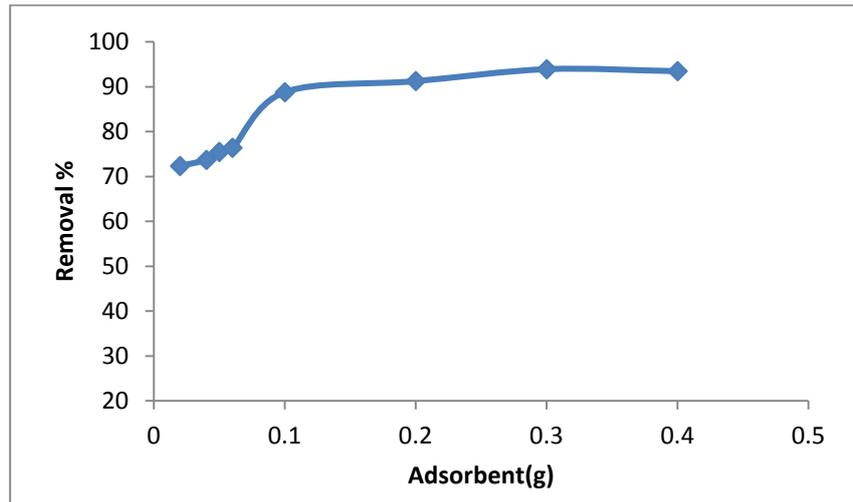
Figure 5. The effect of adsorbent dosage on removal of lead (pH=7.4, C_0: 30 µg mL^{-1}, T: 301 K, time: 10 min)

Langmuir and Freundlich isotherms have been used to describe adsorption phenomena on the adsorbent. The sorption data have been analyzed according to the linear form of the Langmuir isotherm, as represented in Eq. (3)

$$C_e / q_e = (1/Qb) + (1/Q) C_e \qquad (3)$$

b is Langmuir constant and Q is adsorption capacity expressed in mg g^{-1}. The Freundlich isotherm predicts that the concentration of metal ions on the adsorbent will increase as long as there is an increase in the metal ion concentration in liquid, as represented in Eq. (4)

$$q=K_f C_e^n \qquad (4)$$

where n is the Freundlich constant, and K_f is the adsorption coefficient, q is the weight adsorbed per unit weight of adsorbent.
Taking logs gives Eq. (5).

$$\log q = \log K_f + n \log C_e \qquad (5)$$

Freundlich and Langmuir isotherms for the adsorption of Pb(II) on the prepared activated carbon are also presented in Figure 6. The results showed that the adsorption processes can be correlated with both Langmuir and Freundlich isotherms. The values of constants obtained from intercepted and slope of plots and values of calculated according to Eqs. (3) and (5) are given in Table 1.

Effect of ionic strength
Ionic strength is one of the important parameters influencing aqueous phase equilibrium. Generally, adsorption decreases with increasing ionic strength in the aqueous solution. Figures 7 and 8 show the effect of various amounts of NaCl and Na2SO4 on the adsorption of Pb(II) on MFAC. It was seen that there was no significant decrease in the removal efficiency. As, even at high concentrations of the salt, the sorbent still have big percent removal efficiency and can be used to efficiency remove Pb2+ from aqueous solutions with high salt concentration.
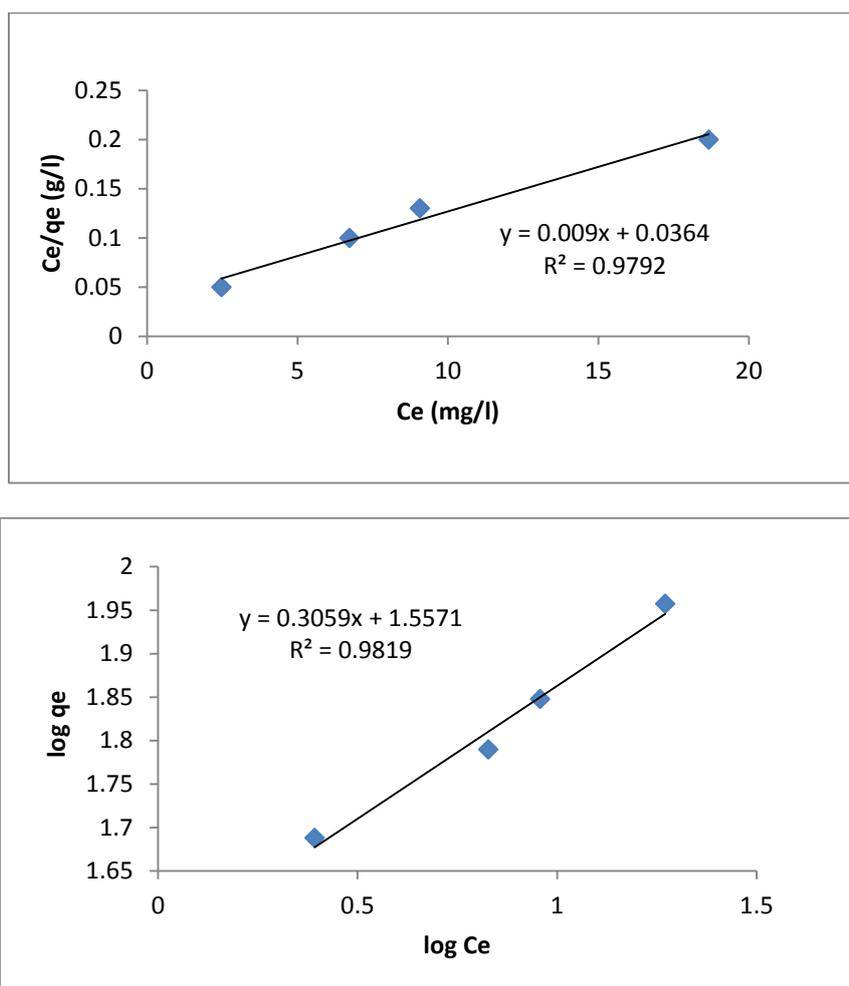
Figure 6. Langmuir and Freundlich and isotherms for the the sorption of lead on MFAC

Table 1. Langmuir and freundlich isotherm constants for lead adsorption on the MFAC.

Sorbent	Langmuir isotherm			Freundlich isotherm		
	$Q(mg\ g^{-1})$	$b(\ L\ mg^{-1})$	R^2	K_f	n	R^2
MFAC	111.11	0.25	0.979	36.06	0.3	0.981
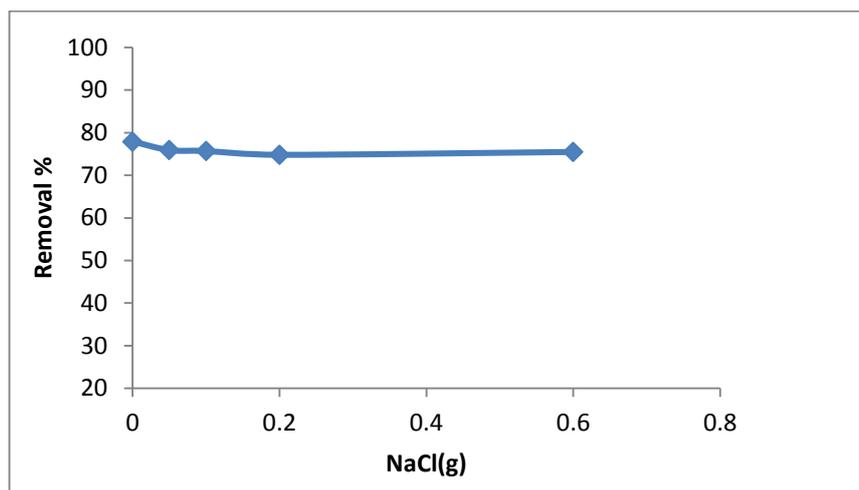
Figure 7. Effect of NaCl on sorption of lead (pH=7.4, C_0: 30 µg mL^{-1}, T: 301 K, time: 10 min, adsorbent: 0.3 g)
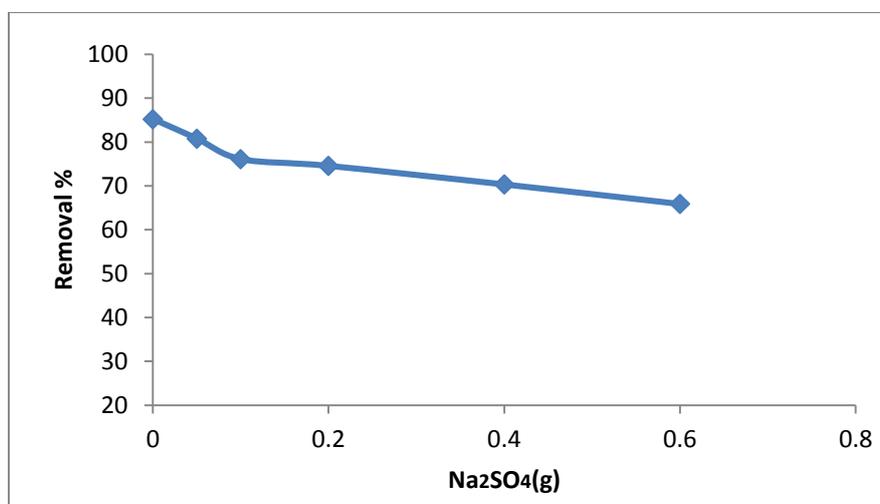
Figure 8. Effect of Na$_2$SO$_4$ on sorption of lead (pH=7.4, C_0: 30 µg mL^{-1}, T: 301 K, time: 10 min, adsorbent: 0.3 g)

Effect of temperature and thermodynamic parameters

The study of the temperature gave valuable knowledge about the enthalpy and entropy changes during adsorption. The removal of Pb(II) onto adsorbent was examined at 301, 307, 311 and 315 K to determine the adsorption thermodynamic parameters. Adsorption ability of the MFAC increased with increasing temperature, that illustrates adsorption of Pb(II) ions onto MFAC is an endothermic process.

The Gibbs free energy change, ΔG^0, is fundamental criterion of spontaneity. The apparent equilibrium constant (K_c) of the adsorption is defined as:

$$K_c = (C_0 - C_e)/C_e \qquad (6)$$

where C_e is the concentration of Pb(II) at equilibrium. The K_c is used in the following equation to determine the Gibbs free energy.

$$\Delta G0 = - RTlnK \qquad (7)$$

The enthalpy (ΔH^0) and entropy (ΔS^0) can be obtained from the slope and intercept of equation of ΔG^0 versus T.

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \qquad (8)$$

R the gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature (K).

As it is shown in Table 2, the values ΔS^0 and ΔH^0 are positive for adsorption of Pb(II) on the MFAC. The positive value ΔH^0 indicates that adsorption process is endothermic and the positive value ΔS^0 shows the increase in degree of freedom or increase the disorder of adsorption.

Conclusion

The present work indicated that the activated carbon prepared from *Melia azedarach* fruit (MFAC), is an effective adsorbent for the removal of Pb(II) from aqueous solutions.

Equilibrium studies showed that the adsorption of Pb(II) onto the new adsorbent followed the Langmuir and Freundlich isotherm and the maximum adsorption capacity of Pb(II) using Langmuir isotherm was determined to be 111.11 mg g^{-1}. The fast adsorptive and low cost and regenerative ability of this adsorbent make it a promising method for cleanup of industrial wastewaters. The adsorption capacity of MFAC was compared with other adsorbents and is presented in Table 3. The adsorption capacity of MFAC was greater than the reported values of other adsorbents. Also, equilibrium time for the proposed adsorbent is shorter than other adsorbents. Negative values of $\Delta G°$ for the adsorption and positive value of $\Delta H°$ suggested that the adsorption process was feasible and spontaneous and endothermic in nature.

Table 2. Thermodynamic parameters for adsorption of lead on MFAC

Temperature (K)	ΔG^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})	ΔH^0 (kJ mol^{-1})
301	-3.56	169.93	47.74
307	-4.26		
311	-4.92		
315	-5.99		

Table 3. Comparison of adsorption capacity and **equilibrium** time of MFAC with other adsorbents to adsorb lead

Adsorbent	Adsorption Capacity $(mg\ g^{-1})$	Equilibrium Time	Ref.
Polygonum orientale Linn activated carbon	13.05	30 min	[13]
Spartina alterniflora activated carbon	99.0	20 min	[17]
Marine green activated carbon	24.15	60 min	[18]
Bamboo activated carbon	0.67	2-4 h	[19]
Lemna minor activated carbon	170.9	30 min	[25]
Organic–inorganic composite	327.87	120 min	[27]
Amygdalus Scoparia shell activated carbon	28.74	10 min	[28]
DNPH-Al_2O_3	100.0	90 min	[29]
Fe_2O_3-Ceramisite	17.4	3-8 h	[30]
Maghemite nanotubes	71.42	60 min	[31]
β-MnO_2	16.72	24 h	[32]
Activated tea waste	81.0	-----	[33]
Sawdust of Meranti wood	37.04	60 min	[34]
Magnetic chitosan	76.90	------	[35]
Pine cone activated carbon	27.53	------	[36]
Cow bone activated carbon	42.3	6 h	[37]
Melia azedarach fruit activated carbon(MFAC)	111.11	10 min	This work

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