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Research Article

Preparation of activated carbon from Pterocarya fraxinifolia and Isotherms and thermodynamics evaluation for Pb (II) sorption

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ABSTRACT

Low-cost activated carbon was prepared from Pterocarya fraxinifolia. To determine the adsorption process the effects of various operating parameters, initial concentration of metal ions (50–200 mg/L) and temperature (298–328 K) were investigated in a batch adsorption technique. Equilibrium data were analyzed by the Langmuir and Freundlich isotherm model. Langmuir and Freundlich isotherms provided the best fit to the equilibrium data and maximum adsorption capacity of 370.370 mg/g at 298 K. The thermodynamic parameters, such as Gibb's free energy change (ΔG), standard enthalpy changes (ΔH) and standard entropy change (ΔS) was evaluated. The value of ΔG was found negative for the adsorption of Pb (II) which confirmed the feasibility and spontaneity of the adsorption process.

Keywords: Pterocarya Fraxinifolia; Isotherm; Thermodynamic; Pb (II); Equilibrium

1. Introduction

Heavy metal ions in water have an adverse effect on human health and the ecosystem. Lead ion, a typical hazardous heavy metal ion, commonly exists in the wastewater streams of various industries, such as acid mining, battery manufacturing, printing, and painting. The presence of lead in water may damage the kidney, nervous system, reproductive system, liver, and brain due to its accumulation in the human body [1]. There are various techniques for reducing the toxicity of heavy metals, including chemical precipitation, adsorption, electrolysis, ion exchange, and membrane separation. Among the aforementioned methods, adsorption has been proven to be one of the simplest and most effective techniques. Currently, activated carbon is widely used as an adsorbent in wastewater treatments. It has highly developed porosity, a large internal surface area, and relatively high mechanical strength. Despite its widespread use in industries, activated carbon remains an expensive material [2]. Carbonization is a good technique for increasing the adsorption capacities of such materials for the removal of heavy metals from water and wastewaters.

The presence of lead ions in the aquatic environment has been of great concern to scientists due to their increased discharge, non-biodegradable, toxic, and other adverse effects on human being as well as the fauna and flora [3]. Many methods such as chemical precipitation, electrochemical reduction, ion exchange, reverse osmosis, and membrane separation have been developed to remove lead from wastewater. However, these technologies are either expensive for the treatment and disposal of the secondary toxic metal sludge or ineffective when lead is present in the wastewater at low concentrations. Currently, activated carbon adsorption is a widely used technology because it is simple, low cost and effective for removing low lead concentration waste streams [4]. Chemical activation involves impregnation of the raw materials with dehydrating chemical agents including phosphoric acid, sulfuric acid, KOH, NaOH, and $ZnCl_2$. The advantages of lower temperature and high carbonization yield of the chemical activation make it be widely used to produce activated carbon.

2. Experimental

Row sorbents was air-dried, crushed and was impregnated with concentrated H_3PO_4. Then materials were activated in a hot air oven at 150 °C for 24 h and then pyrolysed at 450 °C for

5 h. The carbonized material was washed with distilled water and the activated carbon was then soaked in 1% $NaHCO_3$ solution to remove any remaining acid. It was washed with distilled water until the pH of the activated carbon reached 6.5, dried at 105 °C, and sieved to the particle size 0.125 mm. Analytical grade lead nitrate (Merck Ltd, 99% purity) was employed to prepare a stock solution containing 1000 mg/L of Pb (II).The stock solution was diluted with deionized water to the desired Pb (II) concentrations. The effect of pH on the adsorption of Pb (II) was carried out by varying the pH from 2.0 to 7.0 at 25±1 °C using 50 ml of solution with ion concentration 100 mg L-1. For the assessment of amount of adsorbent on adsorption, 100 mg L-1 lead (II) solutions were stirred for 30 min with different amounts of adsorbents. For study the effect of contact time, suspensions consisting of 0.04 g of PFAC and 50 ml of 100 mg L-1 lead (II) solutions were stirred from 1 to 100 min. The amount of adsorbed Pb (II) ions was calculated by equation 1 and 2:

$$q_t = \frac{(C_o - C_e)}{m} \times V$$

$$\%R = \frac{C_o - C_e}{C_o} \times 100$$

where C0 is the initial concentration of Pb (II) ion, V is the volume of the solution, m is the mass of PFAC and C is the residual concentration of Pb (II) ion at any time or equilibrium.

3. Result and discussion

3.1. Effect of pH

pH is an important parameter that highly affects the metal ion adsorption. It not only influences the surface properties of adsorbent but also affects the speciation of the metal ion in solution [5]. An increase in the solution pH led to an increase in %removal for the adsorption of lead (II) ions, especially at pH values greater than 5 (Fig. 1). According to the Pourbaix diagram of lead, lead (II) ion precipitates as $Pb(OH)_2$ at pH values greater than 6.7.

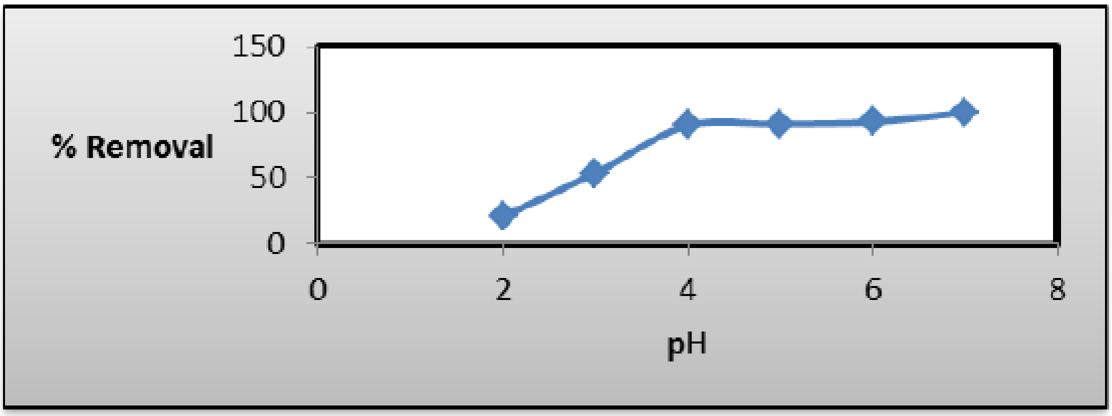


Fig.1. Effect of solution pH on adsorption of lead

3.2. Effect of adsorbent dosage

Adsorbent dosage is an important parameter because it determines the capacity of an adsorbent for a given initial concentration of the adsorbate. Fig. 2. Can be seen that by increasing the amount of adsorbents from 0.01 g to 0.04 g for the adsorbent the amount of adsorbed lead significantly increased from 81.31% to 96.16% and reached plateau. All active sites on the adsorbent surface are then occupied and increase in adsorbent dosage do not provide higher uptake of lead (II) ions.

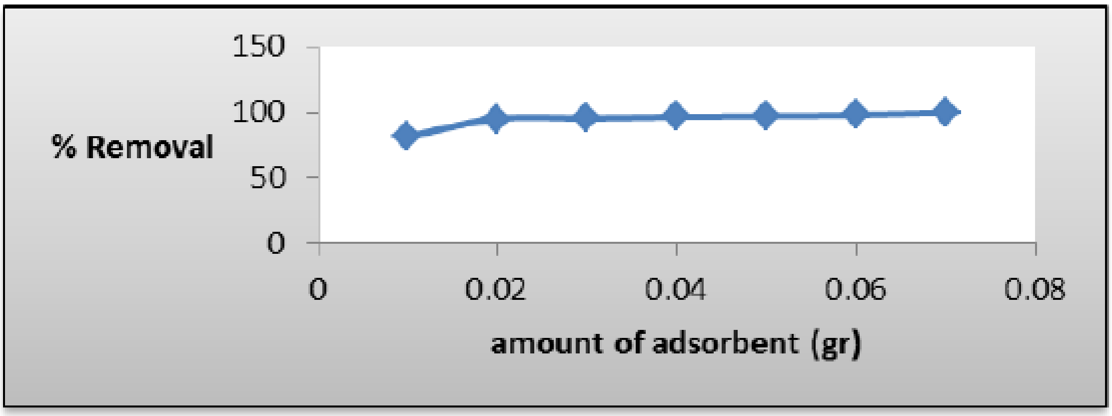


Fig. 2. Effect of adsorbent dosage on adsorption of lead

3.3. Effect of contact time

The time needed for the interaction between the adsorbate and adsorbent is crucial (i.e., the faster the removal, the better the adsorbent). Hence, it is important to study the effect of contact time on the removal of the heavy metal with PFAC. Fig.3. shows the effect of contact time on the adsorption of Pb(II) onto PFAC from aqueous solutions. The % removal of metal ion increased significantly within the first 30 min.

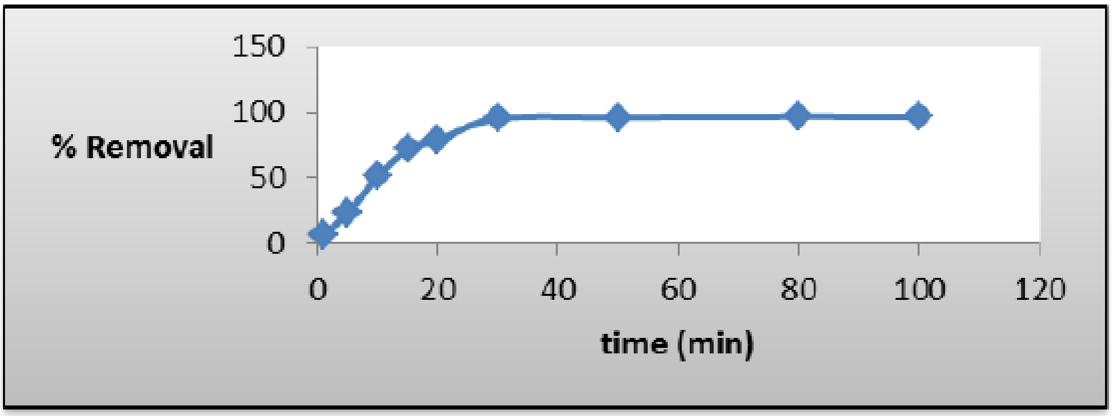


Fig. 3. Effect of contact time on adsorption of lead

3.4. Kinetics of adsorption

The kinetics of Pb (II) adsorption on PFAC was analyzed using pseudo first-order and pseudo second-order. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (R2). The pseudo-first order equation The pseudo-first order equation [6] is generally expressed as:

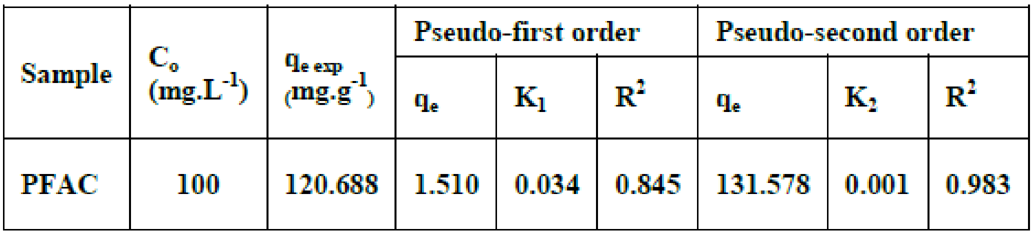
$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$

The pseudo second-order equation the pseudo second-order adsorption kinetic rate equation [6] is expressed as:

$$\frac{t}{q_t} = \frac{1}{k2 q_e^2} + \frac{t}{q_e}$$

Where qe and qt are the amounts of Pb (II) adsorbed (mg/g) at equilibrium and at time t, respectively, and k1 is the rate constant of first order adsorption (min-1). A straight lines were obtained by plotting log(qe − qt) against t. The values of the rate constant k1 and qe were obtained from the slopes and intercepts of the plots, respectively (Table 1).

Table1. Kinetic constant parameters obtained for Pb (II) adsorption on PFAC



Sample	**C_o (mg.L^{-1})**	**$q_{e\ exp}$ (mg.g^{-1})**	**Pseudo-first order**			**Pseudo-second order**		
			q_e	**K_1**	**R^2**	**q_e**	**K_2**	**R^2**
PFAC	**100**	**120.688**	**1.510**	**0.034**	**0.845**	**131.578**	**0.001**	**0.983**

The fitted linear regression plots showed that the experimental data are well fitted to the pseudo-second-order kinetic with higher value correlation coefficient (R2 = 0.983), compared to the pseudo-first-order model.

3.5. Effect of initial concentration and temperature

The initial concentration provides an important driving force to overcome all mass transfer resistance of lead molecules between the aqueous and solid phases. The temperature influences the adsorption equilibrium and its variations produce a displacement from or toward the phase adsorbed. Also, an increase in temperature generally improves the solubility of the molecules (if in liquid phase) and their diffusion within the pores of the adsorbent materials. The adsorption isotherms of Pb (II) on PFAC at 298 K, 313 K, and 328 K are shown in Fig. 4. At lower ion concentrations, an increase in metal removal was occurred due to high ratio of adsorbent sites to ion molecule. At higher concentration of lead, removal percentage decreased significantly due to saturation of adsorbent surface. The amounts adsorbed of lead rose with the decrease of the temperature, indicating the apparent exothermic nature of the entire process.

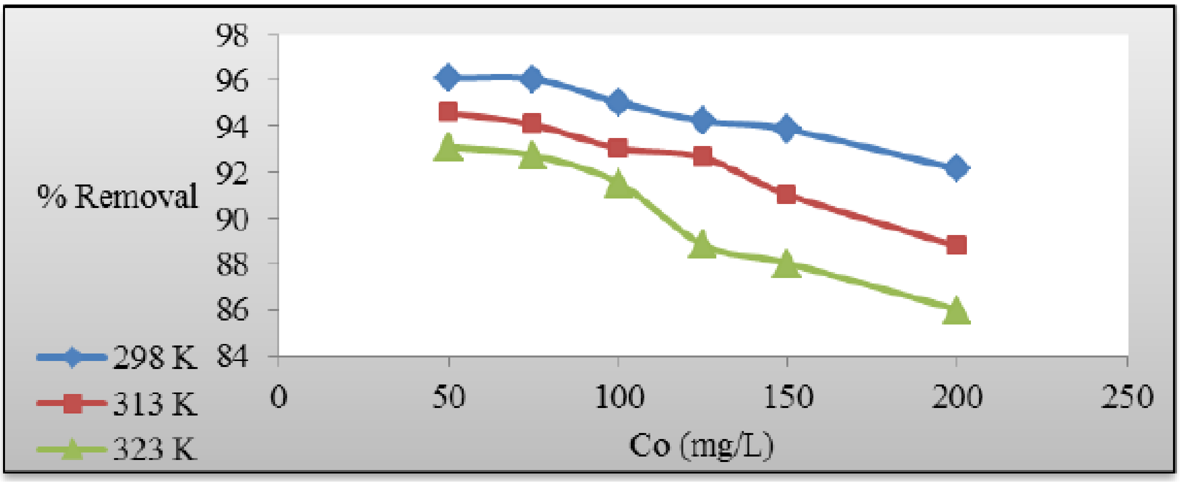


Fig. 4. Effect initial concentration and temperature on adsorption of lead

3.6. Isotherm of adsorption

The isotherm is meaningful to the design of adsorption systems, and its shape provides information about the homogeneity or heterogeneity on the adsorbent surface. Furthermore, the correlation of the equilibrium data with either theoretical or empirical equations is essential to practical operation.

3.7. Langmuir and Freundlich isotherm

The linear form of the Langmuir isotherm [7] is represented as:

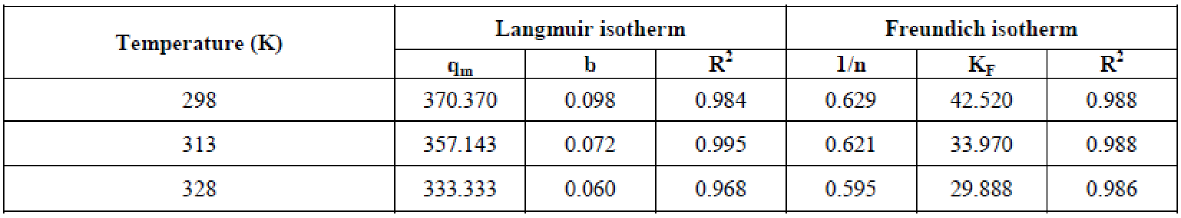
$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m}$$

Where qe is the amount of Pb (II) adsorbed per unit weight of PFAC in mg/g and Ce is the equilibrium solution concentration expressed in mg/L. Qm and b are the Langmuir constants related to the capacity (mg/g) and intensity (L/mg) of adsorption, respectively. Langmuir constants, Qm and b were calculated from the slopes and intercepts of plots of Ce/qe versus Ce, respectively, and are given in Table 1 along with correlation coefficients (R2).The Freundlich isotherm [8] was also modeled to fit the equilibrium data and is given by the following equation:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e$$

Where K_F and 1/n are Freundlich constants related to adsorption capacity and energy of adsorption, respectively. Values of Freundlich constants and correlation coefficient (R2) are given in Table 1. Table 1 show that the Langmuir adsorption capacity (b) increased with increasing the solution temperature from 25 °C to 55 °C and maximum adsorption capacity being 370.370, 357.143 and 333.333 mg/g, respectively. Table 2 show that the values of kF and n for the Freundlich isotherm model vary with solution temperature. The value of 1/n reflects the intensity of the adsorption. In this case, n are equal to 0.629, 0.621 and 0.595 at 25, 40 and 55°C that there is a strong interaction between PSAC and lead ion. The Freundlich and Langmuir isotherm provides the best correlation for the experimental data.

Table2. Langmuir and Freundlich constant obtained for Pb (II) adsorption on PFAC



Temperature (K)	Langmuir isotherm			Freundich isotherm		
	q_m	b	R^2	1/n	K_F	R^2
298	370.370	0.098	0.984	0.629	42.520	0.988
313	357.143	0.072	0.995	0.621	33.970	0.988
328	333.333	0.060	0.968	0.595	29.888	0.986

3.8. Thermodynamics model

The Gibbs free energy (ΔG), the enthalpy (ΔH) and the entropy (ΔS) for the adsorption process were obtained using the formulas as follow:

$$\Delta G = -RT\ln b$$

$$\ln b = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

Where R is the ideal gas constant (kJ/mol.K), T is temperature in K, and b is the Langmuir constant (where the unit of b should be converted to L/mol). The enthalpy change (ΔH) and the entropy change (ΔS) can be calculated from a plot of ln b vs. 1/T (Fig. 5). Thermodynamic parameters, standard free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were calculated and are shown in Table 3. The negative ΔG value suggests that the adsorption process is a spontaneous process and thermodynamically favorable under the experimental conditions. The change in free energy for physical adsorption is between -20 and 0 kJ/mol, and that for chemical adsorption is between -80 and -400 kJ/mol [9]. The values of ΔG obtained in this study are in the range from -7.472 to -6.872 that show physical adsorption. The adsorption process is exothermic in nature.

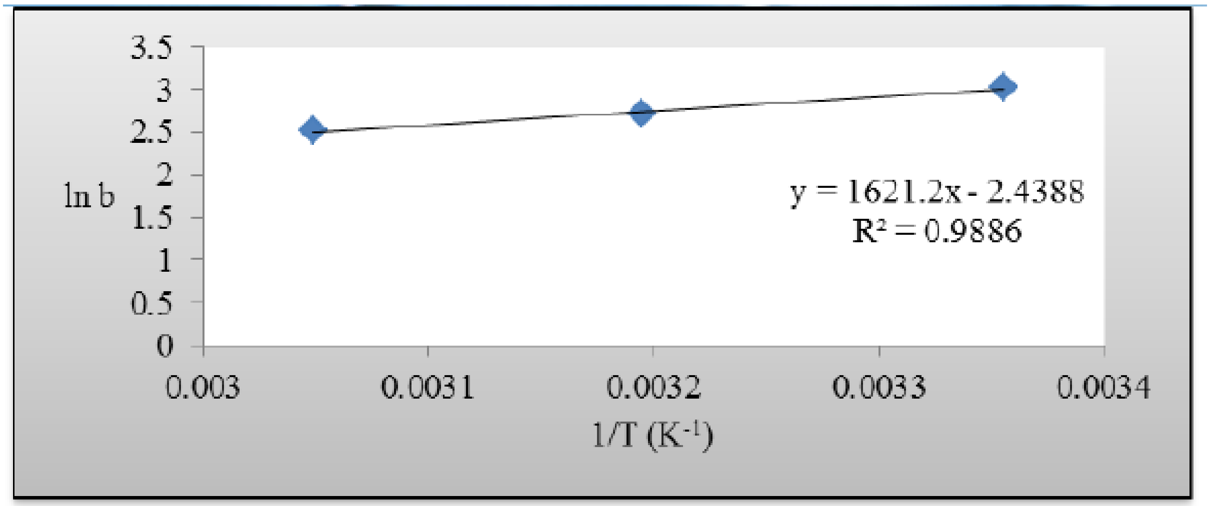


Fig. 5. Plot of the Langmuir constant (ln b) vs. temperature (1/T)

Table 3. Thermodynamic coefficients for Pb (II) ions adsorption on PFAC

T (K)	Ln b	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (KJ/mol/K)
298	3.016	-7.472	-13.478	-0.020
313	2.710	-7.052		
328	2.520	-6.872		

4. Conclusion

The H_3PO_4-activated PF acts as a good adsorbent to adsorb Pb (II) from aqueous solutions. The adsorption of Pb (II) on PFAC increases with the increase in pH and maximum adsorption took place at pH 4.0. The adsorption follows pseudo second-order Kinetics. The adsorption rate (k2) was 0.001 (g/mg.min) for 100 mg/L. it can be observed that PFAC is one of the most effective agro-industrial solid wastes used for the Pb (II) adsorption.

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