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Investigation of Langmuir and Freundlich Adsorption Isotherm of Pb^{2+} Ions by Micro Powder of Cedar Leaf

Gholamali Haghdoost, Hossein Aghaie* and Majid Monajjemi

Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran

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ABSTRACT

In this work, the micro powder was the product of cedar leaf (MPCL) is used as a low-cost adsorbent for the removal of Pb^{2+} ions from aqueous solutions. Bath experiments were used to determine the best adsorption conditionsThe adsorption percentage of Pb^{2+} ions MPCLsamples at different initial pH, contact time (tc), adsorbent dosage and temperature (T) were investigated. Effective removal of metal ions was demonstrated at pH values of 5. Metal adsorption onto MPCLwas evaluated by Langmuir and Freundlich isotherms. Results indicate that the Langmuir isotherm model is the most suitable one for the adsorption process using MPCL(R^2=0.9987), thus indicating the applicability of monolayer coverage of Pb(II) ion on MPCL surface.The relationship between thermodynamic parameters was used to predict the absorption process. According to Thermodynamic analysis, the process exothermic and natural (ΔH=-21.65 kJmol^{-1} and ΔS =- 56.4 Jmol^{-1} K^{-1}).

Keywords: Pb^{2+}; Adsorption; ZMicro powder; Cedar leaf; Thermodynamic; MPCL

INTRODUCTION

Lead and its compounds are toxic and present in wastewater, effluents and soils [1]. Lead is used in some batteries, metal plating, photographic materials, explosive manufacturing and in some other application [2]. The presence of lead compounds in water may damage the kidney, nervous system, Liver, blood composition, reproductive system and brain due to its accumulation in the human body [3]. Treatment processes for metal ions removal from wastewater include precipitation, reverse osmosis, Reduction, filtration, membrane processing, ion exchange, coagulation and adsorption process [4]. Adsorption technique has been developed as an efficient method for treating various wastewaters, in which activated carbons from natural resources have been used as efficient and economical adsorbents for removing heavy metal pollutants [5]. The use of activated carbons to remove Pb (II) from water was proposed because of their high surface areas and active functional groups leading to a search for low-cost adsorbents in recent years.

Indeed agricultural waste for example, has two advantages. First, waste material is converted to useful, value-added adsorbents. Disposal of agricultural by-products has become a major costly waste disposal problem. Second, produced

*Corresponding author: hn_aghaie@yahoo.com

activated carbons are used for removing organic chemicals and metals from wastewater [6-9]. Corn cob, flamboyant pods, apricot stone, almond shell, nut shell, peach stone, oat hulls, coconut husk, coconut shell, hazelnut shell, grape seed, olive stone and Rosa cantina sp. Seeds [10,11] have been used for activated carbon productionZiziphus spina-christi is a plant that grows into a tree with thorny branches and is used as a hedge to form defensive fences for cattle. The fruit has a sweet edible pulp, the leaves are applied locally to sores, and the roots are used to cure and prevent skin diseases [12]. Cedar with scientific name of Zizyphus spina christi grows in Saudi Arabia, north of Africa, and in Iran in provinces of Khuzestan, Fars, and Hormozgan. Such as: Iran. Jujube fruits are consumed fresh or processed into beverage and food. In the present study, MPCLprepared used as an adsorbent to remove Pb (II) from aqueous solutions. The adsorption of Pb^{2+} ions onto MPCLwas studied in batch equilibrium conditions. The effects of different parameters including pH, initial metal ion concentration, contact time, MPCLdosage and temperature were investigated. Langmuir and Freundlich isotherm models were used to analyze the equilibrium data.

EXPERIMENTAL

Apparatus and Materials

An AA 680 model atomic absorption spectrometer (Shimadzu Co.) was used for measuring the concentration of Pb^{2+} ion in studied solutions, a 820A model pH meter (Metrohm Co.) was used to measure pH of solutions and a thermostatic orbit incubator shaker neolab model (India) was used to measure contact time in solution. All chemical materials used in this study were of analytical grade. MPCLprepared by chemical activation with KOH was characterized. Lead nitrate, was purchased from Merck Company.

Batch Adsorption Experiments

Batch adsorption experiments were carried out to determine the Pb^{2+} ions adsorption isotherm onto MPCL and its thermodynamic properties. Pb^{2+} ions stock solution (100 mg.L^{-1}) was prepared by dissolving the appropriate quantity of Pb $(NO_3)_2$ salt in deionized water.

Adsorption isotherms were obtained by using initial Pb^{2+}ions concentration, Co, and its equilibrium concentration, Ce, at 298K.The effect of pH on the Pb^{2+} ions adsorption onto MPCLwas conducted in a pH range of 3-10.The pH of solutions was adjusted by 0.1 M HCl or 0.1M NaOH solutions. For every experiment, 100ml of the solution with Pb^{2+} concentration of 30 mg.L^{-1} was mixed with 50 mg of MPCLin a 250ml glass conical flask. The flask was shaken in a thermostatic orbit shaker at 220rpm for 60min. The mixed was filtered through a 0.45 μm membrane filter. The filtrate was measured by atomic absorption then, the adsorption percentage (%A) was determined as:

$$\%A_e = \frac{A_0 - A_e}{A_0} \times 100 \quad (1)$$

where C_o and C_e are the initial and final concentration of Pb^{2+}ion in solution (mg L^{-1}), respectively. The amount (mg g^{-1}) of Pb^{2+}adsorbed at equilibrium was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where m is the mass of MPCL(g) and V is the volume of the solution (L). To evaluate the thermodynamic properties of the adsorption process, 50 mg of MPCLwas added into the 100 ml solution with pH of 5.0 and initial Pb^{2+}concentration ranging from 30 mg.L^{-1} in every experiment. Each solution was shaken continuously for 60min at 298K [13].

RESULTS AND DISCUSSTON

Adsorption Study

The Effect of pH

Solution pH is one of the most important parameters to determine the adsorption property of an adsorbent that it controlled the kind and amount surface charge of the adsorbent [14]. Table 1 and fig.1 illustrate the effect of the pH of the solution on the adsorption percentage of Pb^{2+} ion adsorbed onto MPCL. The adsorption percentage was increased with pH and optimum pH was 5.0. The decrease of the adsorption percentage in acidic pH can be attributed to the repulsion between positive charge surface of MPCLand Pb^{2+}.

Table 1. The effect of initial pH of the solution on the adsorption percentage (%A) of Pb^{2+} (C_o=30 mg.L^{-1}, m_{MPCL}=50 mg, T=298K, tc=60min)

pH	%A
3	68.3
4	72
5	78
6	77
7	76.4
8	76.2
9	76
10	75.5

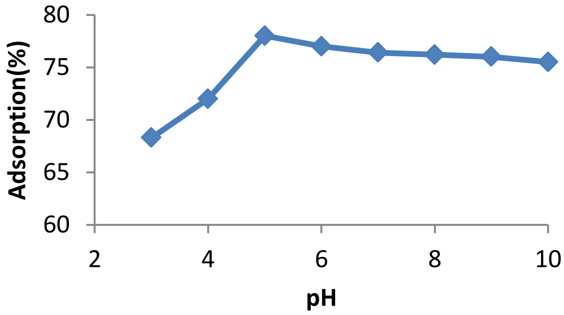

Fig. 1. The effect of initial pH of the solution on the adsorption percentage of Pb^{2+} (C_o=30 mg.L^{-1}, m_{MPCL}=50 mg, T=298 K, tc=60 min).

The Effect of Dosage

The effect of MPCLdosage on the adsorption percentage of Pb^{2+} ion are shown in table 2 and ploted in fig. 2. We concluded that the dosage of 50 mg of MPCLwas the most suitable. After optimum dosage, all active sites are entirely exposed and the adsorption on the surface is saturated.

Table 2. The effect of MPCLdosage on the adsorption percentage (%A) of Pb^{2+}(C_o=30 mg.L^{-1}, pH=5, T=298K, tc=60 min)

m_{MPCL} / mg	%A
10	48
20	49.6
30	52.3
40	58.7
50	59.3
60	56.4
70	56

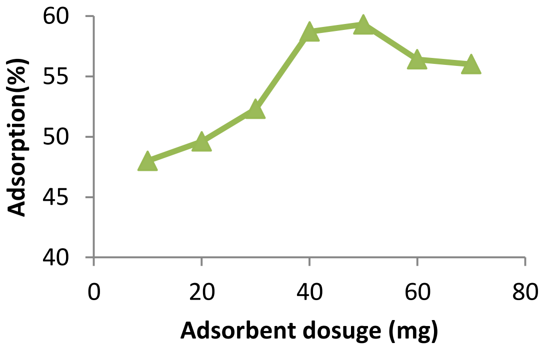

Fig. 2. The effect of MPCLdosage on the adsorption percentage of lead ion onto MPCL (C_o=30 mg.L^{-1}, T=298 K, pH=5, tc=60 min).

The Effect of Temperature

Table 3 and fig.3 show that the adsorption percentage decrease with increasing temperature. Therefore, it may be concluded that the interaction between Pb^{2+} ions and MPCLis exothermic in nature. Adsorption decrease may be due to increase the electrostatic repulsion between of the Pb^{2+} ions.

Table 3. The effect of temperature on the adsorption percentage (%A) of Pb^{2+} (C_o=30 mg.L^{-1}, m_{MPCL}=50 mg, pH=5, tc=60 min)

T / K	%A
298	89
308	83
318	78
328	76.6
338	72
348	68

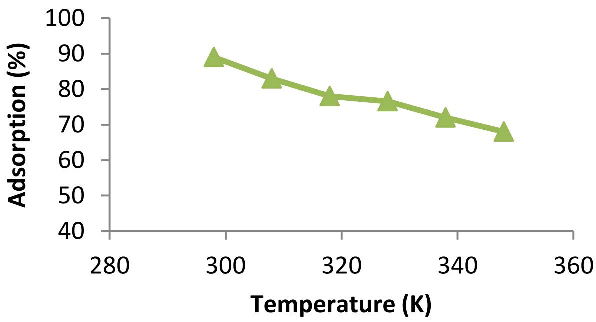

Fig. 3. The effect of temperature on the adsorption percentage of lead ion onto MPCL (C_o=30 mg.L^{-1}, m_{MPCL}=50 mg, pH=5, tc=60 min).

The Effect of Contact Time

The effect of contact time, tc , on the adsorption percentage of Pb^{2+} ion onto MPCLare shown in table 4 and ploted in fig. 4. A rather fast up take occurs during the first 30 min of the adsorption. It becomes slower as the adsorbed amount of Pb^{2+} ion reaches its equilibrium value. It can be seen that the adsorption process is rapid due to the availability of very active sites on the adsorbent surface at initial stage. This may be due to the special one atom layered structure of MPCL[15]. The optimum contact time was obtained as 50 min.

Table 4. The effect of contact time, tc, on the adsorption percentage (%A) of Pb^{2+} ions (C_o=30 mg.L^{-1}, m_{MPCL}=50 mg, pH=5, T=298 K)

tc/min	%A
10	51.6
20	54.8
30	60.1
40	63.2
50	66
60	66
70	66
80	66

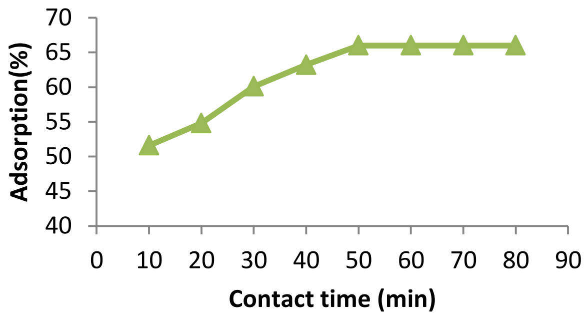

Fig. 4. The effect of contact time on the adsorption percentage of Pb^{2+} ion onto MPCL (C_o=30 mg.L^{-1}, m_{MPCL}=50 mg, pH=5, T=298 K).

Adsorption Isotherm

An adsorption isotherm is characterized by certain constant values, which express the surface properties of the adsorbent and so on the percentages adsorption of Pb^{2+} ion MPCLas a function of initial concentration of Pb^{2+} ions are given in table 5.

Table 5. Adsorption data for Pb^{2+} adsorption onto MPCL (pH=5, tc=50 min, T=298 K, m_{MPCL}=50 mg)

ParameterValue						
C_0 /mg L^{-1}	10	20	30	40	50	60
%A	56.5	58.3	60.1	61.4	62.8	68.13
Ce / mg L^{-1}	4.35	8.3	11.97	15.44	18.6	19.122
q_e / mg g^{-1}	11.3	23.4	36.06	49.12	62.8	81.756
log Ce	0.64	0.92	1.08	1.19	1.24	1.282
log q_e	1.05	1.37	1.56	1.69	1.8	1.91
1/Ce /L mg^{-1}	0.23	0.12	0.084	0.065	0.054	0.052
$1/q_e$ /g mg^{-1}	0.0885	0.0427	0.0277	0.0204	0.0159	0.0122

Equilibrium data of adsorption process can be analyzed on the basis of Freundlich and Langmuire models. The Freundlich equation is an empirical equation based on adsorption on a heterogeneous surface. This isotherm is applicable to both monolayer (chemisorption) and multilayer (physisorption) adsorption [16]. The linear form of the Freundlich isotherm model is described as;

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (3)$$

where K_F (L/g) and n are the Freundlich constants related to adsorption capacity and adsorption intensity [17].The values of K_F and n are determined from the intercept and slope of a plot of log q_e versus log Ce (table 5 and fig.5 that were used to calculate the values of K_F and n (table 6)).

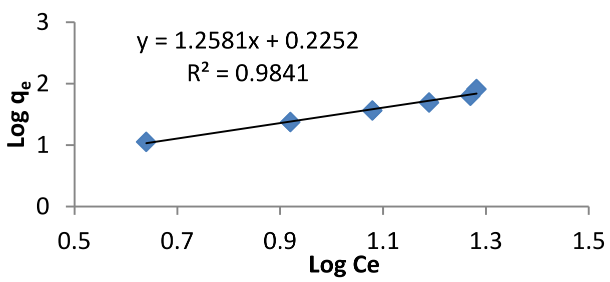

Fig. 5. Freundlich isotherm for lead ion adsorption onto MPCL.

The Langmuire isotherm assumes monolayer adsorption on a homogeneous surface without any interaction between adsorbed ions and with uniform binding sites and equivalent sorption energies [18]. The linear form of Langmuire equation is expressed as:

$$\frac{1}{q_e} = \frac{1}{K_L q_m}\left(\frac{1}{C_e}\right) + \frac{1}{q_m} \qquad (4)$$

where q_m (mgg^{-1}) is the maximum adsorption capacity corresponding to complete monolayer coverage and K_L (L/mg) is the Langmuire constant related to adsorption capacity and energy of adsorption [19].The slope and intercept of plot of $1/q_e$ versus 1/Ce is shown in fig.6 that were used to calculate the values of K_L and q_m (table6).

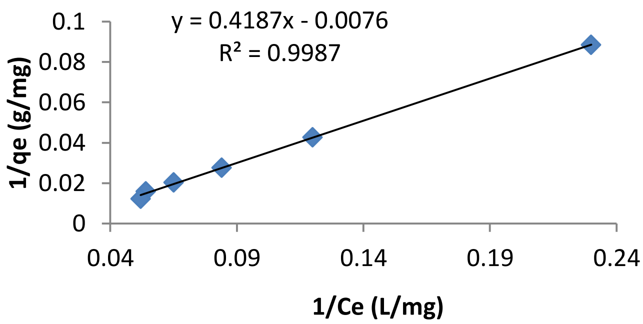

Fig. 6. Langmuire isotherm for lead ion adsorption onto MPCL.

The essential characteristic separation constant factor, R_L, for the Langmuire adsorption is defined as follows:

$$R_L = \frac{1}{1+K_L C_0} \qquad (5)$$

The value of R_L illustrate the shape of the isotherm to be either unfavorable ($R_L>1$), linear ($R_L=1$), favorable ($0<R_L<1$) or irreversible ($R_L=0$). The calculated R_L values versus initial Pb^{2+} concentration are given in table 7, indicating that the Langmuire adsorption of Pb^{2+} onto MPCL is favorable.

Table 6. The resultant values for the studied isotherms in connection to Pb^{+2} ion adsorption onto MPCL at 298K

Isotherm	Parameter	Value
Freundlich	KF /(L g^{-1})	1.7
	n	0.8
	R^2	0.9841
Langmuire	KL / (L mg^{-1})	0.018
	q_m /(mg g^{-1})	131.6
	R^2	0.9987

Table 7. Separation factor for the adsorption of Pb^{2+} onto MPCLin terms of initial concentration of Pb^{2+}

Co / mg L^{-1}	R_L
100.385	
200.24	
300.172	
400.12	
500.111	
600.094	

Thermodynamic Parameters

The thermodynamic parameters of adsorption process can be determined from the variation of thermodynamic equilibrium constant, K [20]. WhereK_o is defined as follow:

$$K = \frac{a_S}{a_e} = \frac{q_e}{C_e} = \frac{C_0 - C_e}{C_e} \qquad (6)$$

where a_S and a_e are the activity of adsorbed Pb^{2+} and the activity of Pb^{2+} in solution at equilibrium, respectively. The adsorption standard free energy change (ΔG) is calculated according to:

$$\Delta G^{\circ} = -RTLnK \qquad (7)$$

The average standard enthalpy change (ΔH) and the average standard entropy change (ΔS) are obtained from the plot of equation (8):

$$LnK = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \qquad (8)$$

In order to obtain the values of ΔH and ΔS, was plotted LnK against 1/T (table 8, fig.7).

Table 8. The effect of temperature on K values (C_o=30 mg.L^{-1}, pH=5, m_{MPCL}=50 mg, tc=50 min)

T/K	%A	K
298	89	8.9
308	83	4.88
318	78	3.55
328	76.6	3.27
338	72	2.57
348	68	2.13

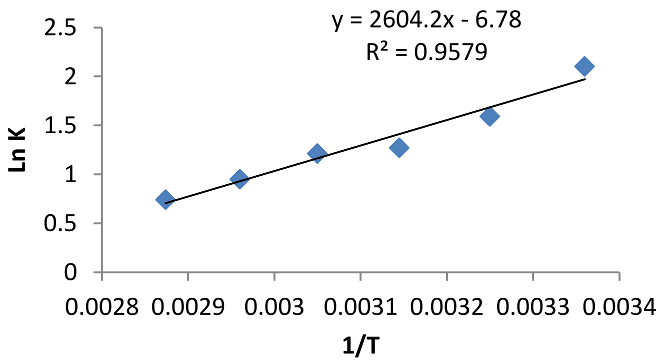

Fig. 7. The effect of temperature on equilibrium constant values.

The obtained values of thermodynamic parameters (ΔG, ΔH and ΔS) are listed in table 9. Negative value of ΔH suggests that the interaction of adsorbed Pb^{+2} with MPCL is an exothermic process, which is supported by the decreasing the amount of lead ion adsorption with increasing temperature. The negative value of ΔS indicates a decrease randomness and mobility at the adsorbent/solution interface during the adsorption of lead ion onto MPCL. The negative values of ΔG reveals the fact that the adsorption process is spontaneous.

Table 9. Thermodynamic parameters for adsorption Pb^{+2} ions onto MPCL

T /K	ΔG°/kJmol^{-1}	ΔH°/ kJmol^{-1}	ΔS° / Jmol^{-1} K^{-1}
298	-5.18	-21.65	-56.4
308	-4.06	-21.65	-56.4
318	-3.35	-21.65	-56.4
328	-3.24	-21.65	-56.4
338	-2.653	-21.65	-56.4
348	-2.188	-21.65	-56.4

CONCLUSION

The results of this research show that MPCLis an effective adsorbent for removal of Pb^{2+} ion from aqueous solution. The experimental data can be fitted with the Langmuire isotherm, thus indicating the applicability of monolayer coverage of Pb^{2+} ion on MPCLsurface. Thermodynamic analysis showed that the adsorption process is exothermic and spontaneous in nature.

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