ISSN: 2586-761x (Print)
ISSN: 2635-5817 (Online)
Vol. 01, No. 02, December 2018
International Journal of Advanced Social Sciences
Source: http://ictaes.org
Manuscript received: November 20, 2018 ; Revised: December 10, 2018 ; Accepted: December 20, 2018

Studies on Adsorption Isotherms and Adsorption Kinetics of the Removal of Pb(II) from Aqueous Solution onto Activated Carbon Prepared from Lapsi Seed Stone

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Abstract

Present study explored the studies on the adsorption isotherms and adsorption kinetic of removal of Pb (II) ion on the activated carbon developed from waste material, Lapsi Seed Stone. Batch adsorption experiments have been investigated for the contact time period of 60 to 240 minutes.180 minutes have been found to be the optimal contact time for the remediation of the heavy metal ions. Similarly the optimum pH for the adsorption of the metal ion was found to be 5.The results of the adsorption data have revealed that Langmuir adsorption isotherm has been found to describe best with higher value of correlation coefficient than that of Freundlich adsorption isotherm with maximum adsorption capacity of 131.0 mg/g. In the same way the analysis of adsorption kinetics data has showed that the Pseudo second order model was found to be the best applied model to describe the adsorption process. It has been concluded that the activated carbon developed from the readily available waste material Lapsi Seed Stone can be applied as an effective adsorbent for the remediation of the heavy metals from aqueous media.

Keywords*: Adsorption, Lapsi seed stone, Adsorption isotherms, Adsorption kinetics, Lead*

1. INTRODUCTION

Lead, a toxic heavy metal, is released into water bodies by anthropogenic activities such as textile dyeing, ceramic, petroleum refining, battery manufacturing, glass industries and mining operations [1].The heavy metal mainly accumulates in sensitive organs such as brain and kidney and other organs like bones, muscles etc. The permissible level of lead in drinking water as set by WHO is 0.01 ppm. The toxic effects of lead include severe damage to kidney, liver, brain, nervous and reproductive system. Lead, therefore, can cause toxic effects at very low concentration. Due to this the metal ions in water should be reduced to lower level to the permissible level before being discharged to water bodies. Many methods have been used over years to remove heavy metals. These methods are chemical oxidation, chemical reduction, precipitation, ion exchange, conventional coagulation, membrane filtration, reverse osmosis and adsorption. Most of these methods have drawbacks such

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as incomplete removal of heavy metals, high cost for the operation and problem for the management of disposing the metallic sludge formed.

Adsorption process being simple and cost effective, therefore, has been mostly applied to remove the pollutants from water. Many researchers have carried out the works to find the cheaper and eco-friendly adsorbent [2].

Many studies have revealed the preparation of low cost activated carbons prepared from locally available and cheaper materials like apricot stone [3], olive stone [4], date stone [5], peanut shell [6], coconut shell [7], palm shell [8], rice husk [9] etc. for the preparation of activated carbon.

The current study explored kinetics of Pb (II) adsorption onto PAALSSC (Phosphoric acid activated Lapsi Seed Stone carbon) through a pseudo-first-order [10, 11] and a pseudo-second-order [12, 13] model. Adsorption isotherm usually gives information about the equilibrium state between the amount of adsorbed metal ion onto the adsorbent surface and the concentration of metal ions in solution. Langmuir [14, 15] and Freundlich [16] are the most commonly applied adsorption isotherms.

2. EXPERIMENTAL

2.1 MATERIALS

The precursor used in this study is Lapsi seed stone as shown in Fig 2, the waste material of Lapsi fruits as shown in Fig 1 left after the production of vitamin – C rich products. The Lapsi seed stones were collected from Paun (vitamin – C rich products) Factory, Godavari, Lalitpur, were washed well with tap water to remove impurities. The seed stones were then washed with deionized water, and dried in a hot box oven at temperature maintained at 105 ^{0}C for 24 hours. The stones were ground by grinder and crushed into the grains of 300 µm by sieve. The ground particles were mixed with 50% H_3PO_4 in the ratio of 1:1 and heated at a temperature of 100ºC for 24 hours and then subjected to carbonization at 400 º C for 4 hours into furnace in nitrogen gas. The activated carbon, thus prepared was left at laboratory temperature for cooling and was washed several times with warm deionized water. The activated carbon thus obtained was then kept in hot box oven at 110 ºC for 24 hours, cooled and sieved to obtain the grains of size 106 µm. The grains of the activated carbon thus prepared was represented as PAALSSC. The full form of the symbol is Phosphoric acid activated Lapsi seed stone carbon. The carbon thus prepared has been used for the study of adsorption process.



Figure 1. Lapsi fruits and Lapsi seed stones

2.2 CHEMICALS AND EQUIPMENTS

The chemical substances and reagents manufactured from Merck and Qualigens Company were used in adsorption experiment. The synthetic solutions of Lead ions used in the adsorption process were prepared using nitrate salt in deionized water. pH value of solution was measured with help of Digital pH meter. The adsorption experiments were carried out using Shaker (Digital VDRL Rotator-RPM-S). The amount of Pb (II) ions adsorbed on the activated carbon was determined by using AAS. In order to maintain the pH of solutions, solutions of NaOH and HCl have been used. The stocks solutions were used to prepare the solutions of required concentrations.

2.3 ADSORPTION PROCESS

The adsorption process was studied by suspending 0.05 g of adsorbent mixed with 25ml of adsorbate solution taken in 50 ml capacity conical flasks which were then stirred well on Digital Shaker to find out the optimum condition for the experiments. Solutions of NaOH and HCl have been utilized to maintain the pH of the solution. The concentration of Pb (II) ions after adsorption was determined by atomic absorption spectrophotometer. The amount of Pb(II) ions uptake can be calculated as follows [17].

$$q_e = \frac{(C_o - C_e) \times V}{W} \quad \ldots\ldots 1$$

C_o = Initial concentration of the metal ions

C_e = Equilibrium concentration of the metal ions

W = Weight of adsorbent in gram (g)

V = Volume in liter (L).

The amount of adsorbed metal ions in percentage (Rem %) can be calculated as follows.

$$\text{Rem}(\%) = \frac{(C_o - C_e)}{C_o} \times 100 \quad \ldots\ldots 2$$

3. RESULTS

3.1 EFFECT OF PH

pH has been found as an important parameter which largely affects on adsorption of the metal ion s. So the adsorption process has been carried out above pH range of 2-7.The role of pH on removal of the metal ions is presented in Fig.3 which shows that removal of Pb(II) ions goes on increasing by in-creasing pH and attains almost constant at pH of 6-7. The adsorption study on higher pH range w as not studied since the precipitation of the metal ions occurs above the pH value. At low pH the per centage of removal of Pb (II) ions was observed as low due to the fact that more concentration of pr ot-ons competes with the metal ions causing decrease in the adsorption process.

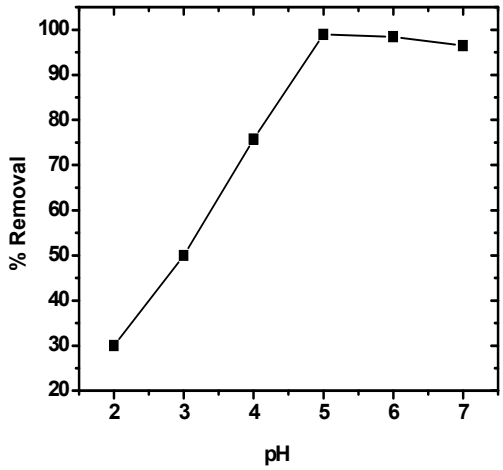


Figure 2. Effect of pH on adsorption of Pb (II)

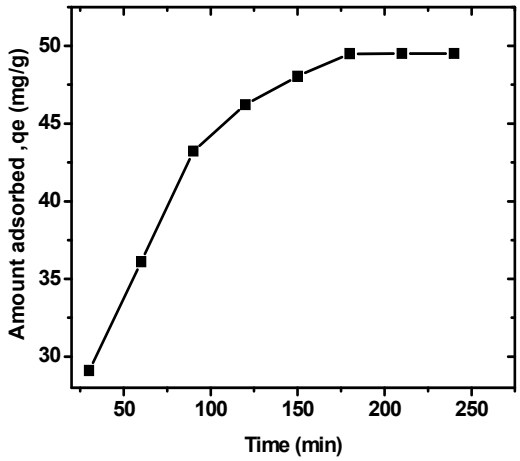


Figure 3. Effect of contact time on adsorption of Pb (II)

3.2 EFFECT OF CONTACT TIME

Contact time is another parameter that affects on the adsorption of the metal ions. The effect is presented in Fig-4 which reveals that in initial state the rate of adsorption has been observed very fast. The fast adsorption may be due to the fact that at initial state higher driving force make transfer of metal ions faster to the surface of adsorbent particles and the presence of the unloaded metal ions on the surface area of the activated carbon. With the further increase in contact time it has taken a long time to attain equilibrium for the adsorption process diffusing slowly into the pores of activated carbon due to the decrease in the presence of the unloaded surface area, the active sites and less driving force. Hence rate of adsorption process was observed slower. The results reveal that 180 minutes was found to be optimal contact time to attain equilibrium for the removal of the metal ions on the activated carbon.

3.3 ADSORPTION ISOTHERM

Adsorption isotherm gives information about how adsorbed molecules will be distributed between two phases i.e. liquid and solid. Langmuir and Freundlich adsorption isotherms are the most commonly used adsorption isotherms to explain the relation between the amount of the metal ions removed and the amount at equilibrium state. Hence this work explored the application of two the adsorption isotherms.

3.3.1 LANGMUIR ISOTHERM

The Langmuir isotherm assumes that a continuous monolayer of adsorbate molecules surround a homogenous solid surface [18]. The linear form of the Langmuir isotherm equation is as follows.

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

Where C_e = Equilibrium concentration of the metal ions (mg/L)

q_e = the amount of the adsorbate adsorbed under equilibrium

q_m= the monolayer adsorption capacity (mg/ g)

b = the Langmuir constant [19, 20]

The slope and intercept of the plot C_e/q_e versus C_e as shown in Fig 5 have been applied to calculate Langmuir constant and adsorption capacity.

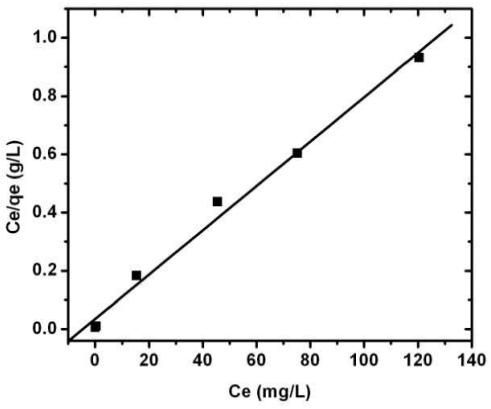


Figure 5. Langmuir adsorption isotherm

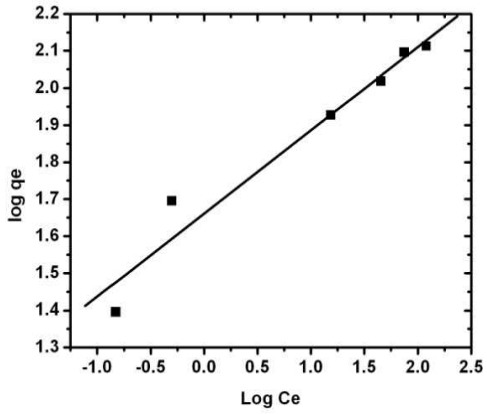


Figure 6. Freundllich adsorption isotherm

3.3.2 FREUNDLICH ISOTHERM

Freundlich isotherm is one of the most commonly applied adsorption isotherms. The isotherm is applied to adsorption processes that take place on heterogenous surface [21].
Freundlich isotherm in linear form may be represented as follows.

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where K_f = Freundlich constant related to adsorption capacity
n = Freundlich constant related to adsorption intensity.

The slope and intercept of the straight line of the plot of log q_e versus logC_e as shown in Fig.6 has been applied to calculate the values of Freundlich constants. The values of Langmuir and Freundlich constants are presented in Table-2.The figures-5 and 6 reveal that the adsorption isotherm data was the best described by Langmuir equation rather than Freundlich equation because higher value of (R^2 = 0.990) in Langmuir isotherm than that in Freundlich isotherms (R^2 =0.955). This is in agreement to fact that the number of active sites available on the surface of activated carbon surface is limited and the adsorption of the metal ions leads to the formation of a monolayer on the surface. Langmuir and Freundllich parameters are presented in Table 1.

Table 1. The values of Langmuir and Freundlich parameters

Heavy metal ions	Langmuir parameters		R^2	Freundlich parameters		R^2
	q_{max} (mg/g)	b		K_f (mg/g)	(n)	
Pb (II)	131.0	0.22	0.990	45.85	4.45	0.955

Adsorption capacity of Pb (II) on the activated carbon is more than that of activated carbons prepared from other adsorbents such as bail leaves, Cotton stalk, Rice husks and Peat as shown in Table 2.fro which it has been concluded that the activated prepared is the best in adsorption of the metal ions than other adsorbents except AC prepared from *Enteromorpha prolifera.*

Table 2. The metal ion-uptake capacity of Pb(II) by different adsorbents

S.N.	Adsorbents	Adsorption capacity q_{max} mg/ g	References
1	Red mud	88.20	Gupta et al., 2001 [22]
2	Peat	95.20	Mckay andHo , 1999[12]
4	Rice husk	91.47	Naiya et al.,2009 [23]
5	AC from cotton stalk by H_3PO_4	119.0	Kunquan Li, 2010[24]
6	AC from *Enteromorpha prolifera*	146.85	Yanhui Li et al., 2010 [25]
7	Bael leaves	104.0	Chakravarty, 2009 [26]
8	PAALSSC	131.0	Present study

4. DISCUSSIONS

4.1 ADSORPTION KINETICS

The study of adsorption kinetic plays an important role to determine the efficiency of adsorption. Most commonly used two kinetic models like pseudo first order and second order kinetic models have been applied to the adsorption kinetic data to analyze rate of adsorption.

4 .1.1 PSEUDO FIRST ORDER

Pseudo first order model was given by Legergren in 1898[27]. According to him the first order equation is represented as follows.

$$\frac{dqt}{dt} = k_1(q_e - q_t) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 5$$

Where q_e = Equilibrium concentration of the metal ions adsorbed (mg/g)

q_t = the amount of the metal ions adsorbed at time't' (mg/g)

k_1 = the pseudo –first order rate constant ($Lmin^{-1}$).

On integration the equation (5) will take the form as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 6$$

The plot of value of log (q_e - q_t) against't 'as shown in Fig. 7 has been applied to test the validity of the kinetic model.

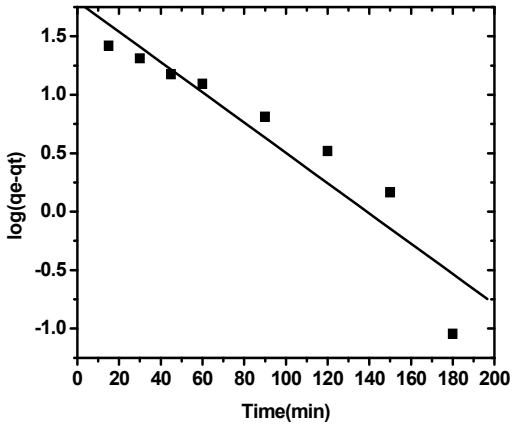


Figure 7. Pseudo first order

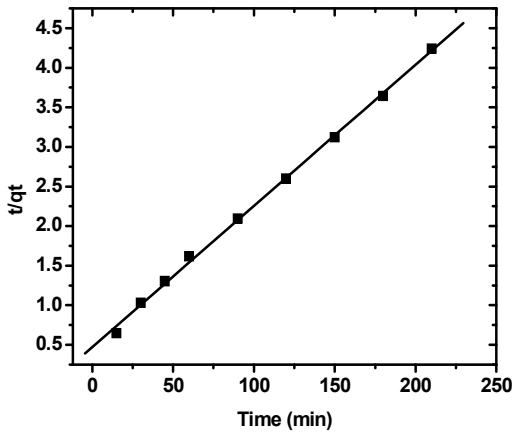


Figure 8. Pseudo second order

The slopes and intercepts of the curves have been applied to calculate the kinetic parameters such as k_1 and equilibrium adsorption capacity. The constants of the kinetic models are given in Table 3.

Table 3. Parameters of Pseudo first and second order kinetics

Heavy metal ions	Pseudo 1st order model			Pseudo 2nd order model			
	q_e(mg/g)	K_1(1/min)	R^2	Experimental value , q_e (mg/g)	q_e(mg/g)	K_2(g/mg min)	R^2
Pb(II)	62.72	0.298	0.888	49.41	56.08	6.733 x 10^{-04}	0.998

4.1.2 PSEUDO SECOND ORDER

Pseudo second order model is also called Ho second order model. The rate equation of pseudo second order is as follows.

$$\frac{dqt}{dt} = k_2(\ q_e - q_t)^2 \text{.....-.....} 7$$

Where k_2 =second order rate constant of adsorption (g mg $^{-1}$ min $^{-1}$).
The equation (7) after integration takes the form as follows.

$$\frac{1}{(qe-qt)} = \frac{1}{qe} + k_2\ \ t \text{.....} 8$$

By rearranging the equation (8) will be as follows

$$\frac{t}{qt} = \frac{1}{qe^2}\frac{1}{k_2} + \frac{t}{qe} \text{.....} 9$$

The plot of value of 't/qt' against 't' as given in Fig. 8 has been applied to test the validity of the kinetics.

5. CONCLUSION

Lapsi seed stone based activated carbon has been applied to study the adsorption isotherms and adsorption kinetic for the adsorption of Pb(II). The removal of the metal ions has been found to be dependent on pH and the maximum adsorption has been observed at pH 5.Optimal contact time for the adsorption of the metal ions has been found to be 180 minutes. The equilibrium data is best described by Langmuir adsorption isotherm with higher correlation coefficient (R^2=0.990) than that of Freundlich isotherm (R^2=0.955) showing a maximum adsorption uptake of 131.0 mg/g. Analysis of adsorption kinetic data has shown that the Pseudo second- order model is found to describe adsorption much better with high correlations coefficient (R^2= 0.998) than that of Pseudo first- order model (R^2= 0.888). The results of current study shows Lapsi seed stone based activated carbon can be used as an efficient adsorbent for removal of lead ions from aqueous media.

ACKNOWLEDGEMENT

The author is especially grateful and thankful to Prof.Dr.Raja Ram Pradhananga, Kathmandu for his guidance, continued support and invaluable suggestions. Besides Pradhananga, the author also expresses gratefulness to Prof.Dr. Amar Prasad Yadav, the President of Nepal Chemical Society for his guidance and valuable suggestions.

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