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Adsorption Isotherm and Kinetic Studies of Cd (II) from Aqueous Solution Using Activated Carbon Prepared from Lapsi Seed Stone by Chemical Activation

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Abstract

The present study explored the investigation on adsorption of Cd (II) on the surface of activated carbon prepared from Lapsi Seed Stone by chemical activation. The batch adsorption experiments were performed using Atomic Absorption Spectroscopy (AAS) Technique. The optimum pH and contact time for adsorption of the metal ions were found to 6 and 180 minutes respectively.Two adsorption isotherms such as Langmuir and Freundlich were applied to analyze the results from the experiments. In order to establish best fit adsorption isotherm model the coefficient of correlation (R2) was determined for each model. The adsorption data was best described by Langmuir with higher value of coefficient of correlation(0.998) as compared to that (0.878) of Freundlich isotherm showing a maximum uptake of 37.0 mg/g. Adsorption kinetic data was in good agreement with Pseudo second order.It has been investigated that the activated carbon prepared from Lapsi can be used as an effective adsorbent for the removal of Cd (II) from aqueous solution.

Keywords: *Activated carbon, Cadmium, Lapsi, Adsorption isotherm, Adsorpion kinetics.*

1. INTRODUCTION

The activities of human beings through industrialization, urbanization, technological development and agriculture discharge heavy metals into water bodies. This has become a matter of global concern over past few decades because the presence of heavy metal ions in water is detrimental to life [1].Heavy metals are not biodegradable and tend to accumulate in living organisms causing various diseases and disorders [2, 3].Cadmium is one of toxic heavy metals released into water bodies through smelting, metal plating, nickel cadmium batteries, alloy industries, mining, sewage sludges, pigments etc. The toxicological effects of Cadmium include camcer, lungs fibrosis, renal damage, hypertension, testicular atrophy, dyspnea, chronic disorders such as itai- itai, weight loss to human beings [4].Cadmium accumulates in human body mainly in kidneys leading to disfunctions of the kidney. The heavy metal, therefore, has been included in the red list priority pollutants by the Department of Environment, UK and in the black list of Dangerous Substance Directive in European Economy Community.US Environment Protection Agency has also classified Cadmium

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as group of B -1 Carcinogen[5].WHO has set 0.003 ppm as the permissible limit for Cd(II) in drinking water. It is, therefore, important to reduce the level of the toxic metal or completely remove from water bodies before being discharged into water.

There are many processes for the treatment of metal- contaminated water including chemical precipitation, membrane filtration, reverse osmosis, ion exchange, and adsorption. However, their use is limited due to various disadvantages such as incomplete metal removal, high capital operational cost and the disposal of residual metal sludge which are not suitable for small scale industries. Adsorption has been proved as one of the most efficient methods for the removal of heavy metals from aqueous media. Adsorption has advantages over other methods for the removal of heavy metals from water because (a) its design is simple (b) it is sludge- free and (c) adsorbent used is low cost. There are many reports showing the development of low cost activated carbon prepared from cheaper and readily available materials such as apricot stone [6], olive stone[7], date stone[8], peanut shell [9],coconut shell[10], palm shell [11], rice husk [12] etc. for the production of activated carbon .

In present study adsorption isotherms of (Cd) II adsorption onto PAALSSC (Phosphoric acid activated Lapsi Seed Stone carbon) studied through Langmuir isotherm [13,14] and Freundlich isotherm [15]. Adsorption isotherm usually describes the equilibrium state between the amount of adsorbed metal ion onto the adsorbent surface and the concentration of metal ions in solution. The kinetics of (Cd)) II adsorption onto activated carbon has been studied through a pseudo-first-order and a pseudo-second-order.

3. MATERIALS AND METHOD

2.1. Materials

The precursor used in this study is Lapsi Seed Stone as shown in Fig.1 (b) , the waste material of Lapsi fruits as shown in Fig.1 (a) after making different vitamin – C rich products. Lapsi seed stones were collected from Paun (vitamin – C rich products) Factory, Godavari, Lalitpur. The seed stones were first washed well with tap water to remove impurities and washed with distilled water. The materials were dried well in a hot box oven at 105 0C for 24 hours. The dried materials were crushed by iron mortar and ground by electric grinder to fine particles. The particles were sieved to obtain the fraction of 300 µm. The particles were mixed with 50% H_3PO_4 in the ratio of 1:1 and dehydrated at 100 ºC for 24 hours in a hot box oven and then carbonized at 400 º C for four hours in a horizontal tube furnace under flow of (75 ml / min) nitrogen.



(a) (b)

Figure 1. a) Lapsi fruits and b) Lapsi seed stones

The activated carbon, thus prepared was cooled at room temperature and was washed several times with warm

distilled water. The material was then dried at 110 ºC for 24 hours, cooled and sieved to obtain the particles of size106 µm. The activated carbon was represented by as PAALSSC (Phosphoric acid activated Lapsi seed stone carbon) and used for adsorption study.

2.2. Chemicals and Instruments

All chemicals and reagents were of analytical grade (Merck and Qualigens Company). Stock solutions of Cd (II) ions were prepared from cadmium nitrate in distilled water. Digital pH meter was used to measure the pH value of the solution. The adsorption experiments were carried out by using Shaker (Digital VDRL Rotator-RPM-S). Atomic absorption spectrophotometer (AAS–VARIAN-AA240FS) has been used to determine the concentration of Cd (II) after adsorption of metal ions onto the activated carbon prepared. Solutions of 0.1 M NaOH and 0.1 M HCl were used to adjust pH. All the working solutions were prepared by diluting the stock solutions with distilled water.

2.3. Adsorption Experiments

In order to study the adsorption of Cd (II) onto PAALSC, Batch experiments of adsorption were carried out in 50 ml Borosil stoppered conical flasks. The flasks were stirred well on Digital VDRL Rotator- RPM-S at 225 rpm for identifying time intervals. Each experiment was carried out by suspending 0.05 g of adsorbent in 25 ml adsorbate solution taken in the conical flasks under the optimum conditions set out for the experiment. The exact residual concentration of Cd(II) ions was determined by atomic absorption spectrophotometer (AAS – VARIAN-AA240FS).The amount of metal ions adsorbed can be calculated by the following equation [16].

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

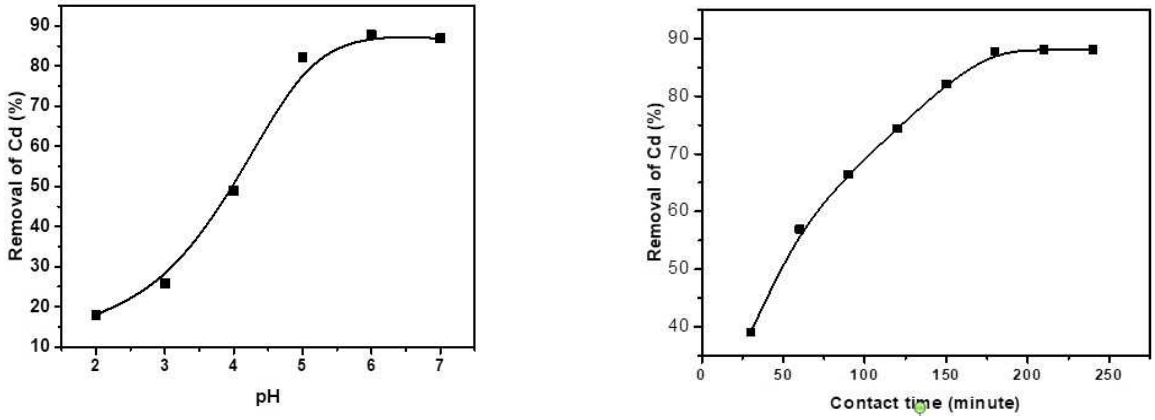
where Co and Ce are initial and equilibrium concentration of metal ion (mg/L) respectively, m is the mass of adsorbent in gram (g) and V was the volume of the solution in liter (L).The percentage of removed metal ions (Rem %) in solution is calculated by using following formula.

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

3. RESULTS AND DISCUSSION

3.1. Effect of pH

pH affects on the metal speciation in aqueous solution as well as the surface properties of adsorbent and therefore can affect the extent of adsorption. So the adsorption behavior of Cd (II) ions on PAALSSC has been studied over a pH range of 2-7 at Laboratory temperature. The percentage removal of metal ions versus pH is shown in Figure 2. The percentage removal of metal ions increases with increase in pH and attains almost constant value at pH range of 6-7. The percentage of removal of Cd (II) is low at low pH. This lower percentage removal of the metal ions may be due to the fact that at lower pH there is a higher concentration of hydrogen ions and that competes with metal ions.



(a) (b)

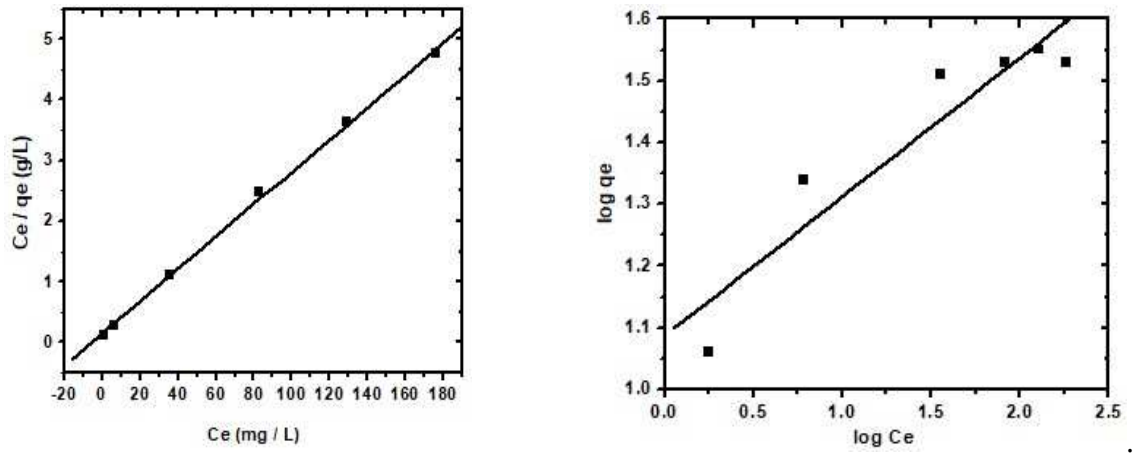
Figure 2. a) Effect of pH on Adsorption of Cd(II) on PAALSSC and b) Effect of contact time on Adsorption of Cd(II) on PAALSSC

3.2. Effect of Contact time

The effect of contact time on the adsorption of Cd(II) onto PAALSSC is shown in Fig 4.The percentage removal of the metal ions increases with increase in time and attains constant value at 180 minutes. The adsorption of metal ions is very fast initially up to 100 minutes and then after it attains equilibrium value slowly. The fast adsorption at initial stage may be due to the higher driving force owing to the availability of the large concentration of active sites for adsorption. After 100 minutes the removal percentage increases gradually and attains constant value at 180 minutes. At equilibrium all the active sites will be occupied by the metal ions and no further adsorption of metal ions occurs. Thus equilibrium time for adsorption of Cd(II) ions is 180 minutes.

3.3. Adsorption isotherm

Adsorption isotherm usually describes the equilibrium state between the amount of adsorbed metal ions onto the adsorbent surface and the concentration of metal ions in solution. Langmuir and Freundlich isotherms are most commonly used adsorption isotherms. So in this study adsorption data was analyzed by these two isotherms as shown in Figure 3.



(a) (b)

Figure 3. a) Langmuir isothern on adsorption of Cd(II) on PAALSSC, and b) Freundlich isothern on adsorption of Cd(II) on PAALSSC

3.1.1 Langmuir isotherm

The Langmuir isotherm assumes that a monolayer of adsorbed material is adsorbed over a uniform adsorbent surface [17].The linear form of the Langmuir isotherm equation is given by

$$\frac{Ce}{qe} = \frac{1}{bqm} + \frac{Ce}{qm} \quad \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

where Ce is the equilibrium concentration of the adsorbate (mg/L) and qe is the amount of the adsorbate adsorbed under equilibrium while qm is the monolayer adsorption capacity (mg/ g) and b is the Langmuir constant [18,19]. Langmuir constant and adsorption capacity are determined from the slope and intercept of the plot Ce/qe versus Ce as shown in Fig 3.

3.1.2 Langmuir isotherm

The Freundlich equation presumes that the adsorption process occurs on a heterogeneous surface [20]. Linear form of Freundlich isotherm may be written as:

$$\log qe = \log K_f + \frac{1}{n}\log Ce \quad \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

where Kf and n are Freundlich constants related to adsorption capacity and adsorption intensity respectively. From the slope and intercept of straight portion of the linear plot obtained by plotting log qe versus log Ce, the values of Freundlich parameters can be calculated as shown in Fig.6.Langmuir and Freundlich constants are given in Table-1. Figures-5 and 6 show that the isotherm data better fit the Langmuir equation than Freundlich equation since the values of the coefficient of determination (R2 = 0.998) are higher than that of Freundlich isotherms (R2 =0.878). This supports the theory that the number of active sites on the carbon surface is limited and uptake of lead ions forms a monolayer on the surface. Langmuir and Freundllich parameters are shown in Table 1.

Table- 1: Langmuir and Freundllich parameters of PAALSSC

Heavy metal-ions	**Langmuir parameters**		**R^2**	**Freundlich parameters**		**R^2**
	q_{max} mg/g	b		**K_f (mg/g**	n	
Cd(II)	37.0	0.19	0.998	12.23	4.44	0.878

3.2 Adsorption kinetics

The adsorption kinetic study gives an information to determine the efficiency of adsorption. In this study pseudo-first-order and pseudo-second-order kinetic models have been applied to analyze the rate of adsorption.

3.2.1 Langmuir isotherm

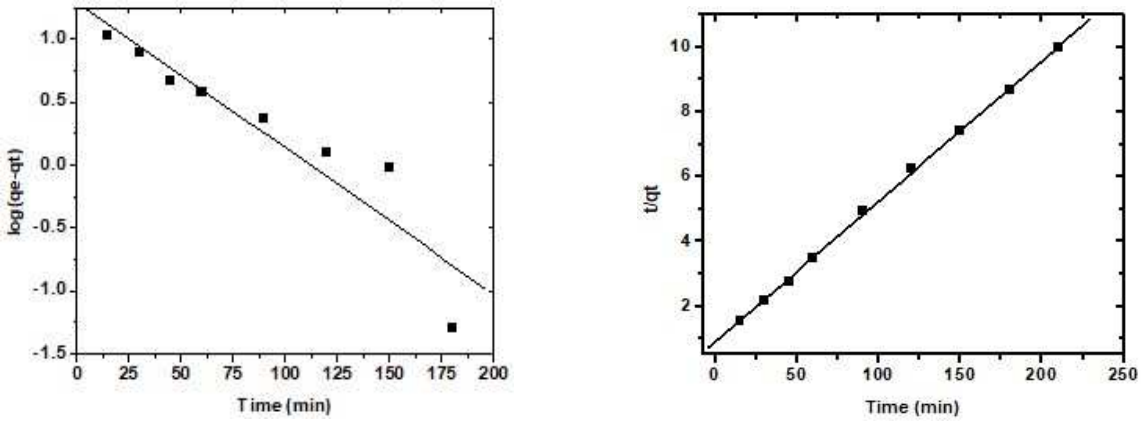
Legergren in 1898 [21] has given pseudo first order equation. According to him the pseudo first order equation is generally represented by the following equation:

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

where qe and qt are the amount adsorbed at equilibrium and time t, respectively (mg/g) and k1 is the pseudo – first order rate constant (Lmin-1).
After integration the equation (5) becomes as follows:

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

The validity of the kinetic model was tested by plotting the value of log (qe - qt) against 't' as shown in Fig. 4.



(a) (b)

Figure 4 a) Pseudo first order plot for Cd(II) adsorption, and b) Pseudo second order plot for Cd(II) adsorption

The slopes and the intercepts of these curves are used to determine the values of kinetics parameters such as k1 and equilibrium adsorption capacity. The pseudo first order and pseudo second order constants are presented in Table 2.

Table 2 Pseudo first order and pseudo second order constants

Heavy metal ions	Pseudo first order model			Pseudo second order model			
	q_e(mg/g)	K_1(L/min)	R^2	Experimental value, q_e (mg/g)	q_e(mg/g)	K_2(g/mg min)	R^2
Cd(II)	19.35	0.266	0.865	21.95	23.95	2.245×10^{-03}	0.999

3.2.2 Pseudo Second Order

Ho second order model is often called pseudo second order. The pseudo second order rate equation is represented as

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

where k2 is the second order rate constant of adsorption (g mg -1 min -1). Integrating the above equation with boundary conditions t = 0 to t = t and qt = 0 to qt =qt it becomes [22].

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

The above equation can be rearranged to obtain

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

The validity of the kinetic model was tested by plotting the value of 't/qt' against 't' as shown in Fig. 8.

5. CONCLUSION

The study reveals the activated carbon prepared from Lapsi seed stone by chemical activation with phosphoric acid in present work can be effectively used in the adsorption of Cd(II) from aqueous media.The optimum pH and contact time for adsorption of the metal ions are found to 6 and 180 minutes respectively.From the study of adsorption isotherms it is observed that the adsorption data is found to be best described by Langmuir isotherm with higher value of coefficient of correlation(0.998) as compared to that (0.878) of Freundlich isotherm showing a maximum uptake of 37.0 mg/g. The results showed that the pseudo first order is not found in good agreement with the kinetic data. The pseudo second order equation has been found to be the best application adsorption kinetics to describe the adsorption process. It has been concluded that the activated carbon prepared from Lapsi seed stone can be used an adsorbent for the removal of Cd(II) from aqueous media.

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