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RESEARCH ARTICLE

Isotherms and Kinetic Studies on the Adsorption of Cd(II) onto Activated Carbon Prepared from Coconut *(Cocos nucifera)* Shell

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Abstract

Activated carbon prepared Coconutshell using Phosphoric acid as an activating agent was investigated to find the feasibility ofits application for removal of Cd(II) from aqueous solution through the adsorption process. The activated carbon thus prepared has been characterized by SEM, XRD, FTIR. SEM morphology has revealed the pores of different diameters while FTIR showed the presence of surface functional groups such as carboxyl, phenolic and lactones. Batch mode kinetics and isotherm studies were carried out to evaluate the effects of contact time, adsorbent dose and pH. The optimum pH, contact time and adsorbent dose needed for the adsorption of the heavy metal have been found to be 6, 180 minutes and 2 g/L respectively. Langmuir and Freundlich isotherm models have been employed to analyze the adsorption equilibrium data. It was found that the adsorption isotherm of Cd(II) onto the activated carbon was the best described by Langmuir with an adsorption capacity of 33.71 mg/g. Kinetic studies showed that a pseudo second-order model was more suitable than the pseudo first-order model. It has been concluded that the activated carbon prepared from Coconut shell can be used as an effective adsorbent for the removal of Cd(II) from aqueous solution.

Keywords: Activated carbon, adsorption, coconut shell, adsorption isotherms, cadmium

Introduction

Cadmium is one of toxic heavy metals released to the environment through the combustion of fossil fuels, metal production, application of phosphate fertilizers, alloy formation, electroplating, production of batteries, etc. [1,2]. This metal is a non-essential and non-beneficial element for plants, animals and human beings. It has a high affinity for sulfhydryl (-SH) groups of proteins for which it competes with Zn(II) in biological systems and is known as a human carcinogen [3]. Due to its low-concentration-long-term effect in drinking water, cadmium belongs to the chemicals list of endocrine disruptors and priority control pollutants issued by USEPA [4,5]. The toxic implications of cadmium in the environment has made the US Environmental Protection Agency (USEPA) set the level of cadmium in drinking water to 0.002 mgL^{-1} and the World Health Organization (WHO) maximum permissible limit for cadmium in drinking water is 0.003 mgL^{-1} [6-9]. The heavy metalis not biodegradable and tends to accumulate in living organisms, causing various diseases and disorders. As far as cadmium is concerned, it causes serious renal damage anemia, hypertensions, testicular atrophychronic disorders such as "itai–itai", lungs fibrosis etc. [10]. The reduction of the pollutant to an acceptable level is needed when the toxic metal is present in the solution. The physicochemical processes such as precipitation, reverse osmosis, ion exchange, adsorption, membrane filtration, electro dialysis, chemical oxidationetc. are employed to treat cadmium-containing effluents. Theprocesses mentioned above with the exception of adsorption are expensive and also have disadvantages such as incomplete metal removal, high reagent, energy requirements and generation of toxic sludge or other waste products that require proper disposal [11]. Because of the problems this research has been focused on using adsorption since it is cheaper, making use of low cost and local Adsorbents, which are adapted inefficiently removing heavy metal ions found in low concentrations in solution. Many

researchers have used a variety of agricultural wastes for the preparation of low cost activated carbon from cheaper and readily available materials. The wastes such as rice husk [12], apricot stone [13], lapsi seed stone [14], olive stone [15], date stone [16], cotton stalk [17] coconut shell [18], peanut shell etc, [19]. have been tested in the production of activated carbon in developing countries. The use of this raw material in the preparation of activated carbon shows from the past studies that they are available at low cost, contain high carbon content and may be effective in the removal of heavy metals.

The present study explored the use of activated carbon prepared from Coconut shell as an adsorbent for the removal of Cd(II) from aqueous solution. The effect of factors such as contact time, pH, the adsorbent dose was investigated. The adsorption kinetics of Cd(II) onto the activated carbon was analyzed by Pseudo first and pseudo second-order models. Experimental equilibrium data were also analyzed by Langmuir and Freundlich isotherms.

Materials and Methods

Preparation of adsorbent

The precursor used in this work is Coconut shell, the waste material left the consumption of edible part. The coconut shells were washed well with tap water and then with distilled water. The washed materials were dried well at 110 ^{o}C and crushed with an iron mortar and electric grinder to obtain the size of 300 µm.The dried mass was mixed with 50% H_3PO_4 in the ratio of 1:1 and carbonized at 400 ^{o}C for 4 hours and cooled after optimizing the parameters like the percentage of phosphoric acid, the ratio of precursor / phosphoric acid, carbonization time and carbonization temperature. The activated carbon was washed with warm distilled water and dried. The carbon was then cooled and sieved to obtain particles of size 106µm. The activated carbon thus prepared was represented by CSPAAC (coconut shell phosphoric acid activated carbon) and used for the adsorption process.

Chemicals and equipment

The chemicals and reagents used in this work are of analytical grade. The stock solution of heavy metals and other solutions were prepared using the distilled water prepared in the laboratory. pH of the solutions was adjusted by 0.1M HCl and 0.1 M NaOH. The adsorption experiments were carried out by using Shaker (Digital VDRL Rotator-RPM-S). The concentrations of heavy metal (II) ions were determined by atomic absorption spectrophotometer (AAS –VARIAN-AA240FS). Digital pH meter was used to measure the pH of solutions.

Adsorption experiment

In order to investigate adsorption, batch experiments were carried out in 50 mL stoppered conical flasks. The flasks were agitated on Digital VDRL Rotator-RPM-S at 225 rpm for identified time intervals. The effect of contact time, adsorbent dose and solution pH was studied. 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 experiments. Since pH is a critical parameter in the process; therefore, the pH of the solutions was adjusted by the addition of 0.1M NaOH and 0.1M HCl. The number of metal ions

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

adsorbed can be calculated by the following equation.

Where C_o and C_e = initial and equilibrium concentration of metal ion (mg / L) respectively,

W= the mass of adsorbent in gram (g) and

V = the volume of the solution in a liter (L).

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

The percentage of removed metal ions (Rem %) in solution is calculated by using the following formula

Results and Discussion

Scanning electron microscope (SEM)

Scanning Electron Microscope (SEM) of the carbon prepared without activating agent and activated prepared with H_3PO_4 as activating agent 50 % H_3PO_4 is presented in Figure 1 and Figure 2 respectively. Figure 1 is the SEM of carbon prepared from Coconut shell without any activating agent. The surface is heterogeneous and hardly any pores are visible. Figure 2 is the SEM images of activatedcarbon prepared by using H_3PO_4 as an activation agent. In the SEM image of Figure 2, a number of pores with different diameters are observed [20]. This development of porous structure may be attributed to the dehydrating effect of H_3PO_4.

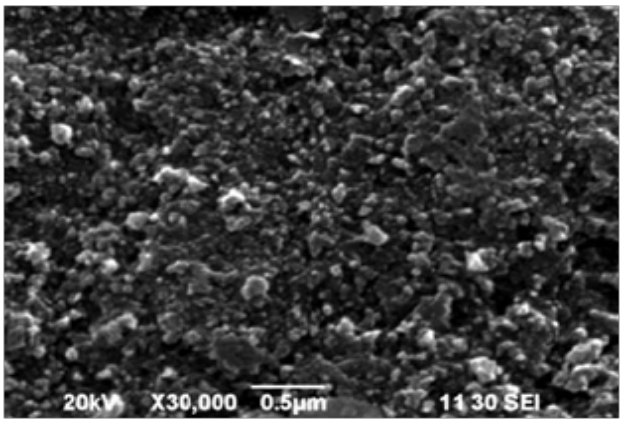

Figure 1: *SEM of carbon without activating agent*

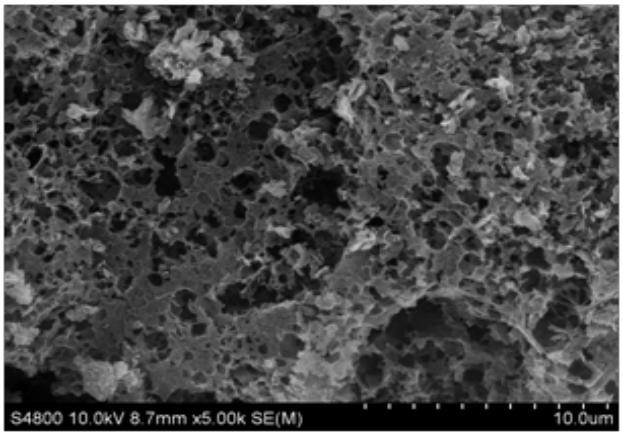

Figure 2: *SEM of activated carbon*

Phosphoric acid being a strong dehydrating agent removes oxygen and hydrogen from coconut shells as water, and that promotes the development of the porous structure.

Fourier transform infrared (FTIR) spectroscopy

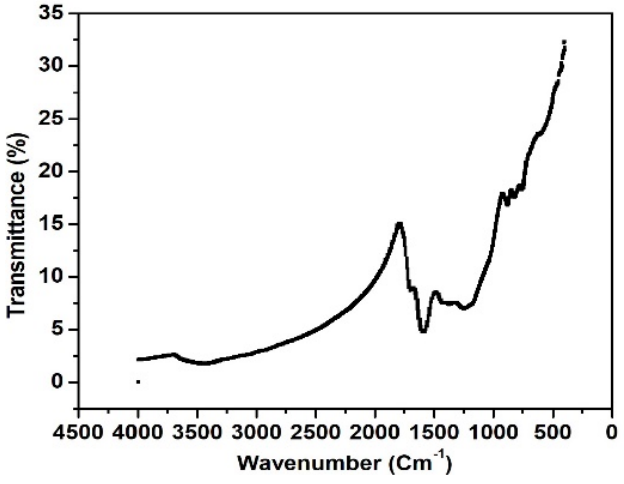

Figure 3: *FTIR spectra of activating agent*

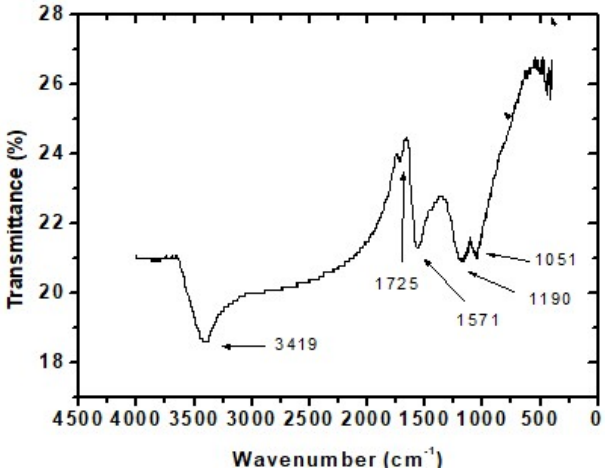

Figure 4: *FTIR spectra of activating carbon*

The FTIR spectra of activated carbon as shown in Figure 4 exhibit a broad band at 3419 cm^{-1} due to the presence of hydroxyl groups on the adsorbent surface. The band located at 1725 cm^{-1} is ascribed to the stretching vibrations of carboxylic groups or to conjugated carbonyl groups (C=O in carboxylic and lactones groups). Asymmetric stretching vibrations of ionic carboxylic groups (-COO-) appeared at 1571 cm^{-1}. The functional groups play an important role in the adsorption of the metal ions by donating electrons to heavy metal ions. These bands observed in the activated carbon are not seen in the carbon prepared without activating agent as shown in Figure 3.

X-ray diffraction (XRD)

XRD of the started as shown shows that the two broad diffraction peaks located near 2θ = 25.5° and 43° reflected from 002 and 100 planes as shown in Figure 5. The appearance of the broad peaks shows

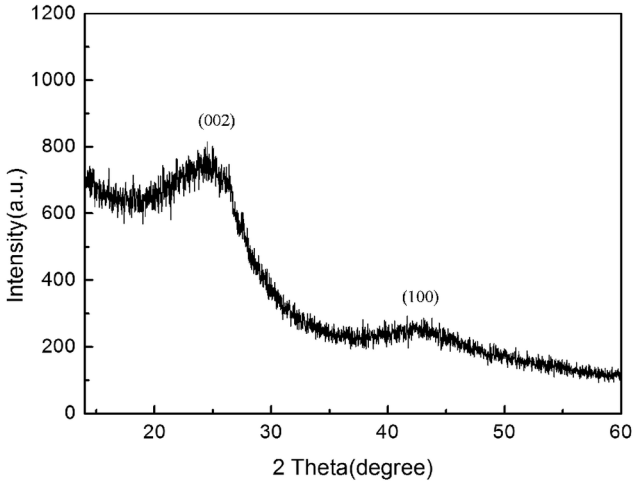

Figure 5: *XRD of activated carbon*

that the activated carbon is amorphous that is the good property of activated carbon for the adsorption.

Adsorption isotherms

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and solid phases, based on a set of assumptions that are related to the heterogeneity/ homogeneity of the solid surface, the type of coverage, and the possibility of interaction between the adsorbate species. In the present study equilibrium data were analyzed using Langmuir and Freundlich isotherms.

Langmuir isotherm

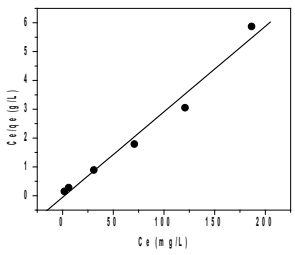

Figure 6: *Langmiur adsorption isotherm for adsorption of Cd (II) on CSAAC*

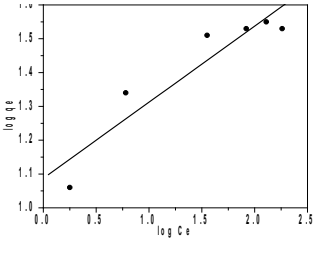

Figure 7: *Freundelich adsorption isotherm for adsorption of Cd (II) on CSAAC*

The Langmuir model assumes that the sorption of metal ions happens on a homogenous surface by monolayer adsorption with no interaction between adsorbed ions. The linear form of Langmuir adsorption isotherm is represented by the following equation.

$$C_e/q_e = (1/ bq_m)+ C_e/q_m \text{.....}\ldots\ldots\ldots\ldots(3)$$

Where, Ce = is the equilibrium concentration of the adsorbate (mg/L)

qe = the amount of the adsorbate adsorbed at equilibrium

qm = the monolayer adsorption capacity (mg /g)

b = Langmuir constant [21].

Adsorption capacity and Langmuir constant can be calculated from the slope and intercept of the plot C_e/q_e versus C_e as shown in Figure 6.

Freundlich isotherm

The Freundlich equation is an empirical equation based on adsorption on a heterogeneous surface. The linear form of the Freundlich isotherm equation can be represented as follows.

$$\log q_e = \log K_f + (1/n) \log C_e \text{.....}\ldots\ldots\ldots\ldots(4)$$

Where, K_f and n = the Freundlich constants related to adsorption capacity and intensity. qe and Ce = the amount of adsorbate adsorbed and equilibrium concentration of the adsorbate respectively.

The values of K_f and 1/n can be determined from the intercept and slope of the plot of log qe versus log Ce as shown in Figure 8. The Langmuir and Freundlich adsorption isotherm parameters are shown in Table 1.

Table 1: *Langmiur and Freundlich parameters of CSAAC*

Heavy metal ions	Langmuir parameters		R^2	Freundlich parameters		R^2
	Q_{max} (mg/g)	b		K_f(mg/g)	n	
Cd (II)	33.71	0.527	0.985	0.031	4.446	0.875

Adsorption kinetics

Adsorption kinetics 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 the rate of adsorption.

Pseudo first-order

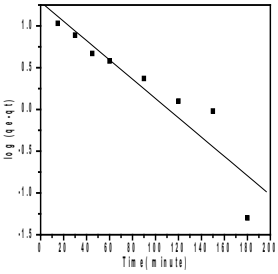

Figure 8: *Pseudo first order kinetics of adsorption of Cd (II) on CSAAC*

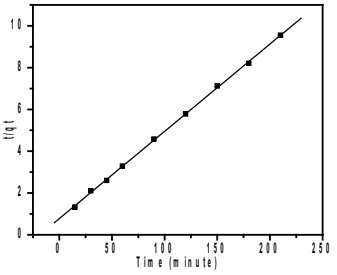

Figure 9: *Pseudo second order kinetics of adsorption of Cd (II) on CSAAC*

The pseudo first-order model was given by Legergren in 1898 [21]. According to him the first-order equation is represented as follows.

$$dqt/ dt = K_1 (q_e - q_t) \text{.....}\ldots\ldots\ldots\ldots(5)$$

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

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

K_1= the pseudo first-order rate constant (L min^{-1}).

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

$$\log (q_e - q_t) = \log q_e - (K_1/2.303)\, t \quad \text{.....(6)}$$

The plot of the value of log $(q_e - q_t)$ against 't' as shown in Figure 8 has been applied to test the validity of the kinetic model.

Pseudo second-order

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

$$dqt/dt = K_2 (q_e - q_t)^2 \quad \text{.....(7)}$$

Where k_2 =second order rate constant of adsorption (g mg $^{-1}$ min $^{-1}$).

The equation (7) after integration takes the form as follows.

$$1/(q_e - q_t) = 1/(q_e \times K_2) + 1/q_e \quad \text{.....(8)}$$

By rearranging the equation (8) will be as follows

$$1/qt = 1/(q_e^2 \times K_2) + 1/q_e \quad \text{.....(9)}$$

The plot of the value of 't/qt' against 't' as given in Figure 9 has been applied to test the validity of the kinetics.

Table 2: *Parameters of Pseudo first and second order kinetics*

Pseudo First-order Model			Pseudo Second-order Model		
q_e (mg/g)	K_1 (1/min)	R^2	q_e (mg/g)	K_2 (g/mg min)	R^2
19.349	0.027	0.865	23.940	2.257×10^{-3}	0.999

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 2.

Conclusion

Adsorption isotherms and adsorption kinetics for the adsorption of Pb (II) have been investigated using the activated carbon prepared from coconut shell. The adsorption of the metal ions has been found to be dependent on pH and the maximum adsorption has been observed at pH 6. Optimal contact time and adsorbent dose have been found to be 180 minutes and 2 g/L respectively. The SEM of the activated carbon has shown the pores of different diameters. Broad peaks in the activated carbon were investigated by XRD. The equilibrium data were best described by Langmuir adsorption isotherm with a higher correlation coefficient (R^2=0.985) than that of Freundlich isotherm (R^2=0.875) showing a maximum adsorption uptake of 33.71 mg/g. Analysis of adsorption kinetic data has shown that the Pseudo second- order model was found to describe adsorption much better with high correlations coefficient (R^2= 0.999) than that of Pseudo first- order model (R^2= 0.865). The results of the present study show that Coconut shell based activated carbon can be used as an efficient adsorbent for the removal of cadmium ions from aqueous solution.

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