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Application of Coconut Shell for the Preparation of Activated Carbon to Remove Heavy Metal from Aqueous Solution

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Abstract

Pollution caused by heavy metals has become one of the most serious environmental problems nowadays. Because of their non-biodegradability and persistence in nature, the removal of heavy metals from aqueous media is a special concern. This study investigates the removal of Cd (II) by adsorption on the activated carbon prepared from Coconut (Cocos nucifera) shell using phosphoric acid as an activating agent. The activated carbon has been characterized by Iodine number, Methylene blue number, SEM, XRD, FTIR. The SEM indicates the pores of different diameters. FTIR spectra exhibit the presence of surface functional groups such as carboxyl, phenolic and lactones groups. 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 2g/L respectively. The Langmuir and Freundlich adsorption isotherms have been utilized to verify the adsorption performance. Langmuir model best described the adsorption data with higher value of coefficient of correlation as compared to that of Freundlich isotherm showing a maximum uptake of 33.71 mg/g. The results show the activated carbon prepared from waste material Coconut shell successfully adsorbed the heavy metal from aqueous media.

Keywords: *Activated carbon; Coconut shell; Adsorption; Adsorption isotherms; Cadmium.*

1. Introduction

Heavy metal pollution in water has posed a threat to the environment and public health because of their toxicity, non-biodegradability and accumulation in the food chain and persistence in nature [1]. Among the heavy metals, Cd(II), is released from nickel-cadmium batteries, smelting, metal plating, phosphatic fertilizers,

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mining, alloy formation, pigments, stabilizers etc. The heavy metal pollution may cause cancer, lung fibrosis, chronic disorders such as “itai –itai”, renal damage, hypertension, testicular atrophy, dyspnea and weight loss to human beings [2] . Cadmium accumulates in the human body especially in kidneys, causing dysfunction of the kidney. So cadmium has been included in the red list of priority pollutants by the Department of Environment, UK and in the black list of Dangerous Substance Directive in European Economic Community. US Environment Protection Agency has also classified Cd as group B1 carcinogen [3]. The Cd(II) from water therefore should be removed.

Many treatment technologies like adsorption, precipitation, membrane filtration, chemical oxidation, electro dialysis, ion-exchange etc. have been used to remove metal ions pollutants from water. However, the treatment methods except adsorption have some limitations like cost effectiveness, production of high sludge, handling, disposal problem and main thing regarding these methods, they are not Eco-friendly anymore. To overcome the limitations of conventional methods it becomes urgent to develop a process which should be superior on these methods. It has been proved by many researchers that “adsorption” is the economical and efficient method for the remediation of heavy metals from aqueous solution. Activated carbon has shown to be an efficient adsorbent for the removal of a wide variety of organic and inorganic contaminants present in the aquatic environment. Because of its high surface areas that range from 500 to 1500 m^2 /g it is widely used in the treatment of wastewaters. The effectiveness of Activated carbon in the purification of polluted water is due to its well-developed porosity structure as well as the presence of surface functional groups. Effectiveness of activated carbons to act as adsorbents for a wide range of contaminants is well noted [4].

In recent years, many researchers have investigated the production of Activated carbons from cheap and renewable precursors such as olive stone [5 and 6], olive kernel [7], peanut shell [8], coconut shell [9], corn stalk [10], cotton stalk [11] etc. Besides these many fruit stones such as apricot stones [12], date stone [13], sea-buckthorn stone [14] etc. have also been used for the production of activated carbons.

Coconut shell is a potential precursor for the production of activated carbons due to its excellent natural structure and low ash content. Conversion of coconut shells into activated carbons which can be used as adsorbents in water purification or treatment of industrial and municipal effluents would add value to these agricultural commodities, help reduce the cost of waste disposal, and provide a potentially cheap alternative to existing commercial carbons. The main objective of this paper is to test the ability of activated carbon for the remediation of Cd (II) from water.

2. Experiment

2.1 Materials

The precursor for the preparation of activated carbon is coconut shell, the waste product of Coconut as shown in Fig. 1. The coconut shells were washed first with tap water and then with deionized water and dried at 110 °C for 24 hours to reduce the moisture content. The dried materials were crushed and sieved to a size range of 300 µm. The particles were mixed with 50 % H3PO4 in the ratio of 1:1 and dehydrated at 100 º C 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. The products were cooled at room temperature and washed with warm deionized water until the pH of the washing solution reached 6–7. The materials were then dried at 110 ºC for 24 hours, cooled and sieved to obtain the particles of size106 µm. The activated thus prepared was represented by Coconut shell activated carbon (CSAC) and was used for further study



a) Coconut shells



b) Coconuts

Figure 1. Coconut shell and Coconut

2.2 Chemicals and Equipment

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

2.3 Adsorption Experiments

To study the adsorption of Cd (II) onto CSAC batch experiments were carried out in 50 ml Borosil stoppered conical flasks. The flasks were then stirred well on Digital VDRL Rotator- RPM-S at 225 rpm for identifying time intervals. The experiment was run by using 0.05 g of adsorbent in 25 ml adsorbate solution taken in the conical flasks under optimum conditions set out for the experiment. The concentration of Cd(II) after adsorption was determined by atomic absorption spectrophotometer (AAS –VARIAN-AA240FS). The metal ions uptake on the adsorbent can be calculated by the equation as follows[15].

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

where C_o and C_e are initial and equilibrium concentration of adsorbate solution. V is the volume of solution in Liter and W is the mass of the adsorbent in gram. The percentage removal of metal ions (Rem %) can be calculated by using following formula

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

Where C_o and C_e are concentration of metal ions in mg/L before and after adsorption experiments

2.4 Methylene blue number and Iodine number

In order to estimate approximate surface area and concentration of micro and mesopores content in activated carbon Methylene blue number and Iodine number were used. Methylene blue number is defined as the amount of the dye adsorbed by one gram of the adsorbent. Whereas the iodine number is defined as the amount of iodine adsorbed per gram of activated carbon at an equilibrium concentration. Iodine being small molecules enters into micropores while methylene blue being a big molecule is absorbed into the mesopores. Methylene blue number can be calculated by the following formula [16]

$$MB_N \text{ (mg/g)} = \frac{(C_o - C_e) \times V}{M} \quad \text{.....(3)}$$

where Co and Ce are initial and equilibrium concentration of MB (mg / L) respectively, M is the mass of adsorbent in gram (g) and V is the volume of the solution in liter.

Iodine number can be calculated as follows.

$$\text{Iodine number} = \frac{\text{Amouont of iodine in mg adsorption by carbon}}{\text{Weight of carbon taken in gram}} \quad \text{.....(4)}$$

2.5 X-ray diffraction

X-ray diffraction analysis was done to determine the degree of crystalline or amorphous nature of the activated carbon. Activated carbon was homogenously spread on the groove of the glass slide and mounted on Rigaku X-ray diffractometer RINT, Japan. The measurement was carried out at 40 kV and 40 mA with Cu-Kα radiation at room temperature for the scanning angle (2θ) range of 3 to 85 ° at scanning speed of 5°/min.

2.6 Scanning Electron Microscope (SEM)

The surface morphology of Activated carbon (AC) was analyzed by scanning electron microscope (SEM). For the SEM image the carbon tape was cut into small pieces and fixed on the disc. Then the upper layer of the disc was removed and very small amount of carbon was placed on the black carbon tape, well fixed just pressing on a clean silicon wafer. The images were recorded in U-8000 Hitachi Co. Ltd., Japan at 5KV.

3. Result and Discussion

3.1 Effect of pH

pH is the important parameter that can affect the adsorption capacity of activated carbon. This may be due

to that fact that hydrogen ions themselves are strong competing species and pH of the solution influences the chemical speciation of the metal ions as well as the ionization of functional groups onto adsorbent surfaces [17]. To evaluate the effect this parameter experiments were carried out at different pH values. The pH ranges are selected from 2 to 8 to avoid precipitation of metal hydroxides. It can be observed from Fig. 2 that the maximum adsorption of Cd(II) was observed at pH 6..

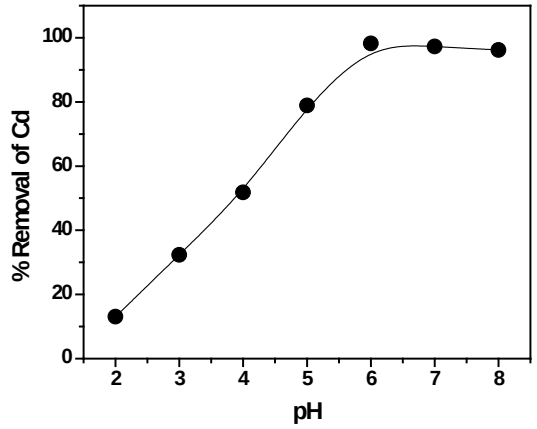


Figure 2. Effect of pH on Cd (II)

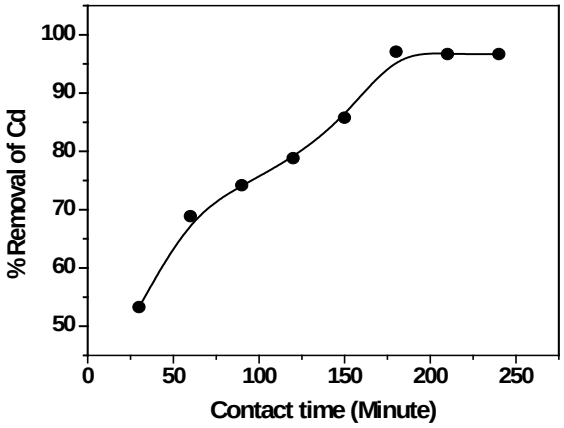


Figure 3. Effect of contact time on Cd (II) adsorption

3.2 Effect of Contact time

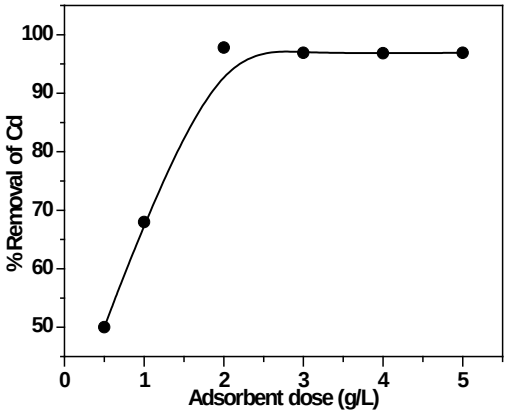
Adsorption efficiency strongly depends upon adsorption time. Therefore, the effect of contact time on adsorption was studied. The result is shown in Fig 3. Equilibrium was attained after 180 min with adsorption capacity of 33.71 mg/g. It was observed that percent removal efficiency increased with time and after equilibrium it become constant.

3.3 XRD (X-ray diffraction)

XRD of the activated exhibits that the two broad diffraction peaks located near at $2\theta = 25.5^{o}$ and 43^{o} reflected from 002 and 001 planes as shown in Fig. 5. The broad peaks show that the activated carbon is amorphous which is the good property of activated carbon for the adsorption.

3.4 Effect of Adsorbent dose

The percentage removal of Cd(II) increased with increase in adsorbent dose from 0.5 g/L to 2 g/L as shown in Fig 4. The increase in percentage removal of metal ions with the increase in adsorbent dose may due to the availability of larger adsorption sites due to increase in adsorbent dose. The percentage removal of the heavy metal ions remained constant when adsorbent dose is more than 2g/L. Adsorbent dose of 2 g/ L has been observed as sufficient contact time for effective adsorption of Cd(II) ions from the aqueous solutions.



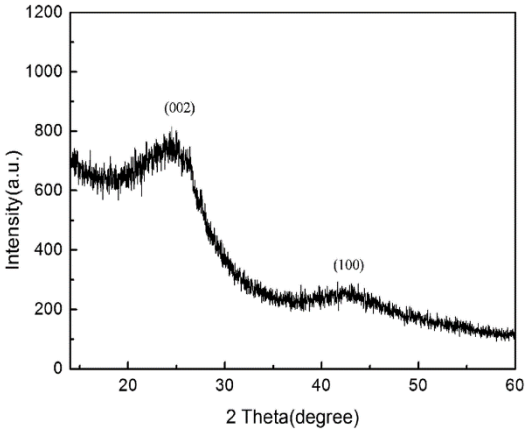
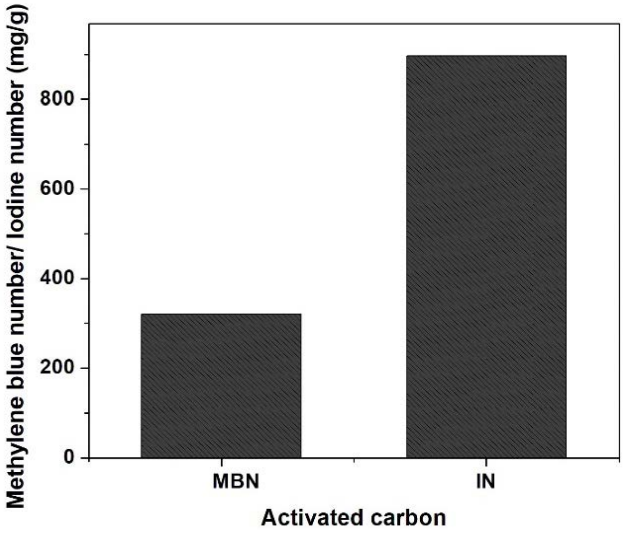


Figure 4. Effect of Adsorbent dose on Cd (II) adsorption

Figure 5. XRD of Activated carbon

3.5 SEM (Scanning Electron Microscope)

SEM image of activated reveals the pores with different diameters as presented in Fig.7. The development of porous structure may be attributed to the dehydrating effect of H3PO4. Phosphoric acid being a strong dehydrating agent removes oxygen and hydrogen from the precursor as water, and that promotes the development of porous structure.



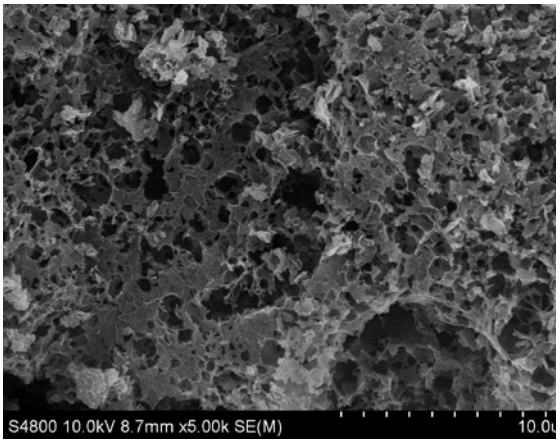


Figure 6. Methylene blue and Iodine Numbers of Activated carbon

Figure 7. SEM of Activated carbon

3.6 FTIR (Fourier Transform Infrared) Spectroscopy

The FTIR spectra of activated carbon 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

important role in the adsorption of the metal ions by donating electrons to heavy metal ions.

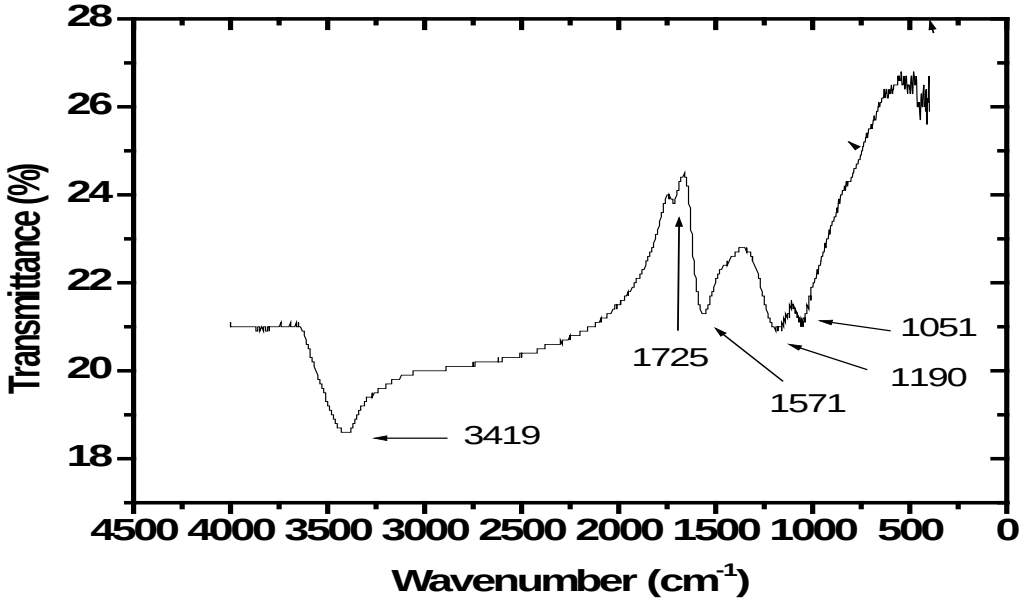


Figure 8. FTIR Spectra of Activated carbon

3.7 Adsorption isotherms

Adsorption isotherm is a curve which relates the amount of adsorbate adsorbed at constant temperature with the concentration of the adsorbate at equilibrium. The equilibrium isotherm of the heavy metal between solid adsorbent and the solution is important to determine the maximum adsorption capacity. Langmuir and Freundlich adsorption isotherm are the most important isotherms generally used to analyze the adsorptive behavior of adsorbate on adsorbent.

3.7.1 Langmuir isotherm

Langmuir isotherm model supposes that the uptake of metal ions on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. Linear form of Langmuir adsorption isotherm is represented by following equation.

$$\frac{Ce}{qe} = \frac{1}{bqm} + \frac{Ce}{qm} \quad \text{.....(5)}$$

where Ce = the equilibrium concentration of the adsorbate (mg/L) and

qe = the amount of the adsorbate adsorbed at equilibrium while

qm = the monolayer adsorption capacity (mg /g)

b = Langmuir constant [18,19]. Adsorption capacity and Langmuir constant can be calculated from the slope

and intercept of the plot Ce/qe versus Ce as shown in Fig. 9.

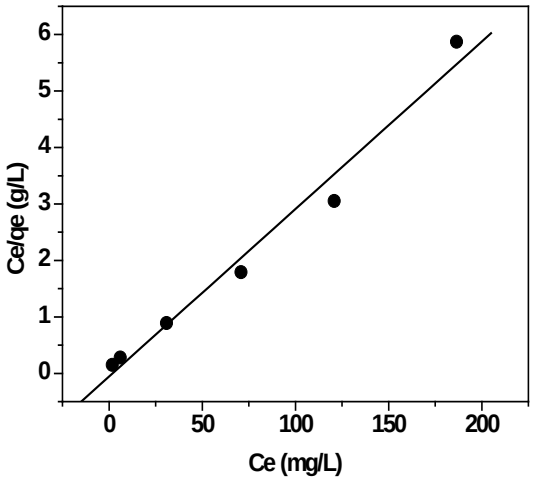


Figure 9. Langmuir Adsorption isotherm

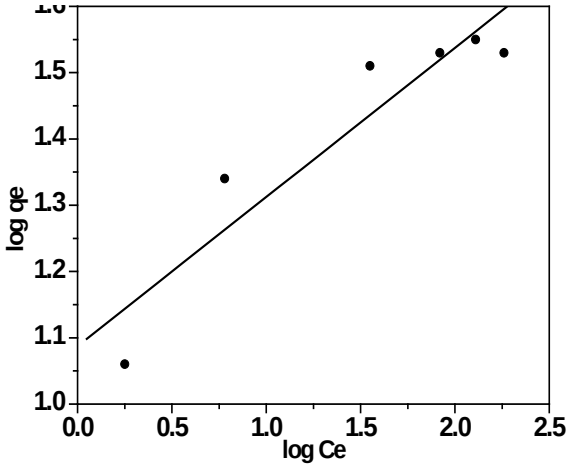


Figure 10. Freundlich Adsorption isotherm

3.7.2 Freundlich isotherm

Freundlich model is based on adsorption on heterogeneous surfaces and does not provide any information on the monolayer adsorption capacity and can be applied to multilayer adsorption [20]. The isotherm was applied to determine adsorption intensity of adsorbent for the adsorbate. The linear form of Freundlich isotherm equation can be represented as follows.

$$\log qe = \log Kf + \frac{1}{n} \log Ce \quad \text{.....(6)}$$

where Kf 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 Kf and 1/n can be determined from intercept and slope of the plot of log qe versus log Ce as shown in Fig. 10. The Langmuir and Freundlich adsorption isotherm parameters are shown in Table 1.

Table 1. Langmiur and Feundlich parameters of CSAC

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

5. Conclusion

The coconut shell activated carbon prepared by using phosphoric acid as an activating agent demonstrated the great advantage in the removal of Cd (II) from aqueous solution. The results exhibited that the pH of the solution is most important parameter for the adsorption of the metal ion on the activated carbon. The adsorption of the metal ions was found to be highly pH dependent and the results indicated that the optimum pH was 6 for the removal of Cd (II).The percentage removal of the metal ions was also dependent on contact time and adsorbent dose and optimum contact time and adsorbent dose for the removal of the heavy metal were found to be 180 minutes and 2 g/ L respectively. FTIR Spectra of the activated carbon indicated the presence surface functional groups such as carboxylic, phenolic and lactones. Presences of pore of different diameters were also exhibited by SEM image. XRD analysis demonstrated the amorphous nature of the activated carbon due to the presence of broad peaks. Methylene and Iodine numbers have been found to be 320 mg /g and 897 mg/g. The adsorption data fitted very well in the Langmuir isotherm equation confirming the monolayer adsorption capacity of 33.71 mg/g. The results indicate that the activated carbon prepared from waste material, Coconut shell, can be used as an effective adsorbent for the remediation of heavy from aqueous solution.

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