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Utilization of Activated Carbon Prepared from Coconut (Cocos nucifera) Shell for the Removal of Pb (II) from Aqueous Solutions

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Abstract

Activated carbon prepared from Coconut (Cocos nucifera) shell by chemical activation with phosphoric acid at 400oC has been utilized to remove Pb (II) from aqueous solutions. The activated carbon was characterized by chemical methods like MBN (Methylene blue number) and IN (Iodine number), and instrumental techniques such as SEM (Scanning Electron Microscope), XRD (X-ray Diffraction), FTIR (Fourier Transform Infrared). The application of the activated carbon for the adsorption of Pb (II) from aqueous solutions was studied by varying the parameters such as pH, contact time and adsorbent dosage. The optimum pH, contact time and the adsorbent dosage have been found to be 5,180 minutes and 2g / L respectively. The most frequently used adsorption Isotherms-Langmuir and Freundlich were applied to verify the performance of adsorption. The results indicated that the adsorption process was fitted best to Langmuir adsorption isotherm as compared to Freundlich isotherm. The maximum adsorption capacity studied at pH 5 was found to be 131.23 mg/g. The present study reveals that the activated carbon prepared from coconut shell can be used an effective adsorbent for the removal of Pb (II) from aqueous solutions.

Keywords: *Activated carbon, Adsorption, Coconut shell, Lead, Adsorption isotherms*

1. Introduction

The water pollution caused by heavy metals is one of the serious problems. The removal of heavy metals is a special concern to scientists and engineers because of their harmful effects on many forms of life [1]. Lead is one

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of the toxic heavy metals. The heavy metal does not undergo biological degradation like organic pollutants and accumulate in living organisms causing various disorders like severe damage to the kidney, nervous system, reproductive system, liver, and brain [2]. The contamination of lead in water is mainly caused by many industries like as metal plating, paints dyes, glass operations, mining and lead batteries [3]. The permissible limit of lead in drinking water and surface water intended for drinking, as set by WHO is 0.010 mgL^{-1} [4]. The heavy metal ions should, therefore, be removed from contaminated water. Many conventional methods have been applied to remove the heavy metal ions. The methods include precipitation, reverse osmosis chemical oxidation, ion exchange, membrane separation, adsorption etc [5]. Most of these methods have some drawbacks such as high operation cost, capital and the disposal of the residual metal sludge which are not suitable for small-scale industries [6]. All these methods except adsorption are, generally expensive and not appropriate for the removal of the heavy metals in trace amounts. Due to this there is a need for developing economic and eco-friendly methods for the minimization of the pollutants and fine tuning of contaminated water [7]. Among the methods adsorption is a user-friendly technique for the removal of heavy metal ions. Many efforts have been made to develop low-cost adsorbents for the removal of heavy metals from aqueous solutions including natural water and industrial wastewater [8].

Many research works have been carried out showing the development of activated carbon prepared from cheaper and readily available materials such as coconut shell [9] apricot stone [10], olive stone [11], rice husk [12] palm shell [13], date stone [14], peanut shell [15], olive kernels [16], cotton stalk [17], Lapsi seed stone [18], sea-buckthorn stones [19] etc. for the preparation of activated carbon.

In current study, coconut shells have been utilized to prepare activated carbon as adsorbents for the removal of Pb (II) from aqueous solutions. The different parameters for adsorption process such as pH, adsorbent dosage and contact time were investigated with respect to the removal efficiency of the metal ions. The adsorption data have been analyzed by two most frequently used adsorption isotherms – Langmuir and Freundlich.

2. Experimental

2.1 Materials

The precursor used in this study is Coconut shell as shown in Fig.1. The material was washed with tap water and distilled water and then crushed and sieved to a size range of 300 μm and was soaked with phosphoric acid solution of 50%. The mixture was dried in an oven at 110 °C and carbonized under high purity nitrogen flow of 75 ml min−1 by raising the temperature at a rate until 400° C and kept at this temperature for 3 hours. The prepared activated carbon was cooled at room temperature and washed with warm distilled water, until the pH of the washing attained 6 –7. The activated carbon thus prepared was indicated as PACSAC (Phosphoric acid activated Coconut Shell Activated Carbon).



Figure 1. Coconuts and coconut shells.

2.2 Chemicals and Equipment

All chemicals and reagents used were of analytical grade. Stock solutions of Pb (II) were prepared from lead nitrate in distilled water. In order to adjust pH of solutions Digital pH meter was used. The adsorption experiments were carried out by using Shaker (Digital VDRL Rotator RPM-S). The concentration of Pb (II) after adsorption onto activated carbon was determined by Atomic absorption spectrophotometer (AAS–VARIAN-AA240FS). The pH of solutions was adjusted by using 0.1 M NaOH and 0.1 M HCl. All the working solutions were prepared by dilution of the stock solutions using distilled water.

2.3 Adsorption Experiments

In order to study the adsorption, batch-mode of adsorption experiments were carried out in 50 mL stopper conical flask. The flasks were stirred well on Digital VDRL Rotator- RPM- at 225 rpm. 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 Pb (II) after adsorption was determined by atomic absorption spectrophotometer (AAS –VARIAN-AA240FS).

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

where CO and C are the initial and equilibrium concentrations of Pb (II) in mg L−1 respectively, V is the volume of the solution in Liter, and W is the mass of adsorbent in gram. The removal of the metal ions in percentage (Rem %) can be calculated by following formula.

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

2.4 Methylene blue number and Iodine number

The amount of mesopore and micropore content in activated carbon was determined by Methylene blue number and Iodine number. Methylene blue number indicates the amount of the dye adsorbed by one gram of the adsorbent while the iodine number is the amount of iodine adsorbed per gram of activated carbon at an equilibrium concentration. Methylene blue number can be calculated by the following formula [20].

$$MB_N \left(\frac{mg}{g}\right) = \frac{(\ C_o -\ C_e\ ) \times 100}{M} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where CO and C are the initial and equilibrium concentrations of Pb (II) in mg L^{-1} respectively, V is the volume of the solution in Liter, and W is the mass of adsorbent in gram. The removal of the metal ions in percentage (Rem %) can be calculated by following formula.

$$\text{Iodine number} \left(\frac{mg}{g}\right) = \frac{\text{Amount of iodine adsorbed in mg by the carbon}}{\text{Weight of the carbon in g}} \ldots. (4)$$

2.5 X-ray diffraction

X-ray diffraction analysis has been used to determine degree of crystalline and amorphous nature of the activated carbon. The 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) has been investigated by Scanning electron microscope (SEM). The carbon tape was cut into small pieces and fixed on the disc to study SEM image. The upper layer of the disc was then 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. Results and Discussion

3.1 Effect of pH

The pH of solution is the important parameter that can affect the adsorption of the metal ions onto activated carbon as shown in Fig. 2. The removal of the heavy metal ions in percentage increased sharply from pH 2 to 4 and then attained a maximum at pH 5. The percentage removal after pH 5 remained almost constant and then decreased from 7 to 8. The percentage of removal of Pb (II) is lower at low pH. This may be due to the fact that at lower pH there is higher concentration of hydrogen ions that compete with the metal ions. The optimum contact time of the adsorption process is found to be 5.

3.2 Effect of Contact time

Fig.3 indicates the effect of contact time on the adsorption of the heavy metal ions. The percentage removal of the metal ions increased with increase in time and attained a maximum value at 180 minutes. The adsorption process is very fast up to 120 minutes and then it attained equilibrium value slowly. The fast adsorption at initial stage may be attributed to the higher driving force due to the availability of the large concentration of active sites for adsorption. After 120 minutes the removal percentage increases gradually and attains plateau value at 180 minutes. At equilibrium all the active sites on the activated carbon will be occupied by the metal ions and no further adsorption of metal ions occurs. Thus equilibrium time for adsorption of Pb (II) on the activated carbon is found to be 180 minutes.

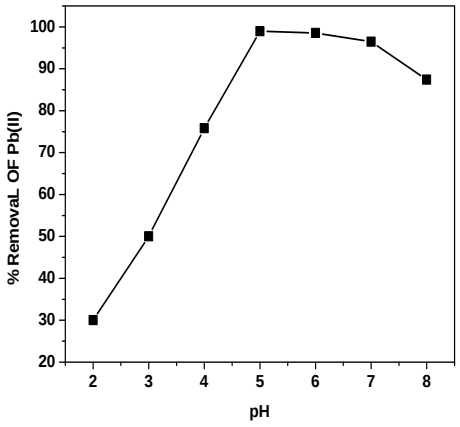


Figure 2. Effect of pH on Pb (II) adsorption.

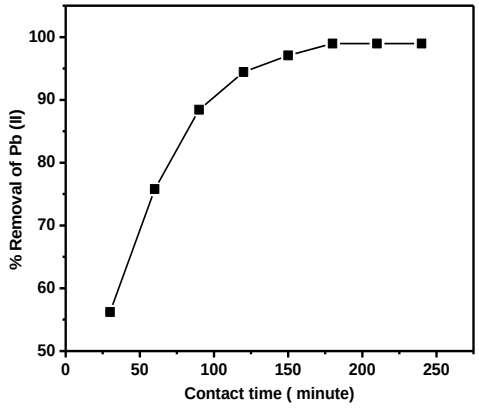


Figure 3. Effect of contact time on Pb (II) adsorption.

3.3 Effect of Adsorbent dosage

The effect of adsorbent dosage on the adsorption of Pb (II) is shown in Fig. 4. The removal of the heavy metal ions increased from 0.5 to 2 g/L and then remained almost constant. This may be attributed to the availability of more adsorption sites because of increase in adsorbent dosage. Adsorbent dosage of 2 g/ L has been observed as sufficient contact time for effective adsorption of Pb (II) ions.

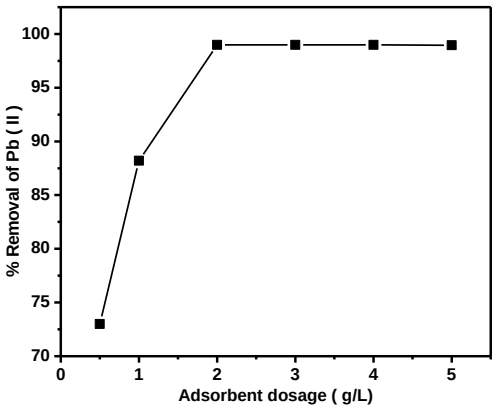


Figure 4. Effect of adsorbent dosage on Pb (II) adsorption.

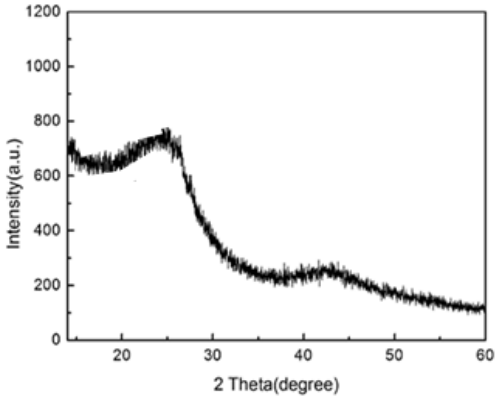


Figure 5. XRD of Activated carbon.

3.4 XRD (X-ray diffraction)

The two broad diffraction peaks located near at $2\theta = 25.5^{o}$ and 43^{o} reflected from 002 and 001 planes have been shown by XRD analysis of the activated carbon as shown in Fig. 5. The broad peaks indicate that the activated carbon is amorphous in nature. The amorphous nature of activated carbon is one of good properties needed for the adsorption.

3.5 SEM (Scanning Electron Microscope)

The surface morphology of activated carbon has been analyzed by SEM which reveals the pores with different diameters as shown in Fig.6. The development of porous structure may be due to the dehydrating action of phosphoric acid. Owing to the dehydrating action it removes oxygen and hydrogen from the precursor as water, and that promotes the development of pores.

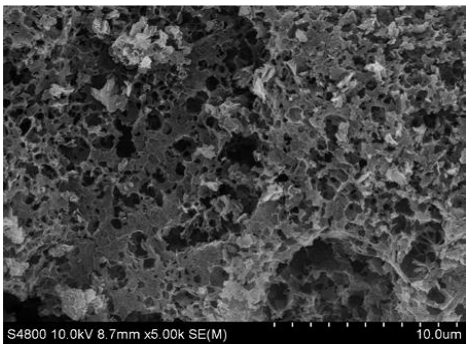


Figure 6. SEM of Activated carbon.

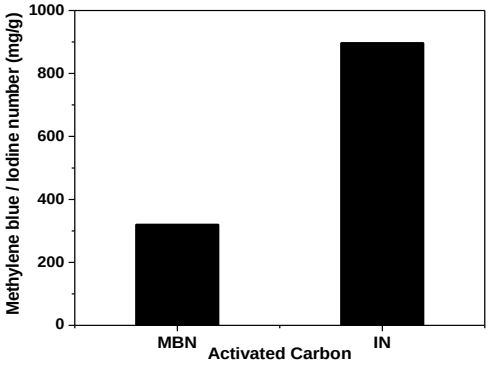


Figure 7. MBN and IN of Activated carbon.

3.6 Methylene blue number (MBN) and Iodine number (IN)

The mesopore and micropore content in activated carbon have been analyzed by Methylene blue number and Iodine blue number as shown in Fig. 7. Iodine blue number and Methylene blue number have been found to be 897.0 mg/g and 320.0 mg/g respectively.

3.7 FTIR (Fourier Transform Infrared) Spectroscopy

The presence of surface functional groups on the surface of the activated carbon has been analyzed by FTIR.The FTIR spectra of activated carbon is shown in Fig.8 which exhibits 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.

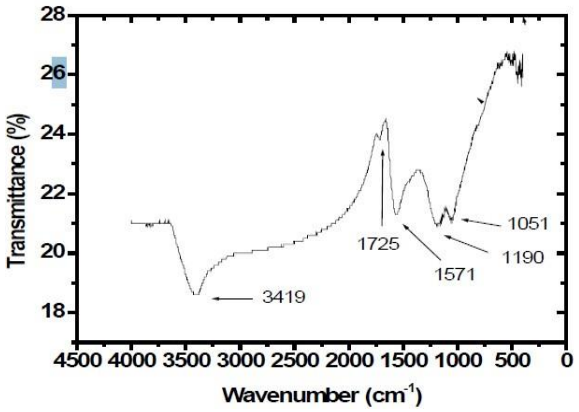


Figure 8. FTIR Spectra of Activated carbon.

3.8 Adsorption isotherms

Adsorption isotherm demonstrates the amount of material that is adsorbed per unit mass of adsorbent as a function of the equilibrium concentration of the adsorbate. Several isotherms are studied in literature to describe experimental data of adsorption. The Langmuir and Freundlich adsorption isotherms are the most frequently employed isotherms. In this work both the adsorption isotherms are used to analyze the adsorptive behavior of adsorbate on adsorbent.

3.8.1 Langmuir isotherm

The Langmuir isotherm is the most commonly used adsorption isotherm for the adsorption of solute from the solution. This adsorption isotherm presumes homogeneous surface adsorption with the formation of monolayer on the adsorbent surface. Linear form of Langmuir adsorption isotherm is represented by following equation [22].

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

where Ce is equilibrium concentration of the adsorbate (mg/L), qe is the amount of the adsorbate adsorbed at equilibrium, qm is monolayer adsorption capacity (mg /g) and b is Langmuir constant.

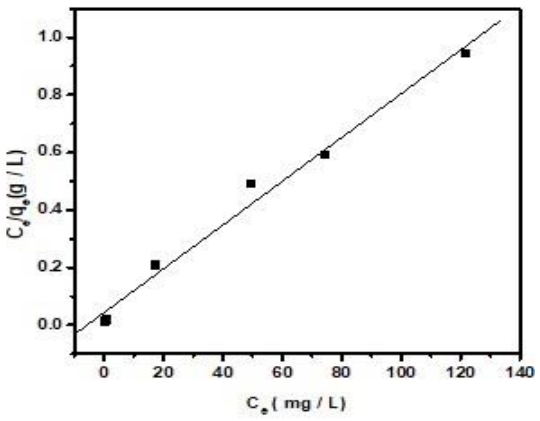


Figure 9. Langmuir isotherm of Pb(II) adsorption onto PACSAC

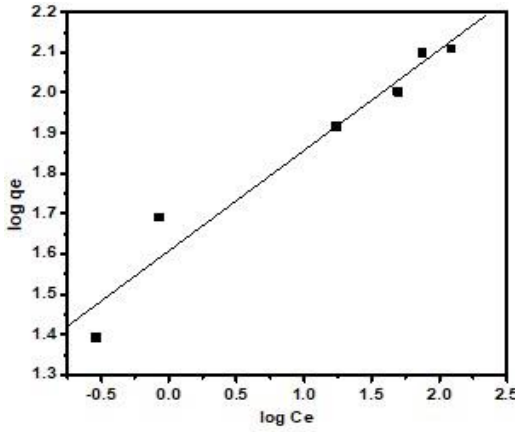


Figure 10. Freundlich isotherm of Pb (II) adsorption onto PACSAC

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.

3.8.2 Freundlich isotherm

The Freundlich isotherm can be applied for non-ideal adsorption heterogeneous surfaces and multilayer adsorption [23].The linear form of Freundlich isotherm equation can be represented as follows.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

where Kf and n are Freundlich constants related to adsorption capacity and intensity. qe and Ce are the amount of Pb (II) adsorbed and equilibrium concentration of Pb (II) respectively.

The Freundlich constants are determined from intercept and slope of the plot log qe versus log Ce. Langmuir and Freundlich parameters of PACSAC are shown in Table 1.

Table 1. Langmuir and Freundlich parameters of PACSAC

Langmuir parameters			**Freundlich parameters**		
Q_{max} (m/g)	**b**	**R^2**	**K_f (mg/g)**	**n**	**R^2**
131.23	0.1770	0.986	40.553	4.015	0.952

4. Conclusion

The results obtained demonstrate that the activated carbon prepared from Coconut shell, is an effective

adsorbent for the removal of Pb (II) from aqueous solutions. The parameters like pH, contact time and adsorbent dosage have influenced the adsorption process. The results indicate that the optimum pH, contact time and adsorbent dosage are 5, 180 minutes and 2 g / L respectively. The presence of surface functional groups such as carboxylic, phenolic and lactones on the activated carbon has been analyzed by FTIR spectra. The pores of different diameters on the activated carbon have been shown by SEM image. XRD analysis exhibits two broad diffraction peaks located near at $2\theta = 25.5$ o and 43 o reflected from 002 and 100 planes. The presence of broad peaks indicates that the activated carbon is amorphous. The amorphous nature of the activated carbon is one of the good properties of activated carbon for adsorption. The mesopore and micropore content in the activated carbon have been exhibited by Methylene blue number and Iodine number which have been found to be 320.0 mg/g and 897.0 mg/g respectively. The adsorption equilibrium data fitted well in Langmuir isotherm confirming the monolayer adsorption with the maximum adsorption capacity of 131.23 mg g^{-1}.

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