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Preparation and Characterization of Activated Carbon from Lapsi (*Choerospondias axillaris*) Seed Stone by Chemical Activation with Potassium Hydroxide

Sahira Joshi, Bhadra Prasad Pokharel

Department of Engineering Science and Humanities, Institute of Engineering, Central Campus, Pulchowk, Tribhuvan University, Nepal

Corresponding email: sjoshi61@hotmail.com

Abstract: Activated carbon (AC) was prepared from Lapsi seed stone by chemical activation with Potassium hydroxide at 400°C. The AC was characterized by pH, moisture content, Fourier transform-infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), methylene blue (MB) and iodine (I_2) number. FT-IR spectra indicated the presence of various oxygen containing functional groups on the surface of AC. SEM images show the highly porous characteristics of AC with full of cavities. The Iodine number of AC revealed that the AC was found to be highly micro-porous. The adsorption of methylene blue by prepared AC was analyzed by the Langmuir and Freundlich adsorption isotherms. The data fitted well to the Langmuir isotherm with monolayer adsorption capacity 158 mg/g. The analysis showed that the AC prepared from Lapsi seed stone activated with potassium hydroxide could be a low-cost adsorbent with favorable surface properties.

Keywords: lapsi seed stone, activated carbon, adsorption isotherm.

1. Introduction

Adsorption is an effective technique for the removal of dissolved pollutants (organic or inorganic) from water. Among many types of adsorbents, activated carbons are the most widely used, because of their large adsorptive capacity and low cost. The adsorption capacity of activated carbon is linked to their large surface area, a high micro porosity and a high degree of surface reactivity [1].

Activated carbons are generally prepared by the carbonization of raw carbonaceous materials in an inert atmosphere followed by the activation of carbonized product. Activation can be carried out by chemical or physical means [2]. Physical activation involves two steps; carbonization of raw material and then activation with an oxidizing gas such as steam or carbon dioxide. In chemical activation, the carbonization and activation are accomplished in a single step by impregnation of raw material with a chemical activating agent and carbonization in an inert atmosphere. Chemical activation is preferred over physical activation due to the lower temperatures (500^oC to 800^oC) needed for activation and high product yields [3]. Among the many different activating agents, the most frequent used are phosphoric acid (H_3PO_4) and zinc chloride ($ZnCl_2$). However others as hydroxides can also be used (i.e. potassium and sodium) [4]. Recently, there is growing interest in alkaline hydroxide activation process and KOH has been found to be one of the most effective activating agents in the production of activated carbons [4, 5].

Agricultural lignocellulosic wastes are potential precursors because of their abundance and low cost. Moreover, use of agricultural wastes for production of activated carbon may help to reduce solid waste disposal problem as well as to convert waste product into a high value material for effluent treatment [6]. Consequently, a wide variety of agricultural by-products and wastes has been investigated as lignocellulosic precursors for the production of activated carbon. These precursors include: coconut shell [7], almond shells [8], pecan shell [9], cherry stones [10], apricot stones [11], peach stones [12], corncobs [13] etc. Among a wide range of lignocellulosic precursors, Lapsi (*Choerospondias axillaris*) seed stones are selected because of their abundance and low cost [14]. Moreover, little work has been reported on the production of activated carbon using Lapsi seed stone. Earlier studies have investigated the production of activated carbons with well-developed porosity from Lapsi seed stone by chemical activation using $ZnCl_2$ and H_3PO_4 [15, 16]. But no information is available concerning the preparation of activated carbon from Lapsi seed stone using basic activating agent. The present work is focused on the characterization of activated carbon prepared from Lapsi seed stone by chemical activation using KOH.

2. Experimental

2.1 Materials

The Lapsi seed stone were purchased from food Industry, Kathmandu, Nepal. The chemicals used for this investigation and analysis were all analytical grade purchased from Qualigen, India were used. Ultra high pure (UHP) nitrogen was used for inert atmosphere during carbonization.

Lapsi seed stones were washed several times with distilled water and dried at 110°C for 24 hrs. The dried seed stones were then crushed, grinded in an electric grinder and sieved to get the particles of size 108 μm.

2.2 Preparation of Adsorbent

Twenty grams of dried, crushed, powdered Lapsi seed stone was mixed with 20 gm Potassium hydroxide (KOH) in ratio of 1:1 by weight. Then added 100 ml distilled water and was shaken in magnetic stirrer at 70°C until the excess water had evaporated. The mixture was dried in the air oven at 110°C for 24 hours. Then the mixture was carbonized in tubular electric furnace at 400°C under atmosphere of nitrogen under a flow (75 ml/min) for 3 hrs. The KOH activated carbon sample was treated with 1N HCl and washed with warm distilled water until free of acid. After that, the carbon sample was dried at 110°C for 24 hrs and sieved to get the particles of size 212 μm. The resulting KOH activated carbon sample was used for textural and chemical characterizations.

2.3 Characterization of Activated Carbons

2.3.1 Thermal Behavior of Lapsi seed stone particles:

Thermal behavior of Lapsi Seed Stone was observed by TGA analysis in atmosphere of nitrogen to find the appropriate temperature for carbonization of Lapsi seed stone for the preparation of Activated carbon.

2.3.2 Characterization of the prepared activated carbon:

Fourier Transform-Infrared (FTIR) Spectroscopy: Surface functional groups of the KOH impregnated activated carbon were determined recording FTIR spectra on the Thermo Electron Corporation, Nicolet 4700 at room temperature. The % of transmission of samples was recorded over 500–4000 cm^{-1}.

Scanning electron microscopy (SEM): Surface morphology of the prepared activated carbon was studied using scanning electron microscopy. SEM samples were prepared on a carbon tape and images were taken using U-8000, Hitachi Co. Ltd. Japan.

Determination of Moisture content: Moisture content of activated carbon is determined according to a standard method ASTM D 2867-99(1999) [32]. Moisture content was obtained by weighing. 1.0 gram of the dried activated carbon placed in washed, dried and weighed crucible then placed in an oven at 105°C to constant weight for 3 h. Then the carbon was cooled and reweighed again. This test was repeated until constant moisture content was obtained. The difference between the initial and final mass of the carbon represents the water content in the sample. In percentage:

$$Moisture\ content\ (\%) = \frac{loss\ in\ wt.on\ drying\,(gm)}{wt.of\ initial\ sample} \times 100$$

Methylene blue Adsorption: The methylene blue number is defined as the milligram of methylene blue adsorbed onto 1.0 gm of adsorbent [17]. Methylene blue number was determined according to Standard Method (JIS K 1470-1991) [18]. In this assay, 0.1 gm of activated carbon was placed in contact with 100.0 mL of a methylene blue (MB) solution at different concentrations (15–100 mg L^{-1}) for 24 hrs at room temperature (approximately 25 °C). After shaking for 24 hrs, the suspensions were filtered and the remaining concentration of methylene blue in the solution was determined spectrophotometrically at λ max of 660 nm using an UV /Vis spectrophotometer (UV- CECIL- CE-100). Standard solutions of methylene blue were used for calibration.

Iodine number (IN): It is the amount of iodine adsorbed (in milligrams) by 1gm of carbon when the iodine concentration of the filtrate is 0.02 N [17]. The iodine number is determined according to ASTM D4607-94 method [19]. In determining the iodine number, 10 ml of 5 % by weight HCl was added to 0.1 gm of activated carbon in a conical flask and the flask was swirled until the carbon was wetted. Then 10 ml of 0.1N iodine solution was added and the content was shaken vigorously for 4 minutes and filtered. The 10 ml of filtrate was titrated with 0.1 N sodium thiosulphate (hypo) in presence of starch as indicator. The concentration of iodine adsorbed by activated carbon was calculated as amount of iodine adsorbed in milligrams.

$$\text{Iodine number} = C * f$$

Where, f is the conversion factor which is calculated as:

$$Conversion\ \ factor\ \ (f) = \frac{Molecular\ \ weight\ \ (126.92) * Normality\ of\ Iodine * 10}{Weight\ \ of\ Activated\ \ Carbon * Blank\ reading}$$

Where,

$$C = (Blank\ reading - volume\ of\ hypo\ consumed\ after\ adsorption\ of\ activated\ carbon)$$

Adsorption isotherm: The performance of activated carbon is evaluated using adsorption isotherms.The most commonly used models includes Freundlich, Langmuir isotherms. Langmuir adsorption isotherm commonly applied in solid/liquid system to describe the saturated monolayer adsorption [21] where as Freundlich adsorption isotherm describes the adsorption equilibrium, based on adsorption on heterogeneous surface [21]. The linearized form of the Langmuir equation can be represented as:

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

Where C_e is the equilibrium concentration of methylene blue in solution (mg/L^{-1}); q_e is the amount of methylene blue adsorbed (mg gm^{-1}); q_m is complete monolayer adsorption capacity (mg gm^{-1}). The parameter q_m can be determined by the slope of the linear plot of $\frac{C_e}{q_e}$ versus C_e.. The linearized form of The Freundlich equation is designed as.

$$\log q_e = \log K + \frac{1}{n}\log C_e$$

Where q_e is the amount of ion adsorbed (mg gm^{-1}); C_e is the equilibrium concentration (mg L^{-1}); K are empirical constant, indicating the adsorption capacity respectively. The plot of log q_e versus log C_e should result in a straight line. From the intercept of the plot, the values for Freundlich parameter K can be calculated. The applicability of the isotherm equations was compared by judging the coefficients of determination R^2.

3. Result and discussion

3.1 Thermogravimetric analysis

In order to predict thermal behavior of the Lapsi seed stone, the rate of weight loss of the sample as a function of temperature was studied (Figure 1).

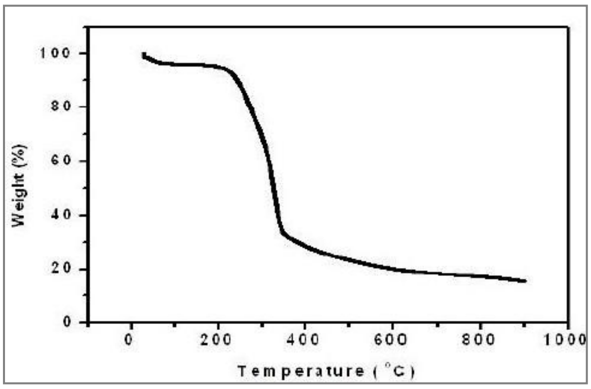

Figure 1: Thermal behavior (TGA) of the Lapsi seed stone

The TGA curve showed that the thermal decomposition of Lapsi Seed Stone starts at about 200°C and there is a continuous decrease in the sample weight from 200°C to 400°C then from 400°C the weight decreases slowly to about 600°C. No more reduction in weight is above 600°C. Generally, biomass consists of hemicellulose, cellulose, lignin, and extractives. The thermal degradation of Lapsi seed stone samples observed from 200°C to 400°C can be attributed to the decomposition of hemicelluloses, cellulose, lignin, water, carbon dioxide and wide range of organic molecules [22]. From the TGA analysis, it is confirmed that, the appropriate temperature for the carbonization of Lapsi seed stone is 400°C.

3.2 Iodine Number

pH, moisture content and Iodine number of KOH activated carbon given in **Table: 1**.The pH of activated carbon was found to be 6.7 which is acceptable for most application such as for water treatment, sugar decolonization etc. Similarly, Iodine number is a measure of the micropore content of the activated carbon (0 to 20 Å, or up to 2 nm.

Table 1: Physicochemical properties of KOH activated carbon

S.No.	**Parameter**	**Value**
1	pH	6.7
2	Moisture content	0.3%
3	Iodine Number (mg/gm)	510

Table 1 shows that the KOH activated carbon gave high Iodine number value of 510 mg/gm. The higher Iodine number of the activated carbon has been attributed to the presence of large micropore structure might have resulted due to the reactivity of the activating agent KOH. During carbonization and activation process, oxygen of the KOH could remove cross-linking and stabilizes the carbon atoms in crystallites. Potassium metal, obtained at the reaction temperature, may intercalate and force apart the separate lamellae of the crystallite. Removal of potassium salts from the internal volume of the carbon by washing creates the micro-porosity in the activated carbon [23].

3.3 Scanning electron microscopy (SEM)

Scanning electron microscopy has been extensively used to study the surface morphology of activated carbons. The SEM images of the KOH impregnated activated carbon are shown (Figure: 2).

The KOH activated carbon (Figure 2.A and Figure 2.B) clearly showed partially developed honey comb like highly defined pores and cavities in its surface. However, the pores are not-uniform. During carbonization process, pores are developed in the carbon and promote the diffusion of KOH molecules into these pores and thereby increase the KOH–carbon reactions which would then create more pores in the activated carbon [24]. This would enhance the surface area and pore volume of the activated carbon so prepared.

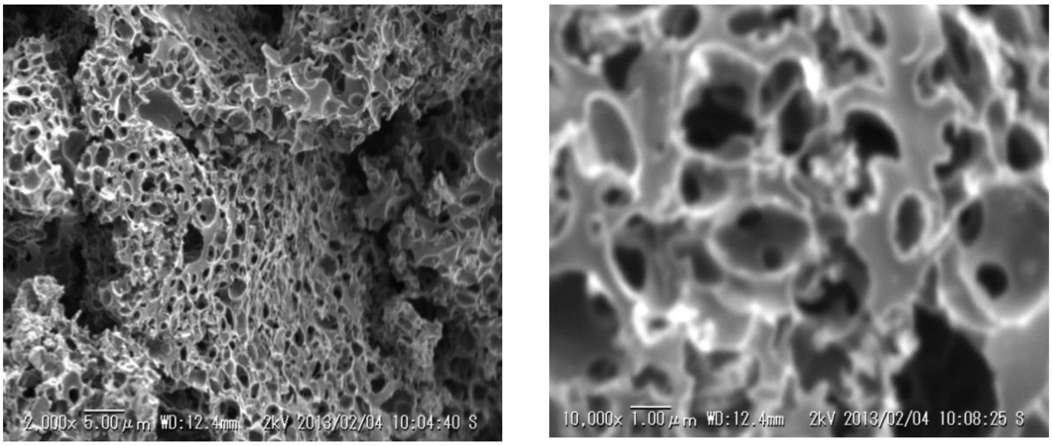

Figure 2.A: KOH activated AC

Figure 2.B: KOH activated AC (High magnification)

Figure 2: SEM Images of the KOH impregnated activated carbon

3.4 Adsorption isotherm

Langmuir isotherm and Freundlich isotherm for adsorption of methylene blue onto KOH impregnated activated carbon is shown (Figure 3). The isotherm represents the specific relation between the concentration of adsorbate and its degree to accumulation onto adsorbent surface at constant temperature [20].

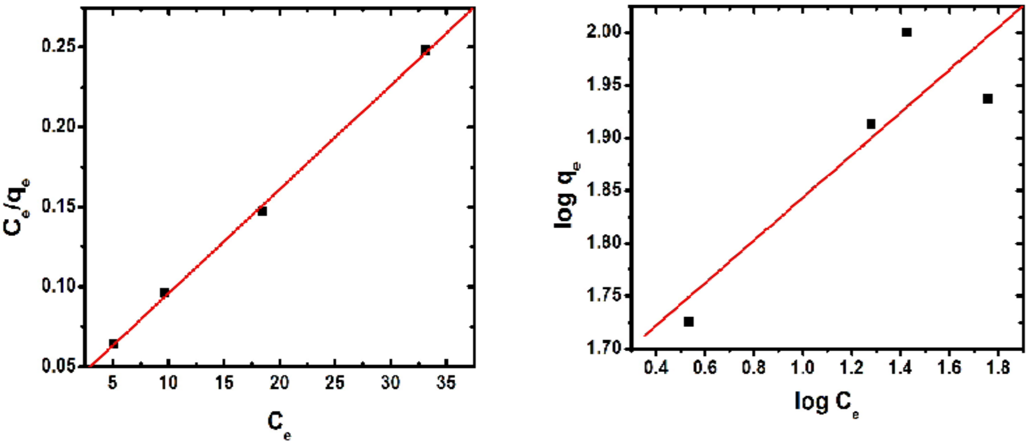

Figure 3.A: Langmuir isotherm

Figure 3.B: Freundlich isotherm

Figure 3: Adsorption Isotherm of KOH activated carbon

Table 2: Langmuir and Freundlich constants for methylene blue adsorption

KOH impregnated AC	Langmuir constants		Freundlich constants	
	q_m (mg/gm)	R^2	Log K	R^2
	154	0.998	1.712	0.969

From the table: 2, It has shown that, the values of coefficient in Langmuir isotherm ($R^2 = 0.998$) was higher than that of Freundlich isotherm ($R^2 = 0.969$) on KOH activated carbon (Figures: 3 A and 3 B) which shows that, the isotherm data better fitted in the Langmuir equation than Freundlich equation. This supports the theory that the number of active sites on the both carbon surface is limited and methylene blue forms a monolayer on the surface [25]. Langmuir constant q_m and adsorption capacity log K were determined from the slope and intercept of the plot are presented (Table: 2). KOH impregnated activated carbon gave fairly high methylene blue value (q_m) of 154 mg/gm which suggests that, KOH activated carbon have a comparatively higher mesoporosity developed as a result of the activation process and favorable to adsorb larger molecules.

3.5 Fourier Transform Infrared (FTIR) Analysis

FTIR spectra were collected for characterization of surface functional groups of prepared carbon (Figure: 4). The adsorption capacity of activated carbon depends upon porosity as well as the chemical reactivity of functional groups at the surface [26]. The presence of various functional groups on the carbon surface contributes to preferential uptake for different molecule species by carbon [20].

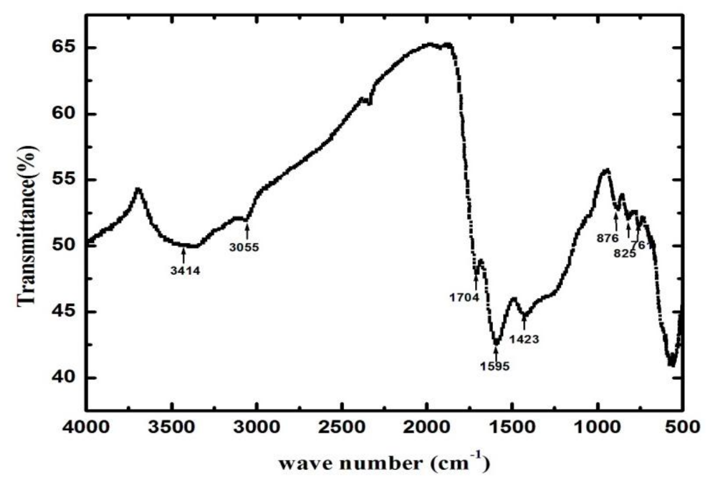

Figure 4: FTIR of KOH activated carbon

FT-IR spectra of the KOH impregnated activated carbon showed three major absorption bands at 1423 cm^{-1}, 1595 cm^{-1}, 1704 cm^{-1}(Figure: 4).The broad adsorption peak at 3414 cm−1 may be assigned to the O–H stretching vibration due to intermolecular hydrogen bonding of polymeric compounds like alcohols, phenols, and carboxylic acids indicating the presence of free hydroxyl groups on the carbon surface [26]. Additionally, the bands in the region of 3055 cm^{-1} are assigned to symmetric aliphatic asymmetric and symmetric C-H bending vibration of $-CH_2$ and $-CH_3$ group [27]. Similarly, the peak at 1704 cm^{-1} corresponds to carbonyl C=O stretching vibration in aldehydes, ester or ketones and carboxyl group [28]. Furthermore, absorption peak in the region of about 1595 cm^{-1} is due to C=C stretching vibrations in the aromatic ring generally found in carbonaceous material, such as activated carbon [29]. The strong bands at 1423 cm^{-1} represent the bending vibrations of C-H group present in alkyl groups such as $-CH_3$ indicative of lignin [30].The bands at 876 - 761 cm^{-1} are assigned to out-of-plane bending vibrations of C-H group in the aromatic rings [31]. However, weak peak appeared slightly above 3000 cm^{-1} in activated carbon demonstrates unsaturation indicating alkenyl C= C stretch [16]. These peaks disappeared in the spectra of activated carbon, indicating the successful removal of hemicelluloses with activation KOH. The FTIR spectra indicate the presence oxygen containing surface functional groups such as hydroxyl groups, carboxyl groups, carbonyl groups in the activated carbon sample.

4. Conclusion

Activated carbon was prepared from Lapsi seed stone by chemical activation with potassium hydroxide (KOH) in ratio of 1:1 by weight at 400°C for 3 hours. The prepared activated carbon was characterized by determining different parameters such as Iodine number, methylene blue number, SEM image, FTIR spectroscopy. FTIR results indicate that KOH activated carbon prepared contains –OH, >C= O, COOH, and lactones as oxygen containing surface functional groups. From SEM micrograph, potassium hydroxide impregnated activated carbon showed well developed pores in its surface. The experimental data of methylene blue adsorption follows Langmuir model with adsorption capacity 154 mg/gm. Lower adsorption capacity for methylene blue compared to iodine (510 mg/gm) indicates microporous structure of the activated carbon. It is concluded that, activated carbon from Lapsi seed stone activated with potassium hydroxide can also be applied as a low cost, possible alternate adsorbent.

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