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Research Article

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Papaya leaf carbon: Its characterization and capacity as an adsorbent towards H⁺

Chaithra P. and J. Ishwara Bhat^{*}

Department of Chemistry, Mangalore University, Mangalagangothri-574199, Karnataka, India

ABSTRACT

Activated carbon (AC) was prepared from papaya leaf petiole (PLP) using physical (PLPC), chemical (ZnCl₂, ZPLPC) and microwave (MWPLPC) activation methods. The synthesized AC's were characterized by powder X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM), Fourier transform infrared spectroscopic technique (FT-IR), thermogravimetric analysis & differential thermal analysis (TGA-DTA). XRD pattern of PLPC, Z PLPC & MW PLPC shows both crystalline and amorphous peaks. Dissimilar size of pores and other adsorption sites were observed in FE-SEM image of the three AC. The surface functional groups were detected using FT-IR spectrometer. TGA- DTA instrument was used to analysis of thermal decomposition of PLP, PLPC, Z PLPC & MW PLPC. Adsorption of acetic acid (AA) on synthesized three AC were studied. Langmuir adsorption isotherm holds good for the present adsorption process. The mechanism of adsorption followed the second order kinetics. Thermodynamic parameters like change in enthalpy, entropy and free energy were calculated.

Keywords: Activated carbon, papaya, adsorbent

INTRODUCTION

Activated carbon (AC) is most familiar adsorbent used for removal of organic chemicals and metal ions from air, gases, portable water and waste water thereby it purifying the environment [1]. The presence of surface pores, functional groups, high surface area and amorphous nature may be reason for the high adsorption potential of AC [2-4]. Acetic acid is most widely used chemical in industries producing acrylic acid, cellulose acetate, terephthalic acid, poly(vinyl alcohol), acetaldehyde[5], high grade phosphate fertilizer, baking powder etc. [6]. The increased demand of acetic acid, results in discharge of waste water containing different concentration of it. Several methods are used to separate acetic acid from aqueous solution that is reactive extraction [7], membrane filtration [8] and bipolar membrane electrodialysis (BMED) [9]. Among these the adsorption onto activated carbon is most widely adapted and efficient method for the removal of acetic acid from aqueous solution. The increasing demand of activated carbon results in search of new raw materials and methods for the production of it. Researchers have reported activated carbons prepared from low cost agricultural wastes products like coconut shell [10], banana peel [11], cashew nut shell [12], rice husk [13], sugarcane bagasse and corn husk [14].

The present research work involves synthesis of activated carbon from papaya leaf petioles employing physical, chemical (ZnCl₂) and microwave activation methods. The synthesized activated carbons were characterized using powder XRD, FE-SEM, FT-IR and TGA-DTA instruments. The acetic acid adsorption capacities of PLPC, Z PLPC & MW PLPC were compared at various experimental conditions. The equilibrium adsorption data were fitted with Freundlich and Langmuir adsorption isotherm. The kinetics and thermodynamics of adsorption were studied.

EXPERIMENTAL SECTION

Extraction of Adsorbent Material: The papaya leaf petiole was collected from agricultural field. It was washed with distilled water and dried in hot air oven at 150 °C. Weighed 20g of dried small pieces of uniform sized papaya

leaf petioles to a petridish. It was heated in hot air oven at 250°C for 8 hr. to become char and then physical activation was done by heating in muffle furnace at 300 °C for 2 hr. The chemical activation involves soaking of hot air oven dried PLP (20g) in 200ml of 1M zinc chloride solution [15] (ZnCl₂) and the char was heated in muffle furnace at 300 °C for 2 hr. 20g of hot air oven dried PLP was grinded in electric mixer grinder to get homogeneous powder and it was activated in domestic microwave oven of the radiation 80W for a period of 280 minutes. The obtained AC was sieved to uniform size (250 μ m) for the adsorption studies.

Selection of Adsorbate: The adsorbate used in the present work is acetic acid glacial 99-100% (AR) (Merk specialities Pvt. Ltd., Mumbai, India). Physical and chemical properties of acetic acid is shown in Table 1.

IUPAC Name	Acetic acid
Systematic IUPAC Name	Ethanoic acid
Chemical formula	$C_2H_4O_2$
Molar mass	60.05g mol ⁻¹
Solubility in water	Miscible
Acidity (pK_a)	4.76
Basicity (pK_b)	9.24

Table 1. Physical and chemical properties of acetic acid

Characterization of Activated Carbon Materials: Characterization was done by XRD, FE-SEM, FT-IR & TGA-DTA techniques.

Powder XRD Analysis: The characterization of the synthesized activated charcoal (PLPC, Z PLPC and MW PLPC) was done by powder x-ray diffractometer (Rigaku Miniflex 600 diffractometer) using Cu-K α (λ =1.5418 Å) operating voltage=40 KV and a current of 15 mA. The diffraction angle range was 2θ =10° to 70°.

FE-SEM Analysis: The surface morphology of activated carbons before and after adsorption was scanned using Carl Zeiss field emission scanning electron microscope. The SEM magnification was 2.50 KX and EHT=5.00kV. **FT-IR Analysis:** Fourier transform infrared spectrophotometer (Shimadzu FT-IR Prestige-21, ATR method) was used to record the surface functional groups present in the raw and synthesized activated carbons. The FT-IR spectra were recorded with wave number range of 4000-500cm⁻¹.

TGA-DTA Analysis: Thermal decomposition of all the three activated carbon was carried out by thermogravimetric analysis (TA) and derivative thermogravimetric analysis (DTA) using a TA-STD Q600 instrument under dry nitrogen atmosphere at the flow rate of 100 mL/min. The samples were heated from 50 $^{\circ}$ C to 700 $^{\circ}$ C at predetermined rate of 20 $^{\circ}$ C/min.

Adsorption Studies: About 0.25g of PLPC, Z PLPC & MW PLPC (adsorbents) were taken in three different reagent bottle. A 50 ml of 0.05M acetic acid (adsorbate) was added to each reagent bottles containing adsorbent. Solutions in these bottles were stirred using magnetic stirrer for about half an hour and filtered. Concentration of acid adsorbed was determined by titrating the filtrate against 0.05N sodium hydroxide (NaOH) solution. The amount of acetic acid adsorbed (q_e) was calculated using following equation [16],

$$q_e = \frac{\left(C_o - C_e\right)}{W} V (1)$$

Where C_0 is the initial concentration of acetic acid (M); C_e is the concentration of AA in the solution after adsorption (M); *V* is the volume of the solution (ml); and *W* is the weight of AC (g).

RESULTS AND DISCUSSION

Powder XRD Analysis

The X-ray diffraction pattern obtained for PLPC, Z PLPC & MW PLPC are shown in Figure 1. From the XRD pattern it is clear that the synthesized activated carbon exhibits both crystalline and amorphous nature on its surface. But the chemical activated charcoal (Z PLPC) showed less peaks than the other two physical and microwave activated charcoal. The diffraction angle θ (degree), Intensity (obtained directly from the XRD) and Lattice spacing d (A⁰), N, reflection plane (hkl) values estimated for crystalline as well as amorphous peaks are presented in Table 2. The d values is in the range of the wavelength of X-ray used. The maximum intensity range varies in the order PLPC > MW PLPC > Z PLPC indicating the high crystallinity nature in case of PLPC than the other two carbon.





Table 2. The diffraction angle θ (degree), Intensity, Lattice spacing d (A⁰), N, and reflection plane (*hkl*) values are calculated for the peaks of PLPC, Z PLPC & MW PLPC

Adsorbent	20(degree)	Intensity	d (A ⁰)	N	hkl
	14.74	361	6.00	1	(100)
	19.39	264	4.57	2	(110)
DI DC	24.28	526	3.66	3	(111)
rLrC	26.58	274	3.35	3	(111)
	28.26	787	3.15	4	(200)
	29.92	339	2.98	4	(200)
	17.06	330	5.19	1	(100)
	18.6	520	4.77	1	(100)
	20.56	387	4.31	1	(100)
	23.88	451	3.72	2	(110)
Z PLPC	24.82	510	3.58	2	(110)
	30.1	406	2.96	4	(200)
	33.46	290	2.67	4	(200)
	35.12	276	2.55	4	(200)
	37.48	233	2.39	4	(200)
	14.94	471	5.92	1	(100)
	18.17	304	4.88	1	(100)
	19.99	326	4.44	1	(100)
MWDI DC	24.44	634	3.64	3	(111)
WIWFLFC	25.98	313	3.42	2	(110)
	28.4	818	3.14	4	(200)
	30.1	424	2.96	4	(200)
	38.32	314	2.96	6	(211)

The crystallite size of AC's were calculated from Scherer's formula [17]. Smaller crystallites are expected to have more active centers leading to higher adsorption. This value varies in the order Z PLPC > MW PLPC > PLPC.

Structural deformation was evaluated using calculated values of defect density and lattice strain [18]. Crystallinity index (*CrI*) of all the three different carbons were calculated [19] and shown in Table 3. The cell volume was found to be the least in MW PLPC among the three activated carbons. The Crystallinity index varies in the order PLPC > MW PLPC > Z PLPC. The defect density and lattice strain varies in the order PLPC > Z PLPC. Crystallite size, defect density and lattice strain values says that physical and microwave activated carbon having more capacity towards adsorption than chemical activated carbon.

Table 3. Cell volume (v), Crystallite size (D), defect density (δ), lattice strain (η) and crystallinity index (*CrI*) values are shown

Adsorbents	$\nu(\mathbf{A}^0)^3$	$D(\mathbf{A}^0)$	δ (A ⁰) ⁻²	η	CrI
PLPC	233.15	0.0538	345.48	26.40	66.48
Z PLPC	125.30	0.0916	119.18	23.38	36.45
MW PLPC	110.77	0.0694	207.62	23.59	60.15

FE-SEM Analysis: The FE-SEM image of synthesized activated carbons and acid adsorbed activated carbons were obtained and are shown in Figure 2a-2f. The FE-SEM image of PLPC,

Z PLPC & MW PLPC are shown in Figure 2a, 2b & 2c. The surface of activated carbons are not very smooth or flat. Probably the roughness is due to the presence of pores, steps, edges and kinks on the surface of synthesized AC. Which leads to the defect density. These defect enhances the adsorption capacity of activated charcoal. The FE-SEM image of acid adsorbed PLPC, Z PLPC & MW PLPC are shown in Figure 2d, 2e & 2f. The morphology of surface of AC is found to be changed drastically after adsorption. Comparison of Figure 2a & 2d indicates that most of the pores have been occupied due to adsorption and which is much more appeared in the case of MW PLPC than other two carbons.



Fig. 2. 2a. SEM image of PLPC, 2b. SEM image Z PLPC, 2c. SEM image of MW PLPC, 2d. SEM image of acid adsorbed PLPC, 2e. SEM image of acid adsorbed Z PLPC, 2f. SEM image of acid adsorbed MW PLPC

FT-IR Analysis

The FT-IR spectra of PLP, PLPC, Z PLPC & MW PLPC are shown in Figure 3. The important observation that can be made from the FT-IR spectra of raw and activated carbons is the change in number of peaks in case of raw

sample the IR peaks are too many and are much more than in activated carbon samples. The FT-IR spectra of papaya leaf petiole shows a broad O-H peak at 3277cm⁻¹ due to the associated water molecule. C-H stretching vibrations at 2929cm⁻¹. These two peaks were not observed in the case of synthesized activated carbons. This indicates the structural changes in AC due to the activation of raw sample. It indicates the loss of functional groups of the raw material during the activation process. The carbonyl (C=O) stretching was observed in PLP (1600cm⁻¹), PLPC (1606cm⁻¹& 1573cm⁻¹), Z PLPC (1560cm⁻¹) and MW PLPC (1697 & 1606 cm⁻¹). The carbonyl functional groups found more in microwave activated carbon than physical or chemical activated carbon. Ether C-O-C stretching was observed at the range from 1035cm⁻¹ to 1031cm⁻¹ for all carbons. The stretching frequency corresponds to 1417, 1384, 1363 & 1382 cm⁻¹ is due to C-N vibration in PLP, PLPC, Z PLPC & MW PLPC respectively. The IR peaks at 1000-750cm⁻¹ corresponds to C-H out of plane bending in all the raw and AC samples. The presence of hetero atoms like O and N helps in the adsorption process and roughness on the surface. Hence activated carbon appeared to be rough as indicated by XRD pattern or SEM image. Three important IR peaks appeared for PLP is lost when AC is formed indicating the decomposition of certain (O-H, C-H & C-O) functional groups due to activation process.



Fig. 3. FT-IR Spectra of a.PLP, b. PLPC, c. Z PLPC & d. MW PLPC

TGA-DTA Analysis: Stability of raw and activated carbon were studied by TGA-DTA analysis. The TGA-DTA pattern of PLP, PLPC, Z PLPC & MW PLPC were shown in Figure 4a, 4b, 4c & 4d.

The thermogravietric plot (weight (%) Vs temperature (°C)) of PLP, PLPC, ZPLPC & MWPLPC shows three distinct decomposition steps. The loosely bound water molecule on the surface gets lost at first stage100°C - 200°C). As the present activated charcoal is of plant origin there it is expected to contain hemicellulose, cellulose and lignin. There is a sharp decomposition probably due to the decomposition of hemicelluloses, cellulose and also some water molecules at higher temperature (step2- 200 to 400 °C) and the decomposition of carbonyl groups present in lignin at step3 (400 to 500 °C). Differential thermogram was obtained by plotting the difference in temperature between sample and inert reference against overall furnace temperature. From DTA plot it was clear that decomposition temperature of raw and activated carbons varies in the order of Z PLPC (586°C) > PLP (486°C) PLPC (454°C) > MW PLPC (452°C). The nature of TGA plot appeared to be almost the same in the case of three activated carbon but they are distinctly different from that of raw sample indicating the structural change between them and which supports our thinking of change in structure of carbon on the basis of XRD.



Fig. 4. 4a. TGA-DTA Pattern of PLP, 4b. TGA-DTA Pattern of PLPC, 4c. TGA-DTA Pattern of Z PLPC, 4d. TGA-DTA Pattern of MW PLPC

Adsorption Studies

Adsorption isotherm: Adsorption experiment was carried out using different concentrations of acid (0.02, 0.03, 0.04, 0.05 & 0.06M) at a given constant temperature. The adsorption data were analysed using Freundlich adsorption isotherm [20] and also Langmuir adsorption isotherm [21] as follows:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \tag{2}$$

Where k_f and *n* are the Freundlich adsorption isotherm constants related to adsorption capacity and adsorption intensity respectively, which are helpful in finding the feasibility of adsorption process and there by comparing the adsorption efficiency of the adsorbent. A plot of log q_e versus log C_e was drawn and is shown in Figure 5a. Plot appeared to be linear and the slope and the intercept of the linear plot gives *n* and k_f values respectively and are shown in Table 4.

Langmuir adsorption isotherm equation can be represented as follows,

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b}$$
(3)

Where C_e is concentration of acid adsorbed at equilibrium, q_e is the amount of acid adsorbed at equilibrium, q_m and b are Langmuir constants which indicates the monolayer adsorption capacity and the adsorption intensity of adsorbent. Linear plot observed for the plot of $C_{e'}q_e$ versus C_e is sown in Figure 5b. From the slope and intercept of this linear plot, value of q_m and b can be calculated. Equilibrium parameter R_L value was calculated, which is an indication of the favorability of adsorption process [22] and shown in Table 4.



Fig. 5. 5a. Freundlich adsorption isotherm plot, 5b. Langmuir adsorption isotherm plot of adsorption of AA on (•) PLPC, (●) Z PLPC & (▲) MW PLPC

Table 4. Freundlich and Langmuir constants for adsorption of acid on PLPC, Z PLPC & MW PLPC

Adsorbents	n	k_f	\mathbf{R}^2	b	R_L	R^2
PLPC	4.739	69.82	0.880	184	0.133	0.976
Z PLPC	1.636	12.35	0.998	23.23	0.533	0.980
MW PLPC	3.568	63.97	0.946	111.5	0.200	0.985

The correlation coefficient value (R^2) was found to be higher, nearing unity for Langmuir adsorption isotherm which is slightly higher than the value observed for Freundlich adsorption isotherm indicating that the Langmuir adsorption isotherm is more suits for the present adsorption system. The Langmuir equilibrium parameter R_L value is within the favorability range for adsorption. Higher adsorption is found in the case of MW PLPC which is little contrasting to the observation made under XRD.

Kinetics and Mechanism of Adsorption: The kinetics of adsorption is the mirror of the mechanism of adsorption process. In the present work adsorption of AA onto AC was studied at different time interval (15, 30, 45, 60 & 75min.). The amount of AA adsorbed was found to increases with the increase in agitation time. The first order and second order rate expression [23] were used to study the kinetics of adsorption as follow:

$$\log(q_{e} - q_{t}) = \log q_{e} - \frac{k_{1}t}{2.303}$$
(4)

Where $q_e \& q_t$ are the amount of acetic acid adsorbed at equilibrium and at time *t* respectively, k_I is the first order rate constant. A plot of $log (q_e - q_t)$ versus *t* was drawn and was found to be non linear. Clearly indicating the non applicability of first order for the present system under the existing condition. The second order rate expression was as shown in eq. 5:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$
(5)

 k_2 is the second-order rate constant rate and was calculated from the slope of linear plot obtained for t/q_t versus t as shown in Figure 6.



Fig.6. Second order kinetic plot for the acid adsorption on PLPC, Z PLPC & MW PLPC

Table 5. Second-order kinetic parameters of the adsorption of AA onto PLPC, Z PLPC & MW PLPC

Adsorbent	$k_2(\text{mol}\cdot\text{g}\cdot\text{min}^{-1})$	$q_e(\text{mol}\cdot\text{g}^{-1})$	R^2
PLPC	0.219	0.116	0.940
Z PLPC	0.109	0.120	0.960
MW PLPC	0.361	0.133	0.981

From the Table 5 it is clear that the second order rate constant for the adsorption of AA onto AC varies in the order MW PLPC > PLPC > Z PLPC. Acetic acid in water dissociates to give RCOO⁺& H⁺. This results in attractive electrostatic interaction between H⁺ ion of acid and the lone pair electrons of O or N present on AC surface. Therefore, rate varies with the surface amount of carbon and also the effectiveness of hydrogen ion. Hence the adsorption of AA onto PLPC, Z PLPC & MW PLPC followed the second order kinetics.

Thermodynamics of Adsorption: Thermodynamics of adsorption were studied at temperature 288K, 303K, 318K & 333K. Thermodynamic parameters like energy of activation (E_a), change in enthalpy (ΔH^{\ddagger}), entropy (ΔS^{\ddagger}) and free energy (ΔG^{\ddagger}) were determined using the following equations [24],

$$\log k = \log A - \frac{E_a}{2.303RT} \tag{6}$$

Where k is concentration of acid after adsorption E_a is the activation energy, A is the Arrhenius parameter, R is gas constant and T is temperature (K). The value of E_a was calculated from the slope of plot of log k versus 1/T (linear) (Figure 7a). The change in enthalpy, entropy and free energy were calculated using absolute theory of rate expression as follows

$$\log\left(\frac{k}{T}\right) = \log\left(\frac{k_B}{h}\right) + \frac{\Delta S^{\ddagger}}{2.303R} - \frac{\Delta H^{\ddagger}}{2.303RT}$$
(7)

Where k_B is the Boltzmann constant, h is plank's constant. The change in enthalpy (ΔH^{\ddagger}) and change in entropy (ΔS^{\ddagger}) was calculated from the slope and intercepts of linear plot of log (k/T) versus *1/T* as shown in Figure 7b. Change in free energy (ΔG^{\ddagger}) can be calculated using following equation,

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T \Delta S^{\ddagger} \tag{8}$$

From the value of (ΔG^{\ddagger}) adsorption constant K_{ads} can be calculated from the eq 9.

$$\Delta G^{\ddagger} = -RT \ln K_{ads} \tag{9}$$



Fig.7.7a. Plot of 2+log k Vs 1/T, 7b. Plot of 5+ log (k/T) Vs 1/T

Table 6. Thermodynamic parameters for the adsorption of AA on Activated Carbon

Adsorbent	$\frac{E_a}{(\mathbf{k}\cdot\mathbf{J}\cdot\mathbf{mol}^{-1})}$	$\frac{\Delta \mathbf{H}^{\sharp}}{(\mathbf{k}\cdot\mathbf{J}\cdot\mathbf{mol}^{\cdot1})}$	$\frac{\Delta S^{\sharp}}{(\mathbf{J} \cdot \mathbf{mol}^{-1} \cdot \mathbf{K}^{-1})}$	$\frac{\Delta G^{\sharp}}{(\mathbf{k} \cdot \mathbf{J} \cdot \mathbf{mol}^{-1})}$	<i>K_{ads}</i> (k •J•mol ⁻¹)
PLPC	-1.010	-3.582	-186.8	54.419	0.978
Z PLPC	-0.965	-3.536	-186.3	54.309	0.978
MW PLPC	-1.394	-3.965	-188.5	54.563	0.978

The Table 6 shows the negative values for activation energy (E_a) for all the three activated carbons. This indicates that no energy is required for the process of activation or it is instantaneous. Both change in enthalpy of adsorption (

 ΔH^{\dagger}) and change in entropy (ΔS^{\dagger}) of adsorption appeared to be negative for all the system of carbon under the existing condition. Hence the adsorption process appeared to be exothermic in nature. The change in free energy ΔG^{\dagger} was found to be positive. Value of K_{ads} is almost equal to unity which might indicates the equilibrium between the surface and the H⁺ adsorption reaction. Adsorption has occurred to a monomolecular on the surface of activated carbon.

CONCLUSION

In the present work activated carbons were synthesized from papaya leaf petiole from physical, chemical (ZnCl₂) and microwave activation methods. The AC's were characterized using powder XRD, FE-SEM, FT-IR and TGA-DTA instruments. The adsorption of acetic acid onto activated carbons were studied and compared. The Langmuir adsorption isotherm is best fit for the adsorption process. The adsorption mechanism followed the second order kinetics. Evaluation of thermodynamic parameter (ΔH^{\ddagger} , $\Delta S^{\ddagger} \& \Delta G^{\ddagger}$) results the exothermic nature of adsorption. The microwave activated carbon has maximum adsorption capacity compared with PLPC or Z PLPC.

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