

Physico-Chemical and Adsorption Studies of Activated Carbon from Henna Leaves and Pungam Bark

Shanthi T^{1*} and Ameeth Basha I²

¹Department of Chemistry, V. M. K. V. Engineering College, Salem, Tamil Nadu, India

²Department of Chemistry, Chemistry, Aarupadai Veedu Institute of Technology, Vinayaka Missions University, Paiyanoor, Karunguzhipallam, Tamil Nadu, India

*Corresponding author: Shanthi T, Department of V. M. K. V. Engineering College, Salem, Tamil Nadu, India, Tel: 04273206009; E-mail: shanthi.thiruvengadam130@gmail.com

Received: July 24, 2017; Accepted: October 05, 2017; Published: October 07, 2017

Abstract

An effective usage of the adsorbent necessitates a deeper understanding of the adsorption characteristics. The present study examined the use of modified activated carbon derived from the widely available plant source of Henna leaves and Pungam tree bark. A series of activated carbon samples were prepared by subjecting the materials to chemical process. The physico-chemical properties and sorption abilities were compared. Adsorption of heavy metals of various concentrations was studied with synthesized activated carbon samples from batch adsorption studies. These materials accrue superior properties and good adsorption behaviors. The adsorption capacities of two of the selected derived carbon samples were much better than the capacities of the other carbon. The results reveal that the synthesized activated carbon could be employed as a low-cost alternative for the removal of heavy metal from waste water and industrial effluents.

Keywords: Activated carbon; Adsorption studies; Heavy metals; Physico-chemical properties; Industrial effluents

Introduction

The industrialization of the world has increased the load of toxic heavy metals in the globe. Day by day, due to industrial revolution and improper treatment of effluents, the pollutant level increases in the earth and in turn it increases the heavy metal wastage. Toxic metals are harmful to living organisms even in small quantities. There are over 20 different toxic heavy metals like arsenic, barium, cadmium, chromium, copper, lead, mercury, nickel which can impair human health and each toxin could produce different behavioral, physiological and cognitive changes to an exposed individual. Hence, the presence of heavy metals beyond the permissible level may cause poisoning, dysfunction of human organs like liver, kidney, reproductive system, central nervous system etc. These metals are concentrated by the food chain, thereby posing the greatest

hazard to organisms [1]. Thus, a greater effort needs to be put in for minimizing these hazardous pollutants to avoid their dangerous effects on the biome. One of the cheapest and effective efforts is adsorption by activated carbon of agricultural wastes and powerful technique for treating domestic and industrial effluents. Activated carbons are used in various forms: powdered activated carbon (PAC), granular activated carbon (GAC) and fibrous activated carbon (FAC). The granulated activated carbon (GAC) has granules of 0.6 mm to 4 mm in size and is hard, abrasion resistance and relatively dense to withstand operating conditions. The most important application of activated carbon is the purification of air and water. The adsorption capacity of an activated carbon for metal ions from the aqueous solutions generally depends on the physicochemical characteristics of the carbon surface, which include surface area, pore size distribution, electro-kinetic properties, the chemistry of the carbon surface and nature of metal ions in the solutions.

Materials and Methods

Henna leaves are opposite, entire, glabrous, sub-sessile, elliptical, and broadly lanceolate (1.5–5.0 cm × 0.5–2 cm), acuminate, having depressed veins on the dorsal surface. The principal colouring matter of henna is lawsone, 2-hydroxy-1:4 naphthaquinone (C₁₀H₆O₃, m.p.190°C decomp.) besides lawsone other constituents present are gallic acid, glucose, mannitol, fats, resin (2%), mucilage and traces of an alkaloid [2]. Seeds contain proteins (5.0%), carbohydrates (33.62%), fibers (33.5%), fatty oils (10%-11%) composed of behenic acid, arachidic acid, stearic acid, palmitic acid, oleic acid and linoleic acid. Pongamia belongs to family Leguminosae and the seeds contain 27% bitter, dark colored, non-volatile oil which contains glabrin, four furano flavones viz. karanjin, pongapin, karanjone and pongaglabrone. It contains diketonepongamol and also fatty acids. These two cheap and easily available agricultural materials were taken for the present study [3].

Carbonization procedures

Acid processes: 500 g of washed and sun-dried plant material (Henna leaves and Pongamia bark) was mixed with 500 ml of concentrated sulphuric acid in the ratio of 1:1 (w/v). The mixing was done with vigorous stirring so that the mixture becomes homogeneous. Charring of the leaves occurs immediately accompanied by evolution of fumes. When the reaction subsided, the mixture was left in hot air oven at 140°C-160°C for a period of 24 h. The product was then washed with approximately 4 L to 4.5 L of distilled water to remove free sulphuric acid and again dried at 110°C. removes the free acid residues. They were dried at 110°C, sieved and finally activated at 800°C [4].

Results and Discussion

Physico-chemical characteristics

Sulphuric acid pre-treatment involves mixing the leaves and bark with concentrated sulphuric acid 1:1 weight ratio followed by washing with distilled water and subsequent drying at 110°C [5,6]. Sulphuric acid treatment introduces new functional groups such as -SO₃ and H₂SO₄. Activation of leaves and bark with sulphuric acid generate more interfaces between carbon layers leading to more micro porosity and more surface area due to its swelling action on the molecular structure of cellulose.

Iron content

The iron content in the sample was determined by the 1, 10 phenanthroline method (ISI 877: 1977). The absorbance at 525 nm was measured against the blank using UV-Visible spectrophotometer [7,8]. The determined values of iron content for

HLC and PBC are shown in TABLE 1. Bark is having more iron content than henna leaves, which may be due to the plant origin.

Moisture content

The moisture content of these carbons is comparatively lesser which facilitates better adsorption properties as higher moisture content reduces the adsorption capacity of carbon due to the fact that water molecules occupy adsorption sites and thus reducing the sites available for metal ions. The values are given in the TABLE 1.

Volatile matter

1 g of test sample dried at $105 \pm 10^\circ\text{C}$ was weighed in a preheated silica crucible. The crucible was kept in the muffle furnace maintained at the temperature of $925 \pm 10^\circ\text{C}$ and was taken out exactly after 7 min. It was then cooled rapidly in a desiccator and weighed (BIS 1350:1969).

$$\text{VM (\%)} = (M_2 - M_3) \times 100/M_1$$

Where, M_1 is the mass of the sample, M_2 is the mass of the crucible with sample and M_3 is the mass of crucible and sample after heating. The percent matter soluble in water are in the order $\text{HLC} > \text{PBC}$. This shows that they have low water-soluble matter because during treatment with sulphuric acid, most of the water soluble matter has already been leached. The values are given in the TABLE 1.

pH

10 g of the dried sample was weighed and transferred into a one-litre beaker. 300 ml of freshly boiled and cooled water (adjusted to pH 7.0) was added and heated to boiling [9]. After digesting for 10 min, the solution was filtered while hot, rejecting the first 20 ml of the filtrate. The remaining filtrate was cooled to room temperature and the pH was determined using a pH meter. The pH value of an activated carbon indicates whether a carbon is acidic or basic. The prepared carbons are acidic due to pre-treatment with sulphuric acid. Because of the acidic nature of these carbons, both were found to have higher ion exchange capabilities. This shows that, activation with sulphuric acid in the case of these carbons introduces ion exchange surface functional groups on the carbon. The values are given in the TABLE 1.

Ash content

2 g of sample under examination was weighed accurately into a silica crucible. The crucible and its contents were placed in an electric oven at $110 \pm 5^\circ\text{C}$ for about 4 h [10]. The crucible was removed from the oven and the contents were ignited in an electric muffle furnace at a temperature of 1000°C for about 3 h. The process of heating and cooling was repeated until the difference between two consecutive weighing was less than 1 mg (the ash was preserved for the determination of iron) (ISI 877: 1977). The determined values of ash content for HLC and PBC are shown in TABLE 1.

$$\begin{aligned} \text{Ash} &= M_1 \times 100 / (M \times (100 - X) / 100) \\ &= 10,000 \times M_1 / M \times (100 - X) \end{aligned}$$

where M_1 is the mass of ash in grams, M is the mass of the sample taken for the test in grams and X is the percentage of moisture content present in the sample taken for the test. The result is given in TABLE 1.

Matter soluble in water

10 g of the sample of unknown moisture content was weighed accurately and transfer into a one-liter beaker. About 300 ml of distilled water was added and heated to boiling with continuous stirring [11]. Stirring was continued for 5 min after the flame was removed. The material was then allowed to settle and the supernatant liquid was filtered through a Gooch crucible fitted with an asbestos mat. The procedure was repeated thrice with the residue in the beaker using 300 ml of water each time. The combined filtrate was concentrated to less than 100 ml over a water bath, cooled and made up to 100 ml mark in a volumetric flask. Exactly 50 ml of the concentrate was transferred to a china dish and evaporated to almost dryness on a boiling water bath and dried in an electric oven, maintained at $110^\circ\text{C} \pm 5^\circ\text{C}$, cooled in a dessicator and weighed. The procedure of drying and weighing was repeated at 30 min intervals until the difference between two consecutive weighing was less than 5 mg. The determined values of matter soluble in water for HLC and PBC are shown in TABLE 1.

$$\text{Matter soluble in water (\%)} = M \times 20000 / (100 - X) \times M_1$$

where, M = mass of the residue in grams

M_1 = mass of the sample in grams

X = percent of moisture present in sample.

Fixed carbon

The fixed carbon content of a coal is determined by subtracting the percentage of moisture, volatile matter and ash from a sample.

$$\text{Fixed carbon} = 100 - (\text{moisture} + \text{volatile matter} + \text{ash})$$

TABLE 1. Physical properties of adsorbents.

Properties	HLC	PBC
Surface area	37.3 m ² /g	20.93 m ² /g
Pore volume	0.01 cc/g	0.08 cc/g
Pore radius	36.739 A	47.822 A
Pore size	42.5001 A	94.4329 A
Ash content	14.10%	9.34%
Moisture	4.21%	2.30%
Volatile matter	18.91%	37.85%
Fixed carbon	64.46%	54.45%
Matter soluble in water	5.10%	4.10%
Iron content	4.07×10^{-3} mg/g	0.018 mg/g
pH	4.5	4.7

Brunauer-Emmet-Teller (BET) sorptometry

The specific surface area of the powder was analyzed by nitrogen adsorption at 77 K applying BET method in Quantasorb (Quanta Chrom-USA). Degassing at 100°C and 2 mm Hg to 10 mm Hg for 2 h was performed prior to measurement. The specific surface area of henna leaves carbon and pongamia bark carbon are given in TABLE 1. The specific surface area values were derived from the isotherm using BET method in the relative pressure range, P/P_0 (P is the adsorption pressure and P_0 is the saturation vapour pressure) where the monolayer coverage is assumed to be complete. The total pore volume was calculated from the amount adsorbed (liquid volume of nitrogen) at a relative pressure of 0.99 [12]. The surface area of Bark and leaves are much lesser, it is compensated by their higher average pore sizes in the removal of heavy metal. Furthermore, the higher ion exchange capacity of carbons favours the adsorption process. The BET constant value and monolayer absorbed gas quantity are given in TABLE 2.

TABLE 2. Monolayer adsorbed gas quantity and BET constant.

S. No.	Adsorbent	Monolayer adsorbed gas quantity (vm)	BET constant (c)
1	Henna leaves carbon	0.07385	173.5973
2	Pongamia bark carbon	0.04903	115.2634

X-ray diffraction (XRD) analysis

X-ray diffraction (XRD) analysis was carried out using Cu $K\alpha$ radiation on a computer controlled Philips make 1050 diffractometer. The scan speed was $0.5^\circ 2\theta$ per minute and step size was $0.02^\circ 2\theta$. XRD Patterns were recorded from 5 to $80^\circ 2\theta$. The XRD patterns for henna leaves carbon, pongamia bark carbon and commercial activated carbon are shown in FIG. 1 and 2. The interlayer spacing is calculated from the Bragg equation as shown below:

$$2d \sin \theta = n\lambda$$

where λ is the wave length of the radiation used and θ is the diffraction angle.

The XRD spectrum of the activated carbon of the bark confirms the presence of carbon, iron and alumina-silicate minerals. The peaks indicated the presence of pearlite, chrophyllite, Kurumsakite, shirokshinite, Babefphite, Ferdasilicate, Glagolevite and Khamrabaevite [13]. The XRD spectrum of the activated carbon of the leaves confirmed the presence of carbon and iron. A peak in this carbon showed the presence of Khamrabaevite. Two activated carbons are containing Khamrabaevite commonly. The d values are given in the TABLE 3 and 3a.

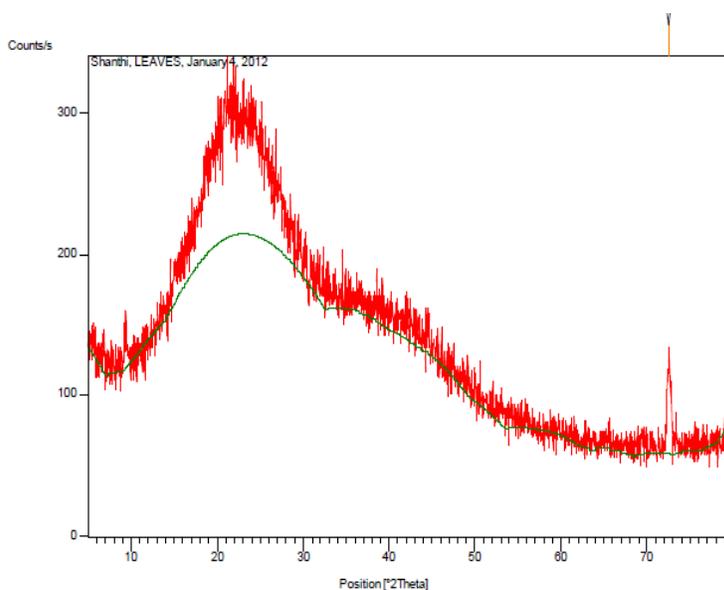


FIG. 1. XRD spectrum of henna leaves carbon.

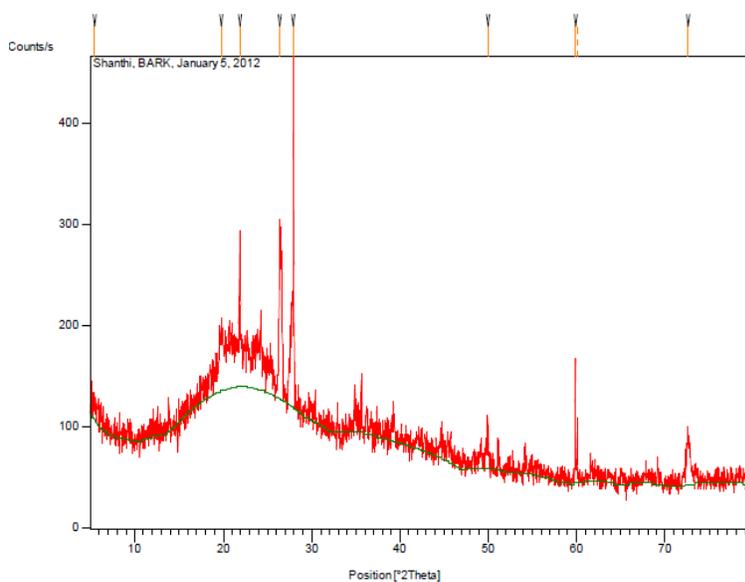


FIG. 2. XRD spectrum of pungam bark carbon.

TABLE 3. Collection of single-phase X-ray powder diffraction patterns for the most intense d values of henna leaves carbon.

Pos. [$^{\circ}2\theta$]	Height [cts]	FWHM [$^{\circ}2\theta$]	d-spacing [Å]	Rel. int. [%]
72.5204	62.48	0.5760	1.30238	100.00

TABLE 3a. Collection of single-phase X-ray powder diffraction patterns for the most intense d values of pongamia bark carbon.

Pos. [2θ]	Height [cts]	FWHM [2θ]	d-spacing [\AA]	Rel. int. [%]
5.4677	17.94	0.9446	16.16344	5.12
19.7648	55.22	0.4723	4.49195	15.77
21.8858	154.72	0.0590	4.06119	44.17
26.3993	150.06	0.1574	4.37619	42.84
27.9342	350.25	0.0590	4.19408	100.00
49.9587	37.45	0.2362	1.82560	10.69
59.8755	126.49	0.0720	1.54350	36.11
72.6226	45.99	0.3840	1.30080	14.1

Scanning electron microscope

Powdered henna leaves carbon and pongamia bark carbon before adsorption were analyzed by Scanning Electron Microprobe (SEM JXO-8100) at 300X magnification and the results are presented in figures. The surface area was analyzed by agitating 1.5 g of the activated carbon sample in 100 ml of diluted hydrochloric acid at a pH=4. Then 30 g of sodium chloride was added while stirring the suspension and then the volume was made up to 150 ml with deionized water. The SEM micrographs for henna leaves carbon and pongamia bark carbon are shown in FIG. 3 and 4.

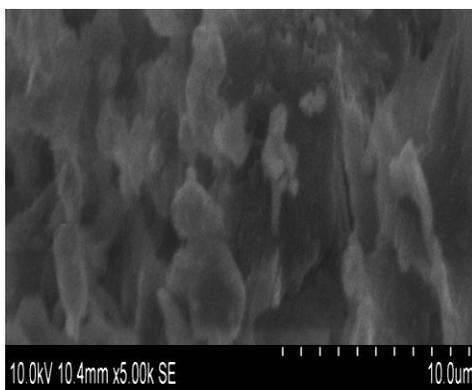


FIG. 3. SEM micrographs for henna leaves carbon.

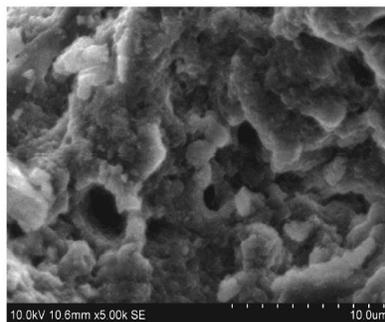


FIG. 4. SEM micrographs for pongamia bark carbon.

FTIR analysis

To know the specific type of functional groups, present on the surface, the synthesized carbon materials were analyzed by FT-IR spectrophotometer. FTIR analysis of the adsorbents was carried out using JASCO make FTIR-3500 spectrophotometer. Pellets (press disk) were used for measuring absorption spectra. The samples were ground with 200 mg of KBr (spectroscopic grade) in a mortar and pressed into 10 mm diameter disks under 10 tons of pressure and high vacuum for FT-IR analysis. The conditions used were 16 scans at a resolution of 4 cm^{-1} measured between 400 cm^{-1} and 4000 cm^{-1} . The results are shown in FIG. 5 and 6.

The surface of the carbon material as synthesized predominantly comprises of C-O type groups present in ethers, acids and esters. Activation in hot air oven leads to the oxidation of carbon surface and resulted in the generation of C=O type carboxyl groups. The extent of oxidation is more in the case of physical activation as evident from the intensity of the peak corresponding to the carboxyl type surface functional groups. The band position, functional group and type of vibration for HLC and PBC are given in the TABLE 4.

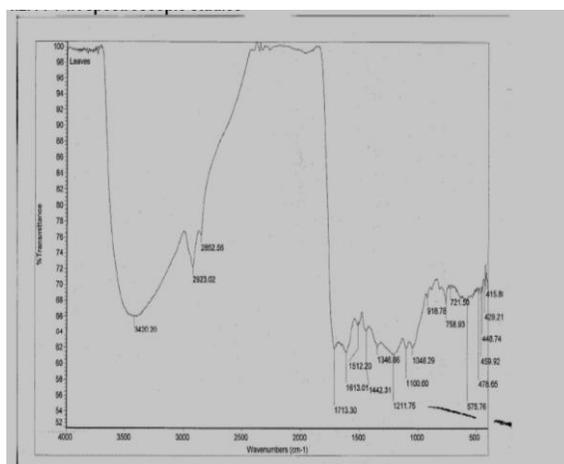


FIG. 5. FT-IR analysis.

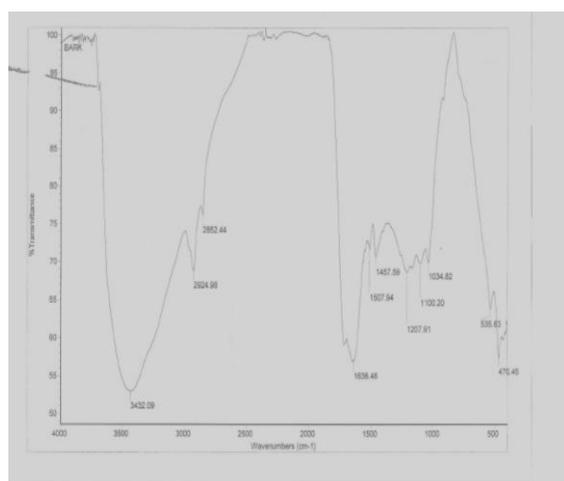


FIG. 6. FT-IR analysis 16 scans at a resolution of 4 cm^{-1} measured between 400 cm^{-1} and 4000 cm^{-1} .

TABLE 4. Assignment of FT – IR bands to specific functional groups of the activated carbon material.

S. No.	Band position cm-1		Functional group	Type of vibration
	HLC	PBC		
1	3420.2	3432.09	O – H	Stretch, H-bonded
2	2924.02 2852.56	2924.98 2852.44	C – H	Stretch
3	1714.20	-	C= O	Stretch
4	1614.01	1636.46	C= C	Stretch
5	1512.20	1507.94	N – O	Stretch
6	1442.31	1457.59	C= C	Stretch
7	1346.66 1211.75 1100.60	1207.91 1100.20	C – N	Stretch
8	1046.29	1034.82	C – O	Stretch

Conclusion

The results of the present study reveal that activated carbons can be synthesized from agricultural wastes in an economic way. The synthesized adsorbents have a substantial variation in the heavy metal removal capacity. The characterization studies are very useful to find the superior grade carbon for adsorption processes. Activated carbon with good surface properties from various treatment procedures were identified, their surface chemical groups can play a key role in removing heavy metals from its aqueous solutions.

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