



Comparison of the Surface Features of the Three Chemically Modified Silk Cotton Hull Activated Carbons

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ABSTRACT

Comparison between three activated carbons having the silk cotton hull origin was done by characterizing them using various methods to find out the changes occur during the modification process. One sample was modified by H_2SO_4 (AC), the second was modified by the mixture of H_2SO_4 and H_2O_2 (AC1) and the third was modified by the mixture of H_2SO_4 and $NH_4S_2O_8$ (AC2). Structural properties of carbons and their oxidized counterparts were determined using sorption of nitrogen. Surface acidity was evaluated using Boehm titration and FTIR spectral analyses. It was demonstrated that, despite the same origin, the carbons significantly differ in their pore structure and surface chemistry. The carbon obtained using H_2SO_4 and H_2O_2 modification is microporous with high surface area $107.23 \text{ m}^2 \cdot \text{g}^{-1}$ (BET). On the other hand, the carbon modified by H_2SO_4 and $NH_4S_2O_8$ contains a high surface acidic oxygenated groups and its surface area is significantly lower. We have used these adsorbents for heavy metal ion removal and got the result more than 90%. In this paper, surface features of these activated carbons were compared.

Key words: SCH, oxidation, surface area, surface acidity.

INTRODUCTION

Various methods are used to manufacture activated carbons. The most common precursors are coal, wood, agricultural waste by-product, peat, and polymers¹. When the so-called physical activation is applied, organic material is first carbonized and then activated at high temperature with steam or CO_2 to introduce porosity^{2,3}. Another method is based on chemical transformations during carbonization⁵. In this method, compounds

such as sulphuric acid, hydrogen peroxide, and ammonium persulphate are used as activating agents at relatively low temperature. This method leads to a very unique sorbent with maximum surface area (around $100 \text{ m}^2/\text{g}$) and a very high volume of pores, all smaller than 30 \AA .

The surface features of carbons such as porosity, surface chemistry, density, and mechanical stability govern the application of activated carbons as adsorbents⁶. The objective of this paper is to

compare the surface features of three SCHACs. The difference in the method of activation results in dramatically different structural and chemical properties of sorbents. One carbon is obtained using the traditional treatment of SCH with sulphuric acid, the second one with the mixture of sulphuric acid and hydrogen peroxide (1:0.4) and the third one with the mixture of sulphuric acid and ammonium persulphate (1:0.1). From the characterization studies it is demonstrated that SCHACs can be applied when sorption or separation of heavy metal ions is taken into consideration.

EXPERIMENTAL

Materials

The silk cotton hull was collected from the campus, Anna University, Tamil Nadu (India). It was washed thoroughly with double distilled water to remove dust and soluble impurities. The samples were cut into small pieces, dried in sunlight until the hulls became crisp. Then the material was powdered by using a jaw crusher and kept it in a hot air oven at 60°C for 24 hours. The completely dried material was then used for the preparation of carbon. According to the literature study⁷ the SCH were soaked in the mixture of a concentrated sulphuric acid, hydrogen peroxide and ammonium persulphate in proper ratios for AC1 & AC2. The material is divided into three equal parts: the first part was soaked in concentrated H₂SO₄ (W/V) at room temperature (30±2°C) over night. The carbonized material was then washed with distilled water several times to remove the free acid. It was finally dried in a hot air oven at 120°C for 6 hours (AC). The second part of the material was soaked in the mixture of concentrated sulphuric acid and hydrogen peroxide in the ratio 1: 0.4 and kept in a hot air oven at 80°C ± 5 for 12 hours, and the same procedure as mentioned above (AC1) was followed. The third part was soaked in the mixture of concentrated sulphuric acid and ammonium persulphate in the ratio 1: 0.1 and kept in a hot air oven at 80°C ± 5 for 12 hours, and the same procedure as mentioned above (AC2) was followed. Finally, the dried activated carbons were sieved to get AC, AC1 and AC2, having an average particle size of 120µm and stored in an air tight container for subsequent experiments.

Methods

Adsorbent characterization was performed by means of spectroscopic and quantitative analyses. The textural characteristics of the adsorbents were determined by the Brunauer Emmette Teller (BET) method, using the Quantachrome version 5.02 instruments.

Surface acidic functional groups and basic sites of the adsorbents determined by the acid-base titration method proposed by Boehm⁸⁻⁹. A half-gram of carbon and 15mL of NaHCO₃ (0.1M), Na₂CO₃ (0.05M) or NaOH (0.1 M) solution was mixed in conical flask, and agitated at 100 rpm for more than two days in room temperature. An aliquot of the solution for each sample was back titrated with HCl (0.1M). The NaHCO₃ neutralizes only carboxylic groups on the carbon surface, Na₂CO₃ does carboxylic and lactonic, and NaOH reacts with carboxylic, lactonic and hydroxyl groups. Accordingly, the difference between the groups neutralized by NaHCO₃ and Na₂CO₃ becomes lactones, the difference between those neutralized by Na₂CO₃ and NaOH is hydroxyls. The same procedure was carried out for the mixture of 0.5g of the carbons and 15mL of HCl (0.1M) solution to determine the basic sites of the carbon surface. The remaining HCl solution was titrated with NaOH (0.1M) after neutralization. Neutralization points were fixed using methyl orange solution indicator for weak base titrated with strong acid, and phenolphthalein solution for strong acid and strong base combination.

Thermal analysis was done using a TA instruments thermal analyzer SDT Q600. An identification of the functional groups was performed, using a Fourier Transform Infrared (FTIR) spectrometer (Shimadzu FTIR-8400) in the range of 400 – 4000 cm⁻¹. A scanning electron microscope (SEM) (Joel JSM-6360) coupled with energy dispersive X-ray (EDX) spectroscopy was used to obtain the surface images and the elemental composition in the adsorbent.

The pH of zero-point charge (pH_{zpc}) of the sample was carried out as follows: 50ml of a 0.1M NaCl was placed in a closed Erlenmeyer flask. The effect of pH on metal ions biosorption can be explained in terms of pH_{zpc} determined by the

method of Leyva-Ramos *et al.* proposed⁹. The pH was adjusted to a value between 2 and 12 by adding 0.1M HCl or NaOH. Then, 0.02 g of each sample was added, and the final pH was measured after 24 h under agitation at room temperature. The pH_{zpc} is the point where the curve pH_{final} versus $\text{pH}_{\text{initial}}$ crosses the line $\text{pH}_{\text{initial}} = \text{pH}_{\text{final}}$.

The bulk densities of all materials were determined following the procedure proposed by No *et al.*,¹¹. One gram of each material was placed in a 15ml tapered graduated centrifuge tube and packed gently by tapping the tube 10 times on the bench top. The volume was recorded and the bulk density expressed in grams per milliliter (g/ml). This procedure was carried out in triplicate and the means reported.

The chemical oxygen demand (COD) in water was determined by means of the dichromate method.

RESULTS AND DISCUSSION

The physico-chemical characteristics of the adsorbent SCHACs are given in Table 1. The adsorption process is affected by surface properties such as surface area and polarity. The BET results revealed that the SCHACs are a microporous material, with a significant specific surface area. Although the three carbons AC, AC1 and AC2 were obtained from the same wood precursors, different methods of activation resulted in completely different

pore structures. The surface area and micropore volumes of AC1 are higher than AC and AC2. For AC2, the surface area and pore volume decreased with significant changes in the range of larger pores. It is noteworthy that the average pore radius is higher than AC and AC1. The observed changes in the pore sizes are the effects of the destruction of some small pore walls and creation of functional groups on the carbon surface. The surface chemistry of carbons studied was evaluated using the "wet" methods providing information about acidic centers (Bronsted type) used here are Boehm. The results of the Boehm titration in terms of the numbers of carboxylic acids, phenols, lactones and bases are collected in Table 1. The results clearly show all the three initial carbons have significant number of surface groups; the overall lower acidity of the AC compared to AC1 and AC2 is demonstrated by its smaller number of strong acids and larger number of base. The oxidation resulted in significant changes in surface chemistry toward an increase in acidity. In the case of AC1 and AC2 the number of acidic groups increased significantly and its total value is found to be greater than total surface basicity. The pH_{zpc} of AC1 & AC2 decreased markedly due to an increase in the amount of the surface acidic oxygen-containing groups^[11] and this was caused by the increase in carboxylic acid groups and protonation of functional groups as indicated by the following equations.

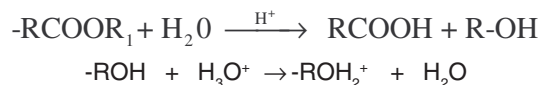


Table 1: Physical characteristics of SCHACs

Characteristics	AC	AC1	AC2
pH_{zpc}	5.1	5.0	4.7
Particle size (μm)	< 120	< 120	< 120
Bulk Density (g/ml)	0.71	0.45	0.42
Surface area (BET) (m^2/g)	102.78	107.23	57.68
Total pore volume (cc/g)	7.621	9.968	6.987
Average pore radius (\AA)	5.2491	3.1579	7.9385
Total surface acidity (mequiv/g)	0.1298	0.1444	0.1609
Carboxyl (mequiv/g)	0.0571	0.0420	0.0605
Lactone (mequiv/g)	0.0679	0.1000	0.0900
Phenolic (mequiv/g)	0.0048	0.0024	0.0104
Total Surface basicity (mequiv/g)	0.1531	0.1356	0.1269

Table 2: Weight loss at various temperatures (%) using TG method

Temperature	AC	AC1	AC2	Proposed group
41 - 95°C	14.32	19.45	24.53	Chemisorbed water
250 - 487°C	34.25	41.44	34.76	Carboxylic acid
479 - 627°C	8.65	18.55	12.77	Lactone
685 - 760°C	-	6.88	16.20	Carboxylic anhydride
773 - 864°C	8.17	4.35	10.85	Phenolic hydroxyl
765°C	-	-	0.33	Residue
> 984°C	26.17	8.09	-	Residue may be quinone

Table 3: FTIR peak assignments of functional groups on carbon surfaces

Group or Functionality	Wave number assignments (cm ⁻¹)
Carboxylic acids	
C=O (Stretching)	1600 - 1800
O-H (Stretching)	3420
Quinones	1616
C-H (Stretching)	2913
Lactones	
C=O (Stretching)	1709
Phenolic groups	
C-OH (stretching)	1207
O-H (Stretching)	2500 - 3620
Acidic Hydroxyl group	3851
Hydrogen bond with water molecules	2421
Sulphate group	1115/610
Organic Sulphates	1378
Isocyanate	2279

Table 4: Chemical composition of SCHACs EDX analysis by weight %

Elements	AC	AC1	AC2
Carbon	75.06	67.69	66.7
Oxygen	23.08	27.57	27.47
Sulphur	0.71	0.61	1.62
Sodium	0.11	3.10	3.14
Aluminium	0.11	0.11	0.11
Silicon	0.10	0.65	0.77
Calcium	0.12	0.27	0.20

Activated carbons with acidic character and lower pH_{zpc} value, can release protons to form net negative surface charges, which is beneficial for the aqueous metal cation adsorption. Bulk Density may not directly relate to the carbon's effectiveness for removing heavy metals but they are important to their commercial utilization.

Thermal Analysis

The effect of oxidation on surface chemistry is also demonstrated from the analysis of DTA curves obtained from the measurement in nitrogen. The TGA for AC, AC1 and AC2 reveals abrupt changes located around 70, 360, 588, 708 & 827°C

as shown in figure 1. This behavior demonstrates the successive decomposition of different species (e.g., H₂O, CO₂, CO). Using the data obtained from,¹³ calculations were made to show the presence of chemisorbed water, carboxylic, lactone, phenolic, carbonyl and quinone group (Table 2). On the TGA curve for AC, AC1 and AC2 indicates a loss of chemisorbed water 14.32, 19.45 and 24.53% between 41 - 95°C. Here, the water is adsorbed by the surface functional groups on the carbon by hydrogen bonding. Once the water molecule is adsorbed on the primary centre, it becomes a secondary adsorption site and the clusters are formed thus enhancing the heavy metal adsorption. Also, we noted that maximum weight losses (34 - 42%) at 360°C which is due to the decomposition

of carboxylic group with the evolution of CO₂. The maximum weight loss percentage is found in AC1 (41.44%). The other three significant weight losses, the first (500 - 600°C), the second (600 - 750 °C) and the third (800°C) corresponds to the presence of lactone, carboxylic anhydride (another form of carboxylic acid), and phenolic group resulting in the emission of CO₂ and CO. Here, the maximum weight losses occur in AC1, 18.55% (509°C) for lactone and for AC2, 16.20% (730 °C) for carboxylic anhydride and 10.85% (810°C) for phenolic group. At the end of the analysis, 26.17 & 8.09% for AC & AC1 (984°C) and 0.33% for AC2 (765°C) of the starting sample was left (Table 3). Here, the residue weight percentage decreased from AC < AC1 < AC2 at 984°C. This shows that the formation of

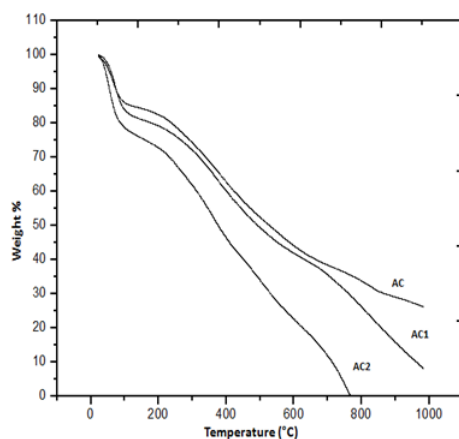


Fig. 1: TGA graph of the SCHACs (AC, AC1, AC2)

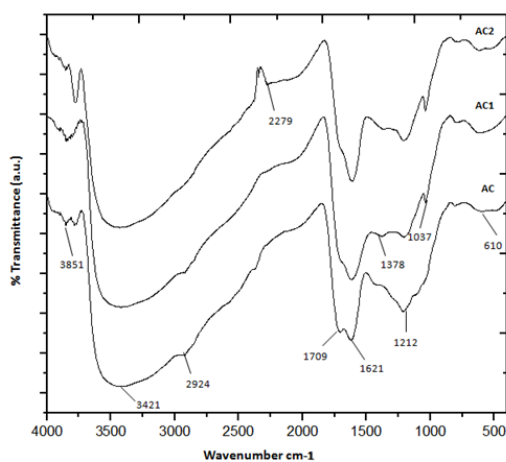


Fig. 2: FTIR spectra of the silk cotton hull activated carbons AC, AC1 and AC2

more acidic oxygenated groups in AC1 and AC2 occurred during modification. Although the total weight losses for these carbons are similar, the differences in surface chemistry are pronounced in the larger weight loss at lower temperature where, strong acids are supposed to decompose and the smaller at higher temperature for AC2 and AC1 compared to AC. As expected based on the titration results, the AC2 and AC1 is more acidic than AC.

Fourier Transform Infrared Spectrum

Fig.2 presents the fundamental peaks of the adsorbent. The broad band at 3420 – 3450 cm^{-1} is attributed to the stretching absorption of the O-H due to inter and intramolecular hydrogen bonding of the polymeric compounds, such as alcohols, phenols and carboxylic acids. The sharp peak at 3851 cm^{-1} is due to the presence of strongly acidic

hydroxyl groups. The band at 1600 – 1800 cm^{-1} suggests the presence of the stretching C=O vibrations arising from groups such as carboxylic acids, lactones and quinones. The small peak observed at 2913 cm^{-1} denotes the presence of the stretching C–H vibration in the quinone group. The bands at 1709 cm^{-1} show the presence of the stretching C=O vibration from the lactone group. The sharp bands at 1616 cm^{-1} are due to the asymmetric stretching of carboxylate anion vibrations¹⁴. The vibration at 1207 cm^{-1} can be attributed to the deformation of C=O, and the stretching formation of the –OH of carboxylic acids and phenols. The strong C–O band at 1037 cm^{-1} due to –OCH₃ group, also confirms the presence of the lignin structure¹⁵ which was found in AC1 and AC2. The additional peak at 810 cm^{-1} can be assigned to the bending modes of aromatic compounds.

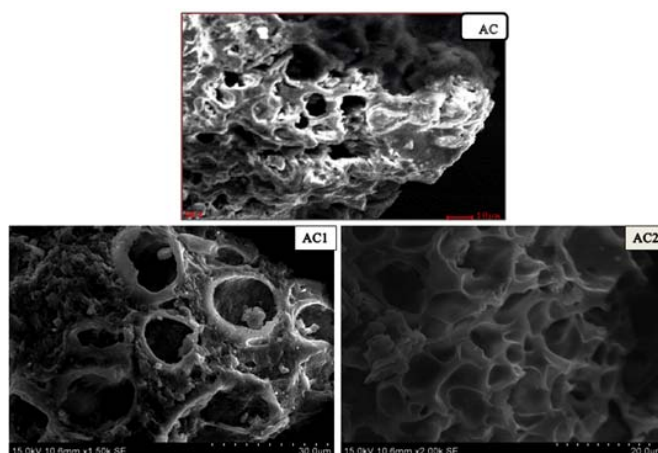


Fig. 3: SEM images of the silk cotton hull activated carbons AC, AC1 and AC2

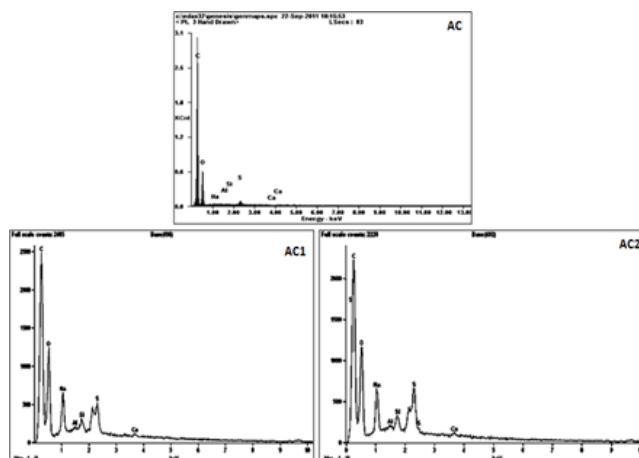


Fig. 4: EDX spectra of the silk cotton hull activated carbons AC, AC1 and AC2

Also, the peaks at 1378cm^{-1} and 1115cm^{-1} indicate the presence of sulphur-oxy compounds which possess a positive charge on the sulphur and a negative charge resonating on the oxygen atoms, making them excellent for adsorption where ionic species are involved¹⁶. A peak at 2279cm^{-1} is found in AC2 which shows the formation of isocyanate group during the modification process. Thus FTIR analysis revealed that $-\text{OH}$, C-H bending, and $-\text{C}=\text{O}$, COO^- , O-H, S-O, $-\text{N}=\text{C}=\text{O}$ stretching were mainly responsible for the adsorption by the SCHAC.

SEM images and EDX spectra

The surface morphology and porous structure of the different carbons were studied by SEM. It is clear from Fig.3 that SCHACs has the microporous structure. From EDX analysis, the carbon content is found to be decreasing from $\text{AC} < \text{AC1} < \text{AC2}$, suggesting that during the modification process, caused the release of organic compounds such as hemicellulose and lignin. The results observed in this study are in complete agreement with the findings of Chen and Wu¹⁷. Thus from the EDX spectra there is reduction in carbon but an increase in oxygen content.

The effect of the modification process

To evaluate the toxicity of the adsorbed solutions, their initial and final COD values were determined. It was found that for the metal ion solution adsorbed by AC, AC1 and AC2, the COD decreases sharply from $282\text{mg O}_2\text{L}^{-1}$ for AC to $60\text{mg O}_2\text{L}^{-1}$ for AC1 and $50\text{mg O}_2\text{L}^{-1}$ for AC2 respectively, indicating the lower toxicity of the solutions after adsorption.

CONCLUSION

In this study, the low values of temperature (80°C) used during the heat-treatment process make this material potentially very useful for applications to remove contaminants from water in a cheapway. From our data, it can be concluded that the adsorbents treated with various oxidising agents enable us to modify the chemico-physical properties of the materials, and it greatly enhances the adsorption capacity. The FTIR, TGA analyses and Boehm titration results confirmed the modification process. Also, it decreased the released COD of the SCH to an acceptable level for wastewater. The BET surface area increased for AC1, whereas it decreased for AC2 after oxidation; however, the total adsorption capacity increased by the total surface acidity facilitating the retention of heavy metal ion that form a complex with the surface groups¹⁸. Also, these render the SCHACs having more acidic sites to release protons to exchange with heavy metal ions in the adsorption process.

Nomenclature

SCH	Silk Cotton Hulls
SCHACs	Silk Cotton Hull Activated Carbons
SEM	Scanning Electron Microscope
EDX	Energy Dispersive X-ray Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
BET	Brunauer Emmette Teller
COD	Chemical Oxygen Demand

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