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## TREATMENT OF TANNERY EFFLUENTS- A COMPARATIVE STUDY BETWEEN MESOPOROUS CARBON AND CARBON/SILICA AS ADSORBENTS

Abinaya. E<sup>1\*</sup>, Stanly Samuel<sup>2</sup> and S. Swarnalatha<sup>3</sup>

**Abstract:** Mesoporous/Microporous carbon and carbon/silica were prepared and characterized for their surface area, pore size, functional groups (FTIR) and surface morphology (SEM). Treatment of Tannery effluent plays a major role in environmental issue because of the presence of Xenobiotic compounds in it. The demand for effective adsorbents for the treatment of tannery effluent is increasing. A comparative study between mesoporous carbon and carbon/silica for the treatment of tannery effluent was carried out using a column reactor. The reactor system was fixed-bed, vertical, downward flow reactor. The effect of various parameters like pH, bed height and contact time were carried out to optimize the conditions for different adsorbents.

**Keywords:** Mesoporous Carbon/Silica matrix, Rice husk, Coconut Shell, Tannery effluent treatment.

### INTRODUCTION

Leather industries in India are one of the export oriented and growth oriented as well as huge water consuming and chemical consuming industry. There are about 3000 tanneries located in India covering large scale, medium scale and small-scale sectors with an annual production capacity of 6 lakh tones and wastewater discharging capacity of 80000 m<sup>3</sup>/day. Leather industries uses broad spectrum of chemicals covering inorganic, natural organic and synthetic organic compounds during the manufacture of leather. Synthetic organic chemicals include sulphonated phenolics, sulphonated naphthalene, phenolic syntans, sulphated / sulphited long chain fatty oils, sulphonated aromatics dye compounds and various other surfactant (Kennedy *et.al.*, 2004a). Organic chemicals used in garment leather manufacturing tanneries shares 510 kg/tonne of skins processed and inorganic chemicals shares 200kg/tonne of skins processed. Among organic chemicals used sulphonated phenolic condensate syntan constitute 40kg/tonne of raw material processed and sulphonated naphthalene constitutes 50kg/tonne.

The tannery wastewater having higher value of COD and BOD, due to high pollution load and toxicity affects the environment and the ground water. It is mandatory that every leather industry should have an effluent treatment plant. The treatment of effluent and the solid residues is specialized and expensive but it is essential to obtain the permissible limit of pollution control board. The leather industries in India have either individual effluent treatment plant or to a common effluent treatment plant (CETP) in which several industries are connected.

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The tannery wastewater is subjected to several primary and secondary treatments such as screening, flocculation, clarification and aerobic or anaerobic digestion treatments, and finally it is subjected to tertiary or advanced treatment (Kennedy *et.al.*, 2004a). The advanced treatment method of the tannery effluents includes Fenton oxidation process, Ozonation process, Electro oxidation process and Catalytic adsorption/removal process (Scott and Ollis, 1995).

Catalytic adsorption/removal process is a recently developed and extensively used in the wastewater and gaseous streams treatment. Activated carbon is one of the commonly used as a catalyst for this process. Activated carbons are utilized as adsorbents in a variety of industrial fields for solvent recovery, gas separation, catalysis etc. (Kennedy *et.al.*, 2007). Their properties related to the adsorptive capacity are attributed to their large internal surface area and porosity as well as a marked surface activity. Advantage of this process for the tannery waste water treatment is due to its cost effective and efficient removal of COD, compared to other processes (Mishra *et.al.*, 1995, Pintar and Levec, 1994). Silica based carbon matrix not only acts as the adsorption but it also acts as the catalyst for the conversion of xenobiotic compounds (Sekaran *et.al.*, 2007).

The objective of this study is to produce a low-cost activated carbon with microporous / mesoporous ranges using  $H_3PO_4$  as activation agents and to compare the different carbons derived from the raw material such as coconut shell and rice husk (carbon/silica matrix) for the treatment of tannery effluent.

## **MATERIALS AND METHODS**

### **Materials**

Phosphoric acid was purchased from Merck (Germany) and used as received. Coconut shell and Rice husk (RH) as the precursor material obtained from the agricultural industry was well washed with  $H_2O$  several times for the removal of dust and used after oven drying at  $110^\circ C$  for 6 h. The dried samples were then sieved to about  $600\text{-}\mu m$  in size, and this fraction was used for the preparation of carbon.

### **Preparation of activated carbons**

The activated carbons were prepared in two sequential steps: pre-carbonization and chemical activation (Kennedy *et.al.*, 2004b). The precursors were packed in an air-tight graphite crucible and heated at  $400^\circ C$  for 4 hours. The pre-carbonized materials were activated, using ortho phosphoric acid ( $H_3PO_4$ ) in the ratio of 1: 2 (carbon :  $H_3PO_4/KOH$ ). The mixture was sealed in an air-tight crucible. This was followed by heating to  $800^\circ C$  at a heating rate of  $5^\circ C/min$  using a temperature programmer and maintained at the final temperature for 1 h before cooling. Finally the activated carbons were washed with hot water to remove the excess phosphorus compounds and alkali until the wash water attained pH 7. The washed sample was dried at  $110^\circ C$  to obtain the final products which were labeled as RH (rice husk carbon) and CS (coconut shell carbon).

## Characterization of activated carbons

### Moisture content of carbons

About 10 g of the carbon was weighed in a weighing bottle. The weighing bottle was then placed in an air oven and maintained at  $110 \text{ }^\circ\text{C} \pm 5 \text{ }^\circ\text{C}$  for about 4 hours. The weighing bottle was covered, cooled in a desiccator and weighed. Heating, cooling and weighing were repeated at 30 minutes intervals until the difference in the two consecutive weighing was approximately less than 5 mg.

$$\text{Moisture content (\%)} = \frac{100 (M_1 - M_2)}{M_1} \quad (1)$$

Where,

$$\begin{aligned} M_1 &= \text{Initial mass of the carbon, g} \\ M_2 &= \text{Mass of the carbon after drying, g} \end{aligned}$$

### Ash content of carbons

About 2 g of the carbon was weighed in a crucible. The crucible and its contents were ignited in a muffle furnace at  $1000 \text{ }^\circ\text{C}$  for 3 hours. The process of heating and cooling were repeated until the difference in the two consecutive weighing was less than 1 mg.

$$\text{Ash (on dry basis) \%} = \frac{10000 M_1}{M (100 - X)} \quad (2)$$

Where,

$$\begin{aligned} M_1 &= \text{Mass of the ash, g} \\ M &= \text{Mass of the carbon, g} \\ X &= \text{moisture content of the carbon, \%} \end{aligned}$$

### Elemental (C H N) analysis of MAC

The CHN content of RH and CS were determined using CHNS 1108 model Carlo – Erba analyzer (New Jersey). About 20 mg of the sample was used for the analysis.

### Surface area and pore size distribution of carbons

The surface area and pore size distribution was determined from the  $\text{N}_2$  adsorption – desorption isotherms. The  $\text{N}_2$  adsorption – desorption isotherm of the carbon samples were measured, using an automatic adsorption instrument (Quantachrome Corp. Nova-1000 gas sorption analyzer). Prior to measurement, carbons were degassed at  $150 \text{ }^\circ\text{C}$  for a night. The nitrogen adsorption – desorption data were recorded at liquid nitrogen temperature  $77 \text{ }^\circ\text{K}$ . The surface areas of the

carbons were calculated, using Brunauer, Emmett, and Teller (BET) equation. The pore size distribution was determined, using Barrett, Joyner and Halenda (BJH) method.

#### **FT-IR spectroscopy of the carbons**

A Perkin-Elmer Fourier transform infrared (FT-IR) spectrometer was used for the investigation of the surface functional groups. The sample was mixed with spectroscopic grade potassium bromide and made into pellets at a pressure of about 1 MPa. The pellets were about 10 mm in diameter and 1 mm in thickness. The sample was scanned in the spectral range of 4000-400  $\text{cm}^{-1}$ .

#### **Scanning Electron Micrograph (SEM) of the carbons**

The surface morphologies of carbons were determined, using JEOL JSM – 6360 scanning electron microscope (SEM). The samples were coated with gold by a gold sputtering device for the clear visibility of the surface morphology.

#### **Treatment of Tannery Effluent:**

##### **Continuous catalytic column**

The influent used in the experiment was taken after the primary treatment from a tannery located at Pallavaram, Chennai. The sample was pumped by peristaltic pump into the reactor as downward flow and the air as upward flow through the peristaltic pump in order to maintain the required amount. The reactor consists of closed glass vertical cylinder with influent inlet and effluent outlet. The bottom section of the

reactor was filled with glass beads stacked by a sand bed. The carbon bed is kept above sand bed. The general dimensions of the reactor is given as

$$\begin{aligned} \text{Height} &= 10\text{cm} \\ \text{Inner Diameter} &= 1.5\text{cm} \end{aligned}$$

The effluent was collected at the bottom via a throttling valve. In parallel two reactors were also operated with same effluent with RH and CS of 600  $\mu$ . Reduction of COD were studied at different flow rates of 4.0, 6.0 and 8.0 ml/min of influent and different bed height of 5, 10 and 15 cm. Optimization of pH (3.0, 7.0 & 9.0) was also done.

#### **Measurement of Chemical Oxygen Demand:-**

Required amount of sample and distilled water to the total volume of 2.5 ml was taken, 1.5ml 0.25 N  $\text{K}_2\text{Cr}_2\text{O}_7$  and add 3.5ml of C.O.D acid (silver sulfate dissolved in concentrated sulfuric acid) was added. The container was closed tightly and kept at 150<sup>o</sup>c for 2hrs. After cooling it was titrated against 0.25 N Ferrous Ammonium Sulphate.

Calculation:-

$$\text{COD} = (\text{Blank} - \text{Sample}) \times \text{N of FAS} \times 8000/\text{volume of sample taken} \quad (3)$$

## RESULTS AND DISCUSSION

### *Physico-chemical characteristics of the carbons*

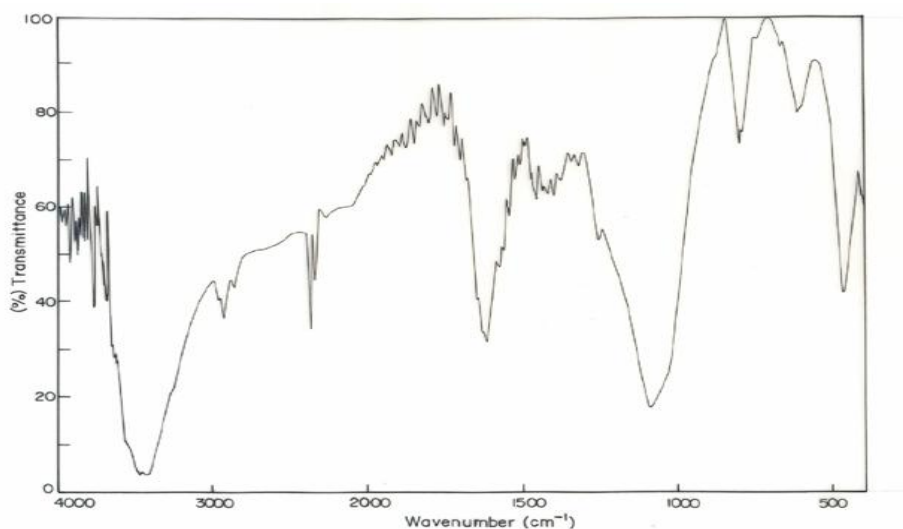
The physico-chemical characteristics of the carbons are presented in Table 1

**Table 1. Physico-chemical characteristics of RH and CS**

S.No	Parameters	RH	CS
1	Moisture content (%)	8.45%	16.2%
2	Ash content (%)	52.0%	35.6%
3	Surface Area	377 m <sup>2</sup> /g	542 m <sup>2</sup> /g
4	Average Pore diameter (Å°)	27.3 Å	8 Å
5	Carbon (%)	38.45	43.45
6	Hydrogen (%)	0.70	1.64
7	Nitrogen (%)	0.10	0.36

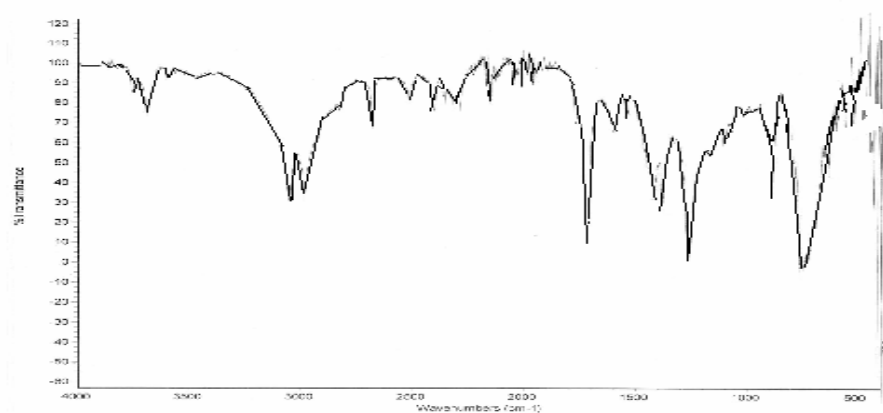
### FTIR spectra of the carbons

FTIR spectra of the RH and CS are shown in Fig. 1 and 2. In RH (Fig. 1) a broad envelope of –OH stretching vibration of –SiOH group at 3433 cm<sup>-1</sup>. A weak band at 3740 cm<sup>-1</sup> may be assigned to the isolated O–H group. The aliphatic C–H groups exhibit its asymmetric and symmetric stretching around 2950 – 2800 cm<sup>-1</sup>. The Si–O–Si stretching overlaps with phosphates arising as a result of phosphoric acid activation and exhibits at 1023 cm<sup>-1</sup> whereas Si–H stretches around 710–720 cm<sup>-1</sup>. Asymmetrical and symmetrical stretching of carboxylate group present in the carbon exhibits around 1515 and 1374 cm<sup>-1</sup> respectively.



**Fig. 1. FTIR spectrum of RH**

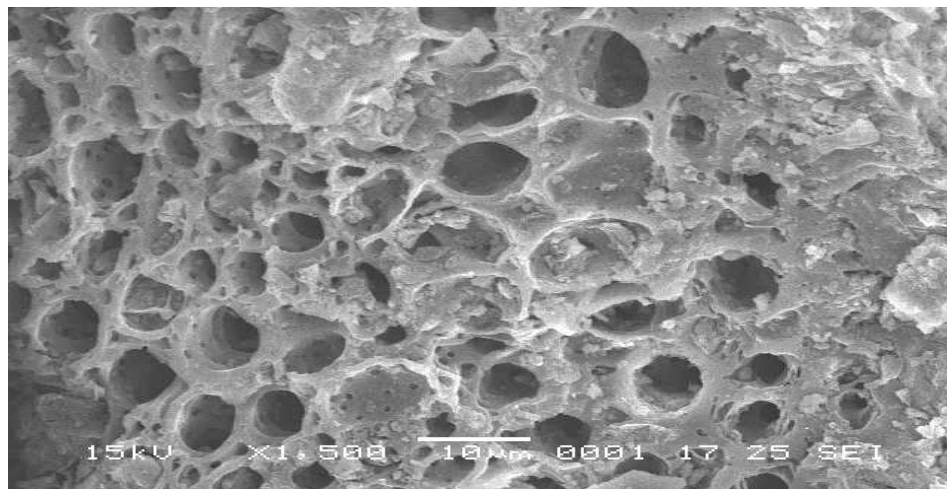
Fig. 2 indicates the IR spectrum of CS. The absence of silica is indicated by the absence of Si-O-Si bond and Si-OH bond. It has a weak band of -OH stretching vibration of due to presence of water molecules around  $3600\text{ cm}^{-1}$ . The aliphatic C-H groups exhibit its asymmetric and symmetric stretching around  $2950 - 2800\text{ cm}^{-1}$ . Asymmetrical and symmetrical stretching of carboxylate group present in the carbon exhibits around  $1651$  and  $1374\text{ cm}^{-1}$  respectively.



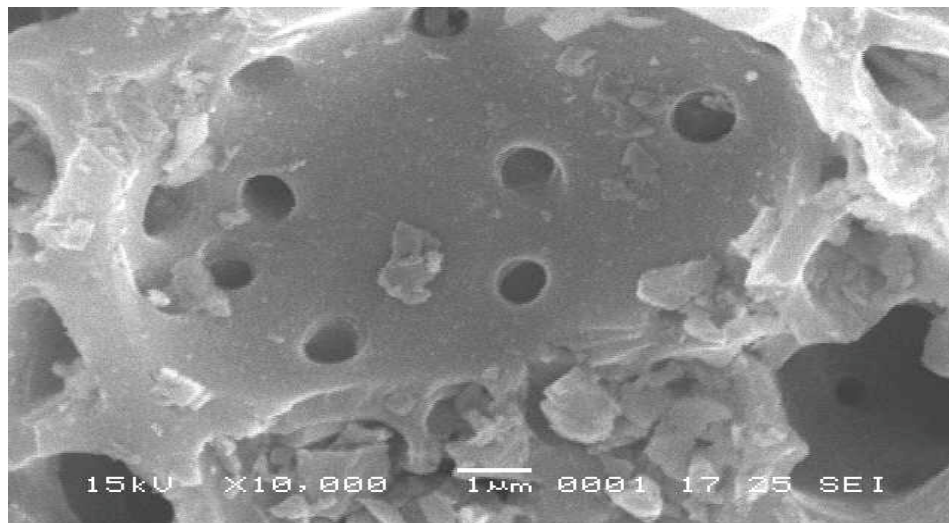
**Fig. 2. FTIR spectrum of CS**

### Surface morphology of carbons

The SEM image of the carbon samples are shown in Fig. 3 and 4. It depicts that the carbons are highly porous in nature. The gases generated from the chemical activant are energized by the thermal energy and erupted with pressure that causes cleavage of the bonding in the network structure of the precursor material used in preparing the carbon matrix. The geometry and distribution of the pores are also controlled by size of the gaseous molecules which are released during activation, bonding characteristics of the precursor material (Swarnalatha and Sekaran, 2007), the activation temperature, pressure employed during the activation and time of activation.



**Fig.3. Surface morphology of RH**



**Fig.4. Surface morphology of CS**

**Treatment of tannery effluent:**

Tannery effluent was treated using parallel reactors filled with RH and CS. Effect of flow rate (contact time) was optimized and effect of pH was also optimized by keeping it in optimized flow rate. And also finally the effect of bed height was also optimized by keeping flow rate and pH constant.

**Effect of flow rate (contact time):-**

Effect of contact time between pollutant and carbon was varied by varying flow rate of influent as 4.0, 6.0 and 8.0 ml/min. The results are tabulated in the tables 2. It shows when flow rate increases, the efficiency of the reactor decreases. It can be due to the less contact time of catalyst with the organics/in-organics present in the inlet water.

**Table 2. Effect of flow rate**

**Conditions:** Bed height of 10 cm; Wt of carbon: CS – 11 g, RH – 6 g, Initial pH – 7.  
Initial Chemical Oxygen Demand = 3920 mg/l

Flow Rate(ml/min)	Carbon	value (mg/l)	% reduction	% Reduction per gm of carbon
4.0	CS	2818.5	28.1	2.55
	RH	2124.6	45.8	7.63
6.0	CS	3085.0	21.3	1.94
	RH	2324.6	40.7	6.80
8.0	CS	3339.8	14.8	1.35
	RH	2516.6	35.8	6.00



**Effect of pH:-**

It is evident from the tables 3 as the pH decreases (acidic), the efficiency of the treatment increases. However the minimum removal was noticed when pH was raised to basic (9.0). The % COD reduction for RH is observed as about 59 at the pH 3.0.

**Table 3. Effect of pH**

**Conditions:** Bed height of 10 cm; Wt of carbon: CS – 11 g, RH – 6 g, Flow rate – 4.0 ml/min  
 Initial Chemical Oxygen Demand = 3920 mg/l

pH	Carbon	value (mg/l)	% reduction	% Reduction per gm of carbon
3	CS	2422.6	38.2	3.47
	RH	1626.8	58.5	9.75
7	CS	2818.5	28.1	2.55
	RH	2124.6	45.8	7.63
9	CS	3034.1	22.6	2.05
	RH	2246.2	42.7	7.12

**Effect of Bed height:**

Effect of bed height is carried at various height such as 5, 10 and 15cm (Table 4). According to bed height weight of the carbon also varies. Though percentage reduction increases as height of the carbon bed increases but % reduction per gm of the carbon reaches the maximum at the bed height of 10cm in both RH (9.75%) and CS (3.47%). For this study the optimized bed height was fixed as 10cm.

**Table 4. Effect of Bed Height**

**Conditions:** Flow rate – 4.0 ml/min, Initial pH – 3  
 Initial Chemical Oxygen Demand = 3920 mg/l

Bed height (cm)	Carbon	Wt. of the carbon (g)	value (mg/l)	% reduction	% Reduction per gm of carbon
5	CS	5.5	3375.1	13.9	2.53
	RH	3	3010.6	23.2	7.73
10	CS	11	2422.6	38.2	3.47
	RH	6	1626.8	58.5	9.75
15	CS	16.5	2179.5	44.4	2.69
	RH	9	1454.3	62.9	6.99

**Comparison between RH and CS:**

Tables 2, 3 and 4 clearly shows that RH has got the good efficiency of 59 % removal at optimized condition compared to only 38% removal in CS. Though surface area is high in CS

compared to RH, the result says RH appears to be a better carbon for tannery effluent treatment. This could be probably mainly due to the two reasons i) Silica is present as a main constituent in rice husk, which was carried in the carbon also. RH not only act as activated carbon, it also acts as carbon/silica matrix, which not only serves as adsorbent but also as a efficient catalyst for the conversion of xenobiotic compounds present in the tannery effluent. ii) Another reason could be microporous nature of CS. Most of the Xenobiotic compounds present in the tannery effluent responsible for high COD content will be in the size of mesoporous range.

## CONCLUSION:

Rice husk carbon, RH (silica based carbon matrix) and Coconut shell carbon (CS) were prepared by two stage carbonization process. Surface area analysis says that CS has got high surface area (542 m<sup>2</sup>/g) when compared to RH (377 m<sup>2</sup>/g). Microporosity was found in CS, whereas mesoporosity in RH. FTIR reveals the presence of Si-O-Si bond in RH around 1070 cm<sup>-1</sup>. Surface morphology of the carbon samples shows the high porous structure of the carbons. RH and CS were employed for the treatment of the tannery effluent, which gives highest percentage conversion of RH and CS are 59 and 38 respectively. Acidic pH (3.0) was optimized for the treatment in both RH and CS. And also the optimization of flow rate and bed height was done. The treatment of tannery effluents by RH is beneficiary when compared with treatment by CS. RH being cost efficient and having catalytic properties, which can be employed in the coming days for a better treatment with less operation cost.

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