

Preparation and application of bio waste based activated carbon on river wastewater treatment

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Abstract : The production of activated carbon (AC) from bio wastes is one of the most environment-friendly solutions by transforming negative-valued wastes to valuable materials. The present work relates to efforts made towards developing a high surface area, activated carbon from rice husk (RH) and sugarcane baggase (SB) by chemical activation process with potassium hydroxide as the activating agent and to ensure the treatment quality of prepared activation carbon on river effluent waste water. The process parameters are characterized and optimized based on the product yield and iodine number (IN) and concentration of activating agent. The adsorption capacity (AC) was found to increase with increasing of initial concentrations activating agents. The quality of activated carbon produced was determined using iodine number test. The higher value of iodine number will increase the adsorption capacity of the activated carbon, hence, the quality of the activated carbon. Activated carbon exhibited high tendency for the reduction of impurities present in effluent waste water. The activated carbon prepared from rice husk and sugarcane baggase in this study had maximum iodine of 639.5 and 670.4 mg/g respectively, with KOH as the activating agent. Their adsorption capacities were comparable to the adsorption capacity of a commercial activated carbon regarding to the reduction in volatile fatty acid, total nitrogen, total phosphorous, cadmium and manganese of the river effluent water.

Keywords: Activated carbon, Chemical activation, Iodine number, Wastewater treatment, Adsorption.

1. Introduction

Activated carbon (AC) has been widely used as a good adsorbent for various applications including the treatment of waste water. The extensive application of activated carbon is mainly due to its high adsorption capacity and cheap or zero cost of the starting carbonaceous materials used for the preparation. Typically, bio waste or wastes such as olive cake, coconut husk, and palm shell are used as the starting materials to prepare AC¹⁻³. In this study, bio waste such as sugarcane baggase (SB) and rice husk (RH) was used as the starting material to prepare AC. Converting this waste to activated carbon will add more value to the product. Moreover, it is a renewable biomass which is environmentally friendly. Commercially activated carbon is manufactured by two major processes, namely physical and chemical activation methods. Physical activation involves activation of carbonaceous raw material using steam/carbon dioxide as activating agent. Chemical activation involves activation of carbonaceous material after pre-treatment with inorganic dehydrating agents like phosphoric acid, zinc chloride etc. Physical activation using steam is the oldest of all activation processes, where steam reacts with carbon resulting in porous activated carbon. The reaction or activation is a highly endothermic process, which must be carried out at very high temperatures (800 to 1000 °C) as compared to chemical activation (400 to 600 °C). In chemical activation, several types of chemicals are used as the activating

agent including ZnCl_2 , H_3PO_4 and KOH . Different activating agents provide activated carbons with different properties. Hayashi and coworkers⁴ found that the greatest specific surface areas of activated carbons were obtained at the carbonization temperature of 600 °C with ZnCl_2 and H_3PO_4 activation. In contrast, the maximum surface areas of activated carbons were obtained at the carbonization temperature of 800°C with alkali metal (KOH , NaOH , K_2CO_3 and Na_2CO_3) activation. Chemical activation methods later came in to practice where dehydrating chemicals are used for activation. Several dehydrating agents like KOH , NaOH , H_3PO_4 , ZnCl_2 , Na_3PO_4 , and NaCl were used on various raw materials to yield appreciable quality of activated carbon. Among the several dehydrating agents, KOH and phosphoric acid are widely employed for commercial manufacture due to its excellent dehydration characteristics. Moreover, chemical activation is reported to give AC with higher specific surface area and much better developed porosity than physical activation^{5,6}. AC manufactured using KOH activation route is gaining significance due to its application in sugar refining, food and Pharma industries and waste water treatment.

The goal of the present study was to investigate the potential application of the activated carbons as adsorbents, derived from SB and RH bio waste and investigated their properties and adsorption capacities for iodine, proximate analysis, yield (%) and other impurities in the water treatment. The effects of preparation parameters such as the concentration of the activating agent KOH and heating temperature were studied to identify an optimum condition for adsorbent production. Adsorption has been found to be superior compared to other techniques in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Moreover, adsorption does not result in the formation of harmful substances. Adsorption using commercial activated carbon is the most commonly used method due to highly porous nature and high adsorption capacity resulting from high surface area of the activated carbon surface. But due to its high cost and 10-15% loss during thermal regeneration, alternative low-cost adsorbents have attracted the attention of several investigators. So, in this work further attempt also conducted the application of prepared AC on river waste water treatment.

2. Experimental

2.1. Preparation activated carbon

The moisture content of the SB and RH is estimated by keeping the samples at 105 °C in air oven until no difference in weight is observed. The samples are prepared by mixing with required ratio of KOH on dry weight of the sample. The impregnation ratio is defined as the ratio of grams of KOH per gram of dry precursor. The reagent can soak with the SB and RH overnight, so that reagents are fully adsorbed in to the raw material. After impregnation, the samples are transferred to a clean glass plate and spread as a thin layer uniformly and kept in the muffle furnace for semi-carbonization. During semi carbonization, the carbonaceous material along with the impregnation agent turns black forming a plastic mass, which turns into a dry powder on continued, heating at 200 °C. The semi-carbonized materials are taken out of the furnace and the furnace is set for higher temperature. After the furnace attained the set temperature the semi-carbonized material is kept in the furnace for activation. After activation at the required temperature the activated material is repetitively washed with distilled water to recover all the unwanted waste from material. The washed material is neutralized with sodium hydroxide solution and later washed thoroughly with distilled water. The product is dried in hot air oven for 4 to 5 h at 105 °C and subjected to size reduction. The dry material is powdered to 300 μm size and subjected for characterization.

2.2. Characterization of the activation carbon

The activation carbon is characterized for yield and iodine number. The yield is defined as the ratio of the weight of activated carbon to the weight of the sawdust used for activation. The IN indicates the porosity of the activated carbon and it is defined as the milligrams of iodine adsorbed per gram of carbon. IN can be used as an approximation for surface area. This was done according to the ASTM D 4607-94 method. 0.1 M sodium thiosulphate solution was titrated against 20.0 ml carbon sample solution (prepared by centrifuging 0.5 g of the AC sample in 25.0 ml of 0.097 M iodine solution). Freshly prepared starch solution (5ml) was used as indicator. Similarly, the quantity of thiosulphate needed to titrate 20.0ml of the blank solution was determined. Each titration was carried out in triplicate and the average titre used in calculating the IN using following equation

$$\text{IN} = (V-x / y) * V/W * M \text{ (mg of Iodine / g of carbon sample)} \quad (1)$$

Where x = volume of the thiosulphate used for carbon free aliquot, y = volume of thiosulphate used for blank solution, W = weight of sample, M = molarity of iodine solution used, and V = volume of iodine solution used for titration.

The moisture content was found by oven-drying test method (ASTM D2867 – 09). A sample of carbon is put into a dry, closed capsule (of known weight) and weighed accurately. The capsule is opened and placed with the lid in a preheated oven (145 – 155 °C). The sample is dried to constant weight then removed from the oven and with the capsule closed, cooled to room temperature. The closed capsule is weighed again accurately. The percentage difference of weight is expressed as the moisture content of the sample. The percentage of volatile matter of the AC samples was determined by the standard method (ASTM D5832 – 98). Approximately 1.0 g of the sample was taken in crucible with cover (of known weight). The covered crucible was placed in muffle furnace regulated at 950 °C for 7 min. Then the covered crucible was cooled to room temperature in a desiccator and recorded the weight. The percentage weight loss was regarded as the percentage of volatile matter. To determine the ash content, dried sample of activated carbon weighed to the nearest 0.1mg was taken into the crucible (of known weight). The crucible was placed in the muffle furnace at 650 °C and ashing was completed when constant weight is achieved. The crucible is cooled to room temperature in a desiccator and the percentage weight of the sample remained was considered as ash content (ASTM D2866 – 94). Fixed carbon is a calculated value and it is the resultant of summation of percentage moisture, ash, and volatile matter subtracted from 100.

$$\text{Fixed carbon (\%)} = 100 - (\text{moisture, \%} + \text{ash, \%} + \text{volatile matter, \%}) \quad (2)$$

The ultimate analysis or elemental analysis was carried out by using CHNS analyzer (Elemental Vario EL CUBE). The percentage of oxygen was calculated by the difference as follows.

$$\text{Oxygen (\%)} = 100 - (\text{C, \%} + \text{H, \%} + \text{N, \%} + \text{S, \%}) \quad (3)$$

The yield of activated carbon (AC) was calculated on a chemical-free basis and can be regarded as an indicator of the process efficiency for the chemical activation process. The yield of AC is calculated as the percentage weight of the resultant activated carbon divided by weight of dried bio waste.

$$\text{Yield (\%)} = (\text{weight of AC} / \text{weight of dry bio waste}) * 100 \quad (4)$$

The adsorption study was performed in a batch system containing 1 L of the water sample from cooum adyar river, Chennai, India. The sample was used for analysis of volatile fatty acids, Total nitrogen total phosphorus, Cd (II) and manganese. 5g prepared activated carbon was put into 500 ml of the effluent water. This was then stirred continuously for 12 h and the samples were filtered before analysed. Organic compounds strongly will adsorbed on AC. Consequently, total nitrogen, Volatile fatty acids, and total phosphorus were analysed. Nitrate as nitrogen was determined by the cadmium reduction metal method ASTM 8036. The adsorption of heavy metals (cadmium and manganese) on carbon aerogel was studied by batch technique. A known weight of adsorbent (5g adsorbent) was equilibrated with 100 ml of the heavy metals solution of known concentration in a stoppered borosil glass flask at a fixed temperature in a thermostatic mechanical shaker (WIDSONS Scientific) for a known period 2h of time. After equilibration, the suspension of the adsorbent was separated from solution by filtration using Wattman No. 1 filter paper. The concentration of heavy metal ions remaining in solution was measured by AAS (GBC 932 AA) using flame method. Determination of volatile fatty acids was done by a spectrophotometric method. The spectrophotometric procedure is based on the well known colorimetric ferric hydroxamate method. Aqueous sample 5 ml was taken into a dry test-tube, and then after the addition of 1.5 ml ethylene glycol reagent and 0.2 ml of 19.5N sulphuric acid the mixture was heated for 3 min in a boiling bath. Then, the content of the test-tube was immediately cooled in cold water. After cooling, 0.5 ml of 10% hydroxylamine hydrochloride solution, 2 ml of 4.5 N NaOH solution and 10 ml of 10% ferric chloride solution were added. The absorbance was measured at 495 nm by spectrophotometer. The standard solutions of acetic acid (1200 mg/L CH₃COOH) were diluted with deionised water to obtain appropriate concentrations in the range of 10 to 1200 mg/L. Phosphorus analyses represent two general steps: (a) Conversion of the phosphorus form of interest to dissolved orthophosphate and (b) colorimetric determination of dissolved orthophosphate into amicro-Kjeldahl flasks. Measure a 5ml sample and add 1ml conc.H₂SO₄ and 5 ml Conc.HNO₃. Digest to a volume of 1ml and then continue until solution becomes colourless to remove HNO₃ - Cool and approximately 20ml distilled water. 0.05 ml (1drop) phenolphthalein indicator, and as much 1N NaOH solution as required to produce a faint pink tinge. Transfer neutralized

solution filtering if necessary to remove particulate material or turbidity, into a 100-ml volumetric flask. Add filter washings to flask and adjust sample volume to 100ml with distilled water. Determine phosphorus by following equation

$$\text{Mg of phosphorus/ml of sample} = (\text{mg of P (in app. final volume)} \times 1000) / \text{ml of sample (5)}$$

3. Results and Discussion

3.1 Properties of rice husk and sugarcane baggase-derived Activated Carbon

From the CHNS (elemental analysis) analysis and proximate analysis it was clearly seen that there was not much difference in the fixed carbon content. Thus, both are practical options for activated carbon production. From the proximate analysis Volatile Matter, Ash Content, Moisture Content was high which may be due to its plant origin. High carbon content is a favourable property of the starting carbonaceous material to be used to produce AC.

Table 1: Proximate analysis of RC-AC (wt %) and SB-AC (wt %)

Component	RH-AC (wt %)	SB-AC (wt %)
Volatile Matter	57.7	31.3
Fixed Carbon	21.7	35.1
Ash Content	20.0	15.5
Moisture Content	0.6	18.1
Total	100%	100%

Table 2: Elemental analysis of Rice husk AC (wt %) and Baggies AC (wt %)

Element	RH-AC (wt %)	SB-AC (wt %)
Carbon	48	29
Hydrogen	5	4.3
Oxygen	38	15.5
Nitrogen	0.6	0.5
Sulphur	0.2	0.21
Chlorine	0	0.19

3.2 Effect of concentration of KOH solution used for producing activated carbons on its iodine number and yield.

The IN and yields (%) of AC prepared from RH and SB are presented in Fig. 1. The iodine values of activated carbons produced had an optimum value of 639.5 mg/g, and the corresponding KOH concentration was 3N. When the concentration was decreased to 1 N, the iodine value was relatively low because of insufficient KOH to react with the sludge to efficiently create the internal pore structures. However, if the concentration of KOH was as high as 4 N or more, the micropore structure of activated carbon deteriorated due to excessive carbonization. The yield of product decreased steeply from 18.0 to 8.0% in the concentration range with increasing iodine value, which may probably be due to the formation of more micropores in the product. The extent of decrease in product yield was lower at higher concentrations of activating agents. In all, we considered the KOH concentration of 3 N to be optimum. Hence, it was used in subsequent experiments.

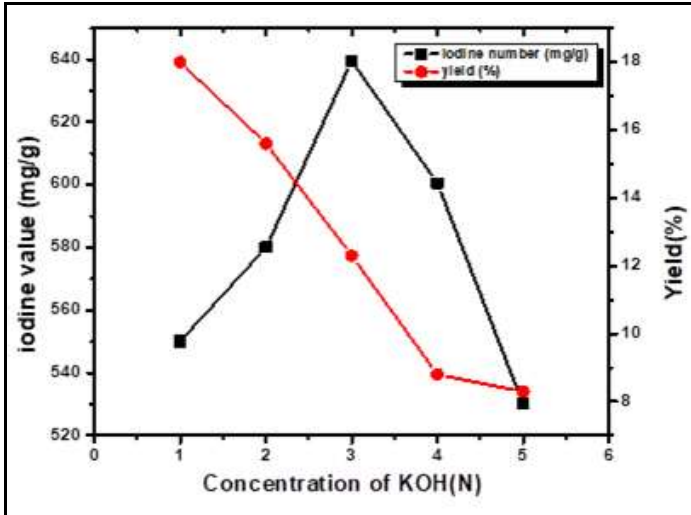


Fig.1: Effect of concentration of activating agent on iodine number and yield of activated carbon (rice husk).

The similar effect also observed on SB based AC. The KOH concentration of 3 N to be optimum and corresponding iodine number was 670.4 mg/g that s shown in Fig.2.

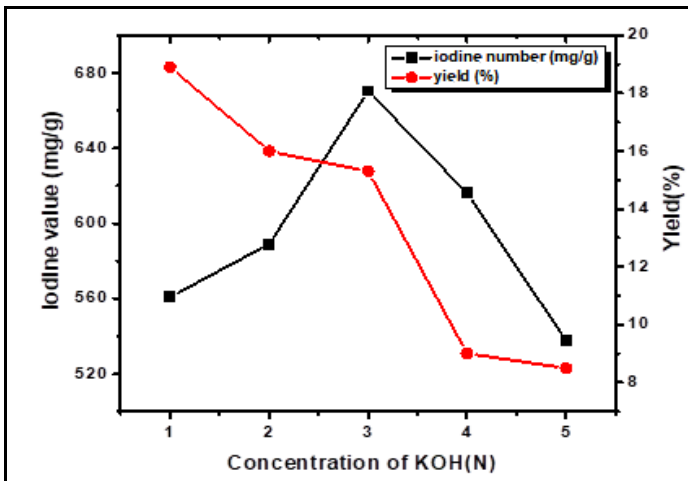


Fig.2: Effect of concentration of activating agent on iodine number and yield of activated carbon (sugarcane baggase).

The IN is the amount of iodine, in milligrams, adsorbed per gram of carbon when the equilibrium concentration (C_e) of iodine is 0.02 M. It has been established that the iodine number in mg/g gives an estimate of the surface area in m^2/g^7 . The removal of iodine by the activated carbons is related to their porosity characteristics which determine the degree of accessibility of these molecules. A lower iodine number can be ascribed to the presence of pores narrower than 1.0 nm, which make up most of the structure of these carbons⁸. Iodine number can be typically used as a measure of the micropore (less than 2 nm).

3.3 Effects of activated carbon on river waste water treatment

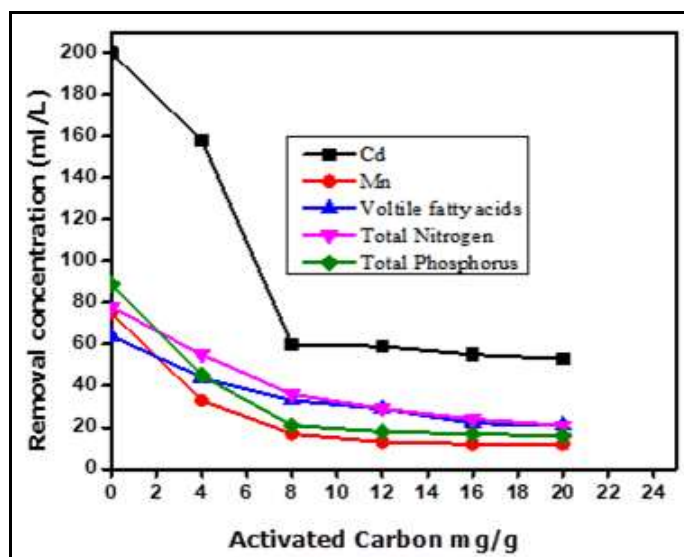


Fig. 3: Effect of sugarcane baggase activated carbon on treatment of waste water in concentration (ml/L).

Effect of SB-AC on treatment of waste water in concentration (ml/L) presented in Fig. 3. Cadmium concentration in the waste water from 280 ml/L into 60 ml/L was achieved. The amount of AC increased after 8g there is no significant effect was found on removal cadmium concentration, i.e., 8g of SB-AC was optimised for cadmium removal of 1L of river waste water. Similarly, at 16g of SB-AC the waste water concentration of 90, 80, 78, and 62 ml/L of total phosphorous, total nitrogen, manganese, and volatile fatty acids reduced into 17, 20, 20 and 15 ml/L respectively. There is no significance effect was found further the addition SB-AC on treatment of waste water. As a result, the prepared AC is significantly influenced on removal of pollutants in waste water.

4. Conclusion

The results of this study show that it is feasible to prepare activated carbons with relatively adsorption capacity and yield (%) from bio waste (sugarcane baggase and rice husk) by direct chemical activation. To characterise AC; iodine number, proximate analysis and ultimate analysis are conducted. Followed by prepared AC was used for treatment of waste water. The iodine number of the activated carbon product increased with concentration of KOH solution (up to 3 N). After, as the impregnation concentration increase iodine value decline sharply. The iodine number for rice husk and sugarcane baggase is 639.5 and 670 mg/g, respectively. According to Thai Industrial Standards Institute, the standard iodine number for a commercial activated carbon must not be lower than 600 mg/g. Thus, the synthesis of AC from bio waste with chemical activation using KOH as the activating agent has a potential to be developed to a commercial scale. As an experimental result on AC would be quite useful in developing an appropriate technology for the removal of heavy metal ions and organic compounds from waste water.

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