

High Surface Area Activated Carbon from Waste Biomass

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Abstract

The present work relates to efforts made towards developing a high surface area, activated carbon from rubber wood sawdust by a two-stage activation process with phosphoric acid as the activating agent. Experiments are conducted in lab scale using muffle furnace under static conditions in a self-generated atmosphere covering process parameters such as impregnation ratio, carbonization time and temperature. The process parameters are characterized and optimized based on the product yield and iodine number. The first stage activation at 200 °C for 15 minutes followed by second stage activation at 500 °C for 45 minutes with impregnation ratio of 1.5 yielded a product with iodine number 1096 with the product yield of 35%. The surface area is analyzed using BET method and found to be 1496 m²/g.

Keywords

activated carbon, saw dust, rubber wood, phosphoric acid

Introduction

Activated carbons are high porosity, high surface area materials manufacture by carbonization and activation of carbonaceous materials. Activated carbons are extensively used in industrial sector for adsorption of pollutants from gaseous and liquid streams. Number of patents on manufacture of activated carbon exists, using a wide range of processing equipment's and process routes. Each route has its significance depending upon the application of activated carbon. Activated carbon is characterized mainly by its adsorption capabilities of various organic and inorganic matters. The pore size distribution plays an important role in the selection of activated carbon for specific applications. Micro pore region implies an average pore diameter of less than 10 Å, macro pore higher than 1000 Å and the meso pore region is in between the micro and macro pore regions.

Activated carbon is manufactured from materials of vegetable sources, which contain appreciable amount of carbon. Manufacture of activated carbon from bio-wastes is gaining significance; as high valued product could be effectively manufactured from almost zero cost raw materials. This also proves a solution for disposal problems of the waste bio mass. 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 pretreatment 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 has to be carried out at very high temperatures

(800 to 1000 °C) as compared to chemical activation (400 to 600 °C). Chemical activation methods later came in to practice where dehydrating chemicals are used for the purpose of activation. Several dehydrating agents like KOH, NaOH, H₃PO₄, ZnCl₂, Na₃PO₄, NaCl, KmnO₄, were used on various raw materials to yield appreciable quality of activated carbon. Among the several dehydrating agents, zinc chloride and phosphoric acid are widely employed for commercial manufacture due to its excellent dehydration characteristics. Although zinc chloride activated carbon can be used as decolorizing carbon, its limitation is felt in food and pharmaceutical industries due to contamination problems. Activated carbon manufactured using phosphoric acid activation route is gaining significance due to its application in sugar refining, food and Parma industries.

Ruiz bevia, et al., [1] studied the effects of different parameters on activation of almond shells with different activating agents such as H₃PO₄, ZnCl₂, K₂CO₃ and Na₂CO₃. They concluded that ZnCl₂ to be the best activating agent for almond shell and the impregnation ratio was found to be the most effective parameter to increase the absorptive power of the carbon. A maximum of 74% reagent recovery was reported. The experiments were carried out in oxygen absent nitrogen medium. Khan and Harbans [2] studied the activation of walnut shells using zinc chloride and phosphoric acid wherein the raw material was digested in reagent solution and activated at 500°C. Zinc chloride was found to be better activating reagent than phosphoric acid based on the quality of the product. Buerge and Alex [3] studied the activation of wood shavings with 50% phosphoric acid in a two-stage process. The mixture was heated for 20 minutes at 170°C followed by activation at 450°C in vapor stream containing 6vol% oxygen for 15 minutes. The product was used to bleach molasses. Kirubakarn et al., [4] studied chemical activation of coconut shell in a laboratory scale static and fluidized bed reactor. The effect of process variable such as time of activation, particle size, temperature, impregnation ratio, fluidizing medium on the yield and quality of activated carbon were studied. Increase in Iodine number and Phenol number was observed up to 1.5 times impregnation ratio beyond which there was no appreciable change in the quality for both H₃PO₄ and ZnCl₂. Zinc chloride was found to be better activating agent than phosphoric acid. The activation temperature was 500°C for 2 hours in a nitrogen medium. No mention was made on the amount of reagent recovered. However Ruiz bevia et al. [1] observed an increase in quality of the product up to an impregnation ratio of 2.

Hassler [5] described activation as a two-stage process. In the first step the macro sized linear chained cellulosic structure with unsaturated hydrogen, oxygen and inorganic elements gets transformed into graphite like crystallographic carbon structure with irregular interstices in between filled by tarry material. The starting material when treated at elevated temperature with activation agent, the cellulosic and other components present are degraded and a plastic mass is formed. In the second stage, activation agent reacts with cellulosic material to change the chemical nature. At high temperature dehydration assists decomposition of organic substances and prevents formation of non-carbonized degraded product. Further at higher temperature the volatilization of tarry material and release of carbon results in porous carbon of high surface area. However Ruiz bevia et al., [1] and Kirubakaran et al., [4] carried out activation in a single stage process. The impregnated raw material is dried around 110°C before activation.

Taking into consideration all the previous work Toles et al., [6] carried out a comprehensive study on the activation of pecan, almond, black walnut, English walnut and macadamia nut shell using phosphoric acid. Based on the literature Toles et al., [6] has classified the activation as standard, continuous, air activation, quench and modified quench covering single stage activation, two-stage activation, air activation and non-air activation methods. The quench method of activation in which the activated material is quenched in a bath of distilled water was found to give higher surface area for all materials as compared to other methods. In the quench method materials were kept at 170°C for 0.5 to 1 hour followed by activation at 450°C whereas in the modified quench method; material after kept in the oven temperature is rammed to 450°C. The work has proved activation only in non-oxygen atmosphere to produce good quality and high yield product was a misconception. Further no significant difference between single stage and two-stage activation was observed.

The present work is an attempt to develop a process for surface area activated carbon from rubber wood sawdust using chemical activation method in particular to phosphoric acid in a self-generated atmosphere. Although no discernible product quality was reported between single stage and two-stage activation process, the present study follows a two-stage activation process due to operational convenience in commercial manufacture. The study covers the effect of operating parameters such as the time and temperature of activation and impregnation ratio on the product quality. The product quality is characterized based on the yield and iodine number. The BET surface area is found for sample that produced highest iodine number.

Experimental

The moisture content of the sawdust 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 phosphoric acid based on dry weight of the sample. The impregnation ratio is defined as the ratio of grams of phosphorous per gram of dry precursor. The reagent is allowed to soak with the sawdust 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. The muffle furnace has the facility to heat the material from ambient temperature to 950°C and the temperature is controlled to an accuracy of $\pm 5^\circ\text{C}$ by means of a temperature controller. 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 acid from material. The reagent recovery is estimated using acid base titration as well as using the density of recovered reagent. Around 7 to 8 washings are required to remove all the acid content from the 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 hours at 105°C and subjected to size reduction. The dry material is powdered to 300 μm size and subjected for characterization.

Characterization of the product

The end product 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 iodine number indicates the porosity of the activated carbon and it is defined as the milligrams of iodine adsorbed per gram of carbon. Iodine number represents the surface area contributed by the pores larger than 10 Å (EPA manual 1973, Bansal et al., 1988). Iodine number can be used as an approximation for surface area. The surface area is predicted by BET technique using surface area analyzer (micromeritics ASAP2000).

Results and discussion

Hassler [5] reported that during semi-carbonization along with moisture content volatile matter releases from cellulose structure accompanied by grouping of carbon into lattice arrangements. The yield and pore formation depends on the lattice arrangement of carbon in aromatic structure. The semi carbonization temperature is indicated to be around 170 °C. Toles et al., [6] carried out semi-carbonization for 0.5 to 1 hour at 170 °C and activated the material at 450 °C. These data's were compared with single stage activation process and reported that there is no need for separate semi-carbonization stage. However they admitted that the material would have had enough time to semi carbonize since the time taken to raise the temperature to 450 °C took more than 45 minutes.

In the present study semi-carbonization stage is demarcated from activation stage as the point at which depolymerised cellulosic material dries to powder form. Since the impregnated raw material during semi carbonization stage transforms in to a plastic like mass, the commercial manufacture demands a specialized equipment to overcome this stage as compared to second stage of activation which deals with dry free flowing powders. Due to the above-mentioned reasons the importance of semi-carbonization stage is considered and the present work follows a two-stage activation process.

The optimum activation temperatures have been reported to be between 400 to 500 °C by most of the earlier researcher irrespective of the time of activation and the impregnation ratio for different precursors. Table 1 and 2 presents the effect of activation temperature and duration of activation for an impregnation ratio of 1.5. An increase in iodine number is observed with increase in activation time up to one hour for activation temperatures of 400 °C, with maximum attained iodine number of 810. However at 500 °C the iodine number is found to reach a maximum of 1096 at 45 minutes of activation time and decrease with further increase in activation time. The yield is found to decrease with either increase in activation time or temperature with 35% yield for the sample corresponding to highest iodine number. The lower activation time as well the temperature results in incomplete burn off resulting in higher yield. The BET surface area corresponding to the experiment 5 and 6 correspond to 1496 and 1312 m²/g. The reduction in surface area beyond the optimum activation time is generally attributed to the increase in the pore size leading to collapse of the small pores.

Table 1. Activation temperature: 400 °C; Impregnation Ratio : 1.5

| Experiment No. | Activation time | Yield | Iodine number |
|----------------|-----------------|-------|---------------|
| 1 | 30 | 63 | 653 |
| 2 | 45 | 68 | 717 |
| 3 | 60 | 53 | 810 |

Table 2. Activation temperature: 500 °C; Impregnation Ratio : 1.5

| Experiment No. | Activation time | Yield | Iodine number |
|----------------|-----------------|-------|---------------|
| 4 | 30 | 37 | 1015 |
| 5 | 45 | 35 | 1096 |
| 6 | 60 | 33 | 334 |

Table 3 presents the effect of impregnation ratio of 1 and 2 at 500 °C for activation time of 45 minutes. It can be observed from the table that the impregnation ratio of 1 as well as 2 yields an activated carbon with iodine number of 892 and 958 much lower than one obtained at impregnation ratio of 1.5. The yield corresponds to 37 and 34%.

Table 3. Activation temperature: 500 °C; Activation time 45 min

| Experiment No. | Impregnation ratio | Yield | Iodine number |
|----------------|--------------------|-------|---------------|
| 7 | 1.5 | 37 | 892 |
| 8 | 2 | 35 | 1096 |
| 9 | 2.5 | 34 | 958 |

Conclusion

A detailed study on the process for activated carbon from rubber wood saw dust using phosphoric acid as activating agent has been carried out. The necessity for a two-stage process as compared to single stage process is highlighted with semi carbonization carried out at 200 °C for 15 minutes. The optimum condition for activation is found to be 500 °C and 45 minute with impregnation ratio of 1.5. The sample corresponding to optimum condition is found to yield a product with 35% yield and iodine number of 1096, which corresponds to a BET surface area of 1496 m²/g, which is much higher than many of the commercially available activated carbons.

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