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Development of micro-mesoporous carbons from several seed hulls under varying conditions of activation

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ABSTRACT

Seed hulls (or coats) of peanut, soybean, cottonseed, lupine, broad beans, and sunflower seeds, were subjected to various treatments in order to get adsorbing carbons. Characterization of porosity was determined by N_2/77 K adsorption isotherms. Simple pyrolysis at 500 °C yields low adsorbing carbons of meso-/macroporous character, whereas steam activation of these chars at 850 °C enhances porosity, in micropores, to a limited extent. Chemical activation with H_3PO_4 at 500 °C exerts the best recommending influence in producing high adsorbing carbons with evenly distributed porosity within micro-mesopore ranges. It was found that phosphoric acid activation of the studied precursors enhanced the yield, surface area and pore volume; 32–46%, 437–1022 m^2/g and 0.444–0.809, respectively, as compared to other treatments. The capacity to remove methylene blue, in single bottle experiments, complements the state of porosity deduced from the gas phase adsorption of N_2. Peanut shells proved the best feasible raw material under all treatment processes, whereas lupine seeds and sunflower seed hulls show relatively the least affected. Dye removal capacity was enhanced by carbon mesoporosity, whereas adversely affected by its increased surface pH and ash content was observed. Low-cost by-products of oil producing industry seem, thus, to be promising precursors for the production of highly valuable adsorbing carbons.

1. Introduction

During the last few decades, there has been growing public concern and awareness regarding the environmental pollution problems. This urged research to device more effective processes for the control and remediation of contamination from its sources, or at its disposal ports to the atmosphere or to the water streams. Adsorption by active materials emerged as one of the best available technologies for this purpose. Carbon adsorbents proved to be of the most efficient materials and were implemented in several countries since many decades allover the world. This type of adsorbents is characterized by well-developed and extensive porosity as evaluated by both the specific surface area and internal porosity. Being non-selective in nature, they find diverse applications in several disciplines of purification and decontamination from both liquid and gas phases. The adsorption capacity of the activated carbons, which is related to the pore structure and the pore size distribution, is largely pre-determined by the nature of the starting material and the history of pyrolysis [1].

Feedstocks for the production of carbon adsorbents were known to be traditionally from three main sources: wood, coal, and coconut shells [2]. It is unreasonable to depend on wood, as the destruction of wood trees is deleterious to the environment as they play a very important role in the balance of atmospheric carbon dioxide. The falling down of woods in many countries caused serious and adverse effects on the ever-prevailing environmental conditions. Coal also plays a keystone as fuel material and thus will diminish by time, and then we should need other feedstocks for the production of carbon adsorbents. Although coconut shells are very favourite raw materials for the production of good adsorbing carbons, yet they are not widely planted except in limited areas and grown under special ecological conditions. It should be noted that a large number of environmentally-concerned countries are joining the international control and remediation club. Most of these countries cannot pay the bill of the advanced decontamination schemes because of the expensive activated carbon systems. This urged the search for locally available, low-price, feedstocks, as well as generation of low-cost technologies for its production, in order to satisfy the increase in demanding and pressing needs for this material.

Accordingly, research has been directed towards the utilization and upgrading of the already available biomass materials from plant origin for the production of carbon adsorbents. These are generated in huge amounts as direct field wastes or consequent to agricultural manufacturing processes, and are meanwhile renewable sources with high carbon and low ash contents. A large

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variety of these source materials has been investigated and reported, e.g. wheat straw [3], banana pith [4,5], sugar cane bagasse [6], rice husks [7], apricot stones [8], oil palm waste fibers [9], date pits [10,11], macadamia nutshells [12], Moringa Oleifera seed hulls [13–15], peach stones [16], cotton stalks [17], soybean hulls [18], rubber seed and palm seed coats [19], pecan shells [20], sunflower stalks [21], and olive oil mill wastes [22].

Carbon adsorbents in various forms can be produced by either thermal or chemical routes. The thermal (or physical) and most common route involves a two-step process; carbonization followed by activation via partial gasification. The sequence is intended to preserve and further develop the pore structure which is inherent to the raw material [23]. For the most part, the reactions are thermally driven. Carbonization is usually conducted at 500–700 °C, where most organic solids undergo reactions leading to the loss of hydrogen and the formation of free radicals which condense to form a rigid cross-linked char. The process causes some increase in porosity, although this is generally insufficient for practical uses, and serves to modify the inherent pore structure to the precursor, as opposed to creating it. This is why the structure and properties of porous carbons are strongly dependent on starting material. Similarly the activation process helps to develop further this structure by the selective gasification of carbon at 850–1100 °C in a stream of steam or carbon dioxide. The removal of carbon atoms increases both the average size of the micropores already accessible to the gas and opens up closed porosity. The principal changes in pore structure with progressive gasification concern the micropores (<20 Å diameter), while changes in the mesoporous (20–500 Å diameter) and macroporosity (>500 Å) are small [2,23]. The second commercial route involves the reaction of a precursor, usually cellulosic, with chemical reagents such as zinc chloride or phosphoric acid in a single heat treatment process. In the chemical activation process, e.g. with H_3PO_4, the temperature of activation is comparatively low, around 400–600 °C, and the volatile losses are low. The relevant reactions primarily involve attack on the cellulosic structures in the precursor. Water is eliminated and cross-linking with increased aromatization is promoted during carbonization. The effect of cross-linking is to bond otherwise volatile products into the precursor structure before reaching the pyrolysis temperature, with consequential increase in the carbon yield and reduction in tar formation. The promotion of cross-linking is somehow related to the development of an extensive pore structure without need of consequent activation in steam or CO_2. Cross-linkage is believed to inhibit shrinkage during heat treatment and help to create the micropore system [11,24–27]. The pore size distribution of the carbon is reported to be dependent on the ratio of chemical activant to precursor (impregnation ratio). A high ratio leads to wider microporosity and more developed meso- and macroporosity.

Activation with phosphoric acid has many advantages over the traditional "physical" methods, as it involves only one heating step, achieved at much lower temperatures, most of the acid used is easily recovered, and the yield of active carbon is mostly higher (40–50%) since the burn-off process encountered at high temperatures (in oxidizing atmospheres) is avoided [6]. This explains the increased studies and special attention, with regards to activation with H_3PO_4, during the last decades as applied to a large number of lignocellulosic materials [6–8,10–12,17,20].

Seed and bean hulls seem to be of the least considered agricultural by-products as renewable carbon precursors, except rice husks. They are generated as by-products in edible oil mills or in other food processing operations and are usually sold to animal feed formulations as low value products. It is now highly desirable to upgrade these by-product source materials by added-value processes that lead to potentially good adsorbents of high economic value. Meanwhile, it is also important to obtain carbon adsorbents in cost-effective processes, which depend on two factors: low-cost precursors and low-cost schemes of preparation.

In the present investigation six discard lignocellulosic materials, from seed and bean hulls (or coats) of different sources, are employed. They are subjected to three thermal treatment processes under optimized conditions: simple carbonization (or devolatalization) at 500 °C, further steam activation at 850 °C, or chemical activation with H_3PO_4 at 500 °C. This aims to demonstrate many aspects: (1) the suitability of these by-products to obtain adsorbing carbons, (2) the best scheme to develop active products as assessed by their surface area and porosity characteristics, (3) capacity of the obtained carbons for the uptake of a standard dye (methylene blue) from aqueous solution, and (4) the most feasible precursor for producing the best adsorbing carbons. In addition this helps to realize two environmental aspects: the economic disposal and utilization of undesirable residues, and to produce an industrially valuable substance for the water/gas treatment purposes, and others.

2. Experimental

2.1. Preparation of carbon adsorbents

Six carbon precursors were utilized; these are oil seed hulls of soybean, cottonseed, sunflower, and peanut, as well as bean coats of lupine and broad beans. The washed dried by-products were milled and the grain size of 0.5–2.0 mm was employed. Three standard schemes of treatment were applied for each waste material as follows: (1) static pyrolysis at 500 °C for 2 h in absence of flowing air (C-series), (2) steam activation, of the above obtained char, at 850 °C under a flow of steam/N_2 for 2 h (S-series), and (3) chemical activation of raw materials with H_3PO_4 which involved soaking with 50% H_3PO_4 and leaving overnight followed by pyrolysis at 500 °C for 2 h (P-series). Previous experience demonstrated that temperatures around 500 °C are efficient to produce maximum development of porosity, although carbonization of the material may be incomplete [6–8,11,17,22,25]. The cooled acid-treated product was thoroughly washed with hot water so as to remove the residual acid until the washings attained a $pH \leqslant 6.5$.

Treatment in the three procedures of preparation was achieved by using a stainless steel reactor tube (40×600 mm) with narrow screw cap openings ($\sim$10 mm) to admit steam and/or to vent evolved gaseous or liquid products. A perforated disc, welded near the end of the tube, prevents falling of the thermally treated material as the process was carried out in a sloping position in order to dispose of the tarry matter. A temperature-controlled tube furnace was employed for the pyrolysis process. The observed values for yield under the three schemes, as well as the ash content for each product, are given in Table 1.

2.2. Characterization of the prepared carbons

An automatic sorptometer was utilized to determine the adsorption isotherms of N_2 at 77 K. Prior to adsorption measurements the carbon samples were subjected to degassing under a pressure less than 10^{-4} mmHg at 200 °C. The adsorption data were analyzed by applying several established procedures in order to get various texture characteristics of the adsorbents under consideration.

1. Surface area by the BET-method (S_{BET}), and the total pore volume (V_p) from the volume adsorbed at a relative pressure of 0.95. An estimate for the average pore radius was calculated by $\bar{r} = 2V_p/S_{BET}$.