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Colloids and Surfaces A: Physicochem. Eng. Aspects 252 (2005) 143–151

COLLOIDS AND SURFACES A

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Textural properties of activated carbons from apricot stones

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Received 29 March 2004; accepted 13 September 2004
Available online 19 November 2004

Abstract

Chemically activated carbons were prepared from apricot stones. Phosphoric acid (25–75 wt.%) was used as an activating agent at 400–600 °C. Zinc chloride-activated carbon were also prepared at 600 and 700 °C using three different zinc chloride:apricot stone ratios of 0.5, 1.0 and 2.0. Steam-activated carbons were obtained by gasifying un-activated carbon obtained by carbonizing apricot stones, at 900 °C to burn-off 25 and 35%. The textural parameters were determined from the nitrogen adsorption data at 77 K. Different adsorption models were considered for the analysis of the adsorption results. Considerable differences between surface areas and pore volume as obtained by considering the different models, have been observed. However, the method of analysis based on comparing the isotherm determined for a given active carbon with the standard isotherm for a non-porous adsorbent seems to be trustworthy.

Keywords: Apricot stones; Activated carbon; Phosphoric acid; Zinc chloride; Steam activation

1. Introduction

Activated carbons are non-specific adsorbents and therefore find wide application in the removal of colour [1–3], odour [4,5], toxic gases [6,7] etc. Activated carbons are now in use for the treatment of potable water [8,9] and waste water [10,11], particularly for the removal of heavy metals [12–15]. The adsorption properties of activated carbons are essentially attributed to their large surface area, large total pore volume, high degree of surface reactivity and favourable pore size distribution [16,17]. The texture (surface area and porosity) of activated carbons can be easily modified or even tailored to suit a specific application [18]. The chemistry of the surface of activated carbon also plays a dominant role in determining its adsorption properties and consequently its use [19,20]. It is also possible to modify the surface chemistry of activated carbons by controlling the amount and strength of the surface functional groups particularly those of the carbon–oxygen type [21,22].

Two conventional methods exist for the preparation of activated carbons from a carbonaceous material. These are: (i) chemical activation, which is based on the carbonization in a limited supply of air or in an inert atmosphere of a mixture of a carbonaceous material and an activating agent (zinc chloride or phosphoric acid) at some intermediate temperatures (400–700 °C), followed by washing and drying [23,24]. (ii) Physical activation based on gasification at a relatively high temperature (900–1000 °C) with an oxidizing gas (steam or carbon dioxide) of a non-activated carbon to certain percentage of burn-off [25]. Cheap raw materials have been recommended for the preparation of activated carbons. Agricultural by-products, which exist in large amounts, represent a solid pollutant to the environment. Many years ago these by-products were used as a fuel in rural areas but now they do not find any application of commercial interest. The preparation of activated carbons from agricultural by-products has therefore been encouraged, since they are cheap precursors and their use in this manner would prevent their accumulation.

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doi:10.1016/j.colsurfa.2004.09.008

Among other countries, Egypt is rich in many agricultural by-products that can be used for the preparation of activated carbon, viz., cotton stalks and corn stalks, rice straw and rice husks, corncobs, date pits, some fruit stones, some nutshells and olive stones. Apricot stones have been used in the present study for the preparation of activated carbons, following impregnation with different percentage of phosphoric acid (25–75 wt.%) or zinc chloride (33–66 wt.%), activation was performed at different temperatures between 400 and 700 °C. Two physically activated carbons were also prepared by gasifying non-activated carbon (prepared by carbonizing apricot stones at 600 °C), with steam at 900 °C to burn-off 25 and 35%. The textural properties of the resulting activated products were determined from nitrogen adsorption studies at 77 K. The adsorption data have been analyzed in terms of different theories and methods of textural analysis.

2. Experimental

2.1. Materials

Dried ground apricot stones were first washed thoroughly with water and then dried again at 383 K. After cooling to room temperature, they were soaked for 72 h in the solution of the activating agent. Activation with phosphoric acid was carried out using various concentrations in the range 25–75 wt.% with occasional shaking. Activation with zinc chloride was carried out using different ratios of zinc chloride to apricot stones = 0.5, 1.0, 2.0 and the appropriate amount of zinc chloride was dissolved in the least amount of distilled water. The treated stones were then filtered and dried to constant weight at 343 K. The dried treated samples were then carbonized in absence of air at temperatures between 400 and 600 °C for phosphoric acid-treated stones and at 600 and 700 °C for zinc chloride-treated stones. The carbonized phosphoric acid-treated products were washed with distilled water until the pH of the resulting wash was ca. 6.0. In the designation adopted below for these carbons, "A" denotes apricot stones and "P" indicates treatment with phosphoric acid, the arabic number following the letter P gives the wt.% of phosphoric acid employed, while the arabic number following the dash gives the carbonization temperature. Thus, for example, AP50–600 stands for an activated carbon prepared from apricot stones by activation with 50 wt.% phosphoric acid followed by carbonization at 600 °C. The carbonized zinc chloride-activated products were washed with 10% hydrochloric acid and then with distilled water until the resulting wash was Cl^--free. In the designation adopted for these carbons, the letter "Z" indicates treatment with zinc chloride, the arabic number following the letter Z gives the zinc chloride/apricot stone ratio, while the arabic number following the dash gives the carbonization temperatures. Thus, for example, AZ0.5–700 stands for an activated carbon prepared from apricot stones by activation with zinc chloride (zinc chloride/apricot stones = 0.5), followed by carbonization at 700 °C. Steam-activated carbons were prepared by gasifying 600 °C, precarbonized apricot stones A-600, with steam at 900 °C to burn-off 25%, giving AS25 or to burn-off 35% giving AS35, where the letter "S" indicates steam activation and the arabic numbers following directly this letter give the percentage burn-off.

3. Techniques

The adsorption of nitrogen at 77 K was determined using a conventional volumetric apparatus. Prior to such measurements, the solids were heated over night at 523 K under high vacuum (10^{-5} Torr).

4. Results and discussion

The adsorption of nitrogen at 77 K proved to be rapid with the equilibrium being attained within less than 40 min at relative pressures less than 0.1 and in less than 20 min at higher relative pressures. This indicates that almost all the pores were accessible to nitrogen molecules at 77 K, this being true for all the carbons investigated. The desorption point were found to lie on the same isotherm as the adsorption data, indicating the absence of hysteresis characteristic of mesoporosity or specific interaction [26], however, AS35 is an exception where pronounced closed hysteresis loop was exhibited. Fig. 1 depicts representative nitrogen adsorption isotherms. With the exception of steam-activated carbons (AS25 and AS35), all the other isotherms are Langmuirian in shape being typical type I in the BDDT classification [27], which is characteristic of adsorption on a microporous adsorbent. On the other hand, the nitrogen adsorption isotherms of AS25 and AS35 are of type II in the same classification.

Application of the Langmuir equation [28,29] was satisfactory and was found to cover a wide range of relative pressure, representative linear Langmuir plots are shown in Fig. 2. Such plots enable the monolayer capacity as well as the specific surface area, S^{L} (m^2/g). The corresponding values of S^{L} obtained are listed in column 2 of Table 1. The conventional BET equation [30] was also applied over the relative pressure range $0.02 \leq p/p_0 \leq 0.2$ to determine the monolayer capacity V_{m} and hence the specific surface area S^{BET} (m^2/g) by adopting the value of 0.16 nm^2 for the cross-sectional area of the nitrogen molecule at 77 K. Representative linear BET plots are depicted in Fig. 3, while the calculated S^{BET} values for the investigated carbons are listed in column 3 of Table 1. The total pore volume V_{T} (ml/g) expressed as the volume of liquid nitrogen adsorbed per gram carbon at relative pressure of ca. 0.98 p/p_0, is listed in column 4 of Table 1. Based on the assumption that the space in the micropores is similar to the space between two parallel plates, the average pore radius $\bar{r}$ (nm) could be calculated from the relationship [31]:

$$\bar{r} = 2V_{\mathrm{T}}\frac{10^3}{S^{\mathrm{BET}}} \quad (1)$$