Available online at www.sciencedirect.com
SCIENCE DIRECT®
Bioresource Technology 97 (2006) 110–115
BIORESOURCE TECHNOLOGY

Process effects on activated carbon with large specific surface area from corn cob

Qing Cao [a,b,*], Ke-Chang Xie [a,*], Yong-Kang Lv [a], Wei-Ren Bao [a]

[a] Key Laboratory for Coal Science and Technology of Shanxi Province and Ministry of Education, Taiyuan University of Technology, Shanxi Province 030024, PR China

[b] Institute of Chemical Engineering and Technology, Taiyuan University of Technology, No. 79, Yingze West Street, Shanxi Province 030024, PR China

Received 15 June 2004; received in revised form 3 February 2005; accepted 10 February 2005
Available online 12 April 2005

Abstract

The main factors that affect the large specific surface area (SSA) of the activated carbon from agricultural waste corn cobs were studied by chemically activated method with solution of KOH and soap which acted as surfactant. The experiment showed that not only the activation temperature, activation time and the mass ratio of KOH to the carbonized material, but also the activated methods using activator obviously influenced the SSA of activated carbon. The experimental operating conditions were as follows: the carbonized temperature being 450 °C and keeping time being 4 h using N_2 as protective gas; the activation temperature being 850 °C and holding time being 1.2 h; the mass ratio of KOH to carbonized material being 4.0; the time of soaking carbonized material in the solution of KOH and soap being 30 min. Under the optimal conditions, the SSA of activated carbon from corn cobs reached 2700 m^2/g. And the addition of the soap as surfactant may shorten the soaking time. The structure of the activated carbon prepared had narrow distribution of pore size and the micro-pores accounted for 78%. The advantages of the method described were easy and feasible.

Keywords: Activated carbon; Corn cob; Biomass; Preparation; Method

1. Introduction

Activated carbons have more and more applications in many fields such as environmental protection, production of fine chemicals and medicines, processing of foods and military activities. Usually, the specific surface area (SSA) of ordinary activated carbons is 1000–1500 m^2/g. However, with the appearance of lots of new technologies such as storage of hydrogen energy, preparation of electric double-layer polar material with super high capacity and low resistance, etc., the activated carbon with ordinary SSA cannot meet these demands. Since the material and the methods used are always very important for production of activated carbon, the explorations about the materials and the methods that can contribute to enhance the SSA of activated carbon were extensively concerned in the past. Although the preparations of activated carbon with large SSA were also reported, the materials used mainly came from the exhausted resources such as coals (Yang et al., 2002), chars of petroleum (Daguerre et al., 2001). The effective use of biomass belonging in the renewable resource plays an significant role for lasting development of the social economy. In our work, the main factors influencing preparation of the activated carbon with large SSA from corn cobs were investigated.

* Corresponding authors. Address: Key Laboratory for Coal Science and Technology of Shanxi Province and Ministry of Education, Taiyuan University of Technology, No. 79, Yingze West Street, Shanxi Province 030024, PR China. Tel.: +86 0351 6018380; fax: +86 0351 6014913.
E-mail address: xieswork@public.ty.sx.cn (K.-C. Xie).

0960-8524/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.biortech.2005.02.026

The corn cobs are the by-product generated during processing corn, which is one of the most widely planted crops in the world. It was estimated that the total yield of corn arrived 6.1×10^8 t in 2001. Only in china, the yield of corn has reached 1.2×10^8 t. Since the ratio between corn grain and corn cobs may reach 100:18, a large quantity of corn cobs were generated. That is to say, the resource of corn cobs are rather abundant. Zdena et al. (1999) extracted the xylan from Corn cobs which are applicable as an additive in papermaking, textile printing and the pharmaceutical industry. Rivas et al. (2002) prepared the fermentable hydrolysate from corn cobs. Cao et al. (2004) investigated the behaviors of pyrolysis of corn cobs as energy source in fixed bed. Perotti and Molina (1988) used the corn cobs as a bacterial substrate for the production of forage protein. The preparations of ordinary activated carbon have also been reported (Tsai et al., 1998, 2001; Aggarwal and Dollimore, 1997) by combination of chemical and physical activation, but the study about how to prepare activated carbon from corn cobs with large SSA is scarce in literature. Therefore, it is necessary to develop a new approach that more effectively utilize the corn cobs and increase its added value of products for adjusting structure of products. This is our aim of the work.

2. Experimental

2.1. Materials

Corn cobs were collected in Taiyuan farm. The amount of main composition such as cellulose, hemicellulose, lignin, moisture and ash in the corn cobs used in the experiment was 35.41, 36.68, 13.01, 8.34 and 1.53 wt% respectively. The corn cobs used in the experiment were pulverized physically and sifted through 60 mesh sieve.

2.2. Chemicals and setup

KOH (AR); Muffle furnace (4 kW) with temperature controller; soap (produced by Yingze soap factory).

2.3. Preparation of activated carbon

The activated carbon with large SSA was prepared by following steps: (1) put about 10 g powdered corn cobs into the column-typed stainless steel tube of 200 ml and use N_2 as protective gas whose flow rate was 80 ml/min; (2) heated the tube to 450 °C at a rate of 30 °C/min and kept this condition for 4 h in order to carbonize the raw materials and then took it out after the furnace was cooled to room temperature; (3) treated the carbonized materials with activator for 30 min; (4) activated the carbonized materials for 1.2 h at 850 °C after drying; (5) washed the products with warm distilled water till neutralization, then, filtered, dried at 120 °C.

Three different methods were used for chemical activation using activator KOH. The first method for the activated procedure was that solid activator KOH was directly added into the carbonized materials (activated carbon obtained in this way denoted AC-01). The second method for the activated procedure was to dissolve KOH in water and became saturated solution in order to reduce the energy consumption required at subsequent drying stage, then put the carbonized material into the saturated solution (activated carbon obtained in this way denoted AC-02). For the third method, the mixed solution of KOH and soap were used to soak the carbonized material (activated carbon obtained in this way denoted AC-03).

2.4. Characterization and measurements of activated carbon

The SSA and porosities of samples for the activated carbon were determined by nitrogen gas adsorption–desorption at 77 K with a sorptomatic 1990 (ThermoQuest corporation, Italy). The nitrogen adsorption–desorption isotherms of the activated carbon were obtained through calculating their Brunauer–Emmeff–Teller (BET) surface areas. The BET surface area was assessed when the range of relative pressures was from 0.05 to 0.3.

3. Results and discussion

3.1. Influence of the methods of addition for activators on SSA of activated carbon

Many chemicals can be used as activators such as $ZnCl_2$ (Tsai et al., 1998), H_3PO_4 (Puziy et al., 2002), KOH (Guo et al., 2000; Tsai et al., 2001), K_2CO_3 (Hayashi et al., 2002), water vapor (Nakagawa et al., 2002; Toles et al., 2000), CO_2 (Linares-Solano et al., 2000), etc. For these activators, KOH as activator not only needs less energy than water vapor, but it also has the least impact on the environment than other activators such as $ZnCl_2$, H_3PO_4. However, different methods that the activator of KOH was added to the material may produce different activated carbon with SSA. The experimental results showed that the SSA of activated carbon obtained from different methods such as AC-01, AC-02 and AC-03 was 2720, 2723 and 2630 m^2/g when the other conditions were the same, respectively. And according yields were 21, 21 and 22 wt%. However, the SSA of activated carbon obtained while the activator of KOH was directly added into raw material (Tsai et al., 2001) was 1600 m^2/g. Compared with the SSAs of activated carbon obtained from carbonized material