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Absorption of ethanol by steam-exploded corn stalk

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ABSTRACT

The aim of this work is to study the feasibility of using a low-cost biomass absorbent steam-exploded corn stalk (SECS) to absorb ethanol in its production by fermentation. Measurement of many the physical properties of SECS showed its specific surface area was about 214 m^2/g and it had a good structure for absorption. Some influencing parameters of using SECS to absorb ethanol in water were studied. Second-order and parabolic diffusion equations excellently described the kinetics of absorption for ethanol. Its absorption isotherm was well described by an improved BET equation, indicating that it was a process of polymolecular layer absorption and had phenomena similar to capillary coacervation. Mesh size did not significantly affect absorptivity, but absorbency decreased with temperature. Absorptivity of SECS for ethanol was compared to that of other absorbents: at 30 °C and 5% initial ethanol, the absorptivity of SECS for ethanol at 5 h was 92 mg/g. When inactivated through use, SECS can continue to be used as an substrate to produce more ethanol, thus avoiding pollution through discarding.

1. Introduction

Cellulose, which accounts for some 35–50% of all kinds of plants, is an abundant and reproducible resource in the world. Corn stalks, rich in natural cellulose, but considered a farm waste, are traditionally burnt in the field without utilization, causing air pollution. Nowadays, with dwindling energy resources, how to use cellulose effectively in the service of mankind has become a problem of global concern.

Of the two common methods of producing ethanol, chemical synthesis and fermentation, the latter is usually used, starting from starch or cellulose as substrate. Absorbents are usually used to remove ethanol from the broth in order to prevent its inhibition on the fermentation process (Zhang et al., 2006). But current absorbents are costly and have limited life spans. Familiar ethanol absorbents include active carbon, molecular sieves (Zhang et al., 2006) and macroreticular resin (Fan, 1999). When active carbon, molecular sieve and macroreticular resin they absorb and desorb repeatedly, the efficiency of absorption diminishes, and it is difficult to regenerate them, thus causing secondary pollution.

Natural cellulose is a porous material and has large specific surface area, which qualifies it as a good absorbent. It has recently been reported that cellulose was used as absorbent in many fields, such as cellulosic waste orange peel to remove dyes from aqueous solutions (Namasivayam et al., 1996), apple pomace and wheat straw to remove dyes from a synthetic textile dye effluent (Robinson et al., 2002), corn stalk to absorb Cr(VI) (Zhang et al., 2004), Fe-modified steam-exploded wheat straw to absorb and remove Cr(VI) (Li et al., 2004), modified wheat and corn residue to absorb phosphate from aqueous solution (Yue et al., 2006; Wang et al., 2008), tea waste to remove Cu and Pb from wastewater (Amarasinghe and Williams, 2007), biomass to absorb water to produce anhydrous ethanol (Han et al., 2007), physical and chemical modified corn stalk to absorb Cu^{2+} and Cd^{2+} (Hao et al., 2007) and Nordmann fir leaves to remove cadmium from aqueous solution (Serencam et al., 2008). Steam explosion serves to expand the pores of corn stalk, thus endowing it with a larger specific surface area for more effective absorption (Chen and Li, 1998). Corn stalk is an abundant and low-cost resource, much cheaper than active carbon, molecular sieve, and macroreticular resin currently used absorbents. When it turns inactive as an absorbent, it can continue to be used as substrate be fermented to produce more ethanol, thus avoiding pollution through discarding waste. Furthermore, it can reduce the cost of fermentation. This article describes the feasibility of using steam-exploded corn stalk as an ethanol absorbent.

2. Methods

2.1. Materials and reagents

Active carbon ZX-40 was obtained from the Guanghua Active Carbon Company in Ningxia, China, and corn stalk was from the suburbs of Beijing. Steam-exploded corn stalk 1 (SECS1) was steam-exploded at 1.3 MPa for 5 min, while steam-exploded corn

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stalk 2 (SECS2) was steam-exploded at 1.7 MPa for 10 min (Chen and Liu, 2007; Peng and Chen, 2008). Other reagents were all analytically pure and were produced in China.

2.2. Measurement of physical properties of SECS1 and SECS2

SECS was crushed by a plant crusher and then separated by a series of standard sieves.

Measurement of bulk density (He and Huang, 1995) was carried out as follows: wg SECS dried to constant weight was placed in a 50 ml triangular flask, pressed carefully to constant volume V, and its cumulate density was calculated as follows:

$$\rho_b = w/V \ (\text{g/ml})$$

Measurement of skeletal density was carried out as follow: 25 ml organic solvent was added to a volumetric flask of 25 ml and their total weight was measured. Then wg (about 1 g) SECS was placed in the flask. The SECS and organic solvent were well mixed by vacuum pumping. After 5 h, their weight was measured again and then additional organic solvent was added to offset the loss of weight by volatilization of organic solvent. The volume V of SECS was measured by using a pipette to remove and measure the excess organic solvent above the 25 ml mark. Then its skeletal density was calculated as follows:

$$\rho_s = w/V \ (\text{g/ml})$$

Measurement of pore volume was carried out as follow: wg (about 1 g) SECS dried to constant weight was placed in a home-made test tube which had scales and a filterable bottom, and then the test tube together with its SECS was soaked in water for 24 h. After centrifugation at 4000 rpm for 15 min for removing to remove the superfluous water, the weight of SECS plus the water it contained was measured immediately. The increase in weight, Δm_{water} represents the weight of water in the SECS pores, and the pore volume of SECS was calculated by

$$V_a = \Delta m_{\text{water}}/(\rho_{\text{water}} * w) \ (\text{ml/g})$$

Then the apparent density of SECS was calculated as follows:

$$\rho_a = w/(V_a * w + w/\rho_s) \ (\text{g/ml})$$

Measurement of specific surface area was based on methylene blue absorption. SECS (0.2 g) and a 400 mg/l solution of methylene blue (50 ml) were placed in a triangular flask to mix for 24 h on a shaking table. After centrifugation, absorbance of the liquor was measured using a spectrophotometer at 665 nm, and the concentration of methylene blue was determined according to a standard curve. Methylene blue absorptivity for SECS was calculated on the basis of a specific surface area of 2.45 m^2 per 1 mg methylene blue.

2.3. Measurement of absorptivity

Measurement of absorptivity of the SECS was carried out as follows: unless otherwise stated, 2 g absorbent was added to 50 ml of 5% (v/v) ethanol solution in a 150 ml triangular flask and shaken for 5 h. Colorimetry (Cai, 1988) was used to measure the ethanol concentration. A blank consisting of 2 g absorbent in 50 ml distilled water without ethanol was used as control.

2.4. Activation of SECS absorbent

To improve its absorbency, absorbent is often activated by removing its absorbed impurities. When corn stalk from agriculture is steam-explored, it has many impurities that should be washed away, such as some components from the soil and the process of steam explosion. SECS was activated by first soaking in water for 24 h followed by boiling at 80 °C for 2 h. It was then washed and dried. Absorptivities of both activated and unactivated SECS were measured.

2.5. Effect of some parameters on SECS absorbing ethanol

Absorptivities for different durations of absorption were measured to determine the time of saturated absorption and describe the kinetics of sorption for ethanol, while different amounts of SECS were used to describe the influence of dosage of SECS on absorption.

Absorptivities of SECS of different mesh sizes, at different temperatures and for different ethanol concentrations at equilibrium were measured to understand some characters of sorption for ethanol.

2.6. Comparison of absorptivity for different absorbents

Absorptivities of ethanol for SECS as well as some other absorbents were measured under the same conditions for comparison.

3. Results and discussion

3.1. Physical properties of SECS1 and SECS2

After being crushed by a plant crusher and separated by a series of standard sieves, SECS was separated into six different size ranges as follow: below 0.080 mm (190 mesh), 0.080–0.110 mm (150 mesh), 0.110–0.177 mm (80 mesh), 0.177–0.250 mm (60 mesh), 0.250–0.420 mm (40 mesh) and 0.420–0.595 mm (30 mesh). The SECS below 0.080 mm was too few and too small to be used as absorbent, so it was discarded.

Shown in Fig. 1, the bulk densities of SECS of different mesh sizes varied slightly except that the bulk density before crushing for either SECS was a little smaller than others, while the bulk density of SECS1 was a little smaller than that of SECS2. SECS2 had a larger specific surface area than SECS1, and that when mesh size of the SECS became smaller, specific surface area became larger.

The skeletal density, pore volume and apparent density were little affected by mesh sizes for both SECS1 and SECS2. Exploding types SECS1 and SECS2, and types of organic solvents cyclohexane and n-hexane hardly did not significantly affected skeletal density, too. The ratio of the difference between the largest and the smallest to the largest pore volume for SECS1 was 18%, and for SECS2 was 9.7%.

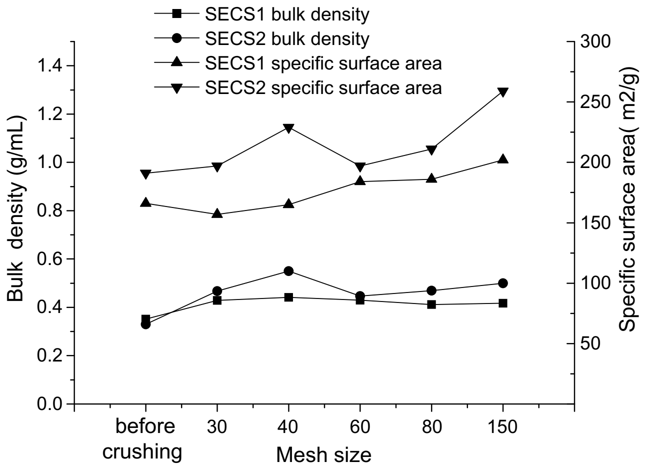

Fig. 1. Bulk density and specific surface area for different mesh sizes of SECS1 and SECS2.