Preparation of CO_2 activated carbon from corncob for monoethylene glycol adsorption

Amphol Aworn [a], Paitip Thiravetyan [b,*], Woranan Nakbanpote [c,1]

[a] The Joint Graduate School of Energy and Environment, King Mongkut's University of Technology Thonburi, Bangkok 10140, Thailand
[b] Division of Biotechnology, School of Bioresources and Technology, King Mongkut's University of Technology Thonburi (Bangkhuntien campus), Bangkok 10150, Thailand
[c] Pilot Plant Development and Training Institute, King Mongkut's University of Technology Thonburi (Bangkhumtien campus), Bangkok 10150, Thailand

ARTICLE INFO

ABSTRACT

Activated carbon was produced from corncob using CO_2 for the activation process. This research investigated the effect of the remaining volatile matter in corncob char combined with CO_2 activation to improve the pore properties of corncob activated carbon. The pore structure was characterized using the Brunauer–Emmett–Teller (BET) surface area test, total pore volume, mesopore volume, micropore volume and average pore diameter. This study discovered that the amount of volatile matter in corncob char is about 17–25% and results in a BET surface area range of 919–986 $m^2 \, g^{-1}$ by the CO_2 activation process. Therefore, the optimum temperature for the activation process should start at 450–550 °C and increase until the temperature reaches to 800 °C. Activated carbon from corncobs at 450–550 °C contained a suitable amount of volatile matter, 17–25%, for pore development. The Langmuir and Dubinin–Radushkevich (D–R) adsorption models were used to study the equilibrium isotherms, the isotherm constants and the adsorption capacity of monoethylene glycol by corncob activated carbon and commercial activated carbon. The values of Langmuir isotherms Q_{max} of corncob activated carbon and commercial activated carbon were 4.509 and 5.910 $mol_{MEG} \, kg^{-1}_{adsorbent}$, respectively. The D–R isotherms were described the adsorption capacity and the free energy (E) of adsorption. The values of E ($kJ \, mol^{-1}$) confirmed that monoethylene glycol adsorption by corncob activated carbon and commercial activated carbon was a physisorption.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Activated carbon is produced from a wide variety of raw materials including coconut shells, palm-oil shells, wood, coal, corncobs, etc. The manufacture of activated carbon involves two main steps: 1) the carbonization of carbonaceous raw material and 2) the physical or chemical activation, and sometimes both of the activation processes. In the carbonization and physical activation, the starting material is pyrolyzed at temperatures below 800 °C in an inert atmosphere so that volatile matter is removed, leaving behind rudimentary structures in the carbon material. Then, the activation begins by introducing activation agents, e.g., air, steam, or carbon dioxide at 800–1100 °C. The adsorbent properties of activated carbon are essentially attributed to their large surface area, high surface reactivity, universal adsorption effect, as well as favorable pore size. These properties make the internal surface accessible,

increase the adsorption rate, and improve mechanical strength [1]. The specific surface area of activated carbon usually ranges from 500 to 3000 $m^2 \, g^{-1}$. The complex network of pores of activated carbon has been classified into micropores (diameter <2 nm), mesopores (diameter 2–50 nm), and macropores (diameter >50 nm) [2].

Recently, Tsai et al. [3] prepared corncob activated carbon by both physical and chemical activation processes. In the physical activation process, corncob was carbonized at 500 °C with a N_2 flow of approximately 500 $cm^3 \, min^{-1}$. Thus, the pyrolysis temperature was increased at a ramp rate of 10 °C min^{-1} in a N_2 flow (200 $cm^3 \, min^{-1}$ at standard temperature and pressure (STP)), then switched to CO_2 flow (200 $cm^3 \, min^{-1}$ at STP) at 800 °C for 1 h. The resulting BET surface area was 437 $m^2 \, g^{-1}$. El-Hendawy [4] investigated the preparation of corncob activated carbons under carbonization at 500 °C followed by activation in steam/N_2 at 600, 700 and 850 °C and found that the BET surface area was 664, 850, and 700 $m^2 \, g^{-1}$, respectively. Chang et al. [5] investigated activated carbon from corncob by physical activation. They reported that the corncob was carbonized at 800 and 900 °C (10 °C min^{-1}) under a constant N_2 stream of 200 $cm^3 \, min^{-1}$. For the activation process, the char obtained from carbonization was activated at the final carbonization temperature for the specified time. For the activa-

* Corresponding author. Tel.: +66 2 4707535 fax: +66 2 4523455.
  E-mail address: paitip.thi@kmutt.ac.th (P. Thiravetyan).
[1] Present address: Department of Biology, Faculty of Science, Mahasarakham University, Mahasarakham, Thailand.

Table 1
Proximate and ultimate analysis of corncob.

Sample	Proximate analysis (dry basis %wt.)			Ultimate analysis (%wt.) (daf)				
	Volatile matter	Fixed carbon	Ash	C	H	N	O[a]	S
Corncob	80.2	18.9	0.9	48.89	6.38	0.18	44.55	0.00

[a] By difference, daf = dry ash free.

tion agent, CO_2 (purity of 99.99%), the flow rate was maintained at 200 cm^3 min^{-1} (measured at room temperature). In the steam runs, water flow rates were 0.6 and 0.05 cm^3 min^{-1} at activation temperatures of 800 and 900 °C, respectively. Activation times of 1 h found that the BET surface area after CO_2 and steam activation were 608 and 897 m^2 g^{-1}, respectively at 800 °C and 1014 and 1063 m^2 g^{-1}, respectively at 900 °C. Fan et al. [6] used oat hull and corn stover to produce chars at approximately 500 °C. After that, the char was heated in an inert atmosphere of nitrogen gas supplied to the retort at a flow rate of 1667 cm^3 min^{-1}. Once the furnace temperature reached 800 °C, water was pumped into the nitrogen gas stream at a rate of 3 cm^3 min^{-1} in order to achieve steam activation. The chars were steam activated for 30, 60, 90, and 120 min. The BET surface areas for oat husk were 349, 431, 522, and 625 m^2 g^{-1}, respectively and those of corn stover were 424, 442, 374, and 311 m^2 g^{-1}, respectively.

For activated carbon production, these studies illustrate the notion that corncob is a suitable precursor for the preparation of activated carbon by physical activation and that the manufacturing of corncob activated carbon was prepared by two main steps: the carbonization of the carbonaceous raw material and the activation of the carbonized product. However, the activation process was investigated only at high temperature (700–900 °C). This means that the N_2 stream was switched to activating agents (CO_2 or steam) at high temperatures. The volatile matter of char has less content at high temperature.

After that the corncob activated carbon and commercial (coconut shell) activated carbon were tested for their efficiency on ethylene glycol adsorption. The ethylene glycol or monoethylene glycol (MEG) was generally used in the plastic industry, including solvent for dyes in textile, coupling printing and water-based coating, as ethylene glycol electrolyte for electrolytic condenser and as an antifreeze component [7].

Nowadays, the wastewater from these industries, in Thailand, contains ethylene glycol and results in high chemical oxygen demand (COD). The effluent standard of COD is less than or equal to 120 mg l^{-1} for the textile and printing manufacturing industry in Thailand.

There are two principal treatment processes for physico-chemical removal of MEG in water and wastewater. The destructive processes such as ozonation, ozonation/UV or H_2O_2/UV oxidation and recuperative processes such as adsorption into activated carbon

or montmorillonite clay [8]. In addition, adsorption using activated carbon for removing the organics from the aqueous solution is an effective separation technology and widely applied in the wastewater treatment [9]. Many researchers investigated poly(ethylene glycol) adsorption by various adsorbents. The adsorbents were hydrophobic zeolite [8], commercial activated carbon (F-400, Calgon) [9], zirconia [10] and alumina [11].

Therefore, the aim of this research was to study the effect of the remaining volatile matters of char on pore development of corncob activated carbon. This study demonstrated that corncob chars activated at 800 °C resulted in lower pore development than corncob chars activated at 450–550 °C and heated continuous temperature to 800 °C by CO_2 activation process. The corncob activated carbon was compared the pore characteristics, the adsorption free energy and the efficiency of MEG adsorption with commercial activated carbon.

2. Materials and methods

2.1. Chemical

The monoethylene glycol was obtained from POCH Spólka Akcyjna Co., Ltd. (Poland) and the molecular weight was 62.07.

2.2. Materials

Corncob (particle size of 1.0–2.0 mm) was obtained from the Betagro Agro-Group Public Co., Ltd. (323 Vibhavadi Rangsit Road, Laksi, Bangkok 10210, Thailand). The proximate and ultimate analysis of the corncob is provided in Table 1. The proximate analysis was calculated on a dry basis by a TGA analyzer (Pyris 1 TGA, PerkinElmer, USA). The standard test method for moisture, volatile matter, and ash content of corncob chars were carried out by ASTM D 2867-96, ASTM D 5832-96, and ASTM D 2866-96, respectively [12]. The ultimate analysis of C, H, N, O and S elements (ASTM D5373-02) [13] was determined by an elemental analyzer (Flash EA 1112, Thermo Finnigan, Germany). The commercial activated carbon was made from coconut shell and obtained from Hexa Thailand Co., Ltd. (67-67/1-3 Soi Samanchan-Babos, Sukhumwit Road, Klongtoey, Bangkok 10110, Thailand).

Table 2
Proximate analysis of corncob char at various carbonization temperatures.

Corncob char (°C)	Proximate analysis (dry basis %wt.)			BET surface area (m^2 g^{-1})	Yield (%)
	Volatile matter	Fixed carbon	Ash		
300	39.7 ± 1.9	57.5 ± 2.5	2.8 ± 0.6	28.94	48.40 ± 0.61
350	34.6 ± 2.8	62.7 ± 3.0	2.7 ± 0.1	30.85	41.39 ± 0.68
400	27.6 ± 0.8	69.6 ± 0.3	2.8 ± 0.5	28.53	36.95 ± 0.09
450	24.2 ± 0.9	72.5 ± 0.5	3.3 ± 0.4	28.27	28.47 ± 0.55
500	20.7 ± 1.6	76.0 ± 1.7	3.3 ± 0.2	29.32	27.75 ± 0.39
550	17.7 ± 2.3	78.5 ± 2.5	3.8 ± 0.3	27.11	27.01 ± 0.29
600	16.5 ± 1.3	80.7 ± 1.6	2.8 ± 0.3	27.64	25.75 ± 0.47
700	14.8 ± 1.5	81.7 ± 1.6	3.5 ± 0.1	28.46	24.98 ± 0.23
800	14.3 ± 1.6	81.9 ± 1.8	3.8 ± 0.2	27.54	24.05 ± 0.21