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Butanol vapor adsorption behavior on active carbons and zeolite crystal

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ABSTRACT

Butanol is considered a promising, infrastructure-compatible biofuel. Unfortunately, the fermentation pathway for butanol production is restricted by its toxicity to the microbial strains used in the process. Gas stripping technology can efficiently remove butanol from the fermentation broth as it is produced, thereby decreasing its inhibitory effects. Adsorption can then be used to recover butanol from the vapor phase. Active carbon samples and zeolite were investigated for their butanol vapor adsorption capacities. Commercial activated carbon was modified via hydrothermal H_2O_2 treatment, and the specific surface area and oxygen-containing functional groups of activated carbon were tested before and after treatment. Hydrothermal H_2O_2 modification increased the surface oxygen content, Brunauer-Emmett-Teller surface area, micropore volume, and total pore volume of active carbon. The adsorption capacities of these active carbon samples were almost three times that of zeolite. However, the un-modified active carbon had the highest adsorption capacity for butanol vapor ($259.6\,\mathrm{mg\,g^{-1}}$), compared to $222.4\,\mathrm{mg\,g^{-1}}$ after 10% H_2O_2 hydrothermal treatment. Both modified and un-modified active carbon can be easily regenerated for repeatable adsorption by heating to 150 °C. Therefore, surface oxygen groups significantly reduced the adsorption capacity of active carbons for butanol vapor.

1. Introduction

The fluctuating price of oil, finite stocks of fossil fuels, and environmental consequences of fossil fuel use have prompted the demand for the production of biofuels from natural resources [1]. Butanol is considered a promising liquid fuel [2] because of its superior fuel properties, such as high energy density [3], low vapor pressure, low corrosivity to aluminum or polymer components in fuel systems [4], and high tolerance to water contamination for long-term storage [5]. In addition, butanol's fuel properties are close to gasoline and it can be used as blend fuel in spark ignition engines without any engine modification [6]. Microbial butanol can be produced by fermentation using different feedstocks, such as sucrose [7], starch [8,9], lignocellulosic biomass [10], glycerol [11], and algae [12]. The concentration of 1-butanol or total organic solvents is approximately 10–20 g/L in aqueous fermentation broth [13–15]. Distillation is generally applied for product recovery, but this is energy-intensive due to the low butanol concentration [16–18].

The product 1-butanol is toxic to bacteria and will inhibit the fermentation process [19]. To overcome this problem, several in-situ product recovery techniques have been developed to remove butanol as it is made. These methods include liquid phase adsorption [20], liquid–liquid extraction [21], pervaporation [22], and gas stripping [23]. While advancements have been made in each of these areas, the expense of recovering butanol from diluted solutions has hindered commercial deployment. Cells and organic compounds in the broth can foul adsorbents. Liquid–liquid extraction technology is limited by toxicity of the organic liquid solvents to the butanol-producing microbes, as well as emulsion formation and loss of extractant. Pervaporation can efficiently recover and concentrate butanol from fermentation broth, but membrane fouling with the microbes and non-volatile organic substances is a challenge [24].

Gas stripping has been suggested as one of the best techniques for butanol recovery [14,23,25], since butanol would be rapidly

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removed from the fermentation broth, and no harmful or expensive extractants or adsobents would be in contact with said broth. To recover butanol from the gas phase, condensation and distillation have been suggested. Unfortunately, both methods are energy intensive, especially for condensation at −60 °C [26]. Therefore, a more efficient means of recovering a dilute butanol vapor from gas stripping is needed.

Active carbon (AC) is a porous material with large surface area, high porosity, and rapid adsorption capabilities, and has been employed to absorb various volatile organic compounds, including benzene, toluene, formaldehyde, n-hexane, and ethanol [27–32]. These studies focused on the adsorption behavior of AC without attention to regeneration. In general, physical adsorption occurs when the solvent is held on the surface and in the pores of the AC by Van der Waals force of attraction. Then, the adsorbed solvent can be easily desorbed by heating the AC. Hence, AC can potentially be used to capture butanol vapor released from fermentation broth via the gas stripping processes. Therefore, it is important to understand butanol adsorption and desorption curves for AC, as well as the relationship between AC properties (pore size, surface area, and functional group) and adsorption capacity. In this study four kinds of AC (original and chemically modified active carbon by hydrothermal H_2O_2 reaction) were investigated for their absorption and desorption behavior with butanol vapor. In addition, the zeolite ZSM-5 was used as a control, since it is known that zeolites are good adsorbents to recover butanol from aqueous solutions [33].

2. Materials and methods

2.1. Materials

Analytical grade butanol, 30% H_2O_2, hydrochloride acid, sodium hydroxide, and ethanol were purchased from Thermo Fisher Scientific Inc. The purity of butanol was >99.8%, which was used to generate vapor directly with helium gas bubbling. Commercial active carbon Sabre Series CR2050C-75 (unmodified AC) was donated by Carbon Resources. Different kinds of modified AC were obtained by reaction between commercial AC and different concentrations of H_2O_2. Another adsorbent, zeolite ZSM-5 (purchased from Sigma), was also used for comparison with the different kinds of AC.

2.2. Methods

2.2.1. Modification of active carbon

Commercial AC was packed into a Soxhlet extractor and washed with boiling water for 2 h. The wet AC was transferred to a beaker and dried at 105 °C for 24 h. Then 5 g of unmodified AC was reacted with 40 ml H_2O_2 at 10%, 20% and 30% concentration (wt.%) in a sealed PTFE reactor (50 ml) at 120 °C for 1 h. After reaction, the reactant was cooled, filtered, and washed with deionized water under vacuum filtration until the pH value of the permeate was ∼7. Finally, the leached reactants were dried in a vacuum oven at 105 °C overnight. The dried modified AC was ground and run through a sieve, and grains falling within US mesh sizes 50–100 were used as adsorbents.

2.2.2. Analytical methods for adsorbents

Nitrogen adsorption/desorption was carried out using Surface Area and Pore Size Analyzers (ASAP 2010, Micromeritics, USA). The total pore volume was determined at relative pressure P/P_0, and the specific surface area was calculated from the Brunauer-Emmett-Teller (BET) method. Density functional theory (DFT) was used to characterize the micropore and pore size distribution.

2.2.3. Gas chromatography mass spectrometer (GC-MS) analytical procedure

GC-MS was applied to analyze the outlet of the sample tube. Chromatographic analysis was performed in a Shimadzu series GC-MS (Shimadzu Corporation, USA) equipped with an RXI capillary column (30 m × 0.15 μm × 15 mm). The initial temperature (40 °C) was held for 1 min and then raised to 200 °C at a rate of 45 °C/min. All samples were injected in split mode. The injection temperature was 150 °C. The mass spectrometer was operated in EI mode. Mass spectra was acquired in full scan mode with repetitive scanning from 45 m/z to 500 m/z in 0.25 s. Ion source temperature was 250 °C.

2.2.4. Adsorption and regeneration procedure

A Micrometrics Autochem II Chemisorption Analyzer, connected to a Shimadzu GC-MS, was employed to investigate the adsorption and desorption behavior of different adsorbents. Fig. 1 shows the schematic diagram of the adsorption system used for testing adsorbents. The flow rate of the vapor, carrier, and reference were set at 5, 5, and 10 cm^3/min, respectively. Experiments were performed at atmospheric total pressure using helium as carrier gas, assuming that helium is not adsorbed on active carbon. Butanol was heated to 50 °C and, as it passed through the sample tube was adsorbed on the adsorbent. Un-adsorbed butanol passed through the analysis chamber and then into the GCMS. The reference chamber recorded the thermal conductivity detector (TCD) readings and plotted them against time. The GC-MS records the intensity of the signal produced by the adsorbate as a function of time approximately once every 10.5 min, and the integral of the curve provides the volume of adsorbate present after adsorption. At least 20 data points were obtained by the GC-MS over the course of the chemisorption analysis. For regeneration, the temperature-programmed desorption (TPD) process pre-programmed into the Micromeritics analyzer was used. The flow rate of the vapor, carrier, and reference were set at 0, 10, and 10 cm^3/min, respectively. The temperature ramp was set at 15 °C/min, starting from 25 to 150 °C with a 1 h end temperature hold.

2.2.5. Surface functional group characterization

TPD analysis was also performed to investigate the oxygen content of the four AC samples. The carbon sample (0.05 g) was placed in a U-shaped quartz tube inside an electrical furnace and heated at 10 °C/min up to 1000 °C using a constant flow rate of helium (the flow rate of the vapor, carrier, and reference were set at 0, 10, and 10 cm^3/min, respectively). The TCD signals were monitored during the thermal analysis, and the corresponding TCD spectra was obtained.

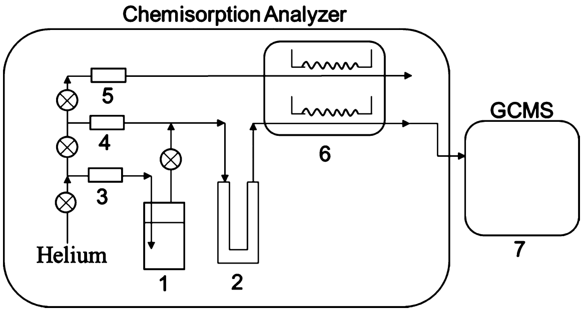

Fig. 1. Schematic diagram of the experimental adsorption system: 1, butanol bath; 2, sample tube; 3, vapor flow rate meter; 4, carrier flow rate meter; 5, reference flow rate meter; 6, TCD detector; 7, GC-MS.