1 **Butanol vapor adsorption behavior on active carbons and**
2 **zeolite crystal**

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23 Abstract

24 Butanol is considered a promising, infrastructure-compatible biofuel.
25 Unfortunately, the fermentation pathway for butanol production is restricted by its
26 toxicity to the microbial strains used in the process. Gas stripping technology can
27 efficiently remove butanol from the fermentation broth as it is produced, thereby
28 decreasing its inhibitory effects. Adsorption can then be used to recover butanol from
29 the vapor phase. Active carbon samples and zeolite were investigated for their butanol
30 vapor adsorption capacities. Commercial activated carbon was modified via
31 hydrothermal H_2O_2 treatment, and the specific surface area and oxygen-containing
32 functional groups of activated carbon were tested before and after treatment.
33 Hydrothermal H_2O_2 modification increased the surface oxygen content, Brunauer-
34 Emmett-Teller surface area, micropore volume, and total pore volume of active
35 carbon. The adsorption capacities of these active carbon samples were almost three
36 times that of zeolite. However, the un-modified active carbon had the highest
37 adsorption capacity for butanol vapor (259.6 mg g^{-1}), compared to 222.4 mg g^{-1} after
38 10% H_2O_2 hydrothermal treatment. Both modified and un-modified active carbon can
39 be easily regenerated for repeatable adsorption by heating to 150°C . Therefore,
40 surface oxygen groups significantly reduced the adsorption capacity of active carbons
41 for butanol vapor.

42 **Keyword:** butanol; biofuel; gas stripping; active carbon; H_2O_2 ; adsorption

43 1. Introduction

44 The fluctuating price of oil, finite stocks of fossil fuels, and environmental

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

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

67 but membrane fouling with the microbes and non-volatile organic substances is a
68 challenge [24].

69 Gas stripping has been suggested as one of the best techniques for butanol
70 recovery [14, 23, 25], since butanol would be rapidly removed from the fermentation
71 broth, and no harmful or expensive extractants or adsorbents would be in contact with
72 said broth. To recover butanol from the gas phase, condensation and distillation have
73 been suggested. Unfortunately, both methods are energy intensive, especially for
74 condensation at -60 °C [26]. Therefore, a more efficient means of recovering a dilute
75 butanol vapor from gas stripping is needed.

76 Active carbon (AC) is a porous material with large surface area, high porosity,
77 and rapid adsorption capabilities, and has been employed to absorb various volatile
78 organic compounds, including benzene, toluene, formaldehyde, n-hexane, and ethanol
79 [27-32]. These studies focused on the adsorption behavior of AC without attention to
80 regeneration. In general, physical adsorption occurs when the solvent is held on the
81 surface and in the pores of the AC by Van der Waals force of attraction. Then, the
82 adsorbed solvent can be easily desorbed by heating the AC. Hence, AC can potentially
83 be used to capture butanol vapor released from fermentation broth via the gas
84 stripping processes. Therefore, it is important to understand butanol adsorption and
85 desorption curves for AC, as well as the relationship between AC properties (pore size,
86 surface area, and functional group) and adsorption capacity. In this study four kinds of
87 AC (original and chemically modified active carbon by hydrothermal H₂O₂ reaction)
88 were investigated for their absorption and desorption behavior with butanol vapor. In

89 addition, the zeolite ZSM-5 was used as a control, since it is known that zeolites are
90 good adsorbents to recover butanol from aqueous solutions [33].

91 **2.0 Materials and methods**

92 **2.1 Materials**

93 Analytical grade butanol, 30% H₂O₂, hydrochloride acid, sodium hydroxide,
94 and ethanol were purchased from Thermo Fisher Scientific Inc. The purity of butanol
95 was >99.8%, which was used to generate vapor directly with helium gas bubbling.

96 Commercial active carbon Sabre Series CR2050C-75 (unmodified AC) was donated
97 by Carbon Resources. Different kinds of modified AC were obtained by reaction
98 between commercial AC and different concentrations of H₂O₂. Another adsorbent,
99 zeolite ZSM-5 (purchased from Sigma), was also used for comparison with the
100 different kinds of AC.

101 **2.2 Methods**

102 **2.2.1 Modification of active carbon**

103 Commercial AC was packed into a Soxhlet extractor and washed with boiling
104 water for 2 h. The wet AC was transferred to a beaker and dried at 105°C for 24 h.
105 Then 5 g of unmodified AC was reacted with 40 ml H₂O₂ at 10%, 20% and 30%
106 concentration (wt. %) in a sealed PTFE reactor (50 ml) at 120 °C for 1 h. After
107 reaction, the reactant was cooled, filtered, and washed with deionized water under
108 vacuum filtration until the pH value of the permeate was ~7. Finally, the leached
109 reactants were dried in a vacuum oven at 105 °C overnight. The dried modified AC
110 was ground and run through a sieve, and grains falling within US mesh sizes 50-100

111 were used as adsorbents.

112 **2.2.2 Analytical methods for adsorbents**

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

118 **2.2.3 Gas Chromatography Mass Spectrometer (GC-MS) analytical procedure**

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

127 **2.2.4 Adsorption and regeneration procedure**

128 A Micrometrics Autochem II Chemisorption Analyzer, connected to a
129 Shimadzu GC-MS, was employed to investigate the adsorption and desorption
130 behavior of different adsorbents. Figure 1 shows the schematic diagram of the
131 adsorption system used for testing adsorbents. The flow rate of the vapor, carrier, and
132 reference were set at $5, 5, \text{ and } 10\text{ cm}^3/\text{min}$, respectively. Experiments were performed

133 at atmospheric total pressure using helium as carrier gas, assuming that helium is not
134 adsorbed on active carbon. Butanol was heated to 50 °C and, as it passed through the
135 sample tube was adsorbed on the adsorbent. Un-adsorbed butanol passed through the
136 analysis chamber and then into the GCMS. The reference chamber recorded the
137 thermal conductivity detector (TCD) readings and plotted them against time. The GC-
138 MS records the intensity of the signal produced by the adsorbate as a function of time
139 approximately once every 10.5 minutes, and the integral of the curve provides the
140 volume of adsorbate present after adsorption. At least 20 data points were obtained by
141 the GC-MS over the course of the chemisorption analysis. For regeneration, the
142 temperature-programmed desorption (TPD) process pre-programmed into the
143 Micromeritics analyzer was used. The flow rate of the vapor, carrier, and reference
144 were set at 0, 10, and 10 cm³/min, respectively. The temperature ramp was set at
145 15°C/min, starting from 25-150 °C with a 1 h end temperature hold.

146 **2.2.5 Surface functional group characterization**

147 TPD analysis was also performed to investigate the oxygen content of the four
148 AC samples. The carbon sample (0.05 g) was placed in a U-shaped quartz tube inside
149 an electrical furnace and heated at 10 °C/min up to 1000 °C using a constant flow rate
150 of helium (the flow rate of the vapor, carrier, and reference were set at 0, 10, and 10
151 cm³/min respectively). The TCD signals were monitored during the thermal analysis,
152 and the corresponding TCD spectra was obtained.

153 **2.2.6 Butanol quantification**

154 To test the impact of surface modification on the butanol adsorption and

desorption capacities of AC, a Shimadzu GC-MS was used. A standard curve was first created by injecting 1 µl volumes of various butanol concentrations in ethanol (1, 5, 10, 20, 30, 50, 60, 75, 93, 170, 235, and 290 mg/ml) and measuring the area beneath the curves. Figure S1A shows the intensity peaks for these butanol: ethanol mixtures. The initial retention times for ethanol and butanol were 1.58 min and 2.23 min, respectively. The peak areas versus butanol concentrations were plotted to generate the standard curve shown in Figure S1B, with an R^2 of 0.99.

To quantify butanol vapor adsorbed on the adsorbent, the butanol concentration of the outlet stream was measured by passing 0.5 ml of outlet stream gas exiting the adsorption column into the GC-MS. Since the GC-MS needs time to cool down, the outlet of the sample tube was measured every 10.5 minutes. The outlet butanol vapor concentration as a function of time gave the breakthrough curve, and the adsorption capacity of the packed column was calculated for each experiment by the following equation:

$$Q = \frac{M_{\text{adsorption}}}{W} = \frac{T_q C_i F_A}{W} \quad (1)$$

The time T_q is estimated according to the equation (2):

$$T_q = \int \left(1 - \frac{C_o}{C_i}\right) dt \quad (2)$$

Where Q is the adsorbed amount (mg mg^{-1}); $M_{\text{adsorption}}$ is the mass of butanol adsorbed (mg); F_A is the volumetric flow rate of the carrier gas (ml min^{-1}); W is the net weight of adsorbent (mg); C_i represents the butanol concentration at the inlet ($\mu\text{g ml}^{-1}$); C_o is the butanol concentration at the outlet ($\mu\text{g ml}^{-1}$).

177 3. Results and Discussion

178 3.1 Physicochemical properties of adsorbents

179 3.1.1 Oxygen-containing functional groups

180 To investigate the functional groups on the surface of the AC samples,
181 temperature-programmed desorption was employed. The carrier gas helium and the
182 detected gases (CO_2 , CO, NO, H_2O , etc.) have different thermal conductivities, and
183 the area under each TCD peak is proportional to the amount of gas produced. At the
184 beginning of each measurement, the TCD base line was zeroed using carrier gas and
185 reference gas. According to Figure 2, which shows the TPD spectra of the AC before
186 and after the oxidative treatments with different concentration of H_2O_2 , there were
187 small peaks for all AC samples from 35 °C to 100 °C, which were caused by the air
188 trapped in the pores of the AC samples.

189 After H_2O_2 treatment, the TCD signal intensities were generally higher than
190 for unmodified AC. The evolution of CO_2 at temperatures of 100-400 °C is usually
191 assigned to the degradation of carboxylic functional group, while at higher
192 temperature (427 °C), CO_2 release is attributed to the decomposition of anhydride and
193 lactone groups [34-36]. Both CO_2 and CO were formed from 400 °C to 1000 °C [37],
194 and the CO may have been derived from the decomposition of phenols, ethers and
195 carbonyls/quinones [38-40]. Based on the peaks that appeared from 100 °C to 1000 °C,
196 it can be concluded that the H_2O_2 treatments of AC were effective in forming acidic
197 oxygen surface groups. The total amount of these groups was greatest in the 30%
198 H_2O_2 treatment, followed by 10% and 20% H_2O_2 treatments, with unmodified AC

199 having the lowest amount of acidic oxygen surface groups.

200 **3.1.2 Micropores of the adsorbents**

201 The micropore (smaller than 2 nm) volume was higher for all H₂O₂
202 hydrothermally treated AC samples compared to the untreated AC control (Table 1).
203 This was likely due to new micropores being generated by etching of the carbon walls
204 by the H₂O₂ hydrothermal treatments, as we observed a slight mass loss of carbon in
205 these treatments (data not shown). Meanwhile, the formation of oxygen groups caused
206 blockage of some macropores (larger than 50 nm) and mesopores (between 2 nm and
207 50 nm), thereby effectively transforming them into micropores. P.C.C. Faria et al. [41],
208 V. Gómez-Serrano et al. [42], and P. Chingombe et al. [43] reported a similar effect
209 caused by carbonyl and carboxylic groups formed during oxidation when using nitric
210 acid. The generated functional groups and the opening of the closed micropores also
211 increased the micropore region of AC samples.

212 In contrast to our work, Pereira et al. found that the micropore volume of AC
213 decreased 10% (from 0.382 to 0.343 cm³ g⁻¹) when hydrogen peroxide oxidation was
214 employed [44]. However in that study oxidation was performed at room temperature,
215 while in this work we conducted hydrothermal H₂O₂ oxidation at 120 °C. The sealed
216 reaction system used herein generated steam, which can help develop pore structure.
217 In addition, the evenly distributed pressure in the sealed system was likely favorable
218 for pore development.

219 While hydrothermal H₂O₂ oxidation did increase micropore volume compared
220 to the control, the effect diminished at higher H₂O₂ concentrations. Thus at 30% H₂O₂

221 treatment, micropore volume was only $0.41 \text{ cm}^3 \text{ g}^{-1}$, compared to $0.39 \text{ cm}^3 \text{ g}^{-1}$ for
222 untreated AC. While low (i.e., 10%) concentrations of H_2O_2 can generate more
223 micropores by serving as an expanding agent and an oxidant, higher concentrations
224 may result in H_2O_2 self-decomposition or convert large micropores into mesopores.
225 Oxygen-containing functional groups formed by higher H_2O_2 levels may also
226 decrease the micropore volume. As for the ZSM-5 adsorbent, the micropore volume
227 was only $0.11 \text{ cm}^3 \text{ g}^{-1}$, or one-third of the unmodified AC sample.

228 **3.1.2 Mesopores of the adsorbents**

229 The adsorption/desorption isothermal curves of the five adsorbents are shown
230 in Figure 3A. There are loops in the five curves between 0.4-1.0 P/P_0 , which
231 demonstrates that all the adsorbents contained mesopores.

232 The TPD profiles of the modified AC samples (Figure 2), indicate that
233 oxidation with H_2O_2 generated many oxygen-containing functional groups. It also
234 showed that oxidation with 10% H_2O_2 was not strong enough to cause wall collapse,
235 but compared to untreated AC, some wall etching increased the mesopore volume
236 from 0.27 to $0.33 \text{ cm}^3 \text{ g}^{-1}$ (Table 1). DFT model simulation results according to the
237 nitrogen adsorption/desorption curve, indicate that the volume of pores between 2 nm
238 and 50 nm are decreased by using 20% H_2O_2 (Figure 3B). As H_2O_2 concentration
239 increased from 10% to 20%, the more robust oxidation caused walls of the mesopore
240 to collapse, thereby reducing mesopore volume from 0.33 into $0.22 \text{ cm}^3 \text{ g}^{-1}$ (Table 1).
241 Additionally, the 20% H_2O_2 level caused more surface oxygen functional groups to
242 form on carbon walls, which further blocked mesopore volume.

243 As H₂O₂ concentration increased to 30%, mesopore volume was partially
244 restored by creating additional pores in the collapsed walls, widening some
245 micropores to mesopores, and opening some closed mesopores in the carbon matrix.
246 Therefore compared with the untreated AC, the mesopore volume only increased
247 slightly with 30% H₂O₂ hydrothermal treatment from 0.27 to 0.28 cm³ g⁻¹ (Table 1).
248 In comparison, the mesopore volume of ZSM-5 was only 0.19 cm³ g⁻¹ (Table 1),
249 which is smaller than all AC samples.

250 3.1.3 Total pore volume and BET surface area of the adsorbents

251 Similar to the trends for micropores and mesopores, hydrothermal treatment of
252 AC with 10% H₂O₂ substantially increased total pore volume from 0.72 cm³ g⁻¹ in
253 untreated AC to 0.86 cm³ g⁻¹ (Table 1). This net increase of 0.14 cm³ g⁻¹ was similar
254 to the combined increase in micro and meso pore volume of 0.13 cm³ g⁻¹ after
255 modification. Therefore, the increase in total pore volume was primarily due to the
256 increase in micro and meso pores. Further increasing the H₂O₂ concentration to 20%
257 resulted in a total pore volume of 0.71 cm³ g⁻¹ (Table 1), which was similar to the
258 untreated AC. Again, this net difference can be explained by the 0.04 cm³ g⁻¹ increase
259 in micropores and the 0.05 cm³ g⁻¹ decrease in mesopores between untreated AC and
260 20% H₂O₂ treated AC (Table 1). Similar correlations can be drawn for the untreated
261 AC versus the 30% H₂O₂ treated AC (Table 1).

262 Some researchers [41, 44] have used oxidized AC for dye adsorption, and
263 reported that higher H₂O₂ concentrations resulted in greater oxidation effectiveness.
264 However, the BET surface area of these AC samples decreased from 972 to 949 m² g⁻¹

265 [41] and from 1032 to 908 m² g⁻¹ [44]. P.C.C. Faria et al. [41] noted that differences in
266 the textural properties of the activated carbons cannot explain the disparity in dye
267 adsorption, leading to the conclusion that surface chemistry plays a key role in
268 adsorption. M F R Pereira et al. [44] found that oxygen-containing groups have a
269 negative effect on adsorption of anionic dyes, but a positive effect for cationic dyes.

270 In this study we found that surface area increased after H₂O₂ oxidation (Table
271 1), and hypothesize that this was because we used hydrothermal H₂O₂ oxidation,
272 instead of oxidation at room temperature [41, 44]. In the study reported herein, the AC
273 samples were also reacted in a sealed reactor at 120 °C. The hydrothermal H₂O₂
274 treatment appears to provide a critical reaction environment, which accelerated pore
275 texture development and increased the BET surface area.

276 In summary, hydrothermal H₂O₂ treatment resulted in different pore structures,
277 with different abilities for butanol adsorption, depending on the H₂O₂ concentration
278 used. As can be seen in Table 1, 10% H₂O₂ treatment resulted in the greatest
279 improvements to AC texture. Surface area, micro and meso pore volume, and total
280 pore volume were increased to the greatest extent. This indicates that a moderate
281 concentration of H₂O₂ can generate additional micropores, while not causing carbon
282 walls of mesopores to collapse. In addition, as can be seen from Figure 2, AC treated
283 with 10% H₂O₂ resulted in more oxygen-containing functional groups compared with
284 the 20% H₂O₂ treatment, however, it had the lowest butanol adsorption capacity of the
285 four AC samples (Figure. 4A). Thus, in addition to pore structure and surface area,
286 functional groups also affect butanol vapor adsorption. Compared to these AC

287 samples, ZMS-5 had less BET surface area ($400 \text{ m}^2 \text{ g}^{-1}$), micropore volume (0.11 cm^3
288 g^{-1}), and total pore volume ($0.32 \text{ cm}^3 \text{ g}^{-1}$), as well as the lowest adsorption capacity for
289 butanol vapor.

290 3.2 Adsorption and desorption of butanol on the adsorbents

291 Figure 4A shows the breakthrough curves for butanol adsorption under
292 atmospheric conditions and 24°C . ZSM-5 was easily saturated by butanol vapor at
293 63.5 min. All four AC samples had longer saturation times, with the longest being
294 168.0 min for unmodified AC.

295 The adsorption capacity (Q value in Table 2) indicates that the three H_2O_2
296 treated ACs had reduced butanol adsorption compared to untreated AC (259.6 mg g^{-1}),
297 but all were significantly higher than ZSM-5 (83.0 mg g^{-1}). Although the AC modified
298 by 10% H_2O_2 had a larger BET surface area compared with the 20% and 30% H_2O_2
299 modified AC samples, it had a lower adsorptive capacity (222.4 mg g^{-1}) due to more
300 oxygen content on the surface (Figure 2). Therefore, adsorption of butanol is affected
301 by BET surface area as well as the surface functional groups.

302 The major factor determining adsorption capacity is pore size. Based on the
303 relative changes in micro and meso pore in Table 1 and adsorption capacity in Table 2,
304 it is apparent that micropore volume is more important. In comparison to ZSM-5,
305 micropore volumes of the ACs were 355-418% higher, while mesopore volumes were
306 only 116-195% higher than ZSM-5. In comparison, adsorption capacity in ACs were
307 298-313% higher than in ZSM-5. Thus adsorption capacity is mainly attributed to the
308 micropores in the adsorbents. This is logical, as the kinetic diameter of butanol is 0.5

309 nm [45], and micropores (smaller than 2 nm) provide a more stable environment to
310 store butanol molecules.

311 Desorption TCD profiles of unmodified AC and AC treated with 10% H_2O_2
312 were obtained via programmed temperature ramping. As is shown in Figure S2,
313 butanol vapor will evolve once desorption starts, even at low temperature (30 °C).
314 Butanol desorption was highest at 110 °C, and was completed when the temperature
315 reached 150 °C. In addition, nearly all of the butanol was removed after 30 min. It also
316 can be seen that the peak of the unmodified AC is higher than that of 10% H_2O_2
317 modified AC, which is corresponded to the adsorption amount calculated.

318 3.3 Regeneration of the adsorbent

319 To investigate the influence of oxidation on repeated adsorption/desorption
320 cycles, unmodified AC (Figure 4B) and AC modified with 10% H_2O_2 (Figure 4C)
321 were evaluated. The break through curves for unmodified AC (Figure 4B) almost
322 overlapped over five rounds of adsorption and desorption, which means that
323 unmodified AC has non-changed adsorption ability after heating regeneration at
324 150 °C. Due to the acidic oxygen surface groups generated by 10% H_2O_2 , the amount
325 of adsorbed butanol from the first round was smaller than these of regenerated AC
326 (the second to fifth adsorption rounds). It indicates that the adsorption capacity
327 increased after regeneration. To investigate the mechanism of this phenomenon, the
328 products from the regeneration was measured.

329 Figure 5A shows butanol desorption of the AC modified by 10% H_2O_2
330 treatment. The outlet was monitored by GC-MS when the TCD signal (1.95) was

331 highest during the desorption process. There was a small amount of butanal produced
332 via oxidation of butanol during regeneration as shown in Figure 5B. Meanwhile the
333 surface oxygen of the AC sample was consumed. After that reaction, the regenerated
334 AC demonstrated much higher dynamic capacity for adsorbing butanol with longer
335 time for the breakthrough (the second to fifth adsorption rounds).

336 4. Conclusion

337 Butanol vapor was adsorbed by AC samples and the zeolite ZSM-5. The
338 adsorption capacity of unmodified AC was 259.6 mg g^{-1} , which was almost three
339 times that of zeolite ZSM-5. Treatment of AC with 10% H_2O_2 increased BET surface
340 area by $205 \text{ m}^2 \text{ g}^{-1}$, micropore volume by $0.07 \text{ cm}^3 \text{ g}^{-1}$, and mesopore volume by 0.06
341 $\text{cm}^3 \text{ g}^{-1}$. However, the adsorption capacity decreased to $222.4 \text{ cm}^3 \text{ g}^{-1}$. Hence, the
342 oxygen-containing function groups generated by oxidation decreased the adsorption
343 ability of AC, because adsorption capacity is related to the pore structure and surface
344 functional groups. Micropores in the adsorbents played an important role in butanol
345 vapor adsorption. The unmodified AC sample were easily regenerated for repeatable
346 adsorption by heating. Although the unmodified AC achieved the best adsorption and
347 desorption performance, surface functional groups of AC samples play a key role in
348 butanol vapor adsorption. This work provides some guidance for designing absorbents
349 for use in industry.

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Figure captions

Figure 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.

Figure 2. TCD signals for TPD spectra of AC samples.

Figure 3. (A) Nitrogen isothermal adsorption of the absorbents. (B) The DFT pore size distribution curves of the absorbents.

Figure 4. (A) Butanol adsorption by different absorbents. (B) Repeating adsorption of butanol with unmodified AC. (C). Repeating adsorption of butanol with 10% H₂O₂ modified AC.

Figure 5. (A) Butanol desorption of 10% H₂O₂ modified AC. (B) GC-MS profile of the outlet at 6.0 min (97 °C).

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A

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Figure 5. (A) Butanol desorption of 10% H₂O₂ modified AC (B) GC-MS profile of the outlet at 6.0 min (97 °C).

Table caption

Table 1 Surface area and pore structure parameters.

Table 2 Adsorption process parameters.

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Sample	$S_{\text{BET}}^{\text{a}}$ ($\text{m}^2 \text{g}^{-1}$)	$V_{\text{Total}}^{\text{b}}$ ($\text{cm}^3 \text{g}^{-1}$)	$V_{\text{Micro}}^{\text{c}}$ ($\text{cm}^3 \text{g}^{-1}$)	$V_{\text{Meso}}^{\text{d}}$ ($\text{cm}^3 \text{g}^{-1}$)	$D_{\text{Average}}^{\text{e}}$ (nm)
Unmodified AC	1157	0.72	0.39	0.27	2.49
ZSM-5	400	0.32	0.11	0.19	3.20
10% H_2O_2	1362	0.86	0.46	0.33	2.53
20% H_2O_2	1216	0.71	0.43	0.22	2.34
30% H_2O_2	1205	0.76	0.41	0.28	2.52

^a BET (Brunauer-Emmett-Teller) surface area

^b Total pore volume, measured at $P/P^0=0.995$

^c Micropore volume, based on density functional theory (DFT)

^d Mesopore volume, based on density functional theory (DFT)

^e Average pore diameter of absorbents, calculated by $4V_{\text{Total}}/S_{\text{BET}}$

Table 2 Adsorption process parameters.

Parameter	Unmodified AC	ZSM-5	10% H_2O_2	20% H_2O_2	30% H_2O_2
F_A^f (ml min ⁻¹)	10	10	10	10	10
T_q^g (min)	108.2	34.6	90.4	103.2	103.1
C_i^h (μg ml ⁻¹)	12.0	12.1	12.3	12.0	12.3
$M_{\text{adsorption}}^i$ (mg)	12.98	4.15	11.12	12.38	12.68
W^j (mg)	50	50	50	50	50
Q^k (mg g ⁻¹)	259.6	83.0	222.4	247.6	253.6

^f Volumetric flow rate of the carrier gas

^g Stoichiometric time determined from the breakthrough curve

^h Butanol concentration at the inlet

ⁱ Mass of butanol adsorbed

^j Net weight of adsorbent

^k Dynamic adsorption capacity of the adsorbent