Adsorption of butanol vapor on active carbons with nitric acid hydrothermal modification

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24 Abstract

25 Butanol can be produced from biomass via fermentation and used in vehicles.
26 Unfortunately, butanol is toxic to the microbes, and this can slow fermentation rates and reduce
27 butanol yields. Butanol can be efficiently removed from fermentation broth by gas stripping,
28 thereby preventing its inhibitory effects. Original active carbon (AC) and AC samples modified
29 by nitric acid hydrothermal modification were assessed for their ability to adsorb butanol vapor.
30 The specific surface area and oxygen-containing functional groups of AC were tested before and
31 after modification. The adsorption capacity of unmodified AC samples were the highest.
32 Hydrothermal oxidation of AC with HNO₃ increased the surface oxygen content, Brunauer-
33 Emmett-Teller (BET) surface area, micropore, mesopore and total pore volume of AC. Although
34 the pore structure and specific surface area were greatly improved after hydrothermal oxidization
35 with 4 M HNO₃, the increased oxygen on the surface of AC decreased the dynamic adsorption
36 capacity.

37 **Keyword:** butanol; hydrothermal; gas stripping; active carbon; HNO₃

1.1 Introduction

High fuel prices and climate change are two critical challenges in the world. Fossil fuels, particularly petroleum-based fuels such as gasoline, diesel fuel, liquefied petroleum gas, and natural gas are mainly used for transportation, and will become increasingly difficult to access in the next few decades (Lin et al., 2011). Liquid biofuels such as biobutanol (Gottumukkala et al., 2013), bioethanol (Kim et al., 2014), and biodiesel (Manickam et al., 2014) have the potential to reduce the need for petroleum fuels. These biofuels can also reduce greenhouse gas emissions compared to petroleum-based fuels (Zhao et al., 2015).

Biobutanol has several advantages over other biofuels such as ethanol, including higher energy density and lower water miscibility, flammability, and corrosiveness. Butanol is also considered an infrastructure compatible fuel, as it can be blended in any ratios with gasoline without requiring engine modifications (Xue et al., 2013). Butanol can also be transported using the same pipelines and distribution networks that are currently used for petroleum products. Butanol is primarily produced via the bacterial acetone-butanol-ethanol (ABE) fermentation pathway (Bellido et al., 2014; Yen & Wang, 2013).

One of the chief limitations of butanol is that it is highly inhibitory to the microbes used to produce it. Levels as low as 13.0 g/L can cause reduced growth and metabolism (Setlhaku et al., 2013). Butanol recovery from dilute fermentation broth is quite expensive, and this has been a major hurdle to commercialization. Distillation (Kraemer et al., 2011) is widely used to recover volatile fermentation products, but is not practical for butanol due to high energy requirements (Oudshoorn et al., 2009b). Membrane distillation (Plaza et al., 2013) and pervaporation (Kujawski et al., 2014) have been suggested, but membrane fouling by organic compounds in the fermentation slurry has been an issue. Liquid phase adsorption (Cousin Saint Remi et al., 2012;

Oudshoorn et al., 2009a; Saint Remi et al., 2011) and liquid-liquid extraction (Ha et al., 2010) are often limited by the toxicity of the liquid absorbents to the microbial culture.

A more economical method of recovering butanol from dilute fermentation streams may be gas stripping (de Vrije et al., 2013; Liao et al., 2014; Plaza et al., 2013). Gas stripping is a relatively simple process in which a gas is continuously bubbled through the fermentation culture to volatilize and carry out the chemical (as well as some water vapor), which are subsequently condensed (Luo et al., 2006). The challenge with applying gas stripping to butanol fermentation is that the gas stream exiting the fermentor would also be very dilute. The condensation temperature required to condense butanol from a vapor stream is directly correlated with the butanol concentration. Therefore, a dilute butanol vapor would require exceptionally cold condensation temperatures, such as that of liquid nitrogen (Liao et al., 2014). These added costs would negate the benefits of gas stripping. To overcome this challenge, an alternative to direct condensation is to pass the gas stripping vapor first into an absorbent to concentrate the chemical. A smaller volume of gas can subsequently be used to displace the chemical from the absorbent, resulting in a higher concentration in this secondary vapor, such that cold water could be used to condense the product.

Activated carbon (AC) has been widely employed to adsorb volatile organic compounds (benzene, toluene, formaldehyde, n-hexane, butanol, and ethanol) from gas streams that are generated from a wide range of industries (Subrenat & Le Cloirec, 2004). AC has a large surface area, high porosity, a variety of pore sizes and structures, and rapid adsorption capabilities. Thus AC may provide an economical option for recovering and concentrating butanol in gas stripping vapor. However, prior work on the adsorption behavior of AC has not adequately addressed the

effects of adsorption temperature, concentration, and regeneration, which are critical for butanol recovery through vapor adsorption (Cao et al., 2015).

It is possible to treat AC to alter the surface functional groups present. For example, acid modification can increase the amount of acidic groups present, making AC ideal for the uptake of heavy metals or bases. Meanwhile, base modification will increase conjugated pi electron systems, making it ideal for uptake of aromatic organic acids (Yin et al., 2007). The performance of AC in most applications is related to its pore structure, specific surface area, and surface functional groups, with modification of its properties being the target of treatment (Soudani et al., 2013). Butanol is neutral with a hydroxyl group. According to the hydrogen-bonding interaction, we hypothesized that butanol adsorption capacity could be increased by generating carboxyl and hydroxyl groups on the surface of the active carbons, which would potentially form hydrogen-bonding interaction with butanol. The aim of this study was to investigate the effects of nitric acid hydrothermal modification on the butanol adsorption /desorption activity of AC.

2.0 Materials and methods

2.1 Materials

HNO₃, butanol, hydrochloride acid, sodium hydroxide, and ethanol were purchased from Thermo Fisher Scientific Inc. All of these chemicals were analytical grade. Commercial AC Sabre Series CR2050C-75 (unmodified AC) was donated by Carbon Resources. Several types of modified AC were generated by reacting the commercial AC at different concentrations of HNO₃.

2.2 Methods

2.2.1 Modification of AC

The commercial AC was washed by boiling water with a Soxhlet extractor for 2 h. The wet AC was dried at 105°C for 24 h. Five g of the dried AC was reacted with 30 ml HNO₃ at 2M,

4M and 6M concentrations in a sealed PTFE reactor (50ml) at 120 °C for 1 h. After reaction, the reactant was cooled and filtered, then washed with deionized water under vacuum filtration until the pH value of the permeate was ~7. Finally, the washed AC was dried in a vacuum oven at 105 °C overnight. Then the dried AC was ground and run through a sieve, and grains falling within US mesh sizes 50-100 were used as absorbents.

2.2.2 Analytical methods for absorbents

Isotherm adsorption of N₂ was carried out using an ASAP 2010 Micropore Analyzer. The total pore volume was determined at relative pressure 0.995 P₀, and the specific surface area was calculated from the BET method. The micropore and mesopore volume and the pore size distribution were determined by the density functional theory (DFT) for samples based on the N₂ isotherm adsorption data.

Temperature-programmed desorption (TPD) was performed using a Micrometrics Autochem II Chemisorption Analyzer to investigate the oxygen content of these four AC samples. The carbon sample (0.1 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, 60, and 60 cm³/min respectively). The thermal conductivity detector (TCD) signals were monitored during the thermal analysis, and the corresponding TCD spectra was obtained.

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 (30m×0.15μm×15mm). 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

129 injection temperature was 150 °C. The mass spectrometer was operated in EI mode. Mass spectra
130 were acquired in full scan mode with repetitive scanning from 45 m/z to 500 m/z in 0.25 s. Ion
131 source temperature was 250 °C.

132 **2.2.4 Dynamic adsorption and regeneration experiments**

133 The Micrometrics Autochem II Chemisorption Analyzer, connected to the Shimadzu GC-
134 MS, was also employed to investigate butanol adsorption and desorption on different adsorbents.
135 Fig. 1 shows the schematic diagram of the adsorption system used for testing the adsorbents. The
136 flow rate of the vapor, carrier, and reference were set at 5, 5, and 10 cm³/min, respectively.
137 Experiments were performed using helium as carrier gas, assuming that helium does not interfere
138 with butanol adsorption on AC (Cao et al., 2015). Pure butanol was heated to 50 °C and sparged
139 with helium at 5 cm³/min. The gas outflow passed through the sample tube with carrier gas at 5
140 cm³/min. The butanol from the outflow was adsorbed by the loaded AC, and what remained
141 passed through the analysis chamber and then into the gas chromatograph. The reference
142 chamber recorded the TCD readings and plotted it against time. The GC-MS recorded the
143 intensity of the signal produced by the adsorbate as a function of time approximately once every
144 10.5 min, and the integral of the curve provided the volume of adsorbate present after adsorption.
145 At least 20 data points were obtained by the GC-MS over the course of the analysis.

146 For regeneration, the TPD process pre-programmed into the Micromeritics analyzer was
147 used. The flow rate of the vapor, carrier, and reference were set at 0, 10, and 10 cm³/min,
148 respectively. The temperature ramp was set at 15 °C/min, starting from 25 °C to the set
149 temperature with a 1 h end temperature hold.

150 **2.2.5 Butanol quantification**

151 To test the impact of surface modifications on the adsorption and desorption capacities of

AC, a standard curve using a GC-MS was created as described previously (Cao et al., 2015). Ethanol was used as solvent to prepare different concentrations of butanol (1.0, 5.0, 10.0, 20.0, 30.0, 50.0, 60.0, 75.0, 93.0, 170.0, 235.0, and 290.0 mg/ml) which were analyzed in a Shimadzu GC-MS to generate a standard curve that was subsequently used to measure butanol levels from the outlet of the sample tube.

To quantify butanol vapor that was not adsorbed onto the adsorbent from the packed column, 0.5 ml of the outlet stream exiting the adsorption column was injected into GC-MS. Since the GC-MS needed time to cool down, the outlet of the sample tube was measured every 10.5 minutes. Determination of the outlet butanol vapor concentration as a function of time allowed us to determine the breakthrough curve and experimentally calculate the dynamic adsorption capacity of the packed column for each experiment. The adsorbed amounts were calculated with 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 absorbed (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 ($\mu\text{g ml}^{-1}$).

3. Results and Discussion

3.1 Physicochemical properties of active carbons

Pore structure and surface area parameters were obtained by the N_2 adsorption method, while micropore volume was determined using the density functional theory (DFT). Fig. 2A

shows the N₂ adsorption/desorption isothermal curves of the four adsorbents. The isotherms were similar for both the original AC and the AC treated with 2 M HNO₃, but when AC was treated with higher HNO₃ concentrations (4 and 6 M), N₂ uptake increased. Table 1 shows that the BET surface areas were larger (1486 and 1277 m² g⁻¹, respectively) for these latter treatments in comparison to the original AC (1157 m² g⁻¹). Table 1 also shows that the pore structures were affected by the higher HNO₃ concentrations. The total pore volumes of the modified AC increased 0.24 and 0.13 cm³ g⁻¹ for the 4 M and 6 M HNO₃ modifications, respectively, in comparison to untreated AC. Total pore volume for the 2 M HNO₃ treatment was similar to the control. Formation of new pores or opening of inaccessible pores are two possible explanations for the increased BET surface areas (Silva et al., 2009).

The nitric acid hydrothermal treatment increased the micropore volumes of modified ACs from 0.39 cm³ g⁻¹ in AC to 0.43, 0.49 and 0.43 cm³ g⁻¹ by using 2, 4 and 6 M HNO₃ modifications, respectively. Increased micropore volume and BET surface area both contributed to enhanced accessibility to the inner part of the micropores by defect creation and/or opening of blocked micropores. Although the micropore volume increased slightly, the total pore volume of the 2M HNO₃ modified AC was similar to the control (0.72 vs 0.73 cm³ g⁻¹), perhaps because this treatment caused mesopore volume to drop (from 0.27 to 0.24 cm³ g⁻¹). This may have been caused by intensive erosion of mesopore walls by HNO₃, resulting in partial destruction or collapse of the porous structure (Soudani et al., 2013; Wang et al., 2009; Yin et al., 2007). Some of the mesopore may have changed into micropore. Table 1 shows that the average pore diameter of the AC decreased from 2.49 into 2.36 nm following treatment with 2 M HNO₃. In addition, the oxygen containing groups introduced by HNO₃ modification were probably fixed at the

active sites at the entrance of the mesopores (Khelifi et al., 2010). These oxygen containing groups could hinder access to the pores.

By contrast, mesopore volume increased greatly for samples modified by 4 and 6 M HNO₃ (Table 1). As is shown in Fig. 2B, DFT model simulation results according to the nitrogen adsorption/desorption curve indicate that the volume of pores between 2 nm and 50 nm were increased from 0.27 to 0.39 (4 M HNO₃) and 0.36 cm³ g⁻¹ (6 M HNO₃), respectively. Higher concentrations of HNO₃ reacted much more strongly, causing more robust oxidation and etching of the carbon matrix of AC, and generating additional micropores and mesopores by eroding carbon walls via strong oxidation. Widening of micropores into mesopores also may have contributed to the greater increase in mesopores. This resulted in the average pore diameter of the ACs modified by 4 and 6 M HNO₃ increasing to 2.58 and 2.66 nm, respectively (Table 1).

In summary, 4 M HNO₃ treatment of AC resulted in the largest changes in AC texture, surface area, micropore volume, and total pore volume. This suggests that a proper concentration of HNO₃ can generate more micropores and mesopores. Due to erosion of reactive sites on the AC, total pore volume increased at higher concentrations of oxidative acid (e.g. 4 and 6 M HNO₃).

Temperature-programmed desorption (TPD) was employed to investigate the functional groups generated by HNO₃ modification. The carrier gas helium and the detected gases (CO, O₂ and CO₂) have different thermal conductivities. TCD signals from the evolved gases were recorded and the areas under the peak were proportional to the amount of gases produced. The TCD readings were zeroed using carrier gas and reference gas at the beginning of each measurement.

Fig. 2C displays the TPD spectra arising from oxygenated groups released as CO and CO₂ from the surface of AC that had been hydrothermally treated with different concentration of HNO₃. The TPD profile measured for the untreated AC was also included. The quantity of oxygenated groups released during treatment was directly related to the HNO₃ concentration used to treat AC. Generally, carboxylic functional groups decompose and release H₂O at lower temperatures (100 °C to 400 °C), while anhydride and lactone groups decompose at higher temperatures (427 °C) (Marchon et al., 1988; Zhuang et al., 1994; Zielke et al., 1996). In this study, the peaks formed between 400-1000 °C were assumed to be CO₂ and CO (Figueiredo et al., 1999), and the CO was possibly derived from the decomposition of phenols, ethers and carbonyls/quinones (Langley et al., 2005; Ruta et al., 2008; Tribolet & Kiwi-Minsker, 2005).

3.2 Adsorption of butanol on the adsorbents

3.2.1 Adsorption of different concentrations of butanol on unmodified AC

To observe the effects of butanol vapor concentration (11.9, 15.9, 19.9, 23.9 and 31.9 µg ml⁻¹) on the breakthrough characteristic of AC, experiments were conducted at atmospheric conditions and 25 °C. As shown in Fig. 3A, the breakthrough time considerably decreased from about 85 min to less than 30 min as the butanol concentration increased from 11.9 to 31.9 µg ml⁻¹.

The widely used Langmuir isotherm has found successful application in many real adsorption processes and is expressed as:

$$q_e = \frac{q_m B P_e}{1 + B P_e} \quad (3)$$

which can be rearranged to obtain a linear form

$$\frac{P_e}{q_e} = \frac{P_e}{q_m} + \frac{1}{q_m B} \quad (4)$$

where q_m refers to the monolayer adsorption capacity, q_e is amount of adsorption at equilibrium, P_e is the partial pressure of butanol vapor at equilibrium and B is the Langmuir

constant.

A linearized plot of P_e/q_e versus q_e was obtained from the model shown in Fig. S1. The fit is good for unmodified AC with butanol vapor under the concentration ranges studied (correlation coefficient, $R^2 > 0.988$). This indicates that the calculated maximum monolayer capacity q_m of butanol vapor onto the unmodified AC is 359.7 mg g^{-1} and the Langmuir isotherm parameter B is 5.24 kPa^{-1} .

3.2.2 Adsorption of butanol on the adsorbents at 25 °C

Fig. 3B shows the breakthrough curves for $11.9 \text{ } \mu\text{g ml}^{-1}$ butanol under atmospheric conditions and 25 °C when adsorbed by the various AC samples. All samples had almost the same saturation time (158 min). The adsorption behavior of untreated AC and AC modified by 2 M HNO_3 were very similar, as the breakthrough curves almost overlapped. The breakthrough time ($C_o/C_i = 0.05$, which is defined as the time that the ratio of outlet to the inlet butanol concentration reaches 0.05) for 2 M HNO_3 modified AC was slightly lower (88.5 min) than the unmodified AC (90.0 min). Values for the key adsorption parameters listed in Table 2 were within the margin of error for the control and the 2 M HNO_3 AC treatment, suggesting that it was not strong enough to change adsorption significantly. This is consistent with the relative lack of change in micropore, mesopore, and total pore volumes noted in Table 1.

On the other hand, after treatment of AC with higher concentrations of HNO_3 (4 and 6 M), butanol breakthrough times were reduced to 75.0 and 58.0 min, respectively. It can be observed (Fig. 3B) that the profile corresponding to the 4 M HNO_3 -modified AC was steeper than that of 6 M HNO_3 -modified AC, which implies a slower butanol adsorption rate for the latter. The AC modified by 4 M HNO_3 had a greater total pore volume ($+0.11 \text{ cm}^3 \text{ g}^{-1}$) and a higher percentage of micropores compared to mesopores than 6 M HNO_3 -modified AC. Oxygen-containing

functional generated during HNO_3 treatment could also cause resistance to butanol diffusion into micropores, making it butanol breakthrough more rapid. Thus the order of butanol breakthrough was $6\text{ M HNO}_3 < 4\text{ M HNO}_3 < 2\text{ M HNO}_3 < \text{unmodified}$ for these AC samples.

It is well-known that both the porous structure and the surface chemistry of AC are important factors affecting adsorption of different compounds. Increasing the surface area of sorbents will generally lead to improved adsorption, but the effects of functional surface groups on the adsorptive characteristics of ACs is closely related to the chemical nature of the adsorbates. As can be seen from Fig. S2, the water contact angle for unmodified AC was 99° , and it decreased to 35° after modification with 2 M HNO_3 . Water contact angles could not be measured on the surface of the 4 and 6 M HNO_3 -modified ACs since water droplets spread out too rapidly. Conversely, butanol spread very rapidly on the surface of the unmodified-AC, while butanol contact angles of 13° , 16° , and 17° were measured for AC treated with 2, 4, and 6 M HNO_3 , respectfully. This indicates that HNO_3 modification changed AC from a hydrophobic into hydrophilic material, and the higher HNO_3 concentration resulted the higher surface hydrophilicity. Butanol has higher affinity for hydrophobic active carbons than hydrophilic active carbon. Hence, the slightly decreased butanol adsorption was partially due to the increased oxygen functional groups, which decreased the affinity of butanol.

Although the AC modified by 4 M HNO_3 had largest BET surface area and highest total pore volume, it had the lowest dynamic saturate adsorption capacity (236.8 mg g^{-1} , Table 2). The kinetic diameter of butanol is 0.5 nm (Borjigin et al., 2012), and the high proportion of micropores (smaller than 2 nm) in the AC modified by 4 M HNO_3 ($0.49\text{ cm}^3\text{ g}^{-1}$) provided a more stable environment to store butanol molecules. However, partial micropores were not able to adsorb the butanol molecules effectively since they were covered with oxygen-containing

functional groups, which repelled the butanol molecules. Therefore, adsorption of butanol is not only dependent on the BET surface but also on the surface functional groups.

3.2.3 Adsorption of butanol on the adsorbents at 30 °C

Fig. 3C shows the breakthrough curves for butanol under atmospheric conditions and 30 °C. The breakthrough time of these four adsorbents was much lower compared with adsorption at 25 °C. Increasing the adsorption temperature decreased both breakthrough time and total adsorption. The unmodified AC still had the highest adsorption capacity (170.0 mg g⁻¹, Table 3), while the 4 M HNO₃-modified AC had the lowest adsorption capacity (139.4 mg g⁻¹, Table 3). The adsorption capacity of the 2 M HNO₃-modified AC (168.2 mg g⁻¹) was statistically similar to the untreated control, but higher than the 6 M HNO₃-modified AC (163.8 mg g⁻¹). Thus the trends in adsorption behavior were similar for both 25 and 30 °C.

Higher adsorption temperatures were also investigated for the unmodified AC. Fig. S2 shows the breakthrough curve shifted further to the left as the temperature was increased to 35 °C, indicating an early saturation of the unmodified AC. Therefore, lower temperature seems to have higher adsorption for the butanol vapor. Since both higher and lower adsorption temperatures require much more energy than the room temperature 25 °C, the optimal adsorption temperature for butanol vapor is 25 °C.

3.3 Regeneration of the adsorbent

Heating was used to recover butanol and regenerate adsorbent from saturated AC samples. Fig. 4A shows the TPD of butanol saturated, unmodified AC at 110, 130, and 150 °C. The TCD signal shows that butanol desorption was positively correlated with regeneration temperature, with the highest amount of butanol evolved at 150 °C. In a subsequent adsorption cycle with the unmodified AC that had been regenerated at 130 °C, we observed a decrease in adsorption

ability compared to fresh, unmodified AC (Fig. 4B). In this case the breakthrough time decreased from 95 to 50 min, and the saturation time decreased from 158 to 126.5 min. This indicates that 130 °C is not high enough to remove all of the adsorbed butanol vapor.

In a separate test we used a regeneration temperature of 150 °C to assess adsorption ability of unmodified AC for four cycles of adsorption/desorption. As is shown in the Fig. 5A, the breakthrough curves for the four cycles were identical, indicating that 150 °C is an appropriate desorption temperature for butanol saturated AC. The almost overlapped adsorptions mean that the unmodified AC has non-changed adsorption ability after heating regeneration at 150 °C.

To investigate the influence of oxidation on repeated adsorption/desorption cycles, AC modified with 6 M HNO₃ was evaluated. The outlet was monitored by TCD and GC-MS during desorption. As shown in Fig. 5B, the adsorption capacity appeared to decrease after the first adsorption and desorption round, but was stable for the second to fourth cycles. From the TCD signals (Fig. 6) for the desorptions, it can be concluded that the adsorption capacities for butanol were almost the same for the second to fourth cycles. However, the breakthrough curve (Fig. 5B) for the first adsorption indicates that it has loaded more butanol than the subsequent adsorption cycles. We hypothesize that surface oxides reacted with butanol and formed new functional groups on the surface in the first round, which partially blocked butanol chemical adsorption sites for cycles two through four.

Fig. 4SA is the GC-MS profile of the outlet at 100 °C for the first regeneration. Besides the butanol peak, there were four peaks. According to the MS profiles (Fig. 4SB) and a similarity search in the GC-MS standard library, peak 1 was 1-butene, peak 2 was butane, peak 3 was butanol, peak 4 was formic acid butyl ester, and peak 5 was n-Butyl ether. The mass spectral

similarities were 98%, 98%, 98%, 98%, and 94%, respectively. Thus, it can be inferred that the modified AC catalytically reacted with butanol. The exact mechanism of the reaction cannot be explained at the present stage of investigation. A detailed analysis will be needed in the future.

4. Conclusion

Hydrothermal modification with 4 M HNO₃ increased BET surface area by 329 m² g⁻¹, micropore volume by 0.10 cm³ g⁻¹, and mesopore volume by 0.12 cm³ g⁻¹. However, the adsorption capacity (dynamic saturate) decreased from 255.8 to 236.6 mg g⁻¹. The oxygen-containing functional groups generated by HNO₃ hydrothermal treatment decreased the butanol adsorption ability of the AC. Overall, the adsorption capacity is not only related to the pore structure but also the surface functional groups. The butanol absorbed by the modified AC cannot be fully recovered after the first adsorption because it partially reacts with the functional groups on the surface.

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Table caption

Table 1 Surface area and pore structure parameters of the absorbents.

Table 2 Key adsorption parameters for butanol adsorption at 25 °C.

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Table 1 Surface area and pore structure parameters of the absorbents.

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
2mol/L HNO ₃	1236	0.73	0.43	0.24	2.36
4mol/L HNO ₃	1486	0.96	0.49	0.39	2.58
6mol/L HNO ₃	1277	0.85	0.43	0.36	2.66

^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 Key adsorption parameters for butanol adsorption at 25 °C.

Items	Unmodified AC	2 M HNO ₃ treated AC	4 M HNO ₃ treated AC	6 M HNO ₃ treated AC
F _A ^a (ml min ⁻¹)	10	10	10	10
T _q ^b (min)	107.47±0.85	106.51±0.97	99.45±1.12	102.56±1.01
C _i ^c (µg ml ⁻¹)	11.90	11.90	11.90	11.90
M _{adsorption} ^d (mg)	12.79±0.10	12.67±0.12	11.83±0.13	12.20±0.12
W ^e (mg)	50	50	50	50
Q ^f (mg g ⁻¹)	255.8±2.0	253.4±2.4	236.6±2.6	244.0±2.4

^a Volumetric flow rate of the carrier gas

^b Stoichiometric time determined from the breakthrough curve

^c Butanol concentration at the inlet

^d Mass of butanol adsorbed

^e Net weight of adsorbent

^f Dynamic adsorption capacity of the adsorbent

Table 3 Key adsorption parameters for butanol adsorption at 30 °C.

Items	Unmodified AC	2 M HNO ₃ treated AC	4 M HNO ₃ treated AC	6 M HNO ₃ treated AC
F _A ^a (ml min ⁻¹)	10	10	10	10
T _q ^b (min)	71.45±0.95	70.71±1.03	58.53±1.31	68.82±1.10
C _i ^c (µg ml ⁻¹)	11.90	11.90	11.90	11.90
M _{adsorption} ^d (mg)	8.50±0.11	8.41±0.12	6.97±0.16	8.19±0.13
W ^e (mg)	50	50	50	50
Q ^f (mg g ⁻¹)	170.0±2.2	168.2±2.4	139.4±3.2	163.8±2.6

^a Volumetric flow rate of the carrier gas

^b Stoichiometric time determined from the breakthrough curve

^c Butanol concentration at the inlet

^d Mass of butanol adsorbed

^e Net weight of adsorbent

^f Dynamic adsorption capacity of the adsorbent

Figure captions

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.

Fig. 2. (A) N₂ isothermal adsorption/desorption on the absorbents; (B) DFT pore size distribution curves of the absorbents; (C) TCD signals for temperature-programmed desorption of AC samples.

Fig. 3 (A) Butanol adsorption capabilities of unmodified AC at different butanol concentrations; (B) Adsorption capabilities of different absorbents at 25 °C; (C) Adsorption capabilities of different absorbents at 30 °C.

Fig. 4. (A) Butanol desorption of unmodified AC at different temperatures; (B) Adsorption curves for fresh and regenerated (at 130 °C) unmodified AC.

Fig. 5. (A) Repeated adsorption of butanol with unmodified AC; (B) Repeated adsorption of butanol with 6 M HNO₃ modified AC.

Fig. 6. Butanol desorption of 6 M HNO₃ modified AC.

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.

A

B

C

Fig. 2. (A) N₂ isothermal adsorption/desorption on the absorbents; (B) DFT pore size distribution curves of the absorbents; (C) TCD signals for temperature-programmed desorption of AC samples.

A

B

C

Fig. 3 (A) Butanol adsorption capabilities of unmodified AC at different butanol concentrations; (B) Adsorption capabilities of different absorbents at 25 °C; (C) Adsorption capabilities of different absorbents at 30 °C.

A

B

Fig. 4. (A) Butanol desorption of unmodified AC at different temperatures; (B) Adsorption curves for fresh and regenerated (at 130 °C) unmodified AC.

A

B

Fig. 5. (A) Repeated adsorption of butanol with unmodified AC; (B) Repeated adsorption of butanol with 6 M HNO_3 modified AC.

Fig. 6. Butanol desorption of 6 M HNO₃ modified AC.