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# PAPER



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# Experimental and DFT investigations on adsorption-regeneration performance and deactivation mechanism over engineered carbon fiber: role of pore structure and functional groups<sup>†</sup>

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Technology based on adsorption of porous carbon is a promising and cost-effective strategy for the recovery of high-value volatile organic compounds (VOCs) or removal of worthless VOCs. However, the deactivation mechanism of porous carbon adsorbents determined by pore structure and functional groups is not clear. This knowledge gap limits their application in the resource utilization or pollution control of VOCs. We investigated the effect of the pore structure and functional groups in relation to adsorption and regeneration of ethyl acetate (EA) over engineered carbon-fiber adsorbents. Experimental and density functional theory (DFT) results indicated that appropriate basic groups were beneficial for EA adsorption, and the physisorption of micropore structure contributed more to the adsorption capacity. However, the strong chemisorption between EA and adsorbents hampered complete regeneration (only 81.5% capacity retention over six cycles of optimal adsorbents). Semi-quantitative methods and identification of intermediates confirmed that deactivation of porous carbon adsorbents was closely related to EA conversion due to strong chemisorption between EA and the adsorbent interface, which resulted in blockade of the pore structure and occupation of interfacial active sites. Our results may guide the design of highly efficient and economic adsorbents with complex micro-interfaces for recovery of high-value VOC.

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#### **Environmental significance**

Porous carbon adsorbents are often at risk of deactivation after repeated adsorption-regeneration. However, the deactivation mechanism is not clear. Herein, we established a correlation between porous carbon interfaces and adsorption-regeneration deactivation from the microscopic viewpoint, revealing the key factors for adsorbent deactivation. An enhanced adsorption capacity was attributable mainly to the physisorption of the micropore structure. The chemisorption of interfacial functional groups (*e.g.*, bases) was conducive to volatile organic compound (VOC) adsorption, but they could also be activated with VOCs during thermal desorption and form polymeric species (which are hard to regenerate). The deactivation of porous carbon adsorbents was closely related to VOC conversion due to strong chemisorption, which resulted in blockade of the pore structure and occupation of interfacial active sites.

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## 1. Introduction

The emission of volatile organic compounds (VOCs) from industrial processes has caused a substantial increase in environmental pollution and health hazards. Oxygenated volatile organic compounds (OVOCs) such as esters, aldehydes, and ketones are common industrial organic solvents as well as the major exhaust waste gas in the chemical industry. Due to their strong reactivity, OVOCs are regarded as important air pollutants. They make a major contribution to the formation of secondary pollutants (*e.g.*, particles  $\leq 2.5$  microns in diameter (PM2.5), tropospheric O<sub>3</sub> and simultaneous photochemical smog) and result in environmental deterioration and chronic respiratory diseases.<sup>1</sup> Therefore, emission control or resource utilization of VOCs are needed to protect environmental sustainability and human health.

Recently, adsorption technology has been considered to be a promising strategy thanks to its economic features and sustainability in resource utilization of OVOCs, especially for capturing highly toxic and value-added compounds from industrial VOCs.<sup>2,3</sup> Activated carbon materials (ACMs) have received increasing attention as desirable and widely used industrial adsorbents for control of OVOCs emission. The adsorption performance of ACMs is largely dependent upon the surface chemistry and structural characteristics of the main skeleton because these active sites, organophilic properties, and the pore structure can directly affect the adsorption and desorption of OVOCs.<sup>4-6</sup> In particular, the pore distribution in ACMs can be regulated to facilitate OVOCs diffusion and to balance adsorption and desorption processes.<sup>7,8</sup> For instance, Wang et al. demonstrated that a well-developed hierarchical pore structure could promote the desorption efficiency of ethyl acetate (EA) on ACMs; the desorption efficiency remained as high as 93% after several cycles of adsorption and desorption.<sup>9</sup> In general, ACMs with a controlled and homogeneous pore structure can provide good porosity for interfacial interactions by maintaining an interlaced carbon-skeleton structure that makes the most of the surface area available for the mass transfer that underpins adsorption.<sup>10,11</sup> Microporous ACMs commonly have a high adsorption capacity owing to their higher specific surface area and more active sites. However, the adsorption capacity of ACMs often suffers a sharp decrease after desorption regeneration due to VOCs molecules reacting with an active interface. This phenomenon results in the formation of some high boiling-point products and subsequent blockade of the microporous structure.<sup>12,13</sup> Meanwhile, the higher steric hindrance of microporous ACMs increases time and energy costs during the regeneration of adsorbents as compared with mesoporous ACMs because of the low diffusion rate of VOCs in microporous ACMs. Chiang et al. corroborated that the diffusion rate of acetone  $(10^{-7})$ cm<sup>2</sup> s<sup>-1</sup>) was substantially lower in a microporous ACM than in mesoporous carbon  $(10^{-4} \text{ cm}^2 \text{ s}^{-1})$ .<sup>14</sup> Furthermore, only a few studies have focused on the deactivation mechanism that the pore structure of porous carbon adsorbents interferes with during adsorption-desorption conversion of VOCs.

Besides, the type and concentration of surface functional groups can also strongly affect interaction between VOCs and the adsorption–desorption behaviour of ACM.<sup>15</sup> Zhu *et al.* demonstrated that oxygen-containing groups (*e.g.*, carbonyl, lactone) on an ACM surface can impart more hydrophilicity, thereby increasing the contact force between polar VOC molecules and the adsorption interface.<sup>9</sup> Minsker *et al.* discovered that increasing the number of carboxyl and hydroxyl groups on the ACM surface increased acetaldehyde adsorption by 20%.<sup>16</sup> However, the inhomogeneity of the ACM surface and the synergistic effect of these functional

groups promote physical adsorption while increasing the difficulty of the desorption process.<sup>17</sup> El-Sayed reported that a high-energy interaction between a carboxyl group on the ACM surface and acetaldehyde group increased the desorption energy by 10 kJ mol<sup>-1</sup>.<sup>18</sup> Similarly, Ghimbeu et al. demonstrated that a high-energy interaction between an ether group on the ACM surface and the hydroxyl group on ethanol molecules increased the desorption energy to 105 kJ mol<sup>-1</sup>.<sup>19</sup> As stated above, the pore structure and functional groups of porous carbon adsorbents have important roles in the reactive transport process of OVOCs over a microinterface.<sup>20</sup> However, the relevance of an appropriate pore scale on accessible adsorption-desorption behaviour and mechanism of VOCs conversion has not been established. Also, how VOCs and oxygen-containing functional groups interact on the surface of ACMs is not known. Therefore, the role of pore-structure factors and interactions with the functional groups of a porous carbon surface must be established to gain deeper understanding of the adsorptiondesorption process.21

In this work, the pore structure and functional groups of porous carbon adsorbents were regulated by a slow-pyrolysis method using bacterial celluloses (BCs) as precursors. Then, we investigated the recycling of EA and regeneration of adsorbents. Experimental results revealed that the pore volume and basic groups were positively correlated with the adsorption capacity. Furthermore, the deactivation of adsorbents caused by pore-channel blockade and covering of active sites was demonstrated, which significantly decreased EA adsorption and adsorbent regeneration.

### 2. Experimental section

#### 2.1 Preparation of porous carbon adsorbents

First, porous carbon (PC) adsorbents were prepared. Freezedried BCs (~1 g) was added to a 250 mL reagent bottle containing 100 mL of NaOH solution (0.1 M). The mixture was agitated for 10 h at room temperature before being centrifuged and rinsed with distilled water to achieve a neutral pH. All samples were redispersed with 100 mL of distilled water to create a homogeneous slurry. Following that, BC samples were recovered after 48 h of drying at 75 °C under vacuum conditions (0.1 MPa). Then, the dried precursors were pyrolyzed for 2 h in a tube furnace in an Ar atmosphere at 300 °C, 400 °C, 500 °C, 650 °C, 750 °C, 850 °C and 950 °C at a heating rate of 2 °C min<sup>-1</sup>, respectively. Finally, adsorbents were obtained and denoted as "CBC-*X*", in which "*X*" represented the pyrolysis temperature.

# 2.2 Characterization of adsorbents and density functional theory (DFT) calculations

Scanning electron microscopy (SEM) was used to observe the surface morphology of the adsorbent using a Merlin system (Zeiss). A high-performance adsorption and porosity analyzer (ASAP 2020 PLUS HD88) was used to quantify  $N_2$  adsorption-desorption isotherms and pore-size distribution at 77 K

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(Micromeritics). Functional groups and adsorption products were identified using a Fourier transform-infrared (FTIR) instrument in a wavenumber range of the 4000–500 cm<sup>-1</sup>. Boehm titration was used to determine the number of surface functional groups. Difference scanning calorimetry-thermogravimetric analysis (TGA-DSC) was employed to explore the thermal behaviours of carbon surfaces. The surface chemistry and chemical state of adsorbents were characterized by semi-quantitative methods (temperature-programmed desorption (TPD; see the Supporting Information for details) and X-ray photoelectron spectroscopy (XPS)). DFT computations were carried out with Materials Studio (see the ESI† for details), and construction of the relevant model was based on the literature.<sup>22</sup>

#### 2.3 Adsorption, regeneration and analysis of byproducts

Adsorption experiments were carried out in a circular quartz reactor with a fixed bed at room temperature. To eliminate moisture and contaminants from the material, adsorbents ( $20 \pm 0.1 \text{ mg}$ ) were typically processed at 150 °C for 1 h under a vacuum before cooling to ambient temperature in a N<sub>2</sub> flow. The flow rate of N<sub>2</sub> gas (utilized as an EA carrier in gas-phase adsorption) was kept constant at 30 mL min<sup>-1</sup> to maintain the inflow concentration of EA at 40 ppm (7% fluctuations). Then, the EA content in the output gas was measured continually using an online gas chromatograph equipped with a flame-ionization detector. The adsorption capacity was determined by measuring the difference between inlet VOC concentration and outlet VOC concentration. When the adsorption bed layer was saturated, the adsorption amount (q, mg g<sup>-1</sup>) was calculated as follows (eqn (1)):<sup>23</sup>

$$q = \frac{Q}{m \times 10^{-6}} \int_{0}^{t_{\rm s}} (C_{\rm in} - C_{\rm out}) \mathrm{d}t$$
 (1)

After saturation adsorption, samples were regenerated using a hot N<sub>2</sub> stream at 30 mL min<sup>-1</sup>. N<sub>2</sub> was purged into the sample column at the start of regeneration, and the programmed warming mode was activated to heat up to 120 °C at a rate of 5 °C min<sup>-1</sup>. The output EA concentration was monitored online by GC, and the desorption process took 6 h. Then, the adsorbent was cooled to room temperature before being utilized in the next adsorption cycle. The adsorption/desorption tests were repeated 14 times. The desorption capacity of the adsorbent was calculated on the basis of the desorption curve using eqn (2):<sup>24</sup>

$$q = \frac{V}{1000m} \int_0^t C_t \mathrm{d}t \tag{2}$$

where  $q \text{ (mg g}^{-1})$  is the adsorption capacity, Q is the gas flow rate (mL min<sup>-1</sup>), C in and C out (mg L<sup>-1</sup>) refer to the concentrations of EA at the inlet and outlet, respectively, m(g) is the amount of adsorber in the reactor, and t (min) refers to the adsorption time. The correlation coefficients between adsorption capacity with pore structure and functional groups were obtained by the Spearman correlation analysis according to the test results (data with an abnormal distribution were suitable for Spearman correlation analysis).

After multiple adsorption-desorption recycling, the intermediate byproducts on the adsorbents were extracted by dichloromethane or EA and detected by a GC-MS (see the ESI† for details). EA adsorption on synthesized adsorbents was also analysed by *in situ* diffuse reflectance Fourier transform infrared spectroscopy (see the ESI† for details).

### 3. Results and discussion

#### 3.1 Analysis of pore structure and functional groups

The pore structure and functional group of CBC was regulated by a temperature-dependent method (Fig. 1A). As uncovered by N2 adsorption-desorption isotherms and the corresponding pore-size distributions (Fig. S1 and Table S1<sup>†</sup>), the adsorbents of CBC-300-CBC-950 mainly exhibited type-IV with H4 hysteresis. Usually, this hysteresis loop is associated with the capillary condensation that occurs in mesopores, indicating the appearance of microporous and mesoporous adsorbents after high-temperature pyrolysis, and solids containing narrow and fractured pores.<sup>25</sup> Fig. 1B displays that the specific surface area  $(S_{\text{BET}})$  increased from 20.42  $m^2 \ g^{-1}$  for CBC-300 to 379.7  $m^2 \ g^{-1}$  for CBC-850. Meanwhile, the pore volume increased from 0.058 to 0.247 mL  $g^{-1}$  with increasing pyrolysis temperature, suggesting that a higher carbonization temperature contributed to the formation of a carbon-skeleton structure. According to the range of pores in the DFT calculation (Fig. S2<sup>†</sup>), CBC adsorbents synthesized at different pyrolysis temperatures showed very similar curves, having a maximum centered at 8-14 nm. However, the average pore size was obviously different, ranging from 2.85 nm for CBC-850 to 9.47 nm for CBC-300, and the average pore size was more similar at a high pyrolysis temperature (from 500 °C to 950 °C). According to the basic morphology of CBC (Fig. S3<sup>†</sup>), CBC was interleaved to form flat layered structures, and the superposition of these layered structures



**Fig. 1** (A) CBC preparation. (B) Pore percentage and BET. (C) Concentration of functional groups in CBC prepared at different pyrolysis temperatures.

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often formed many slit pores.<sup>26</sup> The results were very consistent with the results of  $N_2$  adsorption–desorption isotherms. Moreover, the micropore volume of these adsorbents ranged from 0.00211 to 0.160 mL g<sup>-1</sup>, which had a significant positive correlation with the  $S_{BET}$ . According to the results shown above, a high pyrolysis temperature (850 °C for this result) seemed to be more conducive to porous-structure formation with large pore volume and  $S_{BET}$ .

In addition, the concentration of oxygen-containing groups on CBC was monitored by Boehm's titration method. As shown in Fig. 1C and Table S2,<sup>†</sup> the phenolic hydroxyl, carboxyl groups and lactone group (1.443, 2.579 and 2.525  $\mu$ mmol g<sup>-1</sup> for CBC-300) decreased steadily to be very low concentration (0.0400, 0.00226 and 0.0850  $\mu$ mmol g<sup>-1</sup> for CBC-950) with increasing pyrolysis temperature. For basic groups, the concentration first decreased to 0.319  $\mu$ mmol g<sup>-1</sup> (CBC-650) and then increased to 1.323  $\mu$ mmol g<sup>-1</sup> (CBC-950) with increasing pyrolysis temperature, which could be attributed to the interconversion of internal oxygen-containing functional groups. That is, the pyrolysis temperature had a great impact on the decomposition of the functional groups in CBC. To deeply understand the variable functional groups under different pyrolysis temperatures, TG-DSC and FTIR spectroscopy of BC and CBC were carefully carried out (Fig. S4 and S5<sup>†</sup>).<sup>5</sup> The weight loss produced in the 110 °C range, around 5-7 wt%, was attributed to the desorption of adsorbed water. Combined with FTIR spectroscopy data, the main weight loss during CBC pyrolysis ( $\approx$ 58.7 wt%) was generated in the range of 250–310 °C, which corresponded to the carbonization process of the organic matrix, including the loss of C-O bonds, the dehydration and condensation of C–OH and the formation of C=O.<sup>27</sup> From 300 °C to 650 °C, CBC had a slow rate of weight loss (percent weight loss = 12.30%) due to the shedding of C=O and C-OH.<sup>28</sup> Finally, in the pyrolysis temperature range of 650-950 °C, a more noticeable process of weight loss (16.80%) was observed, which was attributed to the side chains of some functional groups on the surface of the raw material becoming broken and detached from the carbon skeleton at a high treatment temperature, thereby resulting in the decomposition of functional groups at the surface.<sup>29</sup> These changes were also confirmed by FTIR spectroscopy (Fig. S5B<sup>†</sup>).

#### 3.2 Adsorption performance and regeneration performance

Based on the experimental results of pore structure and functional groups of CBC adsorbents, the correlation between adsorption capacity and these results was carefully demonstrated (Fig. 2). As observed clearly from Fig. 2A, the adsorption capacity of CBC adsorbents from low to high was 1.288, 2.340, 20.696, 33.267, 50.813, 74.041 and 141.568 mg g<sup>-1</sup>, and the total pore volume ( $V_{\text{total}}$ ) of these adsorbents corresponding to the adsorption capacity was 0.0584 (CBC-300), 0.0603 (CBC-650), 0.107 (CBC-400), 0.153 (CBC-500), 0.142 (CBC-750), 0.166 (CBC-950) and 0.247 mL g<sup>-1</sup> (CBC-850), respectively. The Spearman correlation between the adsorption capacity and  $S_{\text{BET}}$ ,  $S_{\text{mic}}$ , and  $V_{\text{mic}}$  was calculated to be 0.929, 0.929, and 0.929,



**Fig. 2** (A) Correlation characteristics of BET-adsorption capacity, (B) functional group-adsorption capacity of EA adsorption, and (C) corresponding linear dependence between  $ln[\beta_H/RT_p^2]$  and  $1/T_p$  derived from EA-TPD over CBC prepared at different pyrolysis temperatures. (D) Regeneration rate of CBC-850 for EA adsorption.

respectively, which indicated a significant correlation between adsorption capacity and pore volume, especially the micropore volume, which had an obvious positive correlation with adsorption capacity (Table S3, Fig. S6A and B†). The enhancement of adsorption capacity was mainly due to the abundant active sites for adsorption provided by a microporous structure.<sup>13</sup> However, there seems to be no significant correlation between adsorption capacity and  $S_{\text{BET}}$  in conventional wisdom even though adsorbents with high  $S_{\text{BET}}$ tend to have high adsorption capacity for EA overall (Fig. S6C and D†). That is, in terms of pore structure, the enhancement of EA adsorption is mainly determined by the total pore volume, in which micropore volume has a crucial role.

To explore the effects of functional groups further, the correlation between adsorption capacity and functional groups on the interface was studied carefully. As shown in Fig. 2B and Table S3,† there seemed to be no significant correlation between the content of main functional groups and adsorption capacity (Spearman correlations: carboxylic group, -0.857; phenolic group, -0.857; lactonic group, -0.964; basic group, 0.357). That is, too many oxygen-containing functional groups, especially lactonic, carboxylic and phenolic groups, were not conducive to EA adsorption on CBC adsorbents. However, there seemed to be a positive correlation between basic groups and adsorption capacity, which may have been due to the stronger affinity of basic groups to weakly acidic EA by electrostatic attraction. Therefore, in addition to the dominant role of  $V_{\text{total}}$ , fewer oxygen-containing functional groups may be beneficial for promoting the adsorption of EA. For example, although the  $V_{\text{total}}$  and  $S_{\text{BET}}$  of CBC-750 were slightly lower than those of CBC-500, it had higher EA adsorption capacity compared with that of CBC-500, which could be attributed to the low oxygencontaining functional content on its interface. In summary, only basic groups had a slightly positive correlation with the adsorption capacity, and oxygen-containing functional groups

contributed little to the enhancement of the adsorption capacity, which may affect only the binding strength of the adsorbent and EA.

The regeneration performance of adsorbed CBC adsorbents and EA-TPD were investigated to explore the adsorption strength and regeneration difficulty on the surface of CBC adsorbents.<sup>30</sup> As shown in Fig. S7,† the EA desorption rate of CBC adsorbents from low to high was 63% (CBC-400), 66% (CBC-300), 70% (CBC-650), 75% (CBC-500), 76% (CBC-750), 81% (CBC-950) and 88% (CBC-850). The efficiency of EA desorption seemed to be positively correlated with the total pore volume (especially with the micropore capacity) as well as the adsorption capacity. This was because the adsorption of EA on CBC was mainly dependent on physical-adsorption interaction of pore structure. That is, a suitable pore diameter and developed porosity in CBC adsorbents were very beneficial for enhancement of the efficiency of EA desorption. However, the efficiency of EA desorption on these CBC adsorbents could not reach 100%, which could be attributed to chemical interactions between EA and CBC.<sup>31</sup>

EA-TPD experiments were also undertaken at various heating rates (3 to 10 K min<sup>-1</sup>) to determine the desorption activation energy (Ed) of EA onto CBC adsorbents. The Ed of EA on CBC was calculated using the curve of  $\ln(T_p^2/H)$  and  $1/T_p$  (Fig. 2C and Table S3<sup> $\dagger$ </sup>). The Ed value of CBC-400 (36.46 kJ mol<sup>-1</sup>) and CBC-750 (33.75 kJ mol<sup>-1</sup>) was slightly higher than that of EA outside the heat of evaporation  $(32.29 \text{ kJ mol}^{-1})$ , indicating that chemical interactions dominated the adsorption process. In terms of CBC-850, the Ed of adsorbed EA on CBC-850 adsorbents (25.19 kJ mol<sup>-1</sup>) was obviously lower than the heat of vaporization (32.29 kJ mol<sup>-1</sup>) for EA, indicating that physisorption mainly guided the adsorption process.<sup>32</sup> Besides, CBC adsorbents with a high concentration of functional groups at low pyrolysis temperatures and high micropore distribution at high pyrolysis temperatures tended to possess a higher activation energy for EA desorption. Thus, chemical-physical interactions occurred during EA adsorption on CBC adsorbents. Furthermore, the regeneration properties of CBC-850 were investigated (Fig. 2D). After six successive adsorptiondesorption cycles, the EA adsorption capacity of CBC-850 was maintained at >80% of the initial EA adsorption capacity. Although CBC-850 has relatively durable structural characteristics in terms of adsorption-desorption performance, the adsorbent tended to be inactivated gradually. Therefore, the adsorption mechanism of EA on CBC and the deactivation mechanism of the adsorbent warrant further exploration.

#### 3.3 In situ FTIR spectroscopy and DFT computations

EA adsorption *in situ* DRIFTs was recorded to explore the adsorption forms and mechanism of EA adsorption on CBC adsorbents (Fig. 3 and S8†). When EA were introduced into the IR cell at 25 °C for 50 min, a series of peaks were observed. Three peaks in the range of 3000–2800 cm<sup>-1</sup> were the signals of the C–H stretching vibration on EA, whereas peaks at 2991 and



**Fig. 3** Time-dependent *in situ* DRIFTS of EA adsorption over CBC synthesized at different pyrolysis temperatures: (A) CBC-300, (B) CBC-400, (C) CBC-500, (D) CBC-650, (E) CBC-750 and (F) CBC-850).

2896 cm<sup>-1</sup> represented methyl and methylene species, respectively.<sup>33</sup> In the range of 2000–1000: 1764 cm<sup>-1</sup> represented the signal of C=O of EA; peaks at 1438 and 1373 cm<sup>-1</sup> belonged to the C-H of methylene and methyl species, respectively; the peaks at 1240 and 1056 cm<sup>-1</sup> were attributable to the C-O-C stretching vibration peak.<sup>34-36</sup> The typical vibrations at 2993, 2890, 1762, and 1056 cm<sup>-1</sup> were observed immediately, and the intensity of these peaks increased with increasing time of EA adsorption. The peak intensity at 1371 cm<sup>-1</sup> decreased gradually with the extension of adsorption time, indicating that the adsorption forms of EA on CBC adsorbents were rearranged due to the intermolecular competitive adsorption during the transformation process from single-layer to multilayer adsorption.<sup>22,37</sup> The methyl-dominated adsorption form of a part of EA changed gradually to the oxygen-containing-group binding form, which could be attributed to one part of physically adsorbed EA changing to chemically adsorbed EA.38,39 Moreover, as compared with other CBC adsorbents, there was an obvious blue shift at the signals of the C=O stretching vibration on CBC-400 and CBC-500 adsorbents, suggesting that the chemical bond between EA and CBC adsorbent may be formed, such as the formation of hydrogen bonds or the influence of a  $\pi$ -conjugated bond on the adsorbent.40

Furthermore, the adsorption mechanism between EA and functional groups of CBC adsorbents was also explored by DFT calculations (Fig. 4). All functionalized surface and EA molecules were fully geometry-optimized by the GGA-PBE exchange-correlation functional (Fig. S9<sup>†</sup>), and three monolayer and multilayer adsorption configurations were considered (Fig. S10 and S11<sup>†</sup>). For monolayer adsorption, the adsorption energy of pristine porous carbon (pristine PC), COOH, C=O, C-O-C and C-OH at the most stable EA adsorption configuration was -0.487, -0.597, -0.464, -0.207 and -0.521 eV, respectively. Except for a weak van der Waals interaction of C-O-C, other configurations were mainly chemisorption. Thereinto, the chemisorption between pristine PC and EA could be combined primarily through covalent interactions based on the calculation results. Among the four O-containing functional groups, the highest binding



Fig. 4 The most stable EA monolayer and multilayer adsorption configurations.

energy of EA,  $-0.597 \text{ eV} (57.60 \text{ kJ mol}^{-1})$ , was obtained in the COOH group. EA was strongly attracted by the carboxyl groups due to the hydrogen-bonding interaction between the O atom of C=O on EA and the H atom of the COOH group with a bond length of 1.773 Å. Meanwhile, three adsorption configurations of multilayer EA adsorption were also investigated. Except the C=O group, the adsorption energy of pristine PC and other oxygen-containing groupfunctionalized surfaces increased by 23.1-187.4%, which could be attributed to adsorption forms rearranged by the synergy of intermolecular interactions and the strong chemisorption between pristine PC and EA.<sup>2,37</sup> According to the results stated above, although the enhancement of EA adsorption capacity on CBC adsorbents was mainly dependent on physisorption, the strong chemisorption of the CBC interface to EA hampered complete regeneration, which could lead to a significant decrease in the adsorption capacity (and even deactivation of the adsorbent).<sup>11,12</sup>

#### 3.4 In-depth mechanism of adsorbents deactivation

The deactivation mechanism of the adsorbent interface was studied further. As shown in Table S4 and Fig. S12,† the  $S_{\text{BET}}$ ,  $V_{\text{total}}$  and pore diameter of CBC-850 adsorbent decreased obviously after multiple regeneration, which could be attributed to pore blockade of the adsorbent due to the formation of many carbonaceous byproducts at the adsorbent

interface.41 To confirm this observation, semi-quantitative analysis using XPS was used to explore the element composition and state at the surface using CBC-850 as an example (Fig. 5A and B). The C1s spectrum was deconvoluted into sub-peaks located at 284.8, 285.5, 286.8 and 290.0 eV, which were assigned to C=C, C-C, C-O and C=O, respectively.<sup>42</sup> The peaks of O 1s spectra at 530.9, 532.0, 532.8 and 533.9 eV belonged to groups C=O, O=C-O-(C, H), C-O-C (C-OH) and O=C-O-(C, H), respectively.43,44 After six regeneration cycles, obvious peak shifts in C1s and O1s spectra were observed, indicating that a new stable chemical structure had been formed at the interface of the CBC adsorbent during this process.45 To explore the element content of the interface structure, the proportion of total C, total O and other oxygen-containing groups on CBC adsorbents was calculated (Fig. 5C and S13 and Table S5<sup>†</sup>). The total proportion of O clearly increased after regeneration, which could be attributed to the increase of C=O and C-O species.46,47 From the deconvolution of O1s, the main functional groups of C=O (531.2 eV), O=C-O-(C, H) (532.4 eV) and C-O-C (C-OH) (533.6 eV) species increased by 1.17-58.7%, which further confirmed that many oxygen-containing carbonaceous species had formed and accumulated on the CBC adsorbent interface. Nevertheless, the O=C-O-(C, H)species located at 534.9 eV decreased by 49.6%, which could be attributed to the original functional groups of CBC adsorbents becoming covered by newly formed carbonaceous byproducts during the regeneration process.

The  $I_D/I_G$  and  $A_{sp3}/A_{sp2}$  of CBC adsorbents were calculated based on deconvolution of Raman spectra to explore the effect of byproduct accumulation on interface defects (Fig. 5D and Table S6†). Compared with fresh CBC-850, the  $I_D/I_G$  values of regenerated-CBC-850 increased from 2.701 to 3.455. Hence, the interface defects of the CBC adsorbent obviously increased due to the formation of regenerated byproducts caused by the



**Fig. 5** High-resolution X-ray photoelectron spectroscopy (XPS) of C1 s (A, before and after adsorption) and O1 s (B, before and after adsorption). (C) Proportion of relative C species occupied in the total C content. (D) Raman spectra of CBC-850 before and after adsorption.



Scheme 1 Deactivation mechanism of EA adsorption over CBC during regeneration.

incomplete desorption of EA.<sup>46</sup> Meanwhile, the  $A_{sp3}/A_{sp2}$  (0.395) of regenerated-CBC-850 adsorbent was lower than that of fresh CBC-850 adsorbent (0.599), which indicated that new sp2hybrid carbon species (e.g., C=O or C=C carbonaceous species) had formed at the interface of the regenerated CBC adsorbent.48 Furthermore, the dissolved byproducts were extracted and analyzed by GC-MSD (Table S7<sup>†</sup>). The main adsorbed compounds adsorbents were on 1,2-benzenedicarboxylic acid, dihexyl ester and dioctyl phthalate, which could have been due to the reaction between EA molecules or CBC defect sites to form high-boiling carbonaceous byproducts during thermal desorption of EA.49-51 These processes associated with a deactivation mechanism are illustrated in Scheme 1. High-boiling-point products could be formed due to high chemisorption between EA and the adsorbent interface. These products were subsequently transformed into hard-to-separate polymeric species after multiple regeneration of thermal desorption that blocked the structure, 12,13 Besides, accumulation of pore these carbonaceous species could also cause active sites at the interface to be occupied, eventually resulting in gradual deactivation of the adsorbent.52

### 4. Conclusions

For recycling of high-value VOCs (*e.g.*, EA), the big problem faced in VOCs adsorption is deactivation of adsorbents. This problem limits their application in the resource utilization or control of VOCs. We established a correlation mechanism between deactivation and pore structure and the functional groups of the adsorbent from a microscopic viewpoint. We revealed the key influencing factors for the adsorption capacity and regeneration performance of the adsorbent. This is very important for the design of highly efficient and stable adsorbents based on balancing the function of pore structure and functional groups for recovery of high-value VOCs.

### Author contributions

Weiping Zhang conceptualized the study and undertook writing (original draft and editing). Xiaoqin Wang carried out

the investigation and undertook writing (original draft). Haiyong Pan carried out modelling and theoretical calculations. Xingye Zeng carried out theoretical calculations. Guiying Li undertook writing (review and editing). Hongli Liu contributed to investigation of the main content. Jiejing Kong contributed to obtaining resources. Huijun Zhao contributed significantly to conceptualization and manuscript preparation. Taicheng An was the supervisor and contributed significantly to preparation and review of the manuscript.

# Conflicts of interest

There are no conflicts of interest to declare.

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