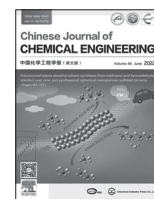




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Full Length Article

Superhigh selective capture of volatile organic compounds exploiting cigarette butts-derived engineering carbonaceous adsorbent

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ABSTRACT

Herein, we develop cost-efficient superhigh-performance of engineering carbonaceous adsorbent from cigarette butts using combined wet-impregnated and re-dispersed method of KOH, which optimizes the implant approach of activator, breaking the restriction of selective capture of toluene using traditional activated carbon. The Brunauer-Emmett-Teller (BET) surface area and pore volume of targeted adsorbent can attain $3088 \text{ m}^2 \cdot \text{g}^{-1}$ and $1.61 \text{ cm}^3 \cdot \text{g}^{-1}$, respectively, by optimizing the temperature-dependent synthetic factor effect of the adsorbent. The adsorption capacity of resultant adsorbent for presenting volatile benzene and toluene shows a positive correlation with increasing carbonization temperature of carbon precursor. Besides, we demonstrated the unsmoked and smoked butts derived adsorbents afford feeble difference in saturated adsorbed capacity of volatile organic compounds (VOCs). The highest adsorption capacity of sample CF-800 for benzene and toluene in CF group is as high as 1268.1 and 1181.6 $\text{mg} \cdot \text{g}^{-1}$ respectively, slightly higher than that of sample UF-800, but far outperforming reported other adsorbents. The predicted adsorption selectivity of CF-800 and UF-800 for $\text{C}_7\text{H}_8/\text{H}_2\text{O}$ (g) using the DIH (difference of isosteric heats) equation reach up to ca. 3800 and 7500 respectively, indicating the weak adsorbability of water vapor on the developed adsorbent and greater superiority of the smoked butts derived adsorbents in selective capture of VOCs at low relative humidity in the competitive adsorption process for practical mixed VOCs.

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1. Introduction

Current days, the issue of urban complex air pollution has increased prominently and the secondary aerosol, photochemical composites pollution problems may also receive widespread attention in society [1–7]. At this junction, the elimination of volatile organic compounds has received much attention to protecting the environment. These volatile organic compounds (VOCs) are excreted from automotive exhaust emissions, paint volatilization and coking industries, and these are one of the most important pollutants of environmental air due to their large total emissions and high toxicity [8]. Hence, the efficacious control and removal of

VOCs pollutants are urgent and significant towards coping with the current atmospheric complex pollution [9].

At present, the riddance of VOCs still mainly relies on adsorption [10,11], photocatalysis [12], incineration [13], thermal-catalysis [14], condensation [15] and biodegradation [16]. Among which, adsorption treatment is regarded as one of the most economical and environmentally friendly industrial technology [17–22] for the elimination of medium and low concentrated VOCs [23]. However, so far, the main difficulty in the adsorption removal of VOCs focus on the efficient selective capture using high surface area and porous volume of adsorbent under humid environment. In general, the adsorption performance of adsorbent is mainly dependent on the structural character of materials. Yang *et al.* [24] reported that the high adsorption amount of acetone, benzene, toluene and ethylbenzene enabled by MIL-101 correspond to 1291 $\text{mg} \cdot \text{g}^{-1}$, 1291 $\text{mg} \cdot \text{g}^{-1}$, 1096 $\text{mg} \cdot \text{g}^{-1}$, and 1105 $\text{mg} \cdot \text{g}^{-1}$,

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respectively, at 25 °C and P/P_0 of 0.5. Despite metal–organic–frameworks (MOFs) materials show strong VOCs capture capability and potential application prospects in the field of environmental governance and protection [25,26]. However, the high cost of preparation and the instability in the humid environment impede its actual production and employment at the great extent.

And all this time, impressively, porous carbonaceous materials (PCMs) have gained exceptional attention due to their high adsorption capacity, renewable, low-cost, and eco-friendly properties [27,28]. Researches have demonstrated the several excellent porous carbon materials affording superior structural and surface characteristic and shows great performance in VOCs treatment. For example, Qi *et al.* [29] prepared nitrogen-doped hollow carbon spheres (NHCS) through an improved “silica-assisted” route, which showed the benzene adsorption capacity was 766 mg·g⁻¹. Qi *et al.* [30] synthesized porous carbon beads (PCBs) via phase inversion route followed by carbonization with BET specific surface area of 1042 m²·g⁻¹ and the static adsorption results indicate the largest adsorption capacities for benzene (1467 mg·g⁻¹), toluene (1229 mg·g⁻¹), *n*-hexane (600 mg·g⁻¹) and acetone (770 mg·g⁻¹). Wang *et al.* [31] utilized polydopamine (PDA) to prepare porous carbon materials by using a two-step synthesis method, and demonstrated that the resultant PDA-derived carbon possesses higher specific surface area of ~3291 m²·g⁻¹ and high-VOCs absorption. However, in these reported methods, spent excessive unique precursors and consisted multiple synthetic steps without exception which is unbearable to practical applications.

The cigarette butt is made up of a plastic-acetate fiber which is disposable after usage. The discarded cigarette butts in America alone were nearly 0.17 billion pounds per year which not only contaminate the environment but also spoil plenty of resources. Accordingly, comprehensive utilization of these cigarette filters becomes attractive especially for preparing porous functional carbon materials, but their resultant specific surface area and pore volume are undesirable. Polarz *et al.* [32] prepared non-graphitic carbons derived from carbonized cellulose acetate using cigarette filters which has lower surface area of 262 m²·g⁻¹, and pore volume of 0.21 cm³·g⁻¹. Chen *et al.* [33] prepared carbonaceous materials via an evaporation-induced self-assembly method using cigarette filters, which showed the surface area of 526 m²·g⁻¹, the pore volume of 0.59 cm³·g⁻¹. However, to our knowledge, this is not enough to achieve excellent adsorption performance for VOCs, and the corresponding report concerning the absorption of VOCs using the carbonaceous adsorbent derived from cigarette filters remains a blank.

Inspired by the above thought, we have developed the CF group and UF group of carbonaceous adsorbent derived from unsmoked and smoked cigarette filters by virtue of a “two-step” hydrothermal carbonization method. Considering the difference of unsmoked and smoked cigarette filters, because the smoked cigarette filters possibly contain more tar, nicotine, and some special residues thereby causing the obvious effect on structural properties of the resultant activated carbon. The prepared carbonaceous materials were characterized carefully to ascertain their physicochemical characters by nitrogen adsorption/desorption measurement, scanning electron microscope (SEM), fourier transform infrared spectroscopy (FTIR), elemental analysis, and thermogravimetric analysis (TG). On the basis of the superior structural performance, the present samples were purposefully employed for the removal of toxic VOCs gas including benzene and toluene. Accordingly, the independent adsorption isotherms of benzene, toluene and water vapor were measured and correlated with the structural characteristic of temperatures dependent-carbonaceous adsorbent. The adsorption heats of benzene, toluene, and water were further estimated through Clausius-Clapeyron equation using the above adsorption isotherms, thereby, the benzene/water and toluene/water

adsorption selectivity was calculated using the (DIH) equation, which implies potential huge superiority for separation of benzene/toluene in the mixed VOCs gases.

2. Experimental

2.1. Materials

The carbonaceous adsorbent precursor cigarette filters (Yunyan) were purchased from Hongyunhonghe Tobacco (Group) Co. Ltd. Potassium hydroxide was obtained from China Sun Specialty Products Co. Ltd. Concentrated hydrochloric acid (37%, by mass), benzene and toluene (>99.0%) were purchased from Yangzhou Shanghai Chemical Reagent Co. Ltd. All chemicals were A.R. grade and used without further purification.

2.2. Synthesis of porous carbonaceous adsorbent

The hydrochar of cigarette filters can be previously achieved according to the typical synthesis method [34]. All of the used cigarette butts in this study belong to the same brand of cigarettes. Clean cigarette butts are marked as C group of carbon, and used cigarettes are denoted as group U of carbon. The typical synthesis procedure starts from the collection of cigarette filters by removing enfolded paper, tobacco and ash content attached to the cigarette butts and grounded the two sets of filters separately until fluffy or flock. Afterward, the ground filters were then mixed with water (1 g filter correspond to 1 ml of water) and poured into a stainless steel reactor for further hydrothermal carbonization reaction at 250 °C (5 °C·min⁻¹) for 2 h. After that, the autoclave was cooled down to room temperature by naturally. Finally, the resulted carbon material is collected and washed with deionized water and dried at 110 °C for 24 h. The hydrothermal carbide is labeled as CF- hydrochar (clean filter) and UF- hydrochar (used filter), respectively.

Before the activation of these above carbides, the hydrochar was mixed with KOH using wet-impregnated and re-grinding dispersed method at mass ratio of 4:1 and ground into a homogeneous state. Specifically, the above obtained carbides were first dispersed into KOH aqueous solution with valid concentration using continuous stirring and ultrasound procedure. Subsequently, the water component was evaporated out from the resulted mixture to obtain the dried carbon precursor and KOH mixtures. Then the obtained KOH and carbon mixture was further ground uniformly to reach the complete dispersion of KOH in carbides. The above mentioned mixtures were placed in a tube furnace and heated to 600, 700, and 800 °C at a heating rate of 5 °C·min⁻¹ in a nitrogen atmosphere, respectively. The resultant sample was incubated at the target temperature for 1 hour and then cooled to room temperature under nitrogen. The carbonaceous adsorbent was recovered by filtration and washed with 1 mol·L⁻¹ HCl and deionized water to a neutral pH. Finally, the powder samples were dried in an oven at 110 °C for 24 h. The final carbonaceous adsorbentaceous adsorbents were marked as CF-T (group C, clean filters) and UF-T (group U, used filters) respectively, where *T* is the activation temperature (600, 700 and 800 °C).

2.3. Characterizations

Thermo-gravimetric analysis (TG) was performed using Pyris Diamond TG-DTA analyzer under flowing air or He conditions, respectively. X-ray diffraction patterns were collected by Shimadzu XRD-6000 diffractometer (Cu K_α radiation) to investigate the structural feature of samples. Scanning electron microscopy (SEM, ZEISS Merlin Compact) was employed to check the morphol-

ogy and structure of the samples. Fourier Transform Infra-Red spectroscopy (FTIR) was obtained using an Agilent Cary FTIR spectrometer, specifically, the samples were uniformly mixed with KBr powder and treated at 100 °C for 1 h. Afterwards, the mixture was pressed into slice state for test. The C, H, and N elemental analysis were performed with the help of Vario E III Analyser. Raman spectroscopic analysis was performed by using a Renishaw inVia reflex Raman spectrometer with a 532 nm laser beam in the range of 500–3000 cm^{-1} . Porosity and textural properties of the material were determined by Belsorp-MAX apparatus for nitrogen adsorption-desorption testing. The test environment was a liquid nitrogen atmosphere ($-196\text{ }^{\circ}\text{C}$), and the carbonaceous adsorbent was degassed under vacuum at 180 °C for 12 h prior to analysis. The specific surface area was calculated by using Brunauer-Emmett-Teller (BET) equation based on nitrogen adsorption data (relative pressure range of 0.05–0.35). The total pore volume is determined by the amount of nitrogen adsorption at $P/P_0 = 0.99$. The pore size distribution curves for identifying the mesopore and micropore were determined by using Barrett-Joyner-Halenda (BJH) and Horvath-Kawazoe (HK) methods. According to clausius-clapeyron principle, the adsorption heats of the prepared samples were calculated using BELmaster/version (6.4.1.0). The X-ray photoelectron spectra (XPS) were acquired on a PHI 5000 Versa Probe X-ray photoelectron spectrometer (ULVAC-PHI, Kanagawa, Japan). The C1s peak at 284.6 eV was used as the reference.

2.4. Measurement of adsorption isotherms of benzene and toluene vapor

Adsorption isotherms of benzene and toluene vapors were measured on carbonaceous adsorbent samples at $-5\text{ }^{\circ}\text{C}$ to $20\text{ }^{\circ}\text{C}$ by using Belsorp Vapor Pretreatment instrument (MicrotracBEL Corporation, Japan) according to standard static volumetric methods. The VOCs vapor is produced using a stainless steel chamber with a thermostatic seal and an automatic air shutoff valve. The sample was placed in a circulating water bath during the test to maintain the adsorption ambient temperature. 30 mg of sample is required for each test. Pretreatment conditions for all samples prior to testing as follows: degassing at 180 °C for more than 6 hrs under vacuum. The absorption cycles were conducted based on the sequential adsorption-desorption process including the pressure-switched adsorption and subsequent 180 °C thermal desorption for 2 h under vacuum condition.

2.5. Measurement of adsorption isotherms of water vapor

The water vapor adsorption on the carbonaceous adsorbent material at $25\text{--}45\text{ }^{\circ}\text{C}$ was tested in a vapor adsorption instrument (MicrotracBEL Corporation, Japan). Prior to each adsorption experiment, approximately 20–30 mg of pre-activated adsorbent sample (heated at $150\text{--}180\text{ }^{\circ}\text{C}$ under vacuum overnight) was charged into the sample pan with an accuracy $\pm 0.1\text{ mg}$ to acquire data. The adsorption test system provides a direct measurement of water vapor adsorption. Further, the temperature and humidity of the adsorption chamber can be controlled by constant temperature water bath and humidifier with an accuracy of $\pm 0.1\text{ K}$ and $\pm 0.1\%$, respectively.

3. Results and Discussion

3.1. Materials characteristics

The synthesis of adsorbent was referred in Fig. 1. The absorption performance of adsorbent predominantly relies on their present structural characteristics. Therefore, the morphological character

of the cigarette filter acetate fiber and resultant carbonaceous adsorbent was discerned by the SEM technique (Fig. 2). The low-magnification SEM images [Fig. 2(a)] shows that the acetate fiber affords integral strip shape with homogeneous and rough surface, while Fig. 2(b) demonstrated the carbonaceous adsorbents possess a broken structure with rich macro- and microporosity, which should be attributed to the pore-forming of KOH activation process. Further, at a higher magnification, the structural similarity was observed in both CF and UF group of adsorbents with respect to various irregular stoma. In turn, mesopores and micropores on the sample surface are unclear in the amplifying SEM images, indicating its integrality at the macro level. Besides, to discern the distributed state of the elements including C, N, and O, the SEM-EDX elemental mapping was presented in Fig. S1 (Supplementary Material), indicating their uniform distribution state on the materials. To ascertain the detail composition of the resultant carbonaceous adsorbent derived from cigarette filter, the elemental distribution was extracted from the elemental mapping results in the case of CF-800 and UF-800, implying the main constituted elements include C, N, and O. Ulteriorly, the elemental composition and concentration of the resultant carbonaceous adsorbent were discerned by virtue of elemental analysis and displayed in Table S1. As shown, the dominant proportion of C element is observed compared to other elements such as H, N, and O in the two CF-800 and UF-800, which can be further supported by XPS results (Fig. S2, see Supplementary Material). Clearly, the increment of C proportion accompanies the decrement of O, N and H element as the carbonization temperature rises, which indicates that the higher degree of carbonization at high temperature was observed after removing the surface organic moiety. Note that, with increasing temperature, H/C and O/C proportion in the two groups of carbonaceous adsorbents show gradual decrement with increased the degree of aromatization and weaken polarity. It means that the higher activation temperature offers better stability to carbonaceous adsorbents and weakening the polarity of material. In contrast, the fine difference in the elemental composition and concentration between CF-800 and UF-800 is still observable, which associates with generated smog ingredients such as nicotine and so on from the smoked process.

The structural character was investigated by means of nitrogen adsorption/desorption measurement and displayed in Fig. 3(A). Both sets of samples exhibit type I isotherms, and corresponding the significant adsorption amount observed at below relative pressure P/P_0 of 0.1 is the characteristic of microporous materials [35]. Table 1 shows the details of BET surface area and pore volume of the carbonaceous adsorbent derived from cigarette filters of CF and UF group prepared at different temperatures. With increasing temperature, the surface area and pore volume of the two groups of carbonaceous adsorbent increases gradually, which should associate with high-temperature driven gasification process of KOH. When the carbonization temperature was reached 800 °C, BET surface area and total pore volume of the two groups of carbonaceous adsorbents attain the highest value as high as $3088\text{ m}^2\cdot\text{g}^{-1}$ and $1.611\text{ cm}^3\cdot\text{g}^{-1}$ in the case of CF-800, and the microporous volume corresponds to a very large value of $1.542\text{ cm}^3\cdot\text{g}^{-1}$, which is slightly higher than those of UF-800 corresponding to the counterpart value of $2938\text{ m}^2\cdot\text{g}^{-1}$, $1.587\text{ cm}^3\cdot\text{g}^{-1}$, and $1.536\text{ cm}^3\cdot\text{g}^{-1}$, respectively. In highlight, both of these carbonaceous adsorbents are much higher than many of the reported carbonaceous adsorbent, template carbon materials and are also comparable to many specifically-designed MOFs materials. To directly observe the configuration of the obtained carbonaceous adsorbents, the TEM technique was utilized for collecting the microscale images. The representative TEM images of CF-800 Fig. 3 (a)–(b) and UF-800 Fig. 3 (c)–(d) are presented as follows in Fig. 3(a)–(d). Specifically, the amorphous character of carbonaceous adsorbents can be

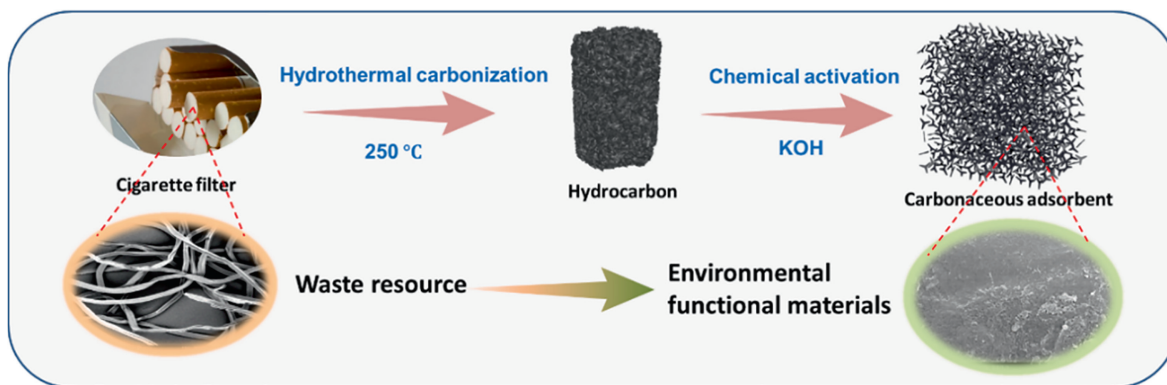


Fig. 1. Schematic illustration of synthesis process of carbonaceous adsorbent from cigarette filters.

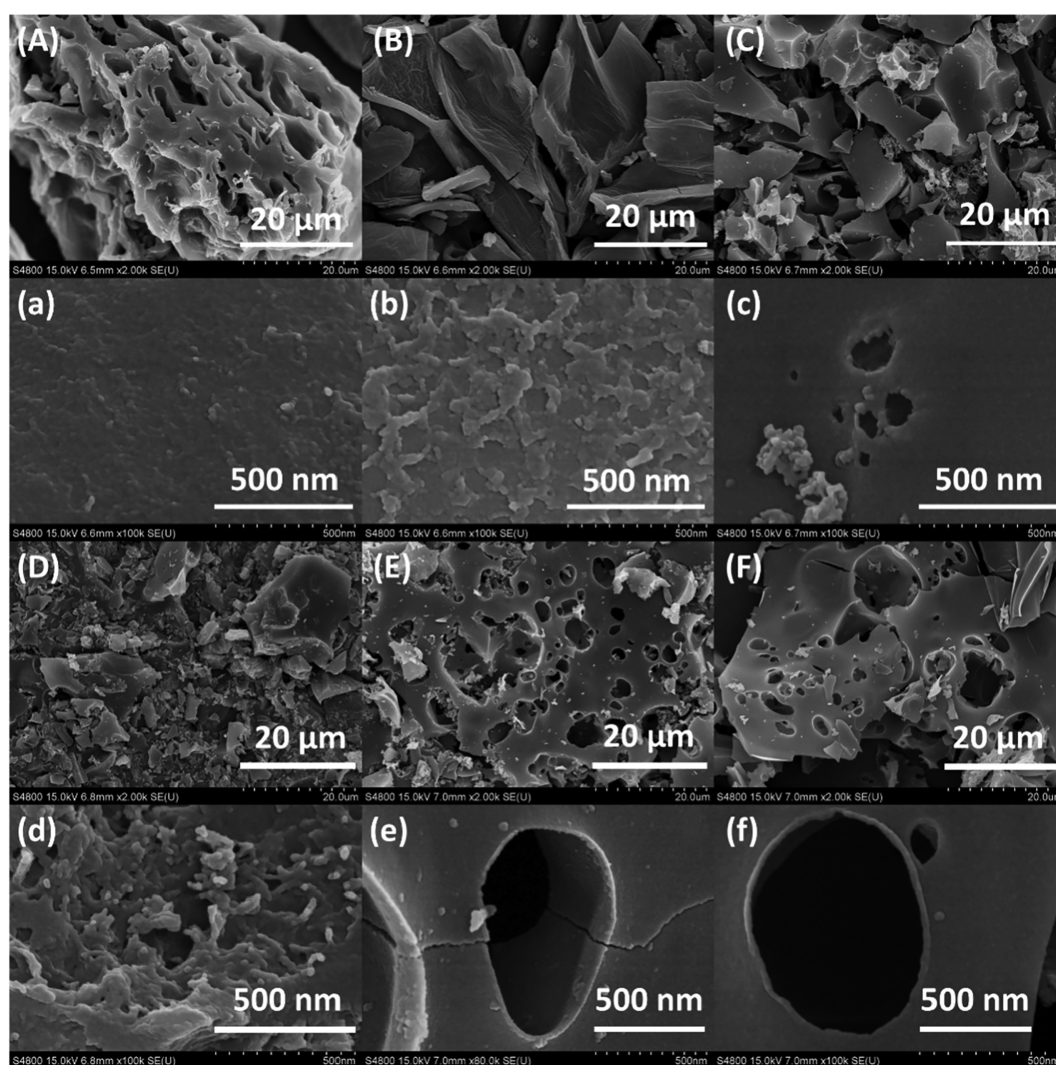


Fig. 2. Representative SEM images of resultant carbonaceous adsorbent derived from cigarette filters(A) (a)CF-600, (B) (b) CF-700, (C) (c) CF-800, (D) (d) UF-600, (E) (e) UF-700, and (F) (f) UF-800.

carefully affirmed, and the present disordered porous structure was also further demonstrated, which reveals the due absorption superiority in terms of the structural property.

Pore size distribution in the means of mesoporous and microporous level of the CF and UF group samples was further ascertained by BJH and HK analysis (Fig. 4), respectively. As observed, with the

enhanced activation temperature of samples from 600 °C to 800 °C, the pore size distribution became wider, and the mesoporous portion (>2 nm) became higher on the basis of the retaining original mesopore, which ascribes to the fact that activation reaction of KOH becomes more intense, thus the further increase in the internal space of the macropore (mesopore) leads to an enhancement in

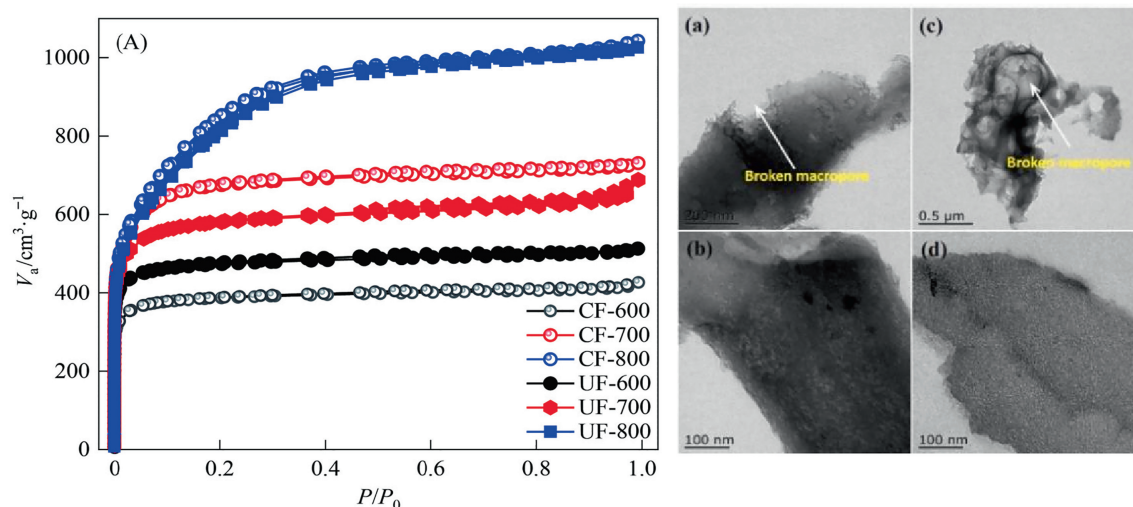


Fig. 3. Nitrogen sorption isotherms of CF and UF series of carbonaceous adsorbents (A) and representative TEM images of CF-800 (a–b) and UF-800 (c–d).

Table 1

Textural parameters of CF and UF series of carbonaceous adsorbents.

Samples	$S_{\text{BET}}/\text{m}^2\cdot\text{g}^{-1}$	$S_{\text{Langmuir}}/\text{m}^2\cdot\text{g}^{-1}$	$V_{\text{total}}/\text{cm}^3\cdot\text{g}^{-1}$	$V_{\text{micro}}/\text{cm}^3\cdot\text{g}^{-1}$
CF-600	1483	1754	0.657	0.616
CF-700	2600	3147	1.129	1.091
CF-800	3088	4656	1.611	1.542
UF-600	1839	2249	0.792	0.756
UF-700	2262	2817	1.057	0.925
UF-800	2938	4630	1.587	1.536

the mesopore capacity of the carbonaceous adsorbent. Apart from that, HK microporous size analysis reveals that all the carbonaceous adsorbent retains small pores of 0.5–0.6 nm even with the increasing carbonization temperature, but the overall distribution of micropore becomes larger in the microporous region. Accordingly, the pore size was enlarged and accompanied by the increment of the pore volume of the original micropores, and the change is the same as that of mesoporous one.

The structural crystalline phase of the obtained porous carbonaceous adsorbent could be ascertained via wide-angle XRD patterns (Fig. 5(a)). Specifically, all the XRD patterns display two broad-like peaks at 22.2° and 42.7° , suggesting that the graphitic structure was only developed to a slight extent. In addition, broad

diffraction peak at ca. 22.2° indicates a disturbed structure due to the randomly oriented aromatic carbon sheets in the carbonaceous adsorbent[36,37], which is beneficial for generating higher specific surface area. To further identify the refined structural properties of these present carbonaceous adsorbent, Raman spectra (Fig. 5(b)) were collected and generally show two Raman shifts at $\sim 1330\text{ cm}^{-1}$ (D peak) and $\sim 1580\text{ cm}^{-1}$ (G peak). The D peak is regarded as the typical carbon defect peak related to the disordered structure of sp^2 lattice, the G peak reflects the symmetry and order of the material, and is attributed to the vibration of the sp^2 lattice of 2D hexagonal structure[38,39]. The intensity ratio of D and G bands (I_D/I_G) is commonly used to analyze the degree of disorder in the carbon layer. As observed, the I_D/I_G of CF group increased slightly from 0.85 to 0.89, and for the UF group further increased from 0.86 to 0.92, as the preparation temperature increased. This observation indicates that the higher activation temperature causes a larger disordered degree of carbonaceous adsorbent, due to the more intense reaction of KOH with carbonaceous adsorbent.

To discern the surface moiety of adsorbent materials, FT-IR technique was employed. Specifically, the FT-IR spectra of carbonaceous adsorbents (Fig. 6) afford three absorption peaks in the range of $500 \sim 4000\text{ cm}^{-1}$, corresponding to 1397 cm^{-1} , 1629 cm^{-1} , and

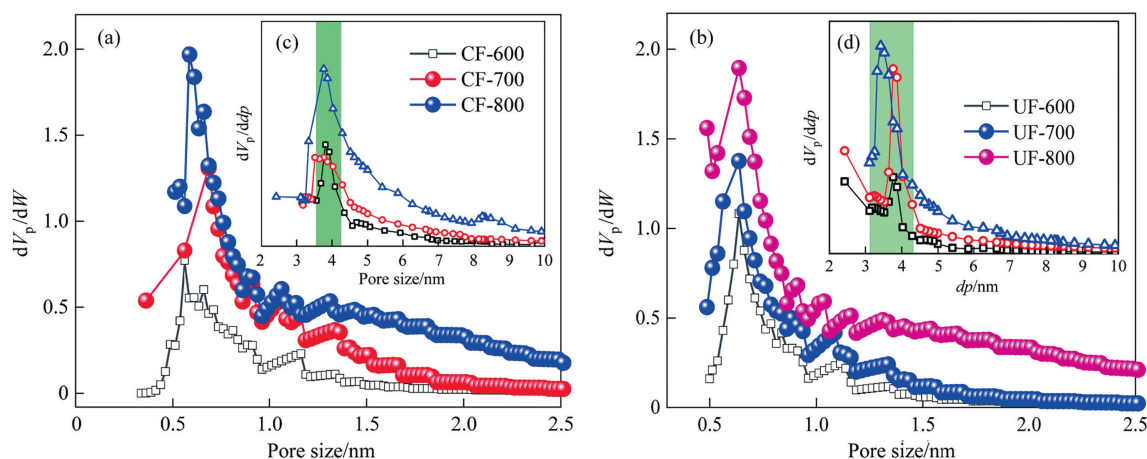


Fig. 4. Pore size distribution in microporous(a) and mesoporous region (c) of series of carbonaceous adsorbent in the CF group; and Pore size distribution in microporous (b) and mesoporous region (d) of series carbonaceous adsorbent in UF group.

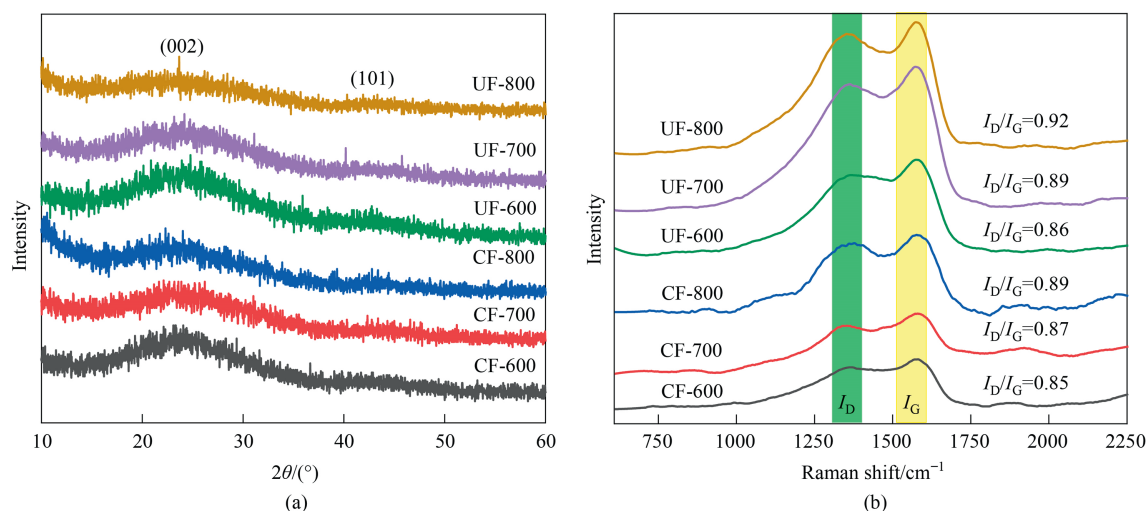


Fig. 5. Wide-angle XRD patterns(a) of and Raman spectra(b) of CF and UF series of carbonaceous adsorbents derived from cigarette butts.

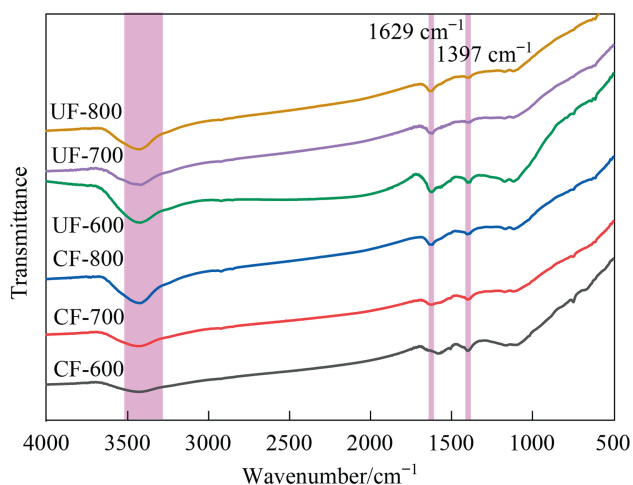


Fig. 6. FT-IR spectra of CF and UF series of carbonaceous adsorbents derived from cigarette butts.

3435 cm⁻¹, among of which the band at 3435 cm⁻¹ is due to the OH stretching vibration of surface OH, COOH, and H₂O of the material, where the absorption peak at 1629 cm⁻¹ is caused by the stretching vibration of C=C bond of the material skeleton and the peak reference map appearing at near 1397 cm⁻¹ is known to be caused by asymmetric and symmetrical COO-vibrations of carbonaceous adsorbent skeleton[40]. These relative simple groups together with the absence of methylene (—CH₂—) indicate the efficient carbonization process of cigarette filter.

Thermogravimetric analysis of these resultant carbonaceous adsorbents and the initial precursor cigarette filters was conducted under air and He gas atmosphere, respectively, to identify their thermal stability and carbonization process, and the obtained results are shown in Fig. 7. The initial mass loss between room temperature and 100 °C under air atmosphere was observed clearly for CF-600 and UF-600. As the temperature increases, the surface water and residual moisture in the pores evaporated to cause mass loss. The material mass drops sharply between 400 °C to 580 °C, which indicates that the carbonaceous adsorbent structure begins to collapse and decompose. At the same time, the TGA curves reveal that the carbonaceous adsorbent prepared at higher temperatures has higher thermal stability in air atmosphere. This observation indicates the thermal stability of the material can be

improved by virtue of higher carbonization temperature triggering the more remarkable aromatization of activated carbon adsorbents. In addition, the carbonization process of cigarette filter could be also reflected, to some extent, by the TG analysis under He gas atmosphere (Fig. 7(b)). Especially, the mass loss reaches as high as 88.4% when the temperature increased to 800 °C, which is almost consistent with that (83.9%) in the real carbonization process.

3.2. Adsorption isotherms of benzene and toluene

The VOCs adsorption including benzene and toluene on these resultant carbonaceous adsorbents were performed at 25 °C and presented in Fig. 8. As shown, the benzene adsorption of the sample CF-800 and UF-800 reach saturation until the pressure P/P_0 was 0.2. The sequence of adsorption amount of samples as follows: CF-800 > UF-800 > CF-700 > UF-700 > UF-600 > CF-600. Interestingly, note that the smaller pore size is more favorable to attracting these adsorbed molecules. When the relative pressure P/P_0 verges to 0.2, the benzene and toluene adsorption of all samples tend to be equilibrated, indicating the prepared carbonaceous adsorbent afford high and rapid adsorption performance, and the adsorption capacity also follows the above sequence, which is positively related to the BET specific surface area and pore volume of the carbonaceous adsorbent sample. This can be accounted by that higher specific surface area supply more adsorption sites and larger space to accommodate more benzene and toluene molecules at higher relative pressures. Besides, we further tentatively fitted the correlation between adsorption capacity and various structural properties, and found the micropore volume dominantly determined the adsorbed amount of VOCs.

To more intuitively see the adsorption capacity of the samples on benzene and toluene, Table 2 lists the adsorption parameters of the adsorbent materials of CF and UF group for benzene and toluene at 25 °C and P/P_0 of 0.6. As shown in Table 2, the adsorption capacity of carbonaceous adsorbent for benzene and toluene in CF and UF groups gradually increases with the increment of activation temperature. Specifically, the adsorption capacity of CF-800 for benzene and toluene in CF group is as high as 16.2 mmol·g⁻¹ and 12.8 mmol·g⁻¹ (1268.1 and 1181.6 mg·g⁻¹), respectively, at 25 °C and P/P_0 of 0.6. Similarly, the best adsorption performance in the UF group corresponds to UF-800, whose adsorption capacities for benzene and toluene are 16.0 mmol·g⁻¹ and 11.6 mmol·g⁻¹ (1250.8 mg·g⁻¹ and 1069.8 mg·g⁻¹), respectively, which are

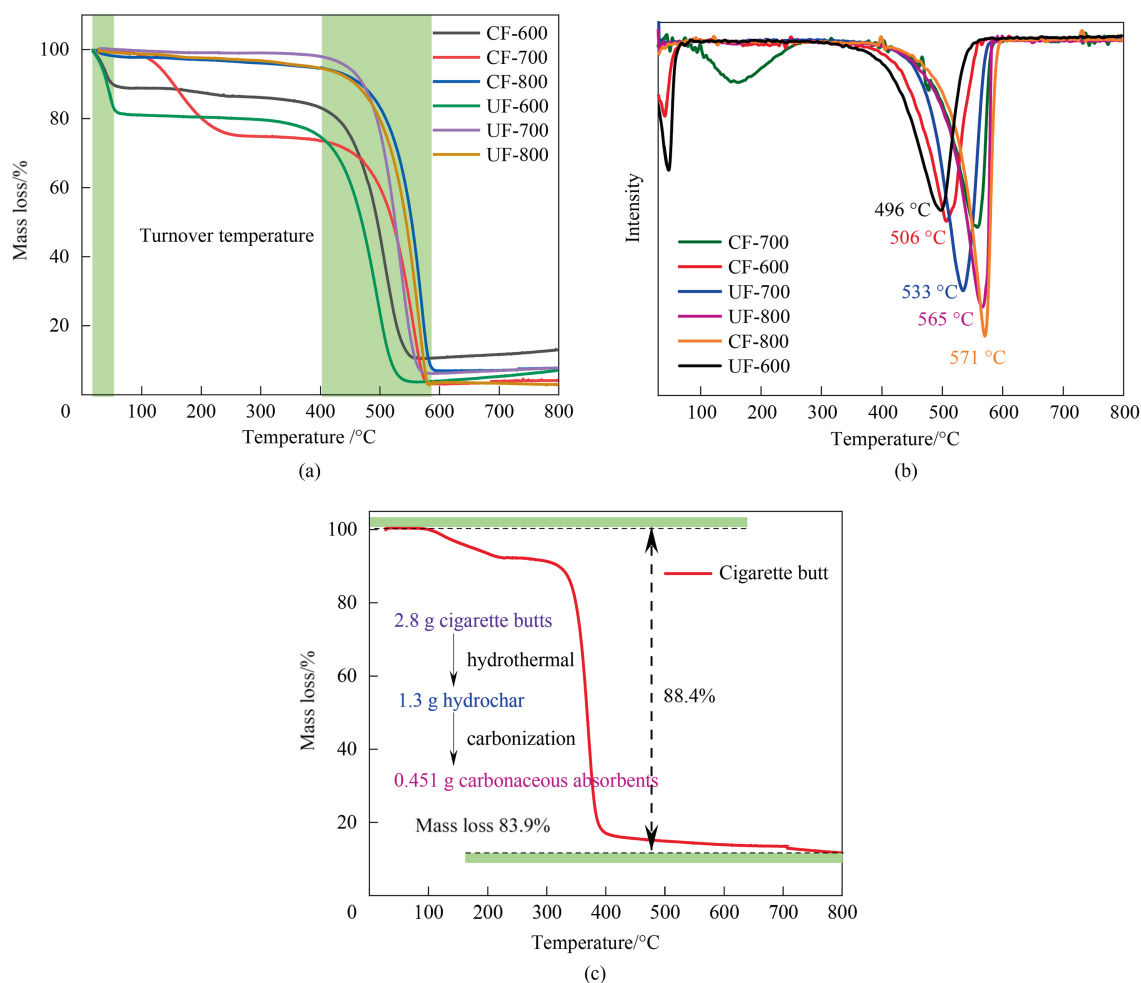


Fig. 7. Thermogravimetric analysis (TGA) curves (a) and differential thermogravimetric analysis (DTG) curves (b) of resultant carbonaceous adsorbents derived from cigarette butts and cigarette butts (acetate fiber) (c).

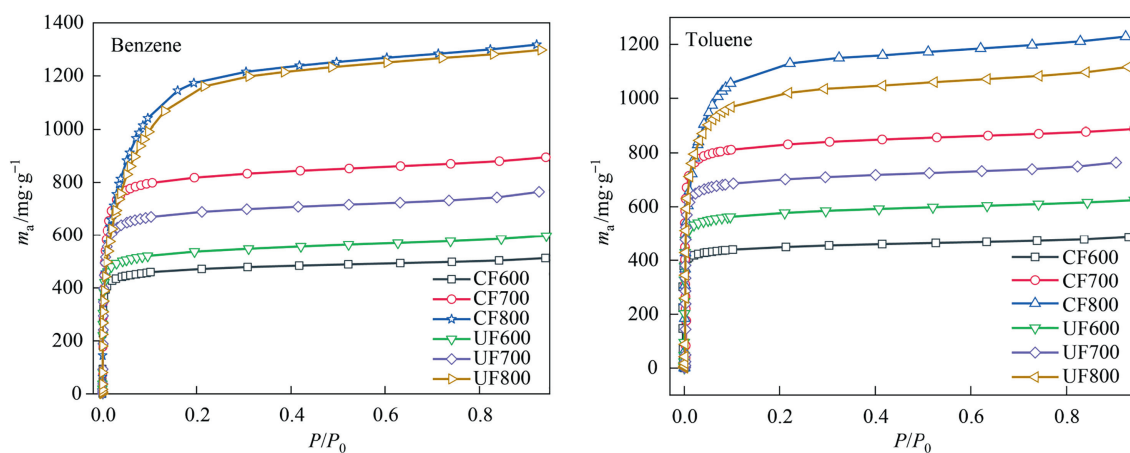


Fig. 8. Adsorption isotherms of benzene (a) and toluene (b) at 25 °C using a series of carbonaceous adsorbents derived from cigarette filters at different temperatures.

slightly lower than those of CF-800. This phenomenon should associate with the exogenous existence of left smog in the smoked cigarette filters, which affects the character of the resultant carbonaceous adsorbents.

To highlight the present adsorption performance of carbonaceous adsorbent resulted from the cigarette filters, Table 3 lists

the adsorption capacities of CF-800, UF-800, and some other reported adsorbent materials for benzene and toluene at 25 °C and P/P_0 of 0.2. As observed, CF-800 and UF-800 exhibit the highest adsorption capacity for benzene and toluene at P/P_0 of 0.2. The adsorption amount Q at P/P_0 of 0.6 is elected as the saturated adsorption amount. When the P/P_0 is 0.2, the adsorption amount

Table 2
Adsorption capacity of carbonaceous adsorbent materials for benzene and toluene.

VOCs	Samples	$Q/\text{mg}\cdot\text{g}^{-1}$	$Q/\text{mmol}\cdot\text{g}^{-1}$	$T/^\circ\text{C}$
Benzene	CF-600	491.5	6.3	25
	CF-700	858.3	11.0	25
	CF-800	1268.1	16.2	25
	UF-600	568.6	7.3	25
	UF-700	721.7	9.2	25
	UF-800	1250.8	16.0	25
Toluene	CF-600	465.2	5.0	25
	CF-700	861.7	9.4	25
	CF-800	1181.6	12.8	25
	UF-600	600.3	6.6	25
	UF-700	731.1	7.9	25
	UF-800	1069.8	11.6	25

Note: Operated adsorption condition is 25 °C, 0.6 of P/P_0

of benzene and toluene on CF-800 were accounted for 93.4% and 95.5% of the saturated adsorption amount, respectively. As such, the percentage of adsorption capacity of benzene and toluene on UF-800 was 91.2% and 95.3%, which ascribes to the fact that the prepared carbonaceous adsorbent belongs to microporous nature material affording super-high the specific surface area and pore volume. As a result, high-capacity adsorption can be rapidly achieved in a low concentration and low-pressure environment. In addition, we noticed that the adsorption capacity of CF-800 and UF-800 almost afford several times increased adsorption value when compared to those of well-designed materials such as zeolite or Cu-BTC and *etc.* Hence, the obtained carbonaceous adsorbents seem to be the superior materials than the above-mentioned adsorbents, thereby shows the potential in practical VOCs treatment application. Besides, we also attribute the excellent VOCs adsorption performance of the developed activated carbon to the results derived from the activator KOH implanting optimization in the activation process of activated carbon. Because the KOH was completely permeated into the existed void of hydrochar and induced the better reaction process between KOH and hydrochar under the high temperature activated process, which superior to the traditional activated carbon preparation.

3.3. Adsorption mechanism of benzene and toluene

The isotherms of benzene and toluene over CF-800 (Fig. 9(a)) and UF-800 (Fig. 9(b)) were carefully discerned. Specifically, when

the $P/P_0 < 0.108$, the adsorption amount of toluene was higher than that of benzene in the case of CF-800. Meantime, the $P/P_0 < 0.04$, the adsorption amount of toluene was higher than that of benzene in the case of UF-800, which indicates that the direct interaction of toluene on the surface of carbonaceous adsorbent is stronger than benzene at low adsorption rate. This ascribes to the adsorbate-adsorbent interaction potential is primarily dependent on the nature of the adsorbate. The polarizability of the adsorbate is one of the most important properties to determine the direct interaction between the adsorbate and adsorbent. Typically, the interaction of the adsorbate with adsorbent increases as the molecular weight increases. To our knowledge, the polarizability of toluene is higher than that of benzene, accounting for the stronger interaction of toluene with the polar surface of the adsorbent than that of benzene. On the other hand, we noticed that the benzene adsorption capacity of CF-800 (UF-800) increases beyond that of toluene at a pressure above $P/P_0 = 0.108$ ($P/P_0 = 0.04$), which derives from the pore volume-limiting effect of the adsorbent. In that case, for a given adsorbent, when the pore volume is constant, and the amount of large-sized molecules adsorbed should be less, accordingly resulting in less adsorption capacity than molecules with large kinetic diameters entering the pores. Since the kinetic diameter of toluene (0.67 nm) is larger than that of benzene (0.58 nm), so given that higher relative pressure, the adsorbent material affords higher adsorption capacity to benzene than toluene.

3.4. Isotherms of water vapor adsorption

In practical VOCs adsorption studies, water vapor in the air will cause adsorption competition and interfere with the adsorption performance of carbonaceous adsorbent on VOCs. Therefore, the water vapor isotherm of the adsorbent referred as a significant thermodynamic property to evaluate the affinity of the adsorbent for water vapor. In general, if the adsorbents having less affinity for water vapor, it referred as a good hydrophobic adsorbent material. Therefore, the isotherms of water vapor on CF-800 and UF-800 at 25 °C were collected and displayed in Fig. 10. These isotherms exhibit an S-shaped isotherm, indicating that the material affords weak adsorption behavior for water vapor at low humidity. Specifically, when the relative humidity is lower than 50%, the water vapor adsorption amount of these two adsorbent materials are very low. And, the water vapor adsorption amounts begin to increase as the relative humidity increase. A sharp increment in the water vapor amount can be observed when the relative humid-

Table 3
Adsorption capacities of CF-800 and UF-800 and reported comparative adsorbent materials directing at benzene and toluene.

VOCs gas	Samples	$Q/\text{mmol}\cdot\text{g}^{-1}$	$Q/\text{mg}\cdot\text{g}^{-1}$	$T/^\circ\text{C}$	Ref.
Benzene	CF-800	15.2	1184.1	25	This work
	UF-800	14.6	1140.9	25	
	MIL-101	15.0	1173.2	25	[31]
	Cu-BTC	3.2	251.0	25	[41]
	MOF-177	8.0	625.7	25	[42]
	HZSM-5	1.7	135.9	30	[43]
	MFOF-1a	4.6	356.2	25	[44]
	SBA-15	1.8	136.7	30	[43]
	Activated carbon adsorbent	7.0	547.55	30	[43]
	CF-800	12.3	1128.3	25	This work
	UF-800	11.0	1009.6	25	
Toluene	MIL-101	5.0	458.9	25	[31]
	Cu-BTC	2.6	234.0	25	[24]
	MOF-177	3.2	294.9	25	[42]
	Silica gel	3.8	353.8	25	[45]
	Activated carbon adsorbent	1.9	176.9	25	[46]
	PCH	1.3	115.2	25	[47]
	Zeolite L	1.1	99.5	25	[48]

Note: Operation condition is relative pressure P/P_0 of 0.2.

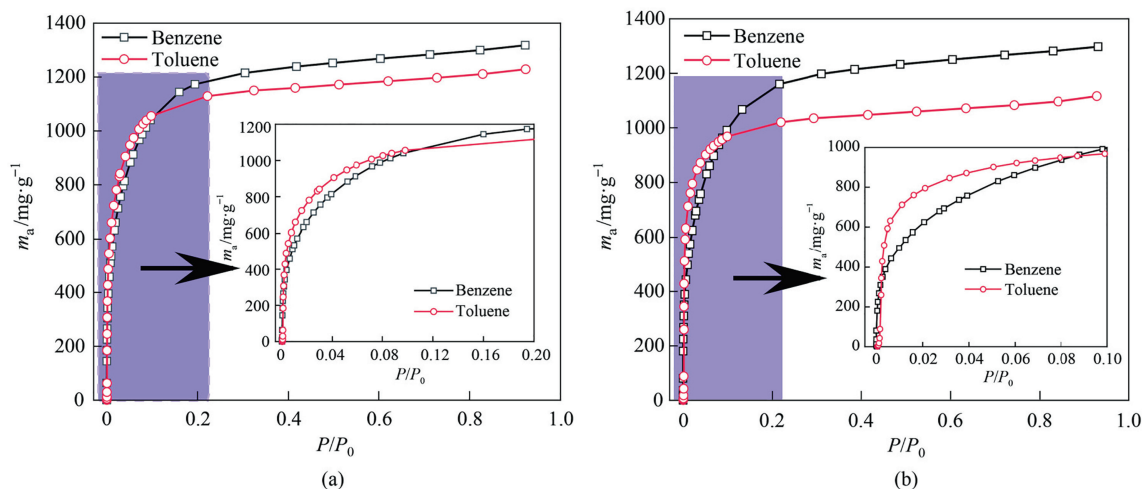


Fig. 9. Comparison of adsorption isotherms of benzene and toluene on CF-800 (a) and UF-800 (b).

ity reaches 60%–80%, whose adsorption amounts of water vapor are founded to be UF-800 > CF-800 in order, when the relative humidity is below that value (the junction point, 74%), because of the higher O/C atomic ratio, the greater surface polarity. Given that O/C atomic ratio of CF-800 is lower than that on the surface of UF-800, so the water molecules are more desire to bind with oxygen and nitrogen atoms on the surface of UF-800 through hydrogen bonding. Withal, the adsorption capacity of water vapor to the sample follows the order of CF-800 > UF-800 at higher relative humidity which derives from the pore volume of the adsorbent.

3.5. Isostatic adsorption heats of benzene, toluene and water vapor

Isostatic adsorption heat is regarded as one of the critical parameters to evaluate the interaction strength between the adsorbate and adsorbent and can provide credible information about the energetic heterogeneity of an adsorbent surface[49]. The isosteric heats of adsorption can be obtained using Clausius-Clapeyron equation[50,51].

$$\ln p = -\frac{Q_{st}}{RT} + C \quad (1)$$

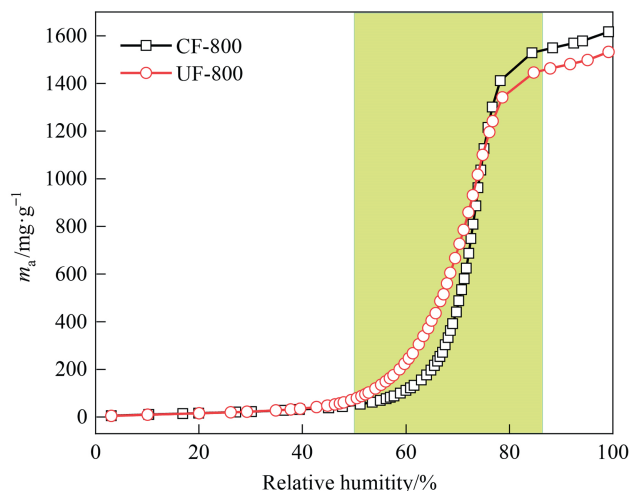


Fig. 10. Adsorption isotherms of water vapor on CF-800 and UF-800 at 25 °C.

where Q_{st} ($\text{kJ} \cdot \text{mol}^{-1}$) is isosteric heat, R ($\text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}$) is the universal gas constant, T (K) is temperature, p (kPa) is pressure, and C is an integral constant.

After measuring the isotherms of benzene, toluene, and water on CF-800 and UF-800 at different temperatures, these isotherms are further converted into adsorption isotherms (See Fig. S3 and Fig. S4). As shown, the adsorption amount of carbonaceous adsorbent to the gas decreases with the increased temperature, indicating that the physical adsorption is dominant in the adsorption process. The adsorption isotherms of the gases at different temperatures were estimated by software to estimate their corresponding adsorption heat. Firstly, the $\ln p$ was plotted against $1/T$ at a given amount adsorbed of adsorbates on the basis of Eq. (1), a straight line with a slope of $-Q_{st}/R$ was plotted (worked in the software, not given). Finally, the isosteric heats (Q_{st}) of these adsorbates adsorption can be calculated directly from the slope $-Q_{st}/R$ of the plotted straight line.

Fig. 11 shows the isosteric heats of benzene, toluene, and water vapor adsorption on CF-800 and UF-800. It is noted that the adsorption heats of benzene and toluene just started at very low value, because, at very low relative pressures, the pressure sensor is not sensitive to pressure changes, resulting in different adsorption temperatures. However, note that the adsorption heat, especially for toluene, gives the variational tendency at a high absorbed amount, indicating the effect of adsorbate absorbed on the carbon for ensuigly absorbed toluene molecule because of the energy inhomogeneous characteristic. Especially, the adsorption heat at low adsorbed amount show certain increased trend which should associate with the filling of large voids when the VOCs enter into the activated carbon on the external surface layer. Afterwards, the adsorption heat became relatively stable as the gradual adsorption process, which accounts for the normal adsorption of VOCs molecules in the dominant micropore. In the final stage of adsorption, the adsorption heat affords the large fluctuation which indicates the possible adsorption process of VOCs entering into the ultramicropore of activated carbon or the stronger interplay between the VOCs adsorbates. The adsorption pressure corresponding to the same adsorption amount is almost similar (when the adsorption capacity of benzene and toluene is 4 mmol, and their corresponding gas pressure is ca. 23 Pa ($P/P_0 = 0.0018$)). Specifically, the adsorption heat of water on the present CF-800 and UF-800 is constant at ca. 45 $\text{kJ} \cdot \text{mol}^{-1}$, but much lower than that of benzene and toluene. This means that CF-800 and UF-800 have ability to facilitate the adsorption of benzene or toluene in water vapor.

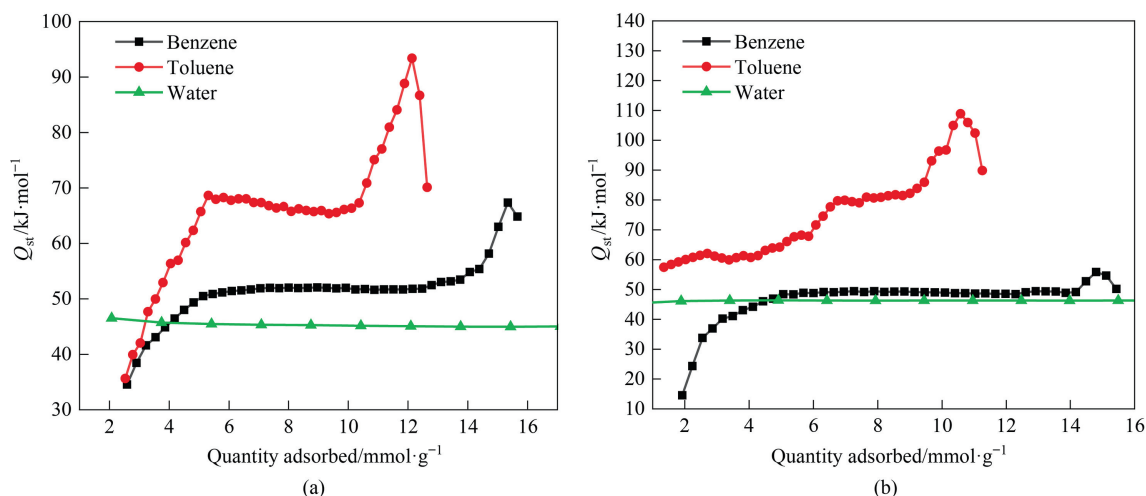


Fig. 11. Isothermic adsorption heats of benzene, toluene, and water vapor adsorption on CF-800 (a) and UF-800 (b) during the adsorption course.

3.6. Estimation of VOCs/ $\text{H}_2\text{O}(\text{g})$ adsorption selectivity on CF-800 and UF-800

Adsorption selectivity emerges as an important parameter to evaluate the adsorption efficiency of adsorbents in practical applications [52]. Herein, the DIH (differential heating difference) equation was selected and used to predict the adsorption selectivity of the gas mixture to the adsorbent, which was proposed by Wang and Cao [53] for the first time and accepted widely at present. The adsorption selectivity of the adsorbent for binary gas mixture is related to the difference in the heat of adsorption of the two kinds of gas, and is independent of the mole fraction of the components in the bulk phase at low pressure. The expression of the DIH equation is expressed as follows [53,54]:

$$S_{\text{ads}}(i/j) = \sqrt{S_{\text{ideal}} S_0} \quad (2)$$

$$S_{\text{ideal}} = \frac{q_i(p)}{q_j(p)} \quad (3)$$

$$\ln S_0 = 0.716 \frac{\Delta Q_{st}^0}{RT} \quad (4)$$

where $q_i(p)$ and $q_j(p)$ are static adsorption amounts of pure component i or j at P . ΔQ_{st}^0 ($\text{kJ}\cdot\text{mol}^{-1}$) is equal to the difference between

isothermic heats of component i and j . R ($=8.314 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) is molar gas constant and T (K) presents temperature.

In this work, we tried to use DIH equation on the basis of isothermic heats of C_6H_6 , C_7H_8 , and water vapor on the samples presented in Fig. 12 to predict the adsorption selectivity of CF-800 and UF-800 for VOCs/ H_2O .

The adsorption selectivities of $\text{C}_6\text{H}_6/\text{H}_2\text{O}(\text{g})$ and $\text{C}_7\text{H}_8/\text{H}_2\text{O}(\text{g})$ for synthesized carbonaceous adsorbent samples were presented in Fig. 12. The results demonstrate that the selectivities of toluene/ $\text{H}_2\text{O}(\text{g})$ of CF-800 and UF-800 were much higher than those of benzene/ $\text{H}_2\text{O}(\text{g})$. The adsorption selectivities of $\text{C}_7\text{H}_8/\text{H}_2\text{O}(\text{g})$ and $\text{C}_6\text{H}_6/\text{H}_2\text{O}(\text{g})$ of CF-800 were in the range of 23–4000 and 10–16, respectively, which mainly ascribed to the stronger interaction of toluene with CF-800 compared with benzene. In contrast, the adsorption selectivities of $\text{C}_7\text{H}_8/\text{H}_2\text{O}(\text{g})$ and $\text{C}_6\text{H}_6/\text{H}_2\text{O}(\text{g})$ of UF-800 were calculated in the range of 200–7500, and 2–11. The selectivity of $\text{C}_7\text{H}_8/\text{H}_2\text{O}(\text{g})$ for UF-800 is much higher than that of CF-800 because UF-800 has more obvious variation in adsorption heat with increased absorbed amount at the same pressure compared to CF-800. The present findings suggested that the observed results or values are more excellent than earlier report used MIL-101(Cr) metal-organic-framework materials which shows adsorption selectivity for $\text{C}_6\text{H}_6/\text{H}_2\text{O}(\text{g})$ and $\text{C}_7\text{H}_8/\text{H}_2\text{O}(\text{g})$ in the range of 0.62–2.04 and 1.97–5.32, respectively [31]. The above results demonstrate that the carbonaceous adsorbents

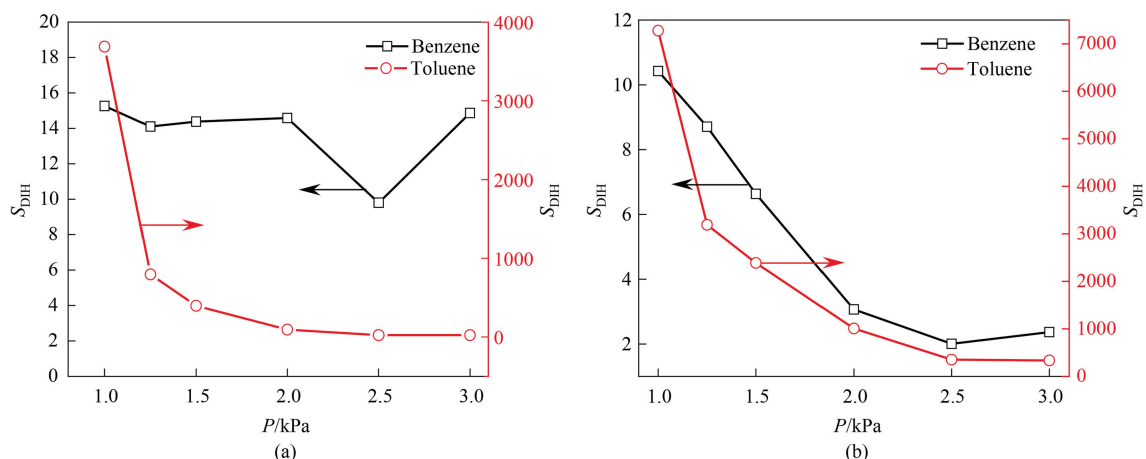


Fig. 12. DIH-equation predicted selectivity for $\text{C}_6\text{H}_6/\text{C}_7\text{H}_8/\text{H}_2\text{O}$ mixtures on CF-800 (a) and UF-800 (b) at 25 °C.

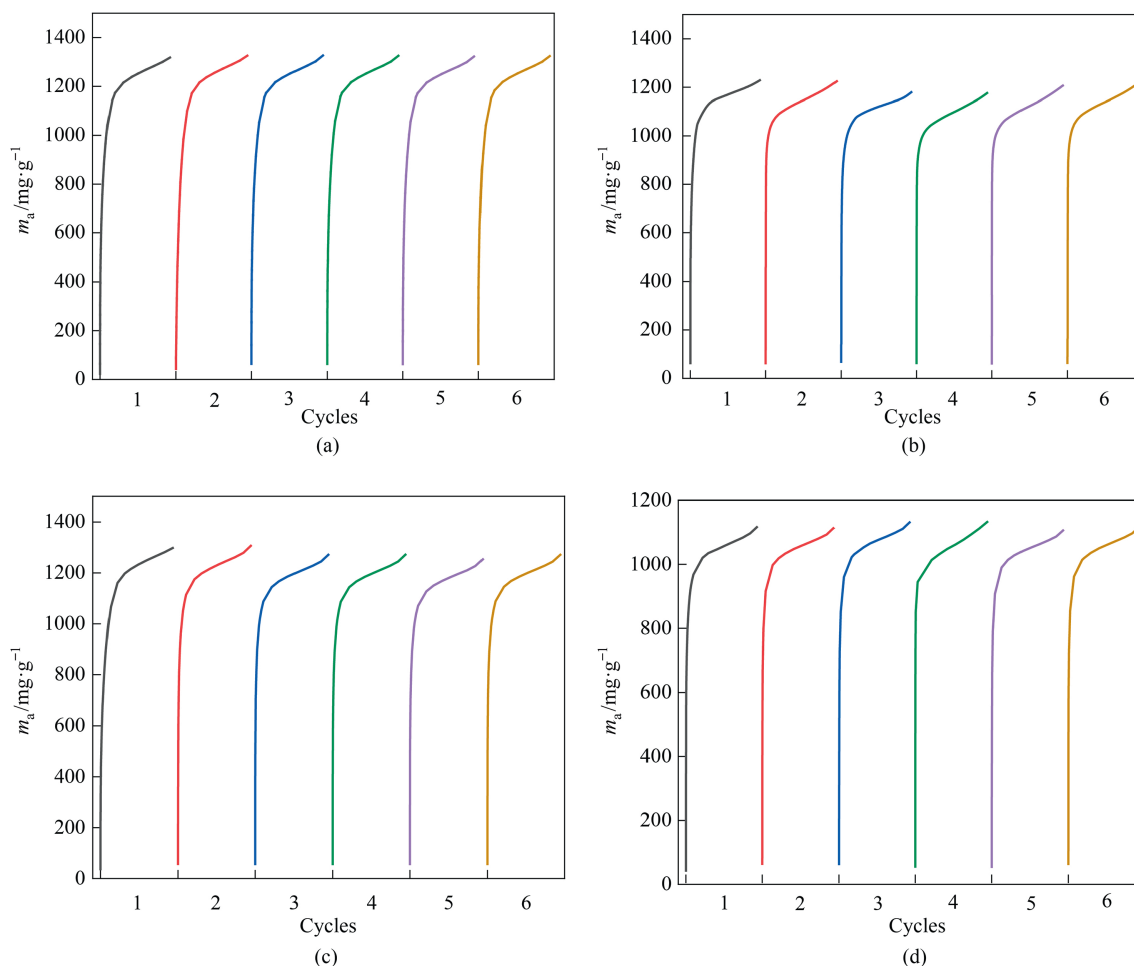


Fig. 13. Recycling test of benzene and toluene absorption using CF-800 (a), (b) and UF-800 (c), (d).

whatever derived from fresh or used cigarette filter had excellent adsorption performance on VOCs even in the humid air, and UF-800 can act as a potential industrial adsorbent for adsorbing VOCs in a realistic application.

In general, application cycle for the evaluation of materials performance is an important factor [55–58], which inspires us to conduct the life assessment of the resultant carbonaceous adsorbent to absorb VOCs such as toluene and benzene. Herein, six absorption cycles isotherms of toluene and benzene of CF-800 and UF-800 are shown in Fig. 13(a)–(d), impressively, great repeatability in several cycles can be observed, implying the reversible absorption–desorption process of benzene and toluene in the applicable microporous channel of carbonaceous adsorbent, which thereof exhibits potential industrial prospect.

4. Conclusions

In summary, novel carbonaceous adsorbents were successfully developed from cigarette filters by chemical activation method. The obtained CF-800 had extremely high adsorption capacities for benzene and toluene of 16.2 and 12.8 mmol·g^{−1} (1268.1 and 1181.6 mg·g^{−1}), respectively, at 25 °C and P/P_0 of 0.6. The adsorbent derived from smoked cigarette butts also has high adsorption capacity for benzene and toluene of 16.0 and 11.6 mmol·g^{−1} at 25 °C and P/P_0 of 0.6. Further, the water vapor isotherm at 25 °C indicates that at a relative humidity below 50%, the amount of water vapor adsorbed is very low, which is critical for the practical

application of carbonaceous adsorbent samples. The DIH equation was used to predict the VOCs/H₂O (g) adsorption selectivity of CF-800 and UF-800. The adsorption selectivity of C₇H₈/H₂O (g) of CF-800 is in the range of 25–186.1, and the measured adsorption selectivity of C₆H₆/H₂O (g) is in the range of 1.7–13.6, which indicates that CF-800 is a potential adsorbent for adsorbing VOCs under humid atmosphere, CF-800 exhibits excellent adsorption properties for benzene and toluene. In addition, it is necessary to solve the problem of large-scale production of the carbons derived from smoked cigarette butts in the future.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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