Adsorption of volatile organic compounds and microwave regeneration on self-prepared high-surface-area beaded activated carbon

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1 Adsorption of volatile organic compounds and microwave
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15

16 **Abstract**

17 Self-prepared beaded activated carbons (SBAC) were derived from carbonized
18 phenolic formaldehyde (PF) resins through an optimal activation procedure (900 °C for
19 4 h) using CO₂. A commercial BAC (termed KBAC) was adopted to compare with
20 SBAC over physicochemical properties, adsorption performance against methyl ethyl
21 ketone (MEK) and toluene (TOL), and the regenerability using microwave irradiation.
22 Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) isotherm models showed
23 good fitting results to explain the adsorption equilibrium. The isosteric heat of
24 adsorption was calculated using the Clausius-Clapeyron equation; the parameters
25 obtained from the D-R isotherm indicate that the interactions between adsorbate and
26 adsorbent were mainly due to physisorption. Microwave heating was applied to the
27 regeneration of saturated adsorbents to examine the effect of irradiation power and
28 heating time on the desorption behavior of adsorbate. Within 12 min of microwave
29 irradiation, excellent desorption efficiencies based on gravimetric method were shown,
30 reaching 110.7 ± 14.4 , 104.4 ± 2.6 , 90.2 ± 2.3 , and $85.5 \pm 5.7\%$ for MEK-SBAC, MEK-
31 KBAC, TOL-SBAC, and TOL-KBAC samples, respectively. After an 8-cycle of
32 adsorption/regeneration, the adsorption capacity for SBAC was significantly decreased

when loaded with TOL, whereas it was more significant than the virgin sample as loaded with MEK. In contrast, KBAC was able to sustain the adsorption capacity after an 8-cycle of regeneration, proving its stability throughout the microwave heating. Kinetic models were further employed to illustrate the desorption of the adsorbates from BAC samples, showing that intraparticle diffusion in SBAC and KBAC was the rate-limiting step during microwave heating. The core kinetic parameters obtained could provide insights for lab-scale adsorbent beds or practical engineering scale design. In conclusion, this study demonstrates the excellent adsorption performance of SBAC and the feasibility of microwave regeneration of BACs.

Keywords: volatile organic compounds, toluene, methyl ethyl ketone, beaded activated carbon, microwave regeneration

1. Introduction

In the past decades, volatile organic compounds (VOCs) emitted from anthropogenic activities have become one group of the significant pollutants harmful to human health and the environment. In addition to the adverse effects, VOCs are also the precursors to the photochemical smog, the near-surface ozone and are responsible for enhancing the global warming effect. Therefore, it is desirable to reduce the

50 emission of VOCs world-wide [1].

51 Up to now, numerous abatement techniques have been proposed and adopted to
52 reduce the VOCs emission from stationary sources, such as thermal/catalytic oxidation,
53 biological conversion, membrane separation, absorption, condensation, and adsorption
54 [2-4]. Among the removal technologies, the adsorption process based on a suitable
55 adsorbent is a compelling method due to its cost-effectiveness and simplicity, and the
56 potential in recovering high-priced VOCs via thermal regeneration followed by
57 condensation [5, 6].

58 One of the widely used porous materials is activated carbon (AC). AC has garnered
59 considerable attention for its remarkable properties: its predominantly hydrophobicity,
60 high thermal stability, low cost, chemical inertness, and low energy consumption for
61 regeneration [7]. Furthermore, because of the non- or weak polar surface of AC,
62 physisorption is typically the dominant adsorption mechanism for VOCs. The overall
63 adsorption performance of AC is mainly attributed to its high specific surface area. It
64 is also dependent on the size, molecular weight, polarizability, concentration, and
65 complexity of the adsorbate [2, 8, 9].

66 To enhance the adsorption performance over specific compounds, ACs are usually

67 subjected to chemical activation using acid/base reagents or physical modification
68 under oxidizing gases (CO₂, steam, or air) at high temperatures (700– 1000 °C) to adjust
69 surface areas and chemical functional groups on the surface [10].

70 A wide variety of ACs with novel morphologies such as monolith, fibrous, and
71 beaded forms have been developed to adapt to different scenarios [11]. Beaded
72 activated carbon (BAC) is employed in a wide range of industrial applications due to
73 its excellent properties such as high mechanical strength, porous structure, large surface
74 area, high micropore volume, good fluidity, and decent adsorption performance [12,
75 13]. A variety of polymeric-based precursors, including phenolic, sulfonated
76 polystyrene, divinylbenzene, and phenol-formaldehyde (PF) have been adopted for
77 BAC manufacturing, and BAC with high mechanical strength, high carbon content, and
78 low ash content could be obtained. However, it is challenging to produce BAC with a
79 perfect sphere and smooth surface without cracks since the types of precursors and
80 adjustment of parameters in stabilization, carbonization, and physical/chemical
81 activation have huge impacts on the resultant products [14, 15]. Our previous studies
82 served as compelling illustrations of this [16, 17]; to deal with the waste bioresources,
83 self-prepared BAC (SBAC) was derived from the mixture of PF-based resin, formalin,

and waste bamboo tar under various experimental conditions. Based on the scanning electron microscope (SEM) micrographs, the non-uniform surface and cracking phenomenon of SBAC became even severe as activation temperature and time increased compared with a commercial product termed KBAC (where K stands for Kureha CORP.). Although the optimal synthesis conditions were acquired according to a series of comprehensive investigations on activation temperature (800, 850, and 900 °C) and activation time (2, 3, and 4 h) during the fabrication of SBACs, the overall adsorption performance for some widely used VOCs and the total surface area were still needed to be improved. Furthermore, our previous studies lacked an in-depth exploration of the effect on the adsorption capacity or regeneration efficiency of adsorbents via cyclic adsorption and microwave regeneration procedures.

Therefore, in continuation to our earlier study (Chen et al. [17]), the present research focuses on (i) establishing equilibria and kinetic mechanisms of BACs, including self-prepared high-surface-area and commercial samples, toward methyl ethyl ketone (MEK) and toluene (TOL), which are the two major species emitted from the polyurethane (PU) industry in Taiwan [18, 19]; (ii) exploring the effect of microwave power output and irradiation time during the regeneration of exhausted BACs; and

finally, (iii) identifying the effect of heel buildup during cyclic adsorption/regeneration of MEK and TOL, and evaluating the feasibility of this technology.

2. Materials and methods

2.1. Adsorbent preparation

The synthesis of SBAC could be broken down into two stages, including carbonization under an inert atmosphere and subsequent activation using CO₂ (99.999%). All the experiments were carried out in a vertical quartz reactor (30-mm i.d.), heated by a conventional temperature-programmed heating furnace (DENGYNG, model D-35). First, commercial PF resin spheres as the raw material of SBAC, were sieved to a selected size (around 150 μm) and placed in the center of the vertical quartz reactor. Then, carbonization took place under 500 °C for 1 h in the N₂ atmosphere (99.999%) to remove volatile contents in the material and to reform the carbon structure. The carbonized PF resin spheres were then physically activated. The temperature increased from room temperature to 900 °C in the N₂ atmosphere at the heating rate of 10 °C min⁻¹; the gas was then switched to CO₂ at 900 °C and held for 4 h, the gas flow rate was controlled at 0.1 L min⁻¹ by a rotameter.

The commercial KBAC used for comparison in this study was heated in an oven at 105

°C over 24 h to remove adsorbed moisture. Afterward, all samples were stored in a desiccator before use.

2.2. Physicochemical characterization of materials

2.2.1. Morphology and pore structure

The surface morphology of virgin and regenerated BACs was analyzed by a field-emission SEM (Hitachi, model S-4800) and a transmission electron microscope (TEM; Hitachi, model H-7100). The N₂ adsorption was carried out at 77 K (Micromeritics, model ASAP 2420) to examine the pore structure of BACs. All samples were degassed at 350 °C for 15 h to remove moisture and impurities before the measurement. Specific surface area (S_{total}) was calculated using the Brunauer-Emmett-Teller (BET) equation. Micropore surface area (S_{micro}) and micropore volume (V_{micro}) were obtained from the t-plot analysis by applying the Harkins and Jura thickness curve, $t = [13.99 / (0.034 - \log(P/P_0))]^{0.5}$. The range of relative pressures used to determine S_{micro} and V_{micro} was based on a statistical thickness t-value of 0.45–0.80 nm. Total pore volume (V_{total}) was determined by the Barrett-Joyner-Halenda (BJH) method and recorded at $P/P_0 = 0.994$. The pore size distribution (PSD) of the mesopore and macropore range was also evaluated by the BJH method. Nonlocal density functional theory (NLDFT) was used

to assess the PSD of the micropore size range.

2.2.2. *Elemental analysis (EA)*

The elemental analysis for C, H, O, N, and S of BACs was performed on an elemental analyzer (Elementar, model vario EL cube). The samples were completely burned and converted into a gas mixture, and the mass fraction of each element was determined by a thermal conductivity detector (TCD) downstream.

2.2.3. *Thermogravimetric analysis (TGA)*

The pyrolysis tests were performed in a thermogravimetric analyzer (SHIMADZU, model TGA-51). The sample was put into a platinum crucible, and the experiments were carried out at atmospheric pressure using N₂ as the purging gas (flow rate = 50 ml min⁻¹) to desorb the species at heating rates of 5, 10, and 20 °C min⁻¹. The weight loss of the sample and the temperature were recorded continuously within a temperature range of 25 to 600 °C.

2.3. *Adsorption and regeneration processes*

2.3.1. *VOCs adsorption measurements and isotherm construction*

The schematic diagram of the adsorption testing system comprises a VOCs vapor generating system, a temperature-controlled adsorption bed, a total hydrocarbon (THC) analyzer, and a data acquisition system (DAQ) is depicted in Figure 1. The selected

153 solvents (MEK and TOL) were injected into a heating furnace (designed by Fortelice
154 International Co., Ltd.) at a constant rate with a gastight syringe (Hamilton Company)
155 and a syringe pump (New Era Pump Systems Inc., model NE 1000). The temperature
156 of the heating furnace was monitored by a K-type thermocouple and set well above the
157 boiling point of both solvents (79.6 °C and 110.6 °C for MEK and TOL, respectively)
158 to ensure the solvents vaporized immediately and mixed with the inert carrier gas (N₂,
159 purity = 99.999%). The injection rates of solvents were adjusted based on the ideal gas
160 law to generate desired VOCs concentrations in the gas stream.

161 The online THC detecting system was a flame ionization detector (FID) (Ratfisch
162 Analysensysteme GmbH, model RS53-T) continuously measuring the outlet
163 concentrations of the adsorption bed. The DAQ system consisted of a Labview software
164 (National Instruments) and a data logger (National Instruments, model USB-6000)
165 acquired one data point per second.

166 The adsorption experiments were carried out in a Pyrex glass tube (40 cm in length
167 and 1 cm in diameter), pre-treated BACs of 20–50 mg were measured and placed in the
168 center of the tube and supported by a sintered glass filter. The adsorption bed was
169 heated by heating tape (Omega). The temperature was well measured and controlled by

a proportional integral derivative (PID) controller with a K-type thermocouple inserting in the adsorption bed; the operating temperature was set at 30, 40, and 50 °C. The adsorption of VOCs onto the tube and glass filter was assumed negligible during the test.

For the adsorption isotherm construction, the concentration of VOCs ranged from 0.0007 to 0.16 P/P₀ and 0.002 to 0.21 P/P₀ for MEK and TOL, respectively. For the dynamic analysis of the adsorption bed, the operating temperature and the inlet concentrations of MEK or TOL were controlled at 500 ppmv and 40 °C. Smooth breakthrough curves were generated, and data were stored for subsequent analysis. The adsorption tests were conducted in triplicate for all experimental concentrations. The total gas flow rate was controlled at 1.6 SLPM by mass flow controllers (Brooks® 5850E).

Two methods were employed to calculate the saturated adsorption capacity. For the gravimetric method, the adsorption capacity was obtained from the weight difference of the BACs before and after the adsorption, which could be calculated by the following equation:

$$\text{Adsorption capacity (\%)} = \frac{W_{AA} - W_{BA}}{W_{BA}} \times 100\% \quad (1)$$

where W_{AA} is the weight of the adsorbent after adsorption and W_{BA} is the weight of the adsorbent before adsorption.

The other approach to calculate the saturated adsorption capacity is by integrating the areas above the breakthrough curves. Therefore, the saturated adsorption capacity was calculated as follows:

$$\text{Adsorption capacity (\%)} = \frac{\int (C_{in} - C_{outlet, i}) \times V_{ad} \times \rho_G}{W_{BA}} \times 100\% \quad (2)$$

where C_{in} is the inlet concentration (ppm_v), $C_{outlet, i}$ is the VOCs outlet concentration (ppm_v) during the period of adsorption at i interval of time, and the time interval was set as one second. V_{ad} is total gas volume (m³), ρ_G is the density of the organic vapor, and W_{BA} is the weight of the adsorbent before adsorption.

2.3.2. Microwave regeneration

Figure S1 shows the setup of the microwave regeneration system. All adsorbents were exposed to MEK or TOL under an inlet concentration of 500 ppm_v at 40 °C until 100% breakthrough before microwave regeneration. The exhausted BAC (20 mg) was placed in a quartz boat within a 1.5 L quartz reactor and heated in a microwave muffle furnace (Milestone, model Pyro 260) operated at 2.45 GHz. The setting power ranged from 400 to 1000 W, and the heating time was 4 to 12 min. To create an oxygen-free

atmosphere, the reactor was purged by N₂ (purity = 99.999%) with a flow rate of 1.5 L min⁻¹ for more than 5 min. The temperature profile of the adsorption bed was obtained using a K-type thermocouple with a ceramic sheath during microwave heating. The desorbed adsorbates were directed to the FID for concentrations measurement.

Furthermore, to comprehensively understand the desorbed species during the microwave regeneration, a portable gas analyzer (HORIBA, model PG-350) was used to measure NO, SO₂, CO, and CO₂ in the exhaust gas stream. The measurement range was set at 0 to 200 ppm for SO₂ and CO, 0 to 25 ppm for NO_x, and 0 to 10% (v/v) for CO₂. The data of the outlet gas concentrations were recorded during the time interval of one second.

The desorption efficiency is defined as:

$$\text{Desorption efficiency (\%)} = \frac{W_{BR} - W_{AR}}{W_{BR} \times q_{500 \text{ ppm}}} \times 100\% \quad (3)$$

where W_{BR} and W_{AR} are the weight of the adsorbent before and after regeneration, respectively, and $q_{500 \text{ ppm}}$ is the adsorption capacity at 500 ppm_v and 40 °C.

2.3.3. Cyclic adsorption/regeneration test

Preliminary tests showed a significant deviation of the adsorption capacities calculated from integration and gravimetric methods. To ensure the accuracy and

consistency of the data, the adsorption capacity after each cycle was calculated by the gravimetric method in the cyclic test. The regeneration performance was evaluated by regeneration efficiency, which was calculated by Eq. (4):

$$\text{Regeneration efficiency (\%)} = \frac{q_r}{q_0} \times 100\% \quad (4)$$

where q_0 is the quantity of adsorbate adsorbed per unit weight of adsorbent and q_r is the quantity of adsorbate adsorbed per unit weight of regenerated adsorbent.

2.3.4. Desorption kinetics analysis

To better describe the interaction between the adsorbate and the adsorbent, the pseudo-first-order model and intraparticle diffusion model were used in this study to obtain the core kinetics coefficients. The kinetics data is necessary and advantageous for designing an adsorption bed appropriately.

Three consecutive steps of a species physisorbed onto a porous adsorbent are (i) transport of the adsorbate from gas film to the external surface of the adsorbent (external diffusion), (ii) transport of the adsorbate within the pores of the adsorbent (intraparticle diffusion), and (iii) adsorption of the adsorbate on the exterior surface of the adsorbent (surface diffusion). Generally, it is accepted that surface diffusion is very rapid [20], and intraparticle diffusion is often considered the rate-controlling step in an

adsorption process [21]. For a desorption process, the pathways of reactions are opposite to the adsorption process.

(1) Pseudo-first-order (PFO) model

If external diffusion was the rate-controlling step, the rate of adsorption could be described by the PFO model [22]:

$$\ln\left(1 - \frac{q_t}{q_e}\right) = -k_1 t \quad (5)$$

where q_e and q_t are the amount of adsorbate adsorbed by the sorbent at equilibrium and time t , respectively, and k_1 is the PFO adsorption rate constant.

(2) Intraparticle diffusion model (IPD)

If intraparticle diffusion was the rate-controlling step, the IPD model proposed by Weber and Morris [23] is widely used for the analysis of adsorption kinetics. The IPD model could be described as:

$$q_t = k_p t^{1/2} + I \quad (6)$$

where q_t is the adsorption capacity at time t , k_p is the IPD rate constant, and I is the intercept reflecting the extent of the boundary layer thickness.

3. Results and discussion

3.1. Adsorbent characterization

3.1.1. SEM and TEM results

The morphologies of SBAC and KBAC were examined by SEM (Figure 2a and b). Both of their appearances were in round shape, which is suitable for fixed-bed packing and fluidity operation. Additionally, the surface of SBAC was smoother than KBAC, indicating the mechanical strength might be higher in SBAC. In addition, well-developed inner structures were found in SBAC while there were only scattered fragments on the surface of KBAC.

The TEM micrographs of SBAC (Figure 2g) reveal a more detailed understanding of the inner structure, suggesting that the 3-D pores were randomly combined and constructed amorphous nanostructures.

The effect of microwave regeneration on BACs was also evaluated via SEM analysis (Figure 2c–f). BACs saturated with MEK and TOL at 500 ppmv and 40 °C (termed MEK-KBAC, TOL-KBAC, MEK-SBAC, and TOL-SBAC) were subjected to microwave regeneration, and the samples regenerated at 800 W for 8 min were chosen for SEM analysis. According to the results, there were no significant differences in the outward appearance between the virgin and regenerated KBAC. However, the pore structure of the regenerated MEK-SBAC (Figure 2c) experienced changes due to the

polarity between the adsorbate and SBAC or the non-uniform heating during the microwave regeneration.

3.1.2. EA results and pore structures of BACs

Table 1 shows the EA results for both virgin and post-regenerated samples (regenerated at 800 W for 8 min). A similar proportion of hydrogen and oxygen in virgin SBAC and KBAC suggested possibly similar polarities on their surfaces. It is said that oxygen-containing groups tend to exchange electrons with the p-orbital electrons of aromatic compounds such as TOL to form chemical adsorption. As a result, the lower oxygen contents of TOL-BACs after microwave regeneration might be caused by chemisorbed TOL remained on the adsorbents since the regeneration temperature was not high enough to remove the adsorbed TOL [24].

The N₂ adsorption-desorption isotherm conducted at 77 K and PSD of BACs are shown in Figure 3. Both SBAC and KBAC followed the type I adsorption isotherm classified by the latest version of the International Union of Pure and Applied Chemistry (IUPAC) definition, which was typically indicative of the microporous character of a porous material. Furthermore, the PSD results examined by NLDFT and BJH methods had revealed that several sharp peaks within 0.5–2.0 nm, indicating that

both SBAC and KBAC were microporous with wider micropores and narrower mesopores.

The overall physical properties of virgin and regenerated BACs are also displayed in Table 1. SBAC synthesized under the optimal experimental conditions (activated at 900 °C for 4 h) according to our previous study (Chen et al. [17]) using PF resins had shown tremendous improvement in surface area, possessing the largest S_{total} of 2114 m² g⁻¹ and V_{total} of 1.361 cm³ g⁻¹ while KBAC used in this study showed a S_{total} of 1210 m² g⁻¹ and V_{total} of 0.602 cm³ g⁻¹, which were lower than that of SBAC. The collapse of micropore structures might cause the decline in the S_{total} and V_{total} of the regenerated BAC samples during the microwave regeneration or the pore blockage by the molecules of MEK or TOL that were unable to desorb.

3.1.3. TGA results

Thermogravimetric analysis (TGA) was employed to understand the desorption pattern of the adsorbate in the adsorbents and could obtain an insight into the optimal microwave regeneration temperature. The virgin BACs were subjected to TGA analysis and showed only slight weight loss during the TGA progress at around 90 °C (Figure 4a). It could be attributed to moisture desorption, usually observed in activated carbon

previously exposed to ambient air [25].

BACs loaded with MEK and TOL were thermally desorbed at heating rates of 5, 10, and 20 °C min⁻¹ from room temperature to 600 °C. For all samples, we found that the desorption of compounds occurred at temperatures between 100 and 400 °C, and the sorbents could be completely desorbed within 400 °C.

On the other hand, the weight loss of saturated BACs became slower at rapid heating rates, resulting from the heel buildup within the adsorbents. Niknaddaf et al. [26] pointed out that the increase of heating rate from 5 to 100 °C min⁻¹ led to 8–52% of capacity loss as well as 4.6–10.5% of heel buildup for activated carbon fiber cloth (ACFC) in five consecutive adsorption/regeneration operations, respectively.

The differential thermal gravimetry (DTG) curve is a plot of the adsorbate's desorption rate as a function of the sample temperature. As a whole, the DTG data were used to evaluate the activation energy (E_d) of different organic materials. Since the desorption peak temperature is related to the adsorption strength, a more robust interaction gives rise to a higher peak temperature. The desorption peak under 100 °C is attributed to water desorption [25]. Assuming that the desorption followed first-order kinetics and the heating rate is constant (i.e., $T = T_0 + \beta t$), based on the Arrhenius

equation, the E_d for desorption could be calculated by the following equation [27]:

$$\ln\left(\frac{\beta}{RT_M^2}\right) = -\frac{E_d}{RT_M} + C \quad (7)$$

where T_M is the peak desorption temperature, β is the heating rate, E_d is the desorption activation energy, R is the universal gas constant, and C is the constant that depends on the desorption kinetics.

The DTG curves for SBAC and KBAC are shown in the Supplementary Materials (see Figure S2–5), and the calculated E_d (tabulated in Table S1) for MEK and TOL in this study was similar to or slightly higher than the heat of vaporization for MEK and TOL (31.2 and 32.8 KJ mole⁻¹ at boiling point for MEK and TOL, respectively), which could be characterized as physical adsorption onto both SBAC and KBAC [25].

3.2. Adsorption and desorption performance

3.2.1. Adsorption isotherm construction

Adsorption isotherm provides essential information to predict the adsorption performance and the maximum adsorption capacity of BACs under various adsorption temperatures and inlet concentrations. The data for VOCs adsorption was fitted by three isotherms, namely Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) isotherms. Detailed description pertaining to these isotherms is presented in Supporting

Information (SI). The inlet concentrations of the VOCs were set in the range within 100 to 20,000 ppm_v for MEK and 100 to 10,000 ppm_v for TOL, respectively, covering the whole range of concentration that could be detected by the FID.

The fitting results of the experimental data based on the integration and gravimetric methods are tabulated in Table S2–4. The R^2 for the gravimetric method was generally higher than that for the integration method with minimum values of 0.894, 0.948, and 0.948 for Langmuir, Freundlich, and D-R isotherms, respectively. The plots of the experimental and Langmuir isotherm modeled data are also presented in Figure 5. Graphically, Langmuir isotherm is characterized by a plateau corresponding to a saturated adsorption capacity (q_s). The q_s calculated by the integration method seemed much higher than that obtained by the gravimetric method. Although the q_s gained from both two methods were similar at the lower concentration range, the q_s showed a significant deviation as the concentration increased. This could result from the response time of the THC detector that amplified the deviation of the breakthrough curve. As a result, the q_s estimated by the gravimetric method appeared to be more accurate. According to the gravimetric results, the q_s of SBAC is consistently higher than that of KBAC, which could be stemmed from the higher surface area and larger pore volume

in SBAC.

Figure 6 shows the plots of Freundlich isotherm fitting results. Judging by the R^2 values, the Freundlich model also fits the experimental data with a level of conformity. The coefficient K_F is related to the adsorption capacity of the adsorbent, and n is a function of the strength of adsorption or surface heterogeneity. The larger the value of n , the stronger the adsorption affinity, indicating more heterogeneous adsorption [28]. As shown in Table S3, in most cases, K_F increased and n decreased with increasing operating temperature. The value of n was more significant than 1 for all scenarios, revealing the heterogeneity of the carbon surface. Owing to its lack of a finite limit under high pressure, the Freundlich isotherm cannot fit broad concentration ranges.

The D-R isotherm parameters are summarized in Table S4, and the plots of the experimental and the D-R isotherm modeled data are presented in Figure 7. The D-R model has been proven to be suitable for the description of adsorption in activated carbon. The experimental data were well fitted by the D-R equation, and the R^2 values were mostly over 0.96. Generally, W_0 is the maximum capacity available for adsorbate, which is determined by pore volume. Therefore, the smaller the value of W_0 , the lower the micropore volume it possesses. As expected, in consistence with the pore structure

analysis shown previously (Table 1), SBACs developed higher proportions of micropores compared to KBAC. However, the calculated W_0 seemed inconsistent with those obtained from N₂ adsorption. The main reason was the difference in the kinetic diameters of the probing molecules (N₂: 4.02 Å, MEK: 5.25 Å, and TOL: 5.85 Å), contributing to the difference in W_0 .

The characteristic energy, E (or $E_0\beta$), is a parameter concerning pore size, surface chemistry, and adsorbate structure [29]. In this study, the characteristic energies of adsorption of MEK and TOL onto SBAC were about 8 to 10 kJ mol⁻¹, suggesting that physical adsorption predominates in the adsorption process. On the other hand, compared with SBAC, the free energy of MEK and TOL adsorbed onto KBAC was higher (10–18 kJ mol⁻¹) but still characterized as physical adsorption.

Once the characteristic energy is gained from the adsorption isotherm data, the characteristic pore dimensions of a porous carbon can also be estimated. There is an inverse proportionality between E and the slit-pore half-width (x_0), which takes the following form:

$$x_0 = k/E_0 \quad (8)$$

For most industrial activated carbons whose E is less than 22 kJ mol⁻¹, the

corresponding values of k are almost constant and can be set approximately to 13 kJ
nm mol⁻¹ [30].

As observed in Table S4, the values of x_0 for SBACs are larger than those for
KBACs. Most results showed an acceptable agreement using MEK or TOL as a probing
molecule. In contrast, some deviated results could be attributed to data errors or
narrower pore sizes in adsorbents, which hindered diffusion of larger molecules. It
should be noted that the VOCs considered in this study is relatively small, and the
adsorption capacity trends may differ from those established here for larger adsorbates
(e.g. polychlorinated dibenzo-p-dioxins and -furans) [31].

3.2.2. *Isosteric heat of adsorption*

The isosteric heats can be calculated using the D-R parameters and Clausius-
Clapeyron equation [9]. However, as mentioned in previous sections, the deviation of
adsorption capacities using different calculation methods was significant. Therefore, to
maintain accuracy and consistency, the D-R isotherm data used in calculating ΔH_s were
based on gravimetric methods. The dependences on adsorbate, temperature, and surface
loading in calculating ΔH_s are illustrated in Figure 8.

A rule of thumb in adsorption is that for adsorption heat < 80 kJ mole⁻¹, the

adsorption process is characterized as physisorption [32]. As shown in Figure 8, the ΔH_s ranges from 35 to 60 kJ mol⁻¹, indicating MEK and TOL are physically adsorbed onto SBAC and KBAC.

The ΔH_s of MEK and TOL on SBAC are nearly constant (≈ 45.47 and 45.52 kJ mol⁻¹, respectively) and are independent of temperature within the range of surface loading. This implies a relatively energetic homogeneity of the adsorbent surface [33]. However, as observed in Figure 8c, the ΔH_s of MEK on KBAC at 30 °C is relatively lower. One explanation is the surface heterogeneity of adsorbent [34], but this also may be attributed to an experimental error in measuring the adsorption isotherm. It should be noted in Figure 8d that ΔH_s for TOL adsorption on KBAC increased drastically at a higher surface loading, which reflected stronger dependence upon surface loading. Such results are consistent with those of Chen et al. [17] and can be explained by the follows: (1) the surfaces of KBAC are energetically heterogeneous towards adsorption of TOL [35], (2) the stronger lateral interactions occurred between the adsorbed molecules at a higher surface coverage [36], or (3) as surface loading increases, more vital interaction between TOL (weak polarity) and the nonpolar adsorbent resulting in high heats of adsorption.

3.2.3. Microwave regeneration

The desorption efficiencies for BACs were evaluated for different power outputs (400, 600, 800, and 1000 W) and durations (4, 8, and 12 min) based on the gravimetric and integration methods with a constant nitrogen gas flow rate of 2.0 SLPM (Figures 9 and 10).

Within 12 min of microwave irradiation, desorption efficiencies based on the gravimetric method reached 110.7 ± 14.4 , 104.4 ± 2.6 , 90.2 ± 2.3 , and $85.5 \pm 5.7\%$ for MEK-SBAC, MEK-KBAC, TOL-SBAC, and TOL-KBAC, respectively. It could be seen that the desorption efficiencies for SBAC were generally higher, probably because the size of SBAC was smaller (spherical diameter of $218.3 \pm 19.3 \mu\text{m}$ and $700.7 \pm 20.3 \mu\text{m}$ for SBAC and KBAC, respectively), therefore enhanced heat retention (i.e., hot spots formation) and accelerated the desorption of VOCs within the carbon bed. Overall, SBAC demonstrated better desorption performance and higher energy utilization efficiency in the desorption process.

In addition, the desorption efficiencies of MEK appeared to be greater than that of TOL on both SBAC and KBAC. It could be attributed to the lower boiling point of MEK, the difference in dielectric permittivity, or the polarizability between the two

442 VOCs [37].

443 It is noteworthy that the desorption efficiencies for MEK and TOL calculated by
444 the gravimetric method were consistently higher than that of the integration method.

445 For MEK-SBAC, the effluent gas analysis results showed CO plus CO₂ weighed
446 approximately 85.52 µg as C, causing an average of 28.01% of efficiency difference.

447 There was no other apparent gas outflow. Thus, the results supported the inference that
448 MEK was decomposed into inorganic compounds during the heating process [38].

449 However, CO and CO₂ released from MEK-KBAC were hardly observed. Instead, a
450 significant SO₂ emission (25.04 µg as S) might be generated from removing sulfur at
451 higher temperatures was considered the main reason for the overestimation of
452 desorption efficiencies based on the gravimetric method, in an average of 22.37% of
453 efficiency difference.

454 On the other hand, for TOL on BACs, the efficiency evaluated by desorption
455 concentration was only slightly lower than that by weight change (-4.31% and -4.48%
456 on average for TOL-SBAC and TOL-KBAC, respectively). A possible explanation was
457 that TOL reacting with oxygen-containing groups on the surface of carbon and
458 transformed into inorganic compounds (i.e., CO or CO₂), which could not be detected

by a THC detector [39]. This was also reflected in the results of elemental analysis (Table 1), in which the percentage of oxygen in the BACs slightly decreased after adsorption and regeneration.

According to the gas analysis results, for TOL-SBAC, CO plus CO₂ was about 57.02 µg as C (causing about 6.19% of efficiency difference). Nevertheless, for TOL-KBAC, the amount of releasing CO plus CO₂ was only 1.37 µg as C (causing only about 0.22% of difference) and accompanied by 3.08 µg as S of SO₂ release. In brief, the results showed that the efficiency differences of TOL-SBAC were possibly associated with the reaction of TOL on the carbon surface. However, the efficiency difference of TOL-KBAC might be due, in large part, to the release of impurities such as sulfur and moisture, accordingly overestimated the efficiency obtained from weight change.

3.2.4. Evaluation on reusability of BACs via cyclic adsorption/regeneration experiments

BAC samples were subjected to 8-cycle of adsorption/regeneration to examine their reusability. In addition, the adsorption capacity in each cycle was evaluated by the gravimetric method.

Figure 11 shows the adsorption capacity/efficiency of BAC samples. The adsorption capacity of KBAC slightly fluctuated in the range of 114.2–115.9 and 237.2–306.4 mg g⁻¹ for MEK and TOL, respectively. The slight decrease in adsorption capacity proved good stability, which the maintained porous properties could explain throughout the cycles.

The adsorption capacity for MEK-SBAC was generally higher than the initial value after each regeneration cycle. However, according to Table 1, the S_{total} and V_{total} of MEK-SBAC (800 W-8min) after the 8-cycle of adsorption/regeneration decreased, indicating the improvement of adsorption capability had nothing to do with the pore structures; instead, the more likely explanation rests in the more critical polarity resulted from the growing H and O ratio.

In contrast, the adsorption capacity of TOL-SBAC gradually decreased throughout the cycles. As shown in Table 1, the total and microporous surface area and pore volume of TOL-SBAC significantly declined after 8-cycle 800W-8min microwave irradiation. It has been proved that coke species grow at higher temperatures and reach molecule sizes larger than pores, the blocking phenomenon becomes severer especially for materials with highly-developed micropore structures such as SBAC in this study. As

a result, TOL being a typical aromatic compound was trapped and prohibited from diffusion within the pore structures during the regeneration process [40]. This could explain the loss in adsorption capacity, or the buildup of heel was not notable in KBAC loaded with TOL throughout the cycles but led to a maximum of 35% of capacity loss in SBAC. Nevertheless, the overall adsorption capacity of SBAC for TOL still prevailed among the two samples over the 8-cycle of adsorption/regeneration even though a severe decrease in adsorption capacity had occurred.

3.2.5. Desorption kinetics of BACs

Desorption kinetics analysis involving mass transfer models is of great importance for simulating lab-scale experiments and practical engineering design. In this section, we used batch experiments to determine the external mass transfer constants (k_l) and intraparticle diffusivities (k_p) for both BAC samples loaded with MEK and TOL at different microwave powers (400, 600, 800, and 1000 W), the simulation results are tabulated in Table S5.

For both SBAC and KBAC, the obtained k_l generally increased as the microwave power increased from 400 to 1000 W. Taking MEK-KBAC for example, the value of k_l at 400, 600, 800, and 1000 W were 0.064 ± 0.017 , 0.068 ± 0.007 , 0.138 ± 0.036 , and

510 $0.204 \pm 0.021 \text{ min}^{-1}$, respectively. When saturated with TOL, as power outputs
511 increased from 400 to 1000 W, the k_l increased from 0.026 ± 0.007 to 0.170 ± 0.009
512 min^{-1} .

513 As for MEK-SBAC, the value of k_l at 400 to 1000 W ranged from 0.309 ± 0.030
514 to $0.372 \pm 0.027 \text{ min}^{-1}$, which were higher than that of TOL-SBAC in which values
515 were ranging from 0.158 ± 0.044 to $0.232 \pm 0.031 \text{ min}^{-1}$. This result could be supported
516 by the aforementioned proposed evidence of stronger interaction between TOL and the
517 nonpolar surface of SBAC or the formation of chemically adsorbed TOL that was hard
518 to remove.

519 The simulation results summarized in Table S5 suggested the rate-limiting step for
520 MEK and TOL desorption would be intraparticle diffusion. In SBAC and KBAC loaded
521 with MEK, there was no much difference in the k_f values at various power outputs.
522 However, the k_f of TOL-SBAC significantly increased within the range of 18.07 ± 1.72
523 to $22.20 \pm 0.98 \text{ mg g}^{-1} \text{ s}^{-1/2}$ while that of TOL-KBAC remained relatively low, ranging
524 from 4.30 ± 1.18 to $11.33 \pm 0.64 \text{ mg g}^{-1} \text{ s}^{-1/2}$ as microwave powers increased from 400
525 to 1000 W. Among each scenario, it is worth noting that the effect of the boundary layer
526 (I) between the bulk phase of desorbed TOL and TOL-SBAC was extremely large,

which could be supported by the explanation of trapping TOL molecules in the micropore structures due to pore blockage by coke species in microporous materials [40].

4. Conclusions

To summarize, self-prepared high-surface-area beaded activated carbon (SBACs) were successfully synthesized using PF resins under optimal conditions of carbonization and physical activation (CO_2). SBAC possessed the largest total surface area of $2114 \text{ m}^2 \text{ g}^{-1}$ compared with bamboo-tar-derived BACs and the commercial KBAC. Additionally, the micropore structures in SBACs contributed to over 98% of the total surface area. The adsorption performance of BACs samples was evaluated by fitting with isotherms, which confirmed physical adsorption dominated the adsorption processes and the amount of the loading adsorbate influenced the adsorption heat. Microwave regeneration was proved to be effective and feasible in regenerating BAC samples within a short period. Cyclic tests verified the regenerability of the exhausted BAC samples and revealed the heel-buildup might occur in the case of SBAC loaded with TOL due to the pore blockage by coke species during the heating process. Kinetics analysis further provided the core parameters of importance to the estimation and designing of either lab-scale or enlarged-engineering scale adsorbent beds. However, a

method to track the actual temperature of samples during regeneration should be developed to analyze the heating behavior of the adsorbent thoroughly. Future studies should also consider regenerating adsorbents in-situ to reduce the complexity and increase the accuracy in multi-cycle adsorption/regeneration tests.

Declarations

Availability of data and materials

All data generated or analyzed during this study are included in this published article and its supplementary materials.

Competing interests

The authors declare they have no competing interests.

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Authors' contributions

Conceptualization, H.C.H., C.W., and J.G.D.; methodology, S.Y.H. and H.C.H.; formal analysis, S.Y.H. and S.W.Y.; data curation, S.Y.H. and S.W.Y.; writing—

original draft preparation, S.Y.H. and H.C.H.; writing—review and editing, S.W.Y. and H.C.H.; visualization, S.Y.H.; funding acquisition, H.C.H., C.W., and J.G.D. All authors read and approved the final manuscript.

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681 **Table 1** Physical and chemical properties of adsorbent

Sample	Component (w.t.% on dry basis)					S_{total} (m ² g ⁻¹)	S_{micro}/S_{total} (%)	V_{total} (cm ³ g ⁻¹)	V_{micro}/V_{total} (%)	d_{avg} (nm)
	C	H	O	N	S					
KBAC	0.12	87.61	0.77	2.95	10.86	1210.4	93.85	0.602	88.70	3.66
SBAC	1.08	82.66	0.09	2.86	11.52	2114.3	98.61	1.361	70.39	2.65
MEK-KBAC 800W8min	0.22	80.81	0.13	4.39	13.68	1104.2	98.16	0.535	94.95	2.82
MEK-SBAC- 800W8min	1.11	85.51	0.37	4.25	14.05	1737.9	98.33	0.785	98.22	2.66
TOL-KBAC 800W8min	0.20	84.37	0.13	4.24	7.11	1115.2	96.76	0.529	91.30	3.11
TOL-SBAC 800W8min	0.95	85.42	0.00	2.63	4.47	1280.1	94.69	0.598	89.30	2.52

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Figure 1 Schematic of adsorption testing system setup

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696 **Figure 2** SEM micrographs of (a) SBAC, (b) KBAC, (c) MEK-SBAC-800W8min, (d) TOL-SBAC-800W8min, (e) MEK-KBAC-800W8min, (f)

697 TOL-KBAC-800W8min, and (g) TEM micrograph of SBAC

Figure 3 Pore structure analysis for adsorbents (a) N₂ adsorption-desorption isotherms and pore size distribution within (b) mesoporous, macroporous, and (c) microporous regime.

Figure 4 TGA curves at heating rates of 5, 10 and 20 °C min⁻¹ for (a) virgin BACs, (b) MEK-SBAC, (c) MEK-KBAC, (d) TOL-SBAC, and (e) TOL-KBAC

Figure 5 Experimental and Langmuir modeled adsorption isotherms for MEK on (a) SBAC, (b) KBAC; TOL on (c) SBAC, (d) KBAC by gravimetric method

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723 **Figure 6** Experimental and Freundlich modeled adsorption isotherms for MEK on (a) SBAC, (b) KBAC; TOL on (c) SBAC, (d) KBAC by
 724 gravimetric method

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Figure 7 Experimental and D-R modeled adsorption isotherms for MEK on (a) SBAC, (b) KBAC; TOL on (c) SBAC, (d) KBAC by gravimetric method

Figure 8 Isosteric heat of (a) MEK and (b) TOL adsorption on SBAC; (c) MEK and (d) TOL adsorption on KBAC

Figure 9 Desorption efficiency evaluated by gravimetric method for (a) MEK-SBAC (b) MEK-KBAC, (c) TOL-SBAC, and (d) TOL-KBAC

Figure 10 Desorption efficiency evaluated by integration method for (a) MEK-SBAC (b) MEK-KBAC, (c) TOL-SBAC, and (d) TOL-KBAC

Figure 11 Variation in adsorption capacity of (a) MEK-SBAC, (b) MEK-KBAC, (c) TOL-SBAC, and (d) TOL-KBAC over an 8-cycle of adsorption/regeneration test

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