Adsorption of Volatile Organic Compounds and Microwave Regeneration on Self-prepared High-surface-area Beaded Activated Carbon

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ABSTRACT

Self-prepared beaded activated carbons (SBAC) were derived from carbonized phenolic formaldehyde (PF) resins through an optimal activation procedure (900°C for 4 h) using CO₂ and compared with a commercial BAC (termed KBAC) over physicochemical properties, adsorption performance against methyl ethyl ketone (MEK) and toluene (TOL), and their regenerability. Langmuir, Freundlich, and Dubinin‒Radushkevich (D‒R) isotherm models showed good fitting results. The isosteric heat of adsorption was calculated using the Clausius‒Clapeyron equation; the parameters obtained from the D‒R isotherm indicate that the physisorption predominates the adsorption process. Microwave heating was applied to regenerate the saturated adsorbents to examine the effect of irradiation power and heating time on the desorption behavior. Within 12 min of microwave irradiation, excellent desorption efficiencies were shown, reaching 110 ± 14.4%, 104 ± 2.6%, 90.2 ± 2.3%, and 85.5 ± 5.7% for MEK-SBAC, MEK-KBAC, TOL-SBAC, and TOL-KBAC samples, respectively. Kinetic models were further employed to illustrate the desorption behavior, showing that intraparticle diffusion in SBAC and KBAC was the rate-limiting step during microwave heating. The core kinetic parameters could provide insights for lab-scale 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 of the significant pollutants that are harmful to human health and the environment. In addition to the adverse effects, VOCs are also the precursors to the photochemical smog and the near-surface ozone, and are partially responsible for enhancing the global warming effect like greenhouse gases do. Therefore, it is desirable to reduce the emission of VOCs worldwide (Montero-Montoya et al., 2018).

Up to now, numerous abatement techniques have been proposed and adopted to reduce the VOC emission from stationary sources, such as thermal/catalytic oxidation, biological conversion, membrane separation, absorption, condensation, and adsorption (Zhang et al., 2017b; Han et al., 2020; Zhang et al., 2020). Among the removal technologies, the adsorption process by using a suitable adsorbent is a compelling method due to its cost-effectiveness and simplicity, and
with a great potential to recover high-priced VOCs via thermal regeneration followed by condensation (Pi et al., 2017; Lv et al., 2020).

One of the widely used porous adsorbents is activated carbon (AC). AC has garnered considerable attention for its remarkable properties: its predominant hydrophobicity, high thermal stability, low cost, chemical inertness, and low energy consumption for regeneration (Wickramaratne and Jaroniec, 2013). Furthermore, because of the non- or weak polar surface of AC, physisorption is typically the dominant adsorption mechanism for VOCs. The overall adsorption performance of AC is mainly attributed to its high specific surface area. It is also dependent on the size, molecular weight, polarizability, concentration, and complexity of the adsorbate (Bansal and Goyal, 2005; Ruthven, 2006; Zhang et al., 2017b).

To enhance the adsorption performance over specific compounds, ACs are usually subjected to chemical activation using acid/base reagents or physical modification under oxidizing gases (CO₂, steam, or air) at high temperatures (700–1000°C) to adjust surface areas and chemical functional groups on the surface (Xu et al., 2018).

A wide variety of ACs with novel morphologies such as monolith, fibrous, and beaded forms have been developed to adapt to different scenarios (Luo et al., 2006). Beaded activated carbon (BAC) is employed in a wide range of industrial applications due to its excellent properties such as high mechanical strength, porous structure, large surface area, high micropore volume, good fluidity, and decent adsorption performance (Wang et al., 2012; Romero-Anaya et al., 2014). A variety of polymeric-based precursors, including phenolic, sulfonated polystyrene, divinylbenzene, and phenolic formaldehyde (PF), have been adopted for BAC manufacturing, and BAC with high mechanical strength, high carbon content, and low ash content could be obtained. However, it is challenging to produce BAC with a perfect sphere and smooth surface without cracks since the size, molecular weight, polarizability, concentration, and complexity of the adsorbate (Bansal and Goyal, 2005; Ruthven, 2006; Zhang et al., 2017b).

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Therefore, in continuation to our earlier study (Chen et al., 2020), the present research focuses on (i) establishing equilibria and kinetic mechanisms of BACs, including self-prepared high-surface-area SBAC and commercial KBAC samples, toward methyl ethyl ketone (MEK) and toluene (TOL), which are the two major species emitted from the polyurethane (PU) industry in Taiwan (Dinh et al., 2016; Zhong et al., 2017); (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 build-up during cyclic adsorption/regeneration of MEK and TOL, and evaluating the feasibility of this technology. KBAC is selected for comparison because this commercial beaded activated carbon has been widely used for VOC adsorption in Taiwan via fluidized-bed operation.

2 METHODS

2.1 Adsorbent Preparation

The synthesis of SBAC (where S stands for self-prepared) 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 (DENGYING, 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 BAC (termed KBAC, where K stands for Kureha CORP.) 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 Adsorbent Characterization

2.2.1 Morphology and physicochemical properties of BACs

Detailed descriptions pertaining to determination of surface morphology and physicochemical properties of virgin and regenerated BACs have been clearly described in our previous works (Chen et al., 2019, 2020) and Supporting Information.

2.2.2 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 standard 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 VOC adsorption measurements and isotherm construction

Detailed descriptions pertaining to VOC adsorption measurements and isotherm construction are shown in Supporting Information. Briefly, the adsorption testing system comprises a VOC vapor generating system, a temperature-controlled adsorption bed, an online total hydrocarbon (THC) analyzer, and a data acquisition system (DAQ) is depicted in Fig. S1. MEK and TOL were selected as the tested adsorbents. Pre-treated BACs of 20–50 mg were measured for their adsorption performance at 30, 40, and 50°C. Both gravimetric method and breakthrough curve integration method are performed for calculating the saturated adsorption capacity.

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 ppm v and 40°C.

2.3.2 Microwave regeneration

Fig. S2 shows the setup of the microwave regeneration system. All adsorbents were exposed to MEK or TOL under an inlet concentration of 500 ppm, 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 1.6 standard 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 NOₓ, 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:
Desorption efficiency (%) = \frac{W_{BR} - W_{AR}}{W_{BR} \times q_{500ppmv}} \times 100

(1)

where $W_{BR}$ and $W_{AR}$ are the weight of the adsorbent before and after regeneration, respectively, and $q_{500ppmv}$ is the adsorption capacity at 500 ppm, 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 the following equation:

Regeneration efficiency (%) = \frac{q_r}{q_o} \times 100

(2)

where:

$q_o$ = quantity of adsorbate adsorbed per unit weight of adsorbent.

$q_r$ = 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. Detailed descriptions pertaining to the desorption kinetics analysis could be found in Supporting Information.

3 RESULTS AND DISCUSSION

3.1 Adsorbent Characterization

3.1.1 Desorption kinetics analysis

The morphologies of SBAC and KBAC were examined by SEM (Figs. 1(a) and 1(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 (Fig. 1(g)) 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 (Figs. 1(c‒f)). BACs saturated with MEK and TOL at 500 ppm, 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.

3.1.2 Elemental analysis (EA) and pore structures of BACs

Table 1 shows the elemental analysis 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 the likeness of 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 (Zhang et al., 2021).
Fig. 1. SEM micrographs of (a) SBAC, (b) KBAC, (c) MEK-SBAC-800W8min, (d) TOL-SBAC-800W8min, (e) MEK-KBAC-800W8min, (f) TOL-KBAC-800W8min, and (g) TEM micrograph of SBAC.

Table 1. Elemental analysis of virgin and regenerated BACs before and after microwave regeneration.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Component (wt.% on dry basis)</th>
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<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>KBAC</td>
<td>85.3</td>
</tr>
<tr>
<td>SBAC</td>
<td>82.7</td>
</tr>
<tr>
<td>MEK-KBAC 800W8min</td>
<td>80.8</td>
</tr>
<tr>
<td>MEK-SBAC-800W8min</td>
<td>85.5</td>
</tr>
<tr>
<td>TOL-KBAC 800W8min</td>
<td>84.4</td>
</tr>
<tr>
<td>TOL-SBAC 800W8min</td>
<td>85.4</td>
</tr>
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</table>

Additionally, the ash content rose to 4.0 and 6.9 wt.%, corresponding to the decrease in oxygen content to 7.1 and 5.4 wt.% for TOL-KBAC and TOL-SBAC, respectively.

The overall physical properties of virgin and regenerated BACs are also displayed in Table 2. SBAC synthesized under the optimal experimental conditions (activated at 900°C for 4 h) according to our previous study (Chen et al., 2020) using PF resins had shown tremendous improvement in surface area, possessing the largest specific surface area ($S_{total}$) of 2114 m$^2$ g$^{-1}$ and total pore volume ($V_{total}$) of 1.361 cm$^3$ g$^{-1}$ while KBAC used in this study showed a $S_{total}$ of 1210 m$^2$ g$^{-1}$ and $V_{total}$ of 0.602 cm$^3$ 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.
Table 2. Surface area and pore volume analysis of virgin and regenerated BACs before and after microwave regeneration.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{\text{total}}$ (m$^2$ g$^{-1}$)</th>
<th>$S_{\text{micro}}/S_{\text{total}}$ (%)</th>
<th>$V_{\text{total}}$ (cm$^3$ g$^{-1}$)</th>
<th>$V_{\text{micro}}/V_{\text{total}}$ (%)</th>
<th>$d_{\text{avg}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KBAC</td>
<td>1210</td>
<td>93.9</td>
<td>0.60</td>
<td>88.7</td>
<td>3.7</td>
</tr>
<tr>
<td>SBAC</td>
<td>2114</td>
<td>98.6</td>
<td>1.36</td>
<td>70.4</td>
<td>2.7</td>
</tr>
<tr>
<td>MEK-KBAC 800W8min</td>
<td>1104</td>
<td>98.2</td>
<td>0.54</td>
<td>95.0</td>
<td>2.8</td>
</tr>
<tr>
<td>MEK-SBAC 800W8min</td>
<td>1738</td>
<td>98.3</td>
<td>0.79</td>
<td>98.2</td>
<td>2.7</td>
</tr>
<tr>
<td>TOL-KBAC 800W8min</td>
<td>1115</td>
<td>96.8</td>
<td>0.53</td>
<td>91.3</td>
<td>3.1</td>
</tr>
<tr>
<td>TOL-SBAC 800W8min</td>
<td>1280</td>
<td>94.7</td>
<td>0.60</td>
<td>89.3</td>
<td>2.5</td>
</tr>
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</table>

*a $S_{\text{total}}$: specific surface area; $S_{\text{micro}}$: micropore surface area; $V_{\text{total}}$: total pore volume; $V_{\text{micro}}$: micropore volume; $d_{\text{avg}}$: average pore diameter.

The N$_2$ adsorption-desorption isotherm conducted at 77K and pore size distribution (PSD) of BACs are shown in Fig. S3. 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.

3.1.3 Thermogravimetric analysis (TGA)

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 (Fig. 2(a)). It could be attributed to moisture desorption, usually observed in activated carbon previously exposed to ambient air (Popescu et al., 2003).

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 (Figs. 2(b–e)). Notably, the weight loss of saturated BACs became slower at rapid heating rates, resulting from the heel buildup within the adsorbents. Niknaddaf et al. (2020) 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 (Popescu et al., 2003). 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 (Cvetanović and Amenomiya, 1972):

$$\ln\left(\frac{\beta}{RT_M^2}\right) = -\frac{E_d}{RT_M} + C$$  \hspace{1cm} (3)

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

The DTG curves for SBAC and KBAC are shown in Supporting Information (Figs. S4–S7), and the calculated $E_d$ (Table 3) for MEK and TOL in this study was similar to or slightly higher than the heat of vaporization for MEK and TOL (31.21 and 32.80 kJ mol$^{-1}$ at boiling point for MEK and TOL, respectively), which could be characterized as physical adsorption onto both SBAC and KBAC (Popescu et al., 2003).
Fig. 2. 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.

Table 3. Peak desorption temperatures at different heating rates and the calculated activation energies for desorption.

<table>
<thead>
<tr>
<th></th>
<th>Peak desorption temperatures (K) at different heating rates</th>
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<tbody>
<tr>
<td></td>
<td>20°C min$^{-1}$</td>
<td>10°C min$^{-1}$</td>
</tr>
<tr>
<td>MEK-SBAC</td>
<td>488</td>
<td>461</td>
</tr>
<tr>
<td>MEK-KBAC</td>
<td>488</td>
<td>468</td>
</tr>
<tr>
<td>TOL-SBAC</td>
<td>494</td>
<td>459</td>
</tr>
<tr>
<td>TOL-KBAC</td>
<td>520</td>
<td>476</td>
</tr>
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</table>

3.2 Adsorption and Desorption Performance

3.2.1 Thermogravimetric analysis (TGA)

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. The inlet concentrations of the VOCs were set in the range within 100 to 20,000 ppm, for MEK and 100 to 10,000 ppm, 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 Tables S1–S3. 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 modelled data are also presented in Fig. S8. 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.

Fig. S9 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 (Do, 1998). As shown in Table S2, 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 S3, and the plots of the experimental and the D–R isotherm modelled data are presented in Fig. S10. 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 2), SBACs developed higher proportions of micropores compared to KBAC. However, the calculated $W_0$ seemed inconsistent with those obtained from $N_2$ adsorption. The main reason was the difference in the kinetic diameters of the probing molecules ($N_2$: 4.02 Å, MEK: 5.25 Å, and TOL: 5.85 Å), contributing to the difference in $W_0$.

The characteristic energy, $E$ (or $E_{o(f)}$), is a parameter concerning pore size, surface chemistry, and adsorbate structure (Chiang et al., 2002). 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:

$$x_0 = \frac{k}{E_0} \tag{4}$$

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$^{-1}$ (Dubinin and Stoeckli, 1980; Ghafari and Atkinson, 2018).

As observed in Table S3, the $x_0$ of SBACs are larger than 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) (Ghafari and Atkinson, 2018).

3.2.2 Isosteric heat of adsorption

The isosteric heats can be calculated using the D–R parameters and Clausius-Clapeyron equation (Ruthven, 2006). 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 $\Delta H_s$ were based on gravimetric methods. The dependences on adsorbate, temperature, and surface loading in calculating $\Delta H_s$ are illustrated in Fig. 3.

A rule of thumb in adsorption is that for adsorption heat $< 80 \text{ kJ mol}^{-1}$, the adsorption process is characterized as physisorption (Sui et al., 2017). As shown in Fig. 3, the $\Delta H_s$ ranges from 35 to 60 kJ mol$^{-1}$, indicating MEK and TOL are physically adsorbed onto SBAC and KBAC.

The $\Delta H_s$ of MEK and TOL on SBAC are nearly constant ($\approx 45.47$ and $45.52 \text{ kJ mol}^{-1}$, respectively) and are independent of temperature within the range of surface loading. This implies a relatively homogeneous distribution of surface energy in these two adsorbents (Buss, 1995). However, as observed in Fig. 3(c), the $\Delta H_s$ of MEK on KBAC at 30°C is relatively lower. One explanation is the surface heterogeneity of adsorbent (Huang, 1972), but this may also be attributed to an experimental error in measuring the adsorption isotherm. It should be noted in Fig. 3(d) that $\Delta H_s$ 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. (2020) and can be explained by the follows: (1) the surfaces of KBAC are energetically heterogeneous towards adsorption of TOL (Park et al., 2002), (2) the stronger lateral interactions occurred between the adsorbed molecules at a higher surface coverage (Chowdhury et al., 2011), or (3) as surface loading increases, more vital interaction between TOL (weak polarity) and the nonpolar adsorbent resulting in high heats of adsorption.

Fig. 3. Isosteric heat of (a) MEK and (b) TOL adsorption on SBAC; (c) MEK and (d) TOL adsorption on KBAC.
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 1.6 standard L min⁻¹ (Figs. 4, 5 and S11). Within 12 min of microwave irradiation, desorption efficiencies based on the gravimetric method reached 110 ± 14.4%, 104 ± 2.6%, 90.2 ± 2.3%, and 85.5 ± 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 ± 19.3 µm and 700.7 ± 20.3 µm 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 VOCs (Kim and Ahn, 2012).

It is noteworthy that the desorption efficiencies for MEK and TOL calculated by the gravimetric method were consistently higher than that of the integration method (Figs. 4 and 5).

For MEK-SBAC, the effluent gas analysis results showed CO plus CO₂ weighed approximately 85.52 µg as C, causing an average of 28.01% of efficiency difference. There was no other apparent gas outflow. Thus, the results supported the inference that MEK was decomposed into inorganic compounds during the heating process (Waring and Spector, 1955). However, CO and CO₂ released from MEK-KBAC were hardly observed. Instead, a significant SO₂ emission (25.04 µg as S) might be generated from removing sulfur at higher temperatures was considered the main reason for the overestimation of desorption efficiencies based on the gravimetric method, in an average of 22.4% of efficiency difference.

On the other hand, for TOL on BACs, the efficiency evaluated by desorption concentration was only slightly lower than that by weight change (~4.31% and ~4.48% on average for TOL-SBAC

![Fig. 4. Desorption efficiency evaluated by gravimetric method for (a) MEK-SBAC (b) MEK-KBAC, (c) TOL-SBAC, and (d) TOL-KBAC.](image-url)
Fig. 5. Desorption efficiency evaluated by integration method for (a) MEK-SBAC (b) MEK-KBAC, (c) TOL-SBAC, and (d) TOL-KBAC.

and TOL-KBAC, respectively). A possible explanation was that TOL reacting with oxygen-containing groups on the surface of carbon and transformed into inorganic compounds (i.e., CO or CO₂), which could not be detected by a THC detector (Bhandari et al., 2014). 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 Reusability of BAC samples via 8-cycle of 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.

Fig. 6 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 2, the S_{total} and V_{total} of MEK-SBAC (800 W-8 min) 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 2, the total and microporous surface area and pore volume of TOL-SBAC significantly declined after 8-cycle 800 W-8 min 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 (Korus et al., 2017). 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 study for 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 ($k_1$) and intra-particle 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 S4.

For both SBAC and KBAC, the obtained $k_1$ generally increased as the microwave power increased from 400 to 1000 W. Taking MEK-KBAC for example, the value of $k_1$ at 400, 600, 800, and 1000 W were $0.064 \pm 0.017$, $0.068 \pm 0.007$, $0.138 \pm 0.036$, and $0.204 \pm 0.021$ min$^{-1}$, respectively. When saturated with TOL, as power outputs increased from 400 to 1000 W, the $k_1$ increased from $0.026 \pm 0.007$ to $0.170 \pm 0.009$ min$^{-1}$. 

Fig. 6. 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.
As for MEK-SBAC, the value of $k_1$ at 400 to 1000 W ranged from $0.309 \pm 0.030$ to $0.372 \pm 0.027 \text{ min}^{-1}$, which were higher than that of TOL-SBAC in which values were ranging from $0.158 \pm 0.044$ to $0.232 \pm 0.031 \text{ min}^{-1}$. This result could be supported by the proposed evidence of stronger interaction between TOL and the non-polar surface of SBAC or the formation of chemically adsorbed TOL that was hard to remove.

The simulation results summarized in Table S4 suggested the rate-limiting step for MEK and TOL desorption would be intraparticle diffusion. In SBAC and KBAC loaded with MEK, there was no much difference in the $k_i$ values at various power outputs. However, the $k_i$ of TOL-SBAC significantly increased within the range of $18.07 \pm 1.72$ to $22.20 \pm 0.98 \text{ mg g}^{-1} \text{ s}^{-1/2}$ while that of TOL-KBAC remained relatively low, ranging from $4.30 \pm 1.18$ to $11.33 \pm 0.64 \text{ mg g}^{-1} \text{ s}^{-1/2}$ as microwave powers increased from 400 to 1000 W. Among each scenario, it is worth noting that the effect of the boundary layer (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 (Korus et al., 2017).

4 CONCLUSIONS

Self-prepared high-surface-area beaded activated carbon (SBACs) with the largest total surface area of 2114 m$^2$ g$^{-1}$ and > 98% microporosity were successfully synthesized using PF resins under optimal conditions of carbonization and physical activation (CO$_2$) in this study. The most innovative findings could be summarized as follows:

(1) Physisorption dominates the VOC adsorption processes and the adsorption amount influences the adsorption heat, which could be thoroughly understood by theoretical adsorption isotherm fittings.

(2) Microwave regeneration is proved to be effective and feasible in regenerating BAC samples within a short period. Additionally, cyclic adsorption/regeneration 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.

(3) Kinetics analysis further provided the core parameters of importance to the estimation and designing of either lab-scale or enlarged-engineering scale adsorbent beds.

Although the excellent adsorption performance of SBAC and the feasibility of microwave regeneration of BACs have been successfully demonstrated, a method to track the actual temperature of samples during regeneration should still 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 multicycle adsorption/regeneration tests.

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DISCLAIMER

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SUPPLEMENTARY MATERIAL

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REFERENCES


