Adsorption of Volatile Organic Compounds and Microwave Regeneration on Self-Prepared High-Surface-Area Beaded Activated Carbon

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1. Adsorbent Characterization

1.1. 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 N$_2$ adsorption was carried out at 77K (Micromeritics, model ASAP 2420) to examine the pore structure of BACs. All samples were degassed at 350$^\circ$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 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.

1.2. 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. VOC Adsorption Measurements

The schematic diagram of the adsorption testing system comprises a VOC vapor generating system, a temperature-controlled adsorption bed, a total hydrocarbon (THC) analyzer, and a data acquisition system (DAQ) is depicted in Fig. S1. The selected solvents (MEK and TOL) were injected into a heating furnace (designed by Fortelice International Co., Ltd.) at a constant rate with a gastight syringe (Hamilton Company) and a syringe pump (New Era Pump Systems Inc., model NE 1000). The temperature of the heating furnace was monitored by a K-type thermocouple and set well above the boiling point of both solvents (79.6°C and 110.6°C for MEK and TOL, respectively) to ensure the solvents vaporized immediately and mixed with the inert carrier gas (N₂, purity = 99.999%). The injection rates of solvents were adjusted based on the ideal gas law to generate desired VOC concentrations in the gas stream.

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

The adsorption experiments were carried out in a Pyrex glass tube (40 cm in length and 1 cm in diameter), pre-treated BACs of 20‒50 mg were measured and placed in the center of the tube and supported by a sintered glass filter. The adsorption bed was 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 standard L min⁻¹ 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:

$$\text{Adsorption capacity (\%) } = \frac{W_{AA} - W_{BA}}{W_{BA}} \times 100\% \quad (S1)$$

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:

$$\text{Adsorption capacity (\%) } = \frac{\int (C_{\text{in}} - C_{\text{outlet, i}}) \times V_{\text{ad}} \times \rho_G \times W_{BA}}{W_{BA}} \times 100\% \quad (S2)$$

where $C_{\text{in}}$ is the inlet concentration (ppm), $C_{\text{outlet, i}}$ is the VOC outlet concentration (ppm) during the period of adsorption at $i$ interval of time, and the time interval was set as one second. $V_{\text{ad}}$ is total gas volume (m³), $\rho_G$ is the density of the organic vapor, and $W_{BA}$ is the weight of the adsorbent before adsorption.
3. Isotherm Construction: Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) Isotherms

The Langmuir isotherm was primarily designed to describe gas-solid phase adsorption. It assumed the adsorption was monolayer and in dynamic equilibrium, the Langmuir equation can be written in the following form:

$$q = \frac{b \cdot P}{1 + bP}$$  \hspace{1cm} (S3)

where $q$ (mg g$^{-1}$) is the adsorption capacity, $q_s$ (mg g$^{-1}$) the saturated adsorption capacity, $b$ (Pa$^{-1}$) the Langmuir constant representing the strength of the adsorbate-adsorbent interactions, and $P$ (Pa) stands for the partial pressure of the adsorbate in the bulk phase.

The Freundlich isotherm is an empirical equation which is applicable to adsorption processes occurred on heterogeneous interfaces. The form of Freundlich isotherm is as follows:

$$q = K_F \cdot P^{1/n_F}$$  \hspace{1cm} (S4)

where $K_F$ and $n_F$ are empirical constants that are generally temperature dependent.

The Dubinin-Radushkevich isotherm is a semi-empirical equation adapted from the earlier Polanyi potential theory and has been widely applied to describe the adsorption in microporous materials (Nguyen and Do, 2001), having the form of:

$$q = \rho W_0 \exp \left[ -\left( \frac{\varepsilon}{E_0} \right)^2 \right]$$  \hspace{1cm} (S5)

and

$$\varepsilon = RT \ln \frac{P_0}{P}$$  \hspace{1cm} (S6)

where $W_0$ is the pore volume filled, $\beta$ the affinity coefficient ($\beta = 1$ for the reference vapor), $\varepsilon$ the adsorption potential, $E_0$ the so-called characteristic energy for a reference vapor (usually benzene), $R$ the universal gas constant (8.314 J mole$^{-1}$ K$^{-1}$), $T$ the absolute temperature (K), and $P_0$ the saturated vapor pressure of the adsorbate.
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.

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 (Singh et al., 2002), and intraparticle diffusion is often considered the rate-controlling step in an adsorption process (Fournel et al., 2010). 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 (Zhou et al., 2015):

\[
\ln \left(1 - \frac{q_t}{q_e}\right) = -k_1 t
\]

where \(q_e\) and \(q_t\) is 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 (Weber Jr and Morris, 1963) is widely used for the analysis of adsorption kinetics. The IPD model could be described as:
\[ q_t = k_p t^{1/2} + I \]  \hspace{1cm} (S8)

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.
5. Supplementary Figures

**Fig. S1.** Schematic of adsorption testing system setup

**Fig. S2.** The scheme diagram of the microwave regeneration system
Fig. S3. Pore structure analysis for adsorbents (a) N₂ adsorption-desorption isotherms and pore size distribution within (b) mesoporous, macroporous, and (c) microporous regime.
Fig. S4. DTG of MEK-SBAC at various heating rates. (a) DTG peaks; (b) linear form providing the heat of desorption.
Fig. S5. DTG of MEK-KBAC at various heating rates. (a) DTG peaks; (b) linear form providing the heat of desorption.
Fig. S6. DTG of TOL-SBAC at various heating rates. (a) DTG peaks; (b) linear form providing the heat of desorption.
Fig. S7. DTG of TOL-KBAC at various heating rates. (a) DTG peaks; (b) linear form providing the heat of desorption
Fig. S8. Experimental and Langmuir modeled adsorption isotherms for MEK on (a) SBAC, (b) KBAC; TOL on (c) SBAC, (d) KBAC by gravimetric method
Fig. S9. Experimental and Freundlich modeled adsorption isotherms for MEK on (a) SBAC, (b) KBAC; TOL on (c) SBAC, (d) KBAC by gravimetric method
Fig. S10. Experimental and D–R modeled adsorption isotherms for MEK on (a) SBAC, (b) KBAC; TOL on (c) SBAC, (d) KBAC by gravimetric method.
Fig. S11. THC desorption curve of MEK-SBAC at different power inputs for 12 min of irradiation time.
6. Supplementary Tables

Table S1. Langmuir parameters for different adsorbate-adsorbent systems at different temperatures

| Integration method | Adsorbate Adsorbent | T (°C) | \( R^2 \) | \( q_s \) (mg g\(^{-1}\)) | \( K_L \) |
|--------------------|---------------------|--------|-----------|-----------------|---------|
| **Langmuir parameter** | **MEK** | **SBAC** | 30 | 0.9571 | 1956.8 | 40.2 |
|                    |        |        | 40 | 0.9559 | 1701.5 | 60.3 |
|                    |        |        | 50 | 0.9904 | 2382.2 | 29.9 |
|                    | **KBAC** | **SBAC** | 30 | 0.9321 | 547.6 | 230.6 |
|                    |        |        | 40 | 0.8572 | 538.9 | 419.2 |
|                    |        |        | 50 | 0.9730 | 568.3 | 238.8 |
|                    | **TOL** | **SBAC** | 30 | 0.8669 | 1686.0 | 64.6 |
|                    |        |        | 40 | 0.8551 | 1222.0 | 168.6 |
|                    |        |        | 50 | 0.9405 | 1433.7 | 105.4 |
|                    | **KBAC** | **SBAC** | 30 | 0.9902 | 593.1 | 176.3 |
|                    |        |        | 40 | 0.9838 | 557.1 | 218.9 |
|                    |        |        | 50 | 0.9866 | 555.6 | 362.9 |
| **Gravimetric method** | **MEK** | **SBAC** | 30 | 0.9683 | 962.7 | 112.5 |
|                    |        |        | 40 | 0.9906 | 770.2 | 100.4 |
|                    |        |        | 50 | 0.8936 | 610.1 | 211.3 |
|                    | **KBAC** | **SBAC** | 30 | 0.9924 | 365.1 | 368.0 |
|                    |        |        | 40 | 0.9849 | 358.8 | 286.0 |
|                    |        |        | 50 | 0.9652 | 377.4 | 255.3 |
|                    | **TOL** | **SBAC** | 30 | 0.9612 | 1323.9 | 71.7 |
|                    |        |        | 40 | 0.9343 | 997.3 | 147.5 |
|                    |        |        | 50 | 0.9456 | 978.2 | 123.7 |
|                    | **KBAC** | **SBAC** | 30 | 0.9944 | 421.8 | 468.6 |
|                    |        |        | 40 | 0.9995 | 413.0 | 491.5 |
|                    |        |        | 50 | 0.9912 | 400.9 | 653.6 |
**Table S2.** Freundlich parameters for different adsorbate-adsorbent systems at different temperatures

| Integration method | Adsorbate | Adsorbent | T (°C) | R²    | n   | K_F  |
|--------------------|-----------|-----------|--------|-------|-----|------|
| **Freundlich parameter** |           |           |        |       |     |      |
| **MEK**            | SBAC      | 30        | 0.9657 | 2.302 |     | 4243.3 |
|                    |           | 40        | 0.9896 | 2.309 |     | 4431.1 |
|                    |           | 50        | 0.9999 | 1.746 |     | 7927.5 |
| KBAC               | 30        | 0.9822    | 4.778  |       |     | 890.8 |
|                    | 40        | 0.9410    | 4.995  |       |     | 954.2 |
|                    | 50        | 0.9931    | 3.352  |       |     | 1360.9 |
| **TOL**            | SBAC      | 30        | 0.9486 | 3.942 |     | 2426.1 |
|                    |           | 40        | 0.9825 | 4.496 |     | 2013.0 |
|                    |           | 50        | 0.9669 | 3.041 |     | 3060.9 |
| KBAC               | 30        | 0.9927    | 7.886  |       |     | 737.1 |
|                    | 40        | 0.9925    | 6.382  |       |     | 783.6 |
|                    | 50        | 0.9967    | 6.662  |       |     | 824.7 |
| **Gravimetric method** |           |           |        |       |     |      |
| **MEK**            | SBAC      | 30        | 0.9483 | 3.336 |     | 1793.6 |
|                    |           | 40        | 0.9769 | 2.531 |     | 2005.2 |
|                    |           | 50        | 0.9637 | 3.105 |     | 1569.8 |
| KBAC               | 30        | 0.9960    | 6.784  |       |     | 518.7 |
|                    | 40        | 0.9946    | 4.407  |       |     | 656.4 |
|                    | 50        | 0.9947    | 3.386  |       |     | 905.4 |
| **TOL**            | SBAC      | 30        | 0.9555 | 3.824 |     | 1988.3 |
|                    |           | 40        | 0.9900 | 3.902 |     | 1777.6 |
|                    |           | 50        | 0.9857 | 3.187 |     | 2107.6 |
| KBAC               | 30        | 0.9989    | 15.97  |       |     | 475.8 |
|                    | 40        | 0.9960    | 12.42  |       |     | 494.1 |
|                    | 50        | 0.9890    | 10.67  |       |     | 515.3 |
Table S3. D-R parameters for different adsorbate-adsorbent systems at different temperature

| Integration method | adsorbate | adsorbent | T (°C) | R²    | W₀ (cm³ g⁻¹) | E₀ (kJ mol⁻¹) | E (kJ mol⁻¹) | x₀ (nm) |
|-------------------|-----------|-----------|--------|-------|--------------|---------------|--------------|---------|
| **D-R parameter** |           |           |        |       |              |               |              |         |
| MEK               | SBAC      | 30        | 0.9685 | 2.711 | 7.44         | 7.20          | 1.747        |
|                   |           | 40        | 0.9778 | 2.536 | 8.17         | 7.92          | 1.592        |
|                   |           | 50        | 0.9949 | 3.367 | 7.30         | 7.09          | 1.780        |
| KBAC              | SBAC      | 30        | 0.9709 | 0.787 | 11.09        | 10.74         | 1.172        |
|                   |           | 40        | 0.9200 | 0.808 | 12.52        | 12.14         | 1.039        |
|                   |           | 50        | 0.9954 | 0.927 | 10.67        | 10.36         | 1.218        |
| TOL               | SBAC      | 30        | 0.9020 | 2.014 | 7.45         | 8.88          | 1.745        |
|                   |           | 40        | 0.9559 | 1.590 | 9.12         | 10.88         | 1.425        |
|                   |           | 50        | 0.9636 | 1.962 | 7.84         | 9.36          | 1.658        |
| KBAC              | SBAC      | 30        | 0.9956 | 0.724 | 10.19        | 12.15         | 1.276        |
|                   |           | 40        | 0.9935 | 0.710 | 10.21        | 12.18         | 1.273        |
|                   |           | 50        | 0.9974 | 0.728 | 11.45        | 13.66         | 1.136        |
| **Gravimetric method** |     |           |        |       |              |               |              |         |
| MEK               | SBAC      | 30        | 0.9690 | 1.389 | 9.22         | 8.92          | 1.410        |
|                   |           | 40        | 0.9932 | 1.219 | 8.67         | 8.41          | 1.500        |
|                   |           | 50        | 0.9477 | 1.008 | 10.34        | 10.04         | 1.258        |
| KBAC              | SBAC      | 30        | 0.9998 | 0.510 | 13.14        | 12.72         | 0.989        |
|                   |           | 40        | 0.9990 | 0.540 | 11.44        | 11.10         | 1.136        |
|                   |           | 50        | 0.9936 | 0.618 | 10.77        | 10.46         | 1.207        |
| TOL               | SBAC      | 30        | 0.9768 | 1.635 | 7.83         | 9.34          | 1.659        |
|                   |           | 40        | 0.9834 | 1.342 | 8.41         | 10.03         | 1.546        |
|                   |           | 50        | 0.9811 | 1.368 | 8.13         | 9.70          | 1.599        |
| KBAC              | SBAC      | 30        | 0.9982 | 0.505 | 14.84        | 17.68         | 0.876        |
|                   |           | 40        | 0.9982 | 0.505 | 14.23        | 16.98         | 0.913        |
|                   |           | 50        | 0.9905 | 0.503 | 14.53        | 17.34         | 0.895        |
Table S4. Kinetic parameters of desorption and correlation coefficient $R^2$ obtained from PFO and IPD kinetic models

| Adsorbate | Adsorbent | Irradiation power (W) | PFO model | IPD model |
|-----------|-----------|----------------------|------------|-----------|
|           |           | $k_1$ (min$^{-1}$)   | $R^2$      | $k_p$ (mg g$^{-1}$ s$^{-1/2}$) | $I$ (mg g$^{-1}$) | $R^2$ |
| MEK       | SBAC      | 400                  | 0.328 ± 0.030 | 0.889 – 0.921 | 9.17 ± 0.49 | -8.23 ± 4.40 | 0.889 – 0.912 |
|           |           | 600                  | 0.372 ± 0.027 | 0.900 – 0.934 | 9.50 ± 0.20 | -7.67 ± 5.55 | 0.886 – 0.916 |
|           |           | 800                  | 0.350 ± 0.009 | 0.895 – 0.926 | 8.60 ± 1.65 | -7.97 ± 6.86 | 0.881 – 0.912 |
|           |           | 1000                 | 0.309 ± 0.030 | 0.875 – 0.904 | 8.75 ± 0.64 | -3.35 ± 6.15 | 0.877 – 0.893 |
| KBAC      | SBAC      | 400                  | 0.064 ± 0.017 | 0.953 – 0.975 | 4.03 ± 0.67 | -25.30 ± 6.39 | 0.973 – 0.985 |
|           |           | 600                  | 0.068 ± 0.007 | 0.842 – 0.987 | 3.87 ± 0.67 | -17.87 ± 8.32 | 0.949 – 0.988 |
|           |           | 800                  | 0.138 ± 0.036 | 0.902 – 0.973 | 5.83 ± 0.55 | -24.30 ± 21.61 | 0.901 – 0.955 |
|           |           | 1000                 | 0.204 ± 0.021 | 0.904 – 0.937 | 7.17 ± 0.12 | -23.43 ± 6.95 | 0.907 – 0.940 |
| TOL       | SBAC      | 400                  | 0.158 ± 0.044 | 0.868 – 0.951 | 18.07 ± 1.72 | -20.17 ± 49.80 | 0.896 – 0.944 |
|           |           | 600                  | 0.230 ± 0.012 | 0.887 – 0.926 | 22.20 ± 0.98 | 7.23 ± 18.65 | 0.874 – 0.905 |
|           |           | 800                  | 0.212 ± 0.019 | 0.803 – 0.870 | 19.90 ± 0.85 | 54.53 ± 13.78 | 0.799 – 0.850 |
|           |           | 1000                 | 0.232 ± 0.031 | 0.814 – 0.895 | 20.43 ± 0.32 | 33.70 ± 42.86 | 0.817 – 0.888 |
| KBAC      | SBAC      | 400                  | 0.026 ± 0.007 | 0.949 – 0.972 | 4.30 ± 1.18 | -35.50 ± 7.66 | 0.958 – 0.976 |
|           |           | 600                  | 0.078 ± 0.026 | 0.981 – 0.985 | 9.33 ± 1.62 | -64.70 ± 8.22 | 0.975 – 0.987 |
|           |           | 800                  | 0.126 ± 0.042 | 0.963 – 0.990 | 11.20 ± 0.70 | -56.93 ± 20.97 | 0.928 – 0.982 |
|           |           | 1000                 | 0.170 ± 0.009 | 0.899 – 0.947 | 11.33 ± 0.64 | -10.13 ± 17.22 | 0.866 – 0.908 |
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