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Supplementary Information

High-capacity petroleum coke–derived activated carbon for bisphenol A and carbamazepine removal: Fixed-bed operation, regeneration, and mechanistic insights

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1.Sections

Section S1

The removal efficiency of pollutants E (%) and equilibrium adsorption capacity q_e ($\text{mg}\cdot\text{g}^{-1}$) of adsorbents were calculated by equation S1 [1] and S2 [2].

$$E = \frac{C_0 - C_e}{C_0} \times 100\% \quad (\text{S1})$$

$$q_e = \frac{(c_0 - c_e)v}{m} \quad (\text{S2})$$

Where C_0 is the initial concentration, $\text{mg}\cdot\text{L}^{-1}$; C_e is the adsorption equilibrium concentration, $\text{mg}\cdot\text{L}^{-1}$; v is the adsorbent dosing amount, L; m is the adsorbent mass, g.

Adsorption kinetics:

The adsorption tests of BPA (25、50、100 $\text{mg}\cdot\text{L}^{-1}$) and CBZ (25、35、100 $\text{mg}\cdot\text{L}^{-1}$) and activated carbon (0.1 $\text{g}\cdot\text{L}^{-1}$) were carried out respectively. The supernatant was obtained by 0.22 μm filter membrane at 0-1440 min without adjusting the initial pH, and then the residual concentration of BPA and CBZ were determined by UV-VIS spectroscopy ($\lambda = 276 \text{ nm}$ 、 285 nm). Four classical models of pseudo-first-order (Eq. S3), pseudo-second-order (Eq. S4), Elovich model (Eq. S5) and intra-particle diffusion (Eq. S6) were used to fit the kinetic experimental data [3].

$$q_t = q_e (1 - e^{-K_1 t}) \quad (\text{S3})$$

$$q_t = \frac{K_2 q_e^2 t}{1 + K_2 q_e t} \quad (\text{S4})$$

$$q_t = \frac{\ln(\alpha\beta)}{\beta} + \frac{\ln t}{\beta} \quad (\text{S5})$$

$$q_t = kt^{0.5} + C \quad (\text{S6})$$

Where q_e ($\text{mg}\cdot\text{g}^{-1}$) and q_t ($\text{mg}\cdot\text{g}^{-1}$) are the adsorption amount towards BPA and CBZ at equilibrium and at time t , respectively. K_1 (min^{-1}), K_2 ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$), α ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$),

β (g·mg⁻¹) and k_i (mg·g⁻¹·min^{-0.5}) are the rate constants of diverse kinetics (Eq. S3-Eq. S6); C is to describe the boundary layer characteristic.

Adsorption isotherm:

The adsorption tests of BPA (10-1000 mg·L⁻¹) and CBZ (10-150 mg·L⁻¹) and activated carbon (0.1 g·L⁻¹) were carried out respectively. Conical flasks filled with pollutant and activated carbon are carried out on a shaker for 24 hours at 298 K, 308 K, 318 K. The initial pH of the solution was not adjusted. In this study, Langmuir (Eq. S7) [4], Freundlich (Eq. S8) and Temkin (Eq. S9) isotherm models were adopted [5].

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (S7)$$

$$q_e = K_F C_e^{1/n} \quad (S8)$$

$$q_e = \frac{RT}{b} \ln(ACe) \quad (S9)$$

Where q_e (mg·g⁻¹) and Q_m (mg·g⁻¹) are the equilibrium and the maximum adsorption capacity, respectively; C_e (mg·L⁻¹) represents the equilibrium concentration of BPA and CBZ; K_L (L·mg⁻¹) and K_F (mg·g⁻¹·min^{1/n}·L^{-1/n}) represent the constants of Langmuir and Freundlich, respectively. $1/n$ (g·mg⁻¹) and A (L·g⁻¹) are the empirical parameters of Freundlich and Temkin, respectively. b is the isothermal adsorption heat of Temkin (kJ·mol⁻¹), respectively.

To further evaluate the influence of adsorption-site heterogeneity, the Sips model was also applied:

$$q_e = \frac{q_m (K_s C_e)^m}{1 + (K_s C_e)^m} \quad (S10)$$

where q_e and q_m are the equilibrium adsorption capacity and maximum adsorption capacity, respectively; C_e is the equilibrium concentration; K_s is the Sips constant; and

mmm is the heterogeneity parameter. When mmm approaches 1, the Sips model reduces to the Langmuir-type behavior.

Thermodynamic analysis:

The effect of activated carbon adsorbed BPA and CBZ was studied 298 K, 308 K, 318 K. Determine the main thermodynamic parameters (ΔS , and ΔG), apply the following formula [6]:

$$K_c = \frac{q_e}{C_e} \quad (S11)$$

$$\Delta G = -RT \ln K_c \quad (S12)$$

$$\Delta G = \Delta H - T\Delta S \quad (S13)$$

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (S14)$$

Where, q_e ($\text{mg} \cdot \text{g}^{-1}$) is the volume of adsorbed BPA and CBZ, C_e ($\text{mg} \cdot \text{L}^{-1}$) is the BPA and CBZ concentration at the time, T (K) signifies the flow temperature and R is the gas law constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), ΔG ($\text{kJ} \cdot \text{mol}^{-1}$) corresponds to Gibbs free energy change, ΔS ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) indicates entropy change, and ΔH ($\text{kJ} \cdot \text{mol}^{-1}$) signifies standard enthalpy variation.

The recovery and reuse of adsorbents are not only related to process costs, but also one of the core indicators that determine their industrial prospects. Based on this, this study was conducted three consecutive adsorption cycle tests on the adsorbent and used the calculation methods in the literature [7] to determine the desorption percentage (%) of each cycle.

$$\text{Desorption}(\%) = \frac{\text{Amount of BPA desorbed}}{\text{Amount of BPA adsorbed}} \times 100 \quad (S15)$$

Yoon–Nelson model:

The breakthrough behavior of BPA and CBZ in the fixed-bed column was analyzed using the Yoon–Nelson model (Eq. S10). The linear equation of the model is given as follows:

$$\ln\left(\frac{C_e}{C_0-C_e}\right)=k_{YN}t-k_{YN}\tau \quad (\text{S16})$$

Where C_0 ($\text{mg}\cdot\text{g}^{-1}$) and C_t ($\text{mg}\cdot\text{L}^{-1}$) are the influent and effluent concentrations at time t , respectively; k_{YN} (min^{-1}) is the Yoon-Nelson rate constant; and τ (min) represents the time required for 50% adsorbate breakthrough.

DFT computational details

Quantum chemical calculations were performed using the ORCA 6.1.0 program package [1]. Geometry optimization, vibrational frequency analysis, and single-point energy calculations were carried out at the $\text{r}^2\text{SCAN-3c}$ level. The optimized adsorption configurations were visualized using VMD 1.9.3.

The binding energy (E_{bind}) between the adsorbate and the PCAC surface model was calculated according to the following equation:

$$E_{bind}=E_{complex}-E_{PCAC}-E_{adsorbate} \quad (\text{S17})$$

where $E_{complex}$ is the total energy of the optimized adsorbate–PCAC complex, E_{PCAC} is the energy of the isolated PCAC surface model, and $E_{adsorbate}$ is the energy of the isolated BPA or CBZ molecule. A more negative E_{bind} value indicates a more favorable interaction between the adsorbate and the PCAC surface model.

2. Figures

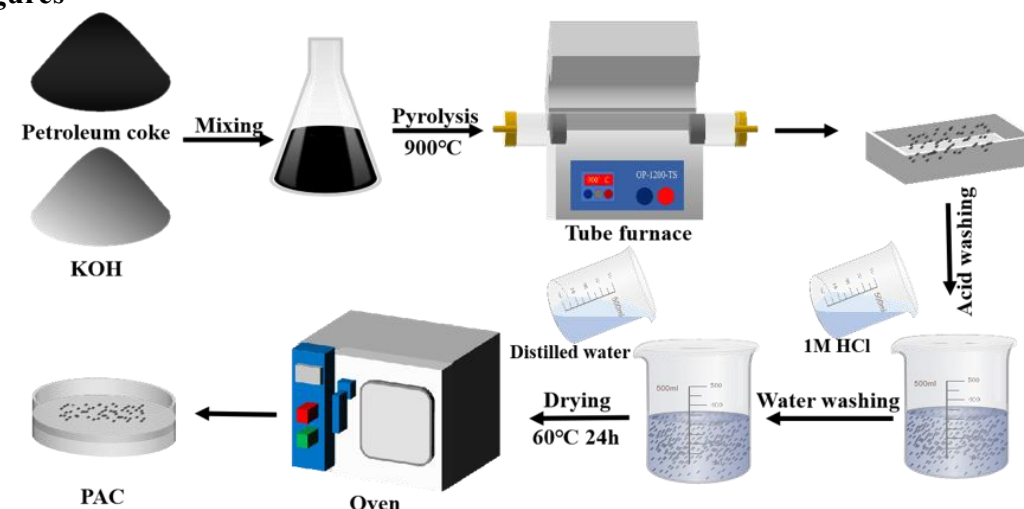


Fig. S1 Schematic diagram of PCAC preparation.

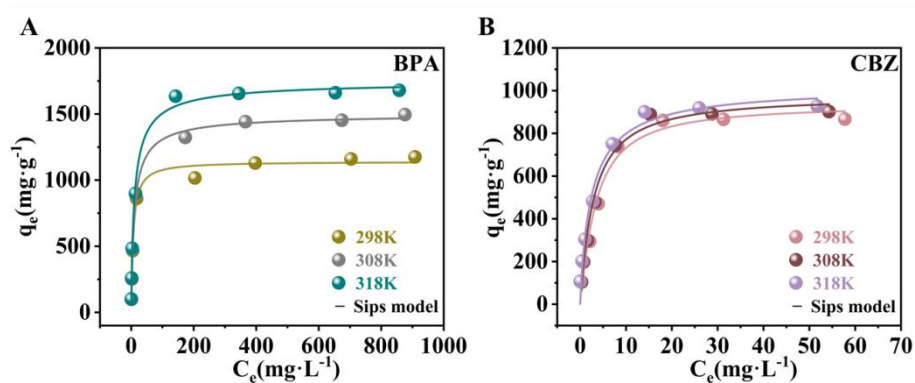


Fig. S2. Sips model fitting of BPA and CBZ adsorption isotherms on PCAC at different temperatures.

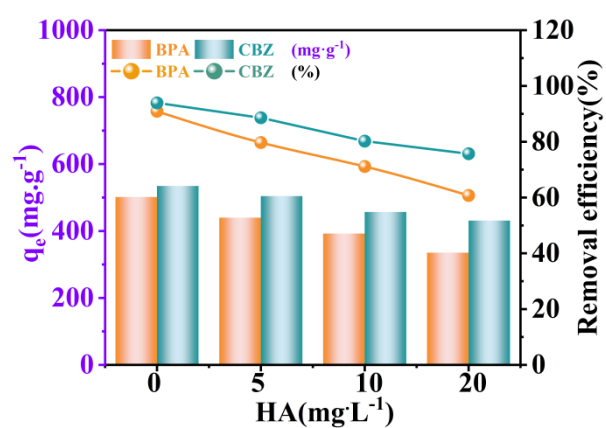


Fig. S3. Effect of humic acid concentration on the removal efficiencies of BPA and CBZ by PCAC. Conditions: $C_0 = 50 \text{ mg} \cdot \text{L}^{-1}$, adsorbent dosage = $0.1 \text{ g} \cdot \text{L}^{-1}$, pH = 7.0, $T = 298 \text{ K}$.

3.Tables

Table S1. Basic water quality characteristics of the real wastewater.

Item	Value
pH	7.1±0.6
Conductivity	1424±11.3 µS/cm
TOC	15±3.2 mg/L
DOC*	8.2±1.5 mg/L
Cl ⁻	84±10.4 mg/L
SO ₄ ²⁻	66±7.2 mg/L
Alkalinity	225±13.7 mg/L as HCO ₃ ⁻

*The DOC value was the TOC determined after filtering water samples through a 0.45 µm filter membrane.

Table S2. Operational parameters of the fixed-bed column used for dynamic adsorption experiments.

Parameter	Value
Column inner diameter	10 mm
Bed height	20 cm
Bed mass	2.0 g
Flow rate	50 mL/min
Bed volume	15.7 mL
EBCT	18.8 s

Table S3. Surface area and pore structure parameters before and after PCAC adsorption.

Sample	Specific Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Pore Size (nm)
PAC	2576.17	1.27	2.15
PAC-BPA	145.2	0.11	3.02
PAC-CBZ	179.32	0.12	2.65

The post-adsorption porosity derived from N₂ sorption reflects N₂-accessible pores; the drastic reduction therefore evidences pore occupation/blocking by adsorbates.

Table S4. Quantitative peak fitting results of high-resolution C1s, O1s, S2p XPS spectrum for PCAC.

Elements	Functional Group	Binding Energy (eV)	Relative Abundance (%)
C 1s	C-C/C=C	283.9	45.7
	C-O	284.9	40.9
	C=O	288.6	13.4
O 1s	C-O-C	530.96	6.5
	C=O	531.89	44.9
	OH	532.44	48.6
S 2p	C-S-C 2p _{1/2}	163.38	67.1
	C-S-C 2p _{3/2}	164.57	26.8
	C-SO _x -C	165.19	6.0

Table S5. Kinetic parameters for the adsorption of BPA and CBZ onto PCAC.

Pseudo-first-order model						
Parameters	BPA (mg·L ⁻¹)			CBZ (mg·L ⁻¹)		
	25	50	100	35	50	100
q_e (mg·g ⁻¹)	32.50	59.24	93.23	44.88	77.90	326.62
K_1 (min ⁻¹)	0.0046	0.0035	0.0044	0.0069	0.0030	0.0062
R ²	0.891	0.912	0.963	0.913	0.882	0.935
Pseudo-second-order model						
Parameters	BPA (mg·L ⁻¹)			CBZ (mg·L ⁻¹)		
	25	50	100	35	50	100
q_e (mg·g ⁻¹)	273.97	476.19	909.09	245.70	322.58	934.58
K_2 (g·mg ⁻¹ ·min ⁻¹)	0.0012	0.0005	0.0004	0.0011	0.0003	0.0001
R ²	0.999	0.999	0.999	0.999	0.999	0.998
Elovich model						
Parameters	BPA (mg·L ⁻¹)			CBZ (mg·L ⁻¹)		
	25	50	100	35	50	100
α (mg·g ⁻¹ ·min ⁻¹)	7.12	1.82	3.35	19.78	40.66	20.76
β (g·mg ⁻¹)	0.1150	0.0771	0.0488	0.0734	0.0518	0.0131
R ²	0.933	0.986	0.977	0.904	0.961	0.955
Intra-particle diffusion model I						
Parameters	BPA (mg·L ⁻¹)			CBZ (mg·L ⁻¹)		
	25	50	100	35	50	100
k_1 (mg·g ⁻¹ ·min ^{-0.5})	7.48	9.18	9.11	12.11	16.68	42.89
C_1	211.62	360.12	777.53	149.18	179.05	440.81
R ²	0.982	0.865	0.989	0.977	0.869	0.969
Intra-particle diffusion model II						
Parameters	BPA (mg·L ⁻¹)			CBZ (mg·L ⁻¹)		
	25	50	100	35	50	100
k_2 (mg·g ⁻¹ ·min ^{-0.5})	0.54	1.34	1.33	0.58	1.88	4.36
C_2	257.70	410.33	863.03	228.46	263.54	797.02
R ²	0.936	0.940	0.898	0.833	0.931	0.806

Table S6. Thermodynamic parameters for the adsorption of BPA and CBZ onto PCAC.

BPA			
T (K)	ΔS (KJ·mol ⁻¹ K ⁻¹)	ΔH (KJ·mol ⁻¹)	ΔG (KJ·mol ⁻¹)
298	0.0846	13.7502	-11.3496
308			-12.3242
318			-13.4888
CBZ			
T (K)	ΔS (KJ·mol ⁻¹ K ⁻¹)	ΔH (KJ·mol ⁻¹)	ΔG (KJ·mol ⁻¹)
298	0.0751	10.3961	-11.8535
308			-12.8234
318			-13.6586

Table S7. Comparison of adsorption capacities of various adsorbents for BPA and CBZ.

Adsorbents	Pollutant	t(min)	$q_e(\text{mg}\cdot\text{g}^{-1})$	References
PAC	BPA	120	1679.39	This study
	CBZ	80	927.22	
MOP-AC	BPA	60	20.14	[8]
OBC	BPA	120	55	[9]
L55C	BPA	1440	8.547	[3]
AC	BPA	20	472	[10]
PC-H	BPA	1800	126.58	[11]
PC-Z	BPA	1800	58.48	[11]
Fe-N-C	BPA	120	54	[12]
CZF-C	BPA	60	101.5	[13]
AC-PGPs	CBZ	60	8.41	[14]
MC	CBZ	480	663.7	[15]
B-nZVI	CBZ	180	142.9	[16]
ZPCNCs	CBZ	60	190	[17]
DPAC	CBZ	1440	14.89	[18]
AC/CB	CBZ	480	243.57	[19]
W-7	CBZ	600	130.81	[20]
C-UiO-66-OH	CBZ	180	186.21	[21]

Table S8 The t-plot-derived pore structure parameters of PCAC before and after adsorption.

Sample	PCAC	PCAC-BPA	PCAC-CBZ
Micropore Area (m²/g)	2079.45	57.80	74.15
Mesoporous Area (m²/g)	496.73	87.40	105.18
Micropore Volume (cm³/g)	0.90	0.02	0.03
Mesoporous Volume (cm³/g)	0.37	0.09	0.10
Micropore Area (%)	80.7	39.8	41.3
Micropore Volume (%)	70.6	19.2	22.4
Micropore / Mesopore Area	4.19	0.66	0.70
Micropore / Mesopore Volume	2.43	0.24	0.29

*Micropore area and volume were calculated using the t-plot method.

Table S9. Yoon Nelson model parameters of BPA and CBZ on PCAC.

Yoon-Nelson model		
Parameters	BPA	CBZ
$k_{YN}(1/min)$	0.005	0.00592
$\tau(min)$	1414.834	1098.998
R^2	0.9894	0.9844

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