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Abstract: Efficient removal of emerging organic contaminants (EOCs) remains a major challenge in water treatment. In this study, petroleum coke was upcycled into a highly porous activated carbon (PCAC) through KOH activation and applied for the adsorption of bisphenol A (BPA) and carbamazepine (CBZ). PCAC exhibited an high BET surface area of 2,576.17 m²·g⁻¹ and a micro–mesoporous structure, providing abundant accessible adsorption sites. The maximum adsorption capacities reached 1,689.44 mg·g⁻¹ for BPA and 961.54 mg·g⁻¹ for CBZ, outperforming many reported carbon-based adsorbents. Kinetic and isotherm analyses suggested rapid chemisorption-involved uptake. Post-adsorption pore analysis revealed a substantial loss of N₂-accessible porosity, confirming pore filling and pore occupation as the dominant adsorption mechanism. Spectroscopic and DFT calculation evidence further indicated that π - π interactions and hydrogen bonding contributed to molecular retention. In fixed-bed experiments, PCAC achieved breakthrough times of 15.8 h for BPA and 11.5 h for CBZ and maintained effective removal in a real wastewater matrix. After five regeneration cycles, more than 70% of the initial adsorption capacity was retained. These findings demonstrate that petroleum coke-derived activated carbon is a high-capacity, regenerable, and practically promising adsorbent for continuous removal of aromatic EOCs from water.

Key Words: petroleum coke; activated carbon; micropollutants; fixed-bed adsorption; water treatment.

1. Introduction

Emerging organic contaminants (EOCs) have been increasingly detected in aquatic environments and are now recognized as a critical challenge for global water security [1-3]. Unlike conventional pollutants, many EOCs exhibit biological activity at trace concentrations and are continuously discharged from domestic, industrial, and medical sources. Among them, endocrine-disrupting chemicals (EDCs) and pharmaceutical residues are of particular concern due to their persistence and ecological risks [1, 4]. Bisphenol A (BPA), widely used in polycarbonate plastics and epoxy resins, has been frequently detected in wastewater effluents and surface waters and exhibits estrogenic effects even at low concentrations [4-6]. Carbamazepine (CBZ), a commonly prescribed antiepileptic drug, is known for its resistance to biodegradation and is often detected in treated wastewater and receiving water bodies [7-9]. Due to its persistence and low removal efficiency in conventional wastewater treatment plants (WWTPs), CBZ is frequently used as a chemical marker of wastewater contamination [7, 8]. The coexistence of BPA and CBZ in urban water systems highlights the need for effective and robust treatment strategies capable of removing chemically diverse micropollutants.

Conventional WWTPs are primarily designed for bulk organic removal (e.g., COD and BOD) and are not optimized for trace-level micropollutant control [2, 3]. Advanced technologies such as ozonation, membrane filtration, and advanced oxidation processes (AOPs) have demonstrated promising degradation efficiencies for certain EOCs [10, 11]. However, their large-scale application is often limited by high

operational costs, complex maintenance requirements, and potential formation of transformation by-products [11, 12]. In contrast, adsorption is widely considered a technically mature and economically feasible approach for micropollutant removal due to its operational simplicity, adaptability, and compatibility with existing treatment infrastructures [13-15]. Activated carbon (AC) remains the benchmark adsorbent owing to its developed pore structure and tunable surface chemistry [14-16].

Nevertheless, adsorption performance reported in laboratory studies is often obtained at relatively high initial concentrations ($\text{mg}\cdot\text{L}^{-1}$ level), whereas environmentally relevant concentrations of EOCs typically occur at $\text{ng}\cdot\text{L}^{-1}$ - $\mu\text{g}\cdot\text{L}^{-1}$ levels [5]. At trace concentrations, adsorption may be governed by micropore diffusion resistance, surface heterogeneity, and competition effects from dissolved organic matter (DOM) and coexisting ions [15-17]. DOM competition has been reported to significantly reduce effective adsorption capacity by occupying active sites or blocking micropores [16-18]. Moreover, while equilibrium adsorption capacity is frequently reported, fewer studies have systematically evaluated dynamic breakthrough behavior and long-term regeneration stability under realistic water matrices [13, 15].

Petroleum coke, a carbon-rich by-product of petroleum refining, has emerged as a promising precursor for high-performance activated carbon due to its high fixed carbon content ($>90\%$), low ash content, and relatively uniform carbon structure [19-21]. Chemical activation of petroleum coke has been reported to generate highly

microporous carbons with specific surface areas commonly ranging from 2000 to 3500 $\text{m}^2\cdot\text{g}^{-1}$, and in optimized cases exceeding 4,000 $\text{m}^2\cdot\text{g}^{-1}$ [20-22]. Existing research on petroleum coke-derived activated carbon has primarily focused on gas adsorption, CO_2 capture, and electrochemical energy storage applications [21-23]. Comparatively fewer studies have explored their performance for aqueous micropollutant removal, especially under environmentally relevant concentration ranges and realistic wastewater conditions.

Micropore-dominated activated carbons may exhibit enhanced adsorption affinity toward small organic molecules through confinement effects and increased dispersion interactions within narrow pores [24-26]. Sub-nanometer pore structures comparable to molecular dimensions can potentially enhance adsorption through steric matching and multipoint interactions [25, 26]. However, whether such pore architectures remain effective at $\mu\text{g}\cdot\text{L}^{-1}$ concentrations and in the presence of competing DOM remains insufficiently understood [16, 18]. Fine micropores may provide high intrinsic capacity, but may also experience accessibility limitations or pore blocking during long-term operation [17, 18]. Therefore, systematic evaluation of petroleum coke-derived super activated carbon under both batch and dynamic conditions is necessary to clarify its engineering applicability.

In this context, the present study investigates an industrial petroleum coke-derived activated carbon (denoted as PCAC) characterized by an high specific surface area ($\sim 2,500 \text{ m}^2\cdot\text{g}^{-1}$) and a narrow pore size distribution centered at approximately 21.5 Å. The molecular dimensions of BPA (5 Å) and CBZ (3.70 Å) are

comparable to the dominant pore size of PCAC, suggesting a potential pore-matching effect that may enhance adsorption affinity through sub-nanometer confinement. This study systematically evaluates (i) adsorption performance under varying pH, dosage, temperature, and concentration conditions; (ii) kinetic and isotherm behavior; (iii) dynamic breakthrough characteristics at $\mu\text{g}\cdot\text{L}^{-1}$ levels in fixed-bed column experiments; and (iv) matrix interference effects in real water samples. By integrating physicochemical characterization with low-concentration dynamic adsorption and real-water evaluation, this work provides practical insights into the applicability of petroleum coke-derived super activated carbon for sustainable micropollutant control.

Unlike many previous studies that mainly emphasized surface area enhancement, this work focuses on how the micropore-dominated architecture of petroleum coke-derived carbon cooperates with molecular-size compatibility and aromatic interactions to deliver exceptionally high uptake of BPA and CBZ under both batch and fixed-bed conditions. In addition, fixed-bed operation, regeneration tests, real wastewater verification, and DFT-supported mechanism analysis were integrated to evaluate both practical applicability and structure-performance relationships.

2. Materials and Methods

2.1 Chemicals and Reagents

Petroleum coke (PC) was obtained from a local refinery in Xi'an, China. Bisphenol A (BPA, $\geq 99\%$, analytical grade) and carbamazepine (CBZ, $\geq 99\%$) were purchased from Macklin Biochemical Co., Ltd. (Shanghai, China). Methanol (CH_3OH , analytical grade), ethanol ($\text{C}_2\text{H}_5\text{OH}$, $\geq 99.7\%$), potassium hydroxide (KOH , $\geq 99\%$), hydrochloric acid (HCl , 37%), and sodium hydroxide (NaOH , $\geq 99\%$) were of

analytical grade and used without further purification. All aqueous solutions were prepared using ultrapure deionized water ($18.2 \text{ M}\Omega\cdot\text{cm}$).

Stock solutions of BPA and CBZ ($1,000 \text{ mg}\cdot\text{L}^{-1}$) were prepared by dissolving appropriate amounts in deionized water. The methanol content in working solutions was kept below 0.05% (v/v) to avoid solvent interference.

2.2 Preparation of Petroleum Coke-Derived Activated Carbon (PCAC)

An industrial petroleum coke-derived activated carbon was prepared through laboratory-scale alkaline activation treatment. The overall preparation process consisted of pretreatment, pre-oxidation, and high-temperature activation stages.

Pretreatment and Pre-oxidation: Raw petroleum coke was crushed and sieved to approximately 100 mesh and dried at $60 \text{ }^{\circ}\text{C}$ for 12 h to remove residual moisture. The dried particles were subjected to pre-oxidation in a tubular furnace under air atmosphere at $300 \text{ }^{\circ}\text{C}$ for 1 h with a heating rate of $10 \text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$.

Chemical Activation: Pre-oxidized petroleum coke was thoroughly mixed with KOH using a mass ratio of 4:1 (KOH:carbon precursor). The mixture was transferred to a tubular furnace and heated to $900 \text{ }^{\circ}\text{C}$ at a rate of $10 \text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ under nitrogen flow ($0.2 \text{ L}\cdot\text{min}^{-1}$) and maintained at this temperature for 60 min.

Post-treatment: After cooling to room temperature under nitrogen, the activated product was washed repeatedly with 1 M HCl solution to remove residual potassium compounds and mineral impurities, followed by washing with deionized water until neutral pH was reached. The material was dried at $60 \text{ }^{\circ}\text{C}$ for 24 h and sieved to obtain uniform particles. The final product was denoted as PCAC.

The synthesis process of PCAC is illustrated in SI, Fig. S1.

2.3 Physicochemical Characterization

Morphology was observed using scanning electron microscopy (SEM, Hitachi FlexSEM1000) coupled with energy-dispersive spectroscopy (EDS). Prior to imaging, samples were sputter-coated with gold.

Nitrogen adsorption-desorption isotherms were measured at 77 K using a surface area and porosity analyzer (TriStar II 3020, Micromeritics). Samples were degassed under vacuum at 300 °C for 12 h prior to analysis. Specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method within the relative pressure range of 0.05-0.30. Pore size distribution was determined using the non-local density functional theory (NLDFT) model assuming slit-shaped pores. The t-plot method was applied to distinguish micropore and mesopore contributions from the N₂ adsorption isotherms.

The crystal structure was analyzed by X-ray diffraction (XRD, PANalytical X'Pert PRO MRD) using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Raman spectra were recorded using a 532 nm laser (LabRam HR Evolution). The degree of graphitization was evaluated from the intensity ratio (ID/IG).

Surface functional groups were characterized by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha) and Fourier transform infrared spectroscopy (FTIR). Zeta potential measurements were conducted using a Malvern Zetasizer Nano ZS90 over a pH range of 2-12. Thermal stability was evaluated using thermogravimetric analysis (TGA, Netzsch STA 449 F3) under nitrogen atmosphere from room temperature to 900 °C at 10 °C·min⁻¹.

Concentrations were determined using a UV-Vis spectrophotometer (BPA: 276 nm; CBZ: 285 nm). Samples were filtered through 0.22 μm nylon membranes prior to analysis.

2.4 Batch Adsorption Experiments

Batch adsorption experiments were conducted in 100 mL conical flasks containing 50 mL pollutant solution.

For equilibrium adsorption, $0.1 \text{ g}\cdot\text{L}^{-1}$ of PCAC was added to $50 \text{ mg}\cdot\text{L}^{-1}$ BPA or CBZ solution and shaken at 160 rpm at $25 \pm 0.5 \text{ }^{\circ}\text{C}$ for 24 h to ensure equilibrium. Preliminary experiments confirmed that equilibrium was reached within this period.

The effects of adsorbent dosage ($0.04\text{-}1 \text{ g}\cdot\text{L}^{-1}$), initial pH (1-13), initial concentration (BPA: $10\text{-}1000 \text{ mg}\cdot\text{L}^{-1}$; CBZ: $10\text{-}150 \text{ mg}\cdot\text{L}^{-1}$), and temperature (25, 35, $45 \text{ }^{\circ}\text{C}$) were systematically investigated. The relatively high initial concentrations in this work were used to ensure reliable concentration gradients and quantifiable residual concentrations for kinetic and isotherm modeling.

For kinetic studies, aliquots were collected at predetermined time intervals (0-1,440 min). All adsorption experiments were conducted in triplicate, and average values were reported, with error bars included in the relevant figures to reflect the variability among parallel measurements. Control experiments without adsorbent were performed to exclude photolysis and volatilization effects.

2.5 Real Water Experiments

To evaluate the applicability of PCAC in complex matrices, its adsorption performance toward bisphenol A (BPA) and carbamazepine (CBZ) was compared in ultrapure water (UW) and simulated real wastewater (RWW). The RWW was collected from the secondary effluent of a municipal wastewater treatment plant. **To characterize the matrix background, basic water quality parameters were measured prior to adsorption tests (Table S1).**

PCAC ($0.1 \text{ g}\cdot\text{L}^{-1}$) was added to UW and RWW solutions containing $50 \text{ mg}\cdot\text{L}^{-1}$ of BPA or CBZ, respectively. Batch adsorption experiments were conducted at 298 K

with continuous shaking until equilibrium was reached (200 min). After adsorption, the suspensions were filtered through 0.45 μm membranes, and the residual concentrations of pollutants were determined.

2.6 Regeneration and Cycling Stability Tests

The reusability of PCAC was assessed using a combined regeneration strategy involving solvent desorption, electrostatic repulsion, and ultrasonic cavitation [27]. After saturation, the spent PCAC was collected and immersed in a regeneration solution consisting of 70% ethanol and 0.1 M NaOH. Ultrasonic treatment was applied at 40 kHz for 30 min. The regenerated material was then rinsed with ultrapure water until neutral pH and dried in a vacuum oven at 60 $^{\circ}\text{C}$ for 6 h. The adsorption-regeneration procedure was repeated for 5 consecutive cycles. All experiments were performed in triplicate to ensure data reliability.

It should be noted that the ethanol-NaOH-ultrasonication process used in this study was designed as a laboratory-scale regeneration protocol to verify adsorption reversibility and material stability, rather than as a final engineering regeneration scheme. From a practical perspective, this method may involve considerable solvent consumption, additional chemical input, and operational complexity associated with ultrasonication. Therefore, more scalable and cost-effective regeneration strategies, such as thermal regeneration, solvent minimization, optimized alkaline washing, and continuous regeneration, should be further investigated before large-scale application.

2.6 Fixed-Bed Column Experiments

Dynamic adsorption experiments were carried out in a transparent acrylic fixed-bed column operated in up-flow mode. The column had an inner diameter of 10 mm and was packed with 2.0 g of PCAC to a bed height of 20 cm. At a flow rate of

50 mL·min⁻¹, the bed volume and empty bed contact time (EBCT) were 15.7 mL and 18.8 s, respectively. Other operational parameters are listed in Table S2.

Influent solutions containing 20 mg·L⁻¹ BPA or CBZ were pumped continuously through the column for 3 days. Ceramic beads and nonwoven filter cloth were placed at both ends of the bed to improve flow distribution and prevent adsorbent loss. Effluent samples were collected at regular intervals and analyzed using a TOC analyzer. Breakthrough curves were obtained by plotting C/C_0 against time, and the breakthrough point was defined as $C/C_0 = 0.05$.

Quantify the equilibrium adsorption capacity (q_e) and removal efficiency (E) using Eqs. S1-S2 in Supplementary Materials (SI, Section S1); The adsorption kinetics, isothermal behavior, and thermodynamic parameters were modeled and fitted using the equations in SI; The desorption efficiency was calculated based on mass balance (Eq. S15, SI).

3. Results and Discussions

3.1 Physicochemical and Morphological Properties

3.1.1 Surface Morphology and Elemental Composition

The surface morphology of the petroleum coke-derived activated carbon (PCAC) was examined using scanning electron microscopy (SEM), as shown in Fig. 1A and B. The material exhibits a rough and fractured surface texture with layered and fissured features. Such structural characteristics are commonly observed in KOH-activated carbons and are generally attributed to chemical etching and carbon matrix reconstruction occurring during high-temperature activation [22].

Energy-dispersive spectroscopy (EDS) analysis (Fig. 1D) indicates that PCAC consists predominantly of carbon (96.4 wt%), confirming its high carbon purity. Oxygen is present at approximately 3.3 wt%, likely associated with surface oxygen-containing functional groups introduced during activation and post-treatment.

These surface functionalities may influence hydrophilicity and contribute to adsorption interactions, particularly through π - π electron donor-acceptor (EDA) interactions and hydrogen bonding. A trace amount of sulfur (0.3 wt%), originating from the petroleum coke precursor, is uniformly distributed across the carbon matrix. Although present at low levels, sulfur species may slightly modify the surface electronic properties.

3.1.2 Pore Structure and Potential “Molecular Capture” Characteristics

PCAC exhibits a highly developed porous structure with a BET specific surface area of $2576.17 \text{ m}^2 \cdot \text{g}^{-1}$ and a total pore volume of $1.27 \text{ cm}^3 \cdot \text{g}^{-1}$ (Fig. 1C and Table S3). The average pore width derived from NLDFT is $\sim 2.15 \text{ nm}$ ($21.5 \text{ \AA}$) [20], indicating that the porosity is mainly distributed in the micro-mesopore transition region and small mesopores, rather than being dominated by sub-nanometer micropores. Such a pore architecture provides both abundant adsorption sites and accessible pore channels for organic micropollutants [28].

Considering the hydrodynamic diameters of CBZ (0.74 nm) and BPA (1.0 nm), the dominant pore width ($\sim 2.15 \text{ nm}$) is approximately 2-3 times the molecular size, which is favorable for confinement-enhanced pore filling: molecules can readily enter the pore network while still experiencing enhanced wall-molecule interactions due to geometric confinement[29]. In narrow pores, the overlap of adsorption potential fields from opposing pore walls strengthens dispersive interactions, thereby promoting the partitioning of hydrophobic aromatics into the carbon phase and enhancing uptake capacity.

3.1.3 Crystalline Structure and Carbon Framework

The microstructural order of PCAC was investigated by X-ray diffraction (XRD) and Raman spectroscopy. As shown in Fig. 2A, the XRD pattern exhibits a broad and

weak diffraction peak around $2\theta \approx 43^\circ$, corresponding to the (100) plane of graphitic carbon [30]. The typical (002) reflection associated with well-ordered graphite stacking is largely diminished, indicating disruption of long-range graphitic ordering during alkaline activation [31]. This suggests that the material predominantly consists of short-range ordered, turbostratic carbon structures.

Raman spectra (Fig. 2B) display two characteristic bands: the D-band at $1,359\text{ cm}^{-1}$, associated with structural defects and disordered carbon, and the G-band at 1587 cm^{-1} , corresponding to in-plane vibrations of sp^2 -hybridized carbon. The intensity ratio (I_D/I_G) of 0.96 indicates a relatively high density of structural defects and edge sites within the carbon matrix [32]. Such defect-rich structures are commonly associated with enhanced surface reactivity and increased interaction sites for aromatic compounds.

3.1.4 Surface Chemical Environment and Functional Groups

The FTIR spectrum (Fig. 2C) shows a broad absorption band at approximately $3,440\text{ cm}^{-1}$ corresponding to O-H stretching vibrations [33]. Peaks at $1,355\text{ cm}^{-1}$ and $1,093\text{ cm}^{-1}$ are attributed to C-O and C-O-C functional groups, respectively [34]. The band near 1633 cm^{-1} corresponds to C=C stretching of aromatic structures [35], indicating the presence of a stable conjugated carbon framework.

High-resolution XPS spectra (Fig. 2D-G) were further analyzed, and the quantitative peak-fitting results are summarized in Table S4. The C1s spectrum is dominated by C-C/C=C (45.7%) and C-O (40.9%), with a smaller contribution from C=O (13.4%), indicating that the carbon framework consists primarily of aromatic structures with abundant oxygen-containing functional groups.

The O1s spectrum shows that O-H (48.6%) and C=O (44.9%) are the major oxygen species [36], while C-O-C accounts for a minor fraction (6.5%). The high

proportion of hydroxyl and carbonyl groups suggests enhanced surface polarity and provides active sites for hydrogen bonding interactions with BPA and CBZ.

In addition, the S2p spectrum reveals the presence of C–S–C (~93.9% combined) and a small amount of oxidized sulfur species (C–SO_x–C, 6.0%) [37]. Although sulfur content is relatively low, its incorporation into the carbon framework may modulate the local electronic structure, thereby facilitating π - π electron donor–acceptor interactions.

3.1.5 Surface Charge Properties and Thermal Stability

Zeta potential analysis (Fig. 2H) shows that the point of zero charge (pH_{pzc}) of PCAC is approximately 3.34. Accordingly, the carbon surface carries a net negative charge under neutral and alkaline conditions. Bisphenol A (BPA), with a pK_a of approximately 9.6, predominantly exists in its non-ionized molecular form at near-neutral pH. Likewise, carbamazepine (CBZ), characterized by pK_{a1} $\approx$ 2.3 and pK_{a2} $\approx$ 13.9, remains largely neutral over a broad pH range relevant to typical water treatment processes.

Under environmentally relevant conditions (pH 6–8), both BPA and CBZ are therefore expected to exist primarily as neutral species. In this pH range, electrostatic interactions between PCAC and the target molecules are unlikely to constitute the dominant adsorption driving force. Instead, adsorption is more reasonably attributed to hydrophobic interactions, pore-filling effects arising from size compatibility between adsorbates and micropores, and π - π interactions between the aromatic rings of the pollutants and the conjugated carbon framework.

Thermogravimetric analysis (Fig. 2I) shows limited weight loss below 100 °C due to moisture and volatile removal, followed by stable mass retention at higher

temperatures under nitrogen. This behavior confirms the formation of a stable carbon structure.

3.2 Batch Adsorption Performance

Operational parameters, including solution pH, adsorbent dosage, temperature, and contact time, play critical roles in determining adsorption performance. In this section, the effects of these parameters on the adsorption of bisphenol A (BPA) and carbamazepine (CBZ) by PCAC were systematically evaluated to establish the fundamental adsorption behavior prior to kinetic and mechanistic analysis.

3.2.1 Effect of Dosage

The effect of PCAC dosage on removal efficiency is presented in Fig. 3A. As the dosage increased from 0.04 to 1.0 g·L⁻¹, removal efficiency increased rapidly at lower dosages and gradually approached a plateau at higher dosages.

At a dosage of 0.1 g·L⁻¹, removal efficiencies for 50 mg·L⁻¹ BPA and CBZ reached 97.90% and 97.21%, respectively. The improvement in removal efficiency with increasing dosage can be attributed to the increased availability of adsorption sites and greater surface area.

However, the equilibrium adsorption capacity per unit mass (q_e) decreased with increasing dosage. This trend is commonly observed and is associated with site underutilization at high adsorbent loading and possible particle aggregation effects, which may reduce effective surface accessibility. Considering both removal efficiency and material utilization efficiency, 0.1 g·L⁻¹ was selected for subsequent experiments.

3.2.2 Effect of pH

Solution pH influences adsorption by regulating both the surface charge of the adsorbent and the ionization state of the adsorbates. As shown (Fig. 3B), PCAC exhibited high removal efficiencies for both BPA and CBZ in acidic to neutral

conditions (pH 1.0-7.0), with maximum removal efficiencies of 97.99% for BPA and 93.99% for CBZ.

When the solution pH increased to alkaline conditions, the removal efficiency decreased. For BPA ($pK_a \approx 9.6$), deprotonation occurs at elevated pH, resulting in negatively charged species. Since the surface of PCAC is negatively charged above its pH_{pzc} (3.34), electrostatic repulsion likely contributes to the observed decline in BPA adsorption under alkaline conditions.

In contrast, CBZ remains predominantly neutral over a broad pH range ($pK_{a1} \approx 2.3$; $pK_{a2} \approx 13.9$). Therefore, the decrease in CBZ adsorption at higher pH cannot be primarily attributed to electrostatic repulsion. Instead, it may be associated with changes in solute solvation behavior and reduced hydrophobic driving forces under alkaline conditions. Overall, adsorption under near-neutral pH appears more favorable, where electrostatic interactions are less influential and non-electrostatic interactions are likely to contribute significantly.

3.2.3 Effect of Initial Concentration and Temperature

The influence of initial concentration and temperature on adsorption performance is shown in Fig. 3C and D. As the initial concentration increased (BPA: 10-1000 $\text{mg}\cdot\text{L}^{-1}$; CBZ: 10-150 $\text{mg}\cdot\text{L}^{-1}$), the equilibrium adsorption capacity increased significantly. The maximum experimental adsorption capacities for BPA reached 1,175.57 $\text{mg}\cdot\text{g}^{-1}$ and for CBZ reached 867.09 $\text{mg}\cdot\text{g}^{-1}$.

The increase in adsorption capacity at higher concentrations is attributed to the enhanced mass transfer driving force resulting from increased concentration gradients [38]. Higher concentration gradients facilitate diffusion from the bulk solution to the adsorbent surface and subsequently into micropores.

Increasing temperature led to a slight enhancement in adsorption capacity for both BPA and CBZ. This trend suggests that the adsorption process may exhibit endothermic characteristics within the investigated temperature range. The temperature effect was more pronounced for BPA, particularly at higher initial concentrations ($>300 \text{ mg}\cdot\text{L}^{-1}$), indicating that elevated temperature may facilitate diffusion and pore-filling processes under high loading conditions. The observed positive temperature dependence is consistent with previous studies on microporous carbon materials, where adsorption may exhibit apparent endothermic characteristics due to enhanced intraparticle diffusion and confinement effects within sub-nanometer pores [14, 39, 40].

3.2.3 Effect of Contact Time

The adsorption profiles as a function of contact time are presented in Fig. 3E and F. Both BPA and CBZ exhibited a two-stage adsorption behavior. A rapid adsorption phase occurred during the initial period (BPA $< 120 \text{ min}$; CBZ $< 200 \text{ min}$), during which more than 90% of total uptake was achieved. This rapid uptake can be attributed to the abundance of accessible surface sites and high concentration gradients [41]. Subsequently, the adsorption rate gradually decreased and approached equilibrium, indicating the increasing importance of intraparticle diffusion and pore-filling processes within the microporous structure. The relatively short time required to reach equilibrium suggests favorable mass transfer characteristics of PCAC under the tested conditions.

3.3 Adsorption Kinetics and Diffusion Analysis

To quantitatively describe the adsorption process of BPA and CBZ onto PCAC and to elucidate the rate-controlling steps, the experimental data were fitted using four kinetic models, including the pseudo-first-order (PFO), pseudo-second-order (PSO),

Elovich, and intraparticle diffusion (IPD) models (Fig. 4A-H). The corresponding kinetic parameters are summarized in Table S5.

3.3.1 Kinetic Model Fitting

Among the tested models, the PSO model provided the best correlation across all investigated concentrations, with correlation coefficients (R^2) exceeding 0.998 and significantly higher than those of the PFO model. In addition, the calculated equilibrium adsorption capacities ($q_{e,cal}$) derived from the PSO model were in close agreement with the experimentally determined values ($q_{e,exp}$).

The superior fitting of the PSO model indicates that chemisorption-related interactions may contribute to the adsorption kinetics under the tested conditions [9]. The Elovich model also showed reasonable correlation ($R^2 = 0.904-0.986$), indicating the heterogeneous nature of the PCAC surface [42]. Given the high specific surface area and complex microstructure, adsorption sites likely vary in energy distribution, including edge defects, oxygen-containing functional groups, and confined microporous domains.

3.3.2 Effect of Initial Concentration on Kinetic Parameters

With increasing initial concentration, the pseudo-second-order rate constant (k_2) decreased. For example, as the BPA concentration increased from 25 to 100 mg·L⁻¹, k_2 decreased from 0.0012 to 0.0004 mg·mg⁻¹·min⁻¹.

This trend can be attributed to increased surface coverage and intensified competition for available adsorption sites at higher concentrations [43]. As adsorption progresses, the probability of molecular interactions within confined microporous environments increases, which may impose steric hindrance and diffusion limitations. Although k_2 decreases with increasing concentration, the enhanced concentration

gradient provides a stronger mass-transfer driving force, resulting in a substantial increase in equilibrium adsorption capacity.

3.3.3 Intraparticle Diffusion and Multistep Mechanism

The IPD model was applied to further analyze the adsorption mechanism. The multilinear plots observed in Fig. 4D and H indicate that adsorption proceeds through multiple stages rather than a single diffusion-controlled process.

The first linear region corresponds to external diffusion, characterized by relatively high diffusion constants (k_{i1}). For BPA, k_{i1} ranged from 7.48 to 9.18 $\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-0.5}$, while for CBZ it ranged from 12.11 to 42.89 $\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-0.5}$. This stage represents rapid mass transfer from the bulk solution to the external surface of PCAC [44]. The higher k_{i1} values observed for CBZ suggest a faster initial uptake, potentially related to differences in molecular structure and interaction affinity with the carbon surface.

The second linear region corresponds to intraparticle diffusion within the microporous structure [44]. The corresponding diffusion constants (k_{i2}) were approximately one order of magnitude lower than k_{i1} , indicating that pore diffusion becomes progressively rate-limiting as adsorption proceeds [45]. This behavior is consistent with diffusion within densely packed sub-nanometer micropores (21.5 Å), where molecular transport is spatially constrained.

Importantly, none of the IPD plots passed through the origin, and the intercept values (C) increased with increasing concentration. This indicates that intraparticle diffusion is not the sole rate-controlling step. Instead, adsorption is governed by a combination of film diffusion, intraparticle diffusion, and surface interaction processes. The synergistic contribution of these mechanisms explains the observed rapid initial uptake followed by a gradual approach to equilibrium.

3.4 Adsorption Isotherm Modeling and Capacity Evaluation

To further elucidate the adsorption behavior of BPA and CBZ on PCAC and to characterize the solid-liquid partitioning process, the equilibrium data at different temperatures (298, 308, and 318 K) were fitted using the Langmuir, Freundlich, Temkin, and Sips isotherm models (Fig. 5A-F, Fig. S2). The corresponding parameters are summarized in Tables 1.

3.4.1 Applicability of Isotherm Models

Among the three models, the Langmuir model provided the best overall fit for both BPA and CBZ adsorption, with correlation coefficients ($R^2 \geq 0.997$), outperforming the Freundlich ($R^2 = 0.832-0.928$) and Temkin ($R^2 = 0.784-0.983$) models. The Langmuir model is more reasonably regarded as an empirical model describing the apparent saturation behavior within the tested concentration range. To further examine the effect of adsorption-site heterogeneity, the Sips model was additionally applied. As shown in Table 1, the Sips model also fitted the experimental data well, with R^2 values of 0.966-0.997. The heterogeneity parameter m ranged from 0.81 to 1.04 for BPA and from 0.92 to 1.16 for CBZ, close to unity [46]. This indicates that although PCAC is structurally heterogeneous, the adsorption behavior approaches Langmuir-type saturation under the investigated conditions [47].

3.4.2 Adsorption Capacity and Structural Correlation

According to the Langmuir model, the maximum adsorption capacity (q_{max}) for BPA reached 1689.44 $\text{mg}\cdot\text{g}^{-1}$ at 318 K, while that for CBZ was 961.54 $\text{mg}\cdot\text{g}^{-1}$. These values are comparatively high relative to many reported biomass-derived and commercial activated carbons under similar conditions [48].

The high adsorption capacity can be attributed to the structural characteristics of PCAC. First, the high specific surface area and significant micropore volume provide

substantial accessible adsorption space. Second, the average pore width (~ 21 Å) is close to the molecular dimensions of BPA and CBZ (~ 4.0 Å), which may promote enhanced confinement interactions within sub-nanometer pores [44]. Such size compatibility can lead to overlapping adsorption potential fields from opposing pore walls, thereby increasing adsorption affinity and packing density within micropores [49]. These structural features collectively contribute to the observed high adsorption capacity.

3.4.3 Temperature Dependence and Adsorption Affinity

The Langmuir affinity constant (K_L) increased with temperature for both pollutants. For BPA, K_L increased from 0.0832 to 0.1351 L·mg⁻¹ as temperature increased from 298 to 318 K, while for CBZ it increased from 0.3407 to 0.6541 L·mg⁻¹ over the same temperature range.

The positive temperature dependence of both K_L and q_{max} suggests that adsorption is thermodynamically favored at elevated temperatures within the investigated range. This behavior is consistent with an apparent endothermic adsorption process [50], which may be associated with enhanced intraparticle diffusion and micropore filling at higher temperatures.

The Freundlich constants (n values ranging from 3.04-3.44 for BPA and 2.32-4.14 for CBZ) fall within the typical range ($1 < n < 10$) indicative of favorable adsorption. The Temkin parameter b remained relatively stable across temperatures, suggesting moderate adsorption heat and consistent adsorbate-adsorbent interactions.

Overall, the isotherm analysis indicates strong adsorption affinity of PCAC toward both BPA and CBZ, particularly under elevated temperature conditions.

3.4.4 Thermodynamic Analysis and Driving Forces of Adsorption

To further elucidate the thermodynamic characteristics and driving forces of the adsorption process, the thermodynamic parameters were calculated using the Van't Hoff equation (detailed in SI, Table S6).

Within the investigated temperature range, the Gibbs free energy change (ΔG) values for both BPA and CBZ were negative, ranging from -11.35 to -13.66 kJ·mol⁻¹, indicating that the adsorption process is spontaneous. Moreover, the magnitude of ΔG became more negative with increasing temperature, suggesting that elevated temperature enhances the thermodynamic favorability of adsorption.

The positive enthalpy changes ($\Delta H = 13.75$ kJ·mol⁻¹ for BPA and 10.40 kJ·mol⁻¹ for CBZ) indicate that the adsorption process is endothermic. This behavior is consistent with adsorption mechanisms involving intraparticle diffusion and micropore filling, where increased temperature may facilitate molecular transport into confined pore domains and partially overcome diffusion resistance.

The positive entropy changes ($\Delta S > 0$) imply an increase in randomness at the solid–liquid interface during adsorption. This entropy gain may be associated with partial desolvation of adsorbate molecules upon transfer from the aqueous phase to the carbon surface. The favorable entropy contribution offsets the endothermic nature of the process and contributes to the overall spontaneity of adsorption.

3.4.5 Comparative Performance Evaluation

The adsorption capacities of PCAC were compared with those reported for representative carbon-based adsorbents (Fig. 5G; Table S7). The maximum capacities for BPA (1689.44 mg·g⁻¹) and CBZ (961.54 mg·g⁻¹) are higher than those of many reported biochars and several modified carbons under comparable conditions.

These results indicate that PCAC exhibits competitive adsorption performance for aromatic micropollutants. The observed capacity enhancement is consistent with its highly developed microporous structure and pore–molecule compatibility.

Overall, PCAC demonstrates strong adsorption capability relative to existing carbonaceous adsorbents.

3.5 Adsorption Mechanism Analysis

To elucidate the adsorption behavior of BPA and CBZ on PCAC, the possible mechanisms were analyzed based on structural characterization before and after adsorption (SEM, XRD, Raman and FTIR; Fig. 6), together with the kinetic and isotherm results discussed above. The adsorption process is interpreted from three complementary aspects: pore filling, confinement effects, and surface interactions.

3.5.1 Pore Filling and Size Compatibility

The high surface area and micropore-rich structure of PCAC provide the structural basis for its high adsorption capacity. After adsorption, SEM images (Fig. 6A, B) show that the initially well-defined layered texture and surface fissures become less distinct, indicating surface coverage by adsorbates.

Consistently, the pore structure parameters change markedly (Table S3). After BPA adsorption, the N₂-accessible surface area decreases from 2576.17 to 145.2 m²·g⁻¹, and the total pore volume drops from 1.27 to 0.11 cm³·g⁻¹. A similar reduction is observed for CBZ (179.32 m²·g⁻¹ and 0.12 cm³·g⁻¹), corresponding to >93% loss of accessible porosity. This drastic decline indicates that BPA and CBZ molecules effectively occupy and block pores that are otherwise accessible to N₂ at 77 K.

To further quantify pore structure evolution, t-plot analysis was conducted (Fig. 6G-I and Table S8). For pristine PCAC, micropores dominate the structure, contributing 80.7% of the surface area and 70.6% of the pore volume. After

adsorption, the micropore area and volume decrease sharply to 57.8-74.2 m²·g⁻¹ and 0.02-0.03 cm³·g⁻¹, respectively. Meanwhile, the micropore contribution drops to ~40%, and the micropore/mesopore ratio declines from 4.19 to below 1.0. These results confirm that micropores are the primary adsorption sites and are preferentially occupied or blocked during adsorption, highlighting micropore filling as the dominant mechanism.

Meanwhile, the apparent increase in average pore size (2.15 → 3.02 nm for BPA; 2.15 → 2.65 nm for CBZ) does not necessarily indicate pore enlargement; instead, it may reflect the preferential masking of smaller pores, leaving relatively larger pores accessible to N₂ and shifting the average value to larger sizes. The stronger reduction after BPA adsorption may be related to its larger hydrodynamic diameter (1.0 nm vs. 0.74 nm for CBZ) and higher hydrophobicity (log_{K_{ow}} 3.32 vs. 2.45), which could facilitate stronger partitioning into the carbon phase and more pronounced pore blocking [51]. These findings align with the blurred/covered pore features observed by SEM after adsorption, jointly suggesting that confinement-driven pore filling and accessibility loss are important contributors to the uptake process.

3.5.2 Carbon Framework Stability and π - π Interactions

The XRD patterns after adsorption (Fig. 6C) retained the characteristic broad diffraction features near $2\theta \approx 24^\circ$ and 43° , corresponding to the (002) and (100) reflections of turbostratic/disordered carbon. No apparent peak shift or emergence of new crystalline phases was observed, suggesting that the carbon framework of PCAC remained structurally stable during adsorption.

Raman spectra of PCAC before and after adsorption (Fig. 6D-E) exhibited the typical D band (~1350 cm⁻¹) and G band (~1580 cm⁻¹), confirming the coexistence of defect/edge sites and sp² graphitic domains. Notably, the intensity ratio (I_D/I_G)

decreased from 0.96 for pristine PCAC to 0.85 and 0.86 after BPA and CBZ adsorption, respectively. This reduction may indicate a lower relative contribution from defect-associated scattering after adsorption, which is possibly related to the preferential occupation/coverage of defect- and edge-rich regions by the aromatic adsorbates, rather than a degradation of the carbon framework. Together with the XRD results, these findings suggest that adsorption did not induce destructive structural reconstruction of PCAC, but instead altered the local surface environment.

Given the aromatic nature of BPA and CBZ, π - π interactions between the delocalized π -electron system of sp^2 carbon domains and the aromatic rings of the adsorbates may contribute to adsorption affinity. The presence of graphitic domains evidenced by the G band provides conjugated surfaces that may be favorable for π - π stacking, while adsorption-induced masking of defect sites as reflected by the decreased I_D/I_G , is consistent with possible interfacial association. Such non-covalent interactions, coupled with pore-filling effects discussed above, likely promote the efficient uptake of both BPA and CBZ.

3.5.3 Contribution of Surface Functional Groups

FTIR analysis (Fig. 6F) revealed slight changes in characteristic functional group vibrations after adsorption. The -OH stretching band around $3,440\text{ cm}^{-1}$ exhibited minor shifts or broadening, and variations were observed in the C-O vibration region ($\sim 1,100\text{ cm}^{-1}$). These changes suggest possible involvement of surface oxygen-containing functional groups in the adsorption process.

Hydrogen bonding between surface hydroxyl or carbonyl groups and the hydroxyl groups of BPA or the amide functionality of CBZ may contribute to adsorption. In addition, surface functional groups can influence local polarity and

induce dipole interactions [52], which may further enhance affinity between PCAC and the adsorbates.

3.5.4 DFT Verification of Interfacial Interactions

To further verify the weak interactions involved in BPA and CBZ adsorption, DFT calculations were conducted using an oxygen-containing carbon cluster as the PCAC surface model [53, 54]. As shown in Fig. 7, all optimized configurations exhibited negative binding energies, confirming the favorable interactions between PCAC and the target pollutants.

For BPA, the H-bonding configuration showed a stronger binding energy ($-60.20 \text{ kJ}\cdot\text{mol}^{-1}$) than the π - π configuration ($-50.88 \text{ kJ}\cdot\text{mol}^{-1}$), suggesting the important contribution of H-bonding. In contrast, CBZ exhibited stronger π - π interaction ($-60.07 \text{ kJ}\cdot\text{mol}^{-1}$) than H-bonding ($-46.94 \text{ kJ}\cdot\text{mol}^{-1}$), indicating that π - π stacking was a dominant interaction for CBZ adsorption.

Therefore, the superior adsorption performance of PCAC should not be attributed solely to its high surface area, but rather to the synergistic effect of micropore-dominated pore filling, molecular-size compatibility, and aromatic interfacial interactions.

3.6 Dynamic and Real Water Performance

3.6.1 Real Wastewater Matrix Effects and Reusability

To clarify the influence of DOM, HA (humic acid) was selected as a representative DOM component. As shown in Fig. S3, increasing HA concentration from 0 to $20 \text{ mg}\cdot\text{L}^{-1}$ decreased the removal efficiencies of BPA and CBZ, indicating that DOM can suppress adsorption. This effect is mainly attributed to competitive adsorption and partial pore blockage by HA molecules. The inhibition was more pronounced for BPA, likely due to its stronger hydrophobicity and higher dependence

on hydrophobic adsorption sites. These results suggest that DOM may weaken adsorption performance in complex water matrices, although PCAC still retained considerable removal capability [54, 55].

To assess the practical applicability of PCAC, BPA and CBZ adsorption was compared in ultrapure water (UW) and real wastewater (RWW). The RWW was collected from the secondary effluent of a municipal wastewater treatment plant, and its basic characteristics are summarized in Table S1. The RWW had a near-neutral pH of 7.1 ± 0.6 , conductivity of $1424 \pm 11.3 \mu\text{S}\cdot\text{cm}^{-1}$, TOC of $15 \pm 3.2 \text{ mg}\cdot\text{L}^{-1}$, DOC of $8.2 \pm 1.5 \text{ mg}\cdot\text{L}^{-1}$, and contained coexisting ions such as Cl^- and SO_4^{2-} . These matrix constituents may interfere with adsorption through competitive site occupation, partial pore blocking, and changes in ionic strength.

As shown in Fig. 8A and B, the initial removal efficiency of BPA decreased from 96.78% in UW to 86.32% in RWW, while CBZ removal decreased from 97.56% to 91.43%. The stronger inhibition observed for BPA may be associated with its higher hydrophobicity and phenolic hydroxyl groups[56], which make it more sensitive to competition from dissolved organic matter and changes in the local interfacial environment. In contrast, CBZ mainly exists as a neutral molecule at near-neutral pH and can maintain favorable interactions with the carbon surface through pore filling and π - π interactions, leading to better matrix tolerance.

After 5 adsorption-regeneration cycles, BPA removal efficiencies in UW and RWW were 85.24% and 71.86%, respectively, while CBZ removal efficiencies were 85.04% and 76.32%, respectively. The greater decline in RWW can be attributed to the cumulative effects of DOM and coexisting ions, which may occupy adsorption sites, block part of the micropores, or weaken adsorbate-surface interactions [57].

Nevertheless, PCAC still maintained considerable removal performance after repeated use in RWW, indicating its potential applicability in complex wastewater matrices.

Overall, these results show that the wastewater matrix moderately suppresses BPA and CBZ adsorption, mainly due to DOM and coexisting inorganic ions, but PCAC retains effective adsorption and regeneration performance under real wastewater conditions.

3.6.2 Breakthrough Curves

To evaluate the practical applicability of PCAC in continuous-flow systems, dynamic breakthrough experiments were conducted for BPA and CBZ. As shown in Fig. 8C and D, under an influent concentration of $20 \text{ mg}\cdot\text{L}^{-1}$ and a flow rate of $50 \text{ mL}\cdot\text{min}^{-1}$; the empty bed contact time (EBCT), calculated as bed volume divided by volumetric flow rate, was 18.8 s under the applied operating conditions (bed volume = 15.7 mL ; flow rate = $50 \text{ mL}\cdot\text{min}^{-1}$). Both pollutants exhibited typical sigmoidal breakthrough curves, with the effluent concentration ratio (C/C_0) increasing progressively over time.

The breakthrough time (t_b , defined at $C/C_0 = 0.05$) was 11.5 h for CBZ and 15.8 h for BPA. The delayed breakthrough of BPA indicates a higher dynamic adsorption capacity of PCAC toward this compound under flow conditions. After 48 h of operation, the effluent concentration approached the influent level ($C/C_0 \approx 1.0$), suggesting that the packed bed had reached adsorption saturation.

The steep breakthrough profiles indicate a narrow mass transfer zone (MTZ), reflecting efficient intraparticle diffusion and favorable mass transfer within the uniformly developed pore structure of PCAC. BPA exhibited a longer breakthrough time, indicating superior dynamic retention. This behavior is attributed to stronger

pore confinement within the sub-nanometer pores ($\sim 21 \text{ \AA}$) and enhanced π - π interactions, which increase resistance to desorption under hydrodynamic shear.

At a flow rate of $50 \text{ mL} \cdot \text{min}^{-1}$, 2.0 g of PCAC treated over 48 L (BPA) and 36 L (CBZ) of simulated wastewater before breakthrough. The sharp breakthrough fronts demonstrate high bed utilization efficiency, highlighting the strong potential of PCAC for continuous-flow removal of emerging organic contaminants.

The breakthrough data of both pollutants were well described by the Yoon-Nelson model (Fig. 8E and F, Table S9), with high correlation coefficients ($R^2 = 0.9894$ for BPA and 0.9844 for CBZ), indicating that the fixed-bed breakthrough behavior of PCAC could be reliably captured by this simplified dynamic model. The larger τ value of BPA (1414.8 min) compared with CBZ (1099.0 min) suggests a longer 50% breakthrough time and thus a stronger dynamic retention of BPA in the packed bed. Meanwhile, the slightly higher k_{YN} value for CBZ (0.00592 min^{-1}) than for BPA (0.0050 min^{-1}) indicates a faster advancement of the mass transfer zone and earlier bed exhaustion for CBZ. These results are consistent with the experimentally observed delayed breakthrough of BPA and support its stronger affinity toward PCAC under continuous-flow conditions.

The fixed-bed test was conducted under laboratory-scale accelerated conditions to obtain measurable breakthrough curves within a practical experimental period. Therefore, these results represent a preliminary evaluation of continuous-flow adsorption feasibility rather than direct full-scale simulation. Further optimization of influent concentration, hydraulic loading, EBCT, bed depth, and regeneration frequency is required for practical scale-up.

4 Conclusion

In this study, a petroleum coke-derived activated carbon (PCAC) was developed as a high-performance adsorbent for aromatic EOCs. Evidence from porosity evolution and spectroscopy indicates that uptake is dominated by confinement-enhanced pore filling/occupation, with π - π interactions and hydrogen bonding providing complementary contributions. In fixed-bed tests, breakthrough was delayed to 15.8 h (BPA) and 11.5 h (CBZ), and PCAC remained effective in a real wastewater matrix. The adsorbent was readily regenerated via an ethanol-alkaline-ultrasonic protocol, retaining >70% of its initial capacity after five cycles. Overall, PCAC offers a reusable and scalable route for continuous EOC removal and value-added utilization of petroleum coke.

It should be noted that the adsorption experiments in this study were mainly conducted at $\text{mg}\cdot\text{L}^{-1}$ -level concentrations to evaluate adsorption capacity, kinetic/isotherm behavior, fixed-bed performance, and adsorption mechanisms. Therefore, these results should not be directly interpreted as removal performance under trace environmental concentrations. Future studies should further verify the removal efficiency of PCAC at environmentally relevant $\text{ng}\cdot\text{L}^{-1}$ - $\mu\text{g}\cdot\text{L}^{-1}$ levels using more sensitive analytical techniques, such as SPE-LC-MS/MS.

Credit authorship contribution statement

Xinhui Tang: Writing-original draft, Data curation; **Liyuan Zhang:** Visualization; **Yongbiao Zheng:** Investigation; **Xinjian Hu:** Formal analysis; **Xinghui Ji:** Methodology; **Dong Ao:** Co-Supervision, Conceptualization; **Ning Wang:** Supervision, Funding acquisition, Writing -review and editing.

Declaration of Competing Interest

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

Data Availability

Data will be made available on request.

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Appendix A. Supplementary data

E-supplementary data of this work can be found in the online version of the paper.

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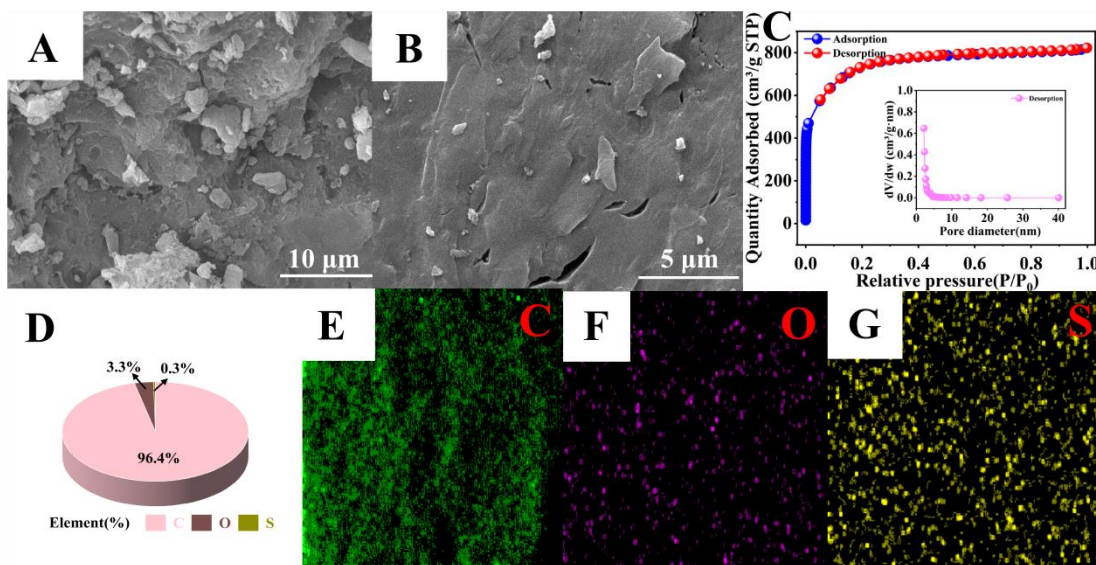


Fig. 1. Morphology and structural characterization of PCAC: SEM images of PCAC (A, B), N₂ adsorption desorption isotherms with corresponding pore size distribution (C), and corresponding EDS elemental mapping images (D-G).

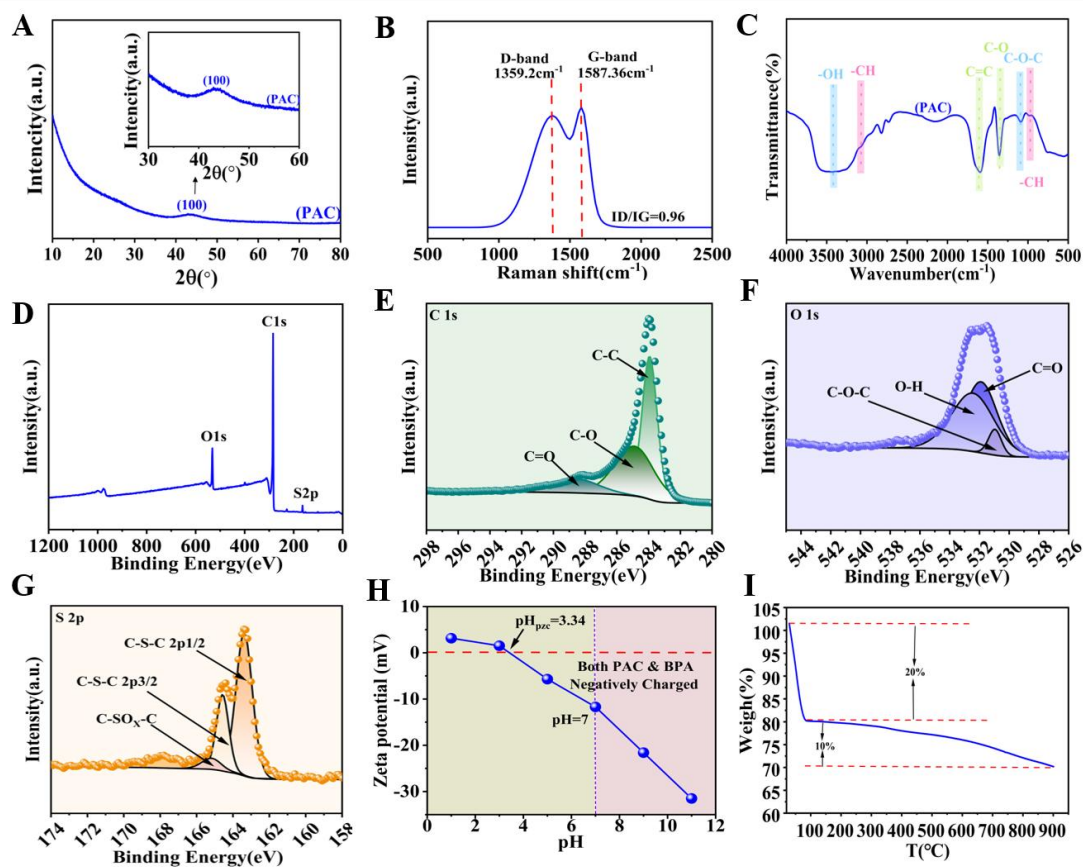


Fig. 2. Structural and chemical characterization of PCAC: (A) XRD pattern, (B) Raman spectrum, (C) FTIR spectrum, (D) XPS survey spectrum, and high-resolution (E) C1s, (F) O1s, (G) S2p spectra, (H) Zeta potential at various pH values, (I) TG curve.

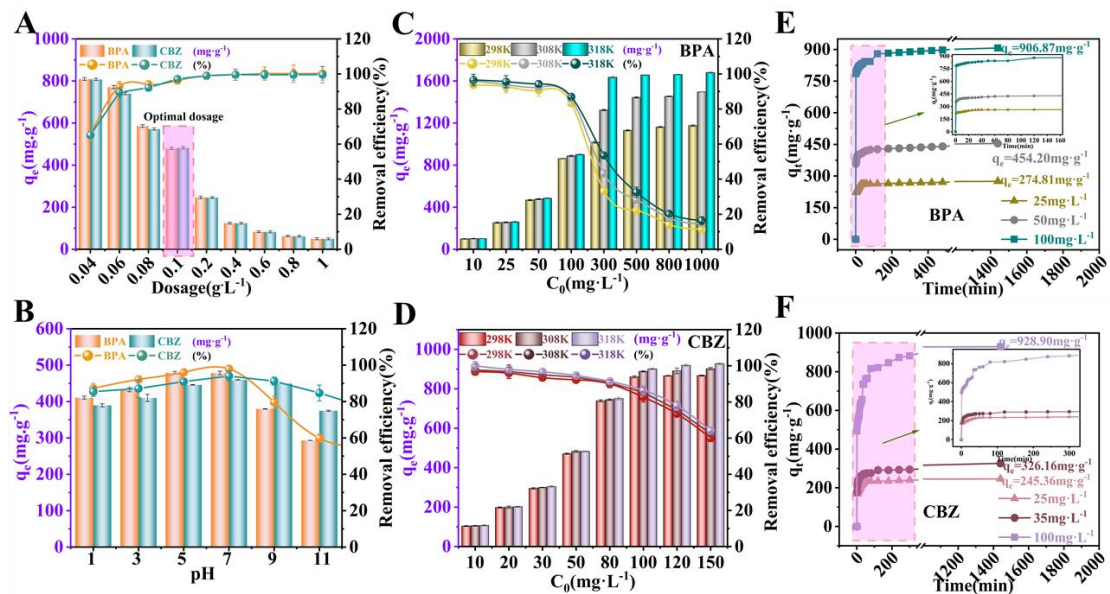


Fig. 3. Influence of batch parameters on BPA and CBZ adsorption: (A) adsorbent dosage, (B) solution pH, (C, D) initial concentration at different temperatures, and (E, F) contact time.

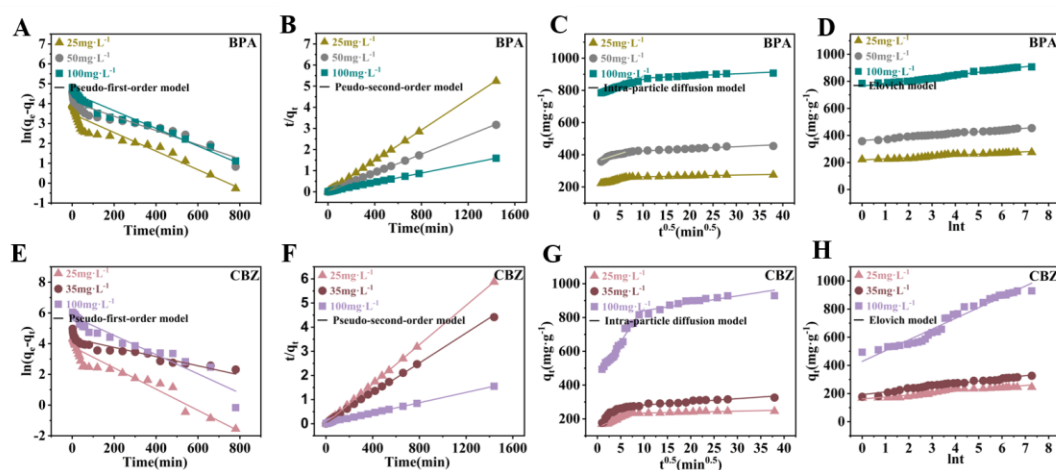


Fig. 4. Adsorption kinetics of BPA and CBZ onto PCAC: (A, E) Pseudo-first-order, (B, F) Pseudo-second-order, (C, G) Elovich, and (D, H) Intra-particle diffusion models.

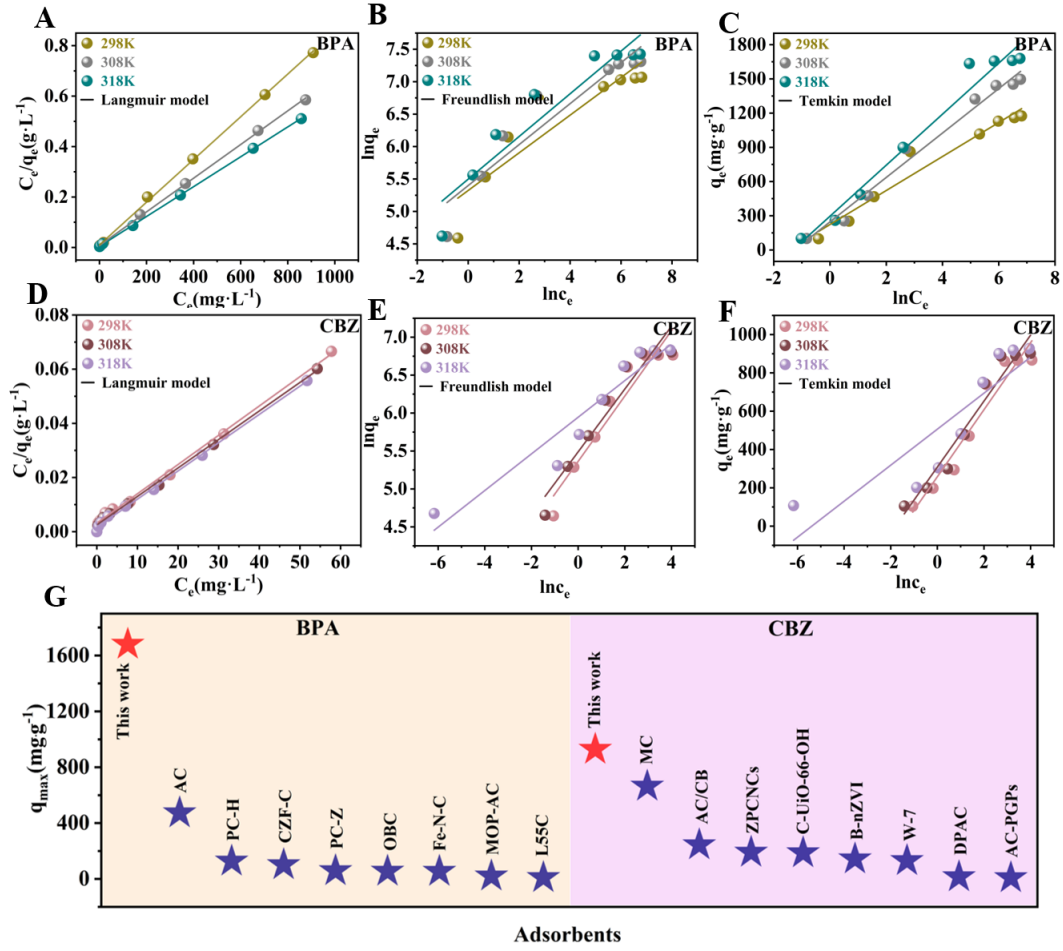


Fig. 5. Adsorption isotherms and adsorption capacity comparison of PCAC

onto BPA and CBZ: Adsorption isotherms of BPA and CBZ onto PCAC fitted by Langmuir (A, D), Freundlich (B, E), and Temkin models (C, F), Comparison of maximum adsorption capacities (q_{max}) of PCAC with reported adsorbents (G).

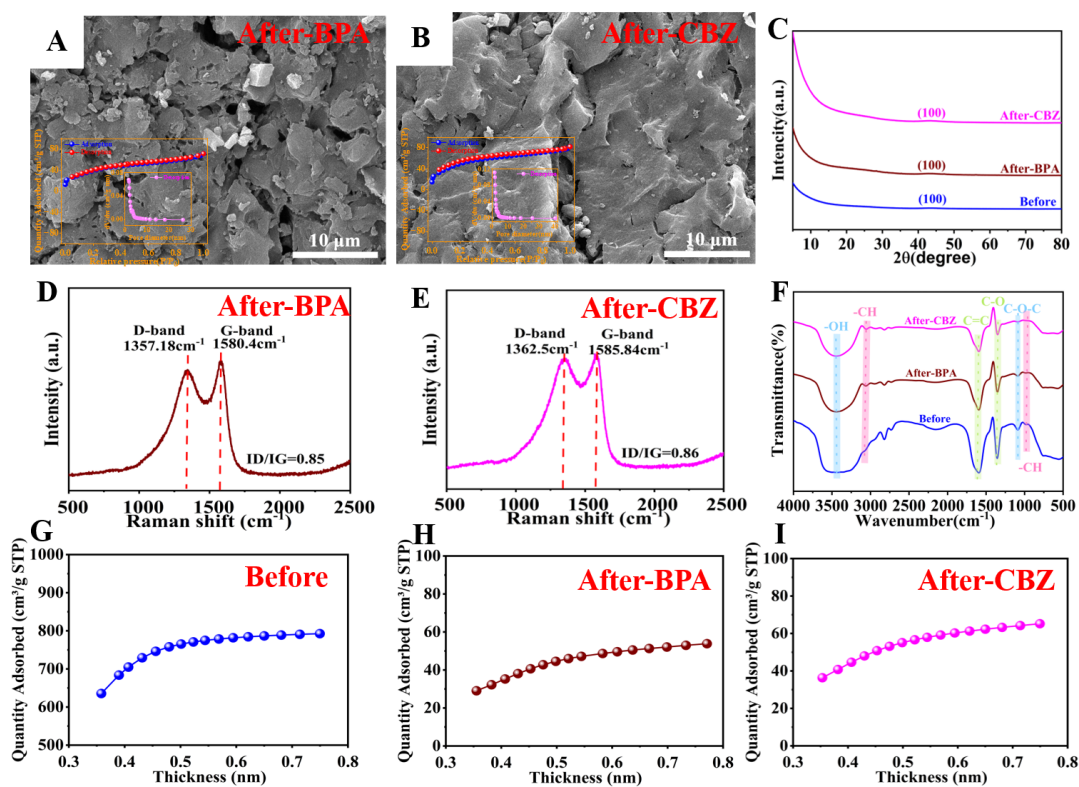


Fig. 6. Characterization of PCAC before and after adsorption: (A, B) SEM comparison, (C) XRD patterns, (D, E) Raman spectrum and, (F) FTIR spectra, (G-I) T-Plots curves of N₂ adsorption before and after adsorption.

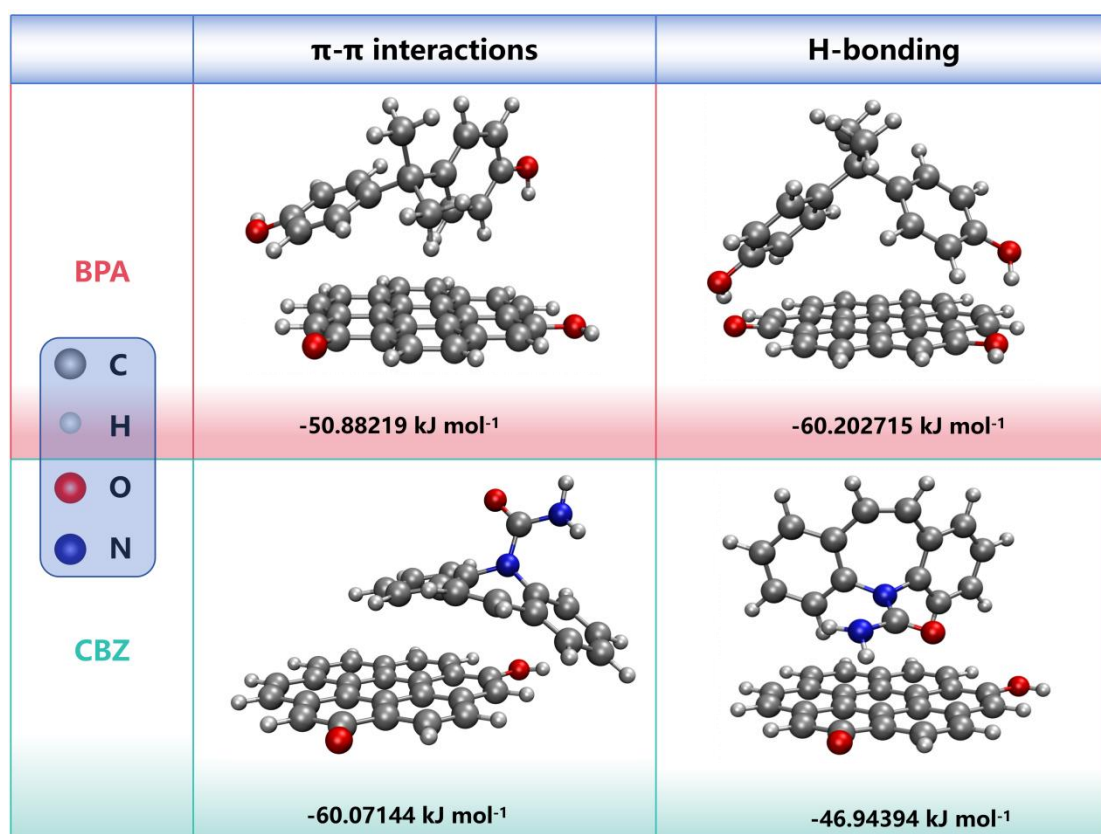


Fig. 7. DFT-optimized configurations and binding energies of BPA and CBZ

adsorption on the PCAC surface model via π - π interactions and H-bonding.

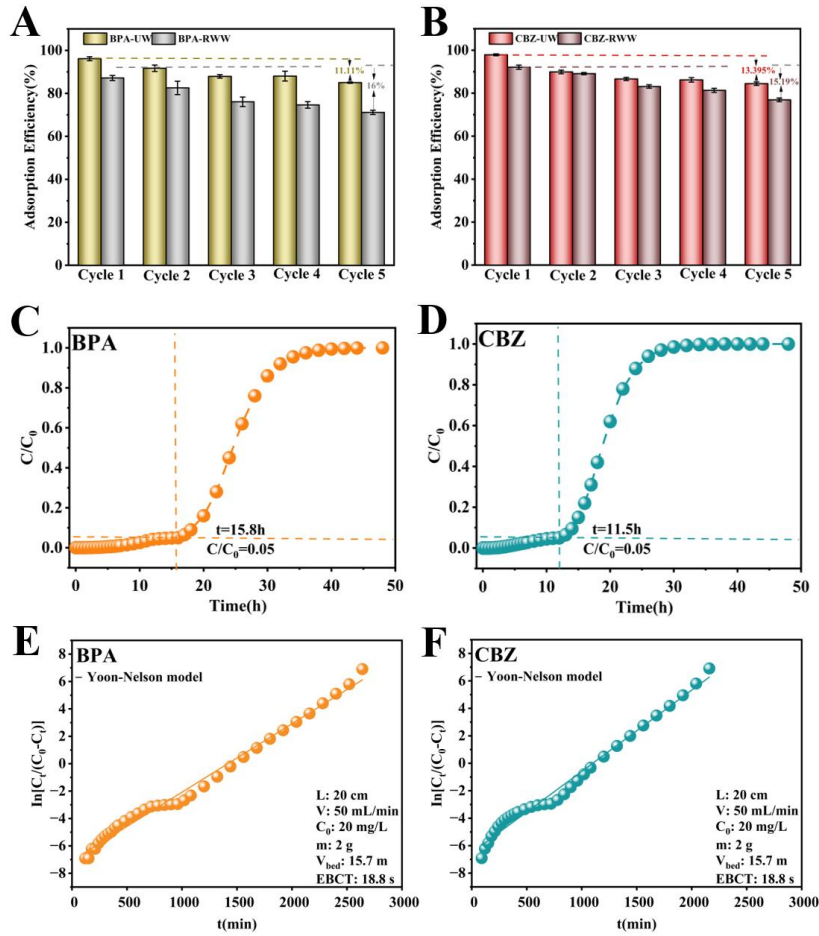


Fig. 8. Reusability and dynamic breakthrough performance of PCAC: (A, B)

Adsorption efficiency over five consecutive cycles in ultrapure water (UW) and real wastewater (RWW) matrix; (C, D) Breakthrough curves in fixed-bed column (Conditions: $C_0 = 20\text{ mg}\cdot\text{L}^{-1}$, flow rate = $50\text{ mL}\cdot\text{min}^{-1}$, bed mass = 2.0 g); (E, F)

Linear fitting of the Yoon-Nelson model for BPA and CBZ, respectively.

951 **Table 1 Isotherm model parameters for the adsorption of BPA and CBZ onto**
952 **PCAC.**

Langmuir model						
	BPA			CBZ		
Parameters	298K	308K	318K	298K	308K	318K
$q_{max}(\text{mg}\cdot\text{g}^{-1})$	1181.25	1497.82	1689.44	925.93	952.38	961.54
$K_L(\text{L}\cdot\text{mg}^{-1})$	0.0832	0.0882	0.1351	0.3407	0.4217	0.6541
R^2	0.999	0.999	0.999	0.997	0.998	0.998
Freundlich model						
	BPA			CBZ		
Parameters	298K	308K	318K	298K	308K	318K
$n(\text{mg}\cdot\text{g}^{-1})$	3.44	3.17	3.04	2.32	2.42	4.14
$K_F(\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{1/n}\cdot\text{L}^{-1/n})$	205.07	221.24	244.17	213.52	242.07	382.01
R^2	0.832	0.891	0.897	0.918	0.928	0.916
Temkin model						
	BPA			CBZ		
Parameters	298K	308K	318K	298K	308K	318K
$A(\text{L}\cdot\text{g}^{-1})$	4.48	3.55	3.76	4.37	5.99	13.59
$b(\text{kJ}\cdot\text{mol}^{-1})$	0.0166	0.0132	0.0118	0.0142	0.0149	0.0281
R^2	0.954	0.983	0.973	0.941	0.949	0.784
Sips model						
	BPA			CBZ		
Parameters	298K	308K	318K	298K	308K	318K
$q_{max}(\text{mg}\cdot\text{g}^{-1})$	1140.05	1503.24	1751.22	936.67	977.65	1023.66

$K_s(\text{L}\cdot\text{mg}^{-1})$	0.1532	0.0995	0.0928	0.2977	0.3455	0.3945
m	1.04	0.83	0.81	1.16	1.06	0.92
R^2	0.987	0.997	0.995	0.976	0.982	0.966

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