Carboxyl-functionalized porous aromatic framework for rapid, selective and efficient removal of cationic pollutants from water

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Abstract
The functionalization of porous aromatic frameworks (PAFs) is essential for task-specific application of these materials as advanced adsorbents in water treatment. In this study, a carboxyl-functionalized PAF was prepared by the post-synthesis modification of a HOCH2-tagged PAF, which was synthesized from a precursor-designed method. The synthesized PAFs were comprehensively characterized. The targeted PAF-COOH showed hierarchical porosity with the coexistence of micropores and mesopores. The carboxyl groups were distributed homogeneously across the whole material, and its content was as high as 4.18 meq g⁻¹. An equilibrium adsorption isotherms study demonstrated that the adsorption of cationic dyes fitted well to the Langmuir model and the maximum adsorption capacities of methylene blue (b-MB) and phenosafranine obtained at pH 10 were 775.19 and 588.24 mg g⁻¹, respectively. The adsorption kinetics of cationic dyes followed the pseudo-second order kinetic model. Quick kinetics was demonstrated with the $k_2$ for a 100 mg L⁻¹ b-MB solution as high as 2.83 g mg⁻¹ min⁻¹ and the equilibrium time was just 0.5 min. In addition, the dye-loaded PAF-COOH could be regenerated easily and showed excellent reusability. These significant characters indicated a promising prospect of the PAF-COOH for water treatment.

Keywords Porous aromatic frameworks · Precursor-designed method · Adsorption · Functionalization · Cationic dye

Introduction
The excessive discharge of various organic pollutants into water systems has caused serious water pollution around the world, which has been a subject of great concern [1]. These pollutants in water systems may cause irretrievable damages to living-being, and bring about detrimental effects on aquatic ecosystems [2]. The removal of organic pollutants from water has attracted increasing interest [3]. Because of the diverse physicochemical properties and low concentrations, the removal of these organic pollutants is of great challenge. Activated carbon (AC) has been the most commonly used adsorbent, and AC adsorption has shown the capacity to remove a broad spectrum of organic pollutants [4, 5]. However, AC suffers from slow kinetics and a low adsorption capacity [5], poor removal of polar pollutants [6], and an energy intensive regeneration process [7]. Therefore, it is of great theoretical and practical significance to explore alternative adsorbents to address these deficiencies of AC.

Recently, novel porous materials based on the ingenious design have been used as promising adsorbents for the removal of multifarious pollutants from water due to their appealing porous structure and properties, such as metal–organic frameworks (MOFs) [8, 9], covalent organic frameworks (COFs) [10, 11], porous organic polymers (POPs) [1, 12] and porous aromatic frameworks (PAFs) [13, 14]. Among these porous materials, PAFs are featured with high surface area, an ordered pore structure and excellent chemical stability, which satisfy the fundamental requirements for qualified adsorbents [4]. Although PAFs or PAF-based composites have been used for the efficient removal of
multitudinous pollutants from water [14–16], the selectivity is still an issue to be addressed for task-specific application. It has been known that the combination with target-specific functionality can facilitate selective adsorption of the desired pollutant molecule. [13, 17].

The chemical structures of PAFs are amenable to functionalization through versatile post-synthesis modification methods, such as chloromethylation [13, 18–21]. The benzyl chloride moieties are extremely reactive, facilitating to convert the chloromethyl groups to other task-specific functionalities, such as thiol group for Hg(II) removal from water [18], quaternary ammonium for anionic pollutants removal from water [20], and cis-diol containing groups for boric acid removal from water [13]. Although the post-synthesis modification method shows the versatile character, the inhomogeneous distribution of the functionalities is an issue to be addressed [22]. The precursor-designed method, which uses building blocks with task-specific functionalities to construct the corresponding task-specific PAFs, is an effective solution to this problems [22]. By this method, task-specific functionalities, such as tertiary amine and carboxyl [23, 24], can homogeneously distributed and precisely located in the whole frameworks with relative high loading. However, the available building blocks or monomers with task-specific functionalities are rare or difficult to synthesize, which severely limits the expanding application of this method in the preparation of task-specific PAFs for water treatment.

The strategy to combine the merits of the precursor-designed method with the versatility of the post-synthesis modification method has been proved to be as an efficient way to prepare versatile task-specific PAFs, which are unfeasible to prepare directly by precursor-designed method [23, 25–27]. In this strategy, a parent PAF was first prepared using a building block containing some active functional groups, such as amino group and tertiary amine moieties [23, 27], through precursor-designed method. Followed by the introduction of some task-specific functionalities through post-synthesis modification of the active functional groups in parent PAF, the targeted PAF could be obtained. And the task-specific functionalities could be located precisely and distributed homogeneously in the whole material. Meanwhile, the synthesis of the building block with the targeted functionalities could be avoided. An elegant example of material embodying this strategy was the quaternary ammonium-functionalized PAFs, which were prepared previously by our group for the selective, rapid and efficient removal of anionic dyes from water [23]. However, this material was impotent to remove cationic dyes. Dyes and other ionized pollutants of various properties and charged states are ubiquitous. The demand for task-specific PAF-based adsorbents for water treatment promotes more possibility of this strategy to be explored.

In this study, exploration was made to prepare functionalized PAF, which integrated the merits of the precursor-designed method with that of the post-synthesis modification method. To this end, 1,5-dibora-2,6-dioxo-sym-hydrindacene-1,5-diol (Di-DHD) was synthesized, which was a benzoxyborole-based building block containing two masked hydroxyethyl groups. By Suzuki coupling polymerization between the Di-DHD and tetrakis(4-bromophenyl)methane (TBPM), a HOCH2-tagged PAF (PAF-OH) was first prepared according to the precursor-designed method. The homogeneously distributed HOCH2– groups were highly reactive, facilitating the occurrence of various post-synthesis modification reactions to generate a wide variety of task-specific adsorbents. Compared with the tertiary amine-functionalized PAF [23], which allowed only a few post-synthesis modification reactions to occur and limited its widespread application, the PAF-OH reported here can be facilely converted to various task-specific PAFs for broad-spectrum applications. As a proof of concept, a carboxyl-functionalized PAF (PAF-COOH) adsorbent was prepared in this study by modifying PAF-OH with maleic anhydride (MAH) for the selective and efficient removal of cationic dyes from water.

**Experimental**

**Reagents and chemicals**

TBPM (98%) was obtained from Zhengzhou Alfa Chemical (Zhengzhou, China). (1,1'-Bis(diphenylphosphino)ferrocene)dichloropalladium(II) (Pd(dpff)Cl2, 99%) and tetrakis(triphenylphosphine)palladium (0) (Pd(PPh3)4, 99.5%) were purchased from J&K Scientific (Beijing, China). Maleic anhydride (MAH, 98.5%), bromobenzene (98%), 1,4-dibromo-2,5-dimethylbenzene (98.5%), bis(pinacolato)diborane (99%), anhydrous KOAc (99%), N-bromosuccinimide (NBS, 99%), anhydrous K2CO3 (99.5%) and benzene-1,4-diboronic acid (BDA, 99%) were purchased from Aladdin Chemistry (Shanghai, China). Phenosafranine, methyl orange (MO), methylene blue (b-MB) and methyl blue (a-MB) were obtained from Alfa Aesar (Shanghai, China) while methanol of HPLC grade was bought from Dikma (Beijing, China). Water used in chromatographic analysis was purified by a Milli-Q Ultrapure Water Purification System (Milford, USA) while deionized water was used throughout all the adsorption experiments.

**Apparatus**

An Agilent 1200 series HPLC system was used for all sample analysis. 1H NMR and 13C NMR characterization were performed on a Bruker Avance III HD 500 MHz instrument...
while the solid-state NMR characterization were carried out on a JEOL JNM-ECZ600R instrument. FT-IR study was completed through a Thermo Nicolet iS10 FT-IR spectrometer with an attenuated total reflection (ATR) accessory in the wavenumber range of 650–4000 cm⁻¹. Zeta potential analysis was performed on the Malvern Zetasizer (Zetasizer Nano). Morphology of the adsorbent was characterized using FEI Quanta 250/Quanta 430 scanning electron microscopy (SEM) and FEI Tecnai G2 20 transmission electron microscopy (TEM). Elemental analysis was performed on a Elementar VARIO EL cube instrument. The thermal property of the adsorbent was performed through thermogravimetric analysis (TGA) with a TA Q500 thermogravimeter over the temperature range from room temperature to 800 °C under nitrogen at a heating rate of 10 °C/min. The pore structure of the adsorbents was evaluated by N₂ adsorption–desorption isotherms at 77 K by an ASAP-2460 instrument. Before any measurement, the samples were degassed under a vacuum at 80 °C for 24 h to remove any impurities.

### Preparation of the PAF-COOH

As shown in Scheme 1, two steps were involved in the preparation procedure. The first step was the preparation of PAF-OH from TBPM and Di-DHD while the second step was the modification of the HOCH₂-tagged PAF-OH with MAH to form the PAF-COOH. PAF-OH was prepared according to our previously reported method with some modification [23]. Briefly, TBPM (0.65 g, 1.02 mmol) and Di-DHD (0.39 g, 2.05 mmol) was added into a round-bottomed flask, followed by the addition of DMF (90 mL) under nitrogen. The mixture was stirred until a homogeneous solution was obtained. The flask was vacuumed and refilled with nitrogen six times. After the addition of an aqueous solution of K₂CO₃ (2 M, 8 mL) and Pd(PPh₃)₄ (100 mg, 0.08 mmol) under nitrogen, the mixture was heated to 110 °C for 24 h. The obtained solid was washed with DMF, water, methanol, dichloromethane and acetone, and dried under vacuum at 60 °C for 24 h, yielding the desired PAF-OH (591 mg, Yield, 98.17%). Anal. Calcd. for \((C_{25}H_{16}O)·(C_{12}H_{8}O_{2})_2\): C, 83.65; H, 5.48; O, 10.87. Found: C, 82.36; H, 5.98; O, 11.55.

PAF-OH (0.30 g), maleic anhydride (MAH, 1.5 g, 15.30 mmol) and DMF (20 mL) were added into a round-bottomed flask and the suspension was stirred under nitrogen at 25 °C for 48 h. The product was collected through centrifugation and washed thoroughly with ethanol and acetone, until the supernatant was colourless. The obtained product was dried under vacuum at 65 °C for 24 h, yielding the targeted PAF-COOH (412 mg, Yield, 95.81%). Anal. Calcd. for \((C_{25}H_{16}O)·(C_{16}H_{12}O_8)_{2}\): C, 69.79; H, 4.11; O, 26.10. Found: C, 68.59; H, 4.38; O, 26.74.

To fully characterize the chemical structure of the designed adsorbents, a non-functionalized PAF, referred as P2, was fabricated from TBPM and BDA following the procedure for PAF-OH preparation and used as a control. The detailed preparation and characterization of P2 was described in Supporting Information.

### Adsorption properties and adsorption isotherms studies

All of the experiments were carried out at ambient temperature. PAF-COOH (5.0 mg) was transferred into a 25 mL vial and 10 mL aqueous solution of a given dye with different initial concentrations (from 100 to 500 mg L⁻¹) was added. The mixture was shaken for 12 h to reach adsorption equilibrium. The suspension was filtered on a glass fiber filter paper and the filtrate was determined by HPLC. The detection wavelengths for phenosafranine, MO, b-MB and a-MB were set at 530 nm, 465 nm, 291 nm and 600 nm, respectively. All experiments were performed in triplicates to obtain average values.

### Adsorption kinetic studies

PAF-COOH (10 mg) was added into a 25 mL vial with a stirring bar, followed by the addition of 10 mL of aqueous solution of dye with different initial concentrations (100 mg L⁻¹,
200 mg L\(^{-1}\) and 400 mg L\(^{-1}\)). The suspension was stirred and samples were collected at a given sampling time from 30 to 1800s. The collected samples were filtered and the filtrate was determined by HPLC. The amount of dye adsorbed by PAF-COOH was determined by the following equation:

\[
q_t = \frac{(C_0 - C_t)V}{m},
\]

where \(q_t\) (mg g\(^{-1}\)) is the amount of dye adsorbed per gram of PAF-COOH at time \(t\) (min), \(C_0\) and \(C_t\) (mg L\(^{-1}\)) are the initial and residual concentration at time \(t\), respectively, \(V\) (L) is the volume of the dye solution; \(m\) (g) is the mass of the PAF-COOH.

**Desorption and reusability**

To evaluate the reusability of PAF-COOH, adsorption–desorption cycles were repeated for 5 times with phenoasafranine at pH 10.0. The tested phenoasafranine concentrations were 50 mg L\(^{-1}\) and 100 mg L\(^{-1}\). Typically, 10 mL of aqueous solution of dye was mixed with PAF-COOH (10 mg) in a 25 mL vial. The suspension was shaken for 12 h and was filtered. The filtrate was determined by HPLC. The dye-loaded PAF-COOH was placed in 5 mL acidic water/methanol/HCl solution (pH 2) and shaken at room temperature for 2 h to desorb the adsorbed phenoasafranine. The desorption process was performed 3 times, followed by being washed with water (5 mL) three times. The regenerated PAF-COOH could be used in the following cycle.

**Results and discussion**

**Preparation of the PAF-COOH**

To prepare the targeted PAF-COOH, a benzoxaborole-based building block (Di-DHD) containing two masked hydroxymethyl groups was synthesized according to previously reported methods [23, 28, 29]. The detailed synthesis process is described in Supporting Information with an overall yield of 63.98%. A model reaction between bromobenzene and Di-DHD was carried out to investigate the feasibility of Di-DHD as a building block in Suzuki coupling polymerization to generate an HOCH\(_2\)-tagged conjugated product. The detailed synthesis and characterization of the model reaction product were described in Supporting Information. The NMR characterization (Fig. S5) confirmed the obtain of the targeted HOCH\(_2\)-tagged conjugated product. Based on this model reaction, HOCH\(_2\)-tagged PAF-OH was prepared from the coupling polymerization between TBPM and Di-DHD with a yield of 98.17%. The active hydroxymethyl could be facilely functionalized by MAH to achieve the targeted PAF-COOH in a yield of 95.81%. According to elemental analysis, the PAF-COOH showed an oxygen atom content of 26.74 wt%, corresponding to 4.18 meq g\(^{-1}\) of the carboxyl groups.

**Characterization**

The chemical structure of the synthesized PAFs was characterized by FT-IR and solid-state \(^{13}\)C-NMR. The FT-IR characterization is shown in Fig. 1. Compared with the two precursors (TBPM and Di-DHD), the spectrum of PAF-OH did not present the C–Br band at 1076 cm\(^{-1}\) of TBPM and a strong B–C band of Di-DHD at 978 cm\(^{-1}\), [14] which preliminarily confirmed the successful coupling of phenyl–phenyl rings through a Suzuki coupling reaction. In addition, the band at 1157 cm\(^{-1}\) in the spectrum of PAF-OH could be attributed to the C–O stretching vibration of the hydroxymethyl groups, indicating the generation of hydroxymethyl groups. When further compared with the FT-IR spectrum of the control PAF (P2) (Fig. S8), the appearance of CH\(_2\)-OH band (at 3360 cm\(^{-1}\)), –CH\(_2\)- band (at 1385 cm\(^{-1}\)) and C–O band (1157 cm\(^{-1}\)) in the spectrum of PAF-OH further demonstrated the formation of the desired HOCH\(_2\)-tagged PAF. From a comparison between the spectrum of PAF-OH and PAF-COOH, the presence of a C=O band (at 1717 cm\(^{-1}\)) and an intense enhancement of the C–O band (at 1157 cm\(^{-1}\)) proved effectuation of the functionalization to convert PAF-OH to PAF-COOH.

The solid-state \(^{13}\)C NMR spectra of P2, PAF-OH and PAF-COOH were shown in Fig. 2. The results of P2 were consistent with the reported ones [30]. Compared with the spectrum of P2, an additional resonance peak at 62.0 ppm was presented in the spectrum of PAF-OH and this peak was attributed to the carbon of methylene (C9). This clearly indicated that the structure of synthesized PAF-OH was identical.
Carboxyl-functionalized porous aromatic framework for rapid, selective and efficient removal...

In the spectrum of PAF-COOH, the resonance peak near 167.1 ppm was attributed to the carbon in C=O groups (C10 and C13), while the resonance peak attributed to the carbon in the –CH=CH– structure (C11 and C12) fused with that of the aromatic carbon (C5 and C6) near 138 ppm. Meanwhile, compared with PAF-OH, the resonance peak attributed to the methylene (C9) shifted to 65.1 ppm, and fused with that of the C1. This was due to the electron-withdrawing effect of the ester group connected to the methylene (C9). These results indicated that all of the HOCH2– groups were modified by MAH and the targeted PAF-COOH with carboxyl groups distributed homogeneously across the whole material was successfully prepared.

The porosity of the prepared PAFs were characterized by nitrogen adsorption and desorption isotherms at 77 K. As shown in Fig. 3a, both PAF-OH and PAF-COOH displayed a rapid uptake at low relative pressure, indicating microporous structure in their frameworks [23]. Meanwhile, both of the PAFs showed a hysteresis loop, especially the PAF-COOH, implying the presence of mesopores [31]. In addition, a rise in the medium to high pressure regions indicated the presence of macropores, which might be due to interparticle porosity or void. The Brunauer-Emmet-Teller (BET) surface areas of PAF-OH and PAF-COOH were found to be 232.10 and 120.02 m² g⁻¹, respectively. As shown in Fig. 3b, the pore size distribution also demonstrated the

Fig. 2 Solid-state ¹³C NMR spectra of P2, PAF-OH and PAF-COOH

Fig. 3 N₂ uptake isotherm (a) and pore size distributions (b) of PAF-OH and PAF-COOH at 77 K
hierarchical nature, manifesting the presence of micropores and mesopores. Compared with PAF-OH, the PAF-COOH showed the absence of micropores at about 0.7 nm, which was due to the introduction of maleic acid moieties.

The morphology and thermal stability of PAF-COOH were also characterized. As shown in Fig. S9, the SEM images (a–c) showed that the PAF-COOH demonstrated rather rough surface and amorphous morphologies. Also, the PAF-COOH was composed of irregularly shaped particles with micrometer sizes. Meanwhile, the TEM image showed in Fig. S9 (d–f) also displayed the amorphous nature and irregular shapes of aggregated particles. The TGA profile of PAF-COOH is shown in Fig. S10. About a 10% weight loss was observed from room temperature to 100 °C, which might be due to the desorption of adsorbed water [31]. Besides, only about an 8% weight loss was observed from 100 °C to 250 °C, indicating the partial decomposition of PAF-COOH at such a high temperature. The porosity, micrometer sizes and high stability as well as the abundant functional groups endowed the PAF-COOH with great potential as an efficient adsorbent [32]. In addition, the surface charge of the prepared PAFs was determined by Zeta potential analysis to get a deep insight into the effect of the chemical structure of adsorbents on the adsorption properties. As shown in Fig. S11, the zeta potential of P2 was measured to be −2.72 ± 1.43 mV, while that of PAF-OH was −25.56 ± 2.09 mV. This difference was due to the weak electronegativity of HOCH2− groups in PAF-OH. When the PAF-OH was converted to PAF-COOH, the zeta potential further decreased to −57.45 ± 1.64 mV, which was attributed to the introduction of negatively charged carboxyl groups into the PAF. These results further confirmed the chemical structure of the prepared PAFs.

**Adsorption properties and adsorption isotherms**

The adsorption properties of the prepared adsorbents, including P2, PAF-OH and PAF-COOH, were investigated by determining the adsorption amounts of dyes at pH 7. As a proof of concept, b-MB was chosen as a model cationic dye, while an anionic dye (a-MB) was used as a control, and the concentrations of the two dyes were 400 mg L−1. As shown in Fig. S12, the P2 and PAF-OH demonstrated a similar adsorption behavior towards a-MB and b-MB, indicating that the HOCH2− groups in PAF-OH did not play an important role for the adsorption of dyes. In addition, the a-MB showed obviously lower adsorption amounts than b-MB on P2 and PAF-OH. This was mainly due to the large molecular size of a-MB, limiting its entrance into the micropores of the adsorbents [33]. When compared PAF-OH with PAF-COOH, although the specific surface area of PAF-COOH was lower than that of PAF-OH, PAF-COOH showed a significantly increased adsorption amount towards b-MB and a marked decrease in the adsorption towards a-MB. This was mainly due to introducing negative –COOH groups, which could adsorb positively charged b-MB through electrostatic interactions and repel negatively charged a-MB [11, 34]. In addition, the lower surface area of PAF-COOH compared with PAF-OH might also make a contribution to the decreased adsorption capacity toward a-MB. These results also manifested the significant role of the –COOH groups in the selective adsorption of cationic dyes.

Equilibrium adsorption isotherms were investigated under pH 7 and pH 10 to deeply evaluate the adsorption performance of PAF-COOH towards cationic dyes, using b-MB as a model cationic dye and a-MB as anionic control. To further confirm the adsorption performance of PAF-COOH, another cationic dye, phenosafranine, was investigated, while MO was used as an anionic control. The structure of the investigated dyes is shown in Fig. 4. Also the isotherm data were analyzed by Langmuir and Freundlich models according to the following linearized equations:

\[
\frac{C_e}{Q_e} = \frac{1}{Q_m^* K_f} \frac{1}{Q_m} + \frac{1}{Q_m^* K_f},
\]

\[
\log Q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e,
\]

In Eq. (2), \(C_e\) (mg L−1) is the equilibrium concentration of the dye, \(Q_e\) (mg g−1) is the adsorbed amount of dye at equilibrium, \(Q_m\) (mg g−1) and \(K_f\) (L mg−1) are the maximum adsorption capacity and the binding energy related to the Langmuir model, respectively. In Eq. (3), \(K_f\) (mg−1) and \(n\) are the Freundlich equilibrium constant and the heterogeneity factor, respectively.

The equilibrium adsorption isotherms of the dyes are shown in Fig. 5, and the linear fitting curves of Langmuir model and Freundlich model are shown in Fig. S13 and Fig. S14, respectively. According to the linear fitting curves, the isotherm parameters were calculated and are summarized in Table 1. As shown in Fig. 5a and Table 1, at pH 7, PAF-COOH displayed an adsorption capacity of 383.14 mg g−1 towards b-MB and a relative low adsorption capacity of 127.71 mg g−1 for a-MB. When the pH was increased to 10, the adsorption capacity of b-MB showed a significant increase to 775.19 mg g−1, while that for a-MB decreased to only 10.02 mg g−1. This high adsorption capacity towards b-MB originated from the high density and homogeneous distribution of the carboxyl groups, and it was much greater than those of the reported adsorbents [35–37]. This phenomenon proved that the electrostatic interaction played a dominant role for the adsorption of cationic dyes. With the increase of pH value, the content of –COO− ions became higher [34, 38]. Consequently, more cationic dye could
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Fig. 4 Molecular structures of b-MB, a-MB, Phenosafranine and MO

![Methylene blue (b-MB)](image)

![Methyl blue (a-MB)](image)

![Phenosafranine](image)

![Methyl orange (MO)](image)

Fig. 5 Adsorption isotherms of b-MB and a-MB (a), phenosafranine and MO (b) at pH 7 and pH 10

Table 1 Langmuir and Freundlich isotherm parameters of the tested dyes onto PAF-COOH at different pH values

| Dyes      | pH  | Langmuir isotherm | Freundlich isotherm |
|-----------|-----|-------------------|---------------------|
|           |     | $Q_{max}$ (mg g$^{-1}$) | $K_l$ (L mg$^{-1}$) | $R^2$ | $K_f$ | $n$ | $R^2$ |
| b-MB      | 7   | 383.14            | 0.2423              | 0.9988 | 193.82  | 0.1319  | 0.9533   |
|           | 10  | 775.19            | 0.4095              | 0.9994 | 540.88  | 0.0751  | 0.8534   |
| a-MB      | 7   | 127.71            | 0.0033              | 0.8510 | 1.79    | 0.6244  | 0.9012   |
|           | 10  | 10.02             | 0.0012              | 0.6907 | 0.0267  | 0.8018  | 0.9616   |
| Phenosafranine | 7 | 344.83            | 0.2071              | 0.9993 | 182.81  | 0.1135  | 0.8801   |
|           | 10  | 588.24            | 0.1037              | 0.9955 | 315.43  | 0.1111  | 0.8734   |
| MO        | 7   | 185.19            | 0.0079              | 0.8859 | 9.67    | 0.4572  | 0.6968   |
|           | 10  | 125.00            | 0.0052              | 0.9740 | 0.2789  | 0.9614  | 0.9612   |
be adsorbed, leading to the dramatical capacity increase. Meanwhile, the repulsive force between the adsorbent and anionic dye was enhanced, resulting in the decrease of the adsorption capacity for anionic dyes. It should be noted that the hydrophobic interaction and π–π interaction also contributed to the adsorption of the tested dyes [14]. As for the adsorption towards phenosafranine and MO, PAF-COOH also showed a strong adsorption affinity towards cationic dyes and repellency for anionic dyes, as shown in Fig. 5b. In addition, as showed in Table 1, for the adsorption of b-MB and phenosafranine, the Langmuir model fitted much better than the Freundlich model by comparing the correlation coefficient ($R^2$) values [31]. These results implied that the adsorption of cationic dyes onto PAF-COOH was mainly a homogeneous monolayer process [35, 39].

Besides, to fully explore the effect of pH value on the adsorption preformation of the PAF-COOH. The adsorption amount of PAF-COOH towards b-MB at 400 mg L$^{-1}$ under different pH conditions were determined. As shown in Fig. S15, the adsorption amount decreased along with lowering the pH value, due to the gradual conversion of –COO$^-$ groups to –COOH groups under lower pH conditions [40]. However, even under pH 2, the PAF-COOH still showed an adsorption capacity of 215.23 mg g$^{-1}$. This was mainly due to the hydrophobic interaction and π–π interaction between b-MB and the aromatic skeleton of PAF-COOH [14].

### Adsorption kinetics

Apart from the adsorption capacity, the adsorption rate and the removal efficiency are essential to adsorbents. The adsorption kinetics of b-MB and phenosafranine were investigated at pH 10 with the initial concentration at 100, 200 and 400 mg L$^{-1}$. The corresponding HPLC spectra of dye solutions with different initial concentrations at different contact times with PAF-COOH are showed in Fig. S16. The experimental data were evaluated using the pseudo-first order model and pseudo-second-order model according to the following equations: [41]

$$\ln (q_e - q_t) = ln q_e - k_1 t,$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2},$$

In Eq. (4) and (5), $q_t$ and $q_e$ (mg g$^{-1}$) are the adsorption amount of dye at time t and equilibrium time, respectively, and $k_1$ (min$^{-1}$) and $k_2$ (g mg$^{-1}$ min$^{-1}$) are the rate constants for the pseudo-first-order model and the pseudo-second-order model, respectively. The kinetic parameters could be calculated from the fitting linear curves (Fig. S17), and are listed in Table 2.

The time-dependent adsorption capacities of b-MB and phenosafranine at different initial concentrations are shown in Fig. 6 and the corresponding time-dependent removal efficiency are presented in Fig. S17. As shown in Fig. 6a and Fig. S16, only 0.5 min was needed to reach the adsorption equilibrium for b-MB at 100 mg L$^{-1}$ and the removal efficiency reached 92.64% (Fig. S18). As for the b-MB at 200 mg L$^{-1}$ and 400 mg L$^{-1}$, just 1 min and 3 min were required to reach the adsorption equilibrium, while the removal efficiency reached 98.03% and 99.24%, respectively. As shown in Fig. 6b, the adsorption equilibrium time for phenosafranine was increased from 1 to 10 min with the initial concentration increasing from 100 to 400 mg L$^{-1}$. Also, the removal efficiencies reached 91.47, 97.45 and 98.93%, respectively. These results demonstrated the rapid adsorption kinetic and high removal efficiency of PAF-COOH towards cationic dyes. [39, 42].

As shown in Fig. S17 and Table 2, the pseudo-second order model showed higher correlation coefficient ($R^2$) values (> 0.999) than those of the pseudo-first order model. The calculated $q_e$ ($q_{e, \text{cal}}$) from the pseudo-second order model were in close agreement with the $q_e$ of experimental data ($q_{e, \text{exp}}$), while the calculated $q_e$ ($q_{e, \text{cal}}$) from the pseudo-first order model varied greatly, implying that the pseudo-second order model was more appropriate to interpret the adsorption behavior of cationic dyes onto the PAF-COOH under chemical adsorption process [39, 42]. The $k_2$ for b-MB at 100 mg L$^{-1}$ was as high as 2.83 g mg$^{-1}$ min$^{-1},$

### Table 2 Kinetic parameters for the adsorption of cationic dyes with different initial concentrations onto the PAF-COOH

| Dyes            | $C_0$ (mg L$^{-1}$) | Pseudo-first-order model | Pseudo-second-order model |
|-----------------|---------------------|--------------------------|---------------------------|
|                 | $q_{e, \text{exp}}$ (mg g$^{-1}$) | $q_{e, \text{cal}}$ (mg g$^{-1}$) | $k_1$ (min$^{-1}$) | $R^2$ | $q_{e, \text{cal}}$ (mg g$^{-1}$) | $k_2$ (g mg$^{-1}$ min$^{-1}$) | $R^2$ |
| b-MB            | 100                 | 94.01                    | 2.28                      | 0.28  | 0.9229  | 92.76                     | 2.83 | 0.9999  |
|                 | 200                 | 196.82                   | 2.49                      | 0.51  | 0.8221  | 196.46                    | 2.24 | 1       |
|                 | 400                 | 397.14                   | 24.88                     | 0.40  | 0.6353  | 396.83                    | 0.048 | 0.9999  |
| Phenosafranine  | 100                 | 93.22                    | 7.35                      | 0.39  | 0.9204  | 93.02                     | 0.15 | 0.9996  |
|                 | 200                 | 195.16                   | 17.76                     | 0.86  | 0.9396  | 193.42                    | 0.13 | 0.9999  |
|                 | 400                 | 398.67                   | 159.84                    | 0.44  | 0.9761  | 403.23                    | 0.0075 | 0.9999 |
which was consistent with the short equilibrium time. Even at 400 mg L\(^{-1}\), a \(k_2\) value of 0.048 g mg\(^{-1}\) min\(^{-1}\) could be obtained. This was much higher than some of the reported adsorbents [37, 41, 43]. As for the adsorption of phosnafranine, the \(k_2\) value decreased from 0.15 to 0.0075 g mg\(^{-1}\) min\(^{-1}\) with the initial concentration increasing from 100 to 400 mg L\(^{-1}\), which was in agreement with the increased equilibrium time required. It is known that strong interactions between the adsorbent and dyes played a significant role in an improved adsorption performance [44]. As shown in Fig. 4, the b-MB and phosnafranine were planar molecules with an aromatic backbone and a positive charge, facilitating the strong \(\pi-\pi\) interaction and electrostatic interaction with the \(\pi\)-electron-rich aromatic skeleton and negatively charged \(-\text{COOH}\) groups of PAF-COOH. These strong interactions were the main source of the rapid adsorption kinetic and high removal efficiency of PAF-COOH. In addition, the adsorption process was based on the mass transfer of solutes from the liquid phase to the adsorbent’s surface and pores to interact with the active sites [39, 44]. The hierarchical porosity of PAF-COOH, which were beneficial for the quick mass transfer of cationic dyes, also made great contribution. So, the quick adsorption kinetics and high removal efficiency could be attributed to the hierarchical porosity, the high density and the homogeneous distribution of the carboxyl groups in PAF-COOH.

**Regeneration and reusability**

The regeneration and reusability are important performance indicators of adsorbents in practical applications. Regeneration could be facilely achieved by washing the dye-loaded PAF-COOH with a water/methanol/HCl solution (pH 2) for three times. FT-IR spectra were recorded to verify the efficient desorption of the adsorbed dye from the adsorbent. The results are shown in Fig. S19. As shown in Fig. S19a, the spectrum of the PAF-COOH after adsorption of b-MB presented the characteristic peaks of b-MB molecular at 1576 cm\(^{-1}\), 1322 cm\(^{-1}\) and 852 cm\(^{-1}\). After desorption, these characteristic peaks disappeared completely, and the spectrum was almost identical to the spectrum before adsorption. This clearly proved the efficient removal of the adsorbed b-MB and the successful regeneration of PAF-COOH. As shown in Fig. S19b, the successful regeneration of PAF-COOH from phosnafranine-loaded PAF-COOH could also be achieved. The regenerated PAF-COOH could be reused in the next adsorption cycle. As shown in Fig. 7, after five adsorption/desorption cycles, the \(q_e\) of phosnafranine at 50 mg L\(^{-1}\) and 100 mg L\(^{-1}\) showed almost no decrease. These results indicated that the PAF-COOH showed
excellent reusability, and the adsorption performance could be well maintained in the five adsorption/desorption cycles.

Conclusions

In conclusion, a carboxyl-functionalized PAF, PAF-COOH, was successfully prepared by combining the precursor-designed method with the post-synthesis modification method. The PAF-COOH showed a hierarchical porosity with the coexistence of micropores and mesopores. In addition, the PAF-COOH was featured with a high density and homogeneously distributed carboxyl groups. Based on these outstanding features, it demonstrated a quick adsorption rate, high adsorption capacity and excellent selectivity towards cationic dyes. All of this, combined with a good thermal stability and reusability, made the PAF-COOH a promising adsorbent for wastewater treatment. Considering the activity of the hydroxyl groups in PAF-OH and the versatility of functional groups could be derived from PAF-OH, which will expand the deep application of PAF-based advanced adsorbents in water treatment.

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