Charge-Enhanced Separation of Organic Pollutants in Water by Anionic Covalent Organic Frameworks

Wei Jiang, Dong Peng, Wei-Rong Cui, Ru-Ping Liang, and Jian-Ding Qiu*

ABSTRACT: The effective removal of organic pollutants in wastewater is a key environmental challenge. In this work, an anionic covalent organic framework (named TpPa-SO$_3$Na) was synthesized through a green two-in-one synthesis strategy with autocatalytic imine formation. The slowly generated acetic acid as a catalyst is favorable to sustain the reversibility of the covalent organic framework (COF) formation reaction and improve the crystallinity of TpPa-SO$_3$Na. TpPa-SO$_3$Na consists of a homogeneous distribution of sulfonate groups to produce negatively charged regular channels. The strong electrostatic and hydrogen-bonding interactions between the sulfonate groups anchored in the nanochannels and the amine groups in organic pollutants improve the adsorption selectivity and capacity. These structures allow a high degree of control over adsorption processes to boost the adsorption kinetics and improve selective separation. TpPa-SO$_3$Na exhibits ultrafast adsorption (<1 min) of cationic antibiotics and dyes (average over 95%). Furthermore, TpPa-SO$_3$Na exhibits high selectivity for the uptake of dye molecules on the basis of the differences in charge and molecular size. This work explored functional designs and green manufacturing of anionic COFs for removal of hydrophilic organic pollutants.

1. INTRODUCTION

With the development of the chemical industry, water resources are seriously contaminated by organic pollutants such as antibiotics and synthetic dyes. Illegal discharges of antibiotics increased bioaccumulation, and dyes might even transform into carcinogenic and mutagenic agents. Adsorption is an effective technique to remove organic pollutants from water owing to its excellent separation efficiency and reusability. To achieve high adsorption capacity, rapid kinetics, and outstanding selectivity, many functional materials have been designed to combat highly water-soluble antibiotic and artificial dye pollution. A series of conventional materials have been developed as adsorbents, such as silica and clay. Nonetheless, only organic pollutants interact mainly with the surface of adsorbents due to their lack of pore structures, limiting adsorption capacity. Because of their high surface area, porous organic polymers offer enhanced adsorption efficiency compared to conventional materials. Though the correlation between surface area and adsorption capacity is often documented, the inner surfaces of open-ended polymers were found to be partially ineffective due to the irregular pore structures and lack of functional groups, compromising binding capacity.

Metal–organic frameworks (MOFs) were used to mitigate this problem due to added functional groups and uniform pore structures, which facilitate the interaction between adsorbents and targeted organic pollutants. However, MOFs with a relative density of functional groups and interpenetrating channels greatly affected site accessibility, thus resulting in a low adsorption affinity and a relatively long adsorption equilibrium time. Therefore, it is highly desirable to develop new types of materials to overcome these limitations.

Covalent organic frameworks (COFs) are a new type of porous crystalline material that integrate organic building blocks into predetermined nanometric networks. The functionalization of COFs with specific functional groups on the organic building blocks can efficiently tune their adsorption properties. In two-dimensional (2D) COFs, the layered structures stack via π–π interactions and form regular channels running along the stacking direction. Thus, the functional groups can be uniformly distributed on the surface, and the density of functional groups can be precisely controlled. Anionic COFs, which consist of negatively charged active sites and well-ordered one-dimensional (1D) nanochannels, are a subtype of COF with extraordinary functions. However, the
introduction of ionic sites on the pore walls needs ionic building blocks, which prevents $\pi-\pi$ stacks because of strong charge repulsion, usually leading to low porosity and crystallinity. Homogeneous negatively charged groups in the channels would generate a strong interaction for cationic organic pollutants, improving the binding capacity. Compared with polymers and MOFs, well-defined hydrophilic 1D channels of COFs are favorable for the diffusion of highly water-soluble antibiotics and artificial dyes, increasing the access of pollutants to the surface of channels. Negatively charged 1D nanochannels will generate ionic interfaces to enhance the accessibility of the anionic sites, allowing high adsorption kinetics and selective adsorption. These traits suggest that anionic COFs can be pertinently designed for highly efficient removal of hydrophilic antibiotics and artificial dyes.

In this study, a two-in-one strategy was developed for the synthesis of sulfonate-based covalent organic frameworks (denoted as TpPa-SO$_3$Na) for trapping antibiotics and synthetic dyes. Sulfonates were homogeneously introduced onto the surface of 2D COFs. The negatively charged site can provide strong electrostatic and hydrogen-bonding affinity, which can promote the interaction between cationic pollutants and the anionic sites. Hydrophilic channels are favorable for the diffusion of water-soluble pollutants. Meanwhile, the ionic interface on the 1D channel walls helps to expose the active sulfonate sites and promotes adsorption efficiency and selectivity. TpPa-SO$_3$Na shows ultrafast adsorption kinetics with high removal efficiency (99.0%) in 1 min toward antibiotics such as norfloxacin (NOR). Owing to its charged nanochannels, TpPa-SO$_3$Na exhibits high selectivity to separate cationic dye molecules owing to the differences in molecular size and charge. These results reveal the broad application of the anionic COF to the treatment of organic pollutants.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization. The anionic COF was prepared by condensing aldehydes and amines at an elevated temperature in a mixture of organic solvents and aqueous acetic acid. Acetic acid was used to catalyze imine formation. Compared with polymers and MOFs, well-defined hydrophilic 1D channels of COFs are favorable for the diffusion of highly water-soluble antibiotics and artificial dyes, increasing the access of pollutants to the surface of channels. Negatively charged 1D nanochannels will generate ionic interfaces to enhance the accessibility of the anionic sites, allowing high adsorption kinetics and selective adsorption. These traits suggest that anionic COFs can be pertinently designed for highly efficient removal of hydrophilic antibiotics and artificial dyes.

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Figure 1. (a) Preparation scheme of TpPa-SO$_3$Na and TpPa; (b) graphic view of the eclipsed AA stacking structure of TpPa-SO$_3$Na (top view); and (c) stacking model showing individual layers (side view) (blue, N; red, O; yellow, S; purple, Na; gray, C; white, H).

2.1. Synthesis and Characterization. The anionic COF was prepared by condensing aldehydes and amines at an elevated temperature in a mixture of organic solvents and aqueous acetic acid. Acetic acid was used to catalyze imine formation. The obtained COF was reacted with an organic salt to exchange its protons with metal ions. A tedious preparation process, long reaction time, and strong acid solution are necessary in the entire COF formation reaction. A relatively high concentration of acid in the reaction can damage the reversible reaction of diamines on the linkers, resulting in irregular nanochannels. However, the networks transform into crystalline COFs, and this transformation would be hindered if acetic acid is not present. As mentioned earlier, the COF was controlled using different amounts of AcOH. The slowly generated acetic acid was favorable to sustain the COF formation reaction and improve crystallinity. In our work, a two-in-one synthesis strategy was used for the synthesis of TpPa-SO$_3$Na as illustrated in Figure 1. First, the sulfone acid group of Pa-SO$_3$H reacted with NaOAc to exchange its proton with Na$^+$. The slowly generated acetic acid catalyzed imine formation without additional catalysts, which ensured a low concentration of acid catalyst in the synthetic process. The low concentration of acetic acid pushed the equilibrium toward COF formation and slowed down the entire reaction, improving self-healing and error correction during the crystallization. Meanwhile, the two-in-one synthesis strategy was used for the synthesis of anionic TpPa-SO$_3$Na, avoiding the traditional synthesis procedures that are time- and solvent-consuming. Thus, the dual role of NaOAc is very intriguing as both an ion exchanger and a catalyst in the reaction. The cation exchange reaction was quantitatively confirmed by the inductively coupled plasma optical emission spectroscopy (ICP-OES) measurement of the Na content. The sulfonate groups in TpPa-SO$_3$Na work as anionic sites for efficient adsorption of cationic antibiotics and artificial dyes.
which also provide sites for charge-assisted hydrogen bonds to further improve the affinity. The structure of TpPa-SO$_3$Na was analyzed based on the powder X-ray diffraction (PXRD) pattern (Figure 2a). The highly prominent PXRD peak at 4.8° can be attributed to the \{100\} facet of a regularly ordered lattice, which is arranged in a hexagonal orientation.\textsuperscript{23,24} The sharp diffraction peaks indicate the successful formation of the imine-linked COF, and the acetic acid formed in the two-in-one step reaction is an effective catalyst for the COF. Noticeably, the slowly generated acetic acid is favorable to sustain the reversibility of the COF formation reaction and improve the crystallinity of TpPa-acetic acid.\textsuperscript{25} The broad peak at 27.0° assigned to the \{001\} facet further confirms the formation of 2D COFs in a crystalline and π−π stacking form.\textsuperscript{24,25} Intramolecular hydrogen bonds between the sulfonate units and imine group on the frame can avoid disturbing the π−π stacking between the sheets, forming a highly crystalline structure.\textsuperscript{26} The PXRD profile obtained from the Pawley refinement of the AA stacking mode (Figure 2a, red curve) agrees well with the experimental result. The average interplanar distance was estimated to be 3.4 Å. The AA-stacking mode provides 1D channel, allowing adjacent alignment of sulfonate. This spatial structure efficiently boosted the accessibility of the anionic sites by cationic pollutants.\textsuperscript{17,18} Based on the facts presented above, superior anionic COFs have been synthesized using the two-in-one synthesis strategy. The method also has the advantages of simplified operation and green environmental protection.

The typical FTIR spectra of TpPa-SO$_3$Na are shown in Figure S3. The material exhibits a nanofiber morphology. The SEM image with a 2 μm scale plate shows a randomly shaped aggregate composed of many macroscopic fibers.

2.2. Stability Test. To investigate the stability of TpPa-SO$_3$Na, samples were dispersed in different solutions, including NaOH (6 M) and aqueous HCl (6 M) and boiling water solutions for 7 days. Surprisingly, all of the TpPa-SO$_3$Na samples exhibited intense PXRD patterns without a change in the peak position and intensity, indicating that the high stability is retained under these extreme conditions (Figure 2d). Compared with traditional imine-linked COFs,\textsuperscript{13} irreversible enol-to-keto tautomerization and the hydrogen-bonding interaction can further enhance the chemical stability.\textsuperscript{29,30} The thermogravimetric analysis (TGA) curves exhibit two weight losses in the studied temperature range. The initial weight loss was caused by the removal of the occluded solvent molecules at 50–120 °C, and the second weight loss was derived from the decomposition of the sulfonate groups at 300 °C (Figure S4). This suggested that the obtained COF exhibits superior stability, which is important for its practical applications.

2.3. Adsorption Kinetics. Taking into account the porosity and high density of sulfonate sites within the ordered pore channels in TpPa-SO$_3$Na, its adsorption performance toward the positively charged amine group of antibiotics and artificial dyes was further investigated. The effects of adsorbent dosage on the removal efficiency were investigated. As shown in Figure S5, it can be seen that the removal efficiency increases with the increase of TpPa-SO$_3$Na dose as a result of increased available adsorption active sites and surface area. Taking the adsorption efficiency and cost into consideration, the optimum dosage of TpPa-SO$_3$Na was used in the subsequent investigations. Typically, TpPa-SO$_3$Na was mixed with pollutant solutions at 10 mg L$^{-1}$ under pH 7.0. As shown in Figure 3a, TpPa-SO$_3$Na showed ultrafast adsorption kinetics, and it efficiently removed most of the pollutants such as NOR (∼99%), ciprofloxacin (CIP) (∼98%), enrofloxacin (ENR) (∼98%), tetracycline hydrochloride (TC) (∼91%), methylene blue (MB) (∼96%), and crystal violet (CV) (∼89%) within 1 min. It is worth noting that almost 90% of its maximum adsorption capacity was reached within 30 s. This suggests that TpPa-SO$_3$Na has excellent affinity toward the antibiotics and dyes. The adsorption kinetics studies show that the adsorption process fits well with the pseudo-second-order model (Figure 3b), confirming that the interactions between TpPa-SO$_3$Na and pollutants are mainly controlled by chemical processes. The pseudo-second-order rate constants ($k_{obs}$) of NOR, CIP, ENR, TC, MB, and CV adsorption are 4.78, 3.53, 3.37, 1.64, 2.18, and 1.08 g mg$^{-1}$ min$^{-1}$, respectively (Figure S6). NOR was selected as one of the representative pollutants. The removal rate constant is 1005 cm$^{-1}$.\textsuperscript{22} The Brunauer–Emmett–Teller (BET) surface area for TpPa-SO$_3$Na is 236 m$^2$ g$^{-1}$ (Figure S2). Because of the high surface-to-volume ratio of the COF and internal sulfonate groups, the surface charges may generate abundant adsorption sites for charged organic compounds and enhance the adsorption capacity and affinity. The pore diameter is concentrated at ∼15.2 Å (Figure 2c), and the narrow pore size reflects the successful preparation of the crystalline network.\textsuperscript{28} Owing to the presence of the narrow nanochannels, the internal sulfonate groups can easily interact with amine groups of antibiotics and artificial dyes.\textsuperscript{17} SEM images of TpPa-SO$_3$Na are shown in Figure S3. The material exhibits a nanofiber morphology. The SEM image with a 2 μm scale plate shows a randomly shaped aggregate composed of many macroscopic fibers.

**Figure 2.** (a) Comparison of PXRD profiles of TpPa-SO$_3$Na between the experimental sample (black), the simulated AA eclipsed stacking modes (red), and the simulated AB staggered stacking modes; (b) Fourier-transform infrared spectroscopy (FTIR) spectra of Tp (black), Pa-SO$_3$H (red), and TpPa-SO$_3$Na (blue); (c) pore size distribution of TpPa-SO$_3$Na; and (d) stability tests of TpPa-SO$_3$Na in 6 M NaOH, 6 M HCl, and boiling water.
The excellent removal rate constant should be structure and interactions according to the contaminant of COFs are desirable materials that provide a specific pore structure, organic porous polymers with an irregular pore structure, clays and zeolites with low inherent porosity and amorphous ionic interfaces in TpPa-SO$_3$Na is favorable for diffusion of the antibiotics and dyes compared with the self-interpenetrated nanochannel of MOFs. The ultrafast adsorption kinetics is the key to remarkably reduce the exposure time, especially under extreme conditions, improving the accessibility of the pores. The nanochannel property of TpPa-SO$_3$Na is concentrated at 15.2 Å, which is large enough to allow entry of NOR inside the nanopore and the sulfonate groups of TpPa-SO$_3$Na. In addition, the sufficiently long 1D nanochannels provide more active sites.

2.5. Effect of pH and Reusability. The capture of antibiotics and dyes over a wide pH range is greatly needed for actual sewage treatments. The effect of pH on the adsorption capacity toward NOR was researched from pH 1 to 12 (Figure 3d). The adsorption efficiencies of TpPa-SO$_3$Na toward NOR were over 90% within a wide pH range of 3–10. Meanwhile, the $\zeta$-potentials of TpPa-SO$_3$Na at different pH values were also measured (Figure 3d). As shown in Figure 3d, when pH <6.30, the adsorption capacity of NOR increases with the increase of pH value. The cationic NOR is mainly formed in the solution in this pH range (Figure S8a,b); therefore, the increase in adsorption capacity is attributed to the sharp increase in the negative potential of TpPa-SO$_3$Na. In the range of 6.30 < pH < 8.38, the increase in the negative potential of TpPa-SO$_3$Na slows down, while the content of anionic NOR increases gradually with pH. The adsorption capacity reaches the highest value at pH about 7.0. When pH > 8.38, anionic NOR as the main form exists in the solution (Figure S8a,b). Compared with the expected result, increased adsorption of NOR was obtained in spite of an unfavorable electrostatic interaction in the range. Hydrogen bonding may be one of the potential mechanisms for enhanced adsorption of NOR. The N–H group of NOR is considered to be able to serve as a very strong hydrogen donor for hydrogen bonds. Therefore, NOR can interact efficiently via hydrogen bonds with adsorbents having a hydrogen acceptor. As TpPa-SO$_3$Na has ultrafast adsorption kinetics, a long-time adsorption and desorption experiment was implemented to determine the stability of TpPa-SO$_3$Na. After being treated with NOR solutions for 12 h, the desorption of NOR from TpPa-SO$_3$Na was studied using an HCl solution (0.1 M). No obvious decrease in the adsorption capacity of TpPa-SO$_3$Na for NOR (100 mg L$^{-1}$) was observed even after five adsorption–desorption cycles (Figure S9). The PXRD result also showed that there was no change in the peak pattern after five cycles of reuse compared with the fresh one (Figure S10). Furthermore, all of the characteristic FTIR peaks remained the same after recycling, and no extra peaks were observed (Figure S11). These excellent properties endow TpPa-SO$_3$Na with great capability in the removal of antibiotics and artificial dyes.

2.4. Adsorption Isotherms. The adsorption isotherms of TpPa-SO$_3$Na fitted well with the Langmuir model (Figure 3c and Table S3) with a correlation coefficient $R^2$ of greater than 0.99, suggesting that the uniform and monolayer adsorption isotherm model is more propitious to the adsorption of NOR. It is worth noting that 2D COFs tend to form uniform and controllable 1D nanochannels by the suitable stacking of monolayers. The monolayer adsorption model is consistent with the structural characteristics of stacking of monolayers. The distribution coefficient value ($K_d$) can be applied to further evaluate the interaction between adsorbents and pollutants. Generally, a material with a $K_d$ value of more than 10$^2$ mL g$^{-1}$ can be regarded as an excellent adsorbent. The $K_d$ of TpPa-SO$_3$Na toward NOR is 1.7 × 10$^2$ mL g$^{-1}$ in 10 min (Table S4). The saturation sorption capacity toward NOR was 653 mg g$^{-1}$ at room temperature (Table S3), higher than those of other reported porous pollutant removers (Table S2). The self-adsorption behavior was also tested under dark conditions. Spectroscopic monitoring of NOR solution at different intervals indicated that the concentration of NOR did not exhibit any noticeable change under dark conditions. It is suggested that the self-adsorption behaviors did not significantly impact the adsorption process of NOR on TpPa-SO$_3$Na (Figure S7). Its excellent adsorption capacity is mainly attributed to the strong affinity interaction between antibiotics and the sulfonate groups of TpPa-SO$_3$Na. In addition, the sufficiently long 1D nanochannels provide more active sites.

2.6. Adsorption Mechanism. The adsorption property of 2D COFs is actuated by “horror vacui” and guided by the diffusion and accessibility of the pores. The nanochannel diameter of TpPa-SO$_3$Na is concentrated at 15.2 Å, which is large enough to allow entry of NOR inside the nanopore and its interaction with the sulfonate groups. To further verify the possibility of entering the pore during adsorption, N$_2$ sorption measurements at 77 K after NOR adsorption were made. The experiment results showed a decrease in surface area to 49 m$^2$ g$^{-1}$, corresponding to a drop of 80%, which could indicate that NOR is adsorbed within the pores of TpPa-SO$_3$Na (Figure S12). The $\zeta$-potential of TpPa-SO$_3$Na is higher than those of most reported porous pollutant removers (Table S2). Compared to inorganic porous materials such as clays and zeolites with low inherent porosity and amorphous organic porous polymers with an irregular pore structure, COFs are desirable materials that provide a specific pore structure and interactions according to the contaminant of choice. The excellent removal rate constant should be attributed to TpPa-SO$_3$Na containing nanochannels and compact sulfonate sites, significantly improving the accessibility to these cationic pollutants rather than the amorphous activated carbon with an uneven pore distribution and undefined functional groups. The 1D nanochannel with ionic interfaces in TpPa-SO$_3$Na is favorable for diffusion of the antibiotics and dyes compared with the self-interpenetrated nanochannel of MOFs. The ultrafast adsorption kinetics is the key to remarkably reduce the exposure time, especially under extreme conditions, improving the configurable preservation during sewage disposal.

Figure 3. (a) Adsorption kinetics of TpPa-SO$_3$Na toward different organic pollutants (initial concentration was 10 mg L$^{-1}$; the dosage of TpPa-SO$_3$Na was 0.6 g L$^{-1}$ (for NOR, CIP, and ENR), 0.8 g L$^{-1}$ (for MB and CV), and 1.0 g L$^{-1}$ (for TC); solution volume 100 mL; and pH 7.0). (b) Pseudo-second-order kinetics of adsorption of different organic pollutants. (c) Adsorption isotherms for different organic pollutants on TpPa-SO$_3$Na (initial concentration was 10, 20, 30, 50, 100, 200, 300, and 500 mg L$^{-1}$; the dosage of TpPa-SO$_3$Na was 0.6 g L$^{-1}$ (for NOR, CIP, and ENR), 0.8 g L$^{-1}$ (for MB and CV), and 1.0 g L$^{-1}$ (for TC); solution volume 40 mL; and pH 7.0). (d) Removal efficiency and $\zeta$-potential of TpPa-SO$_3$Na toward NOR at different pH conditions.
negative at pH 1–12 owing to the abundant sulfonate groups.\textsuperscript{11,38} The negatively charged surface of TpPa-SO\textsubscript{3}Na helped in capturing the positively charged antibiotics and artificial dyes. Coupled with the pore structure, the adsorption kinetics and capacity are also influenced by surface charge.\textsuperscript{39} TpPa-SO\textsubscript{3}Na shows a high negative $\zeta$-potential ($-22.2$ mV) before NOR adsorption, suggesting that it prefers to adsorb cationic NOR. The $\zeta$-potential of the NOR-loaded adsorbents was also tested (Figure S13). The results indicate an improvement in the $\zeta$-potential. The adsorption of cationic NOR was promoted by electrostatic attraction. Negatively charged groups may act in concert with pore size to facilitate adsorption of cationic NOR into the channels of TpPa-SO\textsubscript{3}Na. The typical FTIR spectra of TpPa-SO\textsubscript{3}Na before and after adsorption of NOR are shown in Figure S14. The characteristic peaks for N–O at $1101$ cm\textsuperscript{-1} and the S–O stretching vibration at $1024$ cm\textsuperscript{-1} shifted to $1026$ cm\textsuperscript{-1} are attributed to the occurrence of the strong reaction between sulfonate and amine.\textsuperscript{24} This interaction was further confirmed by X-ray photoelectron spectroscopy (XPS). The spectra of N 1s XPS analysis are consistent with the presence of the electrostatic attraction process as the new peak of N–O (401.9 eV) appeared in TpPa-SO\textsubscript{3}Na-NOR (Figure 4a,b). Moreover, the adsorption of NOR. The characteristic peak at $1237$ cm\textsuperscript{-1} may be attributed to the symmetric stretching vibration of O=S. Following the adsorption of NOR, the peak at $1237$ cm\textsuperscript{-1} shifted up to $1232$ cm\textsuperscript{-1}, which signified that a hydrogen-bonding interaction occurred between N-H and O=S. This interaction was further confirmed by XPS. The O 1s core level of S=O–H–N (532.6 eV) shifted to a lower binding energy (532.3 eV),\textsuperscript{26} verifying that the sulfonate sites were the binding sites toward the amine group in NOR by charge-assisted hydrogen-bonding attraction (Figure 4c,d).\textsuperscript{23,24} To further confirm the hydrogen-bonding interaction, NOR was added to TpPa-SO\textsubscript{3}Na in the presence of $6$ M carbamide (Figure 5a).\textsuperscript{46}

![Figure 4](link) **Figure 4.** N 1s of TpPa-SO\textsubscript{3}Na (a) and TpPa-SO\textsubscript{3}Na-NOR (b) and O 1s of TpPa-SO\textsubscript{3}Na (c) and TpPa-SO\textsubscript{3}Na-NOR (d).

O 1s core level of S–O (533.1 eV) shifted to a higher binding energy (533.5 eV) (Figure 4c,d), corroborating the results obtained from the XPS of N 1s. The sulfonate groups are aligned on the nanochannel’s internal surface, and the open nanochannel effectively exposes the active sites, increasing the accessibility to NOR and enhancing the adsorption efficiency toward NOR.\textsuperscript{17,18} Integration of anionic sites into the nanochannel has generated anionic interfaces to accelerate the diffusion of charged NOR in the direction of the channel.\textsuperscript{40,41}

Nanochannels of 2D COFs can offer efficient pathways for the transport of ions and molecules. With decreasing size, the interfacial wettability within nanochannels plays a significant role in the efficient transportation of various molecules.\textsuperscript{32,43} Modulating hydrogen bonding is a powerful strategy to increase the interior wettability of nanochannels.\textsuperscript{14,42} Figure S14 shows the FTIR spectra of TpPa-SO\textsubscript{3}Na before and after adsorption of NOR. The adsorption capacity toward NOR significantly declined with the addition of carbamides in the pollutant solution. The disruptive effect of carbamide further confirms the hydrogen-bonding mechanism. This shows that negative charge-assisted and enhanced H-bonding attraction makes the hydrophilic nanochannels robust. With the hydrophilic modification of nanochannels, the wettability of the material was effectively improved, facilitating diffusion in the direction of the channel.\textsuperscript{38,42}

In addition, to investigate the role of charges in the adsorption, 4-nitrophenol (4-NP) containing only a hydrogen donor (hydroxyl) was tested. As demonstrated in Figure S15, 4-NP was hardly adsorbed by TpPa-SO\textsubscript{3}Na, which showed as low as 2% of adsorption efficiency even after 2 h, implying that the individual hydrogen-bonding effect was not as dominant as expected in the adsorption process because of the lack of charged binding sites. The synergetic electrostatic interaction and charge-assisted hydrogen bonds strongly enhance the binding ability between TpPa-SO\textsubscript{3}Na and NOR.

To get a better idea of the effect of 1D negatively charged nanochannels in NOR removal, the TpPa COF without the sulfonate group was prepared for comparison (Figure S16).\textsuperscript{29} Similarly, 10 mg of TpPa COF was immersed in 20 mL of NOR solution (10 mg L\textsuperscript{-1}; and pH 7.0), and we could find that only 1% of NOR were absorbed, suggesting that the absence of sulfonate sites in the network led to the poor NOR uptake efficiency (Figure 5b). TpPa-SO\textsubscript{3}Na with uniform 1D negatively charged channels exhibited a higher adsorption efficiency than the TpPa COF. The above results show that the negatively charged nanochannels are indispensable for fast and efficient positively charged organic pollutant adsorption from water.\textsuperscript{17,42}

On the basis of these FTIR, XPS, and confirmatory adsorption experiments, a possible adsorption mechanism for the removal of NOR is proposed and described in Figure 6. The synergetic electrostatic interaction and charge-assisted adsorption, 4-nitrophenol (4-NP) containing only a hydrogen donor (hydroxyl) was tested. As demonstrated in Figure S15, 4-NP was hardly adsorbed by TpPa-SO\textsubscript{3}Na, which showed as low as 2% of adsorption efficiency even after 2 h, implying that the individual hydrogen-bonding effect was not as dominant as expected in the adsorption process because of the lack of charged binding sites. The synergetic electrostatic interaction and charge-assisted hydrogen bonds strongly enhance the binding ability between TpPa-SO\textsubscript{3}Na and NOR.
2.7. Selective Adsorption and Separation. The adsorption and separation of hydrophobic organic pollutants are critically important due to serious environmental problems. The adsorption and separation are highly dependent on the porous structures, that is, the pore size and pore environment.\(^\text{47-51}\) Compared with other separation materials, due to the capacity to regulate their pore size and chemical functionalities, MOFs and COFs have received increasing attention in adsorption and separation. MOFs have limitations such as poor chemical stability and interpenetrating channels in the separation of dyes.\(^\text{47}\) COFs overcome the limitations of chemical instability in aqueous and organic and strongly acidic or alkaline media compared with MOFs.\(^\text{13}\) Meanwhile, in 2D COFs, the 1D pores are open and free of interpenetration.\(^\text{37,50}\)

Owing to the availability of functional groups and design of pore size, a pore-surface engineering and skeleton design strategy offers a powerful tool to broaden the diversity of porous structures of COFs in adsorption and separation fields, thus enabling the screening of impact of porous structures on specific organic pollutants.\(^\text{37,47,50}\) Effective selective separation of specific molecules can be achieved based on different interactions between molecules and functional nanochannels.

To demonstrate the charge-selective separation, we treated TpPa-SO\textsubscript{3}Na with various dye molecules, including positively charged MB, positively and negatively charged methyl red (MR), neutral \textit{p}-benzoquinone (\textit{p}-BQ), and negatively charged calcine (CAL) (Figure S17). As shown in Figure 7a, MB was completely adsorbed in 10 min by TpPa-SO\textsubscript{3}Na, MR was removed by 85% (Figure 7b), while CAL was hardly adsorbed at all even after 2 h (Figure 7c). Neutral \textit{p}-BQ was also hardly adsorbed by TpPa-SO\textsubscript{3}Na, which showed as low as 2% of adsorption. \textit{p}-BQ molecules were small enough for entry, the uptake capacity of neutral \textit{p}-BQ was low because of the absence of electrostatic interaction between TpPa-SO\textsubscript{3}Na and \textit{p}-BQ. Therefore, electrostatic interactions appeared to dominate the adsorption, which was conducive to specific target pollutant removal.

To further test the charge separation effect, TpPa-SO\textsubscript{3}Na was utilized in a column experiment. The decrease of the UV spectra after the column treatment suggested that the dye mixture was completely separated with a sharp decrease of MB concentration (Figure 7d). The concentration change was 2 and 100% for CAL and MB (Figure 7d), respectively, suggesting the effective separation of the two molecules. However, when treated with TpPa, a poor separation selectivity toward CAL and MB was observed under the same conditions (Figure S19), suggesting that the negatively charged nanochannels play a critical role. Experiments show that the pore environment is essential to cause interactions between pores and guest molecules because the surfaces form the interface that interacts with guests.

We then treated TpPa-SO\textsubscript{3}Na with dye molecules including CV and Alcian blue 8GX (AB8GX) (Figure S17), which have different molecular dimensions and are positively charged, to further confirm the confinement effect of charged nanochannels in selective separation. MB was completely removed in 10 min with TpPa-SO\textsubscript{3}Na, while CV and AB8GX did not exhibit a noticeable change after 95% and 16% adsorption, respectively, for the same time period (Figure 8a,b). The size-dependent separation of dye molecules can be attributed to the effect of the nanochannel structure. In TpPa-SO\textsubscript{3}Na, the 1D pores are open and accessible only from the top and bottom sides of the 2D layers, and they are free of interpenetration. TpPa-SO\textsubscript{3}Na has a uniform and persistent hexagonal shape that enables accurate size recognition.\(^\text{37}\) As displayed in Table S5, the size of AB8GX is larger than the accessible nanochannel diameter of TpPa-SO\textsubscript{3}Na, but the size of MB fits the nanochannel diameter of TpPa-SO\textsubscript{3}Na, leading to size-exclusive behaviors. The molecular size of CV is close to the nanochannel width of TpPa-SO\textsubscript{3}Na. The positive charge of CV assists considerably in the selective adsorption when the molecular size approaches the nanochannel diameter of the

![Figure 6. Proposed mechanism for the removal of NOR by TpPa-SO\textsubscript{3}Na.](image)

![Figure 7. UV absorption spectra of aqueous MB (a), MR (b), and CAL (c) treated with TpPa-SO\textsubscript{3}Na at different intervals.](image)

![Figure 8. UV absorption spectra of aqueous CV (a) and AB8GX (b) treated with TpPa-SO\textsubscript{3}Na at different intervals.](image)
charged COF. Results show that selective adsorption can be specifically tuned by introducing functional sites and modifying their pore size. This would generate a high degree of control over host–guest interactions, improving the adsorptive selectivity and promoting the separation processes.

3. CONCLUSIONS
In summary, an anionic covalent organic framework was synthesized through a green two-in-one synthesis strategy with autocatalytic imine formation. The as-prepared TpPa-SO3Na has ultrafast adsorption kinetics and allows molecular separation on the basis of sulfonate functionalization of nanochannels. Our work can greatly promote the green manufacturing and investigation of anionic COFs with different kinds of binding sites to remove hydrophilic pollutants, further broadening the application of COFs as flexible and tunable materials for wastewater treatment and real-time separation, to cope with challenges of sustainability in the field of chemical and environmental protection technology.

4. EXPERIMENTAL SECTION
4.1. Synthesis of TpPa-SO3Na. Briefly, 0.3 mmol of 1,3,5-triformylphloroglucinol (Tp) and 0.45 mmol of 2,5-diaminobenzenesulfonic acid (Pa-SO3H) were added to 5 mL of mesitylene and 1,4-dioxane mixture (4:1, v/v). Subsequently, the mixture was ultrasonicated for 20 min to form a homogeneous solution. Afterward, 1 mL of 5 M NaOAc was added to the mixture dropwise at room temperature, and then it was flash-frozen under liquid N2. The reaction tube was sealed and then heated under 120 °C for 72 h. Precipitates with red color were successfully obtained and then washed successively with water and tetrahydrofuran five times. Finally, the product was dried at 120 °C under vacuum for 12 h to yield TpPa-SO3Na as a red-colored powder (90% yields). Synthesis of TpPa followed the same process, except that 2,5-diaminobenzenesulfonic acid was replaced by p-phenylenediamine.

4.2. Adsorption Experiments. Norfloxacin (NOR), ciprofloxacin (CIP), enrofloxacin (ENR), tetracycline hydrochloride (TC), methylene blue (MB), and crystal violet (CV) were dissolved in deionized water to obtain the stock solutions (0.5 g L−1). To study the adsorption kinetics, 60 mg of TpPa-SO3Na was added to 100 mL of the target pollutant solution (10 mg L−1) at pH 7.0 for 30 min. After being shaken for different time intervals, 0.5 mL of the solution sample was collected and immediately filtered by a 0.45 μm filter. The concentrations of NOR, CIP, ENR, and TC were determined by high-performance liquid chromatography (HPLC) with an ultraviolet (UV) detector. The concentrations of MB and CV were measured by UV−vis absorption spectroscopy. During the adsorption processes, the pH value of the solution was adjusted using NaOH or HCl solutions (0.1 M). For the regeneration experiments, the used adsorbents were added into the HCl solution (0.1 M). After desorbing for 10 min, the adsorbent was centrifuged with a speed of 8000 rpm for 5 min. Finally, the adsorbent was washed with deionized water and dried for reuse.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04904.

Preparation and characterization of TpPa-SO3Na and TpPa COFs; the sorption isotherm models; adsorption kinetics models; adsorption properties; and adsorption mechanism (PDF)

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Notes
The authors declare no competing financial interest.

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