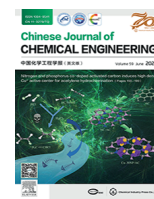




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Synthesis of porous carbon nanomaterials and their application in tetracycline removal from aqueous solutions

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ABSTRACT

The low-cost and efficient elimination of tetracycline from wastewater and to decrease the concentration in soils, sediments, rivers, underground water, or lakes are crucial to human health. Herein, three-dimensional porous carbon nanomaterials were synthesized using glucose and NH_4Cl by sugar-blowing process at 900°C and then oxidized under air atmosphere for surface functional group modification. The prepared 3D porous carbon nanomaterials were applied for the removal of tetracycline from aqueous solutions. The sorption isotherms were well simulated by the Langmuir model, with the calculated sorption capacity of $2378\text{ mg}\cdot\text{g}^{-1}$ for C-450 at $\text{pH} = 6.5$, which was the highest value of today's reported materials. The porous carbon nanomaterials showed high stability at acidic conditions and selectivity in high salt concentrations. The good recycle ability and high removal efficiency of tetracycline from natural groundwater indicated the potential application of the porous carbon nanomaterials in natural environmental antibiotic pollution cleanup. The outstanding sorption properties were attributed to the structures, surface areas and functional groups, strong interactions such as H-bonding, π - π interaction, electrostatic attraction, etc. This paper highlighted the synthesis of porous carbon nanomaterials with high specific surfaces, high sorption capacities, stability, and reusability in organic chemicals' pollution treatment.

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1. Introduction

With the fast development of agriculture, industry, economy and human life quality, large amounts of organic pollutants are inevitably released into the natural environments, although the wastewater is treated strictly before it is discharged into rivers, underground or lakes [1]. Tetracycline, widely used in animal husbandry and human disease treatment, is frequently presented in multi-environmental systems, and thereby causes the safety of antibiotic resistance genes [2]. The efficient elimination of tetracycline from wastewater and to decrease the concentration in soils, sediments, rivers, underground water, or lakes are crucial to human health [3]. In the last decade, large amounts of research works are focused on the elimination of tetracycline through catalytic degradation or sorption strategies [4–6].

Liang *et al.* [7] synthesized $\text{NiAl}_2\text{O}_4/\text{g-C}_3\text{N}_4$ composites and applied for photocatalytic degradation of tetracycline under visible light irradiation. About 90% tetracycline was degraded within 2 h, which was attributed to the high charge transfer and electron-hole

separation. Perumal *et al.* [8] synthesized $\text{Ag}_2\text{CO}_3/\text{BiOBr}/\text{CdS}$ composites and applied for photocatalytic degradation of tetracycline. The high visible light absorption, efficiency $\text{e}^- - \text{h}^+$ pairs separation and charge transfer resulted in the high degradation efficiency of tetracycline, *i.e.*, 99% tetracycline degradation was achieved in 70 min. Wang *et al.* [9] applied $\text{Fe}_3\text{O}_4/\text{PANI-p}$ to activate peroxy-monosulfate for the degradation of tetracycline, and found that 89% tetracycline was degraded in 90 min, which was mainly attributed to the singlet oxygen, superoxide radicals, hydroxyl radicals and sulfate radicals. Wang *et al.* [10] synthesized TCPP/BMO heterojunction catalyst and applied for the photocatalytic degradation of tetracycline. The interfacial interaction between BMO and TCPP promoted the separation of $\text{e}^- - \text{h}^+$ pairs and charge carriers, which were favorable for the high photocatalytic properties. Generally speaking, the photocatalytic degradation of tetracycline is mainly attributed to the properties of the catalysts such as the high visible light absorption, efficient generation and separation of $\text{e}^- - \text{h}^+$ pairs, high adsorption of organic molecules and fast mass transfer *etc.* [11]. However, it is not applicable for high concentrations of organic pollutants and the degradation mechanism is still unclear although the degradation mechanism can be postulated from quenching tests and computational simulation [12–16]. The

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intermediates are very difficult to be on-line measured, and the degradation processes are still “black-box”.

Sorption technique is applied extensively to remove organic pollutants because of its simple operation and in large scale. Generally, the sorption ability of organic pollutants is dependent on the properties of adsorbents and solution conditions. Yukhajan *et al.* [17] applied porous phosphate-carbonate composites for the removal of tetracycline from wastewater, and achieved the sorption capacity of 119 mg·g⁻¹. They concluded the interaction mechanisms of H-bonding and surface complexation from batch and spectroscopy analysis. Jiang *et al.* [18] applied FeCo-MOF-biochar for the removal of tetracycline from solutions, and achieved the sorption capacity of 909 mg·g⁻¹, much higher than most today's materials. Yin *et al.* [19] synthesized MOF-based electrocatalytic membranes and applied for the removal of tetracycline under low current density. The membranes could remove > 99% tetracycline at the current density of 0.01 mA·cm⁻², which was mainly attributed to the ·O₂⁻ and ·OH active free radicals. Yadav *et al.* [20] synthesized Fe₃O₄-MIL101 chitosan composites and used for the removal of tetracycline, and found that > 99% tetracycline was removed from solutions with the sorption capacity of 45 mg·g⁻¹. The H-bonding, π - π interaction, and electron attraction were the main mechanisms for the uptake of tetracycline to the composites. Zhao *et al.* [21] prepared biochar at 500 and 700 °C, respectively, and applied for tetracycline removal from wastewater. The sorption capacities were calculated to be 5.4 mg·g⁻¹ for BC-500 and 5.8 mg·g⁻¹ for BC-700, and the interaction was determined as π - π interaction and hydrophobic interaction. It is a little strange that the biochar had very low sorption capacity as compared to other kinds of biochar, which may be attributed to the poor surface groups and weak π - π interactions. Liu *et al.* [22] activated pharmaceutical sludge by NaOH to prepare biochar with micropore structures, and applied for tetracycline removal from solutions. The biochar achieved the sorption capacity of 380 mg·g⁻¹ and the high sorption ability was attributed to H-bonding, π - π interaction and pore filling in the micropores. Li *et al.* [23] prepared biochar and activated with KHCO₃ to enlarge pore sizes and to increase surface areas, which significantly increased the sorption capacity of biochar (451 mg·g⁻¹, about 40 times higher than that of untreated biochar). The pore filling effect and π - π conjugation were the main mechanisms for the high sorption capacity of KHCO₃ activated biochar. From the abovementioned references, one can see that the sorption mechanisms of tetracycline are relatively clear. However, the sorption capacities of tetracycline on different nanomaterials are quite different, which is mainly attributed to the properties of the nanomaterials such as surface areas, surface groups and porous structures, and the solution conditions such as pH, temperature, coexisting organic/inorganic chemicals *etc.* [24,25].

Adsorption method is widely used in the removal of pollutants [26,27]. Carbon-based nanomaterials have attracted multidisciplinary interests, especially in the preconcentration and separation of pollutants from large volumes of solutions because of their excellent properties such as high sorption ability, high stability, reusability and selectivity [28–30]. However, the sorption capacities of tetracycline were not high enough for most reported materials, which restricted the efficient elimination of tetracycline from natural wastewater. The sorption capacity is mainly dependent on surface areas, surface groups and active sites to bind organic molecules, the structures to form strong complexes or interactions. The high cost of some nanomaterials also limits their application in real works. Thereby, it is urgent to find nanomaterials with low cost and synthesis in large scale. In this work, we reported a 3D porous carbon nanomaterials with high surface areas, abundant functional groups and high sorption capacity for tetracycline, and the interaction mechanism was discussed in detail. The application of the 3D

porous carbon nanomaterials for the real applications in the elimination of tetracycline from natural water environment was also evaluated.

2. Materials and Methods

2.1. Materials and chemicals

The glucose (C₆H₁₂O₆), NaCl, ammonium salt (NH₄Cl), and tetracycline (C₂₂H₂₄N₂O₈) were derived from Aladdin Reagent Co. (China), and used directly without any treatment. The Milli-Q water (18.2 M Ω ·cm⁻¹) was used in the experiments.

2.2. Synthesis of 3D porous carbon nanomaterials

The 3D porous carbon nanomaterial was synthesized by a modified method of previous work [31]. Generally, the glucose was mixed with ammonium salt with mass ratio of 1:1, and heated to 250 °C with the heating rate of 4 (°)·min⁻¹ at argon atmosphere condition, and kept for 1 h at 250 °C. Then the mixture was heated to 900 °C and kept the temperature for 3 h in the tube furnace. Then the temperature was cooled down to room temperature and the derived foam-like product was named as C. The derived C was then post-oxidized at air atmosphere condition at the temperatures of 350, 400 and 450 °C, respectively, for 6 h, and thus achieved porous carbon nanomaterials were named as C-350, C-400 and C-450, respectively.

2.3. Characterization

The morphologies of the prepared materials were observed using scanning electron microscopy (SEM, ZEISS Gemini 300, Germany). Transmission electron microscopy (TEM) images were recorded on a JEM-F200 transmission electron microscope (JEOL, Japan). X-ray photoelectron spectroscopy (XPS) analyses were performed on ESCALAB 250 (Thermo, USA), fitted with a monochromated Al K α X-ray source. The surface functional groups were characterized by Fourier transform infrared spectroscopy (FTIR) by IRTTracer-100 spectrophotometer (SHIMADZU, Japan). The N₂ adsorption-desorption isotherms were measured at -196 °C using HONYEO TriStar II apparatus (micromeritics, USA). The water contact angles were measured using a contact angle goniometer by sessile drop method (KRUS, DSA25S, Germany).

2.4. Tetracycline sorption experiments

The tetracycline solution with initial concentration of 600 mg·L⁻¹ was prepared with Milli-Q water, and then used in the batch sorption experiments. The experiments were carried out at 25 °C, and the concentration of tetracycline was measured at the wavelength of 357 nm. The sorption percentage (%) and sorption amounts of tetracycline by the porous carbon nanomaterials were calculated by the following equations:

$$\text{Removal} = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

where C_0 and C_e are the initial and final concentrations of tetracycline (mg·L⁻¹), respectively. V (ml) is the volume of solution, and m (mg) is the mass of porous carbon nanomaterials. The porous carbon nanomaterials were difficult to be separated from solution using centrifugation technique. Thereby, 0.22 μ m membrane was applied to separate the porous carbon nanomaterials from the aqueous suspensions in the batch experiments.

The sorption isotherms were simulated with Langmuir and Freundlich models, and the kinetic sorption of tetracycline were simulated by pseudo-first order kinetic and pseudo-second order kinetic models [32]:

$$\text{Langmuir model: } q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

$$\text{Freundlich model: } q_e = K_F C_e^{\frac{1}{n}} \quad (4)$$

$$\text{Pseudo-first order kinetic model: } \ln(q_e - q_t) = \ln q_e + K_1 t \quad (5)$$

$$\text{Pseudo-second order kinetic model: } \frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

where q_m , q_t and q_e are the sorption capacity ($\text{mg} \cdot \text{g}^{-1}$), K_L ($\text{L} \cdot \text{mg}^{-1}$) is the Langmuir model constant, K_F ($\text{L} \cdot \text{g}^{-1}$) and n are the Freundlich model constants, t (min) is the time, K_1 (min^{-1}) is the pseudo-first order kinetic constant and K_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) is the pseudo-second order kinetic constant.

3. Results and Discussion

3.1. Characterization of porous carbon nanomaterials

Fig. 1 shows the SEM and TEM images of the prepared C, C-350, C-400 and C-450 samples. One can see that the synthesized C has porous structure with high relative irregular pore surface. After post-oxidation at 350 and 400 °C, the C-350 and C-400 still have the porous structures with highly rough, which provide more sorption sites. Such intricate network structures with mesh pores are favorable for the binding of tetracycline because of the abundant binding sites and high specific surface areas. However, after post-oxidation at 450 °C, the porous carbon nanomaterial is a little more compacted, and the porous structure and intricate network are not obvious as compared to the other three samples. At high temperature of post-oxidation process, the oxidation may result in the collapse of the micropore structures and the micropore becomes smaller. In order to find the inner pore structure of C-450, the TEM images of C-450 are also shown in Fig. 1. Although the intricate network structures were not found in SEM image, it is clear from the TEM image that the C-450 is porous structure, which facilitates the diffusion of tetracycline to the inner pores of C-450.

FTIR spectroscopy was applied to characterize the surface functional groups of the prepared samples. In the FTIR spectra (Fig. 2), one can see that no obvious characteristic peaks in the FTIR spectrum of C sample, suggesting little functional groups on the surface of C sample, which is related to the synthesis of the sample under argon atmosphere conditions. After post-oxidation, it is obviously that O-containing functional groups are introduced to the porous carbon nanomaterials. The characteristic absorption peak at $\sim 3400 \text{ cm}^{-1}$ is corresponding to C—O—H stretching vibrations [33]. The peaks at $\sim 1740 \text{ cm}^{-1}$ corresponds to C=O stretching vibration of carbonyl or carboxyl groups [34]. The peak at about 1200 cm^{-1} is assigned to the vibration of C—O groups, suggesting the formation of oxygen-containing groups, such as hydroxyl groups on basal layers or the epoxide C—O vibration etc. [35]. From the FTIR characterization, one can see that oxygen-containing groups are generated and rise with the increase of post-oxidation temperature, which may be favorable for the formation of surface complexes with pollutant molecules.

Fig. 3 shows the water contact angles of four samples, which show that the four samples are hydrophilic with the contact angles of 70.1° for C-350, 46.0° for C-400 and 35.0° for C-450. It is necessary to note that the C sample is totally hydrophilic and the contact angle is not detected, i.e., 0° . The contact angle decreased with the

increase of post-oxidation temperature, suggesting the implantation of oxygen-containing groups improved the hydrophilic properties of the porous carbon nanomaterials. However, it is necessary to note that the porous carbon nanomaterial was totally hydrophilic before the post-oxidation treatment. The hydrophilic properties of the prepared porous carbon nanomaterials are beneficial for the transfer of the organic molecules from aqueous solution to nanomaterial surface, feasible for the binding to nanomaterials.

The surface areas and pore size distributions were characterized by N_2 BET technique. Fig. 4(a) shows the N_2 adsorption–desorption isotherms, and it is clear to see that the samples of C, C-350 and C-400 had high slope at low pressure and then the adsorption of N_2 reached the peak with the increase of relative pressure. The type-I slope suggested the presence of micropore structures [36]. The N_2 adsorption–desorption isotherms of C-450 are quite different from those of the other three samples, suggesting that C-450 had quite different microstructure as comparing to the other three samples. Fig. 4(b) showed the main peak centered at $\sim 2.5 \text{ nm}$ for the three samples, and non-main peak position was found in C-450. The N_2 BET surface areas of the four samples were calculated to be $1234.6 \text{ m}^2 \cdot \text{g}^{-1}$ for C, $1230.8 \text{ m}^2 \cdot \text{g}^{-1}$ for C-350, $1467.5 \text{ m}^2 \cdot \text{g}^{-1}$ for C-400 and $633.9 \text{ m}^2 \cdot \text{g}^{-1}$ for C-450, which are in good agreement with the SEM analysis. The high BET surface areas are favorable for the interaction of tetracycline on the porous carbon nanomaterials.

XPS spectroscopy was employed to recognize the elements of C and N on the surfaces of four samples (Fig. 5). The C 1s XPS spectrum of C contained the peaks of C=C/C—C bonds (284.7 eV), C=N/C—N bonds (286.0 eV) and C=O bonds (287.9 eV). And the C 1s spectra of C-350, C-400 and C-450 samples were very similar to that of C sample, except for the increase of the peak at 287.9 eV and the decrease of the peak at 286.0 eV due to post-oxidation at high temperature. Three types of N-containing functional groups were found in C, C-350, C-400 and C-450, including pyridinic-N (398.4 eV), pyrrolic-N (399.8 eV) and graphitic-N (401.1 eV). The results of XPS showed that the N content gradually decreased with the increase of post-oxidation temperature. Correspondingly, the content of graphitic-N significantly decreased, accompanied by decreasing content of pyridinic-N and pyrrolic-N.

3.2. Effect of contact time

Effect of contact time on tetracycline sorption is crucial for the elimination of tetracycline from wastewater. The shorter time to reach equilibration or to achieve high sorption capacity, the more economic for real applications and treatment of wastewater. Fig. 6 shows the sorption of tetracycline on the four samples as a function of contact time. It is clear that the sorption of tetracycline on C, C-350 and C-400 reached equilibration in about 3–4 h, and on C-450 reached equilibration in about 6–7 h. The sorption amounts of tetracycline were calculated to be $175 \text{ mg} \cdot \text{g}^{-1}$ on C, $465 \text{ mg} \cdot \text{g}^{-1}$ on C-350, $535 \text{ mg} \cdot \text{g}^{-1}$ on C-400 and $690 \text{ mg} \cdot \text{g}^{-1}$ on C-450 at $\text{pH} = 6.5$ and initial concentration of $20 \text{ mg} \cdot \text{L}^{-1}$. The relative slow sorption of tetracycline may be attributed to the large tetracycline molecular size because the diffusion of tetracycline from solution to the micropores of the porous carbon is resisted. The sorption capacity of tetracycline on C-450 was much higher than those on the other three samples, which was consistent with the hydrophilic properties of C-450. The highest hydrophilic ability of C-450 was related with the post-oxidation process that had implanted the most oxygen-containing groups on C-450 than those on the other three samples. The kinetic sorption data were simulated by pseudo-first order kinetic and pseudo-second order kinetic models, respectively. The experimental data were better simulated by pseudo-second order kinetic model, suggesting that the sorption

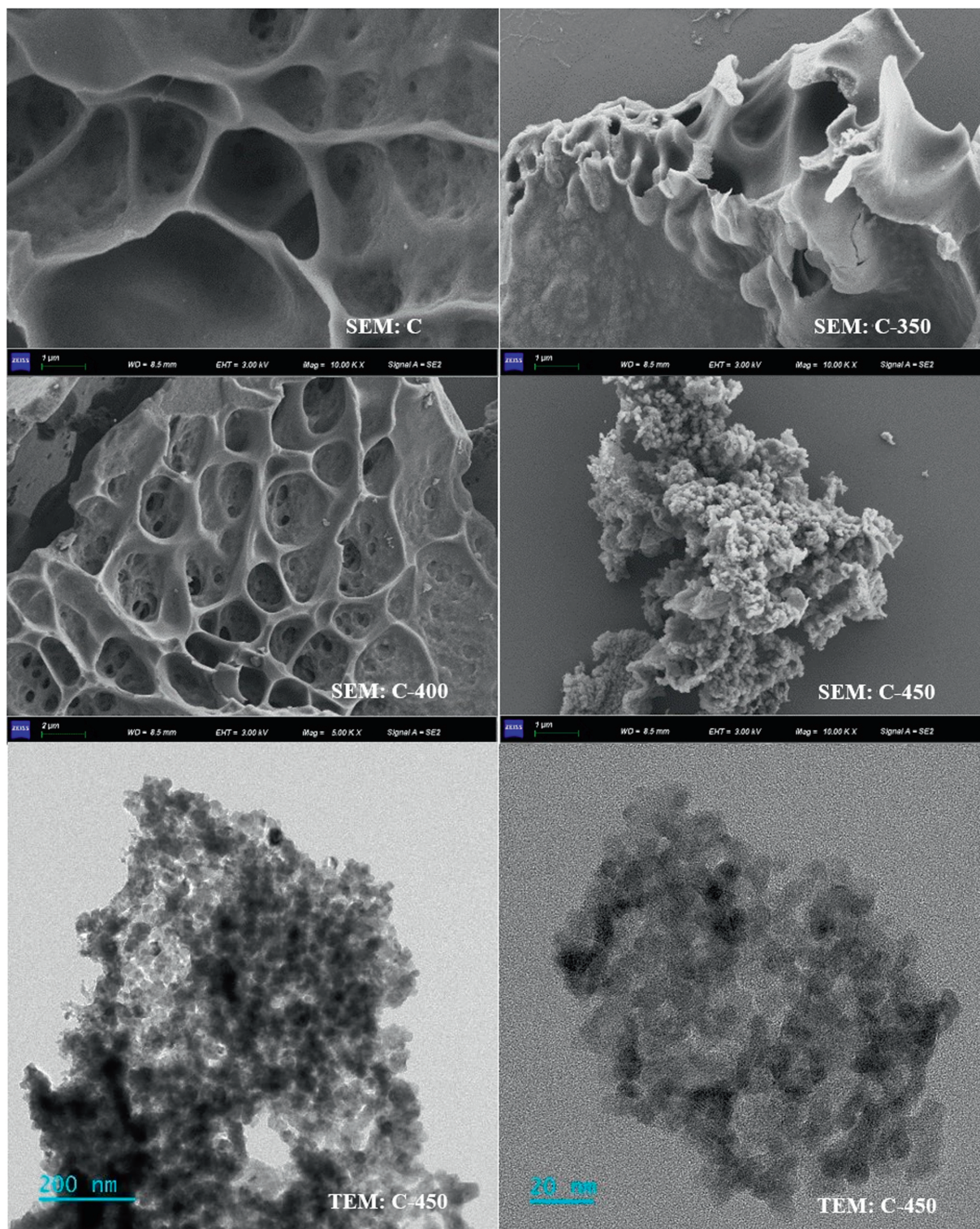


Fig. 1. SEM images of C, C-350, C-400 and C-450 samples and TEM images of C-450.

of tetracycline was mainly dominated by chemical sorption together with physical sorption. After post-oxidation, the sorption of tetracycline increased obviously as compared with C sample, suggesting the modification of porous carbon nanomaterials enhanced the interaction of tetracycline through the strong surface complexation with oxygen-containing groups. The sorption ability increased with the increase of post-oxidation temperature, which was related to the increase of oxygen-containing groups' amounts on the porous carbon nanomaterials.

3.3. Effect of solution pH

Fig. 7 shows the effect of solution initial pH values on the removal of tetracycline from solution to the four samples. It is obvious that the sorption decreased with the increase of solution pH values. The surface charges, active sites and species of tetracycline are related to solution pH values. The surface charge of porous carbon nanomaterials is negatively charged because of the ionization of the oxygen-containing carboxylic or hydroxyl groups

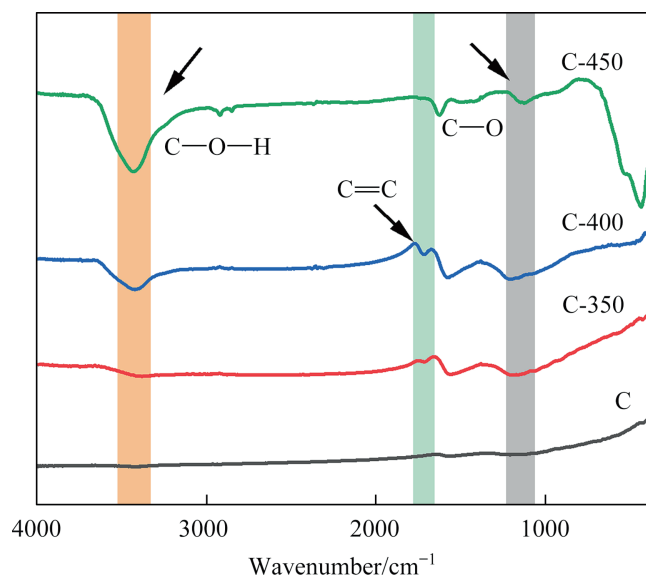


Fig. 2. FTIR spectra of C, C-350, C-400 and C-450 samples.

[37]. At low pH values, the tetracycline is positively charged because of protonation reaction, which is favorable to bind on the negative surface charged porous carbon nanomaterials. With increase of pH, the deprotonation reaction results in the positive surface charge, which results in the mutual repulsion between the negative charged tetracycline and electronegative porous carbon nanomaterials. The sorption of tetracycline by the four porous carbon nanomaterial samples is still high enough at $\text{pH} < 9$ as compared to most reported nanomaterials [17,18,23]. For natural wastewater environment, the pH is generally higher than 5 and lower than 9. The removal of tetracycline is weakly affected by the pH values in this pH range. Thereby, the prepared porous carbon nanomaterials are applicable for the removal of tetracycline from natural wastewater.

3.4. Sorption isotherms

Sorption isotherms are helpful to evaluate the sorption capacities of the porous carbon nanomaterials. The sorption properties of the porous carbon nanomaterials were evaluated by the sorption isotherms of tetracycline at $\text{pH} = 6.5$ and $T = 25^\circ\text{C}$ (Fig. 8). The sorption isotherms of tetracycline on C-350, C-400 and C-450

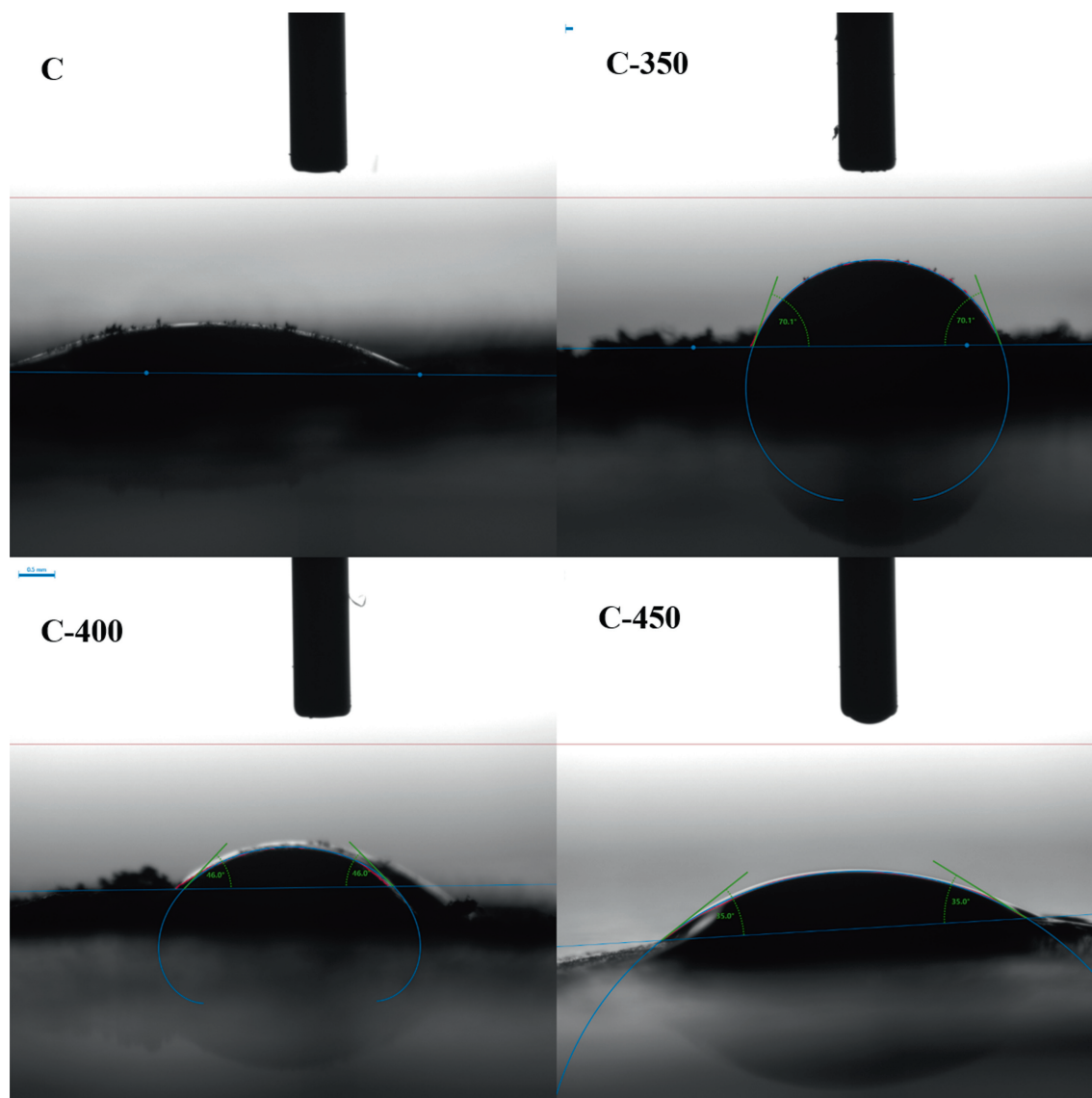


Fig. 3. Contact angle measurements of C, C-350, C-400 and C-450 samples.

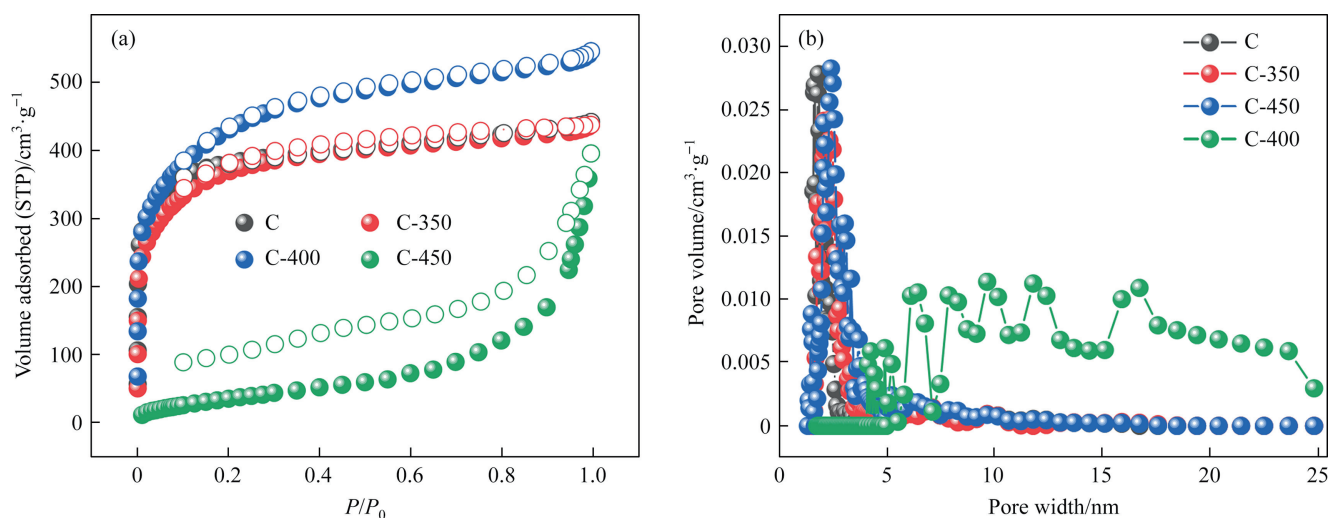


Fig. 4. The N_2 adsorption-desorption isotherms of four samples (a) and the corresponding pore size distribution of four samples calculated from NLDFT simulation (b).

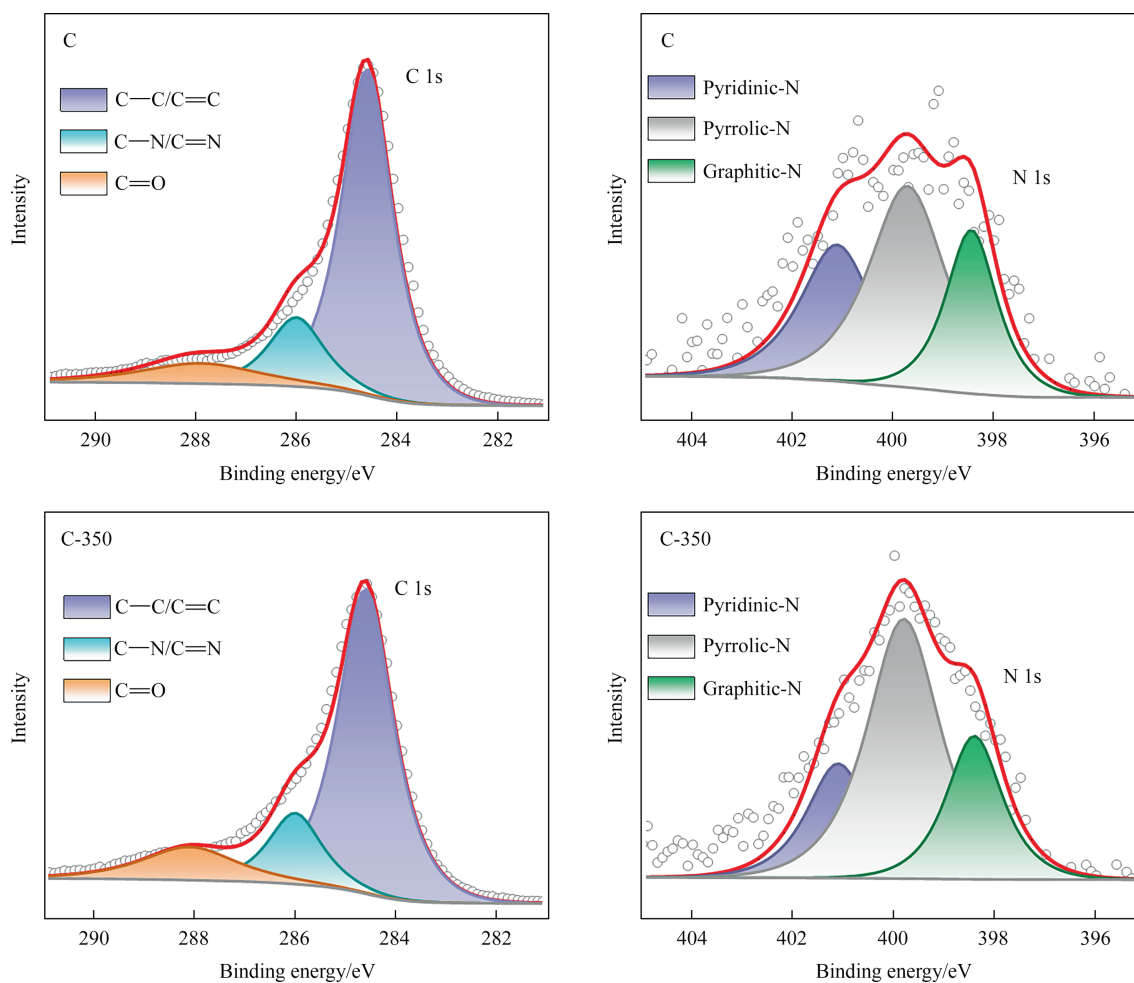


Fig. 5. High XPS resolutions of C 1s and N 1s on the surfaces of four samples.

samples are higher than that on C sample, suggesting that the post-oxidation increases the sorption capacities significantly. Tetracycline sorption isotherms followed the sequences of C-450 > C-400 > C-350, the same trend with the results of hydro-

philic values and the sorption speed, which further confirmed the fact that the post-oxidation treatment had introduced the hydroxyl and carboxyl functional groups to the surfaces of the porous carbon nanomaterials, and the functional groups can interact with the

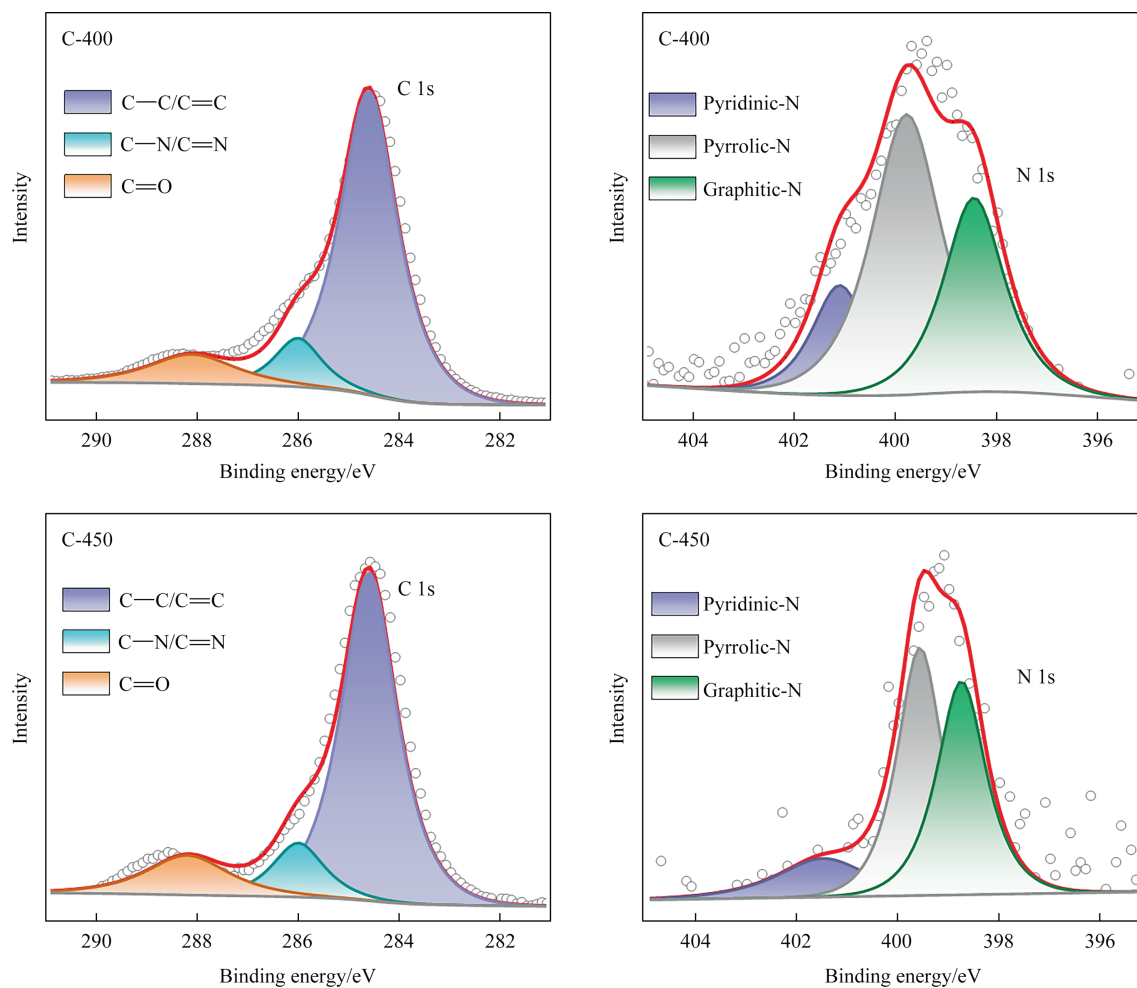


Fig. 5 (continued)

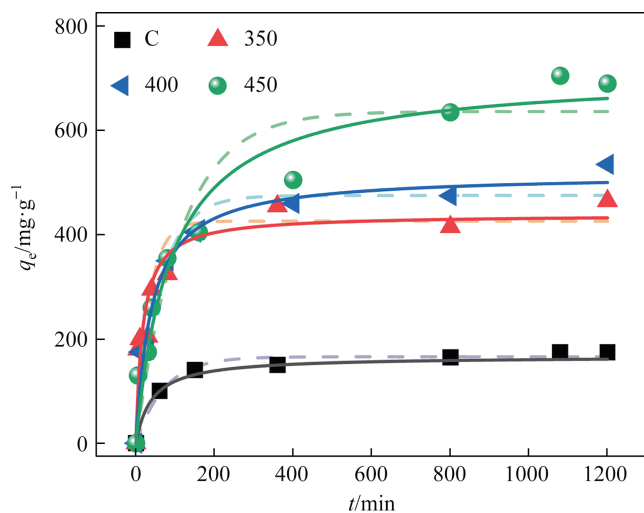


Fig. 6. Effects of contact time on the sorption of tetracycline on C, C-350, C-400 and C-450 samples ($\text{pH} = 6.5$, $[\text{tetracycline}]_{\text{initial}} = 20 \text{ mg}\cdot\text{L}^{-1}$, $T = 25^\circ\text{C}$. The solid line is the pseudo-second order kinetic model simulation, and the dash line is the pseudo-first order kinetic model simulation).

—OH and —CH₃ of tetracycline molecule by hydrogen-bonding and electrostatic attraction [38]. In addition, higher hydrophilicity of C-450 in turn promoting the contact of the carbons with the

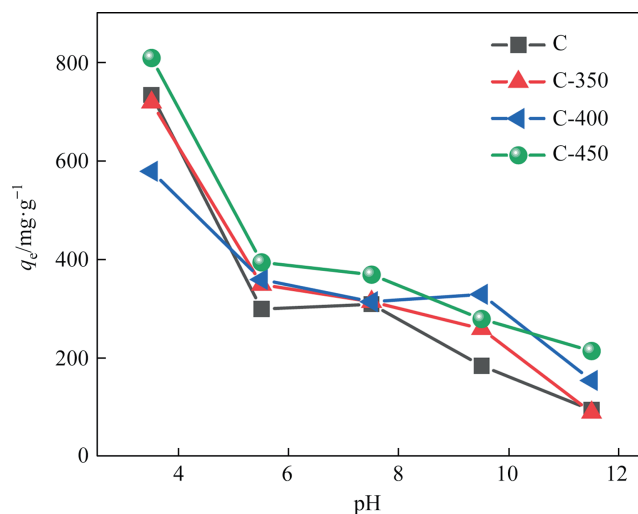


Fig. 7. Effects of pH on tetracycline sorption to C, C-350, C-400 and C-450 samples ($m/V = 0.02 \text{ g}\cdot\text{L}^{-1}$, $[\text{tetracycline}]_{\text{initial}} = 20 \text{ mg}\cdot\text{L}^{-1}$, $T = 25^\circ\text{C}$).

solution, which therefore leading to a more efficient Tetracycline removal process [39]. Thereby, the O-containing groups on the porous carbon nanomaterials are responsible for the high sorption ability of tetracycline, which is in good agreement with the

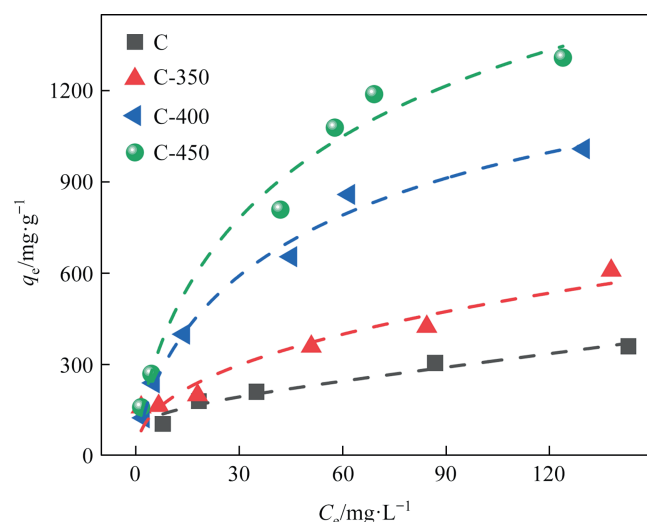


Fig. 8. Sorption isotherms of tetracycline on C, C-350, C-400 and C-450 samples ($m/V = 0.02 \text{ g}\cdot\text{L}^{-1}$, $\text{pH} = 6.5$, $T = 25^\circ\text{C}$. The dash lines are the Freundlich model simulation).

characterization results. The sorption isotherms are better simulated by Freundlich model than Langmuir model, indicating the heterogeneous sorption of tetracycline on the surface of porous carbon nanomaterials. The maximum sorption capacity by C-450 was calculated to be $2378 \text{ mg}\cdot\text{g}^{-1}$ from the Langmuir model simulation. From Fig. 8, it is clear that the amount of tetracycline adsorbed on C-450 reached to $\sim 1300 \text{ mg}\cdot\text{g}^{-1}$, which is still far from the saturation of tetracycline sorption. The value is much higher than those reported on other nanomaterials such as: $370 \text{ mg}\cdot\text{g}^{-1}$ on NaOH treated biochar [22], $119 \text{ mg}\cdot\text{g}^{-1}$ on porous phosphate-carbonate composites [17], $909 \text{ mg}\cdot\text{g}^{-1}$ on FeCo-MOF-biochar [18], $451 \text{ mg}\cdot\text{g}^{-1}$ on KHCO_3 treated biochar [23] etc. From the authors' knowledge, the value is the highest sorption capacity among today's reported materials from published literatures.

3.5. Effect of coexisted cations or anions

In the natural water system, different kinds of foreign cations and anions are generally coexisted. The competition among the coexisted ions and tetracycline on tetracycline sorption should be considered. As C-450 had the highest sorption capacity among the four samples, C-450 was selected to investigate the effect of ionic strength on tetracycline sorption. The effect of competitive

ions on the sorption of tetracycline to C-450 are shown in Fig. 9. In the presence of Na^+ , K^+ , Mg^{2+} or Ca^{2+} ions, one can see that the presence of the cation ions did not affect the sorption of tetracycline obviously. The sorption of tetracycline was not influenced by the concentration of cation ions (1 and $5 \text{ mmol}\cdot\text{L}^{-1}$) either (Fig. 9(a)). The tetracycline is rich of benzene rings, which can interact with the porous carbon nanomaterials via π - π interaction. The introduced O-containing functional groups such as $-\text{OH}$, $\text{C}-\text{O}$, $-\text{COOH}$, can also form strong complexes with tetracycline. The interaction of tetracycline with porous carbon nanomaterials is mainly through H-bonding, π - π interaction and electrostatic attraction, which are not affected by cation ions.

In the presence of NO_3^- , SO_4^{2-} or HCO_3^- anion ions, the sorption of tetracycline on C-450 was obviously decreased as compared in the presence of cation ions (Fig. 9(b)). The competition between tetracycline and anions affected the sorption of tetracycline to the porous carbon nanomaterials. At the main time, the anions can form complexes with tetracycline in solutions, which also decreases the sorption of tetracycline. In natural water environment, such anions should be considered. From the above results, one can conclude that the electrostatic interaction contributes the sorption of tetracycline to C-450.

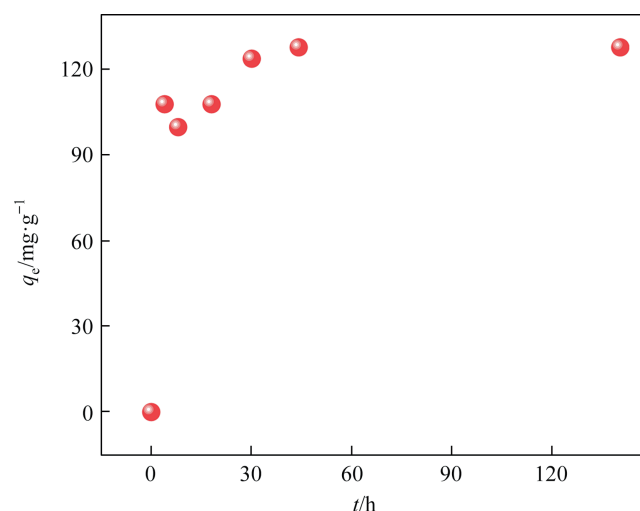


Fig. 10. Efficient removal of tetracycline by C-450 from real ground water ($m/V = 0.01 \text{ g}\cdot\text{L}^{-1}$).

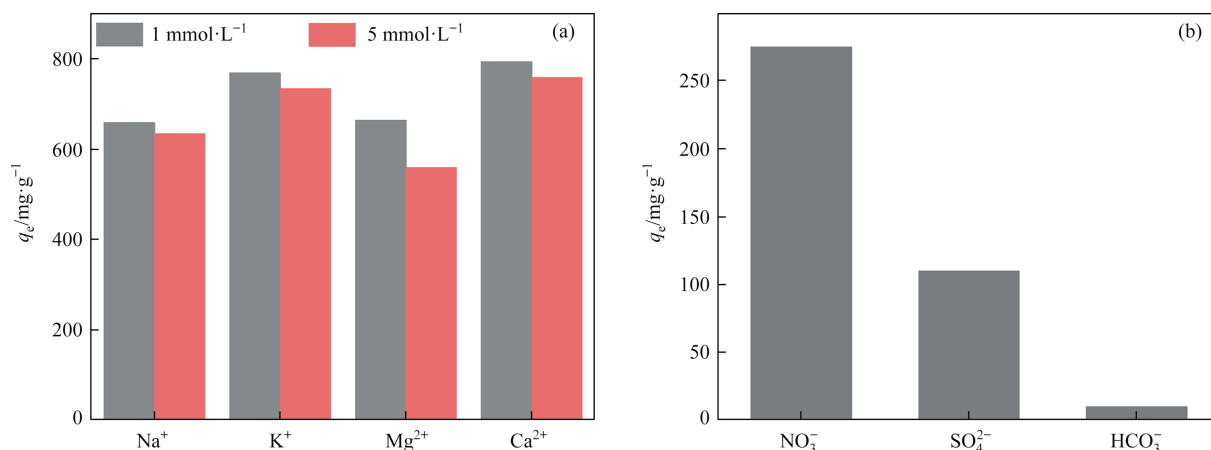


Fig. 9. Effects of different kinds of $1 \text{ mmol}\cdot\text{L}^{-1}$ or $5 \text{ mmol}\cdot\text{L}^{-1}$ cation ions (a) and $1 \text{ mmol}\cdot\text{L}^{-1}$ anion ions (b) on tetracycline sorption to C-450 ($\text{pH} = 6.5$, $T = 25^\circ\text{C}$, $C[\text{tetracycline}]_{\text{initial}} = 20 \text{ mg}\cdot\text{L}^{-1}$).

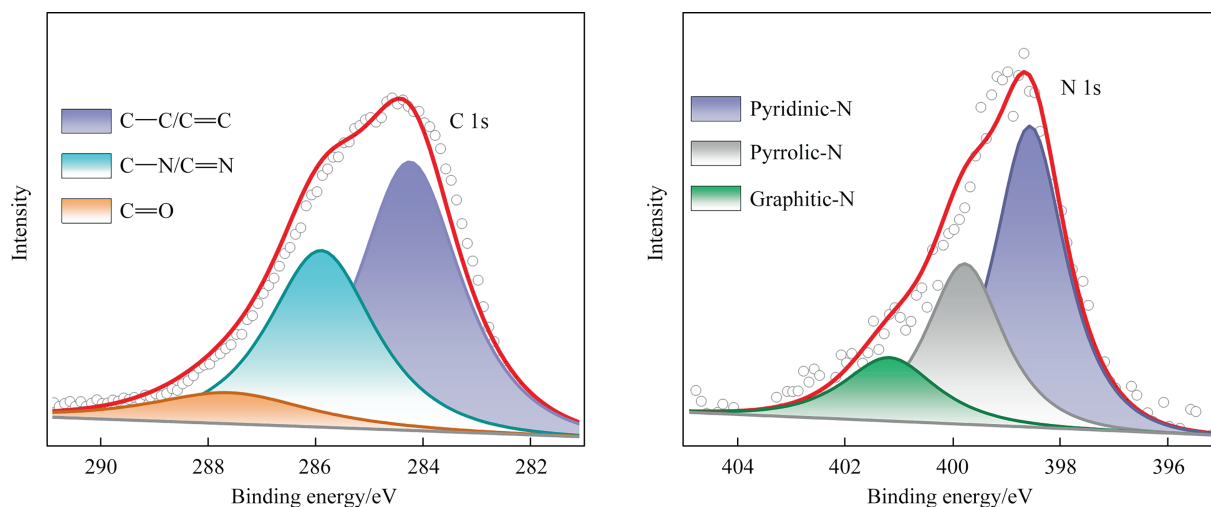


Fig. 11. High XPS resolution spectra of C 1s and N 1s of C-450 after tetracycline adsorption.

The efficient removal of tetracycline from natural ground water is crucial for the real application of the porous carbon nanomaterials. We collected the groundwater from Mentougou county, Beijing, China, and added tetracycline to the groundwater to achieve the initial concentration of $5 \text{ mg} \cdot \text{L}^{-1}$ (the natural concentration of tetracycline in the groundwater was negligible). The sorption of tetracycline to C-450 is quickly to achieve $> 100 \text{ mg} \cdot \text{g}^{-1}$, indicating that the synthesized porous carbon nanomaterials could efficiently remove tetracycline from the groundwater (Fig. 10). Considering the high stability and high removal efficiency, the prepared porous carbon nanomaterials are suitable candidates for the elimination of tetracycline or other kinds of antibiotics from natural water environment.

3.6. XPS analysis after tetracycline adsorption

As shown in Fig. 11, the C 1s spectrum of C-450 after tetracycline adsorption was assigned to three peaks at 284.3, 286.0 and 288.1 eV. The peak belonged to C—C/C=C group of C-450 at 284.6 eV shifted to 284.3 eV, confirming that the π - π interaction participated in tetracycline adsorption [40]. The binding energy of C=O at 288.1 eV of C-450 was slightly shifted due to O-containing moiety as Lewis acid site to combine with N site of tetracycline by H-bonding or π - π interaction [41]. It is the reason that increased tetracycline adsorption performance with the increase of oxygen content caused by post-oxidation temperature. The peaks of N 1s spectrum included pyridinic-N (398.6 eV), pyrrolic-N (399.8 eV) and graphitic-N (401.1 eV), very similar to those of N 1s spectrum of C-450 before adsorption.

4. Conclusions

Porous carbon nanomaterials were synthesized by a simple sugar-blowing process, and then post-oxidized under air atmosphere at different temperature conditions. The oxidized porous carbon nanomaterials had high surface areas and porous structures. The prepared porous carbon nanomaterials had the highest sorption capacity of tetracycline among today's reported nanomaterials, and the interaction was mainly dominated by H-bonding, π - π interaction, electrostatic attraction and strong surface complexation. This work highlighted the simple synthesis of porous carbon nanomaterials and their potential applications in real environmental water pollution cleanup, especially for the antibiotic pollutant treatment.

Data Availability

Data will be made available on request.

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.

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