Removal of Antibiotics from Aqueous Solutions by a Carbon Adsorbent Derived from Protein-Waste-Doped Biomass

Jiamin Yu, Yan Kang, Wenjun Yin, Jinlin Fan, and Zizhang Guo*

ABSTRACT: Antibiotic pollution in water is an urgent environmental problem. A novel carbon adsorbent derived from powdery puFFed waterfowl feather (PPWF)-doped Phragmites australis (PA) was proposed for enhancing the removal of antibiotics from water in this study. Amoxicillin (AMX) and cephalexin (CEX) were selected as typical antibiotics. PPWF-doped (FPAC) and -undoped (PAC) carbon adsorbents were developed to test the adsorption capacities and mechanisms of AMX and CEX. Characterization techniques such as N2 adsorption/desorption, Fourier transform infrared, X-ray diffraction, scanning electron microscopy, elemental analysis, and Boehm titration were used to determine the properties of adsorbents. Results showed that more microporous structure and surface functional groups are exhibited in FPAC compared to PAC. The nitrogen-containing functional groups were introduced in FPAC. Adsorption capacities at different contact times, pH, and initial concentration were investigated by batch experiments. The AMX and CEX maximum adsorption capacities of FPAC are 25.2 and 30.1% higher than those of PAC, respectively. The kinetic data were well represented by the pseudo-second-order model for AMX and CEX adsorption. The equilibrium data agreed well with the Langmuir model for AMX adsorption and the Freundlich model for CEX adsorption. The adsorption mechanism of AMX and CEX was chemisorption, such as electrostatic attraction and covalent bonding.

1. INTRODUCTION
Antibiotics are effective medicines that improve human and animal health and are widely used in medical and aquaculture.1,2 The two common antibiotics amoxicillin (AMX) and cephalexin (CEX) are extensively used in the treatment of bacterial infection and other diseases. It has been reported that about 30–90% of AMX and CEX discharged into the environment through human and animal excrement,3,4 however, they were only partially removed by traditional wastewater treatment plants. Residual antibiotics in the water environment increase the resistance of pathogenic bacteria and pose a great threat to groundwater and surface water; therefore, it remains challenging to remove antibiotics from aqueous solutions. The current methods for removing AMX and CEX are adsorption,5,6 chemical oxidation,7 microbial degradation,8 etc. Among them, adsorption is considered to be an excellent method for treating wastewater containing low concentration of antibiotics because of its high efficiency9 and antitoxic nature.10

The choice of adsorbent is the most critical factor in adsorption. Carbon adsorbents are widely used because they have the advantages of acid and alkali resistance, strong adsorption capacity, and stable properties. Considerable researches11–13 focused on added chemical modifying agents for improving the adsorption capacities of carbon adsorbents for antibiotic adsorption; however, these methods have problems of secondary pollution, high cost, complicated operation, etc. Therefore, a novel protein-waste as a biomass modifier has been proposed in this study, as it protects the environment and is economically favorable.

As a common grass plant, Phragmites australis (PA) is mostly grown in wetlands, and the accumulation of abandoned PA causes blockage of water flow. PA has a high carbon content and is a very suitable material for preparation of a carbon adsorbent.14,15 In modern agriculture, large-scale poultry farming produces a large amount of feather wastes, and only 10–20% of them are used to prepare feed with low utilization and value.16,17 Powdery puFFed waterfowl feather (PPWF) is a common protein waste. As a modifier, it can increase the functional groups of carbon adsorbents. Therefore, PPWF-doped PA was proposed for carbon adsorbent preparation in this study. The prepared adsorbent will have a well-developed
pore structure and abundant surface functional groups, thus having an excellent adsorption removal capacity for antibiotics. The main purposes of this study are: (1) to examine the feasibility of PPWF as a biomass modifier; (2) to explore the properties of prepared carbon adsorbents by N\textsubscript{2} adsorption/desorption, Fourier transform infrared (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), Boehm titration, and elemental analysis (EA); and (3) to investigate the adsorption capacities and mechanisms of AMX and CEX by batch adsorption experiments and characterization results.

2. RESULTS AND DISCUSSION

2.1. Characteristics of Adsorbents. Figure 1 shows the N\textsubscript{2} adsorption/desorption isotherms and crystal structure of PAC and FPAC. As shown in Figure 1a, the adsorbed volume of the two samples had rose very rapidly to a limit at low \( P/P_0 \) and the isotherms exhibited hysteresis loops at high \( P/P_0 \). These two characteristics were consistent with the type I and type IV isotherms; therefore, both PAC and FPAC had a micromesoporous structure. Table 1 lists the Brunauer–Emmett–Teller (BET) surface areas (\( S_{\text{BET}} \)) and pore sizes of adsorbents. As seen, \( S_{\text{BET}} \) and \( V_{\text{tot}} \) of PAC and FPAC were almost equal; however, \( S_{\text{mic}} \) and \( V_{\text{mic}} \) of FPAC (557.7 m\textsuperscript{2}/g and 0.70 cm\textsuperscript{3}/g) were greater than those of PAC (208.1 m\textsuperscript{2}/g and 0.26 cm\textsuperscript{3}/g). The result showed that the modification had little effect on \( S_{\text{BET}} \) and \( V_{\text{tot}} \) but caused an increase in \( S_{\text{mic}} \) and \( V_{\text{mic}} \) which was conducive to removing small molecular pollutants. The XRD pattern in Figure 1b shows that the diffraction pattern of PAC has only one very broad peak, indicating the presence of fully amorphous crystalline phases. No character-

### Table 1. Textural and Chemical Parameters of PAC and FPAC

| samples    | PAC     | FPAC   |
|------------|---------|--------|
| \( S_{\text{BET}} \) (m\textsuperscript{2}/g) | 990.2   | 993.7  |
| \( S_{\text{mic}} \) (m\textsuperscript{2}/g) | 208.1   | 557.7  |
| \( S_{\text{mic}}/S_{\text{BET}} \) (%) | 21.0    | 56.1   |
| \( V_{\text{mic}} \) (cm\textsuperscript{3}/g) | 0.26    | 0.70   |
| \( V_{\text{tot}} \) (cm\textsuperscript{3}/g) | 0.70    | 0.70   |
| \( V_{\text{mic}}/V_{\text{tot}} \) (%) | 21.3    | 59.3   |
| \( D_p \) (nm) | 4.93    | 4.75   |
| carboxylic groups (mmol/g) | 0.427   | 0.777  |
| lactones (mmol/g) | 0.272   | 0.330  |
| phenolic groups (mmol/g) | 0.689   | 0.845  |
| acidic groups (mmol/g) | 1.388   | 1.952  |
| basic groups (mmol/g) | 1.313   | 1.641  |
| total groups (mmol/g) | 2.701   | 3.593  |
| C (wt %) | 72.89   | 63.23  |
| H (wt %) | 4.18    | 6.56   |
| N (wt %) | 0.97    | 3.05   |
| O (wt %) | 19.14   | 23.48  |

Figure 1. N\textsubscript{2} adsorption/desorption isotherms (a), XRD spectrum (b), SEM image of FPAC (c), and FTIR spectrum of PAC and FPAC (d).

The high-resolution SEM image of FPAC (Figure 1c) confirmed that the surface of FPAC was rough and distributed with a large number of pores of different sizes, exhibiting an irregular porous structure. The well-developed pore structure facilitated the adsorption of adsorbates.
FTIR spectra of PAC and FPAC are shown in Figure 1d. The peak at 3427 cm\(^{-1}\) was derived from the \(-\text{OH}\) stretching vibration in the carboxyl group, phenolic group, and \(\text{H}_2\text{O}\),\(^{20}\) while those at 1627 and 1384 cm\(^{-1}\) were derived from the \(\text{C}=\text{O}\) vibration in the carboxyl group or conjugated carbonyl group.\(^{21,22}\) The peak at 1164 cm\(^{-1}\) was the characteristic peak of the \(\text{C}==\text{O}\) contraction vibration in oxygen-containing functional groups.\(^{23}\) There was a difference in the FTIR spectrum of FPAC compared to that of PAC: peaks that symbolize the \(-\text{OH}\) stretching vibration and the \(\text{C}=\text{O}\) vibration were significantly shifted. Peaks at 3417 and 1615 cm\(^{-1}\) in the spectrum of FPAC could be assigned to the stretching vibration of \(\text{N}−\text{H}\) and amide group (\(\text{C}=\text{N}\)),\(^{24,25}\) indicating that nitrogen-containing functional groups were introduced into FPAC. Boehm titration and EA were used to quantify the functional groups and elements of prepared adsorbents, respectively. As can be seen from Table 1, FPAC had more acidic and basic functional groups and elemental contents of N and O. The result showed that the modified adsorbent contained greater surface oxygen-containing functional groups and introduced surface nitrogen-containing functional groups, which was consistent with the analysis results of FTIR.

2.2. Adsorption Kinetics. The adsorption data were analyzed by the pseudo-first-order model (eq 1)\(^{26}\) and pseudo-second-order model (eq 2)\(^{27}\) to explain the kinetics of adsorbents with AMX and CEX adsorption.

\[
\ln(Q_e - Q_t) = \ln Q_e - k_1t
\]  

(1)

\[
\frac{t}{Q_t} = \frac{1}{k_2Q_e^2} + \frac{1}{Q_e}
\]  

(2)
where $Q_e$ and $Q_0$ (mg/g) are the amount of TMP adsorbed on the adsorbents at equilibrium and at time $t$, respectively, and $k_1$ (1/min) and $k_2$ (mg-min) are the rate constants. As shown in Figure 2a,b, almost 85% of AMX and CEX were quickly adsorbed within 6 and 5 h by FPAC, respectively, while PAC took 9 and 6 h to remove the same percentage of AMX and CEX, respectively. FPAC had the faster adsorption efficiency because the nitrogen-containing functional groups of FPAC promoted the chemical combination of adsorbates and adsorbents. The adsorption capacities had a slow rise in a long time until equilibrium was reached as the adsorption time increased. Table 2 shows that the determination coefficient ($R^2$) of the pseudo-second-order model was greater than 0.99, and the equilibrium adsorption capacity experimental value ($Q_{e,exp}$) was near to the calculated value ($Q_{e,cal}$). In contrast, the pseudo-first-order model had a poor fit to the experimental data, and $Q_{e,exp}$ and $Q_{e,cal}$ had significant differences. The ideal pseudo-second-order model fitting showed that the limiting factor in the adsorption process of both adsorbents was the adsorption mechanism.28

### 2.3. Adsorption Isotherms

The adsorption data were fitted using the Langmuir (eq 3)29 and Freundlich (eq 4)30 isotherm models, and constant values in the isothermal equation were calculated to analyze the adsorption isotherms of PAC and FPAC for AMX and CEX adsorption.

$$\frac{C_e}{Q_e} = \frac{1}{Q_0k_L} + \frac{1}{Q_0}C_e$$

(3)

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e$$

(4)

where $Q_e$ (mg/g) is the equilibrium adsorption capacity, $Q_0$ (mg/L) is the equilibrium concentration, $k_L$ (L/mg) is the maximum adsorption capacity, $k_F$ (mg$^{-1}$L/$^1$/g) and $n$ are the Freundlich constants. As shown in Figure 2c,d, adsorption capacities of the two adsorbents increased as the solution concentration increased. Active adsorption sites were sufficient in the low initial concentration range; adsorption capacities increased significantly with the increase of concentration. When the initial concentration exceeded 50 mg/L, adsorption capacities increased slowly until saturation was reached. As can be seen from Table 3, both isothermal models had good fitting results ($R^2 > 0.95$) for the adsorption of AMX and CEX. For AMX adsorption, the $R^2$ of the Langmuir isotherm model was greater than that of the Freundlich isothermal model, and $Q_{e,cal}$ was more consistent with $Q_{e,exp}$. The better fit of the Langmuir isotherm model indicated that the adsorption of AMX by the two samples was mainly concentrated on the monolayer specific site adsorption. Contrary to AMX adsorption, the Freundlich isothermal model was more suitable to describe the isotherm of CEX adsorption. The result showed that the CEX adsorption of the prepared adsorbent was mainly heterogeneous adsorption and many interactions existed between the adsorbate and adsorbent. The constant $1/n$ of the Freundlich model was less than 1, which indicates that CEX was easily absorbed by PAC and FPAC.31

### 2.4. Effect of pH

The adsorption effects of PAC and FPAC on AMX and CEX at different initial pH were studied. As shown in Figure 2e,f, as the solution pH increased, the adsorption capacities increased first and then decreased sharply. Both samples had the highest AMX percent removal at pH = 5.5 and the highest CEX percent removal at pH = 7. The solution pH not only affected the surface properties of the adsorbent but also changed the presence of AMX and CEX. Both AMX and CEX had a hydrolysis equilibrium in an aqueous solution, and their main forms of existence were different at different pHs. AMX$^+$ and CEX$^+$ were the dominant species at low pH, AMX$^2-$ and CEX$^2-$ dominated at $pK_{a1} < pH < pK_{a2}$, and AMX$^-$ and CEX$^-$ were dominant ions in alkaline conditions.32,33 In the strong acidic environment, most of the surface adsorption sites of adsorbents were protonated and exhibited positive charges. AMX$^+$ or CEX$^+$ was electrostatically attracted by a small amount of deprotonated negative charge adsorption sites, so the removal percent was low. As the pH increased, surface adsorption sites were deprotonated and negative charge sites increased, and AMX$^2-$ or CEX$^2-$ was simultaneously adsorbed by the positive and negative charge sites of the surface of the adsorbent. At the same time, electrostatic repulsion was also generated between adsorbates and adsorbents; therefore, the increased trend of AMX and CEX percent removal was slow. The degree of deprotonation was enhanced at pH $> pK_{a2}$, and the repulsion between negative charge sites and anions was pretty intense, resulting in a sharp decrease in the percent removal of AMX and CEX. Based on the above results, electrostatic attraction played an indispensable role in AMX and CEX adsorption.

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**Table 2. Kinetic Parameters of the Pseudo-First Order and Pseudo-Second Order Models for the Removal of AMX and CEX by PAC and FPAC**

| Compounds | Samples | Pseudo-first-order parameters | Pseudo-second-order parameters |
|-----------|---------|-------------------------------|-------------------------------|
|           |         | $Q_{cal}$ (mg/g) | $k_1$ (1/h) | $R^2$ | $Q_{cal}$ (mg/g) | $k_2$ (g/(mg h)) | $R^2$ |
| AMX       | PAC     | 18.9784          | 0.0814       | 0.9776 | 33.0033          | 0.0268          | 0.9953 |
|           | FPAC    | 26.7384          | 0.0783       | 0.9359 | 42.1941          | 0.0171          | 0.9907 |
| CEX       | PAC     | 16.3643          | 0.1040       | 0.9012 | 28.0899          | 0.0325          | 0.9948 |
|           | FPAC    | 22.2446          | 0.0545       | 0.9221 | 39.5257          | 0.0198          | 0.9912 |

**Table 3. Langmuir and Freundlich Constants for the Adsorption of AMX and CEX by PAC and FPAC**

| Compounds | Samples | Langmuir | Freundlich |
|-----------|---------|----------|------------|
|           |         | $Q_0$ (mg/g) | $K_L$ (L/mg) | $R^2$ | $K_F$ (mg/g(L/mg)$^{1/n}$) | $1/n$ | $R^2$ |
| AMX       | PAC     | 74.6269   | 0.0486     | 0.9947 | 8.3095   | 0.4804 | 0.9849 |
|           | FPAC    | 93.4579   | 0.0669     | 0.9919 | 12.4311  | 0.4684 | 0.9901 |
| CEX       | PAC     | 68.0272   | 0.0371     | 0.9766 | 7.4745   | 0.4494 | 0.9918 |
|           | FPAC    | 88.4956   | 0.0540     | 0.9705 | 13.6331  | 0.3956 | 0.9903 |
an increase in the content of C=O or C==N. However, the peak at 1384 cm⁻¹ disappeared, proving that the C=O bond was consumed. The result indicated that new C==N bonds were produced. In addition, the peak at 3417 cm⁻¹ was also enhanced, suggesting an increase in amino groups. The above results were attributed to the following possible chemical combination: (1) the surface carbonyl group of FPAC was substituted with the amine group in AMX and CEX to generate the C==N bond; and (2) the surface carboxyl group of FPAC was dehydrated and condensed with the amine group in AMX and CEX to produce the amino group. This further illustrated the decisive role of chemisorption in the adsorption of AMX and CEX by the prepared adsorbent.

2.6. AMX and CEX Removal Performance of Different Adsorbents. The maximum AMX and CEX adsorption capacities of various adsorbents are shown in Table 4. FPAC was better than other adsorbents for the removal of AMX and CEX from water, demonstrating the great potential of FPAC toward the kind of antibiotic pollutants.

3. CONCLUSIONS

The FFWF-doped FPAC had more microporous structure and surface functional groups, which promoted the adsorption of antibiotic pollutants from water. The associated adsorption kinetics were well fitted to the pseudo-second-order model for AMX and CEX. The adsorption isotherms for AMX accorded with the Langmuir isotherm model, and the adsorption isotherms for CEX accorded with the Freundlich isotherm model. The adsorption capacities of AMX and CEX increased first and then decreased sharply with the increase of solution pH. Chemisorption, such as electrostatic attraction and covalent bonding with surface functional groups, was the primary adsorption mechanism for AMX and CEX adsorption.

4. MATERIALS AND METHODS

4.1. Materials and Chemicals. P. australis used in this study was taken from the Xiaomei River Constructed Wetland in Shandong province, China. It was washed with distilled water repeatedly and dried completely at 105 °C. Then it was crushed to 100 mesh (model Φ 200) as a material for preparing carbon adsorbents. Powdery puffed waterfowl feather (PPWF) was purchased from New Hope Group Co., Ltd., China. Amoxicillin (99.8%, standard grade) and cephalaxin (99.8%, standard grade) were purchased from Aladdin Biological Technology Co., Ltd., China. In this study, all chemicals used in the experiment were of analytical grade, and distilled water was used as the solvent. The pH of the solution was adjusted by HCl and NaOH.

4.2. Preparation and Characterization of Prepared Adsorbents. PA and PPWF were thoroughly mixed in a ratio of 99:1 (g/g) and impregnated in the 85 wt % H₃PO₄ solution with a ratio of 10:0.2 (g/mol) for 10 h, and then the sample was transferred to a muffle furnace and heated to 450 °C for 1 h. After cooling to room temperature, it was washed with distilled water until the solution pH was stable, and then the sample was dried completely and ground to 120 mesh (model Φ 200) to obtain. The adsorbent was referred to as FPAC. The undoped PPWF adsorbent as a control sample was referred to as PAC, and its preparation method was described in our previous work.⁴¹

The specific surface area was determined by N₂ adsorption/desorption at 77 K using a surface area analyzer (TriStar II Plus) by a multipoint Brunauer-Emmett-Teller (BET) method. The micropore surface area (Sₘ) and micropore volume (Vₘ) were calculated using the t-plot method. The total pore volume (Vₜ) was determined from the amount of N₂ adsorbed at a P/P₀ ratio of around 0.95. The average pore diameter (Dₚ) was obtained from Dₚ = 4Vₜ/Sₘ. The crystal phase structure was presented by X-ray diffraction.

### Table 4. Comparison of Results of Different Adsorbents on the Adsorption of AMX and CEX

| Adsorbents | Precursors | Activating Agents | Modifying Agents | Qₘₐₓ (mg/g) | AMX  | CEX  | Reference |
|------------|------------|-------------------|------------------|------------|------|------|-----------|
| PA         | H₃PO₄      |                   |                  |            | 74.20| 66.44| this work |
| PA         | H₃PO₄      |                   | PPWF             | 92.59      | 85.82|      | this work |
| Vine wood  | NaOH       |                   |                  | 2.69       | 7.08 |      | 34        |
| Olive stone| H₃PO₄      |                   |                  | 57.00      |      |      | 35        |
| Graphene nanoplatelets | |                   | magnetically | 14.10      |      |      | 36        |
| Chitosan beads | H₃PO₄     |                   |                  | 8.71       |      |      | 5         |
| Organobentonite |         |                   |                  | 26.18      |      |      | 37        |
| Lotus stalk | H₃PO₄     | Cu(NO₃)₂          |                  | 78.12      |      |      | 38        |
| Amberlite XAD resin | H₃PO₄ | Fe(NO₃)₃          |                  | 75.11      |      |      | 38        |
| Nonimprinted polymers | |                   |                  | 17.70      |      |      | 40        |
| Molecularly imprinted polymers | |                   |                  | 39.70      |      |      | 40        |
an XRD diffractometer (Bruker D8, Germany) and SEM (Zeiss Supra 40, Germany). The surface functional groups were determined by FTIR (Nicolet-460, Thermo Fisher) and Boehm titration.13 The content of main elements was determined by EA (Flash 2000, Thermo Fisher).

4.3. Adsorption Experiments. Batch adsorption experiments were performed to study the effects of different factors (initial concentration, contact time, and initial pH) on AMX and CEX adsorption. Adsorption experiments were conducted by adding a certain amount of adsorbent into 50 mL AMX solution (40 mg/L) or CEX solution (30 mg/L). Experimental samples were shaken at 120 rpm at room temperature (32 ± 1 °C) in darkness for 72 h, and then they were filtered through 0.45 μm filters. The concentration of AMX and CEX were determined with an ultraviolet (UV)—visible spectrophotometer (UV-5100, Shanghai) at the wavelength of 230 nm for AMX and 258 nm for CEX. The adsorption capacity was calculated with an ultraviolet (UV) spectrophotometer.

\[ Q_e = \frac{(C_0 - C_e)V}{M} \]  
(5)

removal (%) = \( \frac{(C_0 - C_e)}{C_0} \times 100 \)  
(6)

where \( C_0 \) is the initial solution concentration (mg/L), \( C_e \) is the equilibrium solution concentration (mg/L), \( V \) is the volume of solution (L), and \( M \) is the mass of the adsorbent (g).

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### Notes
The authors declare no competing financial interest.

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