Salt sealing induced in situ N-doped porous carbon derived from wheat bran for the removal of doxycycline from aqueous solution

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Abstract
In situ N-doped porous carbon (NPC) derived from wheat bran via a convenient salt sealing and air-assisted strategy was prepared for the removal of doxycycline (DOX) from aqueous solution. The NPC was precisely characterized by SEM, FTIR, XPS and BET analysis. Additionally, the experimental variables including contact time, adsorbent dosage of NPC and pH were optimized by using Box–Behnken design (BBD) under response surface methodology (RSM). The predicted adsorption capacity of DOX was found to be 291.14 mg g\(^{-1}\) under optimizing experimental conditions of 196 min contact time, 0.2 g L\(^{-1}\) adsorbent dosage and pH 5.78. The adsorption experimental data fitted Langmuir, Koble-Corrigan and Redlich-Peterson models well, and the pseudo-second-order model perfectly described the DOX adsorption process onto NPC. Thermodynamic parameters of DOX adsorbed onto NPC indicated that the adsorption process was spontaneous and endothermic. Moreover, the adsorption of DOX on NPC was mostly controlled by electrostatic interaction, \(\pi-\pi\) electron–donator–acceptor (EDA) interaction, hydrogen-bonding and Lewis acid–base effect. Besides, the N element of NPC also played a role in capturing DOX. The maximum monolayer adsorption capacity of DOX was turn out to be 333.23 mg g\(^{-1}\) at 298 K, which suggested that the NPC could be a prospectively adsorbent for the removal of DOX from wastewater.

Keywords  Doxycycline · Adsorption · N-doped carbon · Salt sealing · Response surface methodology · Wheat bran

Introduction
Antibiotics had been widely used in the medical and veterinary industries because of its efficacy in the treatment and prevention of various diseases (Peng et al. 2021). A large amount of antibiotics was discharged into the water environment in the process of production and application (Sun et al. 2020a). Unfortunately, it has been reported in the literature that 94 kinds of antibiotics have been detected in water environment of China including underground water, tap water, surface water and sea water (Li et al. 2020b), which could pose a threat to human’s body due to the wide spreading antibiotics in various ecosystems. Therefore, the treatment of antibiotic wastewater had received extensive attention and become an urgent problem to be solved (Saremi et al. 2020).

Among these antibiotics, doxycycline (DOX), as one of the types of tetracycline (Liu et al. 2018), is an inhibitor of protein synthesis (Nooreini and Panahi 2016). It is mainly used in treating various bacterial infections because it could be against gram-positive and gram-negative bacteria, chlamydiae, mycoplasmas rickettsiae and so on (Islam
et al. 2020). Additionally, DOX played a significant role in the treatment of pneumonia in previous viral pneumonia pandemics, which means it may also have a potential utility against COVID-19 (Ali et al. 2021). Unfortunately, DOX is mostly excreted in its original form because it is difficult to decompose in humans or animals’ body (Whelton et al. 1974), which caused serious pollution in the water environment. DOX residues have been found in animals’ body, such as broiler poultry (Islam et al. 2020; Waghmare et al. 2020), grass carp (Xu et al. 2020b) and pigs (Waghmare et al. 2020). These residues in animals were able to amassed in the people’s body through food chain, which may trigger kinds of adverse effect on humans. For example, it will change the gut microbiota and irritate the stomach which may lead to the release of bacterial toxin and severe intestinal inflammation (Islam et al. 2020; Nooreini and Panahi 2016). It will also cause bacteria resistant and make the infections harder to treat, which result tens of thousands of people died every year (Wang et al. 2021). Therefore, how to remove DOX from wastewater quickly and high efficiently has become a world concern problem.

At present, a variety of treatment techniques, mainly including membrane filtration, precipitation, Fenton reaction (Zheng et al. 2017), photocatalysis (Tong et al. 2021), biodegradation (Wen et al. 2020), were applied for the treatment of DOX wastewater. Among these techniques, adsorption is one of the most suitable and efficient techniques owing to its low-cost, high efficiency, non-poisonous and environmental friendly. So far, high-performance adsorbents were prepared using numerous cheap biomass, such as sugarcane (Ho et al. 2005), bamboo shoot shell (Hou et al. 2020) and bean dreg (Wang et al. 2019). The biomass was converted into advanced activated carbon via activation process. Activators in chemical activation are mostly H₃PO₄, KOH and ZnCl₂, which are toxic and strong erosive during the production process. In order to deal with this problem, molten salt activation technique seems like a good choice, which uses inert salt like KCl or NaCl as the activator (Xu et al. 2020a). Surprisingly, the N element in some biomass can be retained due to the protective effect of molten during pyrolysis (Wang et al. 2017). The incorporation of heteroatom doping (N) in the carbon structure is beneficial for enhancing the electronic conductivity and the ability of energy storage. So this technique is widely used in capacitors and electrocatalyst directions (Li et al. 2019a; Wang et al. 2017, 2018; Yin et al. 2014). Recently, it has been reported that the nitrogen atom in carbon structure may provide more activated sites for the adsorption (Hou et al. 2020). With these merits of doping N element in carbon, much attention has been focused on obtaining nitrogen-doped activated carbon. The raw materials like chitosan, glucose and sucrose have been used to prepare nitrogen-doped porous carbon through molten salt template method under N₂ atmosphere (Rehman and Park 2019; Wang et al. 2020; Youssef et al. 2020). However, the protection by inert gases (N₂, Ar₂) may cause high expense and equipment requirements. By comparison, the method without inert gas protection used for energy storage caught people’s eyes (Li et al. 2019a). It was stated that the oxygen in the air permeated into the molten salt and served as an etching agent to produce porous structure during the pyrolysis process (Wang et al. 2017). Therefore, it is suggested that the combination of salt template and air-assisted method could be an inexpensive and green technology for the preparation of activated carbon.

Wheat bran, as one of the major agricultural by-product, contains high contents of carbohydrates and proteins (Bulut et al. 2007), which has great potential for preparing in situ nitrogen-doped porous carbon. In this paper, wheat bran was employed as raw material to prepare in situ nitrogen-doped porous carbon (NPC) via a convenient salt-sealing and air-assisted technique. During the activation process, non-toxic KCl was chosen as salt template, which could fabricate porous structures to achieve higher specific surface area (Kong et al. 2020). The obtained NPC with honeycomb structure provided more adsorption sites for the removal of DOX from wastewater. Adsorption conditions were optimized using response surface methodology (RSM) through exploring three variables (contact time, adsorbent dosage and pH). The adsorption characterizations of DOX onto NPC were studied, and the mechanisms of DOX on NPC were further characterized.

**Experiment**

**Materials**

Wheat bran was collected from local farm in Anyang, Henan Province, China. The antibiotic doxycycline hydrochloride (DOX, ≥ 94%, C₂₂H₂₄N₂O₈·HCl, MW = 480.89) used in this study was bought from Shanghai Macklin Biochemical Co. Ltd. Doxycycline solutions were prepared by dissolving DOX in deionized water. The initial pH of DOX was adjusted by adding 0.1 mol L⁻¹ solutions of NaOH or HCl to the target values. Potassium chloride (KCl) was purchased from Kermel Chemical Reagents Co., Ltd in Tianjin, China.

**Preparation of in situ N-doped porous carbon**

Briefly, wheat bran (WB) was pyrolyzed at 573 K under oxygen-free atmosphere. The carbonizing wheat bran (CWB-573) and KCl were totally grounded in an agate mortar at a certain mass ratio. The mixture was placed into a porcelain crucible and calcined at 1073 K for 139 min in air atmosphere. Subsequently, the calcination black solid was repeatedly washed with deionized water. After filtering, the
sediment was dried in an oven at 378 K for 3 h to produce the in situ N-doped porous carbon (NPC). The above preparation process of NPC is shown in Fig. 1. Additionally, KCl was recycled from filtrate containing the soluble salts through a simple method of evaporation. During the activation process, owing to the abundant protein of wheat bran, the N element was retained in carbon structure due to the protection of salt (Xu et al. 2020a). At the same time, the oxygen in the air, as an etching agent, was beneficial to the formation of pore structure (Wang et al. 2017). To verify the effect of KCl, the wheat bran without KCl was carbonized under nitrogen flow at 1073 K for 139 min, which was named as CWB-1073.

Material characterization

The nitrogen adsorption–desorption isotherms were analyzed at 77 K using the specific surface and aperture analyzer (JW-BK 132F), and the specific surface areas of samples were obtained by using Brunauer–Emmett–Teller (BET) equation. The external surface morphological structures of CWB-573, CWB-1073 and NPC were detected by scanning electron microscopy (SEM, FEI Quanta 200). The samples were sprayed with gold before testing to increase the conductivity. The infrared spectrums of DOX, NPC and NPC after DOX adsorption were observed by using Fourier transform infrared (FTIR) spectrometer (Perkin-Elmer, Spectrum Two, USA) equipped with a pressed KBr pellet within the wave range 500–4000 cm⁻¹. Raman spectrum of CWB-1073 and NPC was operated at room temperature on a confocal micro-Raman spectrometer (HR-800, USA) with a 532 nm laser excitation. A minimum of two acquisitions was done for each sample. These spectra were analyzed by fitting the experimental data using Origin 9.5 peak fitting (Gauss). Two main bands (D band, 1350 cm⁻¹ and G band, 1580 cm⁻¹) were required to accurately fit the experimental Raman spectra. Surface characterizations of NPC and CWB-1073 were performed by X-ray photoelectron spectroscopy (XPS-1730654S, Britain). The spectrum position of each element was calibrated using 284.8 eV as the line position of carbon.

Adsorption experiments

Batch adsorption experiments were performed by adding a certain amount of NPC to a 50 mL conical flask containing 25 mL of 100 mg L⁻¹ doxycycline hydrochloride (DOX) solution. The mixture was agitated in a thermostatic water bath shaker at a constant speed of 130 rpm for a predetermined time interval. After adsorption, the mixture was immediately centrifuged and the supernatants were measured by an UV–Vis spectrophotometer (TU-1810) at λ max 275 nm. The following adsorption experiments were performed twice.

The adsorption uptake of DOX onto NPC at equilibrium (qₑ, mg g⁻¹) is calculated by Eq. (1).

\[ q_e = \frac{(C_0 - C_e)V}{m} \]  

(1)

where \(C_0\) (mg L⁻¹) and \(C_e\) (mg L⁻¹) are the initial concentration and equilibrium concentration of DOX, respectively; \(m\) (g) is the amount of NPC; and \(V\) (L) is the total volume of DOX solution.

Experimental design

To find the optimum adsorption conditions of DOX onto NPC, the Box–Behnken design model (BBD) of RSM was used to optimize experimental factors which had an effect on the adsorption capacity of DOX. The factors containing contact time (\(x_1\)), adsorbent dosage of NPC (\(x_2\)) and pH (\(x_3\))

![Fig. 1 Schematic illustration of the preparation of NPC and its application for removal of DOX](image)
were chosen as input variables for RSM, while the DOX adsorption capacity was the response variable \(Q\). Every independent variable was set with three levels (-1, 0, +1), which are shown in Table 1. Based on BBD experiment design, 17 sets of adsorption experiments used for DOX solution \((C_0 = 100 \text{ mg L}^{-1})\) are summarized in Table 2. For this, quadratic polynomial equation (Eq. (2)) was used to build the relationship between input variables and DOX adsorption capacity (Yang et al. 2009).

\[
Q = \beta_0 + \sum_{j=1}^{3} \beta_j x_j + \sum_{j=1}^{3} \sum_{j=1}^{3} \beta_{ij} x_j^2 + \sum_{j=1}^{3} \sum_{j=1}^{3} \sum_{j=1}^{3} \beta_{ij} x_j^2
\]  

(2)

where \(Q\) is the response value (the predicted adsorption capacity of DOX); \(x_i\) and \(x_j\) are the dimensionless coded predictors of independent variables; \(\beta_0, \beta_j, \beta_{ij}\) and \(\beta_{ij}\) represent the coefficients of constant term, linear term, square term and quadratic interaction term, respectively. A positive coefficient and a negative coefficient represent a synergistic effect and an antagonistic effect on the response value, respectively.

### Results and discussion

#### Response surface methodology analysis

It can be seen from Table 2, the actual adsorptive values were highly close to the predicted adsorptive values, suggesting that this model could predict the relationships between adsorption capacity of DOX and experimental conditions. The quadratic polynomial equation between adsorption capacity \(Q\) and three variables \((x_1, x_2, x_3)\) was used for regression analysis, as follows:

\[
Q = 269.56 + 17.38x_1 - 23.17x_2 + 4.85x_3 - 3.07x_1x_2 - 1.44x_1x_3 - 1.54x_2x_3 - 18.07x_1^2 - 7.48x_2^2 - 20.16x_3^2
\]  

(3)

The analysis of variance for the DOX adsorption capacity is displayed in Table 3. The F-value and P-value were employed to verify the statistical significance of model (Chen et al. 2012; Pinheiro et al. 2020). The higher F-values indicated greater significance of model, while the P-values were greater than 0.05, indicating that the model was non-significant (Onu et al. 2021). The F value of quadratic model was 29.06 and the P value was less than 0.0001, implying that the model terms had a significant effect on the DOX adsorption performance. Furthermore, the “lack-of-fit” P-value of 0.16 showed non-significant, demonstrating that the effect of experimental error on the results was not significant. The correlation coefficient \(R^2\) reached 0.9739 and the adequate precision ratio (APR = 16.606) was greater than 4, indicating that the independent variables of the equation were well related to the dependent variables, so the predicted values fitted well with the experimental values. Additionally, the coefficient of variation (C.V.%  = 2.57%) was less than 10%, demonstrating that the model had reasonably reproducibility (Chen et al. 2012).

According to the F value, the significant intensity order of independent variables was: adsorbent dosage > contact time > pH, and the quadratic model was valid for the DOX adsorption process. The corresponding optimum experimental conditions were contact time 196 min, adsorbent dosage 0.2 g L\(^{-1}\) and pH 5.78, and the predicted adsorption capacity of DOX was 291.14 mg g\(^{-1}\). In order to verify the accuracy of predicted value, six experiments were performed at the optimal conditions and the uptake capacities were 299.39, 291.49, 306.01, 296.66, 293.31, 289.60 mg g\(^{-1}\), respectively. The average value 296.08 mg g\(^{-1}\) was close to the predicted adsorption data, which justified the great applicability of model for DOX adsorption experiment.
Response surface plots

The 3D graphs of the relationships between three variables and adsorption capacity are presented in Fig. 2. It could be seen from Fig. 2a and b that the DOX adsorption capacity \( q \) rose rapidly at first and then decreased slightly with increasing contact time. From Fig. 2a and c, it also could be seen that the values of \( q \) increased first and then decreased by increasing pH value, implying that the neutral condition was favorable for DOX adsorption. From Fig. 2b and c, the adsorption quantity \( q \) decreased as the increase of adsorbent dosage.

Characterization

SEM analysis

The surface morphologies and structures of CWB-537, CWB-1073 and NPC are shown in Fig. 3a-c. The CWB-537 showed large carbon block without evident porous structure, and CWB-1073 had little crevices and pores. Comparing to the CWB-537 and CWB-1073 (Fig. 3a-b), the NPC (Fig. 3c) had more well-developed pores, implying that the abundant pores were produced via a simple salt sealing and air-assisted strategy technique. During the pyrolysis process, the KCl, as salt template, played a crucial role in the preparation of NPC (Kong et al. 2020). In addition, the oxygen in the air was favorable for enhancing porosity (Li et al. 2019a). These honey-combed pores might be beneficial to DOX adsorption in the experiments.

BET analysis

To explore the specific surface area and pore size distribution of NPC, the nitrogen adsorption–desorption isotherm of the NPC at 77 K is described in Fig. 3d. The adsorption uptake of \( N_2 \) rose rapidly at \( P/P_0 \) between 0 and 0.1, which demonstrated the existence of micropores (Yang et al. 2020). It exhibited a type IV adsorption isotherm with a H4-type hysteresis loop. The presence of hysteresis loop was mainly attributed to the capillary condensation, implying the existence of mesopores in the NPC.

The specific surface area and pore structure parameters of CWB-573, CWB-1073 and NPC are listed in Table 4. The specific surface areas \( (S_{BET}) \) of NPC, CWB-573 and CWB-1073 were 1173.97 m\(^2\) g\(^{-1}\), 5.982 m\(^2\) g\(^{-1}\) and 67.18 m\(^2\) g\(^{-1}\) according to Brunauer–Emmett–Teller (BET) equation. The total volume \( (V_p) \) of NPC was 0.851 cm\(^3\) g\(^{-1}\), which was much higher than CWB-573 and CWB-1073. Micropore volume of NPC was 0.257 cm\(^3\) g\(^{-1}\) by t-plot method (Passe-Coutrin et al. 2008). Besides, the average pore diameter \( (D_p) \) of NPC was calculated from \( D_p = 4V_p/S_{BET} \) and the result showed that the average pore size was 2.899 nm. It could be deduced that there were numerous mesopores in NPC, which was in line with the results in Fig. 3c.

FTIR analysis

The characteristic functional groups of samples were obtained by Fourier transform infrared (FTIR) spectrometer equipped with a pressed KBr pellet. The samples were dried in the oven at 378 K for 3 h before FTIR analysis. For DOX (Fig. 3e), the broad band was ascribed to O–H and N–H...
stretching frequencies of alcohols and amines, respectively (Naeimi and Faghihian 2017). The 1704 cm\(^{-1}\) assigned to the amides bands of DOX (Naeimi and Faghihian 2017). The band at 1636 cm\(^{-1}\) represented C=O stretching vibration of DOX, and the peak in 1463 cm\(^{-1}\) represented C–C stretching vibration of benzene rings (Jia et al. 2013; Liu et al. 2017). The peak at 1383 cm\(^{-1}\) was identified as -CH\(_3\) deformation vibration, and the band at 1277 cm\(^{-1}\) was attributed to C–N amine stretching vibration of DOX (Naeimi and Faghihian 2017). The peak at 1050 cm\(^{-1}\) was ascribed to the phenolic C-O stretching (Liu et al. 2017).

As for NPC (Fig. 3e), the broad band at 3440 cm\(^{-1}\) might be attributed to O–H, N–H groups or adsorbed water (Peng et al. 2021). The peaks loaded in 2920 cm\(^{-1}\) and 2842 cm\(^{-1}\) could be ascribed to the C-H stretching and bending vibration of aliphatic series. The band at 1725 cm\(^{-1}\) might be attributed to amides band of NPC (Naeimi and Faghihian 2017). The peaks at 1635 cm\(^{-1}\) might represent C=O group vibration of NPC (Ronix et al. 2017). The band at 1393 cm\(^{-1}\) could be the vibration of -CH\(_3\), and the band in 1081 cm\(^{-1}\) was considered as the C-O stretching of carbon–oxygen surface group (Yu et al. 2019). The carbonyl and hydroxyl of NPC are able to form hydrogen bonds with DOX (Yu et al. 2020a). Compared to NPC, Fig. 3e shows that some peaks of NPC after adsorption DOX had position shifts and intensity changes. The peaks at 1081 cm\(^{-1}\) and 1393 cm\(^{-1}\) were shifted to 1050 cm\(^{-1}\) and 1383 cm\(^{-1}\), respectively. In addition, the new peaks at 1463 cm\(^{-1}\) and 1274 cm\(^{-1}\) indicated that DOX was successfully adsorbed on the surface of NPC.

**Raman spectral analysis**

Raman spectrum was used to reveal the defective framework and graphitization degree of carbonaceous materials. The D band at ~ 1350 cm\(^{-1}\) represents the disordered and defective carbon structure, while the G band at ~ 1580 cm\(^{-1}\) represents the hexagonal lattice stretching vibration of sp\(^2\) carbon (Yu et al. 2020b). Therefore, the intensity ratio of \(I_D/I_G\) was applied to reflect the graphitization degree of materials. The intensity ratio is inversely proportional to the degree of graphitization (Tang et al. 2020). It can be seen from Fig. 4 that the \(I_D/I_G\) of NPC (1.06) was lower than that of CWB-1073 (1.13), indicating the higher graphitization degree of NPC. In addition, the NPC was close to the graphene-based materials because its \(I_D/I_G\) was around 1. It has been confirmed that the adsorption capacity is related to
The graphitization degree (Sun et al. 2020b). The graphitization degree is connection with lots of aromatic rings which are usually regarded as the π-acceptor (Sun et al. 2020b). Thus, DOX, as an π-donor, would be adsorbed on NPC via π-π electron–donator–acceptor (EDA) interaction (Chen et al. 2008).

Fig. 3 The SEM images of CWB-573 (a), CWB-1073 (b) and NPC (c). Nitrogen adsorption and desorption isotherms and the pore size distribution of NPC (d) and FTIR spectra of samples (e).

Table 4 Specific surface area and pore structure parameters of CWB-573, CWB-1073 and NPC

| Samples   | $S_{BET}$ (m² g⁻¹) | $V_{sa}$ (cm³ g⁻¹) | $V_{mic}$ (cm³ g⁻¹) | $S_{mic}$ (m² g⁻¹) | $D_p$ (nm) |
|-----------|-------------------|-------------------|-------------------|-------------------|-----------|
| CWB-573   | 5.982             | 0.015             | 0.002             | 0.055             | 9.991     |
| CWB-1073  | 67.18             | 0.204             | 0.003             | 2.758             | 12.120    |
| NPC       | 1179.97           | 0.851             | 0.257             | 560.167           | 2.899     |
XPS analysis

XPS was further employed to characterize the surface electronic states and chemical states of samples. As displayed in Fig. 5a, the N contents of CWB-1073 and NPC were 0.69 At% and 1.61 At%, respectively. Comparing to NPC, the decrease of N element of CWB-1073 demonstrated that the KCl could protect the main elements from being decomposed by air atmosphere at high temperature (Li et al. 2019a). After DOX adsorption, the content of N atom increased to 2.4 At%, indicating that DOX was successfully adsorbed on NPC.

For the C1s spectrum (Fig. 5b), four peaks were assigned to C = C (284.8 eV), C–C (285.7 eV), C = N (287.5 eV) and C-O (290.6 eV), respectively (Zhu et al. 2017). The energies of C = N and C-O were found from 287.5 eV and 290.6 eV of NPC to 286.2 eV and 289.8 eV of NPC loaded DOX, demonstrating that there was the interaction between DOX and NPC.

For the O1s spectrum (Fig. 5d), the divided Gaussian peaks at 530.8 eV and 532.8 eV were ascribed to the C = O, C-O–H (Li et al. 2019b). The shifts of C = O, C-O–H were observed from 530.8 eV, 532.8 eV of NPC to 531.3 eV and 532.9 eV of NPC-loaded DOX, implying that there could be hydrogen bonding between carbonyl groups of NPC and hydroxyl groups or amidogens of DOX as well as hydrogen bonding between carbonyl groups of DOX and hydroxyl groups of NPC, respectively (Liu et al. 2020). Additionally, it can be seen that the binding energy shifts of pyrrolic N and graphitic N were more obvious among them. It seemed to imply that the Lewis acid–base and π-π EDA interactions were more significant in the DOX adsorption process.

Adsorption isotherms

To study the uptake performance of DOX onto NPC, Langmuir (Eq. (S1)), Freundlich (Eq. (S2)), Koble-Corrigan (Eq. (S3)) and Redlich-Peterson (Eq. (S4)) were employed to fit the adsorption data of NPC, respectively.

In general, the lower $\chi^2$ indicated that the difference between each model and experimental data was not significant (Ghaedi et al. 2012). Nonlinear Chi-square statistical test ($\chi^2$) is shown as:

$$\chi^2 = \sum \frac{(q_{e,\text{exp}} - q_{e,\text{cal}})^2}{q_{e,\text{exp}}}$$

The $q_{e,\text{exp}}$ and $q_{e,\text{cal}}$ are the experimental adsorption capacity of DOX and the calculated adsorption capacity of DOX, respectively.

The adsorption isotherms of DOX onto NPC at three different temperatures are shown in Fig. 6a, and the parameters calculated from the four models are presented in Table 5. The values of correlation coefficient $R^2$ from Langmuir isotherm were greater than 0.99 and the values of $\chi^2$ were relatively lower, which implied that the Langmuir model fitted the DOX adsorption process well. The $q_m$ and $K_L$ increased as the increase of temperature, indicating that the higher temperature was favorable for DOX adsorption (Aldegs et al. 2020).
The Langmuir isotherm assumed DOX molecules were adsorbed onto the homogeneous adsorbent surface, which was mainly monolayer adsorption. The maximum monolayer adsorption \( q_m \) of DOX onto NPC at 298 K, 308 K and 318 K was 333.23 mg g\(^{-1}\), 338.91 mg g\(^{-1}\) and 351.21 mg g\(^{-1}\), respectively. By comparing with the maximum monolayer adsorption of various adsorbents for DOX in Table 6 (Ali and Ahmed 2017; Li et al. 2020a; Wei et al. 2019; Zhang et al. 2018), the NPC is better than other adsorbents, which can be attributed to its higher specific surface area and abundant functional groups.

The Freundlich isotherm usually assumes the DOX molecules were adsorbed onto a heterogeneous surface. As shown in Table 5, the Freundlich model could not describe the adsorption behavior of NPC to DOX well due to the lower \( R^2 \) values and the higher \( \chi^2 \) values. The \( 1/n \) of Freundlich parameter is related to the surface heterogeneity. The 0 < \( 1/n \) < 1 indicates that the adsorption is favorable (Rauf et al. 2008).

The Koble-Corrigan isotherm is a combination of Freundlich isotherm and Langmuir isotherm. The Redlich-Peterson isotherm is a hybrid isotherm basing on

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**Fig. 5** XPS survey spectra of samples (a). XPS spectra of C1s (b-c), O1s (d-e), N1s (f-g) peaks of NPC before and after adsorption.
Freundlich and Langmuir isotherms. The higher $R^2$ values and the lower $\chi^2$ values of K-C and Redlich-Peterson models also indicated that these two models were suited to represent the DOX adsorption process. In addition, the values of constants ($A_K$, $B_K$, $A_R$, $B_R$) were positively proportional to temperature.

**Adsorption thermodynamics**

The thermodynamic parameters including Gibbs free energy ($\Delta G$, kJ mol$^{-1}$), enthalpy ($\Delta H$, kJ mol$^{-1}$) and entropy ($\Delta S$, kJ (mol K$^{-1}$)) are very significant to the adsorption behaviors of DOX on NPC, which are used to study the feasibility and spontaneity of adsorption process for DOX (Yu et al. 2020b). The adsorption thermodynamics calculation equations were as follows:

$$\Delta G = RT \ln K_L$$

(5)

$$\Delta G = \Delta H - T \Delta S$$

(6)

where $R$ (8.314 J/(mol K$^{-1}$)) is the gas constant; $T$ (K) represents the thermodynamic temperature; $K_L$ is the Langmuir constant (L mol$^{-1}$).

The values of $\Delta G$ were -28.93, -31.07, -32.75 kJ mol$^{-1}$ for DOX adsorbed onto NPC at 298, 308, 318 K, respectively. At the same time, the negative values of $\Delta G$ at different temperature indicated that the adsorption process of DOX was spontaneous. The values of $\Delta H$ and $\Delta S$ could be obtained by the intercept and slope of the line based on Eq. (6). The positive value of $\Delta H$ ($\Delta H = 27.97$ kJ mol$^{-1}$) indicated that the DOX adsorption onto NPC was an endothermal process. As it has been documented in the literature, the value of $\Delta H$ between 20.9 kJ mol$^{-1}$ and 418.4 kJ mol$^{-1}$
demonstrated that the chemisorption existed in the adsorption process (Zhu et al. 2021). So the adsorption of DOX onto NPC contained chemical adsorption. Additionally, the positive value of $\Delta S (\Delta S = 0.19 \text{ kJ (mol K)}^{-1})$ confirmed the increasing disorderliness at the adsorbent–adsorbate interface in the adsorptive process of DOX onto NPC (Zhao et al. 2015).

**Adsorption kinetics**

The kinetic experiments of NPC were performed by using 100 mg L$^{-1}$ DOX solution and 0.2 g L$^{-1}$ NPC at 298 K, 308 K and 318 K, respectively. To understand the relationship between the adsorption capacity and time, the pseudo-first-order (Eq. (S5)), the pseudo-second-order (Eq. (S6)) and intraparticle diffusion models (Eq. (S7)) were selected to fit the adsorption kinetic data.

The nonlinear plots of the adsorption capacity of DOX versus time are described in Fig. 6b. The adsorption capacity of DOX rose quickly and then slowly until adsorption–desorption reached equilibrium. The parameters of kinetics models are recorded in Table 7. The values of $R^2$ of the pseudo-second-order model were closer to 1, and the values of $q_{\text{exp}}$ were close to the values of $q_{\text{cal},2}$, implying that the pseudo-second-order model was more suitable for expressing DOX adsorption onto NPC than the pseudo-first-order model. This implied that chemisorption might play an important role during the whole adsorption process, which was consistent with the results of thermodynamic parameter analysis.

The intraparticle diffusion model was used to study the rate-limiting step of the DOX adsorption process. Figure 6c presents that the fitting line was divided into three portions. Each fitted lines did not pass through the origin point, revealing that the DOX adsorption process was driven by the boundary diffusion and intraparticle diffusion (Zhu et al. 2014). Table 7 shows that the values of $K_1$ gradually decreased as the increase of time at the same temperature. In the same state, the $K_1$ and $C$ increased with the increase of temperature, implying that the mass transfer and the thickness of boundary layer increased with the rise of temperature.

### Table 6 Comparison of adsorption capacity of DOX onto different adsorbents

| Adsorbents                                      | $S_{\text{BET}}$ (m$^2$ g$^{-1}$) | $q_m$ (mg g$^{-1}$) | References          |
|------------------------------------------------|----------------------------------|---------------------|---------------------|
| NaY zeolite from wheat straw ash               | 657.44                           | 252.12              | (Ali and Ahmed 2017) |
| The iron-loaded sludge biochar                 | 128.98                           | 128.98              | (Wei et al. 2019)   |
| Fe$_3$O$_4$@SiO$_2$@mSiO$_2$–cyclodextrins      | 119                              | 200                 | (Zhang et al. 2018) |
| BC/MnO$_2$                                     | 64.32                            | 24.69               | (Li et al. 2020a)   |
| NPC                                            | 1179.97                          | 333.23              | This study          |

### Table 7 Kinetics model parameters for the adsorption of DOX onto NPC

| Models                               | Parameters | 298 K | 308 K | 318 K |
|--------------------------------------|------------|-------|-------|-------|
| Pseudo-first-order                   | $k_1$ (min$^{-1}$) | 0.0637 | 0.0640 | 0.0658 |
|                                     | $q_{\text{cal},1}$ (mg g$^{-1}$) | 286.19 | 297.67 | 304.95 |
|                                     | $R^2$      | 0.8940 | 0.8817 | 0.9153 |
| Pseudo-second-order                  | $k_2 \times 10^4$ (g (mg min)$^{-1}$) | 3.5180 | 3.5404 | 3.5874 |
|                                     | $q_{\text{exp}}$ (mg g$^{-1}$) | 294.50 | 309.92 | 315.75 |
|                                     | $q_{\text{cal},2}$ (mg g$^{-1}$) | 305.20 | 315.12 | 325.64 |
|                                     | $R^2$      | 0.9924 | 0.9961 | 0.9966 |
| Intraparticle diffusion              | $K_1$ (mg g$^{-1}$ min$^{-1/2}$) | 23.62  | 25.36  | 25.94  |
|                                     | $C_1$      | 97.92  | 99.02  | 108.18 |
|                                     | $R^2$      | 0.9925 | 0.9598 | 0.9016 |
|                                     | $K_2$ (mg g$^{-1}$ min$^{-1/2}$) | 6.64   | 7.22   | 7.58   |
|                                     | $C_2$      | 206.58 | 212.98 | 218.56 |
|                                     | $R^2$      | 0.9905 | 0.9557 | 0.9755 |
|                                     | $K_3$ (mg g$^{-1}$ min$^{-1/2}$) | 0.88   | 0.90   | 1.00   |
|                                     | $C_3$      | 279.15 | 290.67 | 298.40 |
|                                     | $R^2$      | 0.9660 | 0.8634 | 0.8924 |

### Influence of initial solution pH and adsorption mechanism

The solution pH plays a vital role during the whole adsorption process, which effects the surface charge of NPC and ionization degree of DOX molecules. DOX has three pKa including 3.5, 7.7, 9.1 (Brigante and Avena 2016; Wei et al. 2019), which has different existing species at different pH. The distribution coefficient and ionization constants of DOX are depicted in Fig. 7a-b. The DOX existed mainly as cationic species (DOX$^+$) at pH 2.0 and the DOX$^+$ decreased gradually with increasing pH, while the proportion of DOX$^+$ and DOX$^0$ were equal at pH 3.5. The DOX exists mainly as DOX$^0$ at 3.5 < pH < 7.7 and it presents mainly as anionic species (DOX$^-$, DOX$^{2-}$) at pH > 7.7. The zero point charge (pH$_{zpc}$) of NPC was measured by salt addition method (Slifman et al. 2014). As illustrated in Fig. 7c, the pH$_{zpc}$ of NPC was found around 5.8. It suggested that the NPC has...
a positive charge on its surface at pH < 5.8 and a negative charge on its surface at pH > 5.8.

From Fig. 7d, the adsorptive capacity of DOX was in the range of 216.2 mg g\(^{-1}\) to 298.6 mg g\(^{-1}\) as the pH increased from 2.5 to 10, indicating that NPC exhibited a high adsorption capacity for DOX. It could be observed that the adsorption capacity of DOX exhibited increasing trend with increasing pH and then reached a plateau period, sequentially, declined obviously at pH > 5.8.

The high adsorption capacity of DOX onto NPC was mainly attributed to H-bonding interaction, Lewis acid–base interaction and π-π EDA. As analyzed in FTIR spectrum of the NPC, there are abundant oxygen-containing functional groups including hydroxyl and carbonyl groups on the surface of NPC, which can facilitate DOX adsorption through H-bonding interaction (Yu et al. 2020a). The shifts of C=O, C-O-H in XPS also implied that DOX adsorption mainly occurred via H-bonding between carbonyl groups of NPC and hydroxyl groups or amidogens of DOX as well as via bonding between hydroxyl groups or amidogens of NPC and carbonyl groups of DOX. The pyridinic-N can further behave as adsorption sites to interact with DOX via H-bonding interaction (Hou et al. 2020). Additionally, the pyrrolic-N in the NPC acted as the Lewis-base site (-NH\(_2\), -NH-) to interact with the Lewis-acid site (-OH) of DOX (Liu et al. 2020). Otherwise, the graphitic-N in NPC could act as the π-acceptor capacity due to the strong electronegativity of N; it could enhance the interaction with π-donor capacity of DOX (Sun et al. 2020b). Subsequently, Raman spectrum was further verified that the NPC with high graphitization degree can behave as π-acceptor to interact with DOX via π-π EDA interaction. Therefore, the π-π EDA interaction between NPC and DOX also played an important role in adsorption process.

The effect of electrostatic interaction in the DOX adsorption could be taken into consideration. As pH increased from 2.5 to 3.5, the decrease of DOX\(^+\) leaded to the reduction of electrostatic repulsion force between DOX\(^+\) and the positive charge on the surface of NPC, which promoted the adsorption capacity. At pH > 5.8, the repulsion force between DOX\(^-\)/DOX\(^2-\) and the negative charge on the surface of NPC limited the adsorption capacity. Otherwise, the low adsorption capacity might be due to the reduction of H-bonding interaction for ionization of -OH with the increase of pH. Therefore, the adsorption mechanisms of DOX occurred mainly via hydrogen bonding, Lewis acid–base interaction, π-π EDA interaction and electrostatic interaction. Several possible adsorption mechanisms of DOX onto NPC are visually presented in Fig. 8a.

**Recycling of salt**

The recycling of chemical reagent is significant in a green synthesis route. KCl, as an activator, was recovered by
evaporation during this experiment. The recycled KCl was reused for the next preparation process of NPC, which was denoted as RNPC. It could be seen from Fig. 8b the RNPC still performed a good adsorption capacity of DOX, suggesting that the salt can be reused as activator to produce NPC.

Conclusion

In summary, an efficient adsorbent NPC derived from the agricultural by-product wheat bran was prepared through a simple salt sealing and air-assisted method for the adsorption of DOX from water environment. The conditions affecting adsorption uptake of DOX included contact time, pH and adsorbent dosage, which were optimized by using RSM. The optimum adsorption conditions of DOX were 196-min contact time, 0.2 g L\(^{-1}\) adsorbent dosage, pH 5.78, and the predicted adsorption capacity of DOX was 291.14 mg g\(^{-1}\). The adsorption isothermal and kinetics of DOX onto NPC were further analysis. It was found that the thermodynamic data fitted well with Langmuir, Koble-Corrigan and Redlich-Peterson models and kinetic data were described by the pseudo-second-order model well. The rate-limiting step of DOX adsorption onto NPC includes the boundary diffusion and intraparticle diffusion. The adsorption process of DOX was endothermic and spontaneous according to the calculation of thermodynamic parameters. In addition, the mechanism for the adsorption process of DOX was mainly controlled by \(\pi-\pi\) EDA interaction, electrostatic interaction, H-bonding interaction and Lewis acid–base site. Meanwhile, the presence of N element also made the NPC favorable for DOX adsorption. The maximum monolayer adsorption capacity for DOX was 333.23 mg g\(^{-1}\) at 298 K, suggesting that NPC could be used as a promising adsorbent to remove DOX from antibiotic wastewater.

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Authors Contributions LL designed and performed all experiments, analyzed experimental data and wrote the main manuscript (main author); XH designed and supervised all experiments, analyzed experimental data and revised the manuscript; XN analyzed the experimental data. CC and JC revised the manuscript. All authors read and approved the final manuscript.

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Declarations

Ethical Approval Not applicable.

Consent for publication Not applicable.

Data Availability All data generated or analyzed during this study are included in this published article.

Competing interests The authors declare that they have no competing interests.

References

Aldegs Y, Elbarghouthi M, Elsheikh A, Walker G (2008) Effect of solution pH, ionic strength, and temperature on adsorption behavior of reactive dyes on activated carbon. Dyes Pigm 77:16–23. https://doi.org/10.1016/j.dyepig.2007.03.001
towards antibiotics removal from aqueous solution. J Solid State Chem 289:121492. https://doi.org/10.1016/j.jssc.2020.121492

Sun Z, Zhao L, Liu C, Zhen Y et al (2020b) Fast adsorption of BPA with high capacity based on π-π electron donor-acceptor and hydrophobicity mechanism using an in-situ sp2 C dominant N-doped carbon. Chem Eng J 388:122059. https://doi.org/10.1016/j.cej.2019.122510

Tang Y, Chen Q, Li W, Xie X et al (2020) Engineering magnetic N-doped porous carbon with super-high ciprofloxacin adsorption capacity and wide pH adaptability. J Hazard Mater 388:122059. https://doi.org/10.1016/j.jhazmat.2020.122059

Tong Y, Zhao S, Kang J, Shen J et al (2021) Preparation of small-sized BiVO4 particles with improved photocatalytic performance and its photocatalytic degradation of doxycline in water. Colloids Surf A 620:126412. https://doi.org/10.1016/j.colsurfa.2021.126412

Waghmare RN, Patulkar AM, Vaidya VM, Zende RJ et al (2020) Screening of Antimicrobial Residues and Confirmation of Doxycycline in Samples Collected from Chicken Farms and Processing Units Located Around Mumbai, India. Indian J Animal Res 54:1415–1421. https://doi.org/10.18805/ijar.B-3899

Wang L, Zhu D, Duan L, Chen W (2010) Adsorption of single-ringed N- and S-heterocyclic aromatics on carbon nanotubes. Carbon 48:3906–3915. https://doi.org/10.1016/j.carbon.2010.06.057

Wang C, Wu D, Wang H, Gao Z et al (2017) Nitrogen-doped two-dimensional porous carbon sheets derived from clover biomass for high performance supercapacitors. J Power Sources 363:375–383. https://doi.org/10.1016/j.jpowsour.2017.07.097

Wang C, Wu D, Wang H, Gao Z et al (2018) A green and scalable route to yield porous carbon sheets from biomass for supercapacitors with high capacity. J Mater Chem A 6:1244–1254. https://doi.org/10.1039/c7ta07579k

Wang B, Zhai Y, Wang T, Li S et al (2019) Fabrication of bean dreg-derived carbon with high adsorption for methylene blue: Effect of hydrothermal pretreatment and pyrolysis process. Biotechnol Biofuels 27:525–532. https://doi.org/10.1016/j.biortech.2018.12.022

Wang P, Zhang G, Chen W, Chen Q et al (2020) Molten Salt Template Synthesis of Hierarchical Porous Nitrogen-Containing Activated Carbon Derived from Chitosan for CO2 Capture. ACS Omega 5:23460–23467. https://doi.org/10.1021/acsomega.0c03497

Wang Q, Zhang Z, Xu G, Li G (2021) Pyrolysis of penicillin fermentation residue and sludge to produce biochar: Antibiotic resistance genes destruction and biochar application in the adsorption of penicillin in water. J Hazard Mater 413:125585. https://doi.org/10.1016/j.jhazmat.2021.125385

Wei J, Liu Y, Li J, Zhu Y et al (2019) Adsorption and co-adsorption of tetracycline and doxycycline by one-step synthesized iron loaded sludge biochar. Chemosphere 236:124254. https://doi.org/10.1016/j.chemosphere.2019.06.224

Wen X, Huang J, Cao J, Xu J et al (2020) Heterologous expression of the tetracycline resistance gene tetX to enhance degradability and safety in doxycycline degradation. Ecotoxicology Environmental Safety 191:110214. https://doi.org/10.1016/j.ecoenv.2020.110214

Whelton A, Schach von Wittenau M, Twomey TM, Walker WG et al (1974) Doxycycline pharmacokinetics in the absence of renal function. Kidney Int 5:365–371. https://doi.org/10.1038/ki.1974.52

Xu L, Li X, Li X (2020a) Large-sized and ultrathin biomass-derived hierarchically porous carbon nanosheets prepared by a facile way for high-performance supercapacitors. Appl Surf Sci 526:146770. https://doi.org/10.1016/j.apsusc.2020.146770

Xu N, Li M, Chou WC, Lin Z (2020b) A physiologically based pharmacokinetic model of doxycycline for predicting tissue residues and withdrawal intervals in grass carp (Ctenopharyngodon idella). Food Chem Toxicol 137:111117. https://doi.org/10.1016/j.fct.2020.111127

Yang ZH, Huang J, Zeng GM, Ruan M et al (2009) Optimization of flocculation conditions for kaolin suspension using the composite flocculant of MBFGA1 and PAC by response surface methodology. Biorec Technol 100:4233–4239. https://doi.org/10.1016/j.biortech.2008.12.033

Yang J, Dai J, He J, Wang L et al (2020) A three-in-one strategy for facile fabrication of hierarchically porous n-doped carbons: enhanced CO2 capture and tetracycline removal. J Porous Mater 27:1755–1763. https://doi.org/10.1007/s10934-020-00946-5

Yin H, Lu B, Xu Y, Tang D et al (2014) Harvesting capacitive carbon by carbonization of waste biomass in molten salts. Environ Sci Technol 48:8101–8108. https://doi.org/10.1021/es501739v

Youssef NAE, Amer E, Abo El Naga AO, Shaban SA (2020) Molten salt synthesis of hierarchically porous carbon for the efficient adsorptive removal of sodium diclofenac from aqueous effluents. J Taiwan Inst Chem Eng 113:114–125. https://doi.org/10.1016/j.jtice.2020.07.018

Yu X, Han Z, Fang S, Chang C et al (2019) Optimized Preparation of High Value-Added Activated Carbon and Its Adsorption Properties for Methylene Blue. Int J Chem Reactor Eng 17:20180267. https://doi.org/10.1515/ijcree-2018-0267

Yu H, Gu L, Chen L, Wen H et al (2020a) Activation of grapefruit derived biochar by its peel extracts and its performance for tetracycline removal. Biorec Technol 316:123971. https://doi.org/10.1016/j.biortech.2020.123971

Yu X, Han X, Chang C, Hu Y et al (2020b)Corncob-derived activated carbon for roxarsone removal from aqueous solution: isotherms, kinetics, and mechanism. Environ Sci Pollut Res 27:15785–15797. https://doi.org/10.1007/s11356-020-07942-x

Zhang Y, Jiang F, Huang D, Hou S et al (2018) A facile route to magnetic mesoporous core–shell structured silicas containing covalently bound cyclodextrins for the removal of the antibiotic doxycycline from water. RSC Adv 8:31348–31357. https://doi.org/10.1039/c8ra05781h

Zhao F, Repo E, Yin D, Meng Y et al (2015) EDTA-Cross-Linked beta-Cyclodextrin: An Environmentally Friendly Bifunctional Adsorbent for Simultaneous Adsorption of Metals and Cationic Dyes. Environ Sci Technol 49:10570–10580. https://doi.org/10.1021/acs.est.5b02227

Zheng P, Pan Z, Zhang J (2017) Synergistic Enhancement in Catalytic Performance of Superparamagnetic Fe3O4@Bacillus subtilis as Recyclable Fenton-Like Catalyst. Catalysts 7:349. https://doi.org/10.3390/catal7110349

Zhu X, Liu Y, Qian F, Zhou C et al (2014) Preparation of magnetic porous carbon from waste hydrochar by simultaneous activation and magnetization for tetracycline removal. Biorec Technol 154:209–214. https://doi.org/10.1016/j.biortech.2013.12.019

Zhu M, Zhou K, Sun X, Zhao Z et al (2017) Hydrophobic N-doped porous biochar from dopamine for high selective adsorption of p-Xylene under humid conditions. Chem Eng J 317:15785–15797. https://doi.org/10.1016/j.cej.2017.02.114

Zhu K, Shen Y, Hou J, Gao J et al (2021) One-step synthesis of nitrogen and sulfur co-doped graphene-like carbon nanosheets as a bifunctional material for tetracycline removal via adsorption and catalytic degradation processes: Performance and mechanism. Chem Eng J 412:128521. https://doi.org/10.1016/j.cej.2021.128521

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