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, π - π 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

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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; Waghamare et al. 2020), grass carp (Xu et al. 2020b) and pigs (Waghamare et al. 2020). These residues in animals were able to amass 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 H_3PO_4 , KOH and ZnCl_2 , 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 N_2 atmosphere (Rehman and Park

2019; Wang et al. 2020; Youssef et al. 2020). However, the protection by inert gases (N_2 , Ar_2) 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 (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, $\geq 94\%$, $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_8\cdot\text{HCl}$, 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 pre-determined 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 (q_e , mg g^{-1}) is calculated by Eq. (1).

$$q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

where C_o (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

Table 1 Coded levels and values of experimental variable

Factors	Levels		
	Low (-1)	Central (0)	High (+1)
x_1 : Contact time (min)	40	140	240
x_2 : Adsorbent dosage (g L ⁻¹)	0.2	0.3	0.4
x_3 : pH	2	5	8

Table 2 Experimental design matrix and response values

Run	x_1	x_2	x_3	Q	
				Observed ^a	Predicted ^b
1	40	0.2	5	247.44	246.73
2	240	0.2	5	287.32	287.63
3	40	0.4	5	206.86	206.53
4	240	0.4	5	234.46	235.15
5	40	0.3	2	209.03	207.66
6	240	0.3	2	247.68	245.30
7	40	0.3	8	217.88	220.24
8	240	0.3	8	250.76	252.12
9	140	0.2	2	256.63	258.70
10	140	0.4	2	213.77	215.44
11	140	0.2	8	273.17	271.48
12	140	0.4	8	224.14	222.06
13	140	0.3	5	274.26	269.56
14	140	0.3	5	263.57	269.56
15	140	0.3	5	263.05	269.56
16	140	0.3	5	281.29	269.56
17	140	0.3	5	265.64	269.56

^a Experimental values of response^b Predicted values of response by RSM

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 ($C_0 = 100$ mg L⁻¹) are summarized in Table 2. For this, quadratic polynomial model equation (Eq. (2)) was used to build the relationship between input variables and DOX adsorption capacity (Yang et al. 2009).

$$Q = \beta_0 + \sum_{j=1}^3 \beta_j x_j + \sum_{j=1}^3 \beta_{jj} x_j^2 + \sum_{i=1}^3 \sum_{j=1}^3 \beta_{ij} x_i x_j \quad (2)$$

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; β_0 , β_j , β_{jj} and β_{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_3) was used for regression analysis, as follows:

$$Q = 269.56 + 17.38x_1 - 23.17x_2 + 4.85x_3 - 3.07x_1x_2 - 1.44x_1x_3 - 1.54x_2x_3 - 18.07x_1^2 - 7.48x_2^2 - 20.16x_3^2 \quad (3)$$

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.

Table 3 Analysis of variance for adsorption of DOX onto NPC

Source	Sum of squares	Degree of freedom	Mean square	F-value	P-value Prob > F	Status
Model	10,598.95	9	1177.66	29.06	< 0.0001	significant
x_1	2415.47	1	2415.47	59.6	0.0001	
x_2	4293.4	1	4293.4	105.93	< 0.0001	
x_3	188.57	1	188.57	4.65	0.0679	
$x_1 x_2$	37.3	1	37.3	0.93	0.3669	
$x_1 x_3$	8.32	1	8.32	0.21	0.6641	
$x_2 x_3$	9.52	1	9.52	0.23	0.6428	
x_1^2	1374.23	1	1374.23	33.91	0.0006	
x_2^2	235.33	1	235.33	5.81	0.0468	
x_3^2	1711.01	1	1711.01	42.22	0.0003	
Residual	283.71	7	40.53			
Lack of Fit	30.4	3	10.13	0.16	0.9179	not significant
Pure Error	253.31	4	63.33			
Cor Total	10,882.66	16				

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 $1173.97 \text{ m}^2 \text{ g}^{-1}$, $5.982 \text{ m}^2 \text{ g}^{-1}$ and $67.18 \text{ m}^2 \text{ g}^{-1}$ according to Brunauer–Emmett–Teller (BET) equation. The total volume (V_T) of NPC was $0.851 \text{ cm}^3 \text{ g}^{-1}$, which was much higher than CWB-573 and CWB-1073. Micropore volume of NPC was $0.257 \text{ cm}^3 \text{ g}^{-1}$ by t-plot method (Passe-Coutin et al. 2008). Besides, the average pore diameter (D_p) of NPC was calculated from $D_p = 4V_T/S_{BET}$ 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

Fig. 2 3D surface model graphs of the adsorption capacity versus ► contact time and pH (a), contact time and adsorbent dosage (b) and adsorbent dosage and pH (c)

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 $\text{C}=\text{O}$ stretching vibration of DOX, and the peak in 1463 cm^{-1} represented $\text{C}-\text{C}$ stretching vibration of benzene rings (Jia et al. 2013; Liu et al. 2017). The peak at 1383 cm^{-1} was identified as $-\text{CH}_3$ deformation vibration, and the band at 1277 cm^{-1} was attributed to $\text{C}-\text{N}$ amine stretching vibration of DOX (Naeimi and Faghihian 2017). The peak at 1050 cm^{-1} was ascribed to the phenolic $\text{C}-\text{O}$ stretching (Liu et al. 2017).

As for NPC (Fig. 3e), the broad band at 3440 cm^{-1} might be attributed to $\text{O}-\text{H}$, $\text{N}-\text{H}$ groups or adsorbed water (Peng et al. 2021). The peaks loaded in 2920 cm^{-1} and 2842 cm^{-1} could be ascribed to the $\text{C}-\text{H}$ 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 $\text{C}=\text{O}$ group vibration of NPC (Ronix et al. 2017). The band at 1393 cm^{-1} could be the vibration of $-\text{CH}_3$, and the band in 1081 cm^{-1} was considered as the $\text{C}-\text{O}$ 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 $\sim 1350\text{ cm}^{-1}$ represents the disordered and defective carbon structure, while the G band at $\sim 1580\text{ cm}^{-1}$ 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

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)

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-donor-acceptor (EDA) interaction (Chen et al. 2008).

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

Samples	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{tot} ($\text{cm}^3 \text{g}^{-1}$)	V_{mic} ($\text{cm}^3 \text{g}^{-1}$)	S_{mic} ($\text{m}^2 \text{g}^{-1}$)	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

Fig. 4 The Raman spectra of NPC and CWB-1073

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 carbonyl groups are more obvious than hydroxyl groups, demonstrating that the carbonyl groups of NPC and hydroxyl groups or amidogens of DOX play a major role in the hydrogen bonding.

Generally, N atoms would constitute several bonds with C atoms during the pyrolysis process. The

pyridinic-N consists of sp^2 -hybridized N with two adjacent sp^2 -hybridized C in a ring of the margin, which can be as active sites to produce more H bonding interaction between DOX and NPC (Hou et al. 2020). The pyrrolic-N is formed by the addition of nitrogen to the heterocycle, which mainly acts as the Lewis-base site ($-NH_2$, $-NH-$) to interact with the Lewis-acid site ($-OH$) of DOX (Liu et al. 2020; Wang et al. 2010). The graphitic N is embedded in graphitic carbon structure, which could decrease the surface electron density because of the strong electronegativity of N. It could increase the π -acceptor capacity of NPC to improve the interaction with π -donor capacity of DOX (Sun et al. 2020b). From Fig. 5f–g, the N1s spectra could be divided into three peaks, including pyridinic N (398.6 eV), pyrrolic N (400.2 eV) and graphitic N (401.9 eV). After adsorption of DOX, the binding energies of three species of N shifted from 398.6 eV, 400.2 eV and 401.9 eV to 398.4 eV, 399.2 eV and 401.6 eV of NPC-loaded DOX, which could be deduced that these three species of N-heteroatom in NPC could act as the adsorption sites in adsorption process via hydrogen bonding, Lewis acid–base and π - π EDA interactions (Liu et al. 2020). In additional, 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 χ^2 indicated that the difference between each model and experimental data was not significant (Ghaedi et al. 2012). Nonlinear Chi-square statistical test (χ^2) is shown as:

$$\chi^2 = \sum \frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,exp}^2} \quad (4)$$

The $q_{e,exp}$ and $q_{e,cal}$ 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 χ^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.

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

2008). 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 χ^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

Fig. 6 Four isotherm models for adsorption DOX onto NPC (a) ($C_0=30\text{--}400\text{ mg L}^{-1}$; adsorbent dosage $=0.2\text{ g L}^{-1}$; $t=139\text{ min}$). The fitted kinetics curves for DOX adsorption onto NPC by pseudo-first-order model, pseudo-second-order model (b) and the intraparticle diffusion model (c)

Freundlich and Langmuir isotherms. The higher R^2 values and the lower χ^2 values of K-C and Redlich-Peterson models also indicated that these two models were suited

Table 5 Parameters of adsorption isotherm for DOX onto NPC

Models	Parameters	298 K	308 K	318 K
Langmuir	$q_m\text{ (mg g}^{-1}\text{)}$	333.23	338.91	351.21
	$K_L\text{ (L mg}^{-1}\text{)}$	0.24	0.39	0.50
	χ^2	2.68	0.66	2.06
	R^2	0.9975	0.9972	0.9910
Freundlich	$K_F\text{ ((mg g}^{-1}\text{) (L/mg)}^{1/n}\text{)}$	129.79	151.13	167.40
	$1/n$	0.19	0.16	0.14
	χ^2	47.53	41.27	56.13
	R^2	0.8841	0.8730	0.9084
Koble-Corrigan	A_K	73.63	141.5	167.40
	B_K	0.22	0.41	0.54
	M	1.09	0.91	0.86
	χ^2	2.38	0.47	2.6
	R^2	0.9980	0.9984	0.9932
	R^2	0.9980	0.9984	0.9932
Redlich-Peterson	A_R	80.28	139.14	188.06
	B_R	0.24	0.44	0.57
	g	1.00	0.99	0.99
	χ^2	2.58	1.61	1.67
	R^2	0.9976	0.9981	0.9918
	R^2	0.9976	0.9981	0.9918

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 (ΔG , kJ mol^{-1}), enthalpy (ΔH , kJ mol^{-1}) and entropy (ΔS , 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:

$$\Delta G = RT \ln K_L \quad (5)$$

$$\Delta G = \Delta H - T \Delta S \quad (6)$$

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

The values of ΔG were -28.93 , -31.07 , $-32.75\text{ kJ mol}^{-1}$ for DOX adsorbed onto NPC at 298, 308, 318 K, respectively. At the same time, the negative values of ΔG at different temperature indicated that the adsorption process of DOX was spontaneous. The values of ΔH and ΔS could be obtained by the intercept and slope of the line based on Eq. (6). The positive value of ΔH ($\Delta H=27.97\text{ kJ mol}^{-1}$) indicated that the DOX adsorption onto NPC was an endothermal process. As it has been documented in the literature, the value of ΔH between 20.9 kJ mol^{-1} and 418.4 kJ mol^{-1}

Table 6 Comparison of adsorption capacity of DOX onto different adsorbents

Adsorbents	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	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)
$\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{mSiO}_2\text{-cyclodextrins}$	119	200	(Zhang et al. 2018)
BC/MnO ₂	64.32	24.69	(Li et al. 2020a)
NPC	1179.97	333.23	This study

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 ΔS ($\Delta S = 0.19 \text{ kJ (mol K)}^{-1}$) 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_{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_{fi} gradually decreased as the increase of time at the same temperature. In the same state, the K_{fi} 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.

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 $3.5 < \text{pH} < 7.7$ and it presents mainly as anionic species (DOX^- , DOX^{2-}) at $\text{pH} > 7.7$. The zero point charge (pH_{zpc}) of NPC was measured by salt addition method (Slimani et al. 2014). As illustrated in Fig. 7c, the pH_{zpc} of NPC was found around 5.8. It suggested that the NPC has

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_{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_{fi} ($\text{mg g}^{-1} \text{min}^{-1/2}$)	23.62	25.36	25.94
	C_1	97.92	99.02	108.18
	R^2	0.9925	0.9598	0.9016
	K_{fi} ($\text{mg g}^{-1} \text{min}^{-1/2}$)	6.64	7.22	7.58
	C_2	206.58	212.98	218.56
	R^2	0.9905	0.9557	0.9755
	K_{fi} ($\text{mg g}^{-1} \text{min}^{-1/2}$)	0.88	0.90	1.00
	C_3	279.15	290.67	298.40
	R^2	0.9660	0.8634	0.8924

Fig. 7 Existing species of DOX at different pH (a). Ionization constants of DOX (b). pH_{pzc} of NPC (c) and effect of solution pH on the adsorption of DOX (d) ($C_0 = 100 \text{ mg L}^{-1}$, adsorbent dosage = 0.2 g L^{-1} , $T = 298 \text{ K}$)

a positive charge on its surface at $\text{pH} < 5.8$ and a negative charge on its surface at $\text{pH} > 5.8$.

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 $\text{pH} > 5.8$.

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 $\text{C}=\text{O}$, $\text{C}-\text{O}-\text{H}$ 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 ($-\text{NH}_2$, $-\text{NH}-$) to interact with the Lewis-acid site ($-\text{OH}$) 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^+ led to the reduction of electrostatic repulsion force between DOX^+ and the positive charge on the surface of NPC, which promoted the adsorption capacity. At $\text{pH} > 5.8$, the repulsion force between $\text{DOX}^-/\text{DOX}^{2-}$ 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 $-\text{OH}$ 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

Fig. 8 Schematic illustration of adsorption mechanism of NPC (a) and effect of time on the adsorption capacities of NPC and RNPC (b) ($C_0 = 100 \text{ mg L}^{-1}$, adsorbent dosage = 0.2 g L^{-1} , $T = 298 \text{ K}$)

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 π - π 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.

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