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Study on optimal adsorption conditions of norfloxacin in water based on response surface methodology

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ABSTRACT

The waste pomelo peel was pyrolyzed at 400 °C to prepare biochar and used as adsorbent to remove norfloxacin (NOR) from simulated wastewater. The adsorption conditions of norfloxacin by biochar were optimized by response surface methodology (RSM). On the basis of single-factor experiment, the adsorption conditions of biochar dosage, solution pH and reaction temperature were optimized by Box-Behnken Design (BBD), and the quadratic polynomial regression model of response value Y_1 (NOR removal efficiency) and Y_2 (NOR adsorption capacity) were obtained respectively. The results show that the two models are reasonable and reliable. The influence of single factor was as follows: solution pH > biochar dosage > reaction temperature. The interaction between biochar dosage and solution pH was very significant. The optimal adsorption conditions after optimization were as follows: biochar dosage = 0.5 g/L, solution pH = 3, and reaction temperature = 45 °C. The Y_1 and Y_2 obtained in the verification experiment were 75.68% and 3.0272 mg/g, respectively, which were only 2.38% and 0.0242 mg/g different from the theoretical predicted values of the model. Therefore, the theoretical model constructed by response surface methodology can be used to optimize the adsorption conditions of norfloxacin in water.

Key words: adsorption conditions, biochar, interaction, norfloxacin, RSM

HIGHLIGHTS

- Constructed a reliable response surface model for biochar adsorption of norfloxacin in water.
- The interaction of adsorption conditions and its influence on the adsorption of norfloxacin by biochar have been explored clearly.
- The constructed response surface model can be used to adjust the adsorption conditions of biochar to adsorb norfloxacin in actual water.

1. INTRODUCTION

Antibiotics are widely used in human clinical and animal husbandry to treat infections, saving millions of lives (Cabello *et al.* 2016; Zhou *et al.* 2016). Fluoroquinolones are the most widely used antibiotics (Duan *et al.* 2019), showing good antibacterial activity against both gram-negative and gram-positive bacteria (Chen *et al.* 2013). The excessive use of norfloxacin in animal husbandry, sewage discharge from pharmaceutical factories and hospitals, incomplete metabolism of norfloxacin in animals and other factors has resulted in the widespread presence of norfloxacin in surface water (Jia *et al.* 2012; Van *et al.* 2014; Prutthiwanasan *et al.* 2016), with concentrations up to ng/L and even mg/L (Mir *et al.* 2017). In addition, the non-biodegradability and ecotoxicity of norfloxacin in water induced the generation of some drug-resistant bacteria, which threatened human health (Jojoa *et al.* 2017). Therefore, it is necessary to find an effective method to remove norfloxacin from water. The common methods to remove norfloxacin from water include photocatalysis, electrochemical degradation, biodegradation, Fenton reaction, advanced oxidation process, etc. The adsorption method has been widely used because of its high removal efficiency, low cost and easy operation (Wang *et al.* 2017).

Yang *et al.* studied the adsorption behavior of norfloxacin on porous resin and carbon nanotubes. It was found that the kinetic model and adsorption isothermal model of norfloxacin adsorption by the two materials could be well described by the pseudo-second-order kinetic equation and Langmuir equation respectively (Yang *et al.* 2012). Yan *et al.* studied the adsorption behavior of norfloxacin on barley straw and pretreated barley straw respectively, and studied the potential energy distribution of the adsorption process based on the Dubinin-Astakhov model. The results showed that the pretreated barley straw had higher potential energy, so it had more affinity for norfloxacin (Yan & Niu 2018). Tamiris Chahm *et al.* used sulfuric acid to activate termite feces to study its adsorption performance to norfloxacin, and the results showed that sulfuric acid activated termite feces is an efficient and low cost adsorption material (Chahm *et al.* 2019). Most of these studies focus on the preparation and adsorption behavior of adsorbents. It is also assumed that the factors affecting adsorption capacity are independent of each other. However, it is quite different from the actuality that there is a complex nonlinear relationship between the two factors. Response surface methodology is an effective method to build a model that can predict the whole based on limited experimental data, which can reduce the required preliminary data collection and explore the interaction of multiple factors (Zhou *et al.* 2019; Zhou *et al.* 2020). Therefore, this study intends to use the response surface methodology to establish the nonlinear response relationship between the influencing factors and the output factors, analyze the nonlinear interaction between the factors, and obtain the optimal norfloxacin adsorption conditions.

Pomelo is a fruit widely cultivated all over the world. Pomelo peel accounts for about 45% of the total weight of pomelo (Liang *et al.* 2014), and pomelo peel contains a large amount of cellulose and hemicellulose. However, the majority of pomelo peel is treated as agricultural waste, resulting in a huge waste of resources and environmental pollution (Zhang *et al.* 2018). Therefore, waste grapefruit peel was used as the carbon source of biochar in this experiment. The batch adsorption test was designed by Design Expert software. Box-Behnken Design (BBD) was used to establish the response surface model of biochar dosage, solution pH and reaction temperature on the removal efficiency and adsorption capacity of norfloxacin by biochar. The interaction of factors was discussed and the adsorption conditions were optimized in order to provide reference for similar studies.

2. MATERIALS AND METHODS

2.1. Instruments and materials

Experimental instruments: UV-1810 UV-visible spectrophotometer (Youke, China). PHS-25 digital pH meter (Shanghai thunder magnetic, China). SHA-B digital display constant temperature water bath oscillator (Guohua, China). Norfloxacin (98% purity) reagent was purchased from Aladdin pharmaceutical company (Shanghai, China). Its physical and chemical properties are show in Table 1. The hydrochloric acid and sodium hydroxide used in the experiment were analytically pure. The experimental water was ultra-pure water (UP).

2.2. Preparation of biochar

The recovered grapefruit peel was washed with ultra-pure water and dried at 70 °C to a constant weight. The dried grapefruit peel was stored in a crucible and placed in a muffle furnace, and then heated to 400 °C at a heating rate of 20 °C/min and pyrolyzed at this pyrolysis temperature for 2 h. The biochar was taken out after pyrolysis, ground, passed through a 60-mesh sieve, and placed in a sealed plastic bottle for later use.

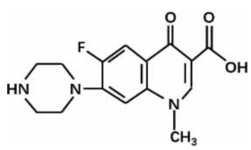
2.3. Adsorption conditions experiment

Biochar dosage: The prepared biochar (0.0025, 0.0050, 0.0075, 0.0100 and 0.0125 g) was placed in a 50 mL centrifuge tube and norfloxacin solution (25 mL, 2 mg/L) was added. It was then placed in a water bath oscillator and oscillated at room temperature for 2 h at 150 rpm.

Solution pH: keeping the above conditions unchanged, biochar dosage was controlled at 0.4 g/L and the pH of norfloxacin solution was 3, 4, 5, 6 and 7, respectively.

Reaction temperature: the biochar dosage was controlled at 0.4 g/L, and the norfloxacin solution concentration was 2 mg/L. Other conditions remained unchanged, and the biochar was oscillated for 2 h at 25, 30, 35, 40 and 45 °C, respectively.

Table 1 | Basic properties of NOR

Molecular formula	Molecular mass	pK_a	lgP	Chemical structure
$C_{16}H_{18}FN_3O_3$	319.33	$pK_{a1} = 6.34$ $pK_{a2} = 8.75$	0.46	

After the adsorption of all samples was completed, the residual concentration of norfloxacin was was measured at 278 nm by UV spectrophotometer after passing a 45 μm needle filter membrane (Jin *et al.* 2014). Except for the experiment to explore the influence of initial solution pH and temperature on the adsorption of NOR by biochar, other experiments were carried out at room temperature (20 ± 1 °C) and the background pH (4.52) of the NOR solution. Each experiment was repeated three times, and the mean value of the experimental data was taken. The removal efficiency and adsorption capacity of norfloxacin by biochar were calculated according to Equations (1) and (2):

$$\mathrm{R} = \frac{C_0 - C_t}{C_0} \times 100\% \tag{1}$$

$$Q_e = (C_0 - C_t) \times \frac{v}{m} \tag{2}$$

where Q_e (mg/g) is the equilibrium adsorption capacity of norfloxacin adsorbed by biochar. C_0 and C_t (mg/L) are the initial concentration of norfloxacin and the residual concentration after adsorption, respectively. m (g) is the biochar dosage. v (L) is the volume of the solution. R (%) is the removal efficiency of norfloxacin by biochar.

Pseudo-first-order, pseudo-second-order kinetics and intra-particle diffusion models were used to analyze the process of biochar adsorption of NOR. The equation is as follows:

Pseudo-first-order kinetic equation:

$$ln(q_e - q_t) = lnq_e - k_1 t \tag{3}$$

Pseudo-second-order kinetic equation:

$$\frac{\mathrm{t}}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \tag{4}$$

Intra particle diffusion equation:

$$q_t = k_3 t^{\frac{1}{2}} + I \tag{5}$$

where q_e (mg/g) is the adsorption capacity of norfloxacin at adsorption equilibrium. q_t (mg/g) is the adsorption capacity of norfloxacin at time t. k_1 (min^{-1}) and k_2 [$g/(mg^{-1}\cdot min)$] are the adsorption rate constants of pseudo first and pseudo second order kinetic equations respectively. k_3 [$mg/(mg\cdot min^{1/2})$] is the interparticle diffusion rate constant, which is related to the diffusion coefficient of particles. I is the constant related to the boundary layer thickness.

2.4. Response surface methodology (RSM): the Box-Behnken design

The effects of biochar dosage, solution pH and reaction temperature on the adsorption of norfloxacin by biochar and their interactions were studied. The experimental process was the same as 2.3. Box-Behnken experimental design was used to optimize the adsorption conditions of norfloxacin by biochar. The norfloxacin removal efficiency Y_1 (%) and norfloxacin adsorption capacity Y_2 (mg/g) were taken as response values to control the initial concentration of norfloxacin at 2 mg/L. Five groups of parallel center point experiments were designed. The coding value and experimental value of 3 factors at 3 level are shown in Table 2. According to the optimization results, the optimal conditions are verified.

Table 2 | Factors and levels of Box-Behnken design

Factor	Symbols	Unit	Coded Levels		
			−1	0	1
Biochar dosage	X_1	g/L	0.3	0.4	0.5
pH	X_2		3	4	5
Temperature	X_3	°C	25	35	45

3. RESULTS AND DISCUSSION

3.1. Effects of single factor on norfloxacin adsorption by biochar

Exploring the effect of time on the adsorption of pollutants by adsorbents is a necessary process to understand the mechanism. As shown in Figure 1, the adsorption of NOR by biochar reached equilibrium at about 120 min, and the Q_e value was 3.75 mg/g. The commonly used pseudo first-order and second-order kinetics are used to fit the experimental data. The results are shown in Figure 1, and the fitting parameters are shown in Table 3. Compared with the pseudo-first-order kinetics, the pseudo-second-order kinetics model has a higher fitting correlation ($R^2 = 0.980$) to the experimental data, and the fitted Q_e value (3.81 mg/g) is closer to the experimental value (3.76 mg/g). Therefore, the adsorption of NOR by biochar is a chemical adsorption process rather than a simple and reversible physical adsorption. In addition, the intra-particle diffusion model is also taken into consideration. As shown in Figure 2, the adsorption of NOR by biochar can be divided into two stages. The first stage is that NOR is adsorbed to the surface of biochar from the liquid interface and has a large adsorption rate $k = 0.124$. The second stage is that NOR diffuses in the pores of the biochar and has a small adsorption rate $k = 0.014$. In addition, some reports on the adsorption of NOR by adsorbents were used to compare with the grapefruit peel biochar prepared in this study (Table 4). Therefore, 120 min was used as the reaction time for subsequent adsorption experiments.

The influence of biochar dosage on norfloxacin removal efficiency and adsorption capacity is shown in Figure 3(a). The removal efficiency increases with the increase of biochar dosage. When the dosage of biochar increased from 0.1 g/L to 0.5 g/L, the removal efficiency increased from 37.15% to 41.62%, the change was not obvious. However, the adsorption capacity of norfloxacin by biochar decreased sharply from 7.43 mg/g to 1.6648 mg/g. The effect of biochar dosage on the adsorption capacity of norfloxacin was greater than that of removal efficiency.

The effect of solution pH on norfloxacin adsorption by biochar is shown in Figure 3(b). When the pH rose from 3 to 6, the removal efficiency of norfloxacin dropped rapidly from 58.78% at pH = 3 to 39.03% at pH = 6, with a decrease of nearly 20%. Meanwhile, the adsorption capacity of norfloxacin by biochar decreased from 2.9390 mg/g to 1.9519 mg/g. When the pH changed from 6 to 7, the removal efficiency and adsorption capacity were almost unchanged.

The influence of temperature on norfloxacin removal efficiency and adsorption capacity of biochar is shown in Figure 3(c). When the temperature rose from 25 °C to 45 °C, the removal efficiency increased by 2.74%, and the adsorption capacity increased from 1.9425 mg/g to 2.0795 mg/g, with a slight increase. This indicates that the adsorption of norfloxacin by

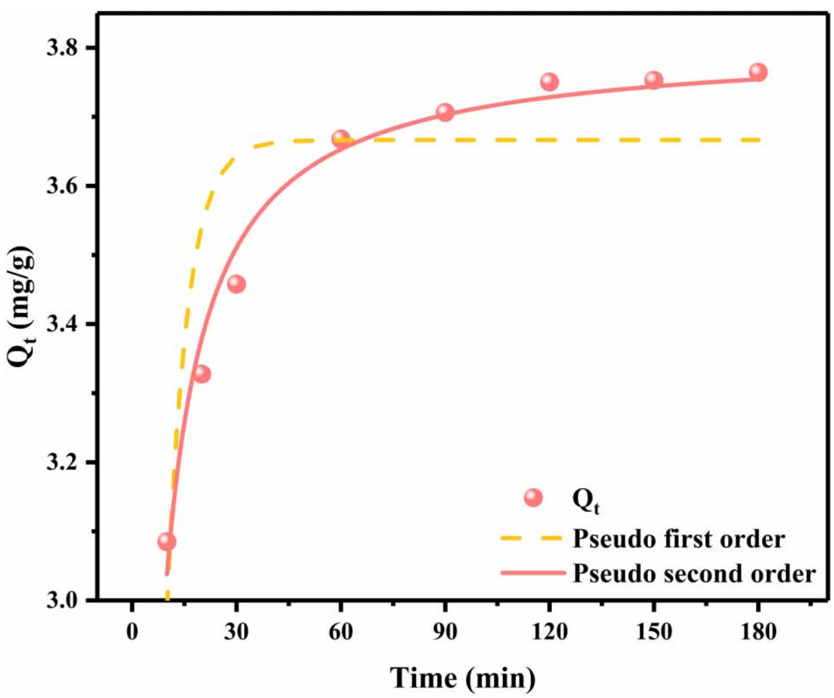


Figure 1 | The effect of time on NOR adsorption and kinetics of biochar.

Table 3 | Fitting parameters of kinetic models for adsorption of NOR by biochar

Kinetic model	*k*	Q_e	R^2
Pseudo-first-order	0.169	3.67	0.738
Pseudo-second-order	0.104	3.81	0.980

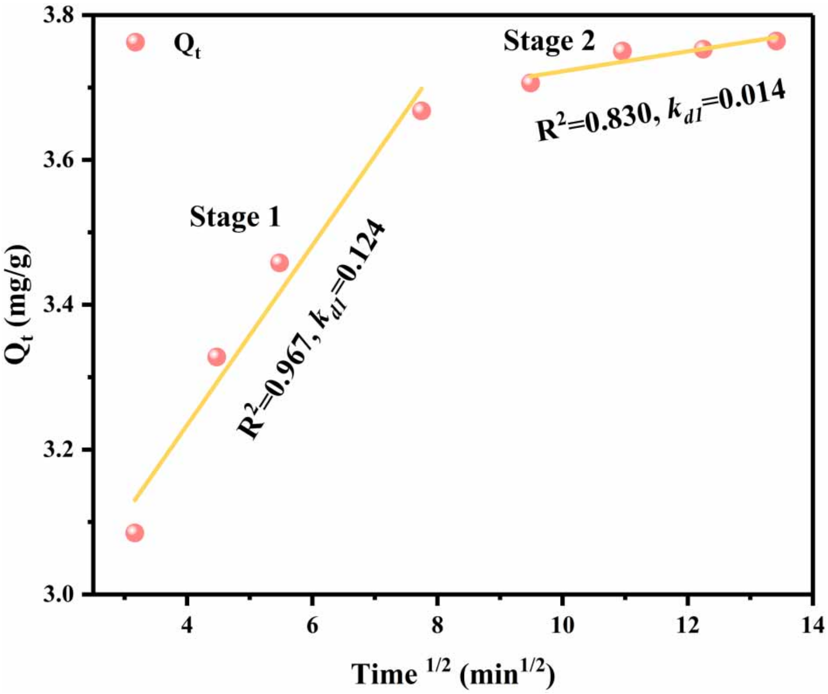


Figure 2 | Intra-particle diffusion model of NOR adsorption by biochar.

Table 4 | Comparison of the adsorption performance of adsorbents for NOR in other reports with this study

Adsorbents	Dosage (g/L)	Concentration (mg/L)	Q_e (mg/g)	Reference
Cauliflower roots biochar	2	10	4.63	Qin *et al.* (2017)
KOH-modified biochar	10	30	2.80	Luo *et al.* (2018)
Magnetic biochar	4	10	2.30	Wang *et al.* (2017)
Hematite–biochar composites	4	8	1.68	Yang *et al.* (2019)
Magnetic biochar-based manganese oxide	2	10	4.64	Li *et al.* (2018)
Pomelo peel-based biochar	0.4	4	3.75	This study

biochar is endothermic (Wang & Zhang 2020), and the increase of temperature is conducive to the adsorption of norfloxacin by biochar.

3.2. Box-Behnken design (BBD) and model analysis

The Box-Behnken experimental design and results of norfloxacin removal by biochar adsorption are shown in Table 5. The data in Table 5 was analyzed by using Design-Expert 11 for variance analysis (ANOVA), and the results are shown in Tables 6 and 7. The comparison between the predicted value and the actual value of the model is shown in Figure 4. The response

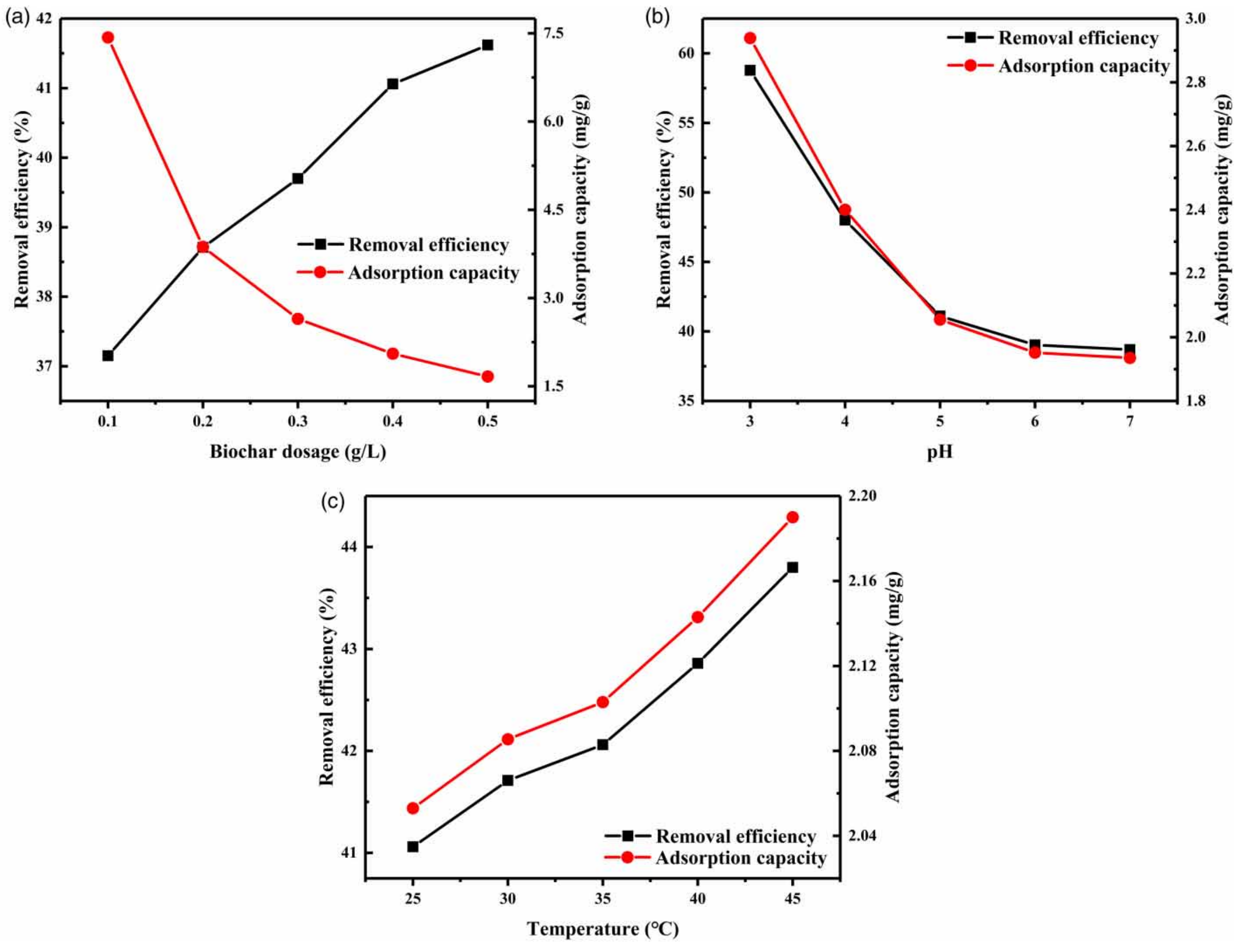


Figure 3 | The effect of biochar dosage (a), pH (b) and reaction temperature (c) on the removal efficiency and adsorption capacity of NOR by biochar.

surface polynomials of norfloxacin removal efficiency (Y_1), adsorption capacity (Y_2) and three factors are as follows:

$$Y_1 = 41.64 + 6.14X_1 - 7.86X_2 + 1.74X_3 - 4.94X_1X_2 + \mathrm{X}_1X_3 + 0.07X_2X_3 + 2.34X_1^2 + 4.97X_2^2 + 2.75X_3^2 \quad (6)$$

$$Y_2 = 2.08 - 0.3106X_1 - 0.3715X_2 + 0.0836X_3 - 0.1733X_1X_2 + 0.0267X_1X_3 + 0.0035X_2X_3 + 0.1947X_1^2 + 0.2494X_2^2 + 0.1364X_3^2 \quad (7)$$

The model predicted the optimal conditions for norfloxacin adsorption by pomelo peel biochar as follows: biochar dosage (X_1) = 0.5 g/L, solution pH (X_2) = 3, reaction temperature (X_3) = 45 °C (corresponding coding value is 1, −1, 1). The verification test is performed according to the optimal adsorption condition. The removal efficiency and adsorption capacity of norfloxacin were 75.68% and 3.0272 mg/g, respectively. The predicted values of the model were 73.30% and 3.003 mg/g, which were almost no different from the experimental values. Figure 4 shows the comparison between the experimental value and the predicted value of the model. It can be found that the relative deviation between the experimental value and the predicted value of the model is small and distributed on both sides of the line. At the same time, it can be drawn from Tables 6 and 7 that the ρ value of the model with two response values of Y_1 and Y_2 is <0.0001, indicating that the fitted regression equation is extremely significant. And the determination coefficient R^2 was 0.9905 and 0.9820 respectively, indicating that the model fitted well with the actual situation and the experimental error was ignorable. Therefore, the regression Equations (6) and (7) can be used to predict and analyze the effects of biochar dosage, solution pH and reaction temperature on removal efficiency (Y_1) and adsorption capacity (Y_2) during norfloxacin adsorption by grapefruit peel biochar.

Table 5 | Box-Behnken design experiment design and results with independent factors

Run	Coded levels X_1	X_2	X_3	Removal efficiency Y_1 (%)	Adsorption capacity Y_2 (mg/g)
1	0	0	0	41.62	2.0810
2	0	0	0	41.75	2.0875
3	0	−1	−1	56.91	2.8455
4	0	0	0	41.58	2.0790
5	1	−1	0	67.00	2.6800
6	1	1	0	43.59	1.7436
7	−1	0	−1	39.80	2.6533
8	0	1	−1	38.85	1.9425
9	−1	0	1	41.80	2.7867
10	0	1	1	41.94	2.0970
11	−1	−1	0	44.43	2.9620
12	0	0	0	41.60	2.0800
13	1	0	−1	49.65	1.9860
14	1	0	1	55.66	2.2264
15	−1	1	0	40.78	2.7187
16	0	−1	1	59.72	2.9860
17	0	0	0	41.65	2.0825

Table 6 | The quadratic regression model of ANOVA for removal efficiency of NOR by biochar

Sources	Sum of squares	df	Mean square	F-value	ρ-value prob. > F
Y_1	1096.26	9	121.81	80.75	<0.0001**
X_1	301.23	1	301.23	199.70	<0.0001**
X_2	494.55	1	494.55	327.86	<0.0001**
X_3	24.19	1	24.19	16.03	0.0052*
X_1X_2	97.61	1	97.61	64.71	<0.0001**
X_1X_3	4.02	1	4.02	2.67	0.1466
X_2X_3	0.0196	1	0.0196	0.0130	0.9124
X_1^2	23.08	1	23.08	15.30	0.0058*
X_2^2	103.95	1	103.95	68.91	<0.0001**
X_3^2	31.76	1	31.76	21.05	0.0025*
Residual	10.56	7	1.51		
Pure Error	0.0178	4	0.0045		
Cor Total	1106.82	16			

Note: **means the difference is very significant (ρ <0.05). *indicates significant difference (ρ < 0.05).

As for the removal efficiency Y_1, it can be judged from the ρ-value in Table 6 that the primary terms X_1 and X_2 are extremely significant and X_3 is significant. The interaction term X_1X_2 was very significant, while X_1X_3 and X_2X_3 were not significant. The quadratic term X_2^2 is extremely significant, while X_1^2 and X_3^2 are significant. For the response value of norfloxacin adsorption capacity Y_2 (Table 7), the primary terms X_1 and X_2 were extremely significant, while X_3 was significant. The interaction term X_1X_2 was significant, while X_1X_3 and X_2X_3 were not significant. The quadratic terms X_1^2, X_2^2 and X_3^2 were all significant.

Table 7 | The quadratic regression model of ANOVA for adsorption capacity of NOR by biochar

Sources	Sum of squares	df	Mean square	F-value	ρ-value prob. >F
Y_2	2.61	9	0.2898	42.45	<0.0001**
X_1	0.7717	1	0.7717	113.03	<0.0001**
X_2	1.10	1	1.10	161.68	<0.0001**
X_3	0.0559	1	0.0559	8.19	0.0243*
X_1X_2	0.1201	1	0.1201	17.59	0.0041*
X_1X_3	0.0029	1	0.0029	0.4192	0.5380
X_2X_3	0.0000	1	0.0000	0.0072	0.9349
X_1^2	0.1596	1	0.1596	23.38	0.0019*
X_2^2	0.2618	1	0.2618	38.35	0.0004*
X_3^2	0.0783	1	0.0783	11.47	0.0116*
Residual	0.0478	7	0.0068		
Pure Error	0.0000	4	0.0000		
Cor Total	2.66	16			

Note: **means the difference is very significant ($\rho < 0.05$). *indicates significant difference ($\rho < 0.05$).

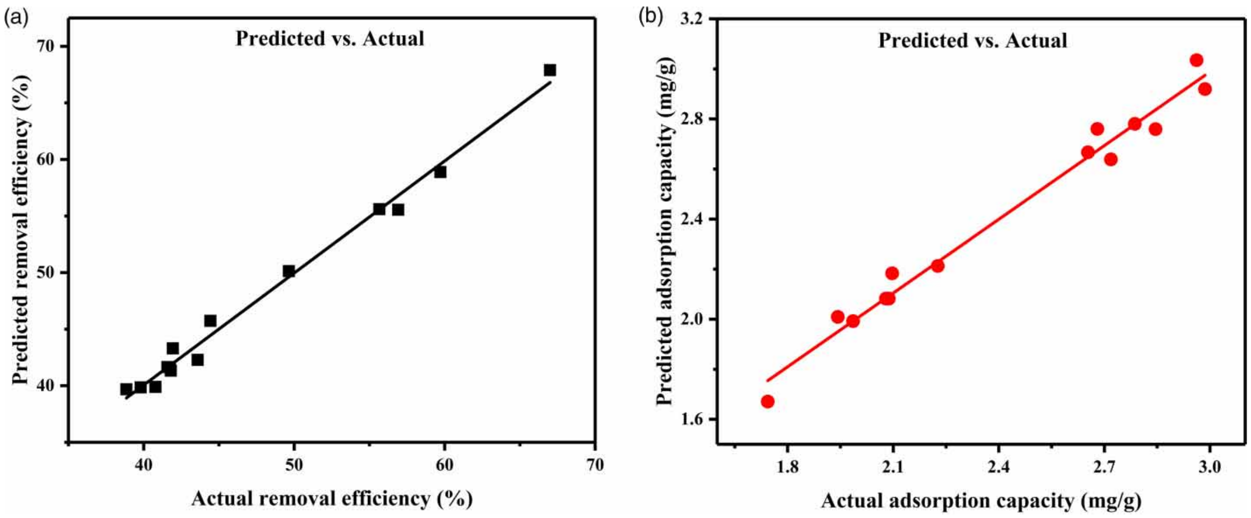


Figure 4 | Relationship between predicated and experimental data for response Y_1 (removal efficiency) (a) and Y_2 adsorption capacity (b).

Comparing the F values in Tables 6 and 7, it can be found that the influence of each single factor on removal efficiency (Y_1) and adsorption capacity (Y_2) is X_2 (solution pH) > X_1 (biochar dosage) > X_3 (reaction temperature) (Wang *et al.* 2021).

3.3. Interaction effects of factors and response surface

The three-dimensional space surface diagram composed of the response value to each experimental factor can directly reflect the influence of each factor and the interaction between each on the response value. The larger the slope of the response surface, the greater the influence of experimental factors on the response value (Wan *et al.* 2018). Using Design Expert software, quadratic multiple regression fitting was performed on the experimental data in Table 5, and the response surface diagram and contour diagram of the quadratic regression Equations (6) and (7) were obtained, as shown in Figures 5 and 6.

For the response values Y_1 (NOR removal efficiency) and Y_2 (NOR adsorption capacity), it can be seen from Figures 5 and 6 that the interaction between X_1 (biochar dosage) and X_2 (solution pH) is very significant, which is reflected in the steep surface. And the closer the contour shape is to the ellipse, the stronger the interaction (Pryseley *et al.* 2010). Both Y_1 (NOR removal efficiency) and Y_2 (NOR adsorption capacity) increased with the increase of X_1 (biochar dosage) and the

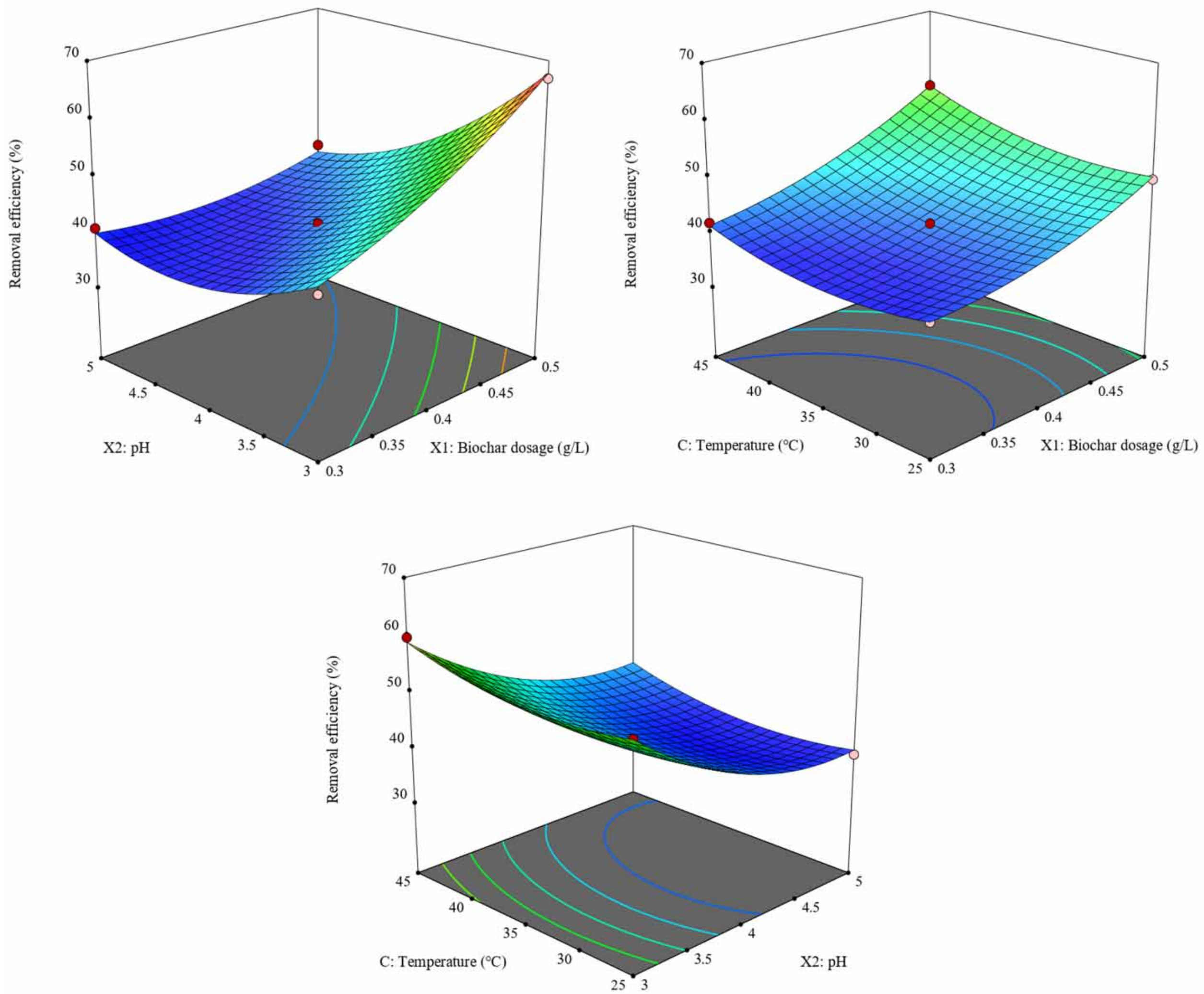


Figure 5 | 3D surface plots of effects of binary interactions among factors X_1 (biochar dosage), X_2 (pH), X_3 (temperature) on response value Y_1 (removal efficiency of NOR).

decrease of X_2 (solution pH), showing an obvious inverse relationship. This is because when the concentration of norfloxacin remains unchanged, the increase of biochar dosage will provide more active sites that can adsorb norfloxacin, improving the removal efficiency and adsorption capacity of norfloxacin. Norfloxacin has two acid dissociation constants pKa values of 6.22 and 8.51 (Kong *et al.* 2014). Therefore, when the pH of the solution rose from 3 to 6, the cation of norfloxacin (NOR^+) dissolved in the water gradually decreased. The zero point charge (pH_{pzc}) of the grapefruit peel biochar is $9.82 > 6$ (Wang *et al.* 2020). The surface of biochar was positively charged, and the cation exchange and H bond between norfloxacin cation (NOR^+) and biochar were weakened, resulting in a great decrease in the adsorption capacity of norfloxacin on the grapefruit peel biochar. The slope of the 3D surface in Figures 5 and 6 is small, indicating that the interaction between X_1 (biochar dosage) and X_3 (reaction temperature), X_2 (solution pH) and X_3 (reaction temperature) has no significant effect on the removal efficiency and adsorption capacity of norfloxacin.

4. CONCLUSION

(1) Box-Behnken Design (BBD) was used to explore the effect of biochar dosage, solution pH and reaction temperature on adsorption of norfloxacin by pomelo peel biochar. Two quadratic multiple regression equations with norfloxacin removal efficiency Y_1 and norfloxacin adsorption capacity Y_2 as response values were constructed. The determination coefficients of the prediction model were 0.9905 and 0.9820, respectively, and the model was significant and reliable.

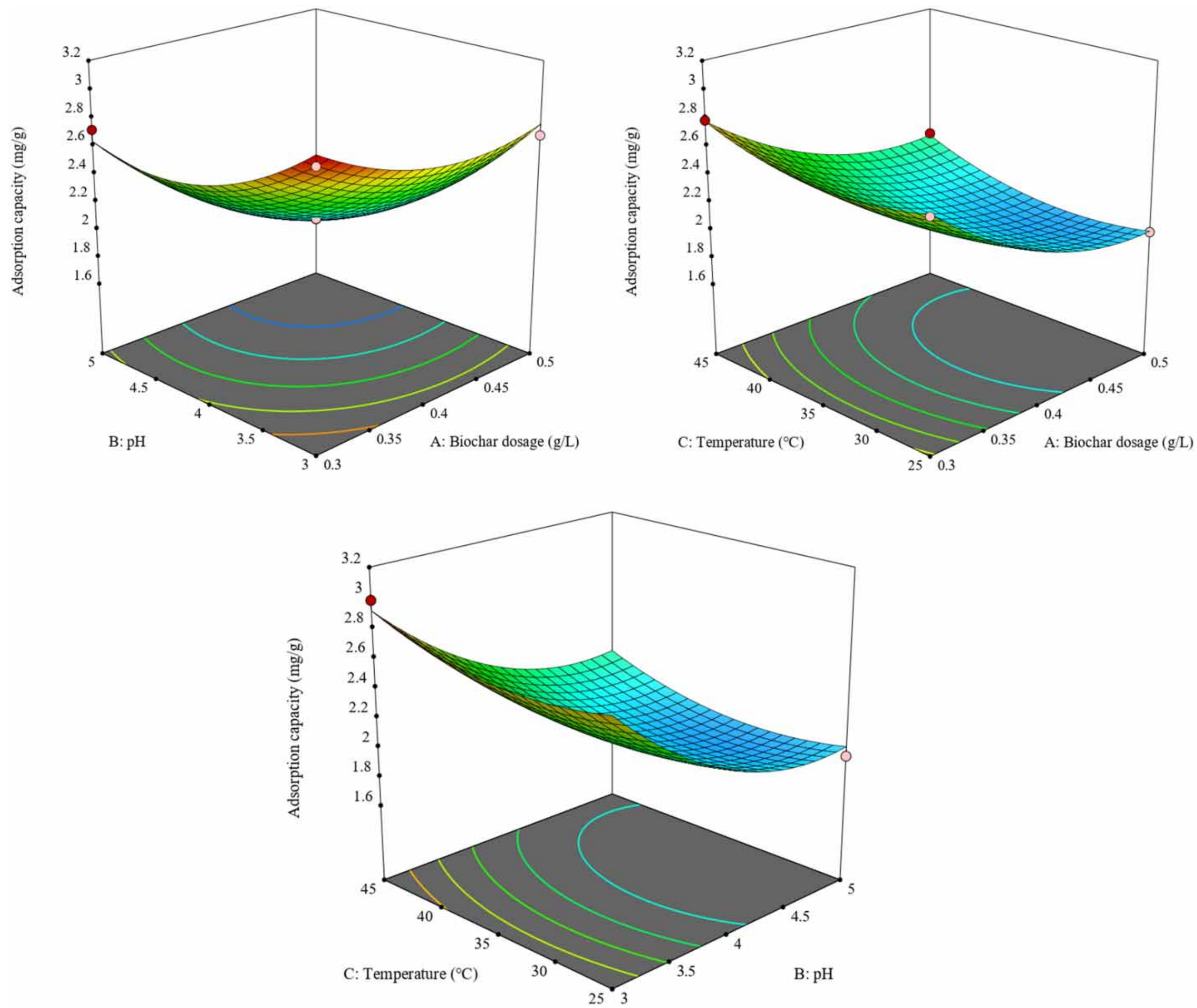


Figure 6 | 3D surface plots of effects of binary interactions among factors X_1 (biochar dosage), X_2 (pH), X_3 (temperature) on response value Y_2 (adsorption capacity of NOR).

(2) Response surface analysis shows that the influence of each single factor on removal efficiency (Y_1) and adsorption capacity (Y_2) is X_2 (solution pH) > X_1 (biochar dosage) > X_3 (reaction temperature). In the interaction, the influence of X_1X_2 (biochar dosage × solution pH) was extremely significant, while that of X_1X_3 (biochar dosage × reaction temperature) and X_2X_3 (solution pH× reaction temperature) was not significant.

(3) Using Design Expert software to optimize the adsorption of norfloxacin by the grapefruit peel biochar, the optimization scheme was X_1 (biochar dosage) = 0.5 g/L, X_2 (solution pH) = 3, X_3 (reaction temperature) = 45 °C. The Y_1 (NOR removal efficiency) and Y_2 (NOR adsorption capacity) obtained in the verification test were 75.68% and 3.0272 mg/g, respectively, and the error was only 2.38% and 0.0242 mg/g. The model established by Box-Behnken Design is verified to be authentic, reliable and accurate.

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CONFLICT OF INTEREST

The authors have declared no conflict of interest.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

Cabello, F. C., Godfrey, H. P., Buschmann, A. H. & Dolz, H. J. 2016 Aquaculture as yet another environmental gateway to the development and globalisation of antimicrobial resistance. *Lancet Infectious Diseases* **16** (7), 127–133.

Chahm, T., De, S. L. F., Dos, S. N. R., Da, S. B. A. & Rodrigues, C. A. 2019 Use of chemically activated termite feces a low-cost adsorbent for the adsorption of norfloxacin from aqueous solution. *Water Science and Technology* **79** (2), 291–301.

Chen, Y. S., Yu, G., Cao, Q. M., Zhang, H. B., Lin, Q. Y. & Hong, Y. W. 2013 Occurrence and environmental implications of pharmaceuticals in Chinese municipal sewage sludge. *Chemosphere* **93** (9), 1765–1772.

Duan, W. Z., Li, M. H., Xiao, W. L., Wang, N. F., Niu, B. H., Zhou, L. & Zheng, Y. A. 2019 Enhanced adsorption of three fluoroquinolone antibiotics using polypyrrole functionalized *Calotropis gigantea* fiber. *Colloids And Surfaces A-Physicochemical And Engineering Aspects* **574**, 178–187.

Jia, A., Wan, Y., Xiao, Y. & Hu, J. Y. 2012 Occurrence and fate of quinolone and fluoroquinolone antibiotics in a municipal sewage treatment plant. *Water Research* **46** (2), 387–394.

Jin, X. Y., Zha, S. X., Li, S. B. & Chen, Z. L. 2014 Simultaneous removal of mixed contaminants by organoclays – Amoxicillin and Cu(II) from aqueous solution. *Applied Clay Science* **102**, 196–201.

Jojoa, S. S. D., Silva, A. J., Herrera, C. E. & Torres, P. R. A. 2017 Elimination of the antibiotic norfloxacin in municipal wastewater, urine and seawater by electrochemical oxidation on IrO_2 anodes. *Science of the Total Environment* **575**, 1228–1238.

Kong, X. S., Feng, S. X., Zhang, X. & Li, Y. 2014 Effects of bile salts and divalent cations on the adsorption of norfloxacin by agricultural soils. *Journal of Environmental Sciences* **26** (4), 846–854.

Li, R. N., Wang, Z. W., Zhao, X. T., Li, X. & Xie, X. Y. 2018 Magnetic biochar-based manganese oxide composite for enhanced fluoroquinolone antibiotic removal from water. *Environmental Science and Pollution Research* **25** (31), 31136–31148.

Liang, Q. H., Ye, L., Huang, Z. H., Xu, Q., Bai, Y., Kang, F. Y. & Yang, Q. H. 2014 A honeycomb-like porous carbon derived from pomelo peel for use in high-performance supercapacitors. *Nanoscale* **6** (22), 13831–13837.

Luo, J. W., Li, X., Ge, C. J., Müller, K., Yu, H. M., Huang, P., Li, J. T., Tsang, D. C. W., Bolan, N. S., Rinklebe, J. & Wang, H. L. 2018 Sorption of norfloxacin, sulfamerazine and oxytetracycline by KOH-modified biochar under single and ternary systems. *Bioresource Technology* **263**, 385–392.

Mir, T. J. A., Parlade, E., Llorca, M., Villagrasa, M., Barcelo, D., Rodriguez, M. S., Martinez, A. M., Gaju, N., Caminal, G. & Sarra, M. 2017 Pharmaceuticals removal and microbial community assessment in a continuous fungal treatment of non-sterile real hospital wastewater after a coagulation-flocculation pretreatment. *Water Research* **116**, 65–75.

Prutthiwanasan, B., Phechkrajang, C. & Suntornsuk, L. 2016 Fluorescent labelling of ciprofloxacin and norfloxacin and its application for residues analysis in surface water. *Talanta* **159**, 74–79.

Pryseley, A., Mintiens, K., Knapen, K., Van, D. S. Y. & Molenberghs, G. 2010 Estimating precision, repeatability, and reproducibility from Gaussian and non- Gaussian data: a mixed models approach. *Journal of Applied Statistics* **37** (10), 1729–1747.

Qin, T. T., Wang, Z. W., Xie, X. Y., Xie, C. R., Zhu, J. M. & Li, Y. 2017 A novel biochar derived from cauliflower (*Brassica oleracea* L.) roots could remove norfloxacin and chlortetracycline efficiently. *Water Science & Technology* **76** (12), 3307–3318.

Van, D. X., Dewulf, J., Van, L. H. & Demeestere, K. 2014 Fluoroquinolone antibiotics: an emerging class of environmental micropollutants. *Science of the Total Environment* **500**, 250–269.

Wan, Y. B., Liu, X., Liu, P. L., Zhao, L. & Zou, W. H. 2018 Optimization adsorption of norfloxacin onto polydopamine microspheres from aqueous solution: kinetic, equilibrium and adsorption mechanism studies. *Science of the Total Environment* **639**, 428–437.

Wang, J. P. & Zhang, M. 2020 Adsorption characteristics and mechanism of Bisphenol A by magnetic biochar. *International Journal of Environmental Research and Public Health* **17** (3), 1075.

Wang, B., Jiang, Y. S., Li, F. Y. & Yang, D. Y. 2017 Preparation of biochar by simultaneous carbonization, magnetization and activation for norfloxacin removal in water. *Bioresource Technology* **233**, 159–165.

Wang, J. P., Zhang, M., Zhou, R. J., Li, J. Y., Zhao, W. & Zhou, J. H. 2020 Adsorption characteristics and mechanism of norfloxacin in water by gamma-Fe_2O_3@BC. *Water Science and Technology* **82** (2), 242–254.

Wang, J. P., Chen, W. Y., Zhang, M., Zhou, R. J., Li, J. Y., Zhao, W. & Wang, L. X. 2021 Optimize the preparation of Fe_3O_4-modified magnetic mesoporous biochar and its removal of methyl orange in wastewater. *Environmental Monitoring and Assessment* **193**, 179–199.

Yan, B. & Niu, C. H. 2018 Adsorption behavior of norfloxacin and site energy distribution based on the Dubinin-Astakhov isotherm. *Science of the Total Environment* **631-632**, 1525–1533.

Yang, W. B., Lu, Y. P., Zheng, F. F., Xue, X. X., Li, N. & Liu, D. M. 2012 Adsorption behavior and mechanisms of norfloxacin onto porous resins and carbon nanotube. *Chemical Engineering Journal* **179**, 112–118.

Yang, X., Zhang, X. L., Wang, Z. W., Li, S., Zhao, J., Liang, G. W. & Xie, X. Y. 2019 Mechanistic insights into removal of norfloxacin from water using different natural iron ore–biochar composites: more rich free radicals derived from natural pyrite–biochar composites than hematite–biochar composites. *Applied Catalysis B: Environmental* **255**, 117752.

Zhang, G. Y., Sun, Y., Guo, Y. L., Liu, J. H., Wu, L. Y. & Lin, J. K. 2018 The application of pomelo peel as a carrier for adsorption of epigallocatechin-3-gallate. *Journal of the Science of Food and Agriculture* **98** (11), 4135–4141.

Zhou, S. L., Zhang, S., Liu, F., Liu, J. J., Xue, J. J., Yang, D. J. & Chang, C. T. 2016 ZnO nanoflowers photocatalysis of norfloxacin: effect of triangular silver nanoplates and water matrix on degradation rates. *Journal of Photochemistry and Photobiology A- Chemistry* **328**, 97–104.

Zhou, R. J., Zhang, M., Zhou, J. H. & Wang, J. P. 2019 Optimization of biochar preparation from the stem of *Eichhornia crassipes* using response surface methodology on adsorption of Cd^{2+}. *Scientific Reports* **9**, 17538.

Zhou, R. J., Zhang, M., Li, J. Y. & Zhao, W. 2020 Optimization of preparation conditions for biochar derived from water hyacinth by using response surface methodology (RSM) and its application in Pb^{2+} removal. *Journal of Environmental Chemical Engineering* **8** (5), 104198.

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