



# Removal of tetracycline in aqueous solution by iron-loaded biochar derived from polymeric ferric sulfate and bagasse

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## Abstract

In this study, the tetracycline (TC) removal performance of iron-loaded biochar (BPFBS) derived from sugarcane bagasse and polymerized iron sulfate was investigated, and the mechanism of TC removal was also explored by study of isotherms, kinetics and thermodynamics and characterization of fresh and used BPFBS (XRD, FTIR, SEM and XPS). The results showed that under optimized conditions (initial pH 2; BPFBS dosage 0.8 g·L<sup>-1</sup>; TC initial concentration 100 mg·L<sup>-1</sup>; Contact time 24 h; temperature 298 K), the removal efficiency of TC was as high as 99.03%. The isothermal removal of TC followed well the Langmuir, Freundlich, and Temkin models, indicating that multilayer surface chemisorption dominated the TC removal. The maximum removal capacity of TC by BPFBS at different temperatures was 185.5 mg·g<sup>-1</sup> (298 K), 192.7 mg·g<sup>-1</sup> (308 K), and 230.9 mg·g<sup>-1</sup> (318 K), respectively. The pseudo-second-kinetic model described the TC removal better, while its rate-controlling step was a combination of liquid film diffusion, intraparticle diffusion, and chemical reaction. Meanwhile, TC removal was also a spontaneous and endothermic process, during which the randomness and disorder between the solid–liquid interface was increased. According to the characterization of BPFBSs before and after TC removal, H-bonding and complexation were the major interactions for TC surface adsorption. Furthermore, BPFBS was efficiently regenerated by NaOH. In summary, BPFBS had the potential for practical application in TC removal.

**Keywords** Bagasse and polymeric ferric sulfate · Iron-loaded biochar · Tetracycline · Adsorption · Potential mechanism

## Introduction

Tetracycline (TC) is one of antibiotics widely used in human medicine and animal husbandry (Guo et al. 2019). However, the effective TCs are very few, which results in that more than 80% of TCs or their metabolic derivatives being excreted in urine and feces (Chen et al. 2021). Due to the low removal efficiency of wastewater treatment plants and the

stability of TCs, they will accumulate in the aqueous environment (He et al. 2021b; Wei et al. 2022), causing serious damage to human health and ecological ecosystems (Gómez et al. 2022; Li et al. 2022b). Therefore, it is essential to effectively remove TCs from the aqueous environment.

In recent years, several methods have been developed to remove TC from the aqueous environment, including photocatalysis (Shi et al. 2020), electrochemistry (Yang et al. 2020b), membrane methods (Amaly et al. 2021), artificial wetlands (Liu et al. 2019), and adsorption (Liao et al. 2022). Among of them, adsorption is more advantageous because of its simple operation, low cost, and high removal effectiveness (Li et al. 2020). The cost and effectiveness of adsorption depend mainly on the adsorbent. The biochar, activated carbon, carbon nanotube, and graphene oxide could be used as adsorbents (Xu et al. 2022). Comparatively, biochar prepared from industrial or agricultural waste has received more attention for TC removal due to its low cost, high efficiency, and environmental friendliness (Wang et al. 2022). In China, sugarcane is one of the most important raw materials for sugar production, resulting in a large amount of bagasse being produced every year, which

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provides sufficient biomass feedstock for biochar preparation (Raj et al. 2022). Moreover, previous studies have showed that bagasse biochar (BB) performed well for the removal of various organic compounds (Ma et al. 2021; Singh et al. 2022). This predicts that BB is a potential adsorbent for TC removal. However, the adsorption capacity of biochar tends to be lower than that of commercial adsorbents due to low type and number of surface functional groups, low ion exchange capacity, and negative surface charge (Shaheen et al. 2022). Therefore, it is necessary to improve the surface properties of biochar in order to increase its removal efficiency of pollutants.

Many scholars believe that loading metals or metal oxides on the surface of biochar is a feasible approach (Xue et al. 2022). Compared to other metals, iron-loaded biochar has better adsorption performance (Li et al. 2022a). And previous studies have also shown that iron-loaded biochar has good performance for TC removal (Hao et al. 2021; Zhou et al. 2017). There are three methods for the preparation of iron-loaded biochar: co-pyrolysis of iron-containing materials with biomass feedstock; loading iron on the surface of biochar (e.g., liquid-phase reduction); and pyrolysis of iron-rich biomass feedstock. Comparatively, the first method is more promising because the physical and chemical properties of the iron-loaded biochar can be further optimized by controlling the process parameters (Zhang et al. 2022c). Water purification sludge is a by-product of drinking water treatment, which consists mainly of suspended matter, organics, microorganisms and coagulants (Kulandaivelu et al. 2020). Due to the high iron content, it has attracted the attention of researchers as a raw material for the preparation of iron-loaded biochar (Lian et al. 2020).

In our previous work, iron-loaded biochar (BPFBS) was successfully prepared by co-pyrolysis of bagasse and polymerized ferric sulfate (PFS). The maximum adsorption capacity of BPFBS for methylene blue was as high as 128.4 mg/g. Therefore, it is presumed that BPFBS also has a good adsorption capacity for TC. In the present study, the optimized conditions and capacity of BPFBS for TC removal were determined by batch experiments. Meanwhile, the potential pathways and mechanisms of TC removal were explored based on the analysis of experimental data and the characterization of BPFBS. Finally, the regenerative nature of BPFBS was also investigated. The results of this study will provide important technical support and theoretical basis for the application of BPFBS in water treatment.

## Materials and methods

### Materials

The bagasse (200 mesh) was commercially available, while the TC and PFS were provided by Shanghai Maclean

Biochemical Technology Co., Ltd and Tianjin Guangfu Fine Chemical Research Institute, respectively. The other reagents (e.g. NaOH, HCl) were purchased from Xilong Scientific Co., Ltd.

### Preparation of biochar

The BPFBS was prepared in the laboratory with the following detailed preparation procedure. First, bagasse and PFS with a mass ratio of 100:1 were thoroughly mixed in ultrapure water. Subsequently, the filtered mixture was dried at 105 °C for 24 h. Then, the dried mixture was heated to 800 °C in a muffle furnace (heating rate: 15 °C/min) and held for 3 h. Finally, the pyrolysis residue after natural cooling was passed through a 100 mesh non-metallic sieve. According to the N<sub>2</sub> adsorption isotherm at 77 K (Beijing High Micro Precision Technology Co., JW-BK200C, China), the specific surface area and pore volume of BPFBS were 407.26 m<sup>2</sup>/g and 0.341 cm<sup>3</sup>/g, respectively. The zero charge point (pH<sub>PZC</sub>) of BPFBS determined by mass titration method (Xia et al. 2020) was 7.

### Adsorption experiments

First, BPFBS samples with different masses (0.01 g, 0.02 g, 0.03 g, 0.04 g, 0.05 g and 0.1 g) were loaded into centrifugal tubes containing 50 mL of TC solution. The initial concentration ( $C_0$ ) and pH of TC solution were in the ranges of 50–200 mg·L<sup>-1</sup> (50 mg·L<sup>-1</sup>, 80 mg·L<sup>-1</sup>, 100 mg·L<sup>-1</sup>, 120 mg·L<sup>-1</sup>, 150 mg·L<sup>-1</sup>, 180 mg·L<sup>-1</sup> and 200 mg·L<sup>-1</sup>) and 2–12 (2, 4, 6, 8, 10 and 12), respectively. Then, the centrifuge tubes were shaken for 0–24 h (0.08 h, 0.17 h, 0.5 h, 1 h, 2 h, 4 h, 8 h, 12 h, 18 h and 24 h; 200 rpm) at different temperatures (298 K, 308 K and 318 K). Finally, the concentration of TC in the supernatant was determined by UV spectrophotometry at 360 nm. All experiments were performed in triplicate. The removal capacity ( $q_t$ , mg·g<sup>-1</sup>) and removal efficiency ( $\varphi$ , %) of TC was calculated by the following equations:

$$q_t = \frac{0.05 \times (C_0 - C_t)}{W} \quad (1)$$

$$\varphi = \frac{C_0 - C_t}{C_0} \times 100\% \quad (2)$$

where  $C_0$  (mg·L<sup>-1</sup>) and  $C_t$  (mg·L<sup>-1</sup>) are the initial concentration and  $t$ -time concentrations of TC, respectively;  $W$  (g) is the mass of the BPFBS sample.

### Isotherms, kinetics and thermodynamics

In this study, linear Langmuir, Freundlich, Temkin, and D-R models were employed to explore the isotherm of TC removal. Meanwhile, linear pseudo-first-order kinetics model (PFO), pseudo-second-order kinetics model (PSO) and Elovich model were used to study the apparent kinetics of TC removal, while liquid film diffusion model (LFD), intraparticle diffusion model (IPDM) and chemical reaction model (CRM) were chosen to examine the mass transfer processes of TC removal. Moreover, Gibbs free energy ( $\Delta G$ ,  $\text{kJ}\cdot\text{mol}^{-1}$ ), enthalpy change ( $\Delta H$ ,  $\text{kJ}\cdot\text{mol}^{-1}$ ) and entropy change ( $\Delta S$ ,  $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ) were used to investigate the thermodynamics of TC removal. The details of these models are shown in Table 1.

### Characterization

The crystal structure of BPFBSBs was characterized by X-ray diffraction (XRD; PANalyteica, X'Pert3 Power, Netherlands). The scanning range was from  $5^\circ$  to  $80^\circ$ , while the scanning speed was  $10^\circ\cdot\text{min}^{-1}$ . The surface functional groups were determined by Fourier transform infrared spectrometry (FTIR; Thermo Fisher, Nicolet. iS10, USA). The test method was the potassium bromide compression method, while the scan range, resolution

and number of scans were  $400\text{--}4000\text{ cm}^{-1}$ ,  $4\text{ cm}^{-1}$  and 5 times, respectively. The scanning electron microscopy (SEM) with X-ray electron spectroscopy (EDS; HITACHI, SU5000, Japan) was used to investigated surface morphology and elemental distribution of BPFBSBs. X-ray photoelectron spectrometer (XPS; Thermo Scientific K-Alpha, USA) was used to explore surface elemental speciation of BPFBSBs. The full spectrum was scanned at a flux energy of 100 eV in steps of 1.0 eV, and the narrow spectrum was scanned at a flux energy of 30 eV in steps of 0.1 eV.

### Regeneration study

The BPFBSB regeneration experiments were also performed in centrifuge tubes. The regeneration agent was NaOH solution ( $0.1\text{ mol}\cdot\text{L}^{-1}$  and  $0.5\text{ mol}\cdot\text{L}^{-1}$ ). Centrifuge tubes containing 100 mL of NaOH solution and used BPFBSB were sonicated for 1.5 h. After centrifugation and separation, the ISBCs were dried to constant weight at  $85^\circ\text{C}$ . The regenerated ISBC was then used to re-adsorb TC under the optimized conditions determined by the adsorption batch experiments. The removal capacity of regenerated BPFBSB ( $q_n$ ,  $\text{mg}/\text{g}$ ) was determined according to the method of batch adsorption experiments, and the regeneration efficiency ( $\varphi_R$ , %) was calculated ( $\varphi_R = q_n/q_0 \times 100\%$ ;  $q_0$  ( $\text{mg}/\text{g}$ ) is the the initial removal capacity).

**Table 1** The details of isotherms models, kinetics models and thermodynamics

| Model           | Expressions                                                                                                 | Parameters                                                                                                                                                                                                                                                                                                                                                                                 |
|-----------------|-------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Langmuir        | $C_e/q_e = 1/(q_{max}k_L) + C_e/q_{max}$<br>$R_L = 1/(1 + k_L C_0)$                                         | $q_e$ ( $\text{mg}\cdot\text{g}^{-1}$ ) is the adsorption capacity of tetracycline at equilibrium; $C_e$ ( $\text{mg}\cdot\text{L}^{-1}$ ) is the concentration of TC in solution at equilibrium; $q_{max}$ ( $\text{mg}\cdot\text{g}^{-1}$ ) is the maximum adsorption capacity of TC; $k_L$ ( $\text{L}\cdot\text{mg}^{-1}$ ) is the Langmuir constant; $R_L$ is separation coefficient. |
| Freundlich      | $\ln q_e = \ln k_F + 1/n_F \ln C_e$                                                                         | $k_F$ ( $\text{mg}\cdot\text{g}^{-1}\cdot\text{mg}^{1/n_F}\cdot\text{L}^{-1/n_F}$ ) is the characteristic constant of the Freundlich model; $n_F$ is the constant indicating the adsorption strength or surface heterogeneity                                                                                                                                                              |
| Temkin          | $q_e = \frac{RT}{b_T} \ln k_T + \frac{RT}{b_T} \ln C_e$                                                     | $T$ (K) is the Kelvin temperature; $R$ is the ideal gas constant; $k_T$ ( $\text{L}\cdot\text{mg}^{-1}$ ) and $b_T$ ( $\text{kJ}\cdot\text{mol}^{-1}$ ) are the characteristic constants associated with the heat of adsorption                                                                                                                                                            |
| D-R             | $\ln q_e = \ln q_{max} + \beta \varepsilon^2$<br>$\varepsilon = RT \ln(1 + 1/C_e)$<br>$E = 1/\sqrt{2\beta}$ | $\beta$ ( $\text{mol}^2\cdot\text{kJ}^{-2}$ ) is a constant related to the adsorption energy ( $E$ ); $\varepsilon$ ( $\text{kJ}/\text{mol}$ ) is the adsorption potential                                                                                                                                                                                                                 |
| PFO             | $\ln(q_e - q_t) = \ln q_e - k_1 t$                                                                          | $k_1$ ( $\text{h}^{-1}$ ) is the pseudo-first-order rate constant. $q_t$ ( $\text{mg}\cdot\text{g}^{-1}$ ) is the amount of adsorption at time $t$                                                                                                                                                                                                                                         |
| PSO             | $\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{t}{q_e}$                                                         | $k_2$ ( $\text{g}\cdot\text{mg}^{-1}\cdot\text{h}^{-1}$ ) is the pseudo-second-order rate constant                                                                                                                                                                                                                                                                                         |
| Elovich         | $q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t$                                            | $\alpha$ ( $\text{mg}\cdot\text{h}^{-1}$ ) is the initial removal rate; $\beta$ ( $\text{g}\cdot\text{mg}^{-1}$ ) is a constant related to the surface coverage and activation energy                                                                                                                                                                                                      |
| LDF             | $\ln\left(1 - \frac{q_t}{q_e}\right) = -k_{LF} t + A$                                                       | $k_{LF}$ ( $\text{h}^{-1}$ ) is the diffusion rate constant; $A$ is the diffusion constant                                                                                                                                                                                                                                                                                                 |
| IPD             | $q_t = k_{ID} t^{0.5} + C$                                                                                  | $k_{ID}$ ( $\text{g}\cdot\text{mg}^{-1}\cdot\text{h}^{0.5}$ ) is the diffusion rate constant; $C$ is the boundary characteristic constant                                                                                                                                                                                                                                                  |
| CR              | $\ln\left(1 - \frac{q_t}{q_e}\right)^{1/3} = k_C t$                                                         | $k_C$ ( $\text{h}^{-1}$ ) is the chemical reaction rate constant                                                                                                                                                                                                                                                                                                                           |
| Thermody-namics | $\Delta G = \Delta H - T\Delta S$<br>$\Delta G = -RT \ln k_L$                                               | $\Delta G$ ( $\text{kJ}\cdot\text{mol}^{-1}$ ) is the Gibbs free energy change, $\Delta H$ ( $\text{kJ}\cdot\text{mol}^{-1}$ ) is the enthalpy change, $\Delta S$ ( $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ) is the entropy change                                                                                                                                               |

## Statistical analysis

In this work, residual root-mean-squared error (RMSE) and chi-square test ( $\chi^2$ ) were used to assess consistency between experimental data ( $q_{i,\text{exp}}$ ) and model prediction data ( $q_{i,\text{cal}}$ ). Their expressions are as follows:

$$RMSE = \sqrt{\frac{1}{N-P} \sum_{i=1}^N (q_{i,\text{exp}} - q_{i,\text{cal}})^2} \quad (3)$$

$$\chi^2 = \sum_{i=1}^N \frac{(q_{i,\text{exp}} - q_{i,\text{cal}})^2}{q_{i,\text{cal}}} \quad (4)$$

where  $N$  is the number of experimental data,  $P$  is the number of model parameters.

## Results and discussion

### Effect of different parameters on TC removal

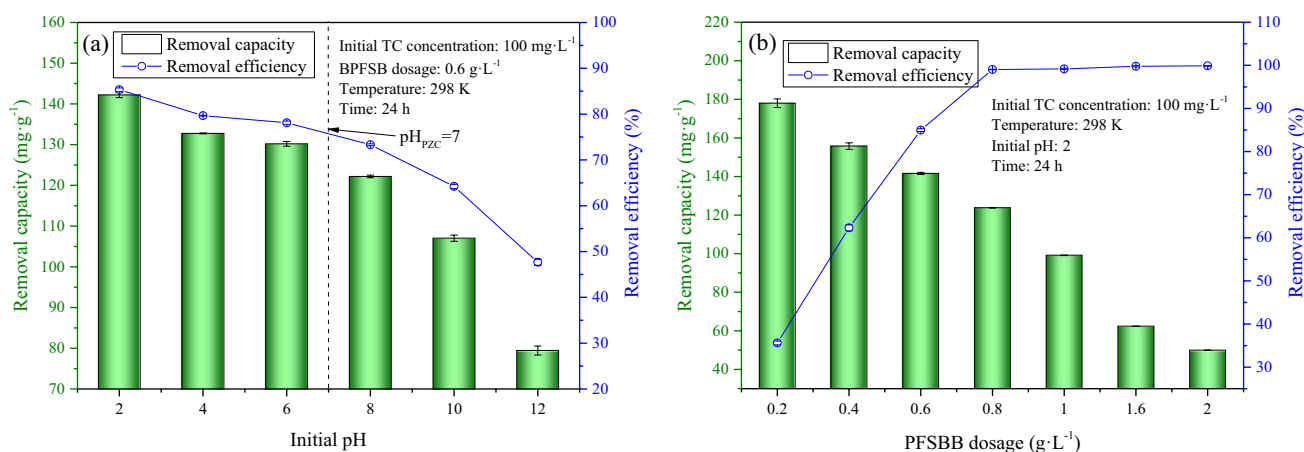
#### Initial pH

In general, the initial pH of the solution significantly affects the removal performance of the adsorbent for adsorbates because it determines the surface properties of the adsorbent and the species forms of the adsorbate. When the initial pH is less than 7 or  $\text{pH}_{\text{PZC}}$ , the surface of the adsorbent is positively charged, while the surface of the adsorbent tends to be negatively charged when the initial pH is greater than 7 or  $\text{pH}_{\text{PZC}}$  (Liu et al. 2020). The TC in solution usually has four forms depending on the pH:  $\text{TC}^+$  ( $\text{pH} < 3.3$ ),  $\text{TC}^0$  ( $3.3 < \text{pH} < 7.7$ ),  $\text{TC}^-$  ( $7.7 < \text{pH} < 9.3$ ) and  $\text{TC}^{2-}$  ( $\text{pH} > 9.3$ ) (Sun et al. 2022). Therefore, the removal

capacity of biochar for TC should theoretically fluctuate at different initial pH values due to the electrostatic interaction (Wu et al. 2022). However, the removal capacity and removal efficiency of TC shown in Fig. 1a trended continuous decrease with the increase of initial pH in the studied range. When the initial pH was raised from 2 to 12, the removal capacity was decreased from  $142.2 \text{ mg}\cdot\text{g}^{-1}$  to  $79.45 \text{ mg}\cdot\text{g}^{-1}$ , while corresponding removal efficiency was declined from 85.32% to 47.67%, suggesting that the electrostatic interactions was non-dominant for the TC removal by BPFBSB, and that the role of other adsorption mechanisms (e.g. hydrogen bonding,  $\pi$ - $\pi$  interaction, pore filling, etc.) was more significant.

#### BPFBSB dosage

The dosage of adsorbent is usually related to the efficiency and cost of pollutant removal. The effect of BPFBSB dosage on TC removal is shown in Fig. 1b. As the dosage of BPFBSB increased from  $0.2 \text{ g}\cdot\text{L}^{-1}$  to  $2.0 \text{ g}\cdot\text{L}^{-1}$ , the TC adsorption capacity decreased from  $178.0 \text{ mg}\cdot\text{g}^{-1}$  to  $49.94 \text{ mg}\cdot\text{g}^{-1}$ . This was due to the fact that high doses of BPFBSB produced aggregation of particles, resulting in overlapping of adsorption sites, reduction of effective surface area (Xu et al. 2019), and prolongation of TC diffusion paths (Zhang et al. 2022b). However, the removal efficiency of TC increased from 35.61% to 99.89% with the increase of BPFBSB dose, which should be attributed to that the higher dose of BPFBSB provided more contact area and adsorption sites (Song et al. 2022a, b). It was of interest that the TC removal efficiency was as high as 99.03% at a BPFBSB dose of  $0.8 \text{ g}\cdot\text{L}^{-1}$ , suggesting that  $0.8 \text{ g}\cdot\text{L}^{-1}$  should be an economic dosage for TC removal.



**Fig. 1** Effect of initial pH (a) and BPFBSB dose (b) on TC removal

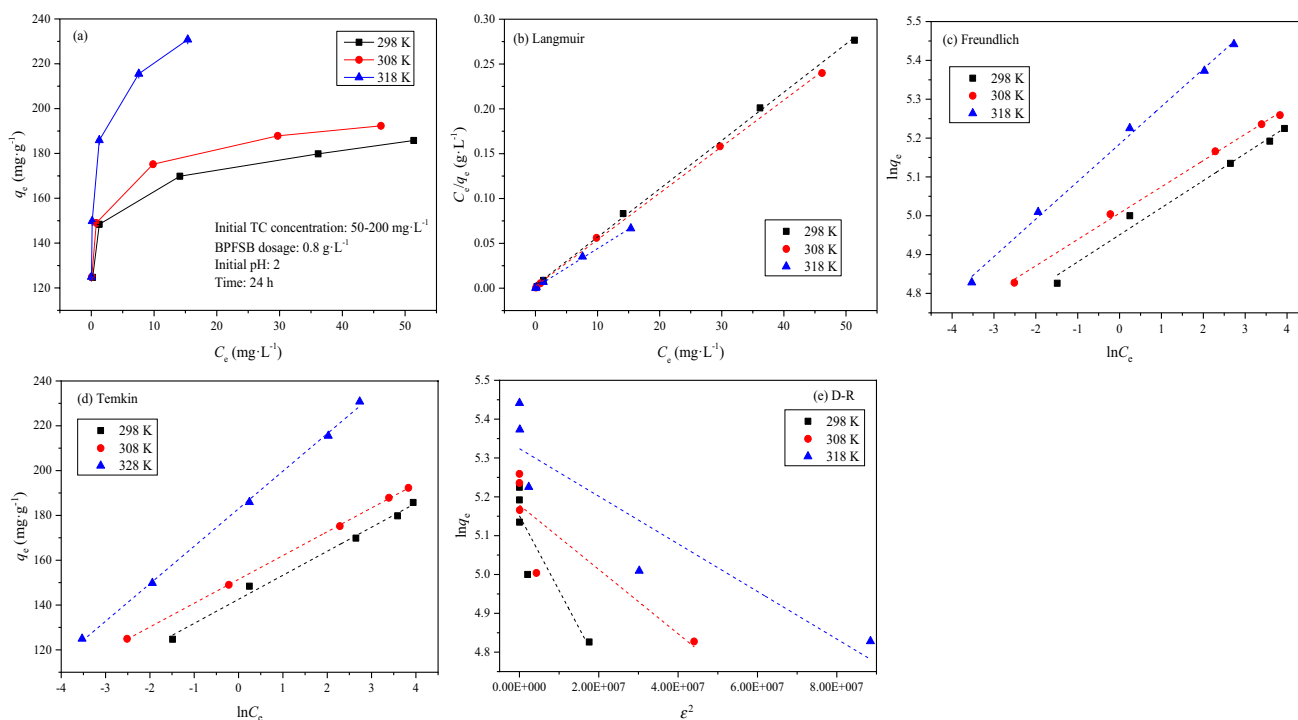
## Adsorption isotherms and thermodynamics

### Isotherms

The isothermal removal performance of BPFBS for TC and its fitting plots are shown in Fig. 2, while the corresponding fitting parameters are listed in Table 2. As shown in Fig. 2a, The TC removal capacity of BPFBS was significantly increased with the increase of TC initial concentration and temperature. This may be due to the following reasons: 1) higher TC concentrations had greater mass transfer force, resulting in rapid migration to BPFBS surface of more TC (Zheng et al. 2021); 2) the high temperature enhanced the thermal motion (Brownian motion) of the TC molecules

and reduced the viscosity of the solution, resulting in an increased opportunity for contact with BPFBS (Sun et al. 2019); 3) the temperature rise activated the adsorption sites, which facilitated the formation of iron-antibiotic complex (Song et al. 2020).

Due to the highest  $R^2$  values and the lowest  $\chi^2$  and  $RMSE$  values, the Temkin model best described the isothermal removal of TC by BPFBS, indicating that the removal of TC was dominated by chemisorption, and that the heat of adsorption was linearly decreased with increasing surface coverage of BPFBS (Zeng and Kan 2022). Since  $R^2$  values were higher than 0.98, the Langmuir and Freundlich models also described the TC removal very well, suggesting that the mechanism of TC



**Fig. 2** Isothermal removal and fitting plots of TC by BPFBS

**Table 2** The fitting parameters of Langmuir, Freundlich, Temkin and D-R models

| T(K) | Langmuir model             |                        |        |          |       | Freundlich model           |                                                          |                        |          |          |       |
|------|----------------------------|------------------------|--------|----------|-------|----------------------------|----------------------------------------------------------|------------------------|----------|----------|-------|
|      | $q_{max}(mg \cdot g^{-1})$ | $k_L(L \cdot mg^{-1})$ | $R^2$  | $\chi^2$ | RMSE  | $n_F$                      | $k_F(mg \cdot g^{-1} \cdot mg^{1/n_F} \cdot L^{-1/n_F})$ | $R^2$                  | $\chi^2$ | RMSE     |       |
| 298  | 185.5                      | 1.739                  | 0.9990 | 104.1    | 43.78 | 14.34                      | 141.3                                                    | 0.9807                 | 0.2222   | 3.247    |       |
| 308  | 192.7                      | 2.370                  | 0.9994 | 288.6    | 56.05 | 14.76                      | 149.4                                                    | 0.9970                 | 0.0452   | 1.528    |       |
| 318  | 230.9                      | 5.166                  | 0.9984 | 323.1    | 63.07 | 10.35                      | 178.5                                                    | 0.9959                 | 0.1317   | 2.738    |       |
| T(K) | Temkin model               |                        |        |          |       | D-R model                  |                                                          |                        |          |          |       |
|      | $b_T(kJ \cdot mol^{-1})$   | $k_T(L \cdot mg^{-1})$ | $R^2$  | $\chi^2$ | RMSE  | $q_{max}(mg \cdot g^{-1})$ | $\beta$                                                  | $E(kJ \cdot mol^{-1})$ | $R^2$    | $\chi^2$ | RMSE  |
| 298  | 230.9                      | 5.89E+05               | 0.9907 | 0.1196   | 2.418 | 172.6                      | 1.92E-08                                                 | 50.98                  | 0.7518   | 3.220    | 13.45 |
| 308  | 240.8                      | 1.53E+06               | 0.9998 | 0.0028   | 0.399 | 177.4                      | 8.28E-09                                                 | 77.69                  | 0.7016   | 4.800    | 16.66 |
| 318  | 157.9                      | 5.58E+04               | 0.9985 | 0.0459   | 1.727 | 205.2                      | 6.13E-09                                                 | 90.33                  | 0.7832   | 7.844    | 22.33 |



removal by BPFBS may be as follows (Zhu et al. 2022): 1) the binding of TC on the homogeneous surface of BPFBS was monolayer, resulting in the continuous generation of a "new adsorbent"; 2) When the removal of TC was close to saturation, van der Waals forces would be dominant in the interaction between TC and BPFBS. Moreover, the separation coefficient  $R_L$  and the separation intensity ( $1/n_F$ ) were in the range of 0–1, indicating that the removal of TC by BPFBS was favorable. In addition, the  $R^2$  values of the D-R models were all less than 0.8, suggesting that the contribution of pore filling to TC removal was insignificant. Meanwhile, the  $E$  values at different temperature were  $50.98 \text{ kJ}\cdot\text{mol}^{-1}$  (298 K),  $77.69 \text{ kJ}\cdot\text{mol}^{-1}$  (308 K), and  $90.33 \text{ kJ}\cdot\text{mol}^{-1}$  (318 K), demonstrating that TC removal by BPFBS was primarily controlled by chemisorption (Yuan et al. 2021). According to the Langmuir model, the maximum removal amounts of TC by BPFBS were  $185.5 \text{ mg}\cdot\text{g}^{-1}$  (298 K),  $192.7 \text{ mg}\cdot\text{g}^{-1}$  (308 K), and  $230.9 \text{ mg}\cdot\text{g}^{-1}$  (318 K), respectively, which were much higher than the adsorbents reported in previous studies (Table 3).

### Thermodynamics

The thermodynamic parameters are listed in Table 4. The negative  $\Delta G$  indicated that the removal of TC by BPFBS was spontaneous, while the increasingly negative  $\Delta G$  with increasing temperature suggested that the process was thermodynamically feasible (Yu et al. 2020). The absolute value of  $\Delta G$  at 318 K was much higher than those of other temperatures, which may be due to the generation of a large amount of Fe-TC complexes (Song et al. 2020). The  $\Delta H$  values was greater than  $40 \text{ kJ}\cdot\text{mol}^{-1}$ , declaring that the removal of TC by BPFBS was an endothermic process dominated by chemisorption (Güleç et al. 2022). In addition, the positive  $\Delta S$  evidenced that the randomness and disorder between the solid–liquid interface was increased during TC removal by BPFBS (Yang et al. 2020a).

**Table 4** Thermodynamic parameters for TC adsorption on BPFBS

| Temperature (K) | $\Delta G$ ( $\text{kJ}\cdot\text{mol}^{-1}$ ) | $\Delta H$ ( $\text{kJ}\cdot\text{mol}^{-1}$ ) | $\Delta S$ ( $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ) |
|-----------------|------------------------------------------------|------------------------------------------------|-----------------------------------------------------------------|
| 298             | -1.370                                         | 43.11                                          | 148.5                                                           |
| 308             | -2.209                                         |                                                |                                                                 |
| 318             | -4.341                                         |                                                |                                                                 |

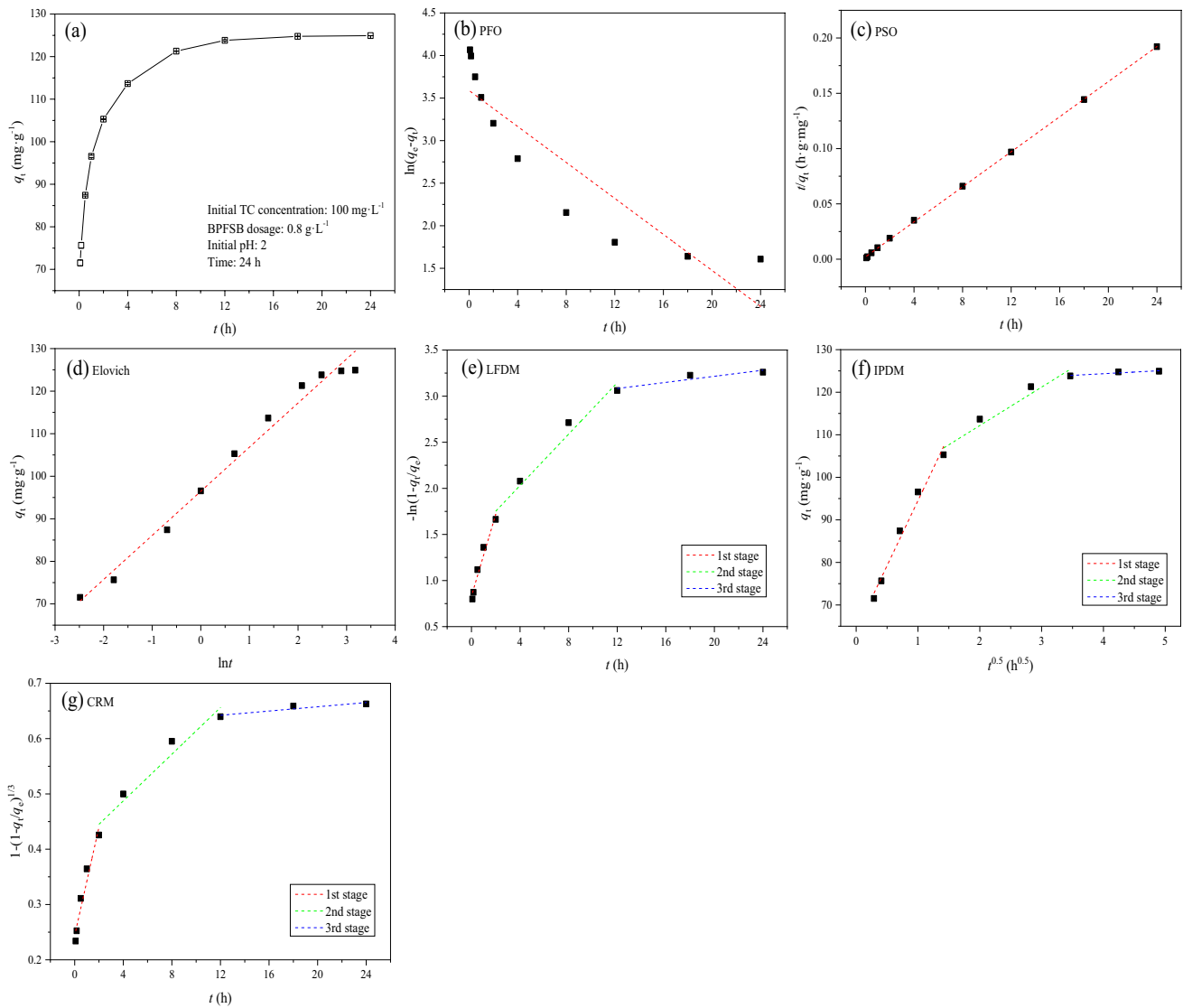
### Adsorption kinetics

The removal capacity of TC at different contact times and its fitting plots are shown in Fig. 3, while their corresponding kinetic parameters are listed in Table 5. As shown in Fig. 3a, the removal capacity of TC increased with the increase of contact time. However, this increasing trend became very slight when the contact time was greater than 18 h, predicting that 18 h could be considered as the equilibrium time. Comparing the fitting results of the PFO and PSO (Fig. 3c and Fig. 3b), the removal of TC by BPFBS better followed the PSO because of greater  $R^2$  value and lower  $\chi^2$  and RMSE values (Table 5), predicting that the removal of TC was mainly dependent on the chemisorption (Xiang et al. 2022), which likely involved the exchange, transfer and sharing of electrons (Jiang et al. 2023). In addition, due to the higher  $R^2$  value (0.9836) and the minimum  $\chi^2$  (0.5001) and RMSE (2.646) values, the TC removal could also be well described by the Elovich model, indicating that the TC removal dominated by chemisorption was heterogeneous (Omidi et al. 2022). Meanwhile,  $\alpha$  was much higher than  $\beta$ , suggesting that the adsorption between BPFBS and TC was very effective (Zhang et al. 2022a).

According to Fig. 3e, Fig. 3f and Fig. 3g, the removal of TC could be divided into three stages: fast removal stage (1st stage; 0–2 h), slow removal stage (2nd stage; 2–12 h) and asymptotic saturation stage (3rd stage; 12–24 h). In the first stage, TC rapidly migrated to the surface of BPFBS and bound to the sufficient adsorption sites due to the large concentration difference between solid and liquid phases. Subsequently, the reduction of the concentration difference

**Table 3** Comparison with adsorbents in previous studies

| Raw materials  | Additives                                                                           | Preparation methods        | pH and temperature (K)  | $q_t$ ( $\text{mg}\cdot\text{g}^{-1}$ ) | Reference                  |
|----------------|-------------------------------------------------------------------------------------|----------------------------|-------------------------|-----------------------------------------|----------------------------|
| bagasse        | polymerized ferric sulfate                                                          | co-pyrolysis               | pH=2.0, T=298, 308, 318 | 185.5<br>192.7<br>230.9                 | This study                 |
| sawdust        | $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$                                            | co-pyrolysis               | pH=6.0, T=298           | 102                                     | Zhou et al. (2017)         |
| hazelnut shell | $\text{FeCl}_3$                                                                     | co-pyrolysis               | pH=6.5, T=298           | 48.3                                    | Hao et al. (2021)          |
| rice straw     | $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ + urea                                     | co-pyrolysis               | T=298                   | 156                                     | Mei et al. (2021)          |
| sewage sludge  | $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2\cdot 6\text{H}_2\text{O}$                  | hydrothermal carbonisation | pH=6.0, T=293.15        | 104.86                                  | Wei et al. (2019)          |
| chicken bone   | $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ + $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ | co-precipitation           | pH=8.0–10.0, T=299.15   | 98.89                                   | Oladipo and Ifebajo (2018) |



**Fig. 3** Effect of contact time on TC removal capacity and its fitting plots by different kinetic models

**Table 5** Kinetic parameters for TC adsorption on BPFSB

| PFO                               |          | PSO                                          |         | Elovich                                          |          |        |         |                             |        |        |         |
|-----------------------------------|----------|----------------------------------------------|---------|--------------------------------------------------|----------|--------|---------|-----------------------------|--------|--------|---------|
| Parameters                        | Values   | Parameters                                   | Values  | Parameters                                       | Values   |        |         |                             |        |        |         |
| $q_{e,cal}$ (mg·g <sup>-1</sup> ) | 36.20    | $q_{e,cal}$ (mg·g <sup>-1</sup> )            | 126.1   | $\alpha$ (mg·h <sup>-1</sup> )                   | 1.14E+05 |        |         |                             |        |        |         |
| $k_1$ (h <sup>-1</sup> )          | 0.1057   | $k_2$ (g·mg <sup>-1</sup> ·h <sup>-1</sup> ) | 0.0314  | $\beta$ (g·mg <sup>-1</sup> )                    | 0.0964   |        |         |                             |        |        |         |
| $R^2$                             | 0.7996   | $R^2$                                        | 0.9998  | $R^2$                                            | 0.9836   |        |         |                             |        |        |         |
| $\chi^2$                          | 3.48E+04 | $\chi^2$                                     | 65.47   | $\chi^2$                                         | 0.5001   |        |         |                             |        |        |         |
| RMSE                              | 102.1    | RMSE                                         | 17.19   | RMSE                                             | 2.646    |        |         |                             |        |        |         |
| LFDM                              |          |                                              | IPDM    |                                                  |          | CRM    |         |                             |        |        |         |
| Parameters                        | Value1   | Value2                                       | Value3  | Parameters                                       | Value1   | Value2 | Value3  | Parameters                  | Value1 | Value2 | Value3  |
| $k_{LF}$ (h <sup>-1</sup> )       | 0.4439   | 0.1394                                       | 0.0166  | $k_{ID}$ (g·mg <sup>-1</sup> ·h <sup>0.5</sup> ) | 30.60    | 9.033  | 0.7775  | $k_{CR}$ (h <sup>-1</sup> ) | 0.0979 | 0.0211 | 0.0019  |
| $A_L$                             | 0.8297   | 1.473                                        | 2.884   | $A_I$                                            | 63.92    | 94.10  | 121.2   | $A_C$                       | 0.2440 | 0.4029 | 0.6190  |
| $R^2$                             | 0.9471   | 0.9584                                       | 0.7882  | $R^2$                                            | 0.9776   | 0.9293 | 0.7882  | $R^2$                       | 0.9244 | 0.9262 | 0.7362  |
| $\chi^2$                          | 0.4363   | 0.0588                                       | 6.71E-4 | $\chi^2$                                         | 0.1469   | 0.0852 | 5.93E-4 | $\chi^2$                    | 0.5697 | 0.0944 | 7.03E-4 |
| RMSE                              | 3.468    | 1.806                                        | 0.2891  | RMSE                                             | 2.110    | 2.220  | 0.2718  | RMSE                        | 3.989  | 2.299  | 0.2959  |

and the decline of the effective adsorption sites led to the decrease of the diffusion rate of TC (liquid film diffusion and intraparticle diffusion), resulting in the weakening of the binding ability of TC to the adsorption sites. When the contact time was extended from 12 to 24 h, the removal efficiency of TC only increased from 99.06% to 99.94%, which indicated that the adsorption was basically equilibrium. As shown in Table 3, the differences in  $R^2$  values for the different stages of the LFD, IPDM and CRM were negligible, and the corresponding  $A_L$ ,  $A_I$  and  $A_C$  values were also non-zero, indicating that the removal rate of TC was determined by a combination of liquid film diffusion, intra-particle diffusion and chemical reaction (or chemical interaction).

### Characterization of biochar before and after TC removal

#### XRD

As shown in Fig. 4a, the crystal structure of BPFBS before TC adsorption was mainly quartz ( $2\theta = 20.81^\circ$ ,  $26.56^\circ$ ,  $36.51^\circ$ ,  $39.44^\circ$ ,  $50.06^\circ$ ,  $59.95^\circ$  and  $68.25^\circ$ ) (He et al. 2021a; Liang et al. 2017), which attributed to the transformation of silica elements in bagasse at high temperatures (Hassan et al. 2020). Moreover, the broad peak around  $2\theta = 22.7^\circ$  related to amorphous carbon structure originated from the pyrolysis of lignin and cellulose (Alchouron et al. 2020). In addition, the characteristic peak of  $Fe^0$  ( $2\theta = 44.3^\circ$  and  $64.6^\circ$ ) (Zhang et al. 2021) was also observed, indicating that the co-pyrolysis of bagasse and PFS may result in the reduction of  $Fe^{3+}$ . (Song et al. 2022a, b). However, no characteristic peaks for other Fe-containing substances were found, which may be due to the following reasons (Ndagijimana et al. 2022; Wen et al. 2022): 1) the distribution of Fe-containing substances was uniform, and their particle size was tiny; 2)

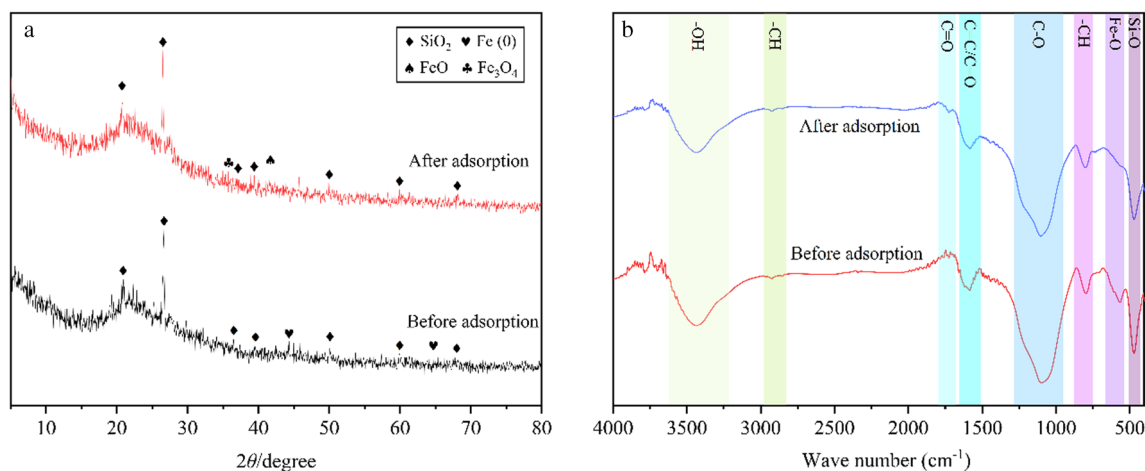
the Fe-containing substances were in non-crystalline or low-crystalline state. After the adsorption of TC, the intensity of  $Fe^0$  characteristic peaks was significantly decreased, and there were new characteristic peaks detected at  $2\theta = 35.75^\circ$  and  $41.7^\circ$  which were associated with  $Fe_3O_4$  and  $FeO$ , respectively. This phenomenon suggested that  $Fe(0)$  may have chemical reactions with TC.

#### FTIR

According to the FTIR spectrum (Fig. 4b), the functional groups on the BPFBS surface are mainly -OH ( $3430\text{ cm}^{-1}$ ), methyl and methylene -CH ( $2923\text{ cm}^{-1}$ ,  $2852\text{ cm}^{-1}$ ),  $C=C/O$  ( $1590\text{ cm}^{-1}$ ), C-O ( $1100\text{ cm}^{-1}$ ), aromatic cyclic -CH ( $780\text{ cm}^{-1}$ ) and Fe-O ( $560\text{ cm}^{-1}$ ) (Gan et al. 2020; Hu et al. 2021; Pi et al. 2019; Tang et al. 2022; Zhao et al. 2019). The characteristic Fe-O peak indicated the presence of iron oxides on the BPFBS surface, which confirmed that the iron oxides presented in a low crystalline or amorphous form. After the adsorption of TC, the characteristic peak representing Fe-O was almost disappeared, and a new characteristic peak referring to C=O was appeared at  $1720\text{ cm}^{-1}$  (Wu et al. 2019). Meanwhile, there was a slight shift for the characteristic peak of -OH. These indicated that the mechanism of TC removal may involve H-bonding and complexation (Ma et al. 2022).

#### SEM

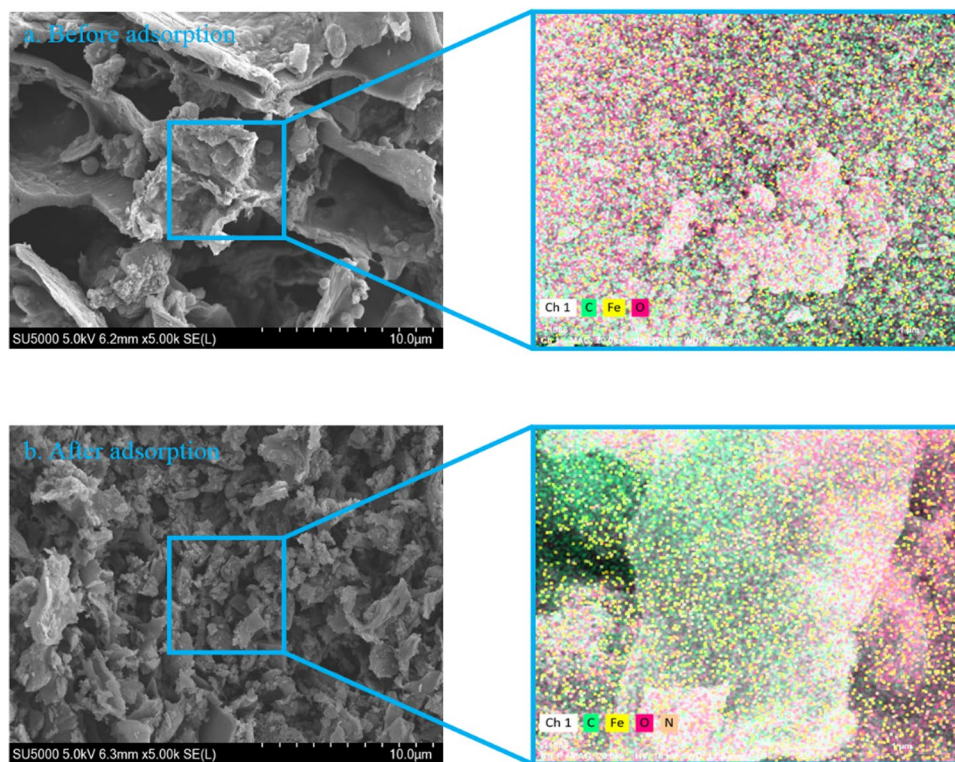
As shown in Fig. 5, the pores of BPFBS were obviously narrowed, and nitrogen elements was appeared on its surface. Meanwhile, the distribution of nitrogen elements was almost the same pattern as that of Fe elements and oxygen elements, indicating that TC may complex with Fe oxides on



**Fig. 4** XRD patterns (a) and FTIR spectra (b) of BPFBS before and after adsorption



**Fig. 5** SEM images and the element distribution mappings of BPFBS before and after adsorption



the surface of BPFBS, and that TC may also combine with oxygen-containing functional groups through H-bonding.

## XPS

The XPS spectra of BPFBS before and after adsorption are shown in Fig. 6. The full-scan spectrum showed a significant increase in the intensity of the characteristic peak representing N1s after TC adsorption (Fig. 6a), indicating that TC was successfully attached to the BPFBS. As shown in Fig. 6b, the characteristic peaks representing C-O, C=O and COO/C-O-C were significantly shifted and their proportions were also reduced after TC adsorption, which may be attributed to strong H-bonding interactions (Jin et al. 2019; Wang et al. 2021b). Comparing the fine scan spectra of O1s (Fig. 6c), the most significant differences before and after TC adsorption involved two aspects: 1) the intensity of the characteristic peaks associated with Fe-O and COO/C-O-C was weakened; 2) the positions of the characteristic peaks related to Fe-O, C=O, C-O/Si-O and COO/C-O were shifted. These confirmed the important contribution of H-bonding and complexation to the removal of TC (Li et al. 2021; Mei et al. 2021; Wang et al. 2021a). As shown in Fig. 6d, there were three forms of Fe 2p: zero-valent iron (Fe<sup>0</sup>), divalent iron (Fe<sup>2+</sup>) and trivalent iron (Fe<sup>3+</sup>). Their proportions were 16.47%, 33.46% and 50.06% before TC adsorption. After TC adsorption, the proportion of Fe<sup>0</sup> and Fe<sup>3+</sup> were individually decreased to 1.73% and

31.38%, while the proportion of Fe<sup>2+</sup> was increased to 66.89%. These predicted that both Fe<sup>0</sup> and Fe<sup>3+</sup> should react with TC.

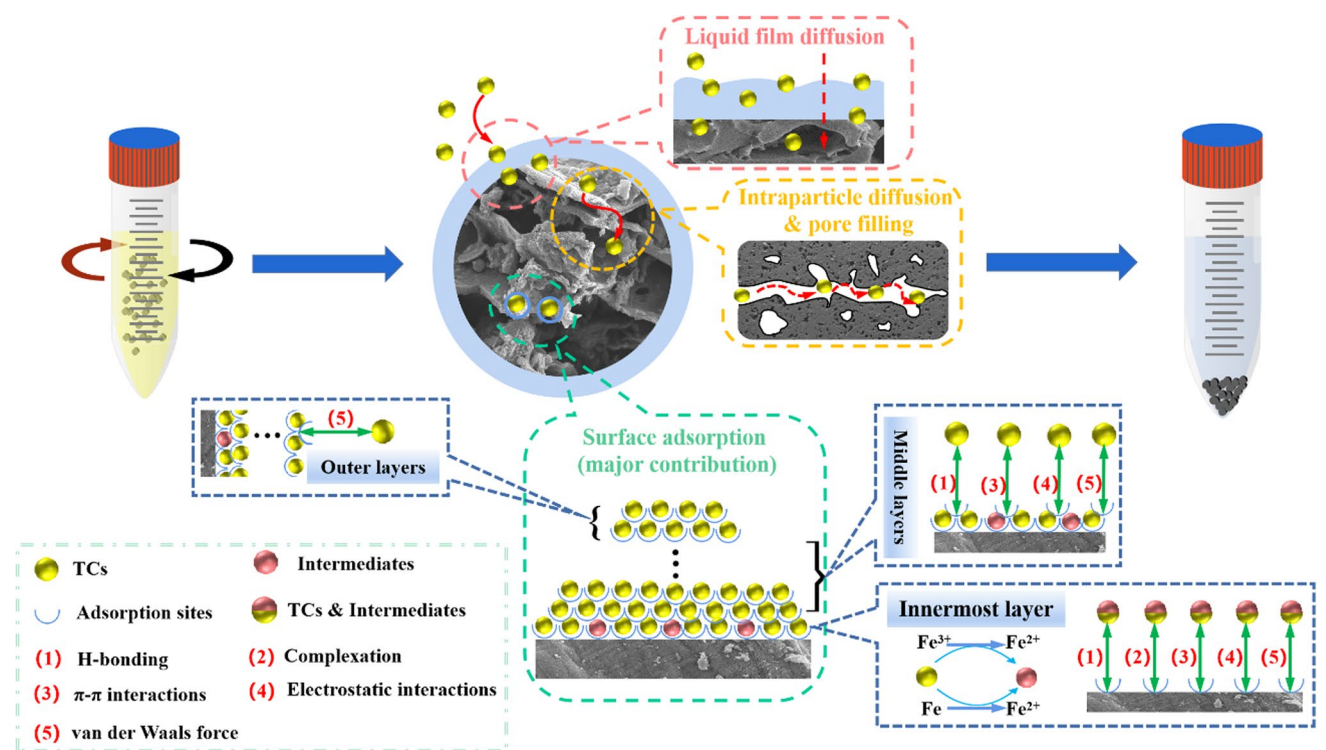
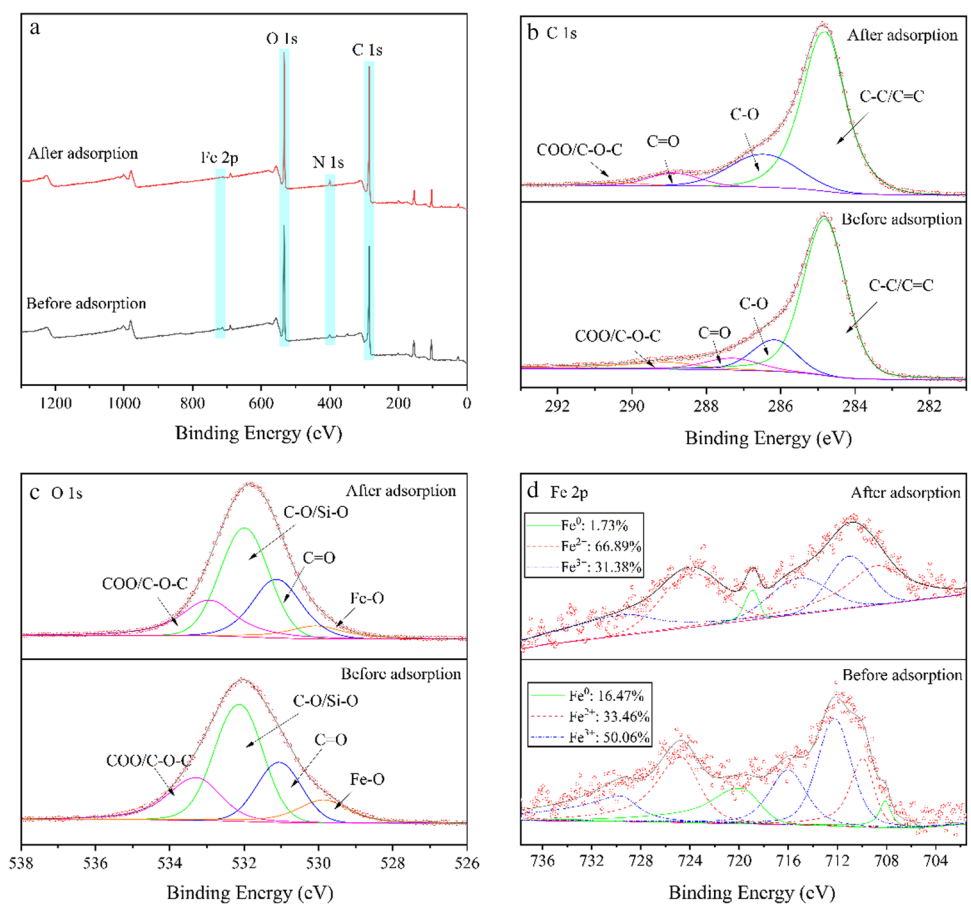
## Potential mechanisms of TC removal

Based on the analysis of experimental data and the characterization of BPFBS, the potential pathways and mechanisms of TC removal by BPFBS were proposed (Fig. 7). First, TC crossed the liquid film and diffused to the surface of BPFBS due to the TC concentration difference between the solid-liquid interface (liquid film diffusion). Subsequently, TC migrated to the blank adsorption sites on the surface of BPFBS and bound with them (surface adsorption). When the adsorption sites on the surface were occupied in large quantities, TC would diffuse to the pores (pore filling). Among them, surface adsorption was dominant.

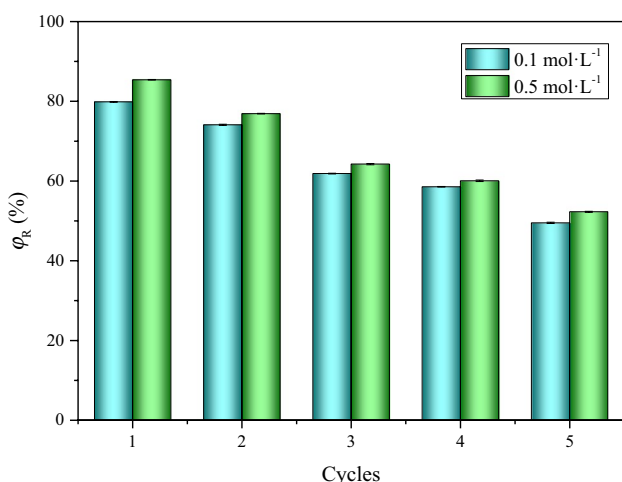
The details of the surface adsorption of TC on BPFBS were as follows. When TC diffused to the adsorption sites, TC bound with them via H-bonding, complexation,  $\pi$ - $\pi$  interactions, electrostatic interactions and van der Waals forces, while H-bonding and complexation may be the main roles. At the same time, TC would react with Fe<sup>0</sup> and Fe<sup>3+</sup> on the surface of BPFBS and produced intermediates (Eq. (4)~Eq. (7)). These intermediates then bound with the adsorption sites by the above actions.



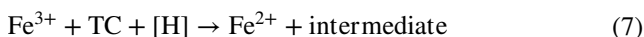
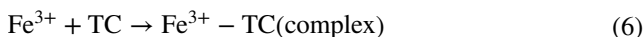
**Fig. 6** XPS spectra of BPFBS before and after TC removal



**Fig. 7** Potential pathways and mechanisms of TC removal by BPFBS



**Fig. 8** Regeneration Performance of BPFBS



When the monolayer adsorption on the surface of BPFBS was completed, a new adsorbent was formed. Subsequently, TC migrated to the adsorption sites on the new adsorbent surface and continued the monolayer adsorption. The interactions of TC with the new adsorbent may be H-bonding,  $\pi$ - $\pi$  interaction, electrostatic interaction and van der Waals forces, among which the contribution of H-bonding may be more significant. The above processes were repeated until the saturation state was approached. Finally, the main interaction of TC attachment to the adsorbent was van der Waals force (physical adsorption).

## Regeneration

The regeneration performance is very important for the practical application of adsorbent. As shown in Fig. 8, the regeneration efficiency of BPFBS was higher (74.11% ~ 85.40%) in cycles 1–2, while in cycles 3–5, the regeneration efficiency of ISBC was significantly lower (49.51% ~ 64.25%). These above may be due to the accumulation of TC on the surface of BPFBS and the longer exposure of the ISBC surface to the regeneration agents (Zeng et al. 2021). Moreover, the regeneration effectiveness of 0.5 mol·L<sup>-1</sup> NaOH solution was better. Compared with previous studies (Li et al. 2022c; Zhu et al. 2022), the regeneration performance of BPFBS was still acceptable, indicating that it had potential for practical applications.

## Conclusion

BPFBS was an adsorbent with superior removal capacity for TC. When the initial pH was 2 and the dose of BPFBS was 0.8 g/L, the removal efficiency of TC was as high as 99.03%. The maximum removal amounts of TC by BPFBS at different temperatures were 185.5 mg·g<sup>-1</sup> (298 K), 192.7 mg·g<sup>-1</sup> (308 K) and 230.9 mg·g<sup>-1</sup> (318 K), respectively. The isothermal removal of TC by BPFBS followed the Langmuir, Freundlich and Temkin model well, indicating that the removal of TC was multilayer adsorption dominated by chemisorption, and the contribution of surface adsorption was major. The pseudo-second-kinetic model described the process better, and the liquid film diffusion, intra-particle diffusion and chemical reaction together determined the TC removal rate. Thermodynamic analysis indicated that the TC removal was a spontaneous and endothermic process, and the randomness and disorder between the solid–liquid interface was increased. In addition, the characterization of BPFBS suggested that TC was mainly attached to the adsorbent surface through H-bonding and complexation. Furthermore, BPFBSs could be effectively regenerated by NaOH. In summary, BPFBSs had the potential to be practically applicable for TC removal.

**Author contributions** Qiaojing Liu: Conceptualization, Methodology, Writing—Original Draft. Xinfeng Cao: Validation, Visualization. Tian-tian Yue: Validation, Visualization. Fengzhi Zhang: Validation, Visualization. Shaoyuan Bai: Resources, Supervision, Funding acquisition, Project administration. Liheng Liu: Conceptualization, Methodology, Resources, Writing—Original Draft, Writing—Review & Editing, Supervision, Funding acquisition.

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**Data availability** The data-set used and/or analyzed during this study are available from the corresponding author on reasonable request.

## Declarations

**Ethical approval** This article does not contain any studies with human participants or animals performed by any of the authors.

**Consent to participate** None of the authors has any objection to participating in the study.

**Consent for publication** All authors agreed with the content all gave explicit consent to submit and they obtained consent from the responsible authorities at the institute/organization where the work has been carried out before the work is submitted.

**Competing interests** The authors have no relevant financial or non-financial interests to disclose.



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