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# The crucial role of different NaOH activation pathways on the algae-derived biochar toward carbamazepine adsorption



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## ABSTRACT

In this study, algae present in wastewater were utilized as precursors for synthesizing a range of biochar (BC) samples to serve as efficient adsorbents for the removal of carbamazepine (CBZ). The impact of modification on BC, activated through the NaOH impregnation method (IBC), and the NaOH dry mixing-pyrolysis (DBC) method, was systematically explored. It was observed that only the surface of IBC became rough due to NaOH impregnation activation, while the DBC structure exhibited additional fine pores within its interior. Furthermore, after NaOH activation, a significant number of oxygen-containing functional groups were introduced onto the surface of the prepared BC samples, with the proportion of O species differing between the two NaOH activation methods. Based on the results from adsorption experiments and kinetic model simulation, CBZ adsorption by BC samples followed a monolayer homogeneous adsorption reaction with excellent pH tolerance, where H-bond (C=O $\cdots$ H–N) was identified as the primary driving force. From an adsorption thermodynamics perspective, it is hypothesized that the high proportion of C=O causes the  $\Delta$ G value to shift from positive to negative, indicating that CBZ adsorption by DBC is a spontaneous reaction. Under optimal conditions, the DBC samples demonstrated an exceptional adsorption capacity, reaching 118.4 mg/g, with the removal rate of CBZ exceeding 99 %. This study offers theoretical insights into the preparation, modification, and adsorption mechanisms of BC-based adsorbents.

## 1. Introduction

The pollution caused by pharmaceuticals in aquatic environments presents a significant danger to the well-being of both humans and animals [1–3]. Carbamazepine (CBZ), a typical antiepileptic drug, is annually consumed at a rate of approximately 1000 tons worldwide, resulting in the release of around 30 tons of CBZ into natural water sources each year [4]. Due to its high resistance to biodegradation and conventional chemical degradation, effectively removing CBZ pollutants from water presents challenges [5].

Given CBZ's high chemical stability, adsorption is generally

considered a simple and promising strategy for its removal from water [6,7]. The effectiveness of traditional adsorbents commonly used in water treatment facilities, such as activated carbon and sludge, in eliminating CBZ is usually below 10 % [8]. Although advanced nano adsorbents (such as modified carbon nanotubes and metal organic frameworks) with excellent removal effects have been developed [9–11], their high cost, complexity of synthesis, and low production yield limit large-scale practical application [12]. Hence, the development of adsorbents that are easily prepared, cost-effective, and efficient in adsorption is of utmost importance [13,14].

Biochar (BC) materials, typically obtained by pyrolysis of biomass

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precursors, have been widely investigated for their potential application in adsorption for pollutant removal from aquatic environments due to their ease of production, economic viability, and environmental friendliness [15-18]. However, the relatively high chemical inertness of BC surfaces limits their adsorption performance to a certain extent [19, 20]. To optimize BC characteristics, chemical activation is a common method used to regulate the structure and micro-chemical environment of BC-based adsorbents [21,22]. Among the activation methods, treating BC with alkali (especially NaOH or KOH) is a mainstream strategy that can be divided into the impregnation method, the dry mixing-pyrolysis method, or a combination of the two methods [23,24]. For example, Lee et al. reported ground coffee residue-derived BC material activated via NaOH impregnation [25]. It was found that the porosity of the BC samples significantly improved after NaOH activation, thereby enhancing the adsorption performance. Liu et al. demonstrated that pharmaceutical sludge-derived BC materials after NaOH dry mixing-pyrolysis activation improved pore formation and the formation of oxygen-containing functional groups [26], which significantly affected the adsorption performance. The above findings suggest that NaOH activation modifies the carbon skeleton structure (porosity/specific surface area) and the surface chemical environment (especially oxygen functional groups) of BC. However, the specific differences in BC modification by different NaOH activation methods have not been clearly elucidated. Furthermore, the difference in adsorption mechanism caused by the structural changes of BC after NaOH activation also requires further investigation.

Therefore, this study utilizes overgrown algae in wastewater as BC precursors to convert waste into high-efficiency adsorbents. A series of BC samples were obtained using different NaOH activation methods, and their structural differences were systematically studied. Additionally, the influence of micro-chemical structural changes of BC samples on the kinetics and thermodynamics properties of CBZ adsorption were analyzed. This study offers significant theoretical guidance for creating BC-centered adsorbents through rational design.

#### 2. Experimental

## 2.1. Preparation and activation of BC samples

Aquatic algae plants were collected and washed thrice with deionized water to remove surface impurities. Subsequently, the plants were air-dried, crushed using a crusher, and then oven-dried at 105 °C for 24 h. The resulting powders were heated to 700 °C for 2 h under an N<sub>2</sub> atmosphere in a tubular furnace, following a procedure previously reported [16,27]. After cooling to ambient temperature, the sample was sieved through a 200-mesh sieve and designated as BC.

## 2.1.1. Preparation of NaOH impregnation activated BC (IBC)

To create IBC (Impregnation-activated BC) using NaOH, 3 g of BC samples were suspended in 50 mL of 3 mol/L NaOH solution at 80  $^{\circ}$ C and stirred for 2 h. Subsequently, the sample was dried at 105  $^{\circ}$ C for 12 h and cooled to room temperature to produce the labeled target sample, designated as IBC.

#### 2.1.2. Preparation of NaOH dry mixing pyrolysis BC (DBC)

For preparing DBC, a mixture of BC (3 g) and NaOH (6 g) powders was homogeneously blended and stirred in a mortar, before undergoing a 2-h heating process at 700  $^{\circ}$ C in a tubular furnace. The resulting sample was then allowed to cool to room temperature, and subsequently labeled as DBC.

It is important to note that all BC samples (BC, IBC, and DBC) were washed and dried before adsorption tests to remove soluble substances and adsorbed impurities.

## 2.2. Adsorption experiments

Batch adsorption experiments were conducted to investigate the effectiveness of BC, IBC, and DBC in removing CBZ from the solution. In 100 mL conical flasks, a predetermined amount of biochar was added to 50 mL of CBZ solution with a specified concentration. Various factors, such as biochar dosage, CBZ concentration, contact temperature, and pH, were studied. The flasks were placed in a thermostatic oscillator operating at 150 rpm under set temperatures. After the adsorption process, the residual solution was collected using a 5 mL syringe and a 0.45  $\mu$ m filter. Each experiment included a control group and was conducted with three parallel samples. The concentration of CBZ was determined using spectrophotometry at the characteristic adsorption wavelength of 268 nm. The removal rate (Eq. (1)) and adsorption capacity (Eq. (2)) were then calculated as follows [28]:

$$R = \frac{(c_0 - c) \times 100\%}{c}$$
(1)

$$q_t = \frac{(c_0 - c)V}{m} \tag{2}$$

Here, the variable  $q_e$  represents the adsorption capacity (in mg/g) of various biochar types for CBZ. While  $c_0$  and  $c_e$  (both in mg/L) refer to the initial and remaining concentrations of CBZ in the solution, respectively. To denote the amount of biochar added (in g) and the volume of the CBZ solution (in L), we use the variables *m* and *V*.

## 2.2.1. Effect of biochar dosage on adsorption performance

To determine the optimal BC sample dosage for CBZ adsorption, varying amounts of BC samples (ranging from 0.12 to 0.4 g/L) were added to 50 mL of CBZ solution (10 mg/L) in 100 mL conical flasks. The mixture was stirred for 2 h at 298 K and pH 7.

### 2.2.2. Effect of reaction time on adsorption performance

To assess the impact of reaction time on adsorption performance, BC samples (0.2 g/L) were introduced into a 50 mL CBZ solution (10 mg/L) and stirred continuously at 150 rpm. The adsorption reaction occurred at 298 K (pH = 7) for varying durations of 0, 10, 30, 60, 120, 180, 240, and 300 min.

#### 2.2.3. Effect of initial CBZ dosage on adsorption performance

To study the influence of different initial CBZ concentrations on adsorption efficiency, experiments were conducted using initial CBZ concentrations of 10, 20, 40, 60, and 80 mg/L. These concentrations were mixed with 0.2 g/L of BC, IBC, and DBC in conical flasks, agitated at 150 rpm for 120 min at a temperature of 298 K and a pH of 7.

## 2.2.4. Effect of temperature on adsorption performance

To investigate the temperature's impact on adsorption performance, BC samples (0.2 g/L) were used to treat 50 mL of CBZ solution (10 mg/L) at three different temperatures: 298 K, 308 K, and 318 K. The mixture was stirred continuously at a rate of 150 rpm for 2 h, with the pH maintained at 7.

# 2.2.5. Effect of pH on adsorption performance

To explore the effect of pH on adsorption efficacy, various biochar materials (at a concentration of 0.2 g/L) were combined with 50 mL of CBZ solution (10 mg/L) in a conical flask. The mixture was agitated for 120 min at a temperature of 298 K, using an oscillation speed of 150 rpm. The pH was adjusted to 4, 5, 6, 7, 8, 9, and 10 by using either 0.1 mol/L HCl or 0.1 mol/L NaOH.

## 2.3. Adsorption model

## 2.3.1. Kinetic models analysis

The pseudo-second-order model was employed to examine the

impact of contact time on CBZ adsorption, while the diffusion mechanism was described by the intraparticle diffusion model. Equations (3) and (4) were utilized to represent the kinetic models used in the study.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

$$q_t = k_{id}t^{1/2} + C_i \tag{4}$$

Here,  $q_t \pmod{g}$  and  $q_e \pmod{g}$  refer to the adsorption capacity at different reaction times (t) and the equilibrium adsorption capacity of biochar for CBZ, respectively. The adsorption rate constant of the pseudo-second-order kinetic model was represented by  $k_2 \pmod{g} \operatorname{mg}^{-1} \cdot \min^{-1}$ ), whereas  $K_{id} (\operatorname{mg/g} \cdot \min^{1/2})$  and  $C_i (\operatorname{mg/g})$  were used to denote the rate constant of the intraparticle diffusion model and the parameter associated with boundary layer thickness, respectively.

## 2.3.2. Isotherm model analysis

The Langmuir model was employed to explore the correlation between CBZ adsorption capacity by biochar and the total amount of CBZ in the equilibrium solution. Additionally, the separation factor ( $R_L$ ) was used for further analysis. Equations (5) and (6) describe the Langmuir model as follows:

$$\frac{c_e}{q_e} = \frac{c_e}{q_{max}} + \frac{1}{q_{max}K_L} \tag{5}$$

$$R_L = \frac{1}{1 + K_L c_0}$$
(6)

here,  $q_{\text{max}}$  and  $K_L$  are parameters used to describe the adsorption capacity of various biochar for CBZ. Specifically,  $q_{\text{max}}$  represents the maximum amount of CBZ (mg/g) that can be adsorbed, while  $K_L$  represents the Langmuir constant (mg/L) indicating the strength of CBZ's adsorption onto the biochar surface. Meanwhile,  $c_e$  (mg/L) and  $q_e$  (mg/g) denote the concentration and adsorption capacity of CBZ at equilibrium, respectively. The  $R_L$  value (0 <  $R_L$  < 1) for initial CBZ concentrations ranging from 10 to 80 mg/L confirms the favorable tendency of CBZ adsorption onto different BCs [29].

#### 2.3.3. Thermodynamic models analysis

The thermodynamic parameters of CBZ adsorption by biochar were evaluated using Equations (7)–(9):

$$K_d = \frac{q_e}{c_e} \tag{7}$$

$$\Delta G = -RT lnK \tag{8}$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{9}$$

here, the thermodynamic partition coefficient is denoted as  $K_d$  (L/g), while the Gibbs free energy ( $\Delta G$ , kJ/mol), enthalpy ( $\Delta H$ , kJ/mol), and entropy ( $\Delta S$ , J/mol·K) are the thermodynamic parameters. *R* (8.314 J/mol·K) and *T* (K) stand for the ideal gas constant and absolute temperature, respectively. The values of  $\Delta H$  and  $\Delta S$  can be obtained by analyzing the slope and intercept of the linear curves of  $lnK_d$  and 1/T, respectively.

## 3. Results and discussion

#### 3.1. Synthesis and characterization of prepared BC samples

Fig. 1a illustrates the preparation and NaOH activation process of BC samples. The original BC sample was obtained through direct pyrolysis of aquatic algae precursors. IBC and DBC were prepared via NaOH impregnation and dry mixing-pyrolysis activation treatments, respectively. Scanning Electron Microscope (SEM) images reveal distinct morphological differences between BC, IBC, and DBC samples. BC presents a massive structure with a relatively smooth surface morphology (Fig. 1b), whereas IBC exhibits a rougher surface due to the etching effect of NaOH. This indicates effective modification of BC's surface and the induction of pit-like structures by NaOH impregnation (Fig. 1c). Furthermore, DBC displays a noticeable pore structure throughout the sample, differing significantly from BC and IBC (Fig. 1d). Brunauer-Emmett-Teller (BET) tests objectively verify the structural alterations of BC, IBC, and DBC. DBC exhibits a notably larger specific surface area of 392.3 m<sup>2</sup>/g, compared to BC and IBC, with specific surface areas of 185.2  $m^2/g$  and 215.3  $m^2/g$ , respectively. This divergence in surface area can be attributed to variations in the pore structure among the different BC samples, as indicated in Fig. S1a. Specifically, the pore size distribution curve of DBC distinctly differs from those of BC and IBC, with additional fine pores (<4 nm) significantly contributing to its specific surface area. Based on these findings, it can be concluded that NaOH activation treatment substantially modifies BC's morphology, wherein the two activation pathways lead to variations in surface morphology for NaOH impregnation and additional pores for dry mixing-pyrolysis treatment.

Further characterization provided detailed structural information. Xray Diffraction (XRD) indicate a broad peak at  $\sim 27^{\circ}$  for all samples, representing the (002) diffraction of graphitic carbon [30], signifying partial graphitization during carbonization. Raman analysis (Fig. 2b) demonstrates an increasing intensity ratio of  $I_D/I_G$  peaks from BC to IBC



Fig. 1. (A) Illustration of the preparation and activation process of BC samples; SEM images of (b) BC, (c) IBC and (d) DBC.



Fig. 2. (A) XRD spectra and (b) Raman spectra of BC, IBC and DBC; high-resolution C 1s XPS spectra of (c) BC, (d) IBC and (e) DBC; (f) proportion of oxygencontaining species in BC, IBC and DBC samples.

to DBC, indicating that the NaOH activation process considerably enhances the disorder degree of the BC skeleton structure. This increase in disorder is attributed to alterations in the carbon skeleton configuration, such as the development of surface roughness, pores, and the incorporation of oxygen-containing functional groups on BC's surface. X-ray Photoelectron Spectroscopy (XPS) analysis confirms an elevated proportion of oxygen atoms in the samples after NaOH activation. Specifically, the proportion of O atoms rises from 15 at% (BC) to 32.9 at% (IBC) and 33.1 at% (DBC). High-resolution XPS spectra of C1s (as shown in Fig. 2c-e) reveal that oxygen functional groups on the sample surface primarily exist in the form of C=O (~288.6 eV) and C-O (~286.0 eV) modifications [31]. However, the relative proportions of C=O and C-O species in BC, IBC, and DBC are quite distinct. As shown in Fig. 2f, the relative proportion of C=O in IBC (34.2 %) or DBC (72.5 %) is higher than in BC (18.6 %), suggesting that C=O may be the primary oxygen-containing functional group introduced into BC samples after NaOH activation treatment. This effect is more pronounced for dry mixing-pyrolysis activation compared to NaOH impregnation activation. Building on the aforementioned results, it can be inferred that the two NaOH activation methods successfully modify the shape and microstructural composition of the BC specimens, albeit with certain distinctions persisted that have been comprehensively elucidated earlier.

### 3.2. Adsorption kinetic properties of prepared BC samples

To study how the BC dosage affects CBZ adsorption efficiency, varying amounts of adsorbents were used in a test with a 50 mL CBZ solution (10 mg/L) (Fig. S2). Results show that when the initial concentration of DBC exceeds 0.2 g/L, CBZ is almost entirely removed with an adsorption rate exceeding 99 %. Conversely, increasing the initial concentration of BC or IBC to 0.4 g/L only yields a relatively low adsorption rate (<20 %). From an adsorption kinetics standpoint, BC, IBC, and DBC reach adsorption equilibrium after 30 min of reaction, with calculated adsorption capacities of 3.5, 4.0, and 45.5 mg/g, respectively (Fig. 3a). Despite IBC and DBC having more oxygencontaining functional groups on their surfaces than BC, their adsorption performance is similar to BC. However, DBC, with its pore structure, exhibits significantly superior adsorption performance compared to BC and IBC, indicating that porous structure and specific surface area predominantly govern the kinetic characteristics of the adsorption reaction. Fig. 3b and Table S1 depict the simulation results of adsorption reaction kinetics. The fitting curves of BC ( $R^2 = 0.998$ ), IBC ( $R^2 = 0.999$ ), and DBC ( $R^2 = 0.999$ ) conform remarkably well to the pseudo-second-order kinetic model, implying that chemical adsorption might be the primary rate-determining step during adsorption [32]. Additionally, the intraparticle diffusion model was employed to investigate the adsorption kinetic process (Fig. S3). The fitting curves of the intraparticle diffusion model reveal two stages, neither of which passes through the origin of



Fig. 3. (A) The effect of reaction time on the adsorption capacity of BC, IBC, and DBC; (b) fitting curves of the pseudo-second-order kinetic model; (c) adsorption capacity of BC samples in different pH environments; (d) distribution of CBZ species in different pH environments; (e) the diagram of CBZ adsorption mechanism.

the coordinate axis. This suggests that intraparticle diffusion may not be the main factor influencing adsorption performance, and that multiple influencing factors likely control the adsorption kinetic process [26,33].

In order to comprehend the adsorption mechanism, the study investigated the adsorption performance of BC samples under various pH conditions. As shown in Fig. 3c, BC, IBC, and DBC exhibit broad pH tolerance during the CBZ adsorption process. Additionally, calculated species distribution results (Fig. 3d) reveal that CBZ molecules exhibit different charge characteristics in different pH environments, primarily existing as CBZ<sup>+</sup> (pH < 4), CBZ<sup>-</sup> (pH > 12), and mixtures (CBZ<sup>+/-</sup>, pH: 4-12). The consistent adsorption performance across different CBZ species confirms that electrostatic adsorption may not be the primary interfacial force during the adsorption reaction [34,35]. These findings align with the evaluation of the intraparticle diffusion model using the pseudo-second-order kinetic approach discussed previously. To explain the driving force of the adsorption reaction at the interface, Fourier Transform Infrared (FT-IR) analysis was conducted before and after DBC adsorption (Fig. S4). The C=O stretching frequency experienced shifts from 1658 cm<sup>-1</sup> to 1621 cm<sup>-1</sup> upon adsorption, indicating the formation of intermolecular H-bonds between C=O and amide groups [36]. However, the wavenumber of C–O (1072  $\text{cm}^{-1}$ ) barely changes after the adsorption reaction [37], suggesting that C=O rather than C-O (forming H-bonds) may be the primary driving force for CBZ adsorption (Fig. 3e).

#### 3.3. Insight into the adsorption thermodynamic properties

The study investigated the impact of varying CBZ concentrations in water on the adsorption capacity of BC samples. As illustrated in Fig. 4a, both BC and IBC display a slight increase in adsorption capacity with rising CBZ concentration. However, DBC demonstrates significantly higher adsorption capacity, reaching up to 118.4 mg/g. This value is 16.9 times and 9.2 times greater than that of BC (7.0 mg/g) and IBC (12.9 mg/g), respectively. The adsorption process of the BC samples is well-matched by the corresponding Langmuir fitting curves (Fig. 4b), with fitting correlation coefficients of 0.999 (BC), 0.994 (IBC), and 0.993 (DBC) (Table S2). Consequently, it can be inferred that homogeneous surface monolayer adsorption best describes the adsorption

process. Thus, the substantial specific surface area of DBC is the primary factor accounting for the significant increase in its adsorption capacity with increasing CBZ concentration. Additionally, the calculated separation factors (RL) for all BC samples are within the range of 0 < RL < 1, suggesting favorable CBZ adsorption nature [29,38].

The CBZ adsorption capacities of BC samples are depicted in Fig. 4c. The results indicate that higher reaction temperatures lead to decreased adsorption capacities, implying that CBZ adsorption by BC samples is an exothermic process. Table S3 presents the thermodynamic parameters for CBZ adsorption by BC samples, revealing negative  $\Delta H$  values consistent with experimental observations, thus supporting the exothermic nature of the adsorption process [39]. Furthermore, negative  $\Delta S$  values suggest reduced disorder and unpredictability for BC, IBC, and DBC surfaces. As shown in Fig. 4d, the adsorption reactions of CBZ by BC and IBC have  $\Delta G$  values of 1.99 kJ/mol and 1.37 kJ/mol, respectively, indicating these reactions are non-spontaneous [40]. In contrast, the adsorption reaction of CBZ by DBC has a  $\Delta G$  value of -12.86 kJ/mol, implying the reaction can occur spontaneously. The driving force for adsorption primarily relies the presence of H-bonding (C=O···H–N), suggesting the variation in  $\Delta G$  value could be attributed to the content of oxygen-containing functional groups and the proportion of oxygen species in BC samples. DBC has a higher content of oxygen-containing functional groups and C=O proportion compared to BC and IBC, resulting in a more spontaneous adsorption reaction.

## 4. Conclusion

In summary, biochar (BC) derived from wastewater algae was successfully synthesized, and we systematically investigated the modification effects of NaOH-impregnated activated BC (IBC) and NaOH drymixed pyrolyzed activated BC (DBC). Our findings elucidate that only the surface of IBC became rough due to NaOH etching, whereas DBC introduced a large number of pores into its interior structure. Based on kinetic experiments and model simulations, we found that the primary driving force for CBZ adsorption on BC samples is the formation of hydrogen bonds, with the specific surface area of BC samples being the main factor influencing the adsorption kinetics. We observed the introduction of additional oxygen-containing functional groups on the



Fig. 4. (A) The effect of initial concentration of CBZ on the adsorption capacity of BC samples; (b) corresponding isotherm fitting curves of Langmuir adsorption model; (c) the adsorption capacities of BC samples under different reaction temperature conditions; (d)  $\Delta$ G values of the adsorption reaction for BC, IBC and DBC.

surface of the prepared BC samples after NaOH activation, although the proportion of oxygen species differed between the two activation methods. We inferred that the high proportion of C—O in DBC caused the  $\Delta$ G value to shift from positive to negative, indicating that CBZ's adsorption onto DBC is a spontaneous reaction. Under optimal conditions, DBC exhibited an impressive adsorption capacity of 118.4 mg/g, with a CBZ removal rate exceeding 99 %, showcasing its broad application prospects.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# Data availability

Data will be made available on request.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.rineng.2023.101509.

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