Characterization of algae residue biochar and its application in methyl orange wastewater treatment

Hao Zhu and Haiming Zou*
Department of Resource and Environment, Anhui Science and Technology University, Fengyang 233100, China
*Corresponding author. E-mail: zouhm@ahstu.edu.cn

ABSTRACT
In this work, Spirulina residue was used as the raw material to prepare different biochars by changing the pyrolysis time. Moreover, the obtained products were characterized by scanning electron microscopy, transmission electron microscopy, Raman spectroscopy, Fourier transform infrared spectroscopy, and X-ray diffraction energy spectrum. This experiment used the batch adsorption method to study the adsorption effect of pH, dosage, and pyrolysis time on methyl orange. The adsorption of methyl orange onto Spirulina residue biochar fitted with the Langmuir isotherm model and pseudo-second-order kinetics. The results showed that the surface functional groups of Spirulina residue biochar obtained by dry pyrolysis were abundant, and it can effectively absorb methyl orange dye in an aqueous solution. The sample prepared at 500 °C for 5 h had the best adsorption effect on methyl orange. The change of pyrolysis time will affect the physicochemical properties of biochar from Spirulina residue, thereby affecting its adsorption effect on methyl orange dye. The analysis showed that the chemical adsorption of Spirulina residue biochar on methyl orange might be the primary way of dye removal. The results can provide a reference for preparing biochar from algae residue and biochar application in the removal of dye wastewater.

Key words: adsorption, algae residue, biochar, characterization, dye removal, pyrolysis time

HIGHLIGHTS
• Resource utilization of production waste.
• Adopting the method of waste treatment to meet the needs of recycling ecological environment protection.
• Characterization and analysis of biochar materials by various characterization and analysis methods.

INTRODUCTION
Spirulina is a kind of microalgae belonging to cyanobacteria. Spirulina has a high growth rate, environmental tolerance, and biomass yield per unit time and area compared with traditional biomass (Chen et al. 2018; Almomani & Bhosale 2021). It does not occupy agricultural arable land, which is easy to obtain and low cost (Venkataraman 1997). Therefore, the resource utilization of Spirulina has attracted wide attention. At present, the utilization of Spirulina is mainly food processing and phycocyanin extraction. The residue of phycocyanin extracted from Spirulina usually accounts for 70% of microalgae biomass (Yan et al. 2010). Treatment of untreated algae residue in the form of sewage discharge will not only cause environmental pollution but also cause waste of resources. These algal residues still contain abundant carbohydrates, proteins, or lipids (Deniz & Kepekci 2015) and are ideal materials for the preparation of biochar.

Biochar is a carbon-rich substance produced by biomass pyrolysis in an oxygen-limited environment (Yu et al. 2018). Previous reports show that biochar is widely used in heavy metals (Hu et al. 2019; Yang et al. 2020; Lee et al. 2021) and organic pollutants (Nguyen et al. 2020; Melo et al. 2021) as an adsorbent due to its low cost and high efficiency. At present, in the study of these pollutants adsorptions, the raw materials for the preparation of biochar mainly include straw (Medyńska-Juraszek et al. 2020; Mao et al. 2021), livestock manure (Yu et al. 2018; Huang et al. 2020), sludge (Diao et al. 2021), and other natural materials. However, there are significant differences in biochar's surface structure and physicochemical properties prepared from different raw materials. These properties are the control factors affecting the adsorption performance of biochar so that the adsorption properties of pollutants are considerably others (Chen et al. 2015; Yang et al. 2020). Compared with other materials, the biochar from algal residues might exhibit superior adsorption behavior because of its different
structure and physicochemical properties. In the existing literature, Zhang et al. used Microcystis aeruginosa to prepare hydrothermal biochar to remove the malachite green dye. The maximum adsorption capacity of this biochar on the malachite green was 89.05 mg/g (Zhang et al. 2017). Yang et al. believed that microalgae residue-derived biochar could effectively adsorb Pb (II). The surface precipitation contributed to a maximum adsorption capacity for high-temperature Chlorella residue-derived biochar and Spirulina residue-derived biochar (600 °C) of up to 151.41 mg/g and 154.56 mg/g, respectively (Yang et al. 2021).

The adsorption capacity of biochar for pollutants is closely related to biochar’s physicochemical properties, such as specific surface area, porosity, and functional groups. The physicochemical properties of biochar are affected by its pyrolysis mode, pyrolysis conditions, and biomass raw materials. Among these conditions, pyrolysis conditions significantly affected biochar’s physicochemical properties and adsorption capacity (Yang et al. 2020; Lee et al. 2021). Therefore, it is necessary to study the effects of different pyrolysis conditions on the physicochemical properties of biochar and the adsorption properties of pollutants. In this paper, the experiment prepared spirulina dry pyrolysis biochar under different pyrolysis times. The adsorption effect of algae residue biochar on methyl orange dye wastewater has been studied.

This paper used high-resolution transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), laser Raman spectroscopy (Raman Spectra), and Fourier transform infrared spectrophotometer (FTIR) to characterize the Spirulina residue biochar (SRBC) prepared at different pyrolysis times. The main structure of methyl orange is the azo structure, which has representative of some dyes. Therefore, this experiment selects methyl orange dye simulated printing and dyeing wastewater as the adsorption object, studies the adsorption effect of algae residue biochar, reveals the specific influence of algae residue biochar on the removal effect of methyl orange dye wastewater, and explores the adsorption mechanism, hoping to provide the theoretical basis for the resource utilization of algae residue and the practical application of biochar in the treatment of dye wastewater.

METHODS

Preparation of SRBC

Methyl orange (MO), sodium hydroxide (NaOH), hydrochloric acid (HCl), potassium bromide (KBr, F.W.), and anhydrous ethanol (C₂H₆O, F.W.) were all analytically pure, and the experimental water was ultrapure. The Spirulina residue used in the experiment was purchased from a phycocyanin processing plant in Fujian Province, China. The extraction process of phycocyanin in this factory was as follows: the fresh Spirulina containing phycocyanin or the pre-soaked Spirulina powder was frozen at −50 °C—10 °C low temperature and then centrifuged at 1,000 r/min ~ 3,000 r/min to obtain the wall-breaking solution containing phycocyanin. The obtained wall-breaking liquid containing phycocyanin was separated, purified, and dried to obtain phycocyanin. Spirulina residue is the filter residue in the process of separation of algae protein from wall-breaking liquid. Taking the SRBC500-3 (SRBC represents Spirulina residue biochar, 500 represents pyrolysis temperature of 500 °C, 3 represents pyrolysis time of 3 h) as an example, the detailed preparation procedures were as follows: the Spirulina residue was washed to neutral with deionized water, transferred to the constant temperature oven at 85 °C for 24 h, broken and ground. 50.0 g algae residue was weighed and placed in the crucible, wrapped with tin paper, transferred to a muffle furnace, heated to 500 °C at a heating rate of 10 °C/min the pyrolysis time was being set to 3 h. After the pyrolysis, the algae residue biochar obtained after the reaction was ground and passed through a 100-mesh sieve. The prepared samples were sealed and stored in a glass sample bottle for use.

Characterization of SRBC

High-resolution transmission electron microscopy (TEM, JEM-2100 F, Japan Electronics Corporation, Japan) and scanning electron microscopy (SEM, EVO-18, Carl Zeiss, Germany) were used to analyze the microstructure of biochar. X-ray diffractometer (XRD, XD-3, Beijing Pursu General, China) was used to analyze the crystal structure characteristics of the biochar. The test range was 2θ = 10°–60°, the scanning speed was 5°/min, the current was 24 mA, and the voltage was 36 kV. The surface functional groups of biochars were characterized by Fourier transform infrared spectrophotometer (FTIR, FTIR-850, Tianjin Gangdong Science and Technology, China) using the KBr tableting method; the wavenumber ranged from 4,000 to 500 cm⁻¹; the resolution was 2 cm⁻¹; scanning number was 32. The molecular structure of biochar was characterized by laser Raman spectroscopy (Raman Spectra, XploRA PLUS, HORIBA Group, Japan); the laser wavelength was 750 nm; the wavenumber was 500–2,000 cm⁻¹.
Absorption experiment

The methyl orange solution with a mass concentration of 1,000 mg/L was configured with ultrapure water and placed in a brown volumetric flask for use.

Effect of pH value of solution: 200 mL of 35 mg/L methyl orange solution was added into a 250 mL conical flask, the pH was adjusted to 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, and 8.0 by 1 mol/L NaOH or HCl, respectively, and 2.0 g/L of the prepared algal residue biochar SRBC500-3 was added. The adsorption reaction was carried out in a constant temperature oscillator at 200 r/min for 360 min. The sample was filtered by 0.45 μm polyethersulfone (PES) filter. The absorbance of methyl orange was measured by the ultraviolet (UV) spectrophotometer at 464 nm, and the mass concentration was being calculated.

Effect of adsorbent dosage: 200 mL methyl orange solution with the mass concentration of 35 mg/L was taken in a 250 mL conical flask. pH was adjusted to 2.0 with 1 mol/L NaOH or HCl, and 1.0 g/L, 1.5 g/L, 2.0 g/L, 2.5 g/L, 3.0 g/L, 3.5 g/L, 4.0 g/L, 4.5 g/L, and 5.0 g/L were added to prepare algal residue biochar SRBC500-3. The adsorption reaction was carried out in a constant temperature oscillator. The sample was shaken at 200 r/min for 360 min. The sample was filtered with 0.45 μm PES filter membrane. The absorbance of methyl orange was measured with UV spectrophotometer at 464 nm, and the mass concentration was being calculated.

Effect of pyrolysis time of algal residue biochar: 200 mL methyl orange solution with 35 mg/L mass concentration was added into a 250 mL conical flask, pH was adjusted to 2.0 with 1 mol/L NaOH or HCl, and 2.0 g/L was added to the prepared algal residue biochars SRBC500-1, SRBC500-2, SRBC500-3, SRBC500-4, and SRBC500-5. The adsorption reaction was carried out in a constant temperature oscillator, shaking at 200 r/min for 360 min. The sample was filtered by 0.45 μm PES filter membrane, and the absorbance value of methyl orange was measured by the UV spectrophotometer at 464 nm to calculate its mass concentration.

Data analysis

The adsorption effect is expressed by the adsorption capacity and removal rate. The calculation method is:

\[ Q_e = (C_0 - C_e)V/m \]  
\[ \eta = 1 - C_e/C_0 \]  

The adsorption isotherms were fitted by the Langmuir isotherm equation and Freundlich isotherm equation. The linear form of the Langmuir isotherm equation and the Freundlich isotherm equation is:

\[ Q_e = Q_mKLC_e/(1 + kLC_e) \]  
\[ Q_e = k_fC_e^n \]  

The adsorption kinetics were studied by quasi-first-order kinetic equation and quasi-second-order kinetic equation. These formulas are given as:

\[ Q_t = Q_e (1 - e^{-k_1t}) \]  
\[ Q_t = k_2 Q et/(1 + k_2 Q et) \]  

where \( Q_e \) is the amount of methyl orange in the adsorption solution of unit mass biochar at equilibrium, mg/g. \( C_0 \) is the mass concentration of methyl orange in the initial solution, mg/L. \( C_e \) is the mass concentration of methyl orange in the solution at equilibrium, mg/L. \( V \) is the volume of the solution, L. \( m \) is the mass of biochar added, g. \( \eta \) is the removal rate, \%. \( Q_m \) is the saturated adsorption amount of biochar, mg/g. \( Q_t \) is the adsorption amount at time t, mg/g. \( K_L \) is Langmuir adsorption characteristic constant, L/g. \( K_f \) is a Freundlich model parameter, mg\(^{1-1/n}\) · L\(^{1/n}\)/g. \( n \) is the Freundlich constant. \( t \) is time, h. \( k_1 \) is the first-order adsorption rate constant, min\(^{-1}\). \( K_2 \) is the second-order adsorption rate constant, g/(mg·h).

All treatments were repeated three times independently, and the average value was used as the measurement result. SPSS 25.0 was used for data analysis, Minitab Statistical Software 20.0 was used for Response surface methodology (RSM) analysis, and OriginPro 18 was used for mapping software.
RESULTS AND DISCUSSION

Characterization results of SRBC

Analysis of TEM and SEM: The high-resolution transmission electron microscopy and scanning electron microscopy images of SRBC500 at different pyrolysis times are shown in Figure 1. High-resolution transmission electron microscopy (TEM) and scanning electron microscopy (SEM) are practical means to measure the microstructure of biochar (Huang et al. 2020). The surface roughness of SRBC increases with the increase of pyrolysis time, and the specific surface area increases. Biochar is granular, with an underdeveloped pore structure and mostly microporous structure. The number of micropores increases with the addition of pyrolysis time, indicating that extending pyrolysis time can provide more adsorption sites for the attachment of pollutants. Moreover, SRBC has a prominent graphite-like lamellar structure. With the increase of pyrolysis time, the biochar lamellar structure becomes thinner and more compact, consistent with the conclusions of XRD and Raman spectra.

X-ray diffraction analysis: XRD spectrum analysis is an essential means to study the crystalline structure of substances (Naga Babu et al. 2020). The crystal structure characteristics of SRBC500 biochar prepared at different pyrolysis times were analyzed by X-ray technology, as shown in Figure 2. There were two dispersive diffraction peaks in the XRD patterns of all biochar samples, namely (002) diffraction peak ($2\theta = 20°–30°$) and (100) diffraction peak ($2\theta = 35°–55°$), which were consistent with the XRD patterns of standard graphite (Howe et al. 2012). It indicated that the biochar from algae residue with different pyrolysis times formed amorphous carbon at 500 °C and had a graphitized aromatic structure, which was consistent with the conclusion of Raman spectroscopy. When the pyrolysis time increased from 1 to 5 h, the intensity of the (002) diffraction peaks and the (100) diffraction peak of biochar increased, indicating that the graphite layer spacing of biochar decreased, the crystallinity increased, and the stability increased with the extension of pyrolysis time.

Fourier transform infrared spectroscopy analysis: The infrared spectrum analysis results of SRBC500 prepared at different pyrolysis times are shown in Figure 3. Fourier transform infrared spectroscopy (FTIR) is one of the effective means to measure the functional groups in biochar (Cole et al. 2019). Pyrolysis time has an important influence on the structure and properties of biochar, which is mainly due to the different carbonization degrees of Spirulina residue, thus changing the functional groups on the surface of biochar. When the pyrolysis time increased from 1 to 3 h, the absorption peak intensity of each functional group in biochar decreased gradually. After 3 h, the absorption peak intensity of each functional group in biochar did not change significantly. 3,405.7 cm$^{-1}$ absorption peak represents O-H, 2,992.1 cm$^{-1}$ absorption peak represents C-H, 1,705 cm$^{-1}$ absorption peak represents C=$\equiv$O, 1,601.8 cm$^{-1}$ absorption peak represents C=$\equiv$C and C=$\equiv$O, 1,104.4 cm$^{-1}$ absorption peak represents C-O and C-O-C (Chen et al. 2008, 2012; Keiluweit et al. 2010; Xiao et al. 2014). This shows that with the increase of pyrolysis time, hemicellulose, cellulose, and lignin components in Spirulina residue are gradually decomposed and dehydrated, and the easily decomposed functional groups are removed by pyrolysis.

Raman spectrum analysis: The Raman spectra of SRBC500 prepared at different pyrolysis times are shown in Figure 4. Raman spectroscopy is one of the effective means to study crystalline and amorphous carbon in biochar materials (especially
Figure 2 | XRD spectra of SRBC prepared at different pyrolytic times.

Figure 3 | FTIR spectra of SRBC prepared at different pyrolytic times.

Figure 4 | Raman spectra of SRBC prepared at different pyrolytic times.
high-temperature preparation materials) (Chia et al. 2012). When the pyrolysis time increased from 1 to 3 h at 500 °C, the ratio of peak area to peak area (ID/IG) of D band (1,350 cm⁻¹) and G band (1,580 cm⁻¹) increased from 0.95 to 1.08. However, there was no significant ID/IG ratio change when the pyrolysis time was further prolonged (Figure 4). This indicated that various oxygen-containing functional groups (Yamauchi & Akio 2009; Smith et al. 2016) such as lignin (Paris et al. 2005) and cellulose (Nanda et al. 2013) in biochars gradually decomposed into stable aromatic carbon structures within 3 h. Although the pyrolysis time was increased again, the temperature remained unchanged, and the functional groups were basically no longer decomposed.

Effect of initial pH

The initial pH value of the reaction solution is an essential factor affecting the adsorption effect of the adsorbent. Figure 5(a) is the methyl orange solution with 35 mg/L mass concentration shows the impact of the initial pH value of different reaction solutions (2.0–8.0) on the treatment of methyl orange dye wastewater by biochar. Figure 5 shows that the change of initial pH of the reaction solution dramatically influences the methyl orange dye wastewater treatment effect by biochar. For methyl orange dye wastewater, when the initial pH of the reaction solution was less than 4.0, with the increase of pH from 2.0 to 4.0, the removal rate decreased gradually, from 46.2% to 2.4%, and the adsorption capacity decreased from 8.09 to 0.41 mg/g. The removal rate and adsorption capacity decreased significantly. However, the removal rate and adsorption capacity of methyl orange did not change considerably from pH 4.0 to 8.0 due to the negatively charged sulfonic acid group on the surface of methyl orange. When the pH was less than 3.5, it was easy to combine with the positively charged algal residue biochar by electrostatic attraction, and the removal rate was higher. In a relatively alkaline environment, OH⁻ in

Figure 5 | Effect of experimental parameters: (a) effect of initial pH; (b) effect of adsorbent dosage; (c) effect of biochar degradation time.
the system competes with the sulfonic acid group on the surface of the methyl orange molecule. The adsorption effect of algae residue biochar on methyl orange molecules becomes worse, thus reducing the removal rate (Subbaiah & Kim 2016; Yu et al. 2018). The experimental results are consistent with the conclusions of removing methyl orange dye in an aqueous solution by activated carbon prepared by (Li et al. 2016) using rice husk residue and biochar prepared by (Yu et al. 2018) using chicken manure. Therefore, to improve the adsorption capacity of algal residue biochar on methyl orange dye solution, the initial pH of the reaction system was adjusted to 2.0 in the other batches of experiments.

**Effect of adsorbent dosage**

The adsorbent dosage is an essential factor affecting the adsorption effect. The effect of adsorbent dosage on the removal of methyl orange is shown in Figure 5(b). With the increase in the biochar dosage from the algal residue, the removal of methyl orange by biochar from algal residue first increased and then tended to be stable, which was related to the increase of specific surface area and active adsorption sites when the adsorbent dosage increased. The adsorption amount of methyl orange on algae residue biochar decreased with the growth of dosage. When the concentration of methyl orange in the solution was 35 mg/L, and the pH value was 2.0, with the increase of biochar dosage from 1.0 g/L to 5.0 g/L, the adsorption amount of methyl orange decreased from 8.60 mg/g to 4.67 mg/g, and the removal rate increased from 24.6% to 66.7%. The above results showed that when the concentration of methyl orange in the solution was constant, the adsorption sites on the biochar surface also increased accordingly with the increase of biochar dosage. A large number of active sites competed for limited methyl orange molecules, which reduced the amount of methyl orange adsorbed by unit mass biochar (Li et al. 2016; Malviya et al. 2019; Huang et al. 2020), but the removal rate of methyl orange by biochar increased gradually.

**Effect of biochar degradation time**

The adsorption capacity of biochar to pollutants is closely related to the physicochemical properties of biochar. Pyrolysis conditions have the most significant effect on the physicochemical properties and adsorption capacity of biochar. Therefore, it is imperative to study the characteristics of biochar to adsorb organic dyes under different pyrolysis conditions. Figure 5(c) shows the effect of varying biochar pyrolysis time on removing methyl orange by biochar. Pyrolysis time has a significant impact on the adsorption amount and removal rate of MO. When the concentration of methyl orange in the solution was 35 mg/L, the pH value was 2.0. The biochar dosage was 2.0 g/L, with the pyrolysis time of biochar gradually extending from 1 to 5 h. The removal rate and adsorption amount of methyl orange by biochar also increased. The adsorption amount increased from 7.48 mg/g to 10.04 mg/g, and the removal rate increased from 42.7% to 57.4%. This is because, with the increase of pyrolysis time, the porosity and specific surface area of algal residue biochar increase, and the surface of algal residue biochar increase more physical adsorption sites that can effectively adsorb methyl orange dye molecules. Therefore, with the rise of pyrolysis time, methyl orange’s adsorption capacity and removal rate on biochar from algal residues increased.

**Adsorption kinetics**

The adsorption process of methyl orange dye on SRBC500-3 was tested by linear fitting of pseudo-first-order kinetic and pseudo-second-order kinetic models. The fitting of ln (q_e – q_t) and t, (t/q_t), and t were studied. The results are shown in Figure 6(a) and 6(b). The correlation coefficient $R^2$ of adsorption kinetics was calculated from Figure 6(a) and 6(b). The $R^2$ of methyl orange dye adsorbed by SRBC500-3 was 0.98874 calculated by quasi-first-order kinetic model fitting, which was smaller than that calculated by quasi-second-order kinetic model fitting, and the $R^2$ of methyl orange dye adsorbed by SRBC500-3 was 0.99325. The equilibrium adsorption amount calculated by theoretical calculation was closer to the actual adsorption amount, indicating that the quasi-second-order kinetic model was more in line with the adsorption kinetics of methyl orange dye adsorbed by SRBC500-3, indicating that the adsorption process of methyl orange dye adsorbed by SRBC500-3 was controlled by physical adsorption and chemical adsorption, mainly by chemical adsorption, supplemented by physical adsorption.

**Adsorption isothermal**

The isothermal adsorption test can provide the physicochemical basis for the applicability of adsorption. Langmuir and Freundlich’s adsorption isotherm models tested the adsorption process of methyl orange dye on algae residue biochar SRBC500-3. The fitting results are shown in Figure 6(c). The results showed that the adsorption of methyl orange dye on SRBC500-3 was consistent with the Langmuir model equation and the Freundlich model equation. The correlation coefficient
The R² of the isothermal adsorption model was calculated from Figure 6(c). The R² of methyl orange dye adsorbed by SRBC500-3 was 0.98493 calculated by Langmuir model fitting. The R² of methyl orange dye adsorbed by SRBC500-3 was 0.90994 calculated by Freundlich model fitting, both of which were greater than 0.90. The correlation coefficient R² showed that the adsorption process of methyl orange on the surface of algae residue biochar SRBC500-3 was more in line with the Langmuir model, indicating that the adsorption of methyl orange on the surface of algae residue biochar SRBC500-3 should be monolayer adsorption behavior. Under the experimental conditions, methyl orange molecules formed monolayer films on the surface of algae residue biochar SRBC500-3, and the properties were uniform. The adsorption energy of each adsorption site of algae residue biochar SRBC500-3 was the same.

**Response surface methodology**

In order to further optimize the experimental parameters, the RSM was used to analyze the experimental results to explore the influence of the interaction between pH, dosage, and pyrolysis time on the removal rate of methyl orange. The surface diagram of RSM between different factors is shown in Figure S1 (Supplementary material), and the Contour diagram RSM between different factors is shown in Figure S2 (Supplementary material).

The results of RSM analysis showed that the effects of pH value, dosage and biochar pyrolysis time on the removal rate of methyl orange changed linearly with the conditions, so the interaction between the three factors had no significant effect on
the removal rate of methyl orange. In actual production, the cost should be calculated to optimize the removal parameters of methyl orange and improve production efficiency.

**CONCLUSION**

SRBC500 prepared by dry pyrolysis of Spirulina residue has a high specific surface area, developed porous structure, and rich surface functional groups. The SEM/TEM analysis showed that with the increase of pyrolysis time, the surface roughness of algal residue biochar increased, the micropores increased, and the graphite layer became thinner. XRD analysis showed that prolonging pyrolysis time would shrink the graphite layer spacing of biochar, increase crystallinity and enhance stability. FTIR analysis showed that the functional groups in algal residue biochar decreased with the increase of pyrolysis time. The pH value of the solution, adsorbent dosage, and pyrolysis time had different effects on the adsorption of methyl orange by algal residue biochar. Analysis of the isothermal adsorption and adsorption kinetics model showed that the adsorption process was a non-spontaneous exothermic process. The increase in temperature was not conducive to the adsorption process. Langmuir’s model could well simulate the adsorption process of methyl orange on algal residue biochar. The adsorption of methyl orange on the surface of algal residue biochar should be monolayer adsorption behavior. The pseudo-second-order kinetics can well reflect the adsorption process of methyl orange on algal residue biochar. Combined with FTIR and adsorption kinetics analysis, it can be seen that the adsorption reaction of algae residue biochar on methyl orange is primarily chemical adsorption, and its mechanism is mainly electrostatic adsorption, formation of complex or precipitation. Current studies have shown that Spirulina residue biochar is a promising low-cost adsorbent for dye wastewater treatment.

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**DATA AVAILABILITY STATEMENT**

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

**REFERENCES**

Almomani, F. & Bhosale, R. R. 2021 Bio-sorption of toxic metals from industrial wastewater by algae strains Spirulina platensis and Chlorella vulgaris: application of isotherm, kinetic models and process optimization. *Sci. Total Environ.* **755** (Pt 2), 142654.

Chen, B., Zhou, D. & Zhu, L. 2008 Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures. *Environ. Sci. Technol.* **42** (14), 5137–5143.

Chen, Z., Chen, B. & Chiou, C. T. 2012 Fast and slow rates of naphthalene sorption to biochars produced at different temperatures. *Environ. Sci. Technol.* **46** (20), 11104–11111.

Chen, T., Zhou, Z., Xu, S., Wang, H. & Lu, W. 2015 Adsorption behavior comparison of trivalent and hexavalent chromium on biochar derived from municipal sludge. *Bioresour. Technol.* **190**, 388–394.

Chen, Y. D., Ho, S. H., Nagarajan, D., Ren, N. Q. & Chang, J. S. 2018 Waste biorefineries – integrating anaerobic digestion and microalgae cultivation for bioenergy production. *Curr. Opin. Biotechnol.* **50**, 101–110.

Chia, C. H., Gong, B., Joseph, S. D., Marjo, C. E., Munroe, P. & Rich, A. M. 2012 Imaging of mineral-enriched biochar by FTIR, Raman and SEM–EDX. *Vibrational Spectroscopy* **62**, 248–257.

Cole, E. J., Zandvakili, O. R., Xing, B., Hashemi, M., Herbert, S. & Mashayekhi, H. H. 2019 Dataset on the effect of hardwood biochar on soil gravimetric moisture content and nitrate dynamics at different soil depths with FTIR analysis of fresh and aged biochar. *Data Brief* **25**, 104073.

Deniz, F. & Kepekci, R. A. 2015 Equilibrium and kinetic studies of azo dye molecules biosorption on phycocyanin-extracted residual biomass of microalgae Spirulina platensis. *Desalination and Water Treatment* **57** (26), 12257–12265.

Diao, Z. H., Dong, F. X., Yan, L., Chen, Z. L., Guo, P. R., Xia, X. J. & Chu, W. 2021 A new insight on enhanced Pb(II) removal by sludge biochar catalyst coupling with ultrasound irradiation and its synergism with phenol removal. *Chemosphere* **263**, 128287.

Howe, J. Y., Rawn, C. J., Jones, L. E. & Ow, H. 2012 Improved crystallographic data for graphite. *Powder Diffraction* **18** (2), 150–154.

Hu, X., Song, J., Wang, H., Zhang, W., Wang, B., Lyu, W., Wang, Q., Liu, P., Chen, L. & Xing, J. 2019 Adsorption of Cr(VI) and Cu(II) from aqueous solutions by biochar derived from Chaenomeles sinensis seed. *Water Sci. Technol.* **80** (12), 2260–2272.

Huang, W., Zhang, M., Wang, Y., Chen, J. & Zhang, J. 2020 Biochars prepared from rabbit manure for the adsorption of rhodamine B and Congo red: characterisation, kinetics, isotherms and thermodynamic studies. *Water Sci. Technol.* **81** (3), 436–444.

Keilwelt, M., Nico, P. S., Johnson, M. G. & Kleber, M. 2010 Dynamic molecular structure of plant biomass-derived black carbon (biochar). *Environ. Sci. Technol.* **44** (4), 1247–1253.
Lee, S., Han, J. & Ro, H. M. 2021 Mechanistic insights into Cd(II) and As(V) sorption on Miscanthus biochar at different pH values and pyrolysis temperatures. *Chemosphere* **287** (Pt 2), 132179.

Li, Y., Zhang, X., Yang, R., Li, G. & Hu, C. 2016 Removal of dyes from aqueous solutions using activated carbon prepared from rice husk residue. *Water Sci. Technol.* **75** (5), 1122–1128.

Malviya, A., Jaspal, D. K. & Khamparia, S. 2019 Kinetics studies on the adsorption of Methyl Orange and Metanil Yellow onto bottom ash: a comparative account. *Water Sci. Technol.* **80** (10), 2714–2723.

Mao, W., Zhang, L., Liu, Y., Wang, T., Bai, Y. & Guan, Y. 2021 Facile assembled N, S-codoped corn straw biochar loaded Bi2WO6 with the enhanced electron-rich feature for the efficient photocatalytic removal of ciprofloxacin and Cr(VI). *Chemosphere* **263**, 127988.

Medynska-Juraszek, A., Cwiela-Łag-Piasecka, I., Jerzykiewicz, M. & Trynda, J. 2020 Wheat straw biochar as a specific sorbent of cobalt in soil. *Materials* **13** (11).

Melo, R. P. F., Carmo, S. K. S., Barros, E. L. B., Camara, A. G., Nunes, S. K. S. & Barros Neto, E. L. 2021 Removal of disperse blue 56 from synthetic textile effluent using ionic flocculation. *Water Sci. Technol.* **83** (11), 2714–2723.

Naga Babu, A., Srinivasa Reddy, D., Suresh Kumar, G., Ravindhranath, K. & Krishna Mohan, G. V. 2020 Sequential synergetic sorption analysis of Gracilaria Rhodophyta biochar toward aluminum and fluoride: a statistical optimization approach. *Water Environ. Res.* **92** (6), 880–898.

Nanda, S., Azargohar, R., Kozinski, J. A. & Dalai, A. K. 2013 Characteristic studies on the pyrolysis products from hydrolyzed Canadian lignocellulosic feedstocks. *BioEnergy Res.* **7** (1), 174–191.

Nguyen, V. H., Van, H. T., Nguyen, V. Q., Dam, X. V., Hoang, L. P. & Ha, L. T. 2020 Magnetic Fe3O4 nanoparticle biochar derived from pomelo peel for reactive Red 21 adsorption from aqueous solution. *J. Chem.* **2020**, 1–14.

Paris, O., Zollfrank, C. & Zickler, G. A. 2005 Decomposition and carbonisation of wood biopolymers – a microstructural study of softwood pyrolysis. *Carbon* **43** (1), 53–66.

Smith, M. W., Dallmeyer, I., Johnson, T. J., Brauer, C. S., McEwen, J.-S., Espinal, J. F. & Garcia-Perez, M. 2016 Structural analysis of char by Raman spectroscopy: improving band assignments through computational calculations from first principles. *Carbon* **100**, 678–692.

Subbaiah, M. V. & Kim, D. S. 2016 Adsorption of methyl orange from aqueous solution by aminated pumpkin seed powder: kinetics, isotherms, and thermodynamic studies. *Ecotoxicol. Environ. Saf.* **128**, 109–117.

Venkataraman, L. V. 1997 *Spirulina platensis* (Arthrospira) physiology, cell biology and biotechnology, edited by Avigad Vonshak. *J. Appl. Phycol.* **9** (3), 293–296.

Xiao, X., Chen, B. & Zhu, L. 2014 Transformation, morphology, and dissolution of silicon and carbon in rice straw-derived biochars under different pyrolytic temperatures. *Environ. Sci. Technol.* **48** (6), 3411–3419.

Yamauchi, S. K. & Akio 2009 Raman spectroscopic characterization of Japanese cedar wood heat-treated at low temperatures. *Eurasian J. For. Res.* **12** (1), 57–63.

Yan, Q., Zhao, M., Miao, H., Ruan, W. & Song, R. 2010 Coupling of the hydrogen and polyhydroxyalkanoates (PHA) production through anaerobic digestion from Taihu blue algae. *Bioresour. Technol.* **101** (12), 4508–4512.

Yang, Z., Liu, X., Zhang, M., Liu, L., Xu, X., Xian, J. & Cheng, Z. 2020 Effect of temperature and duration of pyrolysis on spent tea leaves biochar: physiochemical properties and Cd(II) adsorption capacity. *Water Sci. Technol.* **81** (12), 2533–2544.

Yang, Z., Hou, J., Wu, J. & Miao, L. 2021 The effect of carbonization temperature on the capacity and mechanisms of Pb(II) adsorption by microalgae residue-derived biochar. *Ecotoxicol. Environ. Saf.* **225**, 112750.

Yu, J., Zhang, X., Wang, D. & Li, P. 2018 Adsorption of methyl orange dye onto biochar adsorbent prepared from chicken manure. *Water Sci. Technol.* **77** (5–6), 1303–1312.

Zhang, H., Zhang, F. & Huang, Q. 2017 Highly effective removal of malachite Green from aqueous solution by hydrochar derived from phycocyanin-extracted algal bloom residues through hydrothermal carbonization. *RSC Adv.* **7** (10), 5790–5799.

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