

Adsorption efficiency of biochar produced by aquaculture by-products for removing geosmin in aquaculture environment

Yadi Cui^{a,b,†}, Xi Chen^{a,b,c,†}, Chompoonuch Pitakrattanawong^a, Xiaolu Du^a, Liping Qiu^{b,d,e,f}, Huimin Xu^{b,d,e,f}, Jiazhang Chen^{a,b,d,e,f}, Shunlong Meng^{a,b,d,e,f}, Limin Fan^{a,b,d,e,f} and Chao Song^{a,b,d,e,f,*}

^aWuxi Fisheries College, Nanjing Agricultural University, Wuxi 214081, China

^bFreshwater Fisheries Research Center, Chinese Academy of Fishery Sciences, Wuxi 214081, China

^cCollege of Fisheries, Huazhong Agricultural University, Wuhan 430000, China

^dLaboratory of Quality & Safety Risk Assessment for Aquatic Products on Environmental Factors (Wuxi), Ministry of Agriculture and Rural Affairs, Wuxi 214081, China

^eKey Laboratory of Control of Quality and Safety for Aquatic Products, Ministry of Agriculture and Rural Affairs, Beijing 100000, China

^fKey Laboratory of Freshwater Fisheries and Germplasm Resources Utilization, Ministry of Agriculture and Rural Affairs, Freshwater Fisheries Research Center, Chinese Academy of Fishery Sciences, Wuxi 214081, China

*Corresponding author. E-mail: songc@ffrc.cn

†The authors contribute equally to this work.

ABSTRACT

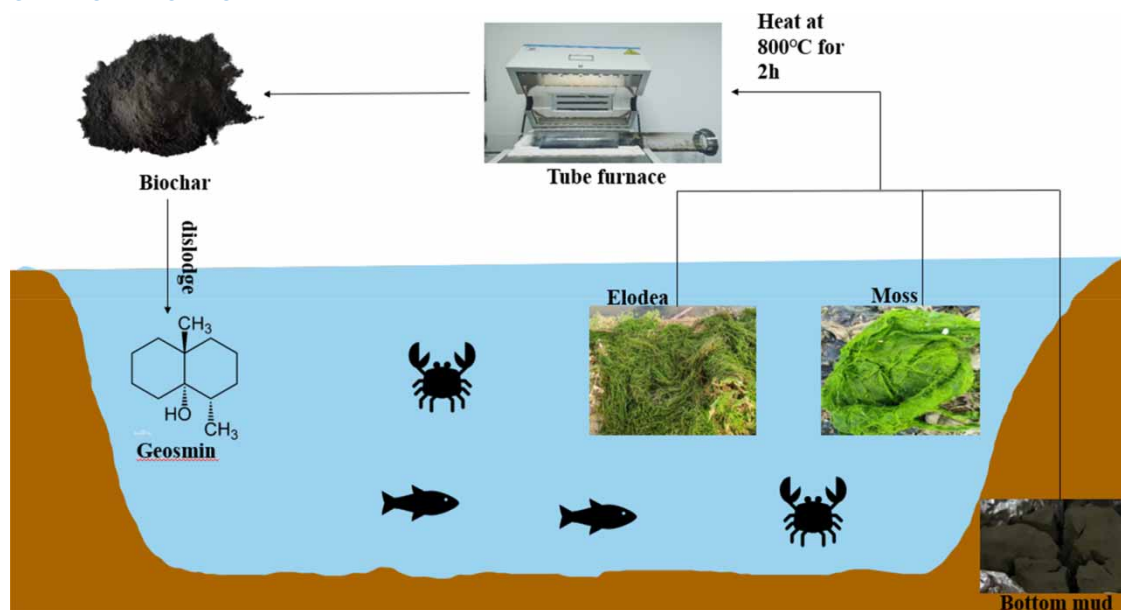
Aquaculture produces numerous by-products like aquatic plants, algae, and nutrient-enriched sediment annually, which are often discarded as waste, are not environmentally friendly, and are harmful to the environment. In this study, aquaculture by-products were utilized to prepare moss biochar at 500, 700, and 800 °C (BC500, BC700, and BC800, respectively); *Elodea* biochar (WBC800) at 800 °C; and sediment biochar (SBC800) at 800 °C. Characterization and experimental results showed that BC800 had the best adsorption effect on geosmin (GSM) under the same conditions; when using BC800 to treat GSM solution with a pH of 7, the adsorption efficiency of GSM was high (97.08%) under the conditions of dosage of 1.0 g, temperature of 25 °C, and adsorption time of 2 min. Adsorption is a multimolecular layer process that involves both physical aspects of porous adsorption and connections between chemical bonds. Biochar, derived from aquaculture by-products, is utilized to eliminate odorous substances in aquaculture environments, thereby promoting resource recycling.

Key words: adsorption efficiency, aquaculture by-product, moss biochar, removal of odorous substances

HIGHLIGHTS

- Aquaculture by-products address environmental issues in aquaculture.
- The removal efficiency of BC800 for earth odorant in aqueous solution can reach 97.08%.
- The adsorption process of BC800 on GSM is both physical and chemical adsorption of multimolecular layer adsorption.

GRAPHICAL ABSTRACT



1. INTRODUCTION

The conversion of biomass energy into biochar through carbonization is now a globally recognized process that can mitigate the problem of climate change, and this process has a clear trend of easy access to raw materials and safe and clean production (Lehmann & Joseph 2015). This can be promoted and used in the fields of ecology and environment, which can sequester carbon and reduce emissions, and can be integrated with agriculture and forestry to alleviate a series of problems caused by waste and greenhouse gas pollution (Liang *et al.* 2006). Using biochar on the field can improve the soil, increase crop yield, and improve the process of sustainable agricultural development, and it also plays a great role in heavy metal pollution adsorption and water purification (Steinbeiss *et al.* 2009). The comprehensive utilization of biochar can be conducive to energy saving and consumption reduction, and it promotes environmental protection and governance, which is of great practical significance to the national environment, energy, and food security (Duan *et al.* 2007). In recent years, China's aquaculture industry has seen rapid development and large-scale expansion; however, pond aquaculture in guaranteeing the effective supply of aquatic products at the same time, the weak infrastructure, and the general lack of drain water treatment facilities of the short board have also been gradually exposed. The ecological environment of the watershed has serious negative impacts, such as aquaculture by-products (moss, *Elodea*, etc.) that cannot be effectively dealt with, wastage of a large number of resources, the process of aquaculture odor produced by the environmental materials and human beings have caused a certain degree of harm but have not been properly dealt with, and the breeding of wastewater pollution of the environment (Nie *et al.* 2023). To better recycle the drain water and achieve resource recycling, aquaculture water treatment should take into account a variety of influencing factors, to minimize the introduction of additional substances that cause pollution or affect the existing ecological environment as far as possible. This is the first study to utilize aquaculture by-products in the production of biochars and then to adsorb odorant substances from drain water, aiming to achieve efficient purification of odorous substances in aquaculture drain water while realizing the recycling of resources and helping the green and high-quality development of fisheries.

Odorants have become one of the water pollutants that have been an increasing concern in recent years (Abd El-Hack *et al.* 2022). In aquaculture, these odorous substances can enter the bodies of aquatic products, which seriously affect the development of aquaculture as well as bringing serious problems to the sale of aquatic products (Wilkes *et al.* 2000). These off-flavors often lead to a loss of consumer interest in consuming fish and shellfish (Sarker *et al.* 2014). Geosmin (GSM) belongs to the monoterpenes of terpenoids, and this terpene alcohol is usually a secondary metabolite of fungi, slime molds, actinomycetes, and cyanobacteria (Gerber & Lechevalier 1965; Boerjesson *et al.* 1993). In our country, GSM produced by algal metabolism are important causes of olfactory problems in drinking water. So far, more than 200 kinds of algae have been

found to produce GSM, including some algae of the genera *Schizophyllum*, *Tremella*, *Sphingomonas*, and fishy algae, and GSM is mainly produced by fishy algae (Jüttner & Watson 2007). Seasonal concentrations of GSM correlate well with the abundance of *Aphanizomenon* (Jüttner *et al.* 1986) and *Anabaena* (Jones & Korth 1995) in nutrient freshwater lakes. Biochar is a porous carbon-containing material produced during the thermochemical decomposition of biomass feedstocks in the presence of little or no oxygen. Biomass feedstock can be any organic waste material, including crop and forest residues, wood chips, algae, sewage sludge, manure, and organic municipal solid waste (Xiang *et al.* 2020). Biochar has a relatively large surface area and an abundance of surface functional groups, which allows it to be used as a green and low-cost adsorbent, providing a sustainable alternative to wastewater treatment technologies (Foong *et al.* 2022). Lin *et al.* (2021) prepared biochar from pyrolyzed bacterial chaff at 400 °C and studied its adsorption effect on the sediment and water quality of aquaculture ponds, and the results showed that this biochar has great potential as an adsorbent for the adsorption of ammonia, nitrogen, sulfide, and other toxic substances in water bodies and sediments. Liao *et al.* (2021) showed that the large specific surface area of biochar can enhance nitrous oxide (N₂O) activity and reduce microorganisms, thus mitigating N₂O emissions.

In the pond culture of Chinese mitten crabs and prawns, the main submerged plants are *Illicium*, black algae, etc. These plants are introduced to improve water quality and provide shelter and food for aquatic animals, but after the culture period, the treatment of the plants is a more troublesome problem. These plants play a key role in water clarity by directly reducing phytoplankton growth through competing with phytoplankton for nutrients and light as well as chemosensory effects (Mulderij 2006; Wang *et al.* 2006; Kong *et al.* 2012). They provide a suitable habitat for crabs, especially during molting; crabs may hide in submerged vegetation to avoid predators or other crabs (Wang *et al.* 2006). They play a key role in the functioning of freshwater ecosystems by influencing the physical and chemical conditions of water and sediments, modifying nutrient cycling, influencing predator-prey interactions, and acting as a source of food, either directly or indirectly through epiphytes (Jeppesen *et al.* 2012). Aquatic plants have a stabilizing effect on the pond culture system, but too many aquatic plants can lead to eutrophication of the water body and can deprive aquatic animals of their living space (Zehnsdorf *et al.* 2015).

Moss is a general term for filamentous algae, and some domestic literature points out that it includes water milfoil, bristle algae, double star algae, and transplants; however, its specific species composition and percentage in some specific environments are rarely reported. According to the data, the outbreak of moss in the Great Lakes of North America is composed almost exclusively of a species of aggregate Chadophorasle (Higgins *et al.* 2008). Bristlenose algae blooms can clog waterworks, produce unpleasant odors, affect landscapes, reduce the ecological value of waters, and pose certain hazards to the aquaculture industry as well (Herbst 1969). Floating algae form loose mats that accumulate on the water's surface. Decay and decomposition of the large number of mats covering the water's surface can cause hypoxia in the water body, which may disrupt natural fluctuations in aquatic animal biomass and elevate the mortality rate of aquatic animals (Norkko & Bonsdorff 1996). In China, moss is a major nuisance in aquaculture, especially in river crab and crayfish breeding ponds. Moss in the pond in large quantities results in thin water, entangled fish and shrimp, a large amount of oxygen consumption at night, the secretion or death of decomposition to produce toxic and harmful substances, and so on. Therefore, moss prevention and control in aquaculture are of great significance.

In pond culture, large amounts of baiting and deposition of fish metabolites lead to the continuous accumulation of organic matter in ponds, resulting in nutrient enrichment of the pond sediment (Dai *et al.* 2022). This shows that the sediment contains a large amount of biomass.

Moss, excess aquatic plants (mainly *Elodea*), and nutrient-enriched sediment are all by-products of the aquaculture ecosystem, as are organic waste materials, as mentioned above. These organic waste materials are calcined into biochar under high temperatures and anaerobic conditions, which is used to adsorb odorous substances in aquaculture. The biochar will not cause secondary pollution to the environment. The problem of the aquaculture environment is solved by utilizing the by-products of aquaculture. In this study, moss, *Elodea*, and pond sediment were made into biochar, respectively, and adsorbed to GSM under the same conditions to investigate their adsorption performance, which provided a solution idea for the by-products in aquaculture to solve the aquaculture environment problem.

2. MATERIALS AND METHODS

2.1. Experimental design

In the aquaculture system in general, there are several kinds of biomass raw materials: sediment, algae, moss, aquatic plants, etc. The aquaculture by-products were selected as the raw material for this experiment for the development of biochar to

remove the odor from the aquaculture water. The aquaculture of Chinese mitten crabs involves the most biomass and is more representative of the whole aquaculture in China.

The moss, *Elodea*, and the sediment were dried and placed in an oven at 105 °C for 24 h, and after drying, they were ground into powder in a grinder and filtered in a 100-mesh sieve, which were bottled and placed in a desiccator for spare parts, respectively.

Moss biochar was prepared by high-temperature pyrolysis: moss powder was placed in a 100 mL quartz boat, stuffed as much as possible, compacted, and spread out. The powder was placed in a tube furnace protected by nitrogen (350 mL·min⁻¹) and heated up to the target temperatures (500, 700, and 800 °C) at 10 °C·min⁻¹ for 2 h. It was cooled down naturally to room temperature and then taken out of the tube furnace, put into bottles, and then put into a desiccator for spare use. The produced moss biochar was labeled BC500, BC700, and BC800, respectively.

Elodea and sediment biochar were prepared using the same method with a target temperature of 800 °C and labeled WBC800 and SBC800, respectively.

2.2. Characterization

The field emission electron scanning microscope (SEM) was used to observe the apparent morphological characteristics of the materials and analyze the elemental content by an organic element analyzer; Fourier infrared spectroscopy (FT-IR) was used to analyze the surface functional groups of the materials, and the fully automatic specific surface and porosity analyzer (BET) was used to analyze the specific surface area and pore structure of the materials.

2.3. Comparison of the adsorption efficiency of biochar prepared from different raw materials

Treatment of the solution to be tested: the use of deodorant standards to prepare a solution to simulate the loose water of the breeding pond containing odorous substances; the use of NaOH and HCl to adjust the pH of the solution; the measurement of 200 mL of deionized water in a 250 mL conical flask; the addition of 600 µL of GSM solution; and then the addition of biochar prepared from different materials to carry out the reaction at 25 °C with 240 r·min⁻¹ in a water bath shaker. Adsorption: After completion of adsorption, the supernatant was aspirated and filtered through a 0.22-µm filter head, and 10 mL was aspirated and kept aside.

Gas chromatography-mass spectrometry (GC-MS) was utilized as the detection method. Also, 10 mL of the water sample was tested by adding 2 g of sodium chloride to a 15 mL headspace injection bottle, screwing the cap tightly, and installing a solid-phase microextraction fiber. The stirring speed was set at 1,200 r·min⁻¹, the temperature was controlled at 60 °C, and the extraction time was 40 min. Immediately after the end of the extraction, the extracted fiber was inserted into the inlet of the GC-MS for determination.

The pH of the GSM solution with a concentration of 300 ng·L⁻¹ was adjusted to 7. BC500, BC700, BC800, WBC800, and SBC800 were added to the configured GSM solution at a dosage of 1.0 g, and the remaining GSM concentration was determined by oscillation at a constant temperature of 25 °C for 2 min.

2.4. BC800 batch adsorption experiment

The pH of the GSM solution with a concentration of 300 ng·L⁻¹ was adjusted to 7. BC800 was added to the configured GSM solution at dosages of 0.2, 0.4, 0.6, 0.8, 1.0, and 1.2 g, respectively, and the residual GSM concentration was determined by oscillation at a constant temperature of 25 °C for 45 min.

The pH of the GSM solution with a concentration of 300 ng·L⁻¹ was adjusted to 2, 5, 7, 9, and 11, respectively, and BC800 was added to the configured GSM solution at a dosage of 1.0 g. The concentration of the remaining GSM was determined by oscillation at a constant temperature of 25 °C for 2 min.

The pH of the GSM solution with a concentration of 300 ng·L⁻¹ was adjusted to 7. BC800 was added to the configured GSM solution at a dosage of 1.0 g. The solution was shaken at a constant temperature of 25 °C for 10 s, 30 s, 1 min, 2 min, 5 min, 7 min, 9 min, 15 min, 30 min, 45 min, and 60 min, and the remaining GSM concentration was determined.

The pH of the GSM solution with concentrations of 100, 200, 300, 400, and 500 ng L⁻¹ was adjusted to 7, respectively, and BC800 was added to the configured GSM solution at a dosage of 1.0 g. The concentration of the remaining GSM was determined by oscillation at a constant temperature of 25 °C for 2 min.

Quasi-primary (Equation (1)) and quasi-secondary (Equation (2)) adsorption models were used to fit the kinetic data and analyze the adsorption mechanism of BC800 on GSM.

Quasi-primary dynamics:

$$Q_t = q_e(1 - e^{-k_1 t}) \quad (1)$$

Quasi-secondary dynamics:

$$\frac{t}{Q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

where q_e and Q_t are the equilibrium adsorption amounts of GSM and the adsorption amounts at moment t , respectively ($\text{ng}\cdot\text{L}^{-1}$), k_1 is the quasi-primary adsorption rate constant ($\text{g}\cdot\text{ng}\cdot\text{min}^{-1}$), k_2 is the quasi-secondary adsorption rate constant ($\text{g}\cdot\text{ng}^{-1}\cdot\text{min}^{-1}$), and t is the adsorption time (min).

The Langmuir (Equation (3)) and Freundlich (Equation (4)) isothermal adsorption models were utilized to fit the isothermal adsorption process.

The Langmuir isotherm model:

$$Q_e = \frac{k_1 q_m C_e}{1 + k_1 C_e} \quad (3)$$

The Freundlich isotherm model:

$$Q_e = K_f C_e^{\frac{1}{n}} \quad (4)$$

where C_e is the adsorption equilibrium concentration ($\text{ng}\cdot\text{L}^{-1}$); Q_e is the equilibrium adsorption amount ($\text{ng}\cdot\text{g}^{-1}$); q_m is the maximum adsorption amount ($\text{ng}\cdot\text{g}^{-1}$), which is related to the adsorption strength; k_L is the Langmuir adsorption constant, which is related to the amount of adsorption; k_2 is the Freundlich adsorption constant; and n is the adsorption strength.

2.5. Data analysis

The data analysis in this study was mainly done using Excel 2016 software, and the plotting and equation fitting were done using Origin 2021 software.

3. RESULTS

3.1. Characterization of biochar prepared from different temperatures and raw materials

SEM results at the 5- μm level show that from the apparent morphology, BC500 starts to volatilize the water in the moss during pyrolysis, and because the temperature is not enough for the charring of the organic matter to initially form many pores, a large number of bio-oil and ash particles will also block the pores of the biochar, so that there are a lot of small particles on the surface and part of the fine pore structure. BC700 has fine particles distributed on the surface, with an obvious pore structure, but the pores are not completely open, and the pores are arranged in a trapezoidal shape. BC800 has a compact structure, with thicker pore walls and fewer impurity particles on the surface, and most of the area can be clearly seen to have a hierarchical pore structure, which shows that the adsorption mode of BC800 on earth odorants is a multimolecule layer adsorption. WBC800 also shows an obvious pore structure, and the loose pore structures are connected with each other. WBC800 also shows an obvious pore structure, and loose pore structures are connected with each other. SBC800 has no obvious pore structure, the surface is rough, and there are a lot of irregular protrusions on the surface. BC800 and WBC800 are biochars prepared from moss and *Elodea*, which are plant-derived biochars, while SBC800 is a substrate-based biochar. Because the composition of substrate raw materials is more complex than that of plant-derived materials, which usually contains organic matter, inorganic minerals, and microorganisms, the characteristics of these materials vary due to pyrolysis, which leads to a big difference in the microscopic morphology of SBC800 compared with that of plant-derived biochars. When pyrolysis occurs at 800 °C, the water in the substrate volatilizes, the organic matter carbonizes to form few pores initially, and a large number of bio-oil and ash particles are generated to block the pores of the biochar, so there are a lot of small particles on the surface, and there is a part of the fine pore structure but with a relatively small number (Figure 1).

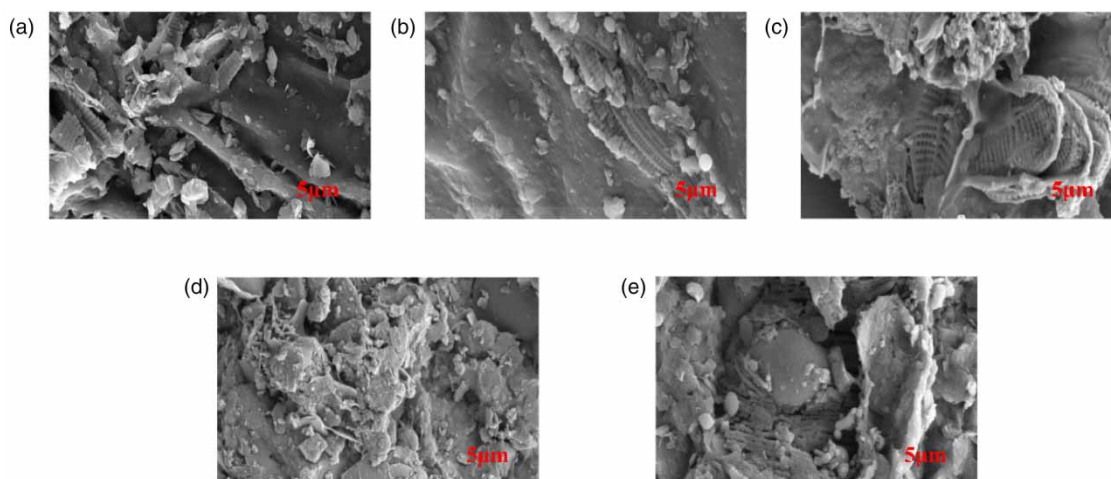


Figure 1 | SEM image of biochar at 5- μm level. (a) BC500; (b) BC700; (c) BC800; (d) SBC800; and (e) WBC800. BC500 has a smooth surface with fewer voids; BC700 has an obvious pore structure but the pores are not completely open, and the pores are arranged in a trapezoidal manner; BC800 has a hierarchical pore structure in most areas; SBC800 has no obvious pore structure and a rough surface with many irregular protrusions; and WBC800 has loose pore structures connected with each other. It can be concluded from the SEM images that BC800 has the best adsorption effect on odor substances and is adsorbed in a multimolecular layer.

The content of each element in biochar can affect its structure and adsorption sites. The pattern of change of the elements in moss biochar varies with the increase of pyrolysis temperature, in which H and O gradually decrease, which originates from the decomposition of organic matter in the process of pyrolysis and the formation of volatile products. The analysis of the elemental contents of the three types of biochars showed that the two types of plant-derived biochars had small differences in the elemental contents of C, H, and N, but differed significantly from that of the sediment biochars. $n(\text{O})/n(\text{C})$ atomic ratio can be used as an indicator to evaluate the degree of aromatization as well as the polarity of the biochars (Zhao *et al.* 2016). Because the bottom mud biochar had the lowest carbon content, its $n(\text{O})/n(\text{C})$ ratio was the largest at 1.2, followed by BC500 at 0.61, and the smallest at BC800. GSM is a hydrophobic organic pollutant (Liu *et al.* 2021); when $n(\text{O})/n(\text{C})$ was low, the hydrophilicity and polarity of biochar were also low, and the affinity of water molecules was reduced, which led to the enhancement of adsorption of hydrophobic pollutants. The little change in the C content and the gradual increase in the S content are due to the anaerobic charring condition, which cannot cause C and S to form gaseous oxides and volatilize but to form solid biochar and sulfide, which increase its content due to the concentration effect caused by the decrease of the total amount of content. The C and O contents of WBC800 are much higher than those of SBC800, and the H contents of both are 0. The N and S contents do not change much, indicating that the biomass content of WBC800 is very low (Table 1).

Infrared spectroscopy can qualitatively analyze the organic functional groups of the materials. The FT-IR results showed that in the BC samples at different temperatures, the absorption peaks in the $2,800\text{--}3,000\text{ cm}^{-1}$ bands gradually weakened or even disappeared with increasing temperature, which was caused by the further decomposition of organic structures such as aliphatic hydrocarbons and other organic compounds such as gaseous hydrocarbons CH_4 , C_2H_4 , C_2H_6 , and so

Table 1 | Elemental content of different biochar (%)

Biochar	C	N	H	O	S
BC500	41.67	2.65	2.07	25.61	3.18
BC700	45.18	1.84	1.11	18.83	3.75
BC800	36.78	1.55	1.49	8.49	4.34
WBC800	17.45	0.67	0	8.23	0.93
SBC800	1.54	0.23	0	1.86	0.10

on, with the increase in the preparation temperature. The decrease in the relative intensity of the hydroxyl absorption peaks in the $3,000\text{--}3,600\text{ cm}^{-1}$ band of the BC700 sample indicates that the dehydroxylation reaction occurred in the biochar sample at $700\text{ }^{\circ}\text{C}$. (The obvious increase in the presence of BC800 cannot be ruled out as a result of the adsorption of water). The relative intensities of the absorption peaks at $1,450\text{--}1,650\text{ cm}^{-1}$ were also significantly reduced and red-shifted toward longer wavelengths, suggesting that the high temperatures affected the backbone structure of the aromatic groups while changing the structures of the hydroxyl and alkyl groups of the biochar. In addition, the relative intensities of C–O groups in the $950\text{--}1,150\text{ cm}^{-1}$ bands were significantly weakened with increasing temperatures, but a deprotonated carboxylate C=O symmetric telescopic vibrational absorption peak appeared at $1,400\text{ cm}^{-1}$, indicating that high charring temperatures are favorable for the enrichment of carboxylate salts on the surface of biochar. In conclusion, BC biochar mainly contains reactive groups such as carboxyl, hydroxyl, and aromatic, and the high-temperature carbonization process can cause the hydrogen bonding between some of the oxygen-containing groups in the biochar to be joined or eliminated and change the structure of the aromatic backbone (Liu *et al.* 2021). The infrared spectra of the samples of WBC800 were similar to those of BC800, and only the relative intensity of the absorption peaks in the $950\text{--}1,150\text{ cm}^{-1}$ band increased significantly, which may be caused by the abundance of polysaccharides in *Elodea* species. However, the infrared spectra of the SBC800 samples basically disappeared in the organic structure characteristic region ($1,200\text{--}1,800\text{ cm}^{-1}$), indicating that the organic components of the SBC800 samples basically disappeared at $800\text{ }^{\circ}\text{C}$, and the samples were mainly inorganic structures such as Si–O (Li *et al.* 2019b; Zhou & Zhang 2022) (Figure 2).

Specific surface area, average pore size, and pore volume of biochar were analyzed using BET. The specific surface areas of BC500, BC700, BC800, WBC800, and SBC800 were determined to be 15.151 , 173.831 , 205.944 , 122.112 , and $4.534\text{ m}^2\cdot\text{g}^{-1}$, respectively, with average pore diameters of 8.80 , 3.52 , 3.87 , 4.21 nm and 2.70 nm and pore volumes of 3.33 , 1.53 , 1.99 , 1.29 , and $3.06\text{ cm}^3\cdot\text{g}^{-1}$, respectively. It was shown that the pyrolysis process results in loss of mass or disproportionate volume reduction of the biomass to form minerals and carbon skeleton but retains the basic pore and structural characteristics of

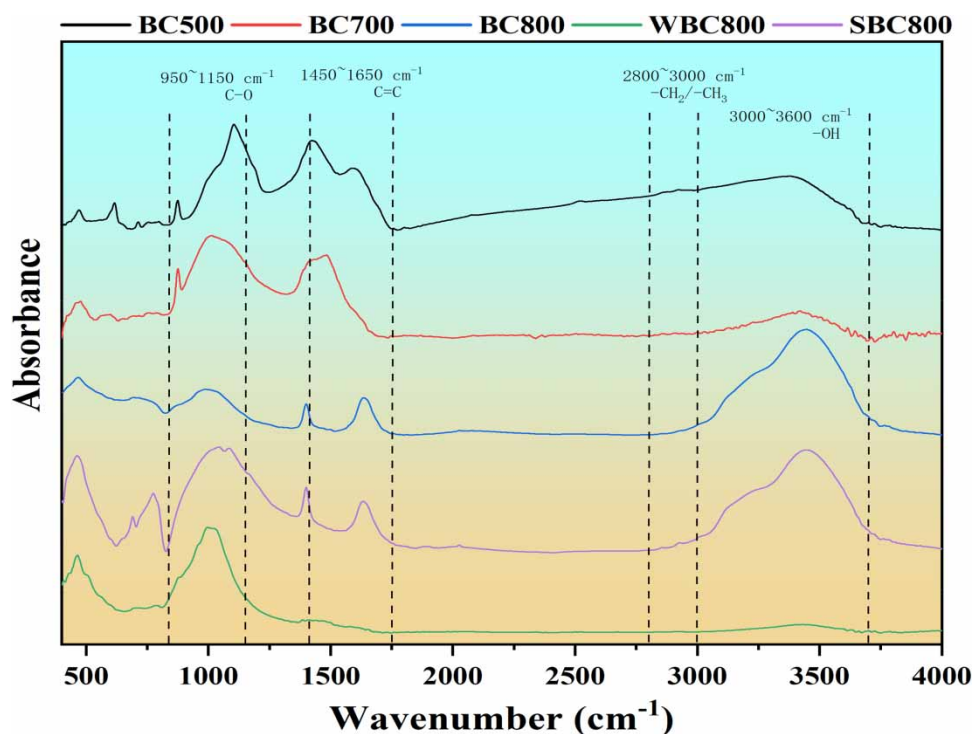


Figure 2 | Infrared spectroscopy was used to analyze various functional groups of biochar and determine the structure of biochar. There is a broad band of –OH absorption vibration at the peak of $3,000\text{--}3,600\text{ cm}^{-1}$; the absorption peak at the peak of $800\text{--}3,000\text{ cm}^{-1}$ is C–H expansion vibration, mainly $-\text{CH}_2$ and $-\text{CH}_3$. The biochars may all be dominated by the aryl ring skeleton, which contains hydroxyl and some oxygen-containing functional groups, but there are differences in the absorption intensity, and there are also C–H and aryl ring with higher chemical stability, indicating that the biochars have the structure of an aryl ring, and some oxygen-containing functional groups, but there are differences in the absorption intensity, and there are also chemically stable C–H and aryl rings, indicating that the biochar has strong stability.

the raw material, so the structure of the biomass feedstock plays a decisive role in influencing the physicochemical properties of the biochar. The smallest specific surface area was found in SBC800, which could be because it had the lowest ash content, which has a large amount of organic matter. The decomposition of organic matter at high temperatures not only generates smoke but also produces a lot of tar-like substances, which will adhere to the surface of SBC800 and lead to clogging of its porous structure. The difference in pore volume of different biochar is not obvious, so the pore volume has little effect on the adsorption capacity of biochar. Overall, the pore structure of biochar with larger specific surface area and smaller pore size is better, which can make it have stronger adsorption capacity, so it is hypothesized that SBC800 has stronger adsorption capacity for GSM (Table 2).

The adsorption effect of biochar prepared from different materials on GSM is very different, and the adsorption effect of biochar prepared from the same material at different temperatures on GSM is also very different. The raw material is the same moss, but the calcination temperature is different, and the adsorption efficiency of the burned-out biochar is very different. Due to high-temperature pyrolysis, the pores are completely opened, which can adsorb the odorous substances very well. The adsorption efficiency of BC800 is the highest, which can be up to 96.90%, while that of BC700 is 25.69% and that of BC500 is 2.38%. The adsorption efficiency of WBC800 is 83.76% and for SBC800 is only 12.62%, probably because the biomass content of *Elodea* is much higher than that of the sediment, and the adsorption capacity is relatively strong. In summary, the moss biochar prepared at 800 °C had the best adsorption effect on GSM, and the adsorption efficiency could reach 96.90% under the same conditions (Figure 3).

Table 2 | Pore analysis of different biochar

Biochar	BET specific surface area (m ² ·g ⁻¹)	Average pore diameter (nm)	Pore volume (cm ³ ·g ⁻¹)
BC500	15.15	8.80	3.33
BC700	173.83	3.52	1.53
BC800	205.94	3.87	1.99
WBC800	122.11	4.21	1.29
SBC800	4.53	2.70	3.06

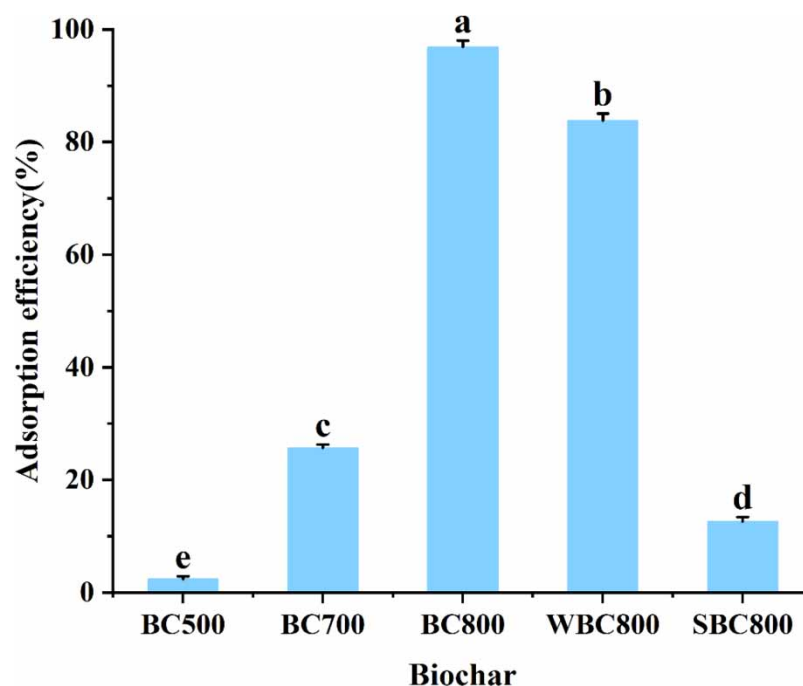


Figure 3 | Biochar made from different materials under the same conditions showed very different removal efficiencies for earth odorants: 2.38% for BC500, 25.69% for BC700, 96.90% for BC800, 83.76% for WBC, and 12.62% for SBC800. BC800 showed the best adsorption of earth odorants.

3.2. BC800 adsorption model

The adsorption effect of BC800 on GSM was different under different dosage conditions. It can be clearly seen that with the increase of BC800 dosage from 0.2 to 1.2 g, the adsorption efficiency increased rapidly, which was mainly due to the fact that with the increase of BC800 dosage, more pores were provided for the adsorption of geotropic odorant, resulting in an increase in the adsorption of geotropic odorant on the adsorbent. However, the adsorption efficiency tends to stabilize as the amount of BC800 dosed exceeds 1.0 g, because the adsorption sites are saturated and the solution system tends to equilibrate when the amount of biochar dosed is 1.0 g. The adsorption efficiency of BC800 in the solution system tends to stabilize. Considering the adsorption effect and the cost of adsorbent, it was determined that the preferred dosage of BC800 for treating a solution with a concentration of 300 ng L^{-1} GSM was 1.0 g (Figure 4).

In the adsorption efficiency of BC800 on GSM in the solution containing odorants under different initial pH conditions, it can be clearly seen that in the pH range of 2–7, with the increase in pH, the adsorption rate curve of GSM is generally increasing and then tends to equilibrium. Because BC800 contains characteristic functional groups that can bind with H^+ , the relationship between H^+ and GSM in solution is competitive adsorption. With increasing pH values, the concentration of H^+ decreases, which reduces the competition on the surface of BC800. Therefore, as the pH value increases, the adsorption capacity of BC800 for GSM is stronger, but the adsorption sites of BC800 are limited, and the adsorption equilibrium will be reached in the end (Figure 5).

Under the condition that the initial concentration of GSM solution is 300-mg L^{-1} , the adsorption process of BC800 on GSM in 60 min using quasi-primary and quasi-secondary kinetic equations to fit the adsorption results found that the adsorption process is divided into two stages of fast adsorption and slow adsorption; the adsorption amount basically reaches saturation within the first 2 min of the adsorption process, which is the stage of fast adsorption. Because this time is the first of the adsorption process, the adsorption amount basically reached the saturation state, which was the fast adsorption stage, because at this time, there was a big difference between the concentration content of GSM in the biochar and the aqueous solution, and the adsorption potential was large, the adsorption sites on the surface of the biochar were more and the adsorption rate was faster, then the adsorption sites on the surface of the biochar were fewer, and the adsorption rate was

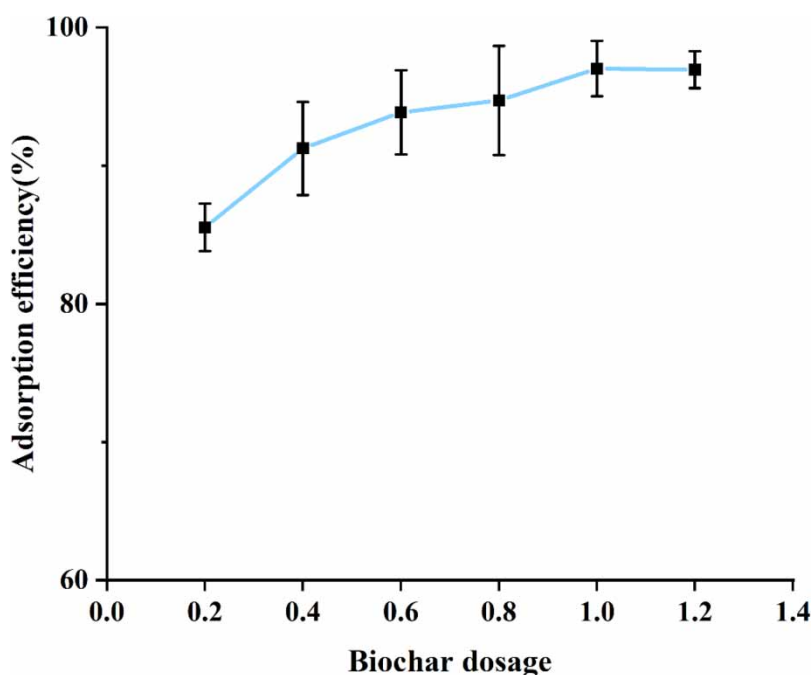


Figure 4 | Under the same conditions, the adsorption effect of BC800 on soil odorant was different with different dosages. The adsorption efficiency of BC800 increased from 0.2 to 1.2 g, and the adsorption efficiency was 87.41, 91.96, 94.42, 95.84, 97.08, and 97.39%, respectively. It can be clearly seen that the adsorption efficiency first increased gradually and finally tended to be equilibrated with the increase in dosage, and the optimal dosage was determined to be 1.0 g, which is the highest dosage for the adsorption of soil odorant. The optimum dosage was determined to be 1.0 g.

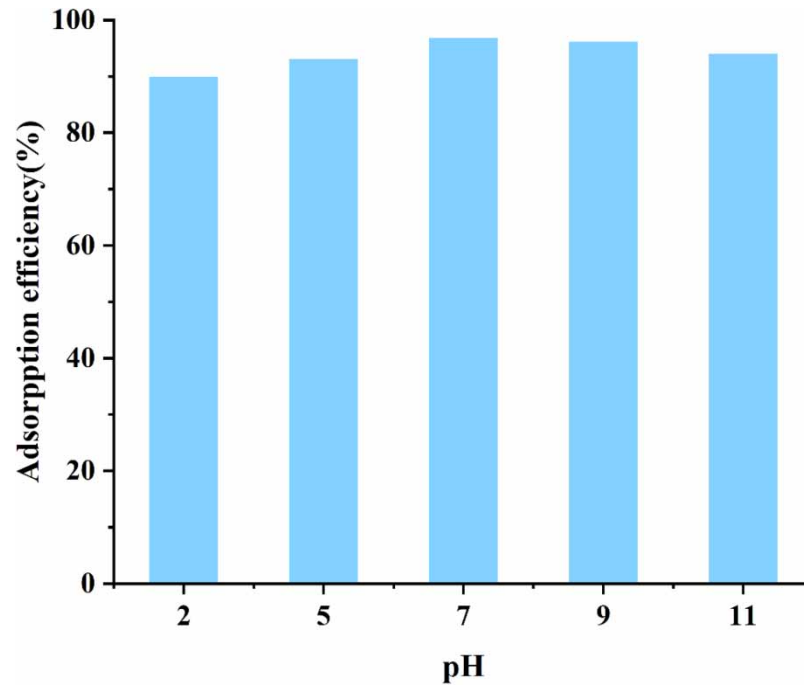


Figure 5 | The adsorption efficiency of BC800 on GSM under the same conditions but different initial pH was the lowest under an acidic condition, the next under an alkaline condition, and the best under a neutral condition. BC800 contains the characteristic functional group that can be combined with H^+ , and H^+ and GSM are in a competitive relationship under acidic conditions, so the adsorption efficiency will increase when the pH is increased, but the adsorption sites of BC800 are limited. The adsorption equilibrium state will be reached at the end.

slowed down to reach more saturation gradually. From the fitting parameters of the adsorption kinetic model, it can be seen that the quasi-secondary kinetic model $R^2 = 0.997$ and the quasi-primary kinetic model $R^2 = 0.989$ of BC800, which can indicate that the two kinetic models can describe the adsorption kinetic behaviors of BC800 on GSM well, and surface chemical adsorption and physical adsorption both play an important role in the adsorption process (Table 3; Figure 6).

The Langmuir isotherm adsorption equation would assume that the biochar contains multiple identical binding sites and that the binding of each adsorbate to each binding site is the same and do not interfere with each other. The Freundlich isotherm adsorption equation is an empirical equation that is applicable to the adsorption on heterogeneous surfaces and predicts the increase of adsorbates on solid surfaces when the concentration of the solute in the solution is increased. The fitted parameter R^2 for the adsorption of GSM by BC800 under different concentration conditions shows that the Freundlich model is larger than the Langmuir model, indicating that it can better describe the isothermal adsorption behavior of GSM by BC800, and this isothermal adsorption process is multimolecular layer adsorption (Table 4; Figure 7).

In summary, the adsorption mechanism of BC800 on GSM is multimolecular layer adsorption with the coexistence of physical and chemical adsorption (Figure 8).

4. DISCUSSION

In this study, moss was used as a raw material to make biochar to adsorb odorous substances for the first time, and good results were achieved. Moss biochar from aquaculture by-products was used to remove the odor produced in aquaculture, which not only solved the problem of aquaculture by-products but also eliminated the impact of odor on the aquaculture

Table 3 | BC800 adsorption kinetic parameters

Biochar	Quasi-first-order kinetic model			Quasi-second-order kinetic model		
	q_e	k_1	R^2	q_e	k_2	R^2
BC800	56.67	3.70	0.989	58.41	0.11	0.997

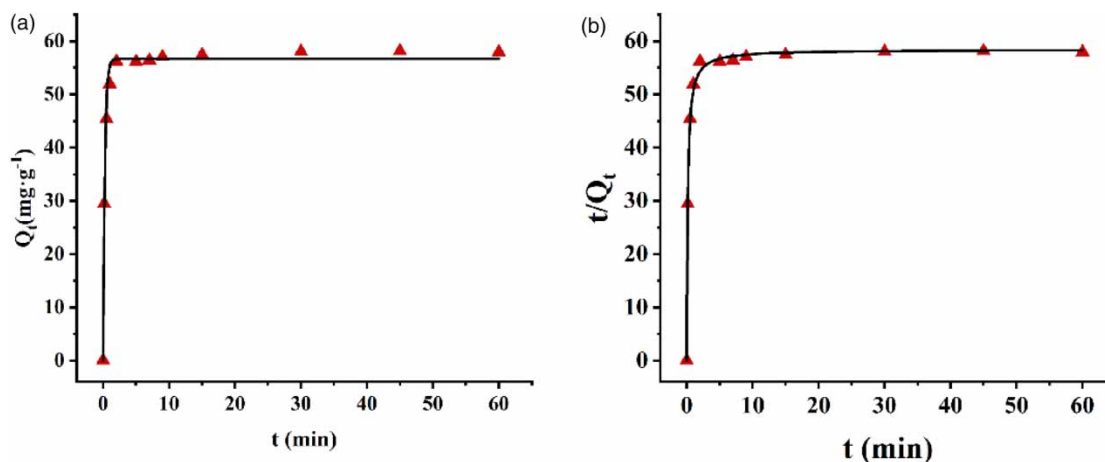


Figure 6 | The kinetic adsorption model of BC800 is a quasi-primary kinetic adsorption model (a) and a quasi-secondary kinetic adsorption model (b). Q_t is the adsorption amount of GSM at the moment of t , where t is the adsorption time, and it is known that (b) $R^2 = 0.997$ and (a) $R^2 = 0.989$ for BC800, which can show that both kinetic models can describe the adsorption kinetic behaviors of GSM by BC800 very well. It can be shown that both kinetic models can well describe the adsorption kinetic behavior of BC800 on GSM, and both surface chemical adsorption and physical adsorption play a major role in the adsorption process.

Table 4 | BC800 isothermal adsorption parameters

Biochar	Langmuir			Freundlich		
	q_{mx}	k_L	R^2	$1/n$	k_f	R^2
BC800	/	/	0.600	0.08	-2.80	0.979

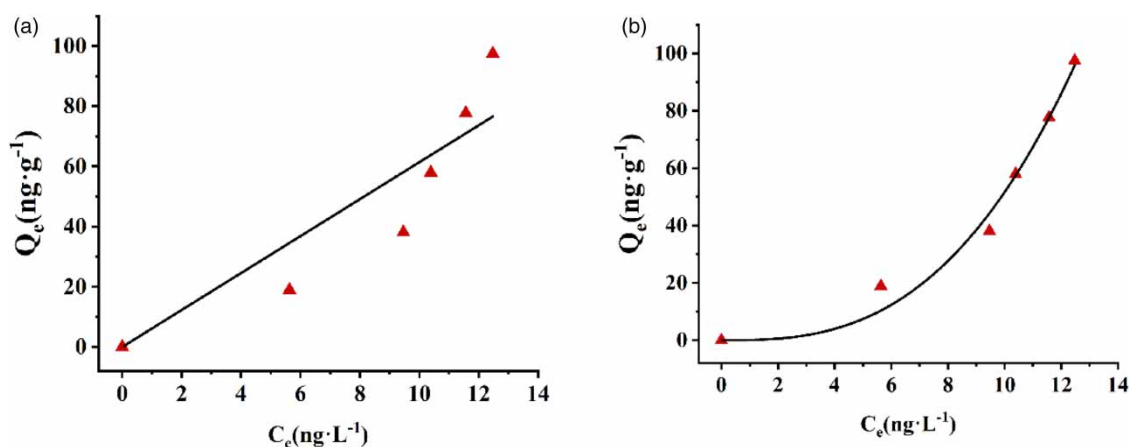


Figure 7 | Isothermal adsorption model for BC800. (a) Langmuir isothermal adsorption model and (b) Freundlich isothermal adsorption model. Langmuir R^2 was 0.600 and Freundlich R^2 was 0.978, and the fitting effect of the Freundlich isothermal equation was much better than that of the Langmuir isothermal equation. It can be seen that the adsorption process of BC800 is multimolecular layer adsorption.

environment, and the resources were recycled without waste. Including biochar production is simple, relatively low-cost, environmentally friendly, and will not produce secondary pollution in the water environment. However, there is no in-depth research on the elution and reapplication of biochar adsorbed with odorous substances.

With the development of human society and population growth, the demand for food and energy has increased dramatically, and humankind and the Earth's terrestrial ecosystems are under unprecedented pressure. Energy shortages and security issues have become global concerns, and these issues urgently require that resources be recycled in our development, production, and living to seek a sustainable path. Biomass, as a renewable energy source, is derived from living organism

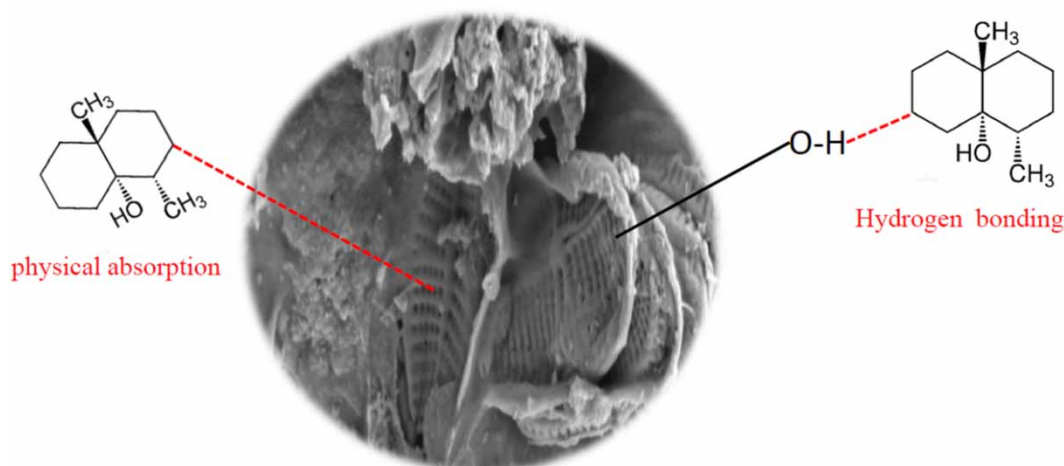


Figure 8 | The adsorption process of BC800 on GSM is multimolecular layer adsorption with both physical and chemical adsorption, which adsorbs GSM through electrostatic attraction, and surface complexation.

materials, most often referred to as plants or plant-derived materials. The recycling of biomass greatly improves the ecological environment and also helps optimize the energy structure (Xu & Chen 2020; Raj *et al.* 2022).

Nowadays, different techniques for the removal of odorous substances, such as adsorption using powdered activated carbon, coagulation, sedimentation, membrane filtration, flocculation, ozonation, electro dialysis, precipitation, co-precipitation, and multi-phase photocatalysis, have been applied to remove color, taste, or odor from water (Fotiou *et al.* 2016; Luo *et al.* 2016). However, each method has its own limitations.

Activated carbon has a large specific surface area, a well-developed microporous structure, and a strong adsorption capacity. Activated carbon will preferentially adsorb organic substances, so it has a good effect on the removal of olfactory substances, mainly through physical adsorption and microbial degradation (Zheng *et al.* 2023). The use of activated carbon adsorption of odor substances is feasible, but it is not easy to regenerate; the production of raw materials is complex with relatively high cost as a drawback (Mustapha *et al.* 2021). Advanced oxidation technology has been identified as the logical choice for the effective decomposition of odorous substances (Garrido-Cardenas *et al.* 2020). Photocatalyst semiconductors such as ZnO, WO₃, and Fe₂O₃ have been developed due to their wide range of technologically useful properties, such as good stability and ease of application, but may cause environmental problems (Banerjee *et al.* 2014). Some research investigated the photocatalytic activity of TiO₂ for the degradation and mineralization of GSM under solar and visible light irradiation (Fotiou *et al.* 2015). However, advanced oxidation is expensive and produces toxic sludge, and the process of removing odorants transfers contaminants from one phase to another without effective removal from the aqueous medium (Wang *et al.* 2023a). In study by Visentin *et al.* (2019) using vacuum UV to remove MIB and GSM, incomplete elimination of these compounds was observed due to the generation of oxidative by-products. Biological treatment is currently widely used in subsurface infiltration and biofilm methods. Ho *et al.* (2007) achieved 100% removal of GSM from surface waters in an Australian catchment through biofilters and conventional treatment processes, with biofilters dominating the removal effect. Biological treatment for the removal of GSM and 2-MIB has the advantages of cost reduction, by-products, and new pollution reduction, but the method is susceptible to a variety of factors such as water temperature, pH, and nutrients, and the treatment effect is not stable enough (McDowall *et al.* 2009; Luo *et al.* 2016).

To summarize, although there are many kinds of technologies to remove GSM, they all have various drawbacks, and to remove GSM, there is no method that has high removal efficiency, is environmentally friendly, and the raw materials are cheap and easy to obtain. The raw material of BC800 used in this study was originally an aquaculture by-product, which is difficult to be treated but cheap and easy to obtain and the process of making it is very simple, and it does not need too much modification and treatment to have a good adsorption effect on GSM, which can be up to 97.08%. Therefore, it is a better technology to use BC800 to adsorb GSM.

Moss is a type of algae that becomes a good adsorbent material when made into biochar, and other algae can also be made into biochar to remove other pollutants. Anthropogenic chemicals, such as heavy metals and organic pollutants, can

frequently be detected in aquaculture products. Among these chemicals, cadmium (Cd^{2+}) and polycyclic aromatic hydrocarbons (FLU, PHE, FLT, and PYR) are two of the most abundant chemicals in aquaculture products, which occasionally exceed safety limits in eastern China due to the presence of contaminants in aquaculture waters (Shin *et al.* 2013; Li *et al.* 2019a). Cd^{2+} in aquaculture ponds may come from road dust and runoff (Pal & Maiti 2018). Polycyclic aromatic hydrocarbons (PAHs), on the other hand, come from biomass combustion and vehicle emissions (Wang *et al.* 2010; Zeng *et al.* 2018). Wang *et al.* (2023b) found that biochar prepared from seabed moss was used to improve water quality in aquaculture ponds, and the removal efficiencies of seabed moss biochar for Cd^{2+} and PAHs were 49, 88, 90, 91, and 88%, respectively.

Chen *et al.* (2018) demonstrated that magnetically modified seashore biochar had a good adsorption effect on Cr. The modification introduced a large number of hydroxyl groups, and the $-\text{OH}$ functional group was protonated to form the positively charged $-\text{OH}_2^+$ functional group, which allowed Cr-containing anions to be adsorbed and migrated to the surface of $\gamma\text{-Fe}_2\text{O}_3$ by electrostatic interactions, and thus electrostatic interactions could be the main mechanism of Cr adsorption by the magnetic biochar (Chen *et al.* 2018). The adsorption mechanism of BC800 on GSM is both physical pore adsorption and chemical adsorption by hydrogen-bonded multimolecular layers.

5. CONCLUSION

Using aquaculture by-products of moss, *Elodea*, and sediment as raw materials, moss biochar, *Elodea* biochar, and sediment biochar were prepared by the high-temperature pyrolysis method, which broadened the source of biochar materials and screened the moss biochar calcined at 800 °C to be the most effective against the main odorous substance (GSM) in aquaculture. When treating a GSM-containing solution with a pH of 7 and a concentration of 300 ng L⁻¹, the adsorption efficiency of GSM reached 97.08% under the conditions of a BC800 dosage of 1.0 g, a temperature of 25 °C, and an adsorption time of 2 min.

The adsorption process of BC800 on GSM conforms to the quasi-primary and quasi-secondary kinetic models, and the Freundlich isotherm model has a good fit for the adsorption process of BC800 on GSM. It shows that the adsorption process of BC800 on GSM is multimolecular layer adsorption with both physical and chemical adsorption, which adsorbs GSM through electrostatic attraction, and surface complexation, and the adsorption process is exothermic.

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DATA AVAILABILITY STATEMENT

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

CONFLICT OF INTEREST

The authors declare there is no conflict.

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