Activated biochar derived from spent *Auricularia auricula* substrate for the efficient adsorption of cationic azo dyes from single and binary adsorptive systems

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**ABSTRACT**

In this study, spent *Auricularia auricula* substrate (AS)-derived biochar (ASBCs) and activated biochar with NaOH (A-ASBC) were evaluated for the adsorption of cationic azo dyes, including methylene blue (MB), rhodamine B (RB), and crystal violet (CV), from single and binary adsorptive systems. A-ASBC showed a higher maximum adsorption capacity for these dyes (MB: 53.62 mg·g⁻¹, RB: 32.33 mg·g⁻¹, CV: 735.73 mg·g⁻¹) than ASBCs in a single system because it had a greater specific surface area and more oxygen containing-functional groups on the surface. The adsorption process of the three dyes onto the adsorbents was in good agreement with the Freundlich adsorption isotherm and fit the pseudo-second-order kinetic model, which revealed sorbate polymolecular layer formation over the adsorbent surface and the involvement of chemisorption. The adsorption mechanism showed that the adsorption of three dyes on adsorbents could be postulated as a multistep process with extraordinary affinity-induced adsorption in terms of both physisorption and chemisorption. In the binary adsorptive system, the results showed that all MB, RB, and CV had antagonistic/competitive effects on each other’s adsorption (Q_{binary}/Q_{single} < 1). Furthermore, a phytotoxic assay affirmed the effectiveness of the adsorbent in adsorbing dye species from aqueous solutions using *Brassica pekinensis* L. seeds as the model. Therefore, activated biochar prepared from AS can be used as a potentially economical and effective adsorbent for treating printing and dyeing wastewater.

**Key words:** adsorption mechanism, antagonistic/competitive effect, base-activated biochar, dyes, pyrolysis temperature, spent mushroom substrate

**HIGHLIGHTS**

- The biochar adsorbent was prepared from the spent *Auricularia auricula* substrate.
- The physicochemical properties of fungus bran biochar were comprehensively analyzed.
- The single and binary adsorption of dyes were compared and the reasons were analyzed.
- Phytotoxicity test was carried out to confirm the effectiveness of adsorption.
- The adsorption mechanism is explained in detail, which provides a theoretical basis.

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INTRODUCTION

With the rapid development of industrialization and urbanization, organic dyes are widely used in textiles, plastics, leather, fiber, paint, and cosmetics, as well as in materials from other industries. These dyes are usually discharged into rivers and lakes in the form of colored wastewater, which will result in serious water pollution (Yagub et al. 2014). According to statistics, approximately $1 \times 10^5$ kinds of dyes are produced annually worldwide, more than $7 \times 10^3$ MT, of which $15\%$ will be discharged as wastewater (Thakur & Chauhan 2018). Cationic azo dyes such as methylene blue (MB), rhodamine B (RB) and crystal violet (CV) are the most common dyes in production and daily life. They can decompose and produce a variety of carcinogenic aromatic amines under certain conditions, which can cause skin allergies of terrestrial organisms, DNA structural changes in the human body, and ecological environmental problems (Balakrishnan et al. 2016). Therefore, effective treatment of dyes in water is imminent.

In recent years, many technologies have been widely used to remove toxic dyes from wastewater, such as adsorption (Zaidi et al. 2019), photocatalytic degradation (Khatarr & Kasiri 2010; Mangindaan et al. 2020), coagulation (Dizge et al. 2008), solvent extraction (Nidheesh & Gandhimathi 2012), and membrane filtration (Rashidi et al. 2015; Febrianto et al. 2019; Gunawan et al. 2019). Among these technologies, adsorption has been popularly applied in many countries due to its low production cost, easy operation, and sustainability (Ngulube et al. 2017). Some materials, such as biochar, biosorbents, chitosan, activated carbon, graphene, natural ores, and carbon nanotubes, are the main adsorbents extensively employed for the removal of dye molecules from different wastewaters (Zhou et al. 2019; Sahu et al. 2021). Biochar has earned extensive research attention for remediation of contaminants as it has abundant oxygen-containing functional groups, such as carboxyl, hydroxyl, and carbonyl groups (Wu et al. 2018), and great potential for practical application as an economical and efficient adsorbent, especially in the removal of dyes, antibiotics, and heavy metals (Ahmad et al. 2014; Dutta et al. 2017). Malik et al. (2007) used groundnut shell waste to prepare the biochar adsorbent to remove malachite green dye from water. The spent Ganoderma lucidum substrate was utilized to prepare a new biosorbent for the removal of Pb$^{2+}$/Cd$^{2+}$ in work of Chang et al. (2017). In another work, the natural nanostructured organic/inorganic composite (i.e., crab shell) was used for pyrolysis of a low-cost but highly efficient dye adsorbent for adsorption of cationic and anionic dye (Dai et al. 2018). Liu et al. (2017a, 2017b) found that biochar prepared from willow catkins can effectively remove organic pollutants and inorganic heavy metals. Two types of commercial biochars (Coconut shell biochar and Bamboo biochar) and one kind of homemade graphene were examined for adsorption of seven different types of antibiotics by Peng et al. (2016). Biochar can be produced from a wide range of...
biowastes, with high efficiency in water treatment and low-cost superiority over many other adsorbents. However, the adsorption performance of biochar relies on its feedstock ingredient and preparation technology.

Spent mushroom substrate (SMS), as a common agricultural waste, is often burned in fields because of its large production, which can easily cause environmental pollution and resource wasting (Paula et al. 2017). The total production of edible fungi in China reached 40 million tons with 200 million tons SMS in 2018, accounting for more than 75% of the global production (China Edible Fungi Association). At present, SMS has gradually become one of the major urban wastes in China (Lou et al. 2017; Sewu et al. 2019). Auricularia auricula is the most popular mushroom because of its largest production and consumption in the world. The produced spent Auricularia auricula substrate (AS) is a kind of fibrous and porous material consisting of cellulose, hemicellulose, lignin, and chitin in intertwined mycelium (Zang et al. 2017). Studies have found abundant functional groups, such as hydroxyl, carbonyl, carboxyl, and amide groups on the AS surface can offer binding sites for dyes in aqueous solution (Wu et al. 2018). Therefore, it may have great value to prepare biochar adsorbents from AS for the treatment of dyeing wastewater. Biochar is obtained by simple pyrolysis without activation, so its pore volume, specific surface area and other microstructure are inferior to activated carbon, which limits its adsorption capacity (Lin et al. 2020). Nevertheless, the high cost of activated carbon limits its wide application (Yagub et al. 2014). Hence, some surface activation strategies based on natural biochar have been provided to enhance the adsorption capacity (Ahmed et al. 2016). For example, it has been reported that acid-treated clay materials enhance the adsorption capacity of sodium leuco-vat dye due to its surface acidity, specific surface area, and porosity (Manyangadze et al. 2020). The base activation enhances the sorption of malachite green dye, Cu$^{2+}$, and Ni$^{2+}$ from water because of the higher surface basicity regarding more oxygen-containing functional groups (Choudhary et al. 2020). Thus, acid/base treatments can be useful methods for activating adsorbents and producing materials with enhanced surface area, porosity, and adsorption properties. However, there are few studies on the adsorption of cationic azo dyes with biochar/base-activated biochar derived from AS in single and binary systems, and the related mechanism is pending investigation.

In this study, biochar prepared from AS at 350 °C and 650 °C and activated by NaOH was used for the adsorption of cationic azo dyes (MB, RB, and CV) in aqueous solution. Adsorption experiments were carried out for single and binary adsorptive systems to understand the synergistic or antagonistic effect of one dye on the adsorption of other dye species. Meanwhile, phytotoxicity assays using Brassica pektinensis L. seeds were studied to analyze the efficacy of the adsorbent in eliminating dyes from aqueous systems. Furthermore, the plausible mechanism of adsorption for MB, RB, and CV were analyzed.

**MATERIALS AND METHODS**

**Materials and reagents**

AS was provided by the Edible Fungus Center of Shanxi Agricultural University. Methylene blue (MB), rhodamine B (RB), crystal violet (CV), NaOH, HCl, NaHCO$_3$, Na$_2$CO$_3$, CsH$_2$O$_3$Na are purchased from Tianjin Hengxing Chemical Reagent Manufacturing Co., Ltd, and ethanol (95%) (CH$_3$CH$_2$OH) is purchased from Tianjin Fuyu Fine Chemical Co., Ltd. The water used for experiments are deionized water. All chemicals and reagents are analytically pure. The characteristic wavelength of maximum absorbance and structures of all dyes used in this study are summarized in Table S1 of supplementary information.

**Preparation of activated biochar**

AS were thoroughly washed with deionized water to remove dust and other impurities and dried in a hot air oven at 60 °C until all moisture was evaporated. The dried biomass was ground by high-speed multi-function pulverizer (SL-100, Zhejiang, China) and sieved through a 0.5 mm sieve to obtain uniform feedstock. Subsequently, AS was carbonized at 350 °C and 650 °C at a rate of 15 °C·min$^{-1}$, and reaches the specified temperature after 25 and 45 min, respectively. Both biochars were kept 3 h under continuous nitrogen flow to avoid oxidation, and the product obtained was labeled biochar (AS350 and AS650). Furthermore, the activation of the biochar was performed by impregnation using NaOH with AS650/NaOH weight ratios of 1:1. The reason why AS650 was chosen to activate is that it has a larger specific surface area and provides more adsorption sites for dyes, with better adsorption capacity. The detailed process of biochar activation was as follows: 40 g NaOH was dissolved in 160 mL deionized water, and then 40 g biochar was added at a 1:1 ratio of AS650/NaOH (Choudhary et al. 2020). In addition, the solution was continuously stirred for 2 h followed by a magnetic stirrer by drying in a hot air
oven at 105 °C for 6 h. Subsequently, the impregnated dried biochar was carbonized for activation at 700 °C under continuous nitrogen flow with a heating rate of 15 °C min⁻¹ for 1 h. After activation, the samples were maintained under continuous nitrogen flow until room temperature was obtained. The obtained samples were thoroughly washed with deionized water until the pH of the filtrate was near that of biochar. The materials were then dehydrated at 105 °C until completely dried, and the resultant activated biochar samples were obtained and labeled A-ASBC.

Characterization techniques

The ash content was determined by a muffle furnace heating at 800 °C for 1 h (Kwak et al. 2019). The pH value of ASBCs and A-ASBC in the mixture (solid to liquid ratio of 1:20) was measured by a pH meter (PHS-4C+, Shanghai, Lei Magnetic) after shaking the mixture for 1 h using a constant temperature shaker (SHZ-82A, Changzhou, China) (Chang et al. 2019). The content of C, H, N and S in the sample was determined by element analyzer (Elementar Vario MACRO Cube, Elementar, Germany). The O content was calculated according to the mass balance, and the O/C and H/C values were calculated in turn. The specific surface area was determined based on Brunner-Emmet-Teller (BET) theories and the pore size was estimated based on Barrett-Joyner-Halenda (BJH) method by specific surface and pore size analyzer (TriStar II 3020, United States Micromeritics) with nitrogen adsorption at 77 K. The thermal stabilities of ASBCs and A-ASBC were analyzed using a thermogravimetric analyzer (TG-hiden MS, PerkinElmer, USA). Nitrogen was used as the inert gas (4 h) for the calculation is given in the Supplementary Information. The dye adsorption amount on single and binary adsorption systems was calculated according to Equation (1).

\[ jQ_{e,i} = \frac{(jC_0 - jC_{e,i})V}{m} \] (1)

where \( jQ_{e,i} \) is the adsorption capacity or equilibrium adsorption capacity of component i at any time in system j, mg g⁻¹; j = S (single system), j = M (composite system: MB + RB; MB + CV; RB + CV); \( jC_0 \) and \( jC_{e,i} \) are the initial
concentration of component i in system j and the concentration at time t or at equilibrium, respectively, mg·L⁻¹; V is the solution volume, L; and m is the mass of the adsorbent, g.

Single and binary adsorption system studies
In this study, single adsorptive systems refer to aqueous systems having one dye at a time with the adsorbent, while binary adsorptive systems refer to aqueous systems having both dye species (MB + RB, MB + CV and RB + CV) at the same time with the adsorbent. All single and binary adsorptive systems were studied using batch experiments for equilibrium time. Experimental data obtained from single adsorption systems were used to study the sorbate-sorbent interactions using two-parameter and three-parameter isotherm models (detailed representation in Table S3 of supplementary information). It was also used to study the kinetics of sorbate-sorbent interactions using models such as pseudo-first-order, pseudo-second-order and intraparticle diffusion models (detailed representation in Table S4 of supplementary information). For binary adsorption systems involving the coexistence of MB, RB, and CV in one system, the relevant equilibrium data were investigated with variable working concentrations of 5 + 5, 10 + 10, 20 + 20, 30 + 30, 40 + 40, and 50 + 50 mg·L⁻¹, and the antagonistic or competitive effect of one dye on the adsorption of another dye was analyzed (Manjunath et al. 2019). For the binary adsorption study, the pH was not adjusted (based on the pH value of the optimal adsorption capacity of different dyes in a single system), and the dosage of adsorbent was the same as that of single adsorption experiment, which was 0.375 g·L⁻¹.

Regeneration studies
To assess the recyclability of the biochar used, the regeneration test was repeated for three cycles with 95% ethanol as the desorption agent. In this test, after the equilibrium adsorption of dye onto A-ASBC was reached, solid liquid was separated by centrifugation at 4,000 rpm for 5 min, and then the supernatant was replaced by 95% ethanol. Subsequently, the mixture was shaken at 200 rpm for 2 h at 25 °C, followed by centrifugation, through addition of deionized water in the centrifuge tube and decanting, through filtration, which is repeated three times, and dried at 60 °C for 24 h. The experimental conditions were the same as those described in section 2.4, and the experiments were conducted thrice.

Phytotoxicity assay
Brassica pekinensis L. seeds were used for phytotoxic assessment of the adsorptive removal of MB, RB and CV in single and binary adsorptive systems. The seed choice was due to its easy availability, since it is a cruciferous vegetable, a popular vegetable that is commonly cultivated in Shanxi Province, China. Importantly, the growth cycle of the seed is relatively short, so the germination status can be understood in a short time. The procedures for seed incubation were performed according to the methods described in previous studies (Luo et al. 2018). Specifically, 5 mL of dye solution without adsorption treatment (control sample plates), dye solution after adsorption treatment (test sample plates) and deionized water (blank plate) were added to a Petri dish covered with filter paper, and then 20 grains of Brassica pekinensis L. seeds were evenly spread on filter paper soaked in culture solution. Here, the concentration of dye solution without adsorption treatment is 50 mg·L⁻¹, and the pH is adjusted to 8. On this basis, 0.015 g biochar was added into a centrifuge tube containing 40 mL dye solution, placed in a 25 °C, 200 rpm constant temperature incubator with oscillation for 24 h, and the solution after adsorption was obtained by filtration. The conditions of dye solution after adsorption treatment are shown in Table S5 of supplementary information. The dish was wrapped with plastic wrap and placed in an incubator at 25 °C in the dark for 72 h. Then, the germination rate was calculated, and the radicle length of the seed was measured.

RESULTS AND DISCUSSIONS
Characterization of adsorbent
Physical and chemical properties of adsorbent
The main physical and chemical properties of ASBC and A-ASBC are shown in Table 1. With increasing pyrolysis temperature, the biochar yields gradually decreased due to the loss of volatile substances in biomass during pyrolysis. The yield of A-ASBC was 34.69%, which was lower than the 38.73% yield of AS650 because activation led to the decomposition of residual cellulose, lignin and hemicellulose in biochar (Choudhary et al. 2020). AS650 and A-ASBC have higher ash contents (26.52% and 28.76%) because of the enrichment of a large number of inorganic mineral components during high-temperature pyrolysis and base activation (Yuan et al. 2011). Compared with
AS350, the higher pH value of AS650 was attributed to the degradation of acidic oxygen-containing functional groups in AS at high temperature (Goh et al. 2019). A-ASBC had a higher C content and lower H, N, and O contents because of its higher carbonization degree, while H, N, and O escaped from the carbon chain and further formed H₂O and volatile nitrogen-containing substances, resulting in loss (Tang et al. 2018). The aromaticity and polarity of the samples were analyzed separately by calculating the ratios of H/C, O/C, and (O + N)/C (Xiao et al. 2016). The large decreases in all atomic ratios of A-ASBC indicated that it had higher aromaticity and less hydrophilicity owing to a greater carbonization and elevated removal of polar surface functional groups compared to ASBCs. The results of the surface functional groups of ASBCs and A-ASBC measured by Boehm titration are shown in Table 2. The content of acidic oxygen-containing functional groups in biochar prepared at high temperature was slightly lower than that of biochar prepared at low temperature. In contrast, the content of basic oxygen-containing functional groups was slightly higher, which was consistent with the increasing pH value. Furthermore, A-ASBC contained the most basic oxygen-containing functional groups, which is one of the reasons for its best adsorption performance.

The thermal stabilities of ASBCs and A-ASBC were studied by thermogravimetric analysis (TGA) (Figure 1). When the temperature reached 1,000 °C, the mass loss rates of AS350, AS650, and A-ASBC were 58.77%, 40.72%, and 37.92%, respectively, which indicated that biochar prepared at high temperature had better thermal

| Material | Yield (%) | Ash (%) | pH   | C  | H  | N  | O  | H/C | O/C | (O + N)/C |
|----------|-----------|---------|------|----|----|----|----|-----|-----|-----------|
| AS350    | 51.70     | 21.48   | 9.25 | 52.01 | 3.09 | 2.38 | 21.04 | 0.06 | 0.40 | 0.45      |
| AS650    | 38.73     | 26.52   | 10.98| 54.29 | 0.90 | 1.58 | 16.71 | 0.02 | 0.31 | 0.34      |
| A-ASBC   | 34.69     | 28.76   | 11.05| 57.17 | 0.81 | 1.40 | 11.86 | 0.01 | 0.21 | 0.25      |

| Sample   | Carboxyl | Lactones | Phenols | Carbonyl | Total oxygen-containing acidic groups | Total oxygen-containing basic groups | Total oxygen-containing functional groups |
|----------|----------|----------|---------|----------|--------------------------------------|-------------------------------------|----------------------------------------|
| AS350    | 0.80     | 0.03     | 0.05    | 0.25     | 1.13                                 | 0.63                                | 1.76                                   |
| AS650    | 0.77     | 0.03     | 0.05    | 0.25     | 1.10                                 | 0.64                                | 1.74                                   |
| A-ASBC   | 0.76     | 0.02     | 0.06    | 0.24     | 1.08                                 | 0.83                                | 1.91                                   |
stability than biochar prepared at low temperature, and the activated biochar had the best thermal stability. From the initial stage to 100 °C, the mass loss of biochar was mainly caused by water evaporation. When the temperature was between 200 °C and 680 °C, the mass loss was primarily derived from the decomposition and volatilization of cellulose, lignin, hemicellulose, and other organic matter. In addition, the large mass loss of the three kinds of biochar appeared between 680 °C and 730 °C, which was mainly due to the thermal decomposition of calcium carbonate. Many studies have shown that thermal decomposition of calcium carbonate mainly occurs at approximately 700 °C (Karunadasa et al. 2019).

**BET and atomic force microscopy analysis**

The specific surface area is an important factor affecting the adsorption performance. The specific surface area, average pore diameter, and pore volume of ASBCs and A-ASBC are shown in Table 3. Compared with AS350, the specific surface area and total pore volume of AS650 and A-ASBC increased, which was mainly due to the increasing pores caused by high-temperature pyrolysis and activation. At the same time, the continuous devolatilization of biochar also contributed to the increasing specific surface area. The specific surface area of A-ASBC was 9.8 times and 4.1 times that of AS350 and AS650, and the pore volume was 2.8 times and 2.2 times that of AS350 and AS650, respectively. As a new type of nanometer observation tool to characterize the apparent morphology, AFM satisfies the study of the complex structure of macromolecules at the molecular level and has a more intuitive and comprehensive understanding of the particle structure (Patra et al. 2020). AFM morphology and particle plane analysis of AS350, AS650, and A-ASBC are shown in Figure 2. Compared with ASBCs, the surface of A-ASBC was conical and compact, and the height of the conical aggregates decreased. In addition, the particle sizes of ASBCs and A-ASBC were at the nanometer level, and the surface roughness was represented by $R_a$. It was found that the A-ASBC nanostructure showed a larger roughness value ($R_a = 0.955 \text{ nm}$), followed by AS650 nanoparticle size ($R_a = 0.877 \text{ nm}$) and AS350 ($R_a = 0.688 \text{ nm}$) after calculation by NanoScope Analysis software. This result was consistent with the BET analysis, which might provide sufficient adsorption sites for dyes.

**Table 3 | Surface area and porosity of ASBCs and A-ASBC**

| Sample | BET(m$^2\cdot$g$^{-1}$) | Average pore diameter(nm) | Total pore volume(cm$^3\cdot$g$^{-1}$) |
|--------|-----------------|-----------------|----------------------------------|
| AS350  | 9.123           | 11.507          | 0.026                            |
| AS650  | 21.772          | 6.143           | 0.033                            |
| A-ASBC | 89.393          | 3.235           | 0.072                            |

**Figure 2 | AFM images of ASBCs and A-ASBC.**
The N$_2$ adsorption-desorption isotherm is shown in Figure 3. The N$_2$ isotherm of AS350 conformed to the type II isotherm defined by the International Union of Pure and Applied Chemistry (IUPAC), indicating the nonporous nature of the material. The specific surface area (9.1234 m$^2$·g$^{-1}$) of AS350 was relatively small as shown in Table 3, which could be attributed to incomplete pyrolysis at low temperature hindering the formation of pores. The N$_2$ adsorption-desorption isotherms of AS650 and A-ASBC belonged to the type IV isotherm with an H3 type hysteresis loop, and showed the mesoporous properties of these two materials (Hu & Hsieh 2017), which was consistent with the pore sizes of AS650 (6.14 nm) and A-ASBC (3.23 nm) as shown in Table 3. Meanwhile, the pore structure of AS650 and A-ASBC was formed by the aggregation of flake particles, and the pore structure was slit pores (Han et al. 2017).

**Zeta potential of adsorbents**

Zeta potential is the potential difference between the continuous phase of the adsorbent and the fluid stabilization layer attached to the dispersed particles. The zeta potential of the adsorbent was measured in aqueous dispersion medium at pH 2–10. The change in zeta potential of ASBC and A-ASBC with the pH of the solution is shown in Figure 4. When pH <4, the zeta potentials of ASBCs and A-ASBC were positive. When the solution...
pH increased to 4.1, 4.2, and 4.7, the zeta potentials of AS350, AS650 and A-ASBC reached zero, the zero charge point (pHpZC). The zero charge point of the adsorbent is an important factor affecting its adsorption capacity (Patra et al. 2020). In general, adsorption is beneficial for cationic adsorbates when pH > pHpzc, and adsorption is favorable for anionic adsorbates when pH < pHpzc. With increasing pH value, electronegativity properties gradually increase, indicating that the number of negative charges increased (Park et al. 2019). In this study, the increase in the amount of negative charges was conducive to the adsorption of cationic azo dyes by electrostatic interactions. Regarding the negative charge concerned, AS350 > AS650 > A-ASBC, indicated that electrostatic interactions were not the key factor affecting the adsorption performance of biochar.

Adsorption study

Single adsorption system

**Effect of pH.** The effect of initial pH on the adsorption process includes the protonation/deprotonation of the adsorbent surface and the change in dye morphology in aqueous solution under different pH conditions. In this study, the adsorption of the cationic azo dyes MB, RB, and CV by ASBC was observed in the pH range of 3 to 10. As shown in Figures 5(a), the adsorption of MB on biochar hardly changed with pH value. When the pH value rose from 3 to 4, the adsorption capacity of ASBC and A-ASBC both decreased slightly. The adsorption capacity (pH: 5–10) was relatively stable. According to zeta potential analysis, ASBC and A-ASBC were positively charged at pH 2–4 and negatively charged at pH 5. Therefore, when the initial pH value was 4, there was electrostatic repulsion between MB and biochar, resulting in a downward trend of adsorption. In addition, biochar showed

![Graph](https://example.com/graph.png)

**Figure 5** | Effect of initial pH value on adsorption of (a) methylene blue (MB), (b) rhodamine B (RB), and (c) crystal violet (CV) by ASBCs and A-ASBC.
a higher adsorption capacity at pH 3. Li et al. (2016) reported that biochar surfaces contain more π electron densities, which can be used as π electron donors, and MB can be used as π electron acceptors. Lyu et al. (2018) pointed out that if the pH_{ZCP} is greater than the solution pH, MB will be adsorbed by π-π stacking interactions. If the pH_{ZCP} is less than the solution pH, MB will be absorbed by electrostatic interactions and π-π stacking interactions. Since the pH_{ZCP} values of ASBCs and A-ASBC were both greater than 3, the higher MB adsorption capacity at pH 3 might be caused by π-π stacking.

On the whole, as shown in Figures 5(b), the adsorption capacity of biochar for RB decreased with increasing pH value, which indicated that adsorption was favorable for RB under acidic conditions. This was because the solution pH value would affect the solubility and color characteristics of RB in water. The solubility of RB in acidic environments was higher than that in basic environments, and RB was prone to discoloration in acidic environments. The other reason was that carboxyl groups in biochar and RB ionized to produce –COO− under base conditions, which led to electrostatic repulsion between biochar and RB. Liu et al. (2017a, 2017b) found that RB molecules might associate with each other to produce dimers or even higher molecular weight aggregates in the base environment, which would cause a certain space resistance effect between them and adsorbents, thereby reducing the adsorption performance of ASBCs and A-ASBC to RB.

However, the adsorption trend of CV was opposite to that of RB. The CV adsorption capacity of ASBC and A-ASBC increased with increasing pH value (Figures 5(c)). As a cationic dye, CV was positively charged at the position containing chromogenic groups after ionization in water. When the pH value was low, the H⁺ in solution would generate electrostatic repulsion with positively charged CV, and H⁺ would also compete with CV for adsorption sites on the surface of biochar. Therefore, the stronger the solution acidity was, the weaker their adsorption capacity was. With increasing pH value, the H⁺ content decreased, and protonation weakened (Sewu et al. 2019). Meaning, the amount of OH⁻ attached to ASBCs and A-ASBC increased. To a certain extent, the negative charge of the biochar surface was enhanced, which can rapidly combine with positively charged CV through electrostatic interactions and achieve adsorption equilibrium in a short time.

**Adsorption kinetics.** The effect of reaction time on the adsorption of the three dyes by biochar is shown in Figs. S1(a-c). The adsorption rate of MB, RB and CV by ASBCs and A-ASBC showed a similar trend as the reaction time. The adsorption rate was fast due to the sufficient active sites of the biochar surface in the initial adsorption stage (the first 120 min). After 120 min, the increase in adsorption capacity slowed, with most of the active sites on the adsorbent surface being occupied by dye molecules, which hindered its further diffusion into the pores of biochar. In addition, the concentration difference between the solution and the adsorbent decreased, resulting in a slow adsorption rate (Malik 2003). The adsorption capacity of ASBCs and A-ASBC was more than 90% of the saturated adsorption capacity within 480 min. As shown in Figs. S1(d-f), the intraparticle diffusion model of three cationic azo dyes adsorbed by biochar can be divided into two linear stages, namely, boundary layer diffusion and intraparticle diffusion (Wu et al. 2000). The straight lines of the intraparticle diffusion model of MB, RB and CV did not pass through the zero point, which indicated that intraparticle diffusion was not the only rate-limiting step. The parameters of the pseudo-first-order, pseudo-second-order, and intraparticle diffusion models are shown in Table 4. Compared with the pseudo-first-order adsorption process (\( R^2 = 0.77–0.98 \)), the adsorption process was more consistent with the pseudo-second-order adsorption process (\( R^2 = 0.92–1.00 \)), and the theoretical adsorption capacity fitted by pseudo-second-order adsorption was also closer to the actual adsorption capacity, indicating that the speed control step of ASBCs and A-ASBC for MB, RB and CV adsorption was chemical adsorption, and the reaction rate was proportional to the number of active sites on the surface of biochar (Inyan et al. 2014; Li et al. 2016). As shown in Table 5, the parameter \( k_{p1} \geq k_{p2} \) indicated that the diffusion rate of the boundary layer was greater, which is consistent with the research results of Nethaji et al. (2018) using activated carbon derived from waste polyurethane foam for adsorption of malachite green.

**Adsorption isotherm analysis.** The adsorption isotherms of MB, RB and CV on biochar are shown in Figs. S2(a-c). The adsorption capacity of ASBCs and A-ASBC for the three dyes increased with increasing equilibrium concentration. Specifically, the adsorption capacity of biochar for the three dyes rapidly increased at low initial concentrations because of more adsorption sites and active groups. With increasing dye initial concentration, the adsorption sites on the biochar surface tend to be saturated, resulting in a slow increase in adsorption capacity.
occurred on nonhomogeneous surfaces (Gunay et al. 2008; Liu et al. 2017b). The Dubinin-Radushkevich isotherm model was not consistent with the experimental data, so the $E_{DR}$ value cannot be related to the adsorption process. Compared with ASBCs, the $m$ value of A-ASBC deviated more from one in the Sips isotherm model, indicating that the surface was more uneven, which was consistent with the results of Freundlich model fitting.

### Table 4 | Parameters of pseudo first order and pseudo second order for methylene blue (MB), rhodamine B (RB), and crystal violet (CV) adsorption on ASBCs and A-ASBC

| Dye    | Sample | $Q_e$ (mg·g\(^{-1}\)) | $Q_e$ (mg·g\(^{-1}\)) | $k$ | $R^2$ | $Q_e$ (mg·g\(^{-1}\)) | $k_2$ | $R^2$
|--------|--------|----------------------|----------------------|-----|-------|----------------------|-------|-------
| MB     | AS350  | 18.48 ± 0.63         | 15.92 ± 0.76         | 0.057 ± 0.014 | 0.83  | 17.03 ± 0.49         | 0.005 ± 0.001 | 0.95  |
|        | AS650  | 26.74 ± 0.86         | 23.51 ± 1.30         | 0.044 ± 0.012 | 0.79  | 24.92 ± 0.92         | 0.003 ± 0.001 | 0.92  |
|        | A-ASBC | 48.77 ± 0.21         | 45.69 ± 2.42         | 0.046 ± 0.013 | 0.77  | 46.28 ± 1.60         | 0.002 ± 0.000 | 0.93  |
| RB     | AS350  | 17.12 ± 0.37         | 16.19 ± 0.53         | 0.012 ± 0.001 | 0.97  | 17.87 ± 0.37         | 8.912*10\(^{-4}\) | 0.000  | 0.99  |
|        | AS650  | 23.78 ± 0.17         | 22.05 ± 0.53         | 0.017 ± 0.002 | 0.98  | 24.07 ± 0.34         | 9.568*10\(^{-4}\) | 0.000  | 1.00  |
|        | A-ASBC | 32.37 ± 0.31         | 30.45 ± 0.70         | 0.020 ± 0.002 | 0.98  | 32.98 ± 0.64         | 8.471*10\(^{-4}\) | 0.000  | 0.99  |
| CV     | AS350  | 174.47 ± 4.23        | 142.76 ± 9.20        | 0.014 ± 0.004 | 0.89  | 158.67 ± 8.09        | 1.146*10\(^{-4}\) | 0.000  | 0.95  |
|        | AS650  | 308.06 ± 1.09        | 294.70 ± 12.63       | 0.014 ± 0.002 | 0.94  | 320.25 ± 11.34       | 6.180*10\(^{-4}\) | 0.000  | 0.97  |
|        | A-ASBC | 729.81 ± 0.85        | 677.81 ± 36.92       | 0.018 ± 0.004 | 0.88  | 729.02 ± 29.18       | 3.799*10\(^{-4}\) | 0.000  | 0.95  |

$Q_e$: Actual adsorption capacity, $Q'_e$: Theoretical adsorption capacity.

### Table 5 | Parameters of intra-particle diffusion for methylene blue (MB), rhodamine B (RB), and crystal violet (CV) adsorption on ASBCs and A-ASBC

| Dye    | Sample | $k_1$ (mg·g\(^{-1}\)·min\(^{-1}\)) | $k_2$ (mg·g\(^{-1}\)·min\(^{-1}\)) | $c_1$ | $c_2$ | $R^1$ | $R^2$
|--------|--------|---------------------------------|---------------------------------|-------|-------|-------|-------
| MB     | AS350  | 1.40 ± 0.24                     | 0.16 ± 0.02                     | 3.09  | 1.22  | 0.92  | 0.93  |
|        | AS650  | 1.83 ± 0.30                     | 0.20 ± 0.02                     | 4.85  | 1.54  | 0.92  | 0.97  |
|        | A-ASBC | 3.05 ± 0.21                     | 0.30 ± 0.05                     | 10.99 | 1.08  | 0.99  | 0.89  |
| RB     | AS350  | 1.13 ± 0.12                     | 0.11 ± 0.02                     | -0.72 | 0.78  | 0.96  | 0.88  |
|        | AS650  | 1.84 ± 0.09                     | 0.14 ± 0.01                     | -1.09 | 0.61  | 0.99  | 0.99  |
|        | A-ASBC | 2.62 ± 0.23                     | 0.15 ± 0.01                     | -0.87 | 1.52  | 0.97  | 0.99  |
| CV     | AS350  | 9.48 ± 1.41                     | 2.36 ± 0.28                     | 3.46  | 9.47  | 0.92  | 0.96  |
|        | AS650  | 18.16 ± 0.68                    | 1.36 ± 0.35                     | 16.37 | 4.59  | 0.99  | 0.82  |
|        | A-ASBC | 41.36 ± 1.69                    | 4.63 ± 1.54                     | 85.21 | 11.32 | 0.99  | 0.83  |

The fitting results of the adsorption isotherms are shown in Table 6. Compared with the other isotherm models, the adsorption process of ASBCs and A-ASBC for the three dyes was more in line with the Freundlich model, indicating that the adsorption of MB, RB and CV on biochar was multimolecular layer adsorption, and occurred on nonhomogeneous surfaces (Gunay et al. 2007; Tran et al. 2017; Guo et al. 2018). The $n$ value and $K_F$ value of Freundlich can be used to judge the adsorption performance of the adsorbent. The $1/n$ ratios of MB, RB and CV adsorbed by ASBCs and A-ASBC were all less than 1, which indicated that adsorption was easily preceded. The $K_F$ values were A-ASBC > AS650 > AS350, indicating that A-ASBC has the best adsorption capacity, followed by AS650 and AS350. The maximum adsorption capacities of A-ASBC for MB, RB and CV calculated by the Langmuir model was 50.57 mg·g\(^{-1}\), 29.95 mg·g\(^{-1}\), and 1,321.81 mg·g\(^{-1}\), respectively. Compared with most adsorbents (Table 7), A-ASBC showed better adsorption performance. In addition, we found that the adsorption capacity of CV was much higher than that of MB and RB. The dimerization constant for CV has been reported to be much smaller than that of MB and RB (Ghasemi & Mandoumi 2008; Liu et al. 2017a, 2017b). MB is a flat and slightly hydrophobic molecule with rigid heterocyclic aromatic rings (Harris et al. 2001). It has a strong tendency to form dimers and trimers due to hydrophobic interactions (Bergmann & O’Konski 1963). Moreover, previous studies have shown that RB molecules may combine to produce dimers or even higher molecular weight aggregates in the adsorption process, resulting in a certain steric hindrance effect between RB molecules and adsorbents (Liu et al. 2017a, 2017b). The Dubinin-Radushkevich isotherm model was not consistent with the experimental data, so the $E_{DR}$ value cannot be related to the adsorption process. Compared with ASBCs, the $m$ value of A-ASBC deviated more from one in the Sips isotherm model, indicating that the surface was more uneven, which was consistent with the results of Freundlich model fitting.
Table 6 | Parameters of adsorption isotherms models for methylene blue (MB), rhodamine B (RB), and crystal violet (CV) adsorption on ASBCs and A-ASBC

| Model                  | Constants | MB AS350 | AS650 | A-ASBC | RB AS350 | AS650 | A-ASBC | CV AS350 | AS650 | A-ASBC |
|------------------------|-----------|----------|-------|--------|----------|-------|--------|----------|-------|--------|
|                        |           | ± 1.11   | ± 3.91| ± 5.31 | ± 1.43   | ± 1.40| ± 2.20 | ± 1.84   | ± 3.92| ± 100.73|
| Langmuir               | Q L       | 19.39    | 50.12 | 50.57  | 17.32    | 19.42 | 29.95  | 185.14   | 437.60| 1,321.81|
|                        | K L       | 0.56     | 0.29  | 0.82   | 0.23     | 0.37  | 0.66   | 0.06     | 0.03  | 0.05   |
|                        | R L       | 0.03     | 0.06  | 0.02   | 0.08     | 0.06  | 0.03   | 0.06     | 0.12  | 0.07   |
|                        | R^2       | 0.83     | 0.71  | 0.76   | 0.83     | 0.81  | 0.81   | 0.71     | 0.90  | 0.99   |
| Freundlich             | K F       | 9.34     | 9.67  | 6.13   | 5.69     | 7.47  | 13.24  | 45.91    | 50.62 | 91.37  |
|                        | n         | 0.20     | 0.81  | 0.19   | 0.54     | 0.82  | 0.24   | 0.26     | 0.39  | 0.64   |
|                        | R^2       | 0.93     | 0.92  | 0.98   | 0.97     | 0.99  | 0.97   | 0.95     | 0.96  | 1.00   |
| Dubinin-Radushkevich  | Q DR      | 17.45    | 24.35 | 46.40  | 14.34    | 16.86 | 26.73  | 160.03   | 291.88| 667.78 |
|                        | K DR      | 3.22×10^{-7} | 2.91×10^{-7} | 4.83×10^{-7} | 8.99×10^{-7} | 177×10^{-7} | 1.60×10^{-5} | 9.68×10^{-6} | 5.28×10^{-6} |
|                        | R^2       | 0.57     | 0.40  | 0.69   | 0.52     | 0.52  | 0.60   | 0.41     | 0.49  | 0.82   |
| Sips                   | Q s       | 19.44    | 29.75 | 49.12  | 17.69    | 19.48 | 28.52  | 186.47   | 405.22| 1,013.6 |
|                        | K s       | 0.55     | 0.20  | 0.88   | 0.22     | 0.37  | 0.79   | 0.06     | 0.03  | 0.08   |
|                        | m         | 0.99     | 1.03  | 0.15   | 0.95     | 0.87  | 1.25   | 0.98     | 1.17  | 1.22   |
|                        | R^2       | 0.83     | 0.70  | 0.74   | 0.85     | 0.82  | 0.74   | 0.72     | 0.87  | 0.98   |

Dye and material

Q: Adsorption capacity; K: Adsorption equilibrium constant; R L: Langmuir coefficient; R^2: Determination coefficient; K: Freundlich constant; 1/n: Freundlich exponent; K DR: Dubinin-Radushkevich constant; m: Sips constant; R^2: Determination coefficient; ASBC: Activated sludge biomass support; A-ASBC: Activated sludge biomass support without adsorption.
The adsorption capacities of the three dyes by A-ASBC in single and binary systems are shown in Figure 6(a)–6(c). In all systems, the adsorption capacity of A-ASBC for the three dyes increased as the initial concentration increased. Clearly, the adsorption capacity of A-ASBC for dyes in a single system was greater than that in binary systems, which might be due to the resistance of mass transfer by one dye species over the uptake of other dye species from binary adsorptive systems at all initial concentrations (Patra et al. 2020). As shown in Figure 6(a) and 6(b), CV had a greater antagonistic effect on MB and RB in the binary system. Compared with other CV adsorption systems, A-ASBC showed the best adsorption capacity of CV in a single system (Figures 6(c)). The difference in affinity between MB and RB might determine its mass transfer resistance, thus affecting individual adsorption capacity (Patra et al. 2020).

The separation factor ($\alpha$) was calculated to evaluate the selectivity of A-ASBC for the adsorption of cationic azo dyes in a binary system. $K_d$ and $\alpha$ can be expressed as Equations (2) and (3), respectively.

$$K_d = \frac{Q_e}{C_e}$$

$$\alpha = \frac{K_{d1}}{K_{d2}}$$

where $K_{d1}$ is the partition coefficient of dye 1, $K_{d2}$ is that of dye 2, $Q_e$ is the equilibrium adsorption capacity, $C_e$ is the equilibrium concentration, and $\alpha$ is the separation factor. For an adsorbent, $\alpha > 1$ represents the selectivity of the adsorbent for dye 1 (Kyzas et al. 2009).

### Table 7 | Comparison of the adsorption capacity of A-ASBC for methylene blue (MB), rhodamine B (RB), and crystal violet (CV) with other reported adsorbents

| Adsorbent | Maximum adsorption capacity (mg g$^{-1}$) | Reference |
|-----------|----------------------------------------|-----------|
| MB        |                                        |           |
| Framboidal vaterite | 27.39 | Saikia & Das (2014) |
| MnO$_2$ nanocorals | 41.26 | Salam (2015) |
| Fe$_3$O$_4$-CNT | 48.06 | Ai et al. (2011) |
| A-ASBC | 53.62 | This work |
| Pine wood hydrochar | 86.7 | Madduri et al. (2020) |
| ZnS: Cu nanoparticles loaded on activated carbon | 106.9 | Asfaram et al. (2015) |
| Dried Biomass of Freshwater Moss Vesicularia Dubyana | 229 | Pipiška et al. (2018) |
| RB        |                                        |           |
| Ni/C nanoparticles | 5.27 | Kim et al. (2018) |
| Zeolite imidazole frameworks-8 | 9.88 | Tran et al. (2021) |
| A-CNT | 25.66 | Banerjee et al. (2017) |
| Palm shell-based activated carbon | 29.98 | Mohammadi et al. (2010) |
| A-ASBC | 32.33 | This work |
| Activated sugar-based carbon (ASC) | 123.46 | Xiao et al. (2020) |
| CV        |                                        |           |
| Polycatechol modified Fe$_3$O$_4$ nanoparticel | 66.01 | Hua et al. (2018) |
| SnFe$_2$O$_4$@activated carbon magnetic nanocomposi | 158.7 | Rai et al. (2015) |
| Cellulose based adsorben | 218.8 | Zhou et al. (2014) |
| sugarcane bagasse modified with EDTA dianhydride | 327.83 | Gusmão et al. (2013) |
| A-ASBC | 755.73 | This work |
| Steam activated biochar from spent mushroom substrate | 1,057 | Sewu et al. (2019) |
As shown in Table 8, the $\alpha$ value was less than 1, indicating that A-ASBC had no selectivity for MB of MB$^+$CV and RB of RB$^+$MB and RB$^+$CV, while the $\alpha$ value was greater than 1 in other binary systems, thus A-ASBC showed efficient selective adsorption and separation for cationic azo dyes.

The ratio of $Q_{\text{Binary}}$ to $Q_{\text{Single}}$ was calculated to understand the influence of one solute on adsorption of the other solute by A-ASBC ($Q_{\text{Binary}}$ and $Q_{\text{Single}}$ represent the maximum adsorption capacity of dyes in binary and single adsorptive systems, respectively.). The specific analysis basis is as follows: (a) $Q_{\text{Binary}}/Q_{\text{Single}} = 1$, i.e., non-interaction of individual components in binary system; (b) $Q_{\text{Binary}}/Q_{\text{Single}} < 1$, i.e., the antagonistic effect on adsorption of individual components by others in the binary system and (c) $Q_{\text{Binary}}/Q_{\text{Single}} > 1$, i.e., the synergistic effect on adsorption of individual components over the other in binary systems (Manjunath & Kumar 2018). The $Q_{\text{Binary}}/Q_{\text{Single}}$ for all dyes was less than 1 in this study; hence, all MB, RB and CV had antagonistic/competitive

### Table 8 | Selectivity exhibited by A-ASBC in mixtures of methylene blue (MB), rhodamine B (RB), and crystal violet (CV)

| Dye | Mixture | $K_{d1}$ | $K_{d2}$ | $\alpha$ | $Q_{\text{Binary}}/Q_{\text{Single}}$ |
|-----|---------|---------|---------|--------|------------------|
| MB  | MB + RB | 1.30    | 0.73    | 1.78   | 0.82             |
|     | MB + CV | 0.90    | 11.17   | 0.08   | 0.63             |
| RB  | RB + MB | 0.73    | 1.30    | 0.56   | 0.89             |
|     | RB + CV | 0.41    | 13.82   | 0.03   | 0.55             |
| CV  | CV + RB | 13.82   | 0.41    | 33.71  | 0.88             |
|     | CV + MB | 11.17   | 0.90    | 12.41  | 0.84             |
effects over each other’s adsorption on the A-ASBC surface in binary systems. This result was consistent with the study of Patra et al. (2020), that is, the adsorption of individual dye species in multicomponent adsorptive systems was influenced by the presence of other dye species.

**Recyclability studies**

The recyclability of an adsorbent is one of the key factors for practical applications. In this study, the ethanol washing method was used to desorb A-ASBC after the adsorption of MB, RB and CV and to analyze the resorption performance. As shown in Figure 7, the adsorption property of A-ASBC decreased with increasing sorption−desorption cycles, which might be attributed to the formation of inert or noninert compounds on the surface and pores of biochar after many sorption−desorption cycles. The size of these compounds will gradually increase as the cycles increase, and they cannot escape from the pores when the size is larger than the pore size of the adsorbent (Patra et al. 2020). In addition, continuous adsorption-desorption will cause the abrasion of adsorption sites and further destroy the surface morphology of the adsorbent (Choudhary et al. 2020). The damage degree increases with increasing cycle times. After 3 adsorption-desorption cycles, the adsorption capacities of MB, RB, and CV by A-ASBC were 74.30%, 72.43%, and 86.61% of the initial adsorption capacity, respectively, indicating that A-ASBC had good adsorption performance.

**Phytotoxicity assays and analysis**

The phytotoxicity assay was carried out to assess the effectiveness of the adsorbent in eliminating MB, RB, and CV species by analyzing the toxic effects of dye solutions (before and after adsorption) on the germination of *Brassica pekinensis* L. seeds. After germinating the seeds for 72 h, the length of radicles from all samples was measured and reported as depicted in Figure 8 and Fig. S3. The mean root length of the *Brassica pekinensis* L. seeds germinated in deionized water (blank sample plate) was 0.66 cm, and the germination rate was 100%, which gradually reduced for seeds germinated and germination rate in dye samples before adsorptive treatment (control sample plates). Conclusively, it can be reported that all MB, RB, and CV dyes in single and binary forms were toxic for seed germination. However, the indices of the seeds germinated in dye samples after adsorptive treatment with A-ASBC (test sample plates) were better than those in control sample plates. The detailed data are given in Table S6. Thus, it can be reported that seeds germinated in dye samples after adsorption showed an improved growth in radicle length to indicate the effective adsorptive removal of dyes by A-ASBC.

**Adsorption mechanisms**

The BET results indicated that ASBCs and A-ASBC were mesoporous materials. Both high-temperature pyrolysis and activation processes enhanced the specific surface area of the adsorbents (Table 3). In general, the larger the specific surface area, the stronger the adsorption capacity. The adsorption capacity results were as follows:

![Figure 7](http://iwaponline.com/wst/article-pdf/doi/10.2166/wst.2021.222/896150/wst2021222.pdf)
A-ASBC > AS650 > AS350, which indicated that the adsorbent with a large specific surface area can provide more adsorption sites for dye molecules (Choudhary et al. 2020).

Fourier transform infrared spectroscopy was carried out on the surface functional groups of the samples to further understand the adsorption mechanism (Figure 9). Compared with AS650 and A-ASBC, AS350 contained more surface functional groups, which indicated that pyrolysis and activation caused the loss of some functional groups. With increasing pyrolysis temperature and activation, most absorption peaks changed. In comparison to AS350, the peak intensities of AS650 and A-ASBC between 3,417 cm$^{-1}$ and 2,852 cm$^{-1}$ sharply dropped or even disappeared, which might be caused by the cleavage of hydrogen bonds in hydroxyl groups and the dehydration and decomposition of aliphatic compounds (Khanday et al. 2016). The weakening of the stretching vibration peak at 1,618 cm$^{-1}$ and the bending vibration peak at 780 cm$^{-1}$ may be due to the activated carbon atoms condensing into aromatic structures at high temperatures (Liu et al. 2014; Silverstein et al. 2014). The increased peak intensities at 1,438 cm$^{-1}$ and 869 cm$^{-1}$ suggested that high temperature and base activation were beneficial to the formation of carbonate minerals (Choi & Kan 2018), which is consistent with the XRD results that the high intensity peaks of carbonate minerals were found in AS650 and A-ASBC (Fig. S4). After adsorption of MB and RB on A-ASBC, the absorption peaks at 3,417 cm$^{-1}$ (–OH and –NH) were weakened, indicating that there were hydrogen bond forces during the adsorption process (Du et al. 2014). However,
little change was observed after adsorption of CV, showing that no hydrogen bonding was involved in dye adsorption. After adsorption of MB, RB, and CV on A-ASBC, the absorption peak at 1,618 cm\(^{-1}\) (C=C) weakened or disappeared. This result suggested that the adsorption process underwent π-π stacking between aromatic π electrons on biochar and π electrons on the benzene ring structure in the dye (Wu et al. 2014). XRD results showed that both ASBCs and A-ASBC contain a certain amount of calcium oxalate crystals (CaC\(_2\)O\(_4\)) (Fig. S4). There was a planar eight-electron π system in C\(_2\)O\(_4^{2-}\), which might be π-π stacking with the structure of the dye benzene ring. In addition, through Boehm functional group titration, it can be seen that biochar contains a large number of oxygen-containing functional groups, such as carboxyl groups, phenols and other acidic groups, and some basic groups, which have a strong negative charge and can produce electrostatic gravitation with positively charged chromogenic groups after ionization of MB, RB and CV. The positively charged chromogenic group produces electrostatic attraction (Lai et al. 2018). Meanwhile, the absorption peaks at 1,438 cm\(^{-1}\) and 869 cm\(^{-1}\) also decreased, which indicated that the carbonate minerals in biochar participated in the dye adsorption process. Many studies have found that CO\(_3^{2-}\) in carbonate minerals can adsorb cationic dyes through electrostatic interactions (Chowdhury & Saha 2010; Zhang et al. 2017).

In summary, the adsorption process of MB, RB, and CV by ASBCs and A-ASBC mainly includes pore filling, hydrogen bonding, π-π stacking interactions and electrostatic interactions. The specific adsorption mechanism is shown in Figure 10.

**CONCLUSIONS**

In conclusion, biochar was prepared using a spent *Auricularia auricula* substrate, and the pyrolysis temperature had a great effect on the surface physicochemical properties of biochar. The adsorption capacity of biochar prepared at high temperature to dyes was higher than that of biochar prepared at low temperature. The biochar was further activated with NaOH impregnation and resulted in higher BET surface area (89.393 m\(^2\)·g\(^{-1}\)) and higher amount of oxygen-containing functional groups. The adsorption capacity of activated biochar for dyes (53.62, 32.33 and 735.73 mg·g\(^{-1}\) for MB, RB and CV) was significantly increased compared with that of AS650 (33.04, 20.13 and 354.07 mg·g\(^{-1}\) for MB, RB and CV). In particular, the adsorption capacity of MB and CV...
were 1.62 times and 2.08 times higher than AS650. The pseudo-second-order kinetic model and Freundlich model better fit the experimental data for all MB, RB, and CV. The adsorption mechanism of cationic azo dyes on A-ASBC was observed to be pore filling, hydrogen bonding, π-π stacking interactions, and electrostatic interactions. The A-ASBC maintained >70% adsorption of initial capacity even after three adsorption-desorption consecutive cycles, which showed A-ASBC has remarkable reusability, indicating that it might be a potential adsorbent for printing and dyeing wastewater treatment.

**AUTHOR CONTRIBUTIONS**

Long Su: Conceptualization, Methodology, Writing-original draft preparation. Haibo Zhang, Kokyo OH, Na Liu, and Yuan Luo: Data curation, Visualization. Hongyan Cheng: Supervision, Writing – review & editing. Guosheng Zhang and Xiaofang He: Investigation, Data curation.

**NOTES**

The authors declare that they have no known conflict of interest or personal relationships that could have appeared to influence the work reported in this paper.

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**DATA AVAILABILITY STATEMENT**

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

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