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# Preparing Shrimp Shell-Derived Chitosan with Rice Husk-Derived Biochar for Efficient Safranin O Removal from Aqueous Solution

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#### ABSTRACT

In this study, the shrimp shell-derived chitosan was coated onto rice husk-derived biochar to form chitosan/biochar bio-composite beads. The physicochemical properties of biochar (BC) and chitosan/biochar beads (CS@BC) were characterized by BET, SEM-EDX, FTIR, and pH<sub>pze</sub> analyses, which were then tested for their capacity to remove Safranin O (SO) from water. In kinetics, the pseudo-second-order model was found to well represent experimental data, indicating the adsorption was mainly a chemical process. The intra-particle diffusion model was not the sole rate-limiting step, because the results did not pass through the origin. In isotherms, both the Langmuir and Freundlich models described well the equilibrium adsorption data. The CS@BC adsorbent showed adsorption capacity at 77.94 mg/g for SO, which is higher than BC adsorbent with 62.25 mg/g (experimental conditions: pH ~ 7.0, dosage = 0.2 g, contact time = 240 min, and temperature = 298 K). The findings revealed that the biochar-loaded chitosan can improve the adsorption capacity of SO. It is predicted that the enhancement in the functional groups (i.e., -NH<sub>2</sub> and -OH groups) of CS@BC could contribute to the electrostatic interactions and the complexation between SO and CS@BC, thereby enhancing the Safranin O adsorption from water.

Keywords: adsorption, biochar, chitosan, rice husk, Safranin O, shrimp shell.

# **INTRODUCTION**

Dyes are used to impart color to materials, possessing complex organic compounds and aromatic structure. The dyes are discharged into natural water bodies mainly from several industries, such as leather industry, rubber industry, textile industry, cosmetic industry, food industry and paper industry. The dye-contaminated industrial effluents contain huge amounts of inorganic and organic compounds, which are highly toxic to the environment and humans, thus requiring immediate attention. Some of the dyes, such as a basic dye Safranin O, persist as aquatic pollutants, inhibit photosynthesis activity, cause depletion of dissolved oxygen and thereby pose a threat to aquatic ecosystems. They may be toxic, mutagenic, carcinogenic, even can contribute to biomagnification that poses a genuine threat to humankind (Lellis et al. 2019). Safranin O has been extensively used in paper technology as counterstain to cotton blue stain for fungal hyphae, and as a general botanical stain.

Various methods and processes are used for removing dyes from water, for instance, electrochemical oxidation (Wang et al. 2020), biological treatment (Paz et al. 2017), coagulation–flocculation-based (Gadekar et al. 2020), and adsorption methods (Dutta et al. 2021). A growing interest in adsorption processes for vigorously removing organic dyes has been observed recently, mainly due to their versatility, effectiveness, easy operating and low cost (Alguacil et al. 2021). Different adsorbents generally used for dye removal are activated carbon (Kheddo et al. 2020), zeolite (Hammood et al. 2021), biochar (Sutar et al. 2022), clay (Kausar et al. 2018), and metal-organic framework (Uddin et al. 2021). Various studies have proven that biochar has a great potential for organic dye removal in aquatic systems. Nevertheless, biochar has been found to be an inconsistent adsorbent because of its heterogeneous nature, high pH and negatively charged surface [12]. To address these restraints, new trends in activation and modification of biochar have been developed in recent years. Previous studies revealed that when biochar is engineered with foreign materials, its pore structure, its desirable functional groups, its recalcitrance potential and its adsorption efficiency are generally improved (Sajjadi el al. 2019; Wang L et al. 2020; Srivatsav et al. 2020; Udawattaet al. 2022).

Chitosan is a biodegradable natural polymer with biocompatibility, nontoxicity, and excellent adsorption properties (Kurita, 2006). Chitosan is obtained from chitin by deacetylation in the presence of alkali at high temperature. Basically, chitosan comprises two different structural units, N-acetyl glucosamine unit and D-glucosamine unit. Each C2 position on D-glucosamine unit contains a free amino group, and depending on the pH, this amino group can exist in free  $(-NH_2)$ form and protonated (-NH<sub>3</sub><sup>+</sup>) form (Chitosan- $NH_2 + H_2O^+ \leftrightarrow Chitosan-NH_2^+ + H_2O)$ . The presence of the protonated  $(-NH_2^+)$  form can make chitosan to be a potential ligand capable of binding heavy metal ions (Amalraj et al. 2020) or a potential adsorbent of dye anions in water (Dotto et al. 2012). Therefore, chitosan has been used extensively for metal chelation (Perumal et al. 2019) and dye removal (Le el al. 2018; Crini et al. 2019).

Recently, it was found that when chitosan is combined with carbon-based materials as biochar, the modified materials obtained the benefits provided by the high chemical affinity of chitosan, together with the advantages provided by the porous network of biochar (Zhou et al. 2013). In addition, chitosan can be an organic glue for the pollutants onto biochar; therefore, chitosan combined with biochar can promote the adsorption of pollutants (Lyu et al. 2022). Furthermore, the chitosan-modified biochar material composites can exhibit higher chemical stability and mechanical strength compared to the pristine biochar or raw chitosan (Ahmed et al. 2020).

Preparation, modifications and adsorption applications of chitosan-modified biochar to water pollutants has been reviewed in several papers (Ahmed et al. 2020; Pang et al. 2021; Gao et al. 2022). However, most previous studies mainly focus on the removal of heavy metal ions in water (Dewage et al. 2018; Zhang et al. 2019; Song et al. 2021), and there are also limited studies on the adsorption of ciprofloxacin (Afzal et al. 2018), dissolved organic matter (Shi et al. 2020), ofloxacin (Zhu et al. 2018), phloridzin (Ma et al. 2021), Malachite Green and Rhodamine B dyes (Vigneshwaran et al. 2021). As far as the authors of this paper are aware, there has been no research done on adsorption of Safranin O dye from their aqueous solutions by using chitosanmodified biochar hydrogel beads. Hence, this work firstly reported the production of chitosan from shrimp shells, the pyrolysis of biochar from rice husk, the synthesis of chitosan-modified biochar hydrogel beads. Thereafter, this work investigated the physicochemical characteristics of synthesized adsorbents by using different techniques and measurements, including SEM, EDX, FTIR techniques, N<sub>2</sub> adsorption (77K) and pH<sub>nzc</sub> measurements. Finally, this work explored the adsorption capacities toward Safranin O from aqueous solutions using batch experiments by varying the pH solution, the mass of adsorbent, the contact time and the initial SO concentration, the mechanism was also explored by using various isotherm and kinetic models.

# MATERIALS AND METHODS

#### Chitosan preparation

In this study, *Penaeus monodon* shrimp shell waste was used as the raw material for chitosan extraction. The production of chitosan was outlined in Figure 1, involving the following basic steps: (i) pretreatment by washing and grinding, (ii) deproteinization by 5% NaOH, (iii) demineralization by 0.25M HCl, (iv) decoloration by 0.315% NaOH, and (v) deacetylation by 50% NaOH (Radwan et al. 2012). The resulting samples from this step are identified as chitosan (CS).

#### **Biochar preparation**

The process of making biochar was followed the procedure adopted in authors' previous paper (Phuong and Loc. 2022), as outlined in Figure 2. The resulting samples from this step are identified as biochar (BC).



Figure 3. Preparation of chitosan-modified biochar

#### Chitosan-modified biochar preparation

Chitosan-modified biochar was prepared following the protocol summarized in Dewage et al. (2018) and displayed in Figure 3. The resulting chitosan-modified biochar samples are identified as CS@BC.

## Characterization of adsorbents

The micrographs and elemental compositions of the BC also CS@BC were evaluated by scanning electron microscopy (SEM), energy dispersive X-ray (EDX) spectroscopy (SEM-EDX Hitachi S4800, Japan), while their functional groups were analyzed using a Fourier transform infrared spectroscopy (FTIR, FTIR-PerkinElmer Spectrum 10.5.2). The textural characterization of BC and CS@BC was obtained from the nitrogen adsorption-desorption isotherms determined at 77K in a Nova Station A (Quantachrome Instruments version 11.0, USA).

#### **Batch adsorption experiments**

The batch adsorption experiments were used to evaluate the effect of solution pH, adsorbent dose, initial SO concentration and adsorption time. The adsorption experiment was performed by using #15 mL conical centrifuge tubes, in which a fixed amount of BC or CS@BC was added into 10 mL SO solution. The mixtures were then agitated in a rotary shaker (HS 250 Basic, IKA Labortechnik) at an agitation speed of 120 rpm and under room conditions ( $25 \pm 2$  °C) for a fixed time. After filtering with Whatman No. 6 filter paper, the residual SO in the remaining solution was analysed by using an UV-Vis spectroscopy (Shimadzu UV-1900, Japan; at an optimal wavelength of 530 nm) and applying Eq. 1:

$$Q_e = \frac{C_i - C_e}{m} V \tag{1}$$

where:  $Q_e$  (mg/g) – refers to adsorption at equilibrium;

 $C_i$  (mg/L) and  $C_e$  (mg/L) – refer the SO concentrations at initial and equilibrium, respectively;

m(g) – refers the mass of adsorbent;

V(mL) – refers the volume of the solution.

All the experiments in this study were conducted in triplicate (n = 3), and data were expressed as the mean  $\pm$  standard deviation.

## **RESULTS AND DISCUSSION**

# Physicochemical characteristics of adsorbent materials

#### **BET** analyses

The evaluation of BET specific surface area provides a good indication of the extent of porosity and surface adsorption sites. In this study, CS@BC had slightly lower specific surface area (107.97  $m^2/g$ ) and pore volume  $(0.134 \text{ cm}^3/\text{g})$  than that of BC (115.59 m<sup>2</sup>/g for specific surface area; 0.121 cm<sup>3</sup>/g for pore volume), while the average particle size of CS(a)BC (2.34 nm) is higher than that of BC (2.26 nm)nm) (Table 1). These findings are consistent with the results of previous studies (Zhou et al. 2013; Dewage et al. 2018; Vigneshwaran et al. 2021). The smaller specific surface area could be due to the blockage of partial pores by the incorporation of chitosan in biochar matrix, or the alterations in the chemical compositions of the biochar surface so that N<sub>2</sub> has relatively little affinity towards surface adsorption (Zhou et al. 2013).

# pH<sub>nrc</sub> analyses

The "drift method" (Karam et al. 2021) was used for determining the pH value of BC and CS@BC at the point of zero charge  $(pH_{pzc})$ . From Table 1, the  $pH_{pzc}$  of CS@BC ( $pH_{pzc}$ ) = 7.26) was higher than that of BC ( $pH_{pzc} = 6.48$ ). The slight increase in pH<sub>pzc</sub> of CS@BC could be due to the addition of -NH, and -OH groups after chitosan were added on the precursor biochar surface (Dewage et al. 2018). Below these pH<sub>pre</sub>, the CS@BC and BC surface charges are positive, while above  $pH_{pzc}$  their surfaces are negative. Therefore, the chitosan loaded on the biochar derived from rice husk increased the positive charge, and these findings were similar to the chitosan loaded on the biochar derived from bamboo (Huang et al. 2022).

**Table 1.** The surface area, pore volume, particle size and  $pH_{nze}$  of CS@BC and BC

Parameter	CS@BC	BC		
Specific surface area (m²/g)	107.97	115.59		
Pore volume (cm <sup>3</sup> /g)	0.134	0.121		
Median particle size (nm)	2.34	2.26		
pH <sub>pzc</sub>	7.26	6.48		

# SEM-EDX analyses

The SEM micrographs revealed that the surface morphology of CS@BC was obviously different from the surface morphology of BC (Fig. 4). The SEM picture of BC (Fig. 4A) was the same as in other rice husk-derived biochar SEM images (Liu et al. 2017; Xiang et al. 2021), which possessed cylindrical, layered and porous structure forms. Compared with BC, the surface of CS@BC (Fig. 4B) had an irregular surface, which might be due to the incorporation of chitosan in the biochar surface. Therefore, these SEM results showed that the biochar surface could be covered by the chitosan, and even the biochar pores could be penetrated by the chitosan, thereafter the porosity structure of biochar surface was altered, similar to other observations (Ahmed et al. 2016; Huang et al. 2022).

The EDX spectra mapping of BC material shows that the BC composed of C (61%), O (22%), Si (14.6%), K (0.88%), Ca (0.78%), and Al (0.75%) (Fig. 5A), which are considered as common elements existing in the biochar derived from rice husk biomass (Liu et al. 2017). After coating of chitosan, the percentages of these

elements were slightly changed in the EDX spectra mapping of CS@BC material (Fig. 5B). Importantly, a new peak of N (accounted for nearly 3% atomic weight) appeared in the EDX spectra of CS@BC, together with an increase in the percentage of O (from 22% to 26% atomic weight), indicating the presence of  $-NH_2$  and -OH groups into CS@BC composites. The N content of 2.5% after tapioca peel biochar modified with chitosan was also reported (Vigneshwaran et al. 2021).

# FTIR analyses

Figure 6 displayed the spectrum of CS@BC in comparison with the spectrum of BC, recorded in the range of 4000 – 400 cm<sup>-1</sup>. The FTIR spectrum of BC in this study shows several groups. For example, a strong peak around 3430 cm<sup>-1</sup> represents O–H stretching vibrations. The absorption peak at around 2959 and 2857 cm<sup>-1</sup> is attributed to the asymmetric and symmetric stretching vibrations of C–H of aliphatic CH<sub>3</sub>. The weak bands appearing around 1758 cm<sup>-1</sup> and 1492 cm<sup>-1</sup> are usually assigned to the carboxyl group (–CO–) and C=C group, respectively. Furthermore, a strong absorption band at 1031 cm<sup>-1</sup> is usually presented of



Figure 4. The SEM images of BC (A) and CS@BC (B)



Figure 5. The EDX analysis of BC (A) and CS@BC (B)

C-O-C stretching vibrations of ether. Finally, the bands at around 798 cm<sup>-1</sup> and 488 cm<sup>-1</sup> are associated with Si-O stretching vibration and SiO, tetrahedra, respectively (Jindo et al. 2014; Palniandy et al. 2019; Zhang et al. 2019). In comparison, the FTIR spectrum of CS@BC also possesses most of these functional groups; however, some of these characteristic peaks shifted compared with the BC spectrum, for example, the absorption peaks at around 3430, 2857, 1492, 1031, 798 and 489 cm<sup>-1</sup> in the FTIR spectrum of BC were shifted to lower or higher frequencies at around 3411, 2868, 1396, 1075, 819 and 506 cm<sup>-1</sup> in the FTIR spectrum of CS@BC, respectively. It should be emphasized that several new functional groups that are usually found in the FTIR spectrum of chitosan also appeared the FTIR spectrum of CS@BC, including free N-H stretching vibrations (appeared in the bands at  $3856 \text{ cm}^{-1}$ ), C=O stretching vibration of amide I (appeared in

the bands at 1651 cm<sup>-1</sup>), N–H bending vibration of amide II (appeared in the bands at 1531 cm<sup>-1</sup>), C–N stretching vibrations of amide III (appeared in the bands at 1396 cm<sup>-1</sup>) (Liu et al. 2017; Mehmood et al. 2020). Therefore, these absorption bands confirmed the presence of amide I, amide II and amide III in the FTIR spectrum of CS@BC.

In brief, the results obtained from the analyses of EDX and FITR can support the conclusion that several functional groups, such as amino and hydroxyl groups, were added during the incorporation of chitosan hydrogels into biochar.

#### **Batch sorption studies**

#### Effect of pH solution

It is obvious from Figure 7 that the adsorption capacities for SO depended highly on pH solution,



Figure 6. FTIR analysis of biochar (BC) and chitosan-biochar (CS@BC)



Figure 7. Effect of pH on SO sorption onto CS@BC and BC

where the SO adsorption capacity increased along with solution pH. Specifically, by increasing the pH from 2 to 10, the amount of SO adsorbed increased from 5.41 mg/g to 9.63 mg/g for CS@BC and increased from 4.77 mg/g to 9.65 mg/g for BC.

To explain, increasing the pH value, that beyond the pH<sub>pzc</sub> value of 7.26 for CS@BC and 6.48 for BC, basically leads to the increasing degree of dissociation of the hydroxyl groups, thereby making the negative charge on BC and CS@BC even more negative, as shown in the Eq. 2 and Eq. 3, respectively (Sahu et al. 2015).

$$-BC-OH + OH^{-} \leftrightarrows -BC-O^{-} + H_2O \qquad (2)$$

$$-CS@BC-OH+OH^{-} \leftrightarrows -CS@BC-O^{-}+H_{2}O(3)$$

In addition, since the dissociation constant  $(pK_a)$  of SO is 11, thus, when the pH solution is less than the pK<sub>a</sub> value, SO is protonated and exists in SO<sup>+</sup> form. Therefore, there was an increase in electrostatic attraction between the negative charges (i.e.,  $-BC-O^-$  and  $-CS@BC-O^-$ ) and the SO<sup>+</sup> molecules, thereby increasing the adsorption capacity of SO dye in alkaline solutions, as shown in Eq. 4 and Eq. 5.

$$-BC-O^{-} + SO^{+} \leftrightarrows -BC-O^{-} \cdots SO^{+} \qquad (4)$$

$$-CS@BC-O^{-}+SO^{+} \leftrightarrows -CS-BC-O^{-} \cdots SO^{+} (5)$$

Briefly, an increase in pH can lead to an increase in electrostatic attraction between the BC or CS@BC surface and the SO<sup>+</sup> molecules, thereby increasing the adsorption capacity of SO dye.

#### Adsorption kinetic mechanism

The experimental data was analyzed by the pseudo-first-order (PFO) and pseudo-second-order

(PSO) kinetics; their nonlinear models described by Eq. 6 and Eq. 7, respectively:

$$Q_t = Q_e (1 - exp^{-k_1 t})$$
(6)

$$\frac{dQ_t}{dt} = k_2 \left(Q_e - Q_t\right)^2 \tag{7}$$

where:  $Q_t(mg/g)$  and  $Q_e(mg/g)$  – refer to adsorption capacity at given time t and at equilibrium;  $k_1$  (1/min) and  $k_2$  (g/mg·min) – refer to rate constant of PFO adsorption and PSO adsorption, respectively.

The experimental data of BC and CS@BC fitted with PFO and PSO kinetic models are shown in Figure 8, while their kinetic parameters for SO adsorption are summarized in Table 2.

According to Table 2, it was observed that the R<sup>2</sup> values obtained by the PSO kinetic were greater than R<sup>2</sup> values from the PFO kinetic in both BC and CS(a)BC; in particular, the R<sup>2</sup> value of PFO kinetic equation was 0.68 for CS@BC and 0.93 for BC, while that of PSO kinetic was 0.91 for CS@BC and 0.98 for BC. This indicated that the adsorption process on either BC or CS@BC followed PSO. The PSO adsorption rate constant  $k_{2}$  was 0.054 for CS@BC and 0.010 for BC, in addition to the equilibrium adsorption capacity values  $(Q_{e cal})$  calculated by PSO kinetics of both CS@BC and BC showed closer to that obtained by experiments  $(Q_{eexp})$  than PFO kinetics. These may imply that the adsorption of SO on the two adsorbents is mainly a chemisorption-based mechanism (Vigneshwaran et al. 2021).

In the case of BC adsorbent, the chemisorption mechanism emphasizes the electrostatic interactions between the negatively charged groups, including the carboxyl –COO<sup>-</sup> and hydroxyl –OH<sup>-</sup> groups,



Figure 8. Fitting of kinetic models for SO adsorption on BC and CS@BC

Adsorbent	Q <sub>e,exp</sub> (mg/g)	Kinetic model												
		PFO						PSO						
		Q <sub>e,(</sub> (mg/	<sup>cal</sup> (g)	<i>k</i> 1 (1/min	)		R <sup>2</sup> Q <sub>e,cal</sub> (mg/g		) (9	k <sub>2</sub> (g/mg.min)		R <sup>2</sup>		
CS@BC	12.73	12.1	10	0.355	0.355		.683 12		12.40		0.054		0.910	
BC	11.44	10.9	93	0.073		(	0.935		11.22	0.010		0.979		
	IPD													
	Stage I					Stage II			Stage III					
	C₁ (mg/g	) (mg/g	g.min)	R <sup>2</sup>	(mį	C <sub>2</sub> k <sub>ic</sub> (mg/g) (mg/g		<sup>d2</sup> J.min)	R <sup>2</sup>	2 C3 (mg/		k <sub>id3</sub> (mg/g.min)		R <sup>2</sup>
CS@BC	1.864	4.	35	0.998	0.1	73	'3 10.72		0.943	0.02	22	12.25		0.992
BC	1.66		'12	0.997	0.6	0.673		0.846		0.05	057 10.2		22	0.991
	Isotherm model													
			La	ngmuir				Freundlich						
	<b>Q</b> <sub>m</sub> (1	mg/g)	k,	(L/mg)	R <sup>2</sup>				1/n	(mg/kg	<i>k<sub>F</sub></i> (mg/kg)/(mg/L) <sup>1/n</sup>		R <sup>2</sup>	
CS@BC	77	.94	(	0.003		0.992			1.324	C	0.576		0.986	
BC	62	0.004			0.995			1.370		0.587		0.984		

Table 2. Kinetic and isotherm parameters for the adsorption of SO on CS@BC and BC at room temperature

and the positively charged  $N^+$  atoms of the SO molecules (Fig. 9A). In the case of CS@BC adsorbent, the chemisorption of SO on the CS@BC not only emphasizes the electrostatic interactions (similar to BC material), but also the surface complexation between the SO dye and CS@BC in water (Fig. 9B).

To study the diffusion process of SO adsorption onto BC and CS@BC, the intra-particle diffusion IPD (Weber-Morris) model was applied, as shown in Eq. (8):

$$Q_t = k_{id} t^{\frac{1}{2}} + C \tag{8}$$

where:  $Q_t (mg/g)$  – refers to adsorption capacity at given t time;  $k_{id} (mg/g \cdot min)$  – refers to the diffusion rates; C – refers to the intercept.

The IPD plots for SO adsorption capacity were shown in Figure 10, while IPD parameters were also provided in Table 2. Figure 10 revealed that, over the whole experiment period, the adsorption process for SO onto BC and CS@BC was not a straight line and was separated into three stages: (i) boundary layer diffusion stage; (ii) gradual adsorption stage, and (iii) equilibrium adsorption stage. The R<sup>2</sup> values from these stages were found between 0.85 and 0.99, indicating IPD mechanism also plays a crucial role in the adsorption process. However, Table 2 shows the calculated  $C_{j}$ ,  $C_{2}$ ,  $C_{3}$  values also were all non-zero, demonstrating that the IPD was not the sole rate-limiting step. In addition, Table 2 also shows that the rate constant of stage I ( $k_{id1}$ ) was higher than the rate constant of stage II ( $k_{id2}$ ) and stage III ( $k_{id3}$ ), demonstrating the boundary layer diffusion also involved in the process.

Therefore, the adsorption process for SO onto either BC or CS@BC was a complex process, involving chemical interaction, external and intraparticle diffusion.



Figure 9. The chemisorption mechanism for the adsorption of SO by BC (A) and CS@BC (B)



Figure 10. IPD plots for SO adsorption on BC and CS@BC

#### Adsorption isotherms

To predict the adsorption behavior of BC and CS@BC for the SO adsorption process, both Langmuir and Freundlich models were employed to fit the isotherm data. The nonlinear forms of the Langmuir and Freundlich models are shown in Eq. 9 and Eq. 10, respectively:

$$Q_e = \frac{Q_m k_L C_e}{1 + k_L C_e} \tag{9}$$

$$Q_e = k_F C_e^{\frac{1}{n}} \tag{10}$$

where:  $Q_e$  (mg/g) – refers to the equilibrium capacity;

 $Q_m (mg/g)$  – refers to maximum capacity;  $C_e (mg/L)$  – refers to the equilibrium concentration of adsorbate;

 $k_L$  (L/mg) and  $k_F$  ((mg/kg)/(mg/L)<sup>1/n</sup>) – refer to the Langmuir and Freundlich adsorption constant, respectively;

*n*(unitless) – refers to adsorption intensity.

The fitting of the Langmuir and Freundlich models of the experimental data is displayed in Figure 11, and the isotherm parameters obtained are presented in Table 2. From the fitted results, two isotherm models provided good fitting with the experimental data of CS@BC and BC, with the determination coefficient R<sup>2</sup> of these models having very high values, ranging from 0.98 to 0.99. The fitting of the Langmuir model indicated a monolayer adsorption process on a homogenous surface, while the fitting of the Freundlich model indicated multilayer adsorption process on a heterogeneous surface. Therefore, both monolayer adsorption and multilayer adsorption could occur in the process.

Under the optimum adsorption conditions  $(m_{adsorbent} = 0.2g, t = 240 \text{ min}, \text{pH} \sim 7, T = 298\text{K})$ , the maximum equilibrium adsorption capacity (obtained from the Langmuir model, as summarized in Table 2) of CS@BC was 77.94 mg SO/g and BC was 62.25 mg SO/g, demonstrating



Figure 11. Fitting of isotherm models for SO onto BC and CS@BC

that the combination between chitosan and biochar can help to enhance the adsorption of Safranin O from water, in particular, the adsorption capacity of CS@BC was almost 1.3 times more SO sorption than BC. Several studies also reported similar enhanced findings. For example, CS@BC exhibited nearly twice more phloridzin sorption than the BC produced from apple branches at 300 °C (Ma et al. 2021); nearly 2.5 times more Cd(II) sorption than the BC produced from bamboo at 900 °C (Huang et al. 2022), and nearly 3 times more Pb(II) sorption than the BC produced from pine wood at 425 °C (Dewage et al. 2018).

## CONCLUSIONS

This study investigated the physicochemical characteristics of BC and CS@BC adsorbent materials and explored their potential applications in Safranin O removal from water. The results of batch sorption experiments suggest that chitosan hydrogels coated onto biochar matrix can help to improve the adsorption capacities toward Safranin O of biochar produced from rice husk by almost 1.3 times ( $Q_{m, CS@BC} = 77.94$  mg SO/g,  $Q_{m, BC} = 62.25$  mg SO/g). It is predicted that this enhancement could be more likely because of the increasing the number of -NH<sub>2</sub> and -OH groups on the surface of biochar after chitosan modification. Both Freundlich and Langmuir isotherms corresponded well with the experimental data, with  $R^2$  being more than 0.98. The kinetic data for SO adsorption was well-fitted to pseudo-secondorder model as well as intra-particle diffusion model, implying that the chemical mechanism and intra-particle diffusion mechanism could be the controlling mechanisms for SO adsorption process. Briefly, a simple and inexpensive chitosan-modified biochar composite was successfully developed and can be applied as a bio-adsorbent for the removal of Safranin O from water.

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