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Adsorption Isotherm and Kinetic Studies of Chitosan–Coffee Husk Carbon Composite Beads for the Removal of Congo Red and Methylene Blue

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Abstract. Investigation of adsorption of Congo Red (CR) and Methylene Blue (MB) dyes by coffee skin carbon chitosan composite beads (CCCB) has been carried out. The adsorbent was synthesized with varying mass ratio of chitosan and carbon. The composite was synthesized with PVA as a crosslinker agent. This research was carried out in several stages for adsorbent preparation, the effect of contact time (adsorption kinetics), and isotherm adsorption. Adsorption studies were carried out using a batch system. The effect of adsorption contact time was carried out at a contact time of 15 - 150 minutes, adsorbent dose of 10 g/L with dyes volume of 10 mL and initial dyes concentration of 25 mg/L. The optimum adsorption time of MB was obtained at 90 minutes with the adsorption percentage of 91.50% with 1:1 carbon chitosan composite beads. The optimum adsorption time of CR was obtained at 150 minutes with the adsorption percentage of 96.01% with chitosan beads. The kinetics result is in line with pseudo second order rate equation for all application. The isotherm studies almost follow the Langmuir isotherm models.

Keywords : Beads composites; congo red; isotherm; kinetics; methylene blue.

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Introduction

The textile industry in Indonesia has been rapidly developing in response to the increasing human need for clothing. The ever-changing fashion trends have driven the textile industry to increase its production capacity, thereby resulting in greater waste emissions. Liquid waste is the main type produced by the textile industry, particularly from the dyeing process, and can pose serious environmental problems if not properly treated [1].

Various dye wastewater treatment techniques have been developed, including biological treatment, chemical adsorption, coagulation, membrane filtration, and photodegradation. One of the more popular methods is adsorption, which is a mass transfer process that occurs on the surface of the adsorbent's pores and takes place in two phases: gas-solid or liquid-solid. This method is favored due to its efficiency, simple procedure, low cost, and low energy consumption [2]. Various materials can be used as adsorbents, including natural-based materials and seafood processing waste such as chitin and chitosan.

Chitosan is a derivative of chitin, commonly obtained from the exoskeletons of arthropods such as crab shells, shrimp skins, and lobster shells. Bengkulu is a province with a long coastline and abundant marine resources. Waste from seafood processing, such as crab shells, shrimp skins, and lobster shells, has the potential to be processed into chitosan, which can then be used as an adsorbent. Chitosan is a biomaterial with polycationic properties that can adsorb heavy metals as well as textile dyes from wastewater [3]. Several studies have examined the use of chitosan for dye adsorption, such as for Congo Red (CR) [1], Direct Blue (DB) [4], Remazol Black (RB) [5], Methylene Blue (MB), and Reactive Brilliant Red (RBR) [6]. However, the use of chitosan as an adsorbent has limitations because it is easily soluble in acidic environments. Moreover, as a polycationic biomaterial, chitosan tends to more easily adsorb negatively charged dyes.

To enhance its surface area and stability, chitosan can be combined with activated carbon, which is a porous material that increases the surface area of the adsorbent and improves its adsorption capacity. The addition of fillers in composites can also improve the mechanical properties of the composite matrix. Charcoal can be produced through the pyrolysis of lignin-, cellulose-, or lignocellulose-containing materials [7]. As a tropical country, Indonesia is one of the world's major coffee producers. According to the 2023 Coffee Statistics (Indonesian Central Bureau of Statistics, 2023), Indonesia's coffee production reached 758.73 thousand tons, with Bengkulu ranking as the fifth-largest coffee-producing province, contributing 7% of the national production. With such a high coffee production volume, much coffee husk waste is inevitably generated. Due to a lack of public knowledge about coffee husk processing, it is often used merely as animal feed or discarded [8]. The high cellulose and lignin content in coffee husks makes them suitable for the production of activated charcoal.

The chitosan–activated carbon composite made from Coffea canephora coffee husks is synthesized in bead form to facilitate easier application as a dye wastewater adsorbent, allowing for easy separation of the adsorbent from the filtrate. However, there has been no research on the synthesis of chitosan–activated carbon beads made from coffee husks or their application as adsorbents for both anionic (Congo Red) and cationic (Methylene Blue) dyes. Therefore, this study presents an engaging and valuable research topic.

Experimental

The equipment used in this study included a hot plate stirrer, analytical balance, mortar and pestle, a set of pyrolysis tools, oven, 100-mesh sieve, Buchner funnel, and other glassware. The analytical instruments included a Fourier-transform infrared spectrophotometer (Bruker, Germany), a UV-Visible spectrophotometer (Agilent Technology), and a scanning electron microscope (Phenom ProX G6 Desktop SEM).

The materials used in this study included coffee skin waste, NaOH (Merck), HCl (Merck), polyvinyl alcohol (Sigma) with molecular weight = 13,000–23,000, chitosan with a degree of deacetylation >75% (Himedia), acetic acid (Merck), Congo Red (Merck), Methylene Blue (Merck), distilled water, and Whatman No. 42 filter paper.

Preparation of HCl-Activated Carbon. Charcoal was prepared via pyrolysis at 300°C for 6 hours. The resulting charcoal was then activated using 0.1

M HCl for 24 hours, followed by separation and rinsing with distilled water until a neutral pH was reached. The activated carbon was dried at 105°C until constant weight.

Synthesis of Coffee Skin Carbon Chitosan Composite Beads (CCCB) and Chitosan Beads (CB). The synthesis of CCCB followed a previously established method [9] with slight modifications. First, 0.5 g of PVA powder was dissolved in 25 mL of distilled water and stirred with a magnetic stirrer at 70°C. Separately, 0.2 g of activated carbon was dispersed in 25 mL of 3% acetic acid, and then 0.8 g of chitosan was added and stirred until a gel-like mixture was formed. The two mixtures were then combined and stirred continuously for 10 minutes at 70°C.

The resulting mixture was dropped using a 1 mL syringe into a beaker containing 2.5 M NaOH solution. The formed beads were stirred for 1 hour, then filtered and rinsed with distilled water until neutral pH. The neutralized adsorbent was dried in an oven at 60°C until constant weight [10]. The same procedure was repeated with chitosan-to-carbon ratios of 1:0 (CB) and CCCB with ratios of 4:1, 2:1, and 1:2.

Adsorbent Characterization. Functional group analysis of activated carbon, chitosan, chitosan beads, and coffee skin carbon chitosan composite beads was carried out using FTIR (Fourier Transform Infrared Spectroscopy). Surface morphology analysis using SEM was conducted on CB and CCCB at magnifications of 3000x and 10,000x.

Adsorption Study. The adsorption study included isotherm and kinetic analyses. Kinetic studies were conducted using 0.1 g of adsorbent in Methylene Blue and Congo Red dye solutions (25 mg/L) with contact times of 15, 30, 45, 60, 90, 120, and 150 minutes. Meanwhile, isotherm studies were conducted at optimal contact times with varying concentrations of 10, 25, 50, 100, 150, and 200 mg/L. Adsorption capacity was calculated using the following equation [11].

$$qe = \frac{(Co - Ce)V}{m} \quad (1)$$

Where qe = adsorption capacity (mg/g); Co = initial concentration of solution (mg/L); Ce = final concentration of solution (mg/L); m = adsorbent mass (g); V = volume (L).

Adsorption Kinetics. Adsorption kinetics were analyzed using the Ho and McKay (1999) pseudo-second-order model [12], in which qt is the amount of adsorbate adsorbed at time t (mg/g), qe is the amount of adsorbate at equilibrium (mg/g), and k1' is the rate constant of the pseudo-first-order reaction (1/min). By plotting t/qt versus t, qe, and k2 values were determined from the slope and intercept [13].

Pseudo first order: $\ln (qe - qt) = \ln (qe) - k_1 t$ (2)

Pseudo second order:

$$\frac{t}{q_{(t)}} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

Adsorption Isotherms. Isotherm analysis was conducted using the Langmuir (1918) and the Freundlich (1906) models [14]. A linear regression for the Langmuir isotherm was obtained by plotting Ce (equilibrium concentration) versus Ce/qe, where qe is the adsorption capacity. Meanwhile, for the Freundlich model, the linear regression equation was derived by plotting log Ce versus log (x/m).

Langmuir Isotherm models

$(Ce/(qe) = 1/KLqm + Ce/qm$ (4)

Freundlich Isotherm models

$\text{Log } qe = \log K + 1/n \text{ Log } Ce$ (5)

Result and Discussion

FTIR Analysis of Adsorbent. The FTIR spectrum of CCCB is shown in **Figure 1**. Chitosan exhibited absorption bands at 3275.80 cm^{-1}, 2873.51 cm^{-1}, 1559.90 cm^{-1}, 1371.07 cm^{-1}, and 1018.04 cm^{-1}, corresponding to –OH/NH stretching overlap, –CH stretching, –C=O, –CN, and amide –NH scissoring vibrations, respectively [15]. Coffee skin activated carbon displayed absorption at 3292.22 cm^{-1}, 1578.32 cm^{-1}, and 1018.18 cm^{-1}, indicating –OH, =O stretching, and C-O from carboxylates. FTIR spectra comparisons indicate that the composite beads exhibited combined features from their constituent materials.

Shifts in wavenumbers from 2873 cm^{-1} to 2906 cm^{-1} for NH_2 and from 3292 cm^{-1} to 3267 cm^{-1} for –OH suggest a reduction in hydrogen bonding, resulting in more free amine and hydroxyl groups that increase adsorption capacity [15].

Surface Characteristics of Adsorbents. SEM analysis results are presented in **Figure 2**, showing

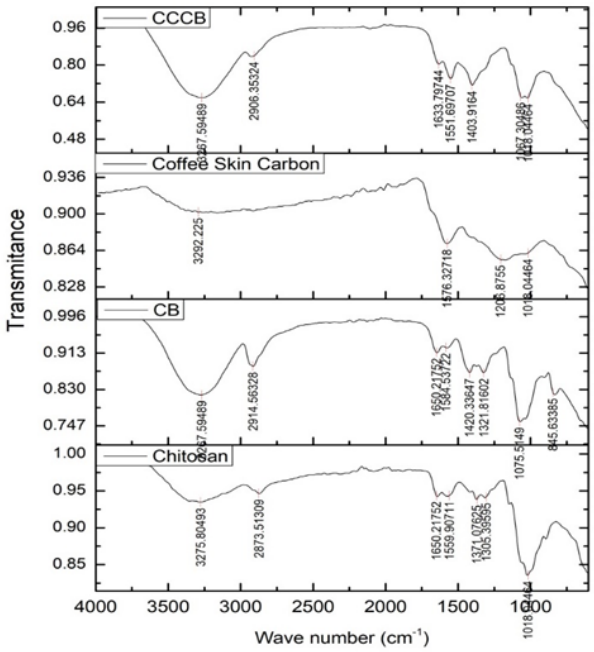

Figure 1. FTIR spectrum of the material

surface differences between CB and CCCB. CB had a smooth, homogeneous, and non-porous surface, while CCCB showed a rough, heterogeneous surface with visible pores, indicating the presence of activated carbon, a porous material. This suggests that carbon pores were not entirely covered by chitosan, allowing adsorption via functional group interaction and pore filling.

Adsorption Kinetics. The effect of contact time on Methylene Blue and Congo Red adsorption by CB and CCCB was investigated using 25 mg/L dye solutions and 0.1 g of adsorbent over contact times of 30, 45, 60, 90, 120, and 150 minutes. As shown in Figure 3, Methylene Blue and Congo Red were rapidly adsorbed within the first 30 minutes, followed by a slower rate. The adsorption rate depends on the number of active sites available on the adsorbent surface, which is initially high and declines due to steric hindrance as sites become occupied [16]. Hence, Methylene Blue adsorption reached equilibrium at 60 minutes, while Congo Red adsorption reached equilibrium at 150 minutes.

Both pseudo-first-order and pseudo-second-order models were applied to study the adsorption kinetics of CB and CCCB on Methylene Blue and Congo Red. The kinetic parameters are shown in Table 1. Based on Table 1, the pseudo-second-order model had higher R^2 values than the pseudo-first-order model for both CB and CCCB, indicating that the pseudo-second-order model better explained the adsorption kinetics in this study. Theoretically, this model assumes that adsorption involves more than one active site [10].

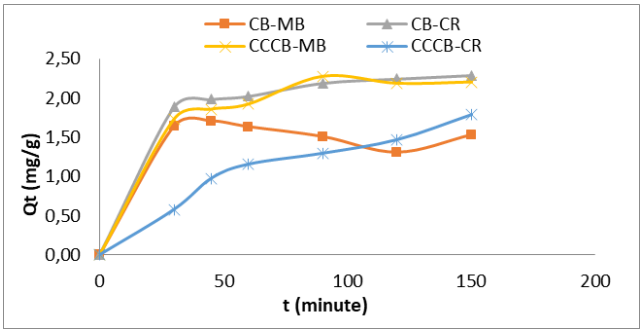

Figure 3. Effect of contact time on adsorption capacity for Methylene Blue and Congo Red

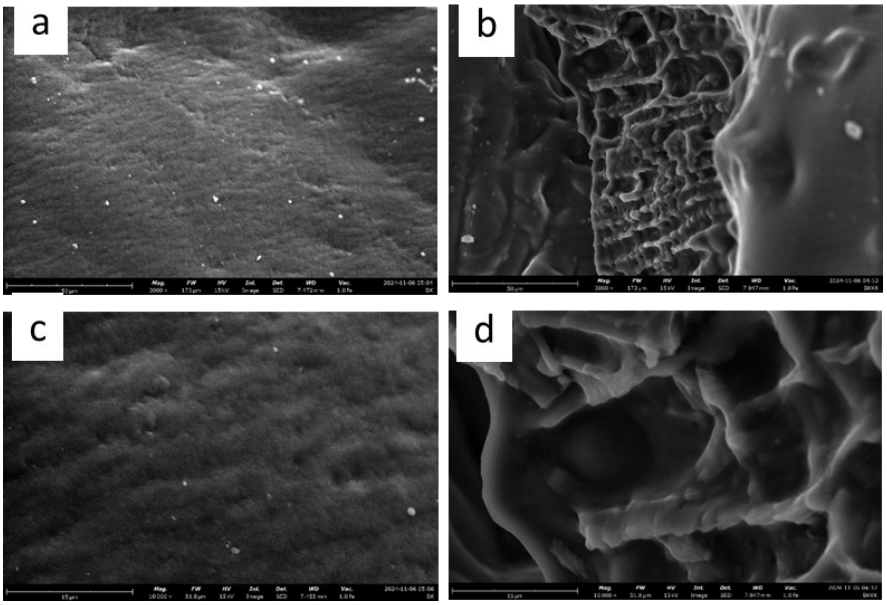

Figure 2. Surface morphology: a. CB (3000x), b. CCCB (3000x), c. CB (10,000x), d. CCCB (10,000x)

Table 1. Adsorption kinetics parameters

Adsorbent	Kinetic Model	Parameter	*Methylene Blue*	*Congo Red*
CB	*Pseudo first order*	*Qe*	0,0138	6,790
		k_1	$2,2x10^{-2}$	$5,98x10^{-2}$
		R^2	0,4268	0,5617
CCCB		*qe*	1,147	6,395
		k_1	$1,71x10^{-2}$	$3,81x10^{-2}$
		R^2	0,7540	0,7149
CB	*Pseudo second order*	Qe	1,3815	2,439
		k_2	$1,158x10^{-1}$	$3,97x10^{-2}$
		R^2	0,9766	0,9994
CCCB		*qe*	2,4102	2,9386
		k_2	$3,42x10^{-2}$	$3,2x10^{-3}$
		R^2	0,9942	0,9110

Adsorption Isotherm. The greater the dye concentration used, the higher the adsorption capacity becomes. This increase in adsorption capacity is associated with an enhanced mass transfer driving force between the solid and liquid phases. As the adsorbate concentration increases, the frequency of collisions also rises, facilitating adsorption [17]. Based on Figure 4, it is evident that the adsorption capacity of CCCB for Methylene Blue was significantly higher compared to CB. Conversely, chitosan beads exhibited a higher adsorption capacity for Congo Red. This observation aligns with theoretical expectations: chitosan beads, containing $–NH_2$ functional groups, are more effective in adsorbing negatively charged dyes like Congo Red. Meanwhile, the modification of chitosan beads with activated carbon introduces additional –COOH and –OH groups into the adsorbent, enhancing their capacity to adsorb positively charged dyes such as Methylene Blue. The maximum adsorption capacities of each adsorbent for Methylene Blue and Congo Red are presented in Table 2.

Table 2. Adsorption Capacity of CB and CCCB for Methylene Blue and Congo Red

No.	Adsorbent	Adsorption Capacity (mg/g)	
		MB	CR
1.	CB	9,19	12,09
2.	CCCB	20,018	6,86

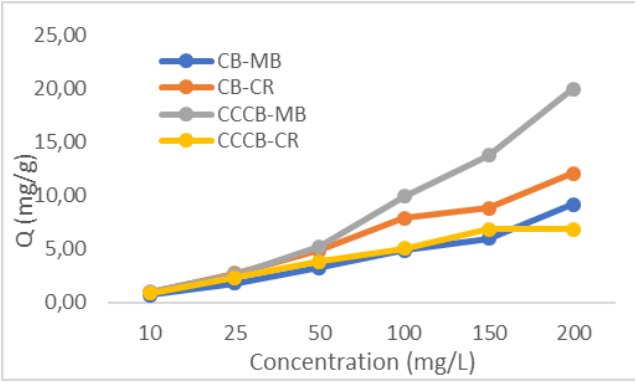

Figure 4. Effect of adsorbate concentration on the adsorption capacity of adsorbents for Methylene Blue and Congo Red

Based on Table 3, the adsorption of Congo Red by both chitosan beads and coffee skin carbon chitosan composite beads yielded higher R^2 values when modeled using the Langmuir isotherm equation. The same result was observed for Methylene Blue adsorption by chitosan beads. This suggests that the adsorption occurred in a monolayer on the adsorbent surface [18]. However, Methylene Blue adsorption using the coffee skin carbon chitosan composite beads showed an R^2 value closer to 1 when fitted to the Freundlich isotherm model, indicating that the Methylene Blue adsorption process on this adsorbent occurred in multilayers [17].

Conclusion

The chitosan-carbon composite beads demonstrated superior adsorption capacity com-

Table 3. Adsorption Isotherm Parameters

Adsorbent	Adsorbate	Langmuir (Ce/qe) = 1/KL qm + Ce/qm			Freundlich log(qe) = log K_F + 1/n log Ce		
		qm (mg g^{-})	K_L (Lmg^{-})	R^2	N	K_F (mg g-($L\ mg^{-}$)$^{1/n}$)	R^2
CB	MB	8,49	0,026	0,9962	1,616	2,832	0,9804
CCCB	MB	112,36	0,018	0,4823	1,002	1,787	0,9921
CB	CR	11,53	0,170	0,9408	5,21	4,617	0,9224
CCCB	CR	7,28	0,112	0,9884	2,755	1,33	0,9796

pared to chitosan beads for Methylene Blue, with an optimum capacity of 20.018 mg/gram. However, their adsorption capacity for Congo Red decreased to 6.86 mg/gram. Thus, the adsorption kinetics of both adsorbents for Methylene Blue and Congo Red followed the pseudo-second-order kinetic model. The adsorption of CB-MB, CB-CR, and CCCB-CR followed the Langmuir isotherm model, whereas CCCB-MB followed the Freundlich isotherm mode.

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Author Contribution

Ria Nurwidiyani : writing-original draft, visualization, investigation, data curation, data analysis. Deni Agus Triawan : writing-review, data curation, visualization. Chelin Dion Sigiro : writing -original draft, data curation, visualization.

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