

Performance of Chitosan Beads after treatment with spent coffee grounds for the adsorption of methylene blue

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ABSTRACT

Spent coffee grounds are one of the ingredients that are abundantly available today and can be used as a crosslinking material with other materials. The objective of this work was chitosan (CS) beads and treatment spent coffee grounds (TCG) made into beads to determine their ability to adsorb methylene blue (MB). The ratios of CS to TCG (by weight) were varied to make beads with the following composition: 1:0 (CS), 1:1 (CS/TCG 3%), 1:2 (CS/TCG 6%), and 1:3 (CS/TCG 9%). Glutaraldehyde crosslinking was performed to increase the stability of the beads in water; these beads were used to test the capacity to adsorb MB. The beads of different compositions were assessed using several techniques, including scanning electron microscopy (SEM), Fourier-transform infrared (FTIR) and ultraviolet-visible spectroscopy (UV-Vis). The results of the morphological analysis showed that adding TCG resulted in the formation of more pores and cavities in each sample. It enhances its effectiveness as an adsorbent. Analysis of the composition of TCG via XRF showed the presence of a carbon atom, a precursor of activated carbon. The FTIR spectrum indicated that functional groups played a crucial role in adsorption. The UV-Vis results showed that the degradation percentage increased with an increase in the weight ratio of CS/TCG beads. The CS beads treated with TCG could be used to adsorb MB for up to seven repetitions, with an adsorption percentage of 87.8%. Therefore, it is concluded that the measured CS/TCG data were numerically fitted using Langmuir and Freundlich models to analyze the adsorption isotherm behavior.

Key words: Waste coffee ground; chitosan; beads; pollutant; robusta.

1 INTRODUCTION

Water pollution can be caused by hazardous waste from various industries, such as textiles, paper, cosmetics, paint, rubber, ink, and food. More than 100,000 varieties of dyes are used, and 7×10^5 tons of dyes are produced worldwide annually (Gayathri; Palanisamy, 2020). Methylene blue (MB) is commonly used in the textile industry for dyeing because of its water solubility and cationic properties. As it provides exceptional dyeing qualities, it is favorable for textile manufacturers (Jain; Dwivedi; Waskle, 2016). The presence of dyes in water can harm aquatic ecosystems as it interferes with light penetration and the photosynthesis of plants. Additionally, suspended solids in dyes can dissolve and create microtoxicity (Gayathri; Palanisamy, 2020). Additionally, the breakdown of MB can result in gastritis, diarrhea, and skin diseases in humans (Liu et al., 2022). Therefore, dye waste, such as MB, needs special treatment to render them harmless before being released into the environment.

Different techniques, including physical, chemical, and biological, have been developed to remove dyes from water (Ayalew; Aragaw, 2020). However, the adsorption method is preferred because the adsorbent is easy to obtain and has higher efficiency (Khan; Nazir, 2015). Spent coffee grounds (TCG) are an environmental problem because they contain a lot of water after brewing. Hence, they quickly cause rot or mold, resulting in secondary ecological pollution. However, after treatment, TCG can be used as an adsorbent (Lee et al., 2021).

Spent coffee grounds (TCG) can serve as an effective adsorbent for several reasons. First, its surface is highly porous, which facilitates the absorption of various substances. Additionally, it is rich in functional groups like methoxyl, carboxyl, or carboxyl due to its cellulose, hemicellulose, and lignin content. Finally, as it can be recycled, it could become an option for managing water treatment waste. This approach reduces processing expenses and promotes sustainable environmental practices (Kang et al., 2022). TCG has active sites, such as hydroxyl and carboxyl groups, which can bind to MB (Anastopoulos et al., 2017). However, using only powdered coffee grounds as an adsorbent has certain disadvantages, for example, separating MB from the coffee grounds is not an ideal option. It is also not sustainable. Thus, additional materials are required to separate the adsorbent and MB. Treating TCG with other materials before use can enhance its performance.

Many researchers have investigated chitosan (CS) as an adsorbent due to its excellent capability to adsorb various contaminants found in water, including metal cations and anions, drugs, and dyes (Wang; Zhuang, 2017; Sowmya; Meenakshi, 2014; Hsu et al., 2024). The presence of OH and NH_2 functional groups in CS facilitates this adsorption process through electrostatic attraction. However, as an adsorbent, CS also has some disadvantages, such as low adsorption capacity, mechanical strength, and lack of selectivity (Wang; Zhuang, 2017). Therefore, other materials need to be added to improve its adsorption and mechanical abilities. The objective of this work was to add coffee grounds and CS beads to adsorb MB

and facilitate the separation between the adsorbent and the adsorbate. We analyzed the effect of adding coffee grounds on the morphological structure, functional groups, and adsorption ability of MB and assessed adsorption isotherms to understand the adsorption behavior of the beads.

2 MATERIAL AND METHODS

2.1 Materials

The materials used in the experiments included CS at 85% deacetylation and a molecular weight of 87,000 g/mol, MB, and glutaraldehyde at 25% weight to volume in water. These materials were purchased from Sigma-Aldrich (USA). The raw coffee grounds were purchased from a local Indonesian brand that uses 100% Robusta beans. Acetic acid (100%) was purchased from Brataco (Indonesia). All chemicals were of analytical grade and used in the experiments without further purification.

2.2 Synthesis of CS/TCG Beads

In this study, pre-treatment methods for raw coffee grounds described in another study were used (Lessa; Nunes; Fajardo, 2018). After the coffee was made, the residue left behind was referred to as TCG. To synthesize CS/TCG, 3 g of CS was added to a 100 mL solution of 5% acetic acid and mechanically stirred for 7 h. This mixture was left undisturbed overnight to remove air bubbles and establish a stable CS solution. Next, varying masses of waste coffee grounds (3 g, 6 g, and 9 g) were thoroughly mixed with a CS solution. The resulting mixture was added dropwise using a burette to a precipitation bath containing 500 mL of 0.5 M NaOH, forming uniform beads. This mixture was allowed to soak overnight, after which, the beads were isolated and rinsed with distilled water to eliminate the alkaline residue.

The crosslinking solution was prepared by mixing glutaraldehyde (GA) and distilled water to create a 5.0 wt% GA solution. Adding GA prevented the beads from getting hydrated in the aqueous solution. Next, the wet beads were crosslinked with GA for 2 h under gentle stirring at ambient temperature. After agitation, the beads were separated from the mixed solution and washed multiple times with deionized water to attain a neutral pH. Finally, the beads were dried at 60 °C under controlled conditions in an oven and stored in a desiccator. This approach was adopted to ensure optimal preparation of the beads.

2.3 Characterization

A Micromeritics Gemini VII-type analyzer was used to examine the surface area and porosity. Before determining the characteristic-specific surface area and porosity, the sample was prepared with a piece degas system

(Micromeritics Flow Prep 060). Fourier-transform infrared (FTIR) spectroscopy was performed to assess the functional groups of the beads using a Shimadzu's FTIR spectrometer 8201PC. The morphological characteristics of the beads were examined using a JSM-6510LA scanning electron microscope (SEM). The same instrument was used to analyze the FTIR spectra and morphology of the reusable beads. The MB aliquot was analyzed using a Shimadzu UV-1700 UV-Vis spectrophotometer, and an absorption peak was detected at 664 nm.

2.4 Adsorption Experiments

Batch adsorption experiments were performed in 50 mL conical flasks with a 10 mL solution of MB (10 mg/L) under controlled conditions and agitation at 200 rpm. A 0.3 g sample containing CS and CS/TCG beads was used for adsorbing MB. The pH of the MB solution was maintained at three initial values of 4, 7, and 10. The effect of the concentration of the adsorbent on the removal efficacy of MB was investigated. Briefly, 10 mL of MB (10 mg/L) was mixed with different quantities of the adsorbent (0.1, 0.2, or 0.3 g) at pH 7 and ambient temperature. The reusability of the samples was assessed. The samples were dried in an oven at 60 °C for 2 h, and then, they were used again to adsorb MB by adding 0.2 g of beads to 10 mL of MB solution (10 mg/L). The maximum amount of a substance that can be adsorbed onto a material and the effectiveness of the removal process (expressed as a percentage) were determined using Equations (1) and (2) (Ho; Malarvizhi; Sulochana, 2009).

$$Q_e = (C_0 - C_e) \times \left(\frac{V}{M} \right) \quad (1)$$

$$R = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

Here, Q_e (mg/g) indicates the maximum amount of substance that can be adsorbed onto a surface at equilibrium, R (%) indicates the elimination ratio, V (L) indicates the volume of the solution, which was fixed at 10 mL, C_0 (mg/L) indicates the concentration of MB at the beginning of the experiment, C_e (mg/L) indicates the concentration of MB at equilibrium in the solution, and M (g) indicates the mass of the adsorbent.

After producing MB solutions at different concentrations (5, 10, 15, and 20 mg/L) and adjusting their pH value to neutral, the adsorption kinetics and isotherm curves were derived. Next, a consistent mass of 0.3 g of adsorbent was added to the solutions and stirred continuously for 24 h. The formulae for the isotherm adsorption are as follows:

For linear Langmuir fittings, Equation (3) was used (Ho et al., 2005)

$$\frac{1}{Q_e} = \frac{1}{Q_{\max} K_L C_e} + \left(\frac{1}{Q_{\max}} \right) \quad (3)$$

Equation (4) was used for linear Freundlich fittings (Ho et al, 2005).

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

Here, C_0 denotes the initial dye concentration and C_e denotes the concentration of the dye at equilibrium (both in mg/L). Q_e denotes the amount of dye adsorbed at equilibrium. $Q_{\max}$ denotes the maximum adsorption capacity of the dye (mg/g), while K_L denotes the Langmuir constant (L/mg). K_F and n denote adsorption isotherm constants, which indicate the removal capacity (L/mg) and parameters related to adsorption intensity, respectively.

3 RESULTS

3.1 Characterization

The physical properties of the CS and CS/TCG 9% beads are presented in Table 1. The measured surface areas of the CS beads and the CS/TCG 9% beads were 0.2961 m²/g and 0.3129 m²/g, respectively.

Table 1: Physical properties of CS and CS/TCG 9% beads

Physical Properties	Characteristic Value	
	CS	CS/TCG 9%
Surface area using BET	0.2961 m ² /g	0.3129 m ² /g
Temperature	~60°C	~60°C
pH	Stable in various pH	Stable in various pH
Adsorption average pore diameter by BET	0.9668 nm	3.4433 nm
Desorption average pore diameter by BET	0.7933 nm	2.3816 nm

The FTIR spectra of CS and CS/TCG beads are shown in Figures 1a and 1b. However, small variations were found for the spectra of CS/TCG 3% (Figure 1c), CS/TCG 6% (Figure 1d), and CS/TCG 9% (Figure 1e), respectively. The characteristics of the functional groups in the CS/TCG 9% sample were analyzed before and after using the samples for adsorption once and seven times. The results are illustrated in Figure 1f.

A morphological analysis of the beads that were repeatedly used was conducted with SEM. Figure 2a was the original chitosan beads. Figure 2b shows the CS/TCG 3%. Figure 2c shows the CS/TGS 6%. However, the CS/TCG 9%

beads shows in Figure 2d. Figure 2e shows that CS/TCG 9% beads used for adsorption seven times.

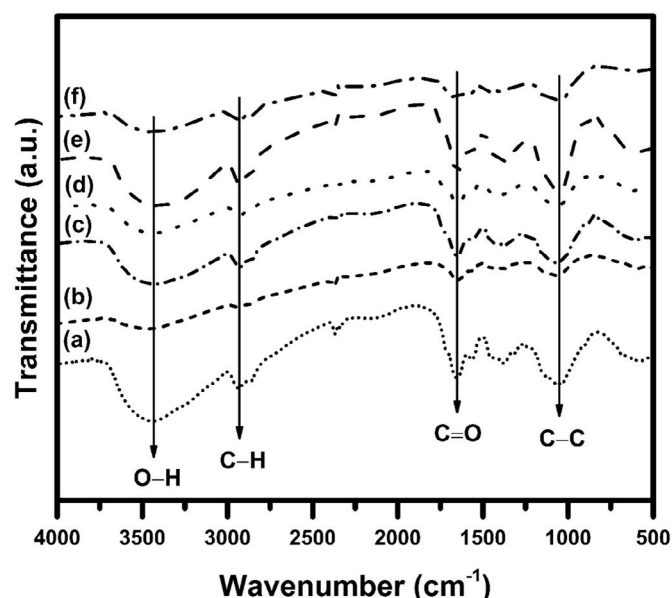


Figure 1: FTIR spectra of the starting materials (a) CS, (b) CS/TCG 3%, (c) CS/TCG 6%, and (d) CS/TCG 9%, followed by CS/TCG 9% after using (e) once and (f) seven times.

3.2 Adsorption experiments

The influence of composite composition and pH was tested on the adsorption of MB, as illustrated in Figure 3. The results of the aquadest solution (Figure 3a) showed that the adsorption process was rapid during the first 10 min, but it started slowing down in the next minute and reached 92.9% after 60 min. Under acidic conditions, the adsorption percentage was only 24.1% after 60 min (Figure 3b). The adsorption percentage was 70.1% at pH 7.0 (Figure 3c). In this study, the adsorption percentage in the alkaline solution was 78.4% (Figure 3d).

3.3 Adsorption isotherm models

The isothermal adsorption curve of CS/TCG beads based on the Langmuir model is shown in Figure 4a. The Freundlich model for the adsorption curve of CS/TCG is shown in Figure 4b. The beads that were reused for the adsorption process seven times are shown in Figure 4c. The Langmuir and Freundlich parameters were evaluated from the linear plot using the linear regression analysis listed in Table 2.

4 DISCUSSION

The physical properties result suggested that the CS/TCG 9% beads had more surface area than the CS beads. A higher surface area increases the adsorption capacity (Moosavi et al., 2020). The mechanical stability of the

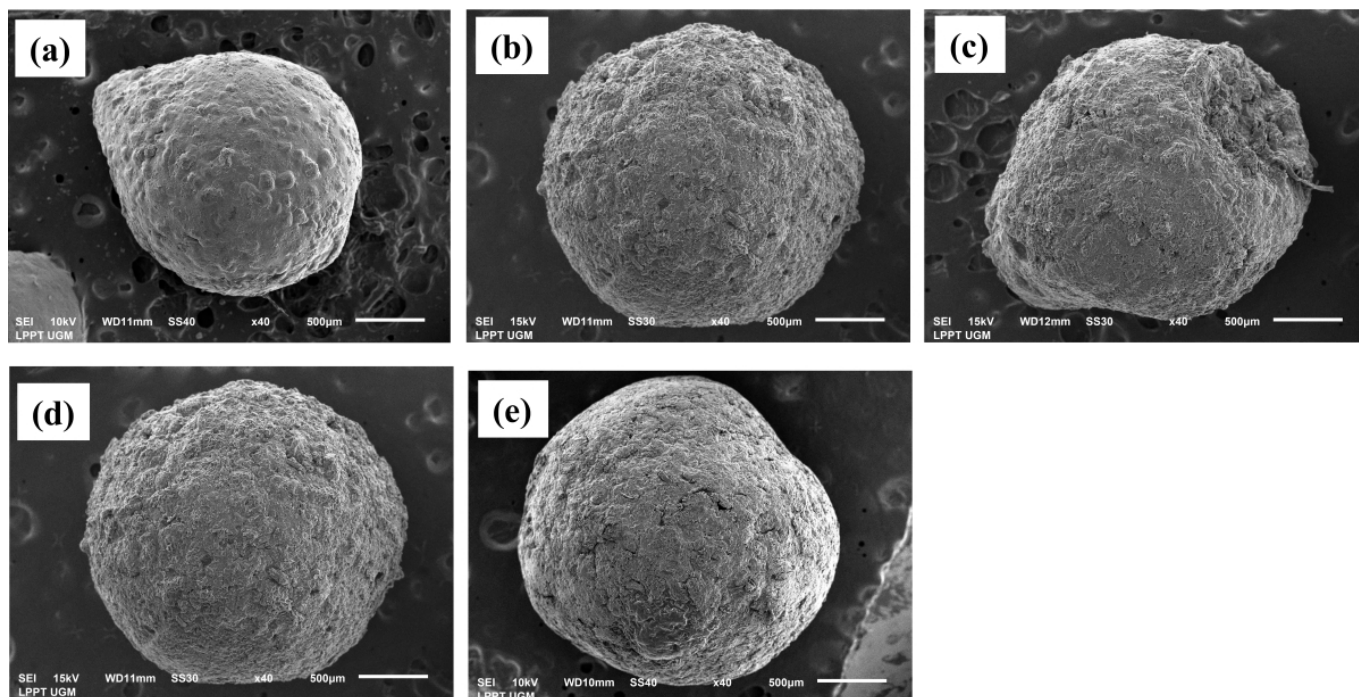


Figure 2: SEM images of the starting materials (a) CS (b) CS/TCG 3%, (b) CS/TCG 6%. (d) CS/TCG 9%. Followed by (e) CS/TCG 9% after seven times usage.

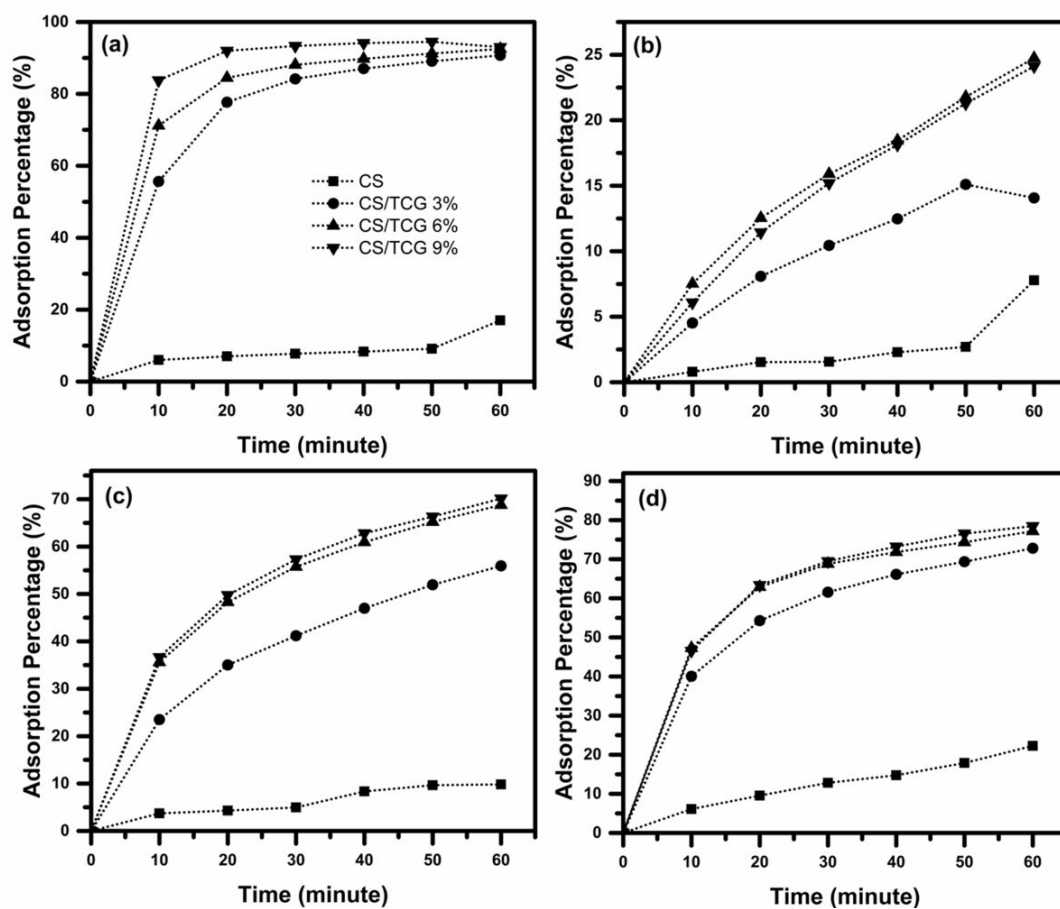


Figure 3: Contact time curves of various adsorbents for the adsorption of MB under different conditions: (a) distilled water, (b) acidic solvent at pH 4.0, (c) neutral solvent at pH 7.0, and (d) alkaline solvent at pH 10.

beads remained consistent at approximately 60 °C across all pH values. The FTIR analysis can be used to identify the functional groups present carboxyl and hydroxyl on the surface of an adsorbent because each group has a unique energy absorption band (Bhatti et al., 2017). A wide band at 3425.58 cm^{-1} was associated with O–H strain vibrations, and the band at 2924.09 cm^{-1} was attributed to aliphatic C–H strain vibrations. The bands at 1651.07 cm^{-1} and 1527.62 cm^{-1} were associated with the C=O carbonyl stretch of hemicellulose and chlorogenic acid and the stretching vibration of the C–N caffeine bond polymer (Ballesteros; Teixeira; Mussatto, 2014). The band at 1381.03 cm^{-1} was related to CH_3 , while the band at 1249.87 cm^{-1} was attributed to the C–O–C bonds of lignin, chlorogenic acid, and caffeine. The band at 1064.71 cm^{-1} corresponded to the C–O–H bonds commonly found in polysaccharides (Lessa; Nunes; Fajardo, 2018).

Analysis of the spectrum of the CS beads revealed a distinct band ranging from 3448.72 cm^{-1} to 2931.8 cm^{-1} , corresponding to the bond strain vibration of the O–H and N–H bands. Additionally, the C=O strain (amide I) and the N–H deformation vibration (amide II) were detected at 1651.07 cm^{-1} and 1566.2 cm^{-1} , respectively. The band at 1056.99 cm^{-1} was related to the C–O–H bond of the glycosidic bond (Alves et al., 2016). The infrared spectrum of CS/TCG beads exhibited the characteristic bands of CS and TCG. The intensity of the O–H stretching vibration band of the CS/TCG spectrum was lower than the intensity of the corresponding band of CS and TCG. The broadband related to the O–H and C–H stretching vibrations (3700–3000 cm^{-1}) was shifted to a lower wavenumber region, which indicated that the presence of TCG decreased hydrogen bonding between the two polymers. These finding align with the research conducted by (Lessa; Nunes; Fajardo, 2018) who conducted membranes from polyvinyl alcohol, chitosan and waste coffee ground.

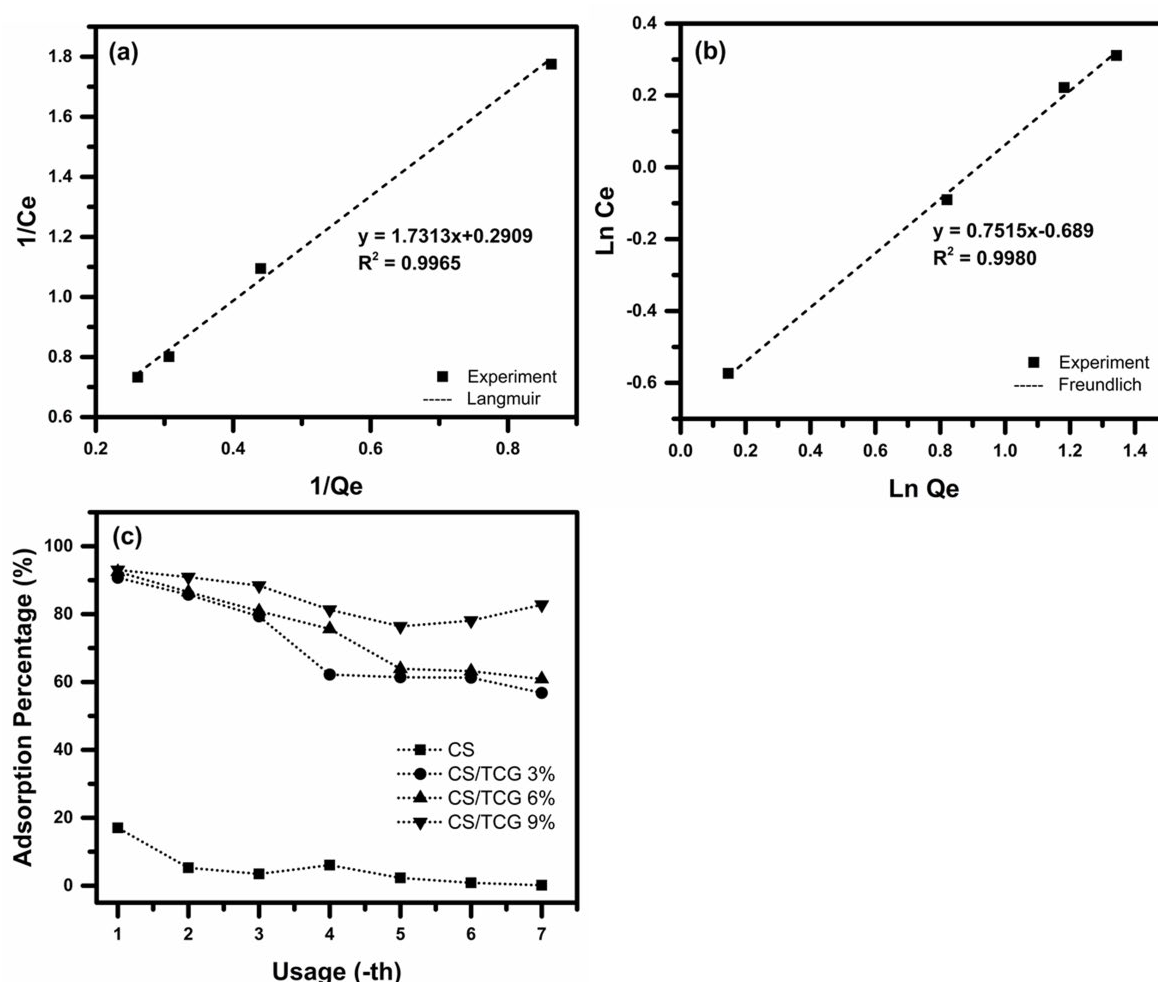


Figure 4: Isothermal adsorption of CS/TCG 9% beads for MB was determined using the (a) Langmuir and (b) Freundlich isotherm models. (c) The reusability of CS/TCG 9% was tested seven times.

Table 2: Adsorption isotherms of CS/TCG 9% beads.

Langmuir			Freundlich		
$Q_{\max}$ (mg/g)	K_L (L/mg)	R^2	$1/n$	K_F (mg/g)	R^2
3.44	0.39	0.996	0.75	0.5	0.998

The O–H stretching band became broader and shifted toward a lower wavenumber after adsorption, indicating the formation of H bonds between the hydroxyl groups of CS/TCG 9% and MB. The vibrational peak of the bound hydroxyl groups shifted from 3433.29 cm^{-1} to 3402.43 cm^{-1} . The vibration of the C=O strain of carboxylic acids with fixed intermolecular hydrogen bonds was 1651.07 cm^{-1} . However, in the first and seventh repetitions, the strain vibrations of the bonded hydroxyl groups and the stretching vibrations of the C=O carboxylic acid with intermolecular hydrogen bonds shifted from 3402.43 cm^{-1} and 1651.07 cm^{-1} to 3425.58 cm^{-1} and 1658.78 cm^{-1} , respectively. Some changes were also observed in the range of $1700\text{--}1600\text{ cm}^{-1}$, possibly due to the stretching of the C=O groups of CS/TCG 9%, which interacted with MB and the C=O groups of MB. Additionally, the band at 1527.79 cm^{-1} , which indicated N–H stretching, shifted to 1566.2 cm^{-1} . No shift was recorded in the other functional groups before adsorption or after the samples were used once or seven times for adsorption. The functional groups were stable, remaining unchanged before and after adsorption for multiple uses, indicating that their interaction with MB was too weak to alter their vibrational frequencies. The results of the FTIR analysis showed that the adsorbent of CS/TCG beads mainly contained O–H, C=O, and N–H groups, which adsorbed MB through chemical binding. The adsorption of MB was primarily driven by O–H, C=O, and N–H functional groups (Nizam et al., 2021).

After using the beads repeatedly, a morphological analysis was conducted with SEM. The original sample had a rough and grooved surface with various cavities (Figure 2a–d). These cavities could be characterized as channels opening on the surface of the dye waste (Taleb et al., 2020). The CS/TCG 3% beads had a rougher texture (Figure 2b). A higher adsorption capacity of the sample is shown in CS/TCG 6% in figure 2c (Liakos et al., 2021). In CS beads, the addition of TCG led to the formation of more pores. However, the CS/TCG 9% beads had smaller, more uniform, and symmetric pores than the TCG 3% and 6% beads. The CS/TCG 9% beads that were not used for adsorption had a rougher surface with many pores and cavities (in Figure 2d). The surface looks smooth after the adsorption process once compared to the surface before the adsorption process was carried out by Figure 2e. The results of the FTIR analysis and the adsorption repetition test indicated a decrease in adsorption potential due to the filling of the pores and cavities by MB and functional groups, which were

mutually bonded with pollutants. The test results after 6–7 rounds of adsorption showed that the adsorption ability of the CS/TCG 9% beads decreased in repetitions 1 to 5 and then increased (see the repetition graph in Figure 4c). The CS/TCG 9% beads used for adsorption seven times formed sufficiently long fractures.

4.1 Adsorption Experiment

The active sites and pores were bound and filled with MB pollutants. Initially, a significant fraction of the sites on the surface remained unoccupied, which provided adsorbate adhere to the surface. Washed coffee grounds provide higher adsorption capacity compared with raw coffee ground (Nurmayasari et al., 2023). Washed coffee grounds provide higher adsorption capacity for powder form compared to beads. However, as adsorption continued, filling the remaining empty surface sites became increasingly difficult because of the repulsion between the adsorbate molecules and the solid phase. Also (Fu et al., 2015), stated the microsphere shape increased the capacity of adsorbent for removal MB. Hence, the adsorption rate decreased because of the availability of fewer active sites on the adsorbent material. The number of H^+ ions in the system increased, which caused the adsorbent surface to accumulate a positive charge by adsorbing H^+ ions. This positive charge prevented the adsorption of MB ions onto the adsorbent surface because of electrostatic repulsion and competition between H^+ ions in the system and the cationic groups on MB for the adsorption sites. However Han, Wang and Ma (2011) showed that in an alkaline solution, MB is adsorbed more efficiently onto an adsorbent. Consequently, the adsorption of the molecules of the cationic dye increases due to electrostatic attraction.

The adsorption capacity of cationic dyes, such as MB, increases with the pH. Also, (Hu et al., 2019), the adsorption can be attributed to the reaction of positively charged ions of the dyes with OH^- ions present in aqueous solutions. The pH of the solution plays a crucial role in adsorption, as an increase in the pH increases the number of negatively charged surface sites on the adsorbent. The excellent performance of the composite might be attributed to the integration of TCG into the CS matrix. The presence of TCG enhances the functional portion of the bead, causing adsorption on MB. Functional groups (–OH, –NH, and –COOH) and the carbonic (aliphatic and aromatic) backbone of the TCG components can increase the interaction between MB and the CS/TCG composite by providing extra H bonds.

4.2 Adsorption isotherms model

In this study, the adsorption of MB was evaluated using the Langmuir and Freundlich isotherm models. The $Q_{\max}$ and K_L parameters obtained for MB were 3.43 mg/g and 0.39 L/

mg, respectively, and the regression curves matched the experimental data with a high correlation coefficient (R^2) of 0.99. For the samples containing CS beads, the K_L values were 0.3, 0.2, 0.15, and 0.1 when the MB concentrations were 5, 10, 15, and 20 ppm, respectively. The value of K_L was between 0 and 1, indicating a beneficial procedure because the adsorption and desorption processes did not occur simultaneously (Nandiyanto et al., 2020).

The Freundlich parameter $1/n$ is associated with surface heterogeneity. From the fitting results, the value of $1/n$ was found to be between 0 and 1, and thus, the adsorption and desorption processes did not occur simultaneously. Additionally, the values of $n > 1$ indicated that the process occurred physically. (Nandiyanto et al., 2020) showed that the carbonizing pineapple waste fit to Freundlich model with the values of $n > 1$. The fitting between the Langmuir and Freundlich models was balanced. The first adsorption process occurred in a monolayer and the next in a multilayer. The adsorbent form, such as beads or membranes, provides multiple benefits, such as the efficiency and ease of repeated use, and facilitates the separation between the adsorbent and the adsorbate. Omer et al. (2022) showed composite beads could be easy to separate from pollutant and reusable.

The results of the repetition test showed that CS/TCG 9% had a high percentage of adsorption even after repeated use up to seven times. CS/TCG 9% has adsorption percentage of 93% after first adsorption and sorption percentage was 87.8% after seven times. It was considerably higher than that of CS/TCG 3% (56.7%) and CS/TCG 6% (60.9%) after seventh time repetition. The adsorption rate indicated that the adsorption capacity was reusable. The repetition results suggested that the adsorption occurred in a multilayer manner, and active sites and pores were available for the adsorption process. However, in CS beads, CS/TCG 3%, and CS/TCG 6%, the adsorption efficiency decreased as the number of repetitions increased. Hence, the performance decreased because the number of active sites, pores, and cavities decreased.

5 CONCLUSION

It is conclude that adding TCG to the CS bead increased the number of pores and cavities on the surface of the adsorbent. Additionally, the FTIR characterization results indicated the availability of active sites of TCG that enhanced the adsorption efficiency. The fitting results showed that CS/TCG beads exhibited a balanced adsorption following both Langmuir and Freundlich isotherm. The percentage of degradation of MB increased as the amount of TCG added to the CS beads increased. Adding more beads also induced the degradation of MB. Additionally, increasing the pH increased the adsorption capacity to 78.4%, and the CS/TCG adsorbent beads could be reused seven times, with an adsorption percentage of 87.8%.

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7 AUTHORS' CONTRIBUTION

Conceptual Idea: Nugraheni, A.D., Methodology design: Nugraheni, A.D.; Nurmayasari., Data collection: Nurmayasari., Data analysis and interpretation: Nugraheni, A.D.; Nurmayasari.; Sholihun., and Writing and editing: Nugraheni, A.D.; Nurmayasari.; Sholihun.

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