

Adsorption of Methylene Blue Dye from Aqueous Solution Using Activated Cogon Grass (*Imperata cylindrica*) Fixed on Alginate

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The continuous discharge of large volumes of colored effluents into water bodies has been contributing to environmental problems over the years. Extensive research has been conducted, over time, to investigate various treatment methods for effectively removing methylene blue (MB) dye from textile wastewater. In this study, activated cogon grass-alginate beads (ACAB) were successfully prepared by fixing the activated cogon grass in an alginate matrix using dropwise extrusion in calcium chloride solution. The adsorbent before and after adsorption was characterized using Energy Dispersive X-ray Spectroscopy (EDX) for elemental percentages, Fourier Transform Infrared Spectroscopy (FTIR) for functional groups, and Scanning Electron Microscope (SEM) for surface morphology. Batch adsorption experiments were carried out to determine the effect of increasing adsorbent dosage and effect of increasing pH on the adsorption of MB on ACAB. The findings showed that the highest color removal efficiency reached 96.34 %, resulting in a final total color units (TCU) concentration of 4.09 ppm and an adsorption capacity of 6.02 mg/g (at 8 % adsorbent dosage, pH 8.0, agitation at 300 rpm and contact time of 1 h). The MB adsorption process on ACAB adhered to the Flory-Huggins isotherm and demonstrated a good fit with a pseudo-second-order model. The inherent spontaneity of this adsorption phenomenon, coupled with an increasing degree of disorder, was verified through the analysis of thermodynamic parameters. Specifically, the values of ΔG (-4.62 kJ/mol) and ΔS (+15.48 J/K·mol) provided compelling evidence for the thermodynamic favorability and the associated rise in entropy during the process.

1. Introduction

Globally, large volume of wastewater is produced every year by textile manufacturing processes. The high demand for synthetic dyes, with annual industrial production of approximately 700,000 t (Oladoye et al., 2022), contributes to the significant environmental concern surrounding the presence of residual dyes in textile wastewater effluents. Highly-colored wastewater not only creates an unsightly appearance but also disrupts the aquatic ecosystem by hindering sunlight penetration, as noted by Rubio et al. (2018). Synthetic dyes, upon release into waste streams, pose a significant challenge due to their inert nature, making them resistant to biodegradation (Amon and Lawagon, 2021), and persisting in the environment for extended periods. Both synthetic dyes and their breakdown products may possess carcinogenic or toxic properties even at low concentrations (Meili et al., 2019). Methylene Blue is a basic and a cationic dye used in textiles particularly in cotton, wool and silk. Exposure to methylene blue can result in a range of adverse effects on human health such as methemoglobinemia and mental confusion, and severe exposure may lead to difficulty in breathing, irritation to the gastrointestinal tract, and permanent eye injury (Hameed et al., 2008). Among several treatment processes available, adsorption is known as a favorable process in dye removal in wastewater due to its low-energy input, easy-handling, high efficiency, low cost, and availability of different natural adsorbents (Liu et al., 2012). Activated carbon, although widely used for dye removal, faces limitations in widespread application on a larger scale due to its high operational costs, particularly in regenerating used adsorbents (Pavan et al., 2008)

and presents challenges due to filtration difficulties (Dahlan et al., 2017). Consequently, there has been extensive research on low-cost alternative adsorbents with higher adsorption capacity and regeneration ability, aimed at reducing the overall cost of treatment technology (Senthamarai et al., 2013). The use agricultural waste as a source of carbonaceous material offers several benefits, including wide availability, low cost, renewability, and viable for regeneration (Phuong et al., 2021). Cogon grass (*Imperata cylindrica*), often regarded as garden waste with no economic value, can serve as an adsorbent for pollutant removal in wastewater treatment (Su et al., 2014). Activated carbon derived from biomass is known to have low adsorption capacity and low regeneration capacity (Girish, 2018). To enhance the adsorption of synthetic dyes such as methylene blue (MB) and methyl orange, from aqueous solutions, activated carbon from biomass can be immobilized in a supporting medium, such as a hydrogel derived from materials like starch, chitin, chitosan, and sodium alginate (Dahlan et al., 2017). Alginate is a structural component in marine brown seaweed *Sargassum* (*Phaeophyceae*) and serves as a bioadsorbent because of the functional groups present in its cell wall, enabling the electrostatic attraction and complexation of metal ions in aqueous solutions (Freitas et al., 2017). It is a heteropolysaccharide composed of α -L-guluronic acid (G) and β -D-mannuronic acid (M) (Sosnik, 2014). It forms stable gels in water by crosslinking with divalent cations through a process called ionotropic gelation in which the carboxylic acid groups of the guluronic sugar subunit chelate divalent cations (Sun and Fugetsu, 2013). This study investigated the performance of cogon grass-derived activated carbon immobilized on alginate for removing methylene blue dye from aqueous solution.

2. Materials and Methods

2.1 Preparation of the activated cogon grass-alginate beads (ACAB)

The activated carbon derived from cogon grass powder was prepared following the method outlined by Hanafiah et al. (2008) with some modifications. Collected cogon grass was washed with tap water and rinsed with distilled water before sun-drying for seven days. It was further dried in an oven at 100 °C for 8 h then treated with KOH in a 1:3 ratio and dried in the oven at 100 °C for 7 h. The dried sample was ground and carbonized at 800 °C for 1.5 h. The activated cogon grass was then cooled to room temperature and washed with 0.1 M HCl for neutralization then was washed several times with cold water then hot water. The acid-washed activated cogon grass was oven dried at 100 °C and was pulverized using mortar and pestle. ACAB was prepared using the method outlined by Mahamadi and Mawere (2014), with modifications. The immobilization process involved mixing 2 g of activated cogon grass with 100 mL of 2 % (w/v) sodium alginate solution to achieve a 2 % (w/v) adsorbent dosage. The mixture was stirred using a magnetic stirrer for one hour until a homogeneous polymer solution was achieved. The same method was used to prepare adsorbent dosages of 4 %, 6 %, and 8 % (w/v). Beads were formed by drop-wise extrusion using a Pasteur pipette in a 4 % (w/v) CaCl₂ solution. The beads were immersed in the solution for 24 h, followed by filtration and washing with distilled water to eliminate any remaining CaCl₂ solution, and then dried in an oven at 60 °C for 4 h.

2.2 Preparation of Methylene Blue (MB) Stock Solution

A 500 ppm MB stock solution was prepared by dissolving 500 mg of analytical grade Methylene Blue (MB) dye in distilled water. Desired working solutions were prepared by simple dilution. The concentrations of MB in the solution before and after adsorption were measured by UV-vis spectrophotometer and the pH were checked using Milwaukee pH 600.

2.3 Characterization of ACAB

Fourier Transform Infrared (FTIR) Spectroscopy was utilized to identify the functional groups within the adsorbent, Scanning Electron Microscopy (SEM) was employed to examine its morphology and microstructure, and SEM-Electronic Dispersive X-ray Analysis was conducted to determine the elemental composition.

2.4 Effect of Adsorbent Dosage

The effect of adsorbent dosage on the adsorption of MB was investigated by using 0.2 g of ACAB with adsorbent dosage of 2, 4, 6, and 8 % (w/v) each in a 50 mL beaker containing 25 mL of 50 ppm MB solution. The initial pH of the solution was adjusted to pH 8 and agitated at 300 rpm for 1 h at room temperature. The concentration of the remaining dye was measured using UV-vis spectrophotometer. The adsorption capacity in mg/g, (q_t), which represents the amount of adsorbate adhered to the surface of the adsorbent after 1 h, is calculated using Eq(1).

$$q_t = (C_o - C_t) \frac{V}{m} \quad (1)$$

where: C_0 is the initial concentration of adsorbate (mg/L); C_t is the concentration of adsorbate (mg/L) after 1 h, V is the volume of the aqueous solution (L), and m is the mass of the adsorbent (g).

2.5 Effect of pH

The effect of pH on MB adsorption was determined by varying the pH from 6 to 10 using 0.1 M HCl and 0.1 M NaOH. A 0.2 g of 8 % ACAB was added to 25 mL of 50 ppm solutions (8 % ACAB was used because it was the most efficient based on the effect of adsorbent dosage experiment). The mixture was agitated at 300 rpm for 1 h at room temperature. Dye concentration was then determined using UV-vis spectrophotometer.

2.6 Kinetics and Isotherm Studies

Kinetics and isotherm studies were conducted using 0.1 g of 8 % ACAB to 50 mL of 2, 4, 6, 8, and 10 ppm in 150 mL beaker. The initial pH was adjusted to pH 8 since this showed the most efficient adsorption in the preceding experiment, agitation was at 300 rpm and at room temperature. The absorbance was measured at 5-min interval for the first 20 min and then at 10-min intervals for the succeeding readings. This was done until constant absorbance reading was observed.

3. Results and Discussion

3.1 Characterization of Aqueous MB Solution

The prepared 50 ppm MB aqueous solution has initial pH of 6.9 and initial total color unit (TCU) of 111.81 ppm. The MB solution showed maximum absorbance at 666 nm, serving as the standard for measuring absorbance across all solutions.

3.2 Characterization of ACAB

The strong peak at $3,416.97\text{ cm}^{-1}$ as shown in Figure 1 corresponds to the stretching vibration from the hydroxyl groups on the surface of the ACAB. Upon adsorption of MB onto the beads, this peak shifts to $3,407.66\text{ cm}^{-1}$, indicative of H-bonding and electrostatic interactions between the alginate beads and the MB dye. The adsorption peak at $2,920\text{ cm}^{-1}$ was assigned to $-\text{CH}$ stretching vibrations. The stretching vibration of $-\text{C}=\text{O}$ shifted from $1,600.52\text{ cm}^{-1}$ to $1,605.06\text{ cm}^{-1}$, accompanied by a significant increase in peak intensity following MB adsorption. This change suggests the presence of electrostatic interactions and hydrogen bonding between ACAB and the MB molecules. The peak at $1,421.37\text{ cm}^{-1}$ represents $-\text{COH}$ bend and at $1,076.88\text{ cm}^{-1}$ represents $-\text{CO}$ in general and primary alcohols. The FTIR results showed that ACAB has $-\text{OH}$ and $-\text{C}=\text{O}$ functional group which are considered as active adsorption sites for interaction making the adsorption of cationic dyes like MB possible.

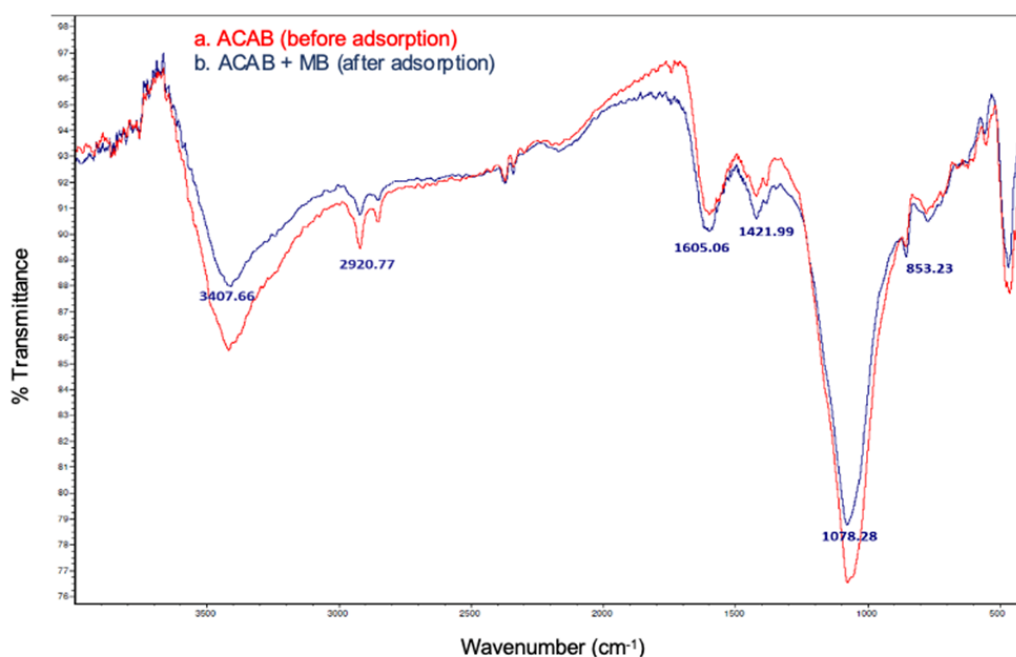


Figure 1: IR spectra of (a) ACAB before adsorption and (b) ACAB after adsorption

The surface morphology of ACAB before and after adsorption was analyzed using SEM as shown in Figure 2a. The average particle diameter of ACAB before adsorption ranges from 2.00 - 2.49 μm . In general, the ACAB displays smooth surface. Following adsorption, SEM images reveal that the beads enlarged and exhibited uneven surfaces with cracks. The extended stirring and saturation of MB molecules might have caused the cracks to open further, generating additional active sites for the adsorption of MB. EDX analysis reveals that the ACAB predominantly comprises oxygen and carbon, as illustrated in Figure 2b. The presence of Ca^{2+} is due to formation of complex with the cross-linking of Ca^{2+} metal and alginate. The trace percentage of silicon can be associated with the vapor of silica gel used during storage to prevent moisture on the ACAB.

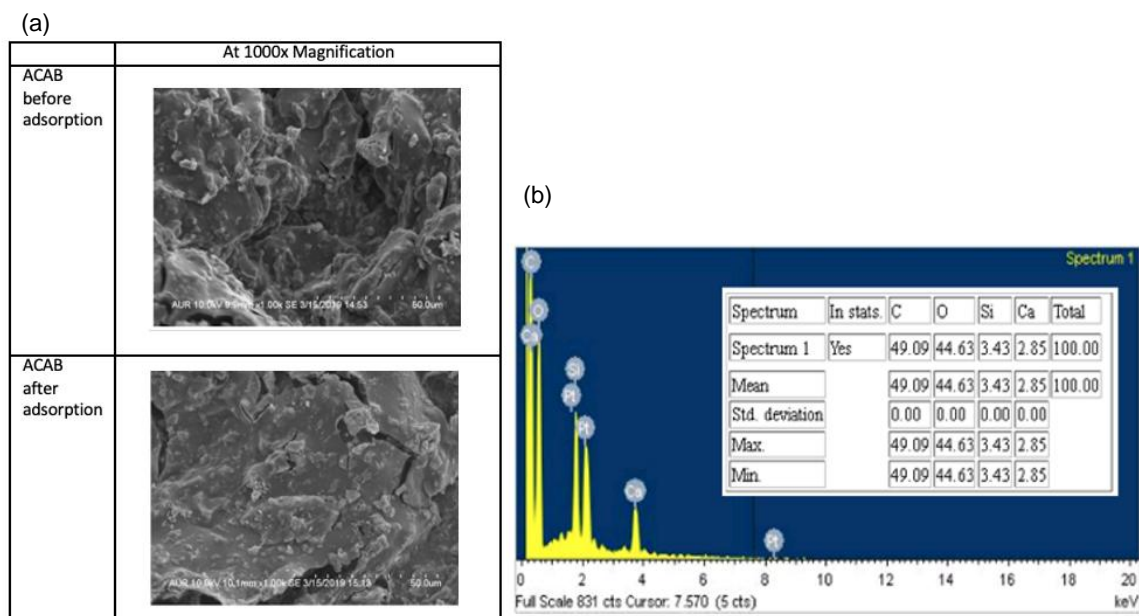


Figure 2: (a) SEM micrographs of ACAB before adsorption and after adsorption and (b) Elemental analysis

3.3 Effect of Adsorbent Dosage

Table 1 shows the effect of adsorbent dosage on the removal of MB dye. The experimental results show that increasing the adsorbent dosage increases the average percent MB removed from the aqueous MB solution with the highest removal of 96.34 % at 8 % adsorbent dosage. This increase can be attributed to the availability of more sorption or binding sites facilitated by the additional adsorbent dosage. The results, at a 95 % confidence level, indicate significant differences, except for those obtained from 6 % and 8 % adsorbent dosage. This suggests that utilizing ACAB with a 6 % adsorbent dosage would be more cost-effective.

Table 1: Effect of adsorbent dosage on the removal of MB from aqueous solution

Adsorbent Dosage (%)	Average % Removal	Average q_t (mg/g)	Final TCU (ppm)
2	79.42	4.9630	23.01
4	92.07	5.7547	8.86
6	95.56	5.9726	4.96
8	96.34	6.0214	4.09

3.4 Effect of pH

One of the important parameters in adsorption of dyes is the initial pH of the solution since adsorption of MB is due to the attraction between the positive charges of MB and the negative charges present on the adsorbent. The effect of pH on adsorption of MB on ACAB was investigated from pH 6 to pH 10 using 8 % ACAB. The results show that the optimum pH for the adsorption process is at pH 8 resulting in 91.18 % removal and that the amount of dye adsorbed (mg) per unit mass of adsorbent (g) is 5.6145, as depicted in Table 2. The increase in adsorption capacity results from the increase in hydroxide ions on the adsorbent and additional adsorption sites provided by the carboxylic functional groups of alginate as pH rises. This elevated presence of hydroxide ions and carboxylate functional groups enhances the electrostatic interaction between MB molecules and ACAB. The lowest adsorption capacity of MB occurred at pH 6. A possible explanation for this is that in acidic medium

the excess hydrogen ions compete with the MB dye for the adsorption sites on ACAB. At 95 % confidence level, it was found that the effect of pH is significant since the p value is less than 0.05.

Table 2: Effect of pH on the removal of MB from aqueous solution

pH	Average % Removal	Average q_t (mg/g)	Final TCU (ppm)
6	87.13	5.3260	14.39
7	88.39	5.1439	12.99
8	91.18	5.6145	9.86
9	88.84	5.4529	12.48
10	89.09	5.5245	12.20

3.5 Adsorption Isotherms and Kinetics

Despite achieving an R^2 value of 0.966 using the Langmuir isotherm model, as illustrated in Table 3, the maximum adsorption capacity (Q_L) is -1.124 mg/g which suggests that this isotherm model inadequately explains the adsorption process. The negative adsorption intensity parameter (R_L) also indicates unfavorable adsorption. The experimental adsorption data fit the Flory-Huggins model better compared to other isotherm models, as it yielded the next highest R^2 value of 0.934. The negative ΔG value from this isotherm indicates the spontaneous nature of the adsorption process, and the positive value of ΔS indicates the good affinity of ACAB for the MB and the increasing disorderliness at the solid-solution interface during the adsorption process. The R^2 values obtained from the pseudo-second order model were higher than those from the pseudo-first order model. Therefore, the pseudo-second order model was identified as the most suitable kinetic model for the adsorption of MB dye on ACAB, indicating a predominant chemisorption mechanism. MB, being a cationic dye, adsorbs primarily via electrostatic interactions on the adsorbent's surface, involving functional groups such as -COOH and -OH. Additionally, chemisorption may occur through complexation between the MB molecule and ACAB's functional groups. ACAB, with hydroxyl groups in its carboxylic and alcohol functional groups resulting from alginate immobilization, acts as a chelating agent capable of binding the cationic MB molecule.

Table 3: (a) Isotherms and (b) Kinetics constants of different adsorption and kinetic models

(a) Isotherm Models			(b) Kinetic Models					
Model	Parameter	Constant	Model	Rate constants	R^2			
Langmuir	Q_L (mg/g)	-1.124	Pseudo-first order	k_1 (min^{-1})	R^2			
	K_L (L/mg)	-0.799				10 ppm	0.018	0.864
	R_L	-0.143				8 ppm	0.020	0.837
	R^2	0.966				6 ppm	0.018	0.911
Freundlich	K_f (mg/g)	3.896	4 ppm	0.020	0.887			
	N	0.413	2 ppm	0.021	0.955			
	R^2	0.872						
Dubinin-Radushkevich	Q_D (mg/g)		10 ppm	0.003	0.999			
	B_D (mol^2/kJ^2)	0.363				8 ppm	0.004	0.991
	E (kJ/mol)	1.173				6 ppm	0.004	0.962
	R^2	0.860				4 ppm	0.014	0.912
Flory-Huggins	K_{FH}	6.436	2 ppm	0.040	0.963			
	n_{FH}	1.391						
	ΔG (J/mol)	-4,615.359						
	ΔS (J/mol-K)	15.479						
	R^2	0.934						

4. Conclusions

Activated carbon derived from cogon grass and fixed on alginate was successfully produced for use in adsorption experiments. Batch experiments were conducted to investigate the influence of adsorbent dosage and pH on the adsorption processes. It was observed that higher doses of adsorbent led to increased adsorption capacity and a higher percentage of removal of MB dye. Results show that using a 6 % adsorbent dosage yielded statistically similar results to using 8 %. The most effective adsorption occurred at a pH of 8 when using 8 % ACAB, resulting to a 91.18 % removal efficiency. This pH level was deemed optimal as it provided stability to the alginate beads without being overly acidic or basic, enhancing the adsorption of MB, which is cationic in nature. The Flory-Huggins model was identified as the best fit isotherm model, indicating that the adsorption process is spontaneous. Additionally, the adsorption kinetics followed a pseudo-second-order model, suggesting the presence of chemisorption mechanisms. This finding was supported by the strong electrostatic interactions observed between the positively charged nitrogen atom of the MB molecule and the negatively

charged carboxylate and hydroxide ions on the surface of ACAB. Overall, the results demonstrated the potential of ACAB as an effective adsorbent for the removal of cationic dyes, such as MB from aqueous solutions.

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