



## Article Info

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## Functionalised Seed Pods for the Sorption of Crystal Violet from Aqueous Solution: Kinetics and Equilibrium Studies

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The release of dye-containing effluents from several industries into natural water bodies continues to pose a serious threat to the ecosystem. Even though several conventional wastewater treatment technologies abound, their usage in developing nations has been limited due to their high cost. This has prompted research into the use of low-cost materials, such as agricultural waste biomass for sequestering such dyes from wastewater. The ability of CH<sub>3</sub>COOH-functionalised *Milletia thonningii* seed pods (FMTP), an agricultural waste, as an adsorbent for the sequestration of Crystal Violet (CV) dye from aqueous solutions is investigated in this study. Fourier Transform Infrared (FTIR) spectroscopy was used to characterize the functionalized adsorbent and its precursor. The pseudo-first-order, pseudo-second-order, and Elovich's kinetic models were used to analyze the kinetic data, while Langmuir and Freundlich isotherm models were used to analyze the equilibrium data using the non-linear regression method. To evaluate the adsorption data and identify the best-fitting kinetic and isotherm models, four error functions were used: Coefficient of Determination (R<sup>2</sup>), Chi-Square (χ<sup>2</sup>), Sum of Error Squares (SSE), and Percent Deviation (% D). The adsorption kinetics was best described by Elovich's kinetic model, while the adsorption equilibrium was better described by the Freundlich model, indicating that the mechanism of adsorption is predominantly chemisorption onto a heterogeneous adsorbent surface. The maximum adsorption capacity of the functionalized adsorbent was 34.8270 mg/g as given by the Langmuir Q<sub>max</sub>. Experimental results revealed that acetic acid functionalized biomass is a suitable adsorbent for removing CV from aqueous solutions. Its application in the treatment of industrial wastewater should be investigated further.

**Keywords:** Adsorption, Nonlinear Regression, Crystal Violet, Sequester, Error Function, Wastewater.

## 1. Introduction

Environmental pollution caused by dye-containing effluents discharged from a variety of industries has become a source of concern for environmentalists in recent decades. The continuous discharge of such coloured dye-containing effluents from industries is regarded as a major environmental threat, particularly because the majority of these dyes are typically non-biodegradable into non-toxic forms. Crystal Violet (CV) has numerous applications as a dye and stain for textiles, forensic, biological, and analytical samples. It is used in veterinary and human medicine as a staining agent and diagnostic dye<sup>1</sup>. It is also a known carcinogen and can cause neonatal blindness<sup>2,3</sup>. The noxious

properties of this dye, makes it critical to investigate its removal from aqueous systems.

Adsorption has been found as the most practical, low-cost, and straightforward method for removing dyes from solution. Adsorption with activated carbon as an adsorbent is the most explored adsorption method. However, because it is costly, its applicability is limited. This has prompted several researchers to investigate and develop more affordable and effective adsorbents. Agricultural waste has been reported to be a cost-effective and environmentally friendly alternative adsorbent

for wastewater remediation<sup>4</sup>. Many have been used to remove inorganic as well as organic contaminants from natural aqueous streams. Since most agricultural biomass are lignocellulosic, they contain functional groups like the phenolic, hydroxyl, and carboxylic groups, that confer them with sorptive ability. These functional groups can be chemically modified to improve the adsorption capacity of any biomass.

A number of studies have examined the use of chemically modified agro-waste-derived biomass as inexpensive adsorbents for dye sorption from aqueous streams<sup>5,6,7</sup>. Adsorption of a number of contaminants onto waste biomass reduces environmental pollution while also lowering wastewater treatment costs.

*Millettia thonningii* seed pods (MTP) are woody seed pods that fall off after the seeds have been released, resulting in a dense litter of pods with limited commercial value. In this study, MTP was treated with acetic acid to modify its surface functional groups and its applicability in adsorbing CV dye from an aqueous solution was evaluated. This research investigates the adsorption properties of Crystal violet on acetic acid-functionalized *M. thonningii* seed pods.

## 2. Materials and Methods

### 2.1 Materials

All of the reagents used were of Analar grade. The reagents are glacial acetic acid, NaOH and HCl, and Crystal violet (CV). All solutions were prepared using deionized water.

At room temperature, an aqueous solution of CV dye (C<sub>25</sub>H<sub>30</sub>N<sub>3</sub>Cl, molecular weight = 407.99, max = 589 nm) at pH 7 was used for all adsorption studies. The dye stock solution was prepared by dissolving accurately weighed dye in distilled water to a concentration of 500 mg/L. The dye solution starting concentrations were obtained by diluting the dye stock solutions in appropriate proportions to achieve distinct initial concentrations.

### 2.2 Adsorbent preparation

A simple and unique technique was used to prepare the low-cost biosorbent. *M. thonningii* seed pods (MTP) were obtained from Sabon Gari, Zaria in Kaduna State. The seeds were removed and the pods were first washed with tap water, then with deionized water to remove dirt from their surface before being air-dried for 7 days to eliminate moisture. The dried precursors were crushed in a ball mill and sieved to a particle size of 2-4 mm using conventional sieves, before being stored in clean air-tight containers and denoted as MTP. Approximately 20 g of MTP was soaked in 200 mL acetic acid, in a ratio of 3:1(acid: biomass) for 24 hrs. The acid-treated seed pods were washed thoroughly with distilled water until pH~7, oven-dried at 110 °C until a constant weight was reached, and kept in glass vials. This processed material was denoted 'FMTP'.

### 2.3 Characterization of the Pristine and Modified Biomass

The major functional groups on the surface of the MTP and FMTP prior to and after dye adsorption were identified using a Fourier Transform Infrared (FTIR) Spectrophotometer (FTIR-CARY 630, Agilent Technologies).

### 2.4 Adsorption Kinetic and Isotherm Experiments

Kinetic experiments were performed by agitating 0.1 g of FMTP with 50 mL of 10 mg/L CV solutions at a constant speed of 300 rpm. At appropriate time intervals (10–200 minutes), samples were withdrawn, centrifuged and the absorbance of the supernatants was measured spectrophotometrically with the necessary calibration curves created prior to the analysis. Under the same conditions the kinetic tests, isotherm experiments were carried out using initial dye concentrations ranging from 10 to 50 mg/L for a predetermined equilibrium time of 180 minutes. The solutions were centrifuged at 1500 rpm for 3 minutes, and the initial and residual dye concentrations were measured with a UV-Vis spectrophotometer (Agilent CARY 300) at the absorption maxima of 589 nm for CV. Eqs. (1) and (2), were used to compute the amount of dye adsorbed onto

the adsorbent at time  $t$ ,  $q_t$  (mg/g) and at equilibrium time  $q_e$  (mg/g) respectively.

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

To ensure reproducibility, all adsorption tests were performed in triplicate, with the mean values utilized during data analysis. The best fitting kinetic and equilibrium isotherm models were determined using non-linear regression analysis.

## 2.5 Analysis of Data

The nonlinear forms of pseudo-first-order (PFO), pseudo-second-order (PSO), and Elovich's kinetic models [8,9,10] were applied to analyze the kinetic experimental data. Equations (3), (4), and (5) represent the equations for the PFO, PSO, and Elovich's models, respectively.

$$q_t = q_e (1 - e^{-k_1 t}) \quad (3)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (4)$$

$$q_t = \frac{1}{\beta} \ln(1 + \alpha \beta t) \quad (5)$$

where  $q_e$  and  $q_t$  are the amounts of dye adsorbed (mg/g) at equilibrium and at time  $t$  (min), respectively,  $k_1$  ( $\text{min}^{-1}$ ) is the pseudo-first-order rate constant,  $k_2$  ( $\text{min}^{-1}$ ) is the pseudo-second-order rate constant,  $\alpha$  (mg/g min) and  $\beta$  (mg/g) are the Elovich's constants relating to initial adsorption rate and the degree of surface coverage respectively.

The isothermal equilibrium experimental data were fitted into the nonlinear Langmuir and Freundlich models expressed in equations 6 and 7 respectively

$$q_e = \frac{Q_{max} K_L C_e}{1 + K_L C_e} \quad (6)$$

$$q_e = K_F C^{1/n} \quad (7)$$

where  $q_e$  is the equilibrium adsorption capacity of adsorbent (mg/g),  $Q_{max}$  is the Langmuir saturation adsorption capacity,  $C_e$  is the equilibrium adsorbate concentration (mg/L),  $K_L$  is the Langmuir equilibrium adsorption constant (L/mg), and  $K_F$  and  $n$  are the Freundlich constants associated with adsorption capacity and intensity respectively.

The experimental data from the kinetic and equilibrium experiments were analyzed using four distinct statistical error functions, which

are represented in equations 8-11: coefficient of determination ( $R^2$ ), chi-square ( $\chi^2$ ) test, the sum of square error (SSE) and percent deviation (%D). Error functions are statistical functions that are used to calculate the difference between experimentally obtained data and the values theoretically predicted by the models. Lower error values are indicative of a better performance of the predictive models. The model with the best fit is the one with the largest  $R^2$  value and the lowest value of SSE,  $\chi^2$ , and % D.

$$R^2 = 1 - \frac{\sum (q_{e,exptal} - q_{e,calc})^2}{\sum (q_{e,exptal} - q_{e,mean})^2} \quad (8)$$

$$\chi^2 = \sum \frac{(q_{e,exp} - q_{e,calc})^2}{q_{e,calc}} \quad (9)$$

$$SSE = \sum_{i=1}^n (q_{e,exptal} - q_{e,calc})^2 \quad (10)$$

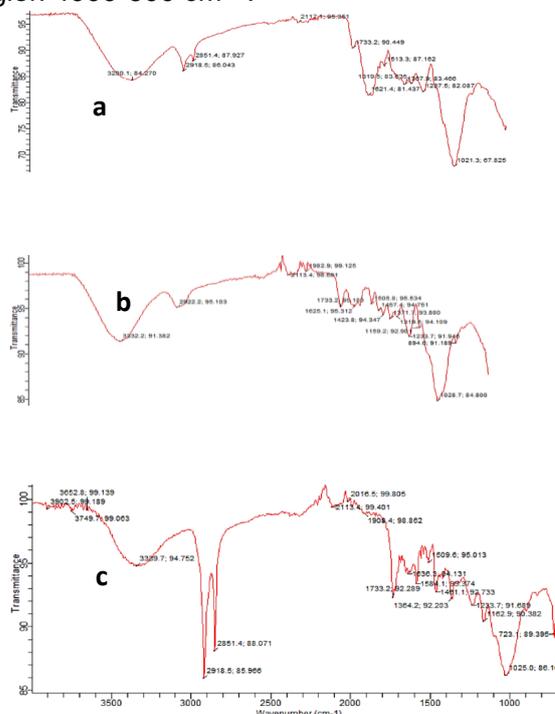
$$\%D = \frac{1}{N} \sum \left| \frac{q_{e,exptal} - q_{e,calc}}{q_{e,calc}} \right| * 100 \quad (11)$$

## 3. Results and Discussion

### 3.1 Results

#### 3.1.1 FTIR Characterization studies

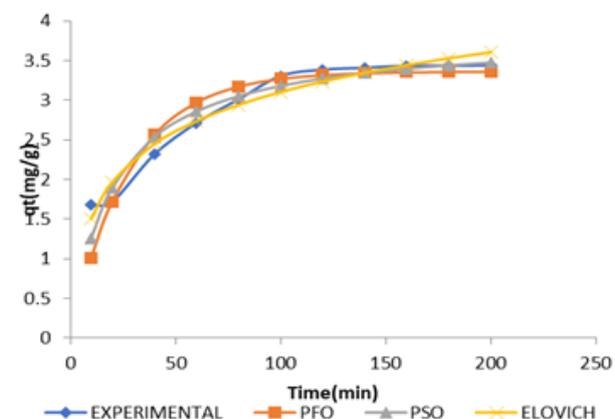
Figure 1 depicts the FTIR spectra of unmodified and chemically modified FMTP (before and after adsorption) recorded in the region 4000-600  $\text{cm}^{-1}$ .



**Figure 1:** FTIR Spectra of (a) pristine MTP (b) FMTP and (c) FMTP after CV adsorption

### 3.1.2 Adsorption Kinetics

Figure 2 depicts a graphical relationship between the kinetic experimental data and the theoretical predictions (the PFO, PSO, and Elovich models) for the adsorption system.



**Figure 2:** Kinetic Plots of the adsorption of CV onto FMTP

The kinetic parameters and error functions determined from nonlinear regression analysis for each model equation are shown in Table 1.

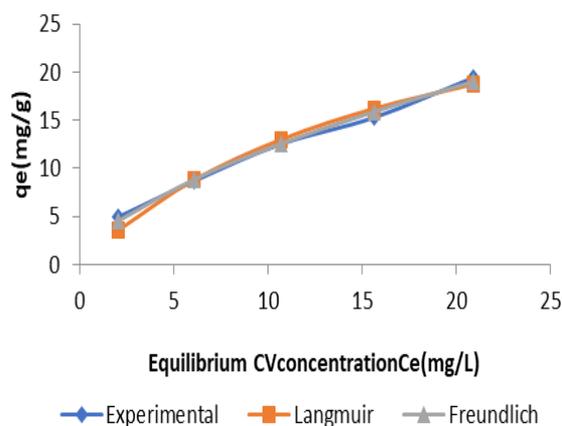
**Table 1:** Kinetic Parameters for kinetic models studied for the adsorption of CV onto FMTP

Kinetic model	Equation	Parameter	
Pseudo-first order	$qt = qe \cdot (1 - \exp(-k_1 \cdot t))$	$qe$ (mg/g)	3.3645
		$k_1$ ( $\text{min}^{-1}$ )	0.0358
		SSE	0.6266
		$R^2$	0.8688
		$\chi^2$	0.5017
		%D	10.1011
Pseudo-second order	$qt = \frac{qe^2 \cdot k_2 \cdot t}{1 + qe \cdot k_2 \cdot t}$	$qe$ (mg/g)	3.8324
		$k_2$ (g/mg min)	0.0127
		SSE	0.3141
		$R^2$	0.9342
		$\chi^2$	0.1961
		%D	6.9517
Elovich	$qt = \frac{1}{\beta} \ln(1 + \alpha\beta t)$	A	0.4956
		B	1.3647
		SSE	0.2173
		$R^2$	0.9545
		$\chi^2$	0.0917
		%D	5.3258

### 3.1.3 Equilibrium Studies

The experimental isotherm and individual model curves for the Langmuir and

Freundlich isotherm model equations generated from the studied error functions are shown in Fig. 3.



**Figure 3:** Equilibrium Isotherms of CV Sorption onto FMTP

Table 2 shows the equilibrium parameters and error functions derived for each Isotherm model equation via the nonlinear regression analysis

**Table 2:** Parameters for Isotherm Models Studied for the Sorption of CV onto FMTP

Isotherm model	Equation	Parameter	CV
Langmuir	$q_e = \frac{Q_{max} K_L C_e}{1 + K_L C_e}$	$Q_{max}$ (mg.g)	34.8270
		$K_L$	0.0055
		SSE	3.4387
		$R^2$	0.9733
		$\chi^2$	0.6311
		%D	10.5833
Freundlich	$q_e = K_f C_e^{1/n}$	$K_f$	2.8788
		N	1.6098
		SSE	0.7506
		$R^2$	0.9942
		$\chi^2$	0.0759
		%D	3.3946

## 3.2 Discussion

### 3.2.1 FTIR Analysis

The FTIR spectrum of the pristine MTP (Fig. 1a) revealed six prominent significant peaks at  $3280.1 \text{ cm}^{-1}$ ,  $2918.5 \text{ cm}^{-1}$ ,  $2851.4 \text{ cm}^{-1}$ ,  $1733.2 \text{ cm}^{-1}$ ,  $1621.4 \text{ cm}^{-1}$  and  $1021.3 \text{ cm}^{-1}$ . These peaks are characteristic of the -OH, -

CH<sub>3</sub> (methyl), -CH<sub>2</sub> (methylene), -CO stretching carbonyl functional groups respectively. FMTP (Fig. 1b) shows a partial modification in its functional group properties. An increase in the intensity of the broad peak at 3232.2 cm<sup>-1</sup> and the appearance of the peak at 2922.2 cm<sup>-1</sup> could be attributed to -OH vibrational frequency and -CO stretching of the carboxyl functional group, respectively which indicate a successful functionalization of the biomass. Increased intensity of the C = O band at 1733.2 cm<sup>-1</sup> indicates an increase in carboxylic groups<sup>11</sup>. The peak at 1621.4 cm<sup>-1</sup> and 1021.3 cm<sup>-1</sup> (Fig 1a) shifted to 1625.1 cm<sup>-1</sup> and 1025.0 cm<sup>-1</sup> (Fig 1b).

Figure 1c shows the post-CV adsorption spectra of FMTP, which was recorded to gain a better understanding of the nature of the dye adsorption mechanism. The appearance of peaks from 3652.8 to 3902.5 cm<sup>-1</sup> can be accounted for by H<sub>2</sub>O and N-H stretching from interaction with the dye molecule. The intensity of the OH group increased with a broader peak appearing at 3339.7cm<sup>-1</sup> which is attributed to hydrogen-bonded OH groups, the -NH stretch and chemisorbed water. Jin *et al.*<sup>12</sup> reported a similar observation in the functional group properties of citric acid-modified cellulose waste whose FTIR spectrum displayed an increased broadening of the O-H group thus indicating an increase in carboxylic O-H groups. The disappearance of the signal at 2922.2cm<sup>-1</sup> following CV adsorption indicates that the -CO carbonyl stretch is involved in dye adsorption. New peaks appeared at 2918.5 and 2851.4 cm<sup>-1</sup>, corresponding to the C-H stretch of alkanes. The intensity of the -CO (carboxyl group stretching vibration) peak at 1733.2 cm<sup>-1</sup> rose as well. As a result, CV adsorption by FMTP was a chemical adsorption process, with -OH and -COOH groups serving as the primary active adsorption sites.

### 3.2.2 Kinetic Experiments.

Figure 2 indicates that the rate of dye removal from solution onto FMTP rose steadily during the first 80 minutes of contact, after which it appeared to remain stable, indicating that equilibrium was reached at around 180 minutes. The pseudo-first-order

(PFO) kinetic model<sup>10</sup>, which is based on the premise that the adsorbate molecule is adsorbed onto only one active site on the adsorbent's surface, presented the lowest R<sup>2</sup> value (0.8688) and the highest  $\chi^2$  (0.5017), SSE (0.6266), and % D (10.1011). This means that it does not fit the CV adsorption data well. The PFO has previously been described as being unsuitable during the whole course of the adsorption process<sup>9</sup>.

The pseudo-second-order (PSO) model proposed first by Blanchard *et al.*<sup>9</sup> describes the adsorption process as being controlled by chemisorption involving electron sharing between the adsorbent and the adsorbate. It assumes the adsorption of the adsorbate onto two active sites of the adsorbent surface. The relative kinetic parameters for CV adsorption (Table 1) reveal that the PSO model has a higher R<sup>2</sup> value (0.93420) than the PFO model.

The Elovich model provided the best correlation to the experimental data as it exhibited the highest nonlinear R<sup>2</sup> (0.9545) values and lowest  $\chi^2$ (0.0917), SSE (0.2173), and % D (5.3258). The Elovich model assumes heterogeneity of the adsorption sites on the adsorbent<sup>12</sup>. The best fit by Elovich's model implies that the surface of the biosorbent is heterogeneous<sup>13</sup>. Based on the close-fitting of both the Elovich and PSO models, it can be implied that the sorption dynamics are predominantly chemical (chemisorption) proceeding via a chemical reaction.

### 3.2.3 Equilibrium studies

Figure 3 depicts an almost linear increase in the FMTP's equilibrium sorption capacity for CV with increasing initial dye concentration. The error functions for the isotherm models reveal that the best fitting isotherm is the Freundlich model with the highest nonlinear R<sup>2</sup> (0.9942) values and lowest  $\chi^2$ (0.0759), SSE (0.7506), and % D (5.3258) thereby providing the best correlation to the experimental data. The Freundlich exponent, 1/n, obtained in this research was 0.6212 (n value =1.6098) (Table 2), showing a favourable CV adsorption process, where exponent values between 0 and 1 indicate adsorption process favorability<sup>14</sup>. The maximum saturated monolayer adsorption

capacity of an adsorbent, which may be used to characterize the interaction between adsorbate and adsorbent, was measured as the Langmuir  $Q_{max}$  (mg/g) and was found to be 34.8270 mg/g in the examined range of adsorbate concentration (10-50 mg/L).

#### 4. Conclusion

FMTP was produced in this study by modifying MTP with acetic acid, and its adsorption ability for CV was studied. The Elovich model offered the greatest fit for the experimental kinetic data, whereas the Freundlich model better described the CV adsorption, which is controlled by the active adsorption sites (-OH and -COOH) on the FMTP surface, based on isotherm investigations. The maximum adsorption capacity of the functionalized adsorbent was 34.8270 mg/g as given by the Langmuir  $Q_{max}$ . The acetic acid functionalized biomass is a suitable adsorbent for removing CV from aqueous solutions.

#### Authors' Contributions

EEJ and VOA conceived the idea and designed the experiment. EEJ, JCO and IB conducted the experiments and analysed the results. EEJ prepared the manuscript and all authors read the manuscript.

#### Conflict of interest

The authors declare no conflict of interest.

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