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Isotherm Study of Crystal Violet on Activated Carbon Synthesized from Millet Stover

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Abstract. Continuous release of synthetic dyes from industrial effluent into surface water poses a huge environmental threat and health hazard to humans and aquatic life. The need to right the wrong occasioned by the inimical industrial practice of uncontrolled release of carcinogenic dyes into the surface water calls for research into effective treatment technologies for the treatment of dye-contaminated industrial effluent. The isotherm of Crystal Violet (CV) solution on activated carbon (AC) synthesized from millet stover was investigated and presented herein. Samples of AC were synthesized from millet stover at 120°C using phosphoric acid as the activating agent. Employing varying mix ratios of stover-to-phosphoric acid (1:0, 1:1, 1:2, 1:3, and 1:4), respective samples of AC were synthesized. The batch adsorption process of the various samples of the AC in 15 mg/l initial concentration of an aqueous solution of CV was carried out at varying times. The CV's change in the sorbate's concentration was monitored using a UV spectrophotometer. The optimum adsorption time was 240 min. The optimally synthesized activated carbon was the 1:2 sample having an equilibrium sorbent concentration of 0.74 mg/L and sorbate uptake of 95.1%. Langmuir, Freundlich and Temkin isotherm models were employed for the isotherm analysis. The R^2 values of the Langmuir, Freundlich and Temkin models were 0.99, 0.90, and 0.94, respectively. The isotherm constants for the Langmuir, Freundlich and Temkin models were -1.52 l/mg, -4.08 , and 0.005 l/min, respectively. The Langmuir isotherm model best fitted the adsorption mechanism with a maximum equilibrium adsorption capacity of 14.0 mg/g.

Keywords: millet stover, activated carbon, crystal violet, isotherm model.

1 Introduction

Activated carbon is a porous adsorbent with a highly developed internal pore structure and large surface area prepared from the activation of biomass. Activated carbon possesses active sites and is applied for the adsorption of sorbate molecules. They are usually applied in wastewater and municipal water treatments and in air purification [1].

Globally, the annual production of activated carbon was estimated to be about 100,000 tonnes [2]. The feedstock used for activated carbon production is agricultural materials which normally are disposed of as wastes [3, 4]. Examples of the agricultural wastes used in the synthesis of activated carbon include coconut shell [5], rice husk, sugarcane bagasse, sawdust [6], yam peels, potatoes peels, cassava peels, durian peel [7, 8], and watermelon. The carbon content of these materials ranges from 40 to 90% wt. [9, 10]. Activated carbon is produced by the activation process involving the thermal activation of a biomass feedstock in the presence of a chemical activating agent in an inert atmosphere. The most used activating agent for the synthesis of activated carbon is potassium

hydroxide (KOH), sodium hydroxide (NaOH), zinc chloride (ZnCl), phosphoric acid (H_3PO_4) and potassium carbonate (K_2CO_3).

Recent studies on the statistics of activating agents employed for the synthesis of the activating agent over the last two decades have shown that used KOH, NaOH, ZnCl, H_3PO_4 , K_2CO_3 , and new activating agents were 22.0, 11.0, 18.5, 21.0, 14.0, and 13.5%, respectively.

The active sites of activated carbon contain functional groups such as carboxyl, carbonyl, phenol, lactone, and quinone responsible for adsorbing contaminants. The functional group in a particular activated carbon is a function of the biomass feedstock used for the synthesis and the synthesis condition. The mechanism and extent of adsorption of sorbate molecules on activated carbon is a function of the functional group present on the active site and their chemical affinity with the sorbate molecules [2].

This work aimed to study the isotherm of adsorption of crystal violet contaminated water over a low temperature synthesized activated carbon using millet stover biomass feedstock.

2 Research Methodology

Materials used include; raw millet stover collected from a farm in Janguza, Ungogo Local Government Area of Kano State – Nigeria, Phosphoric acid, crystal violet powder, and distilled water. Equipment includes weighing balance (Model; PE-160), shaker (KJ-201 BS OSCILLATOR), UV-Vis spectrophotometer (Model; Zuzi-4201/20), milling machine, and laboratory oven. Apparatus used include measuring cylinder, conical flask, crucibles, beakers, and spatula.

Synthesis of activated carbon was synthesized at low temperatures using phosphoric acid as the activating agent. Different samples of the AC were prepared to measure a constant weight of millet stover in each case and to add a varying dosage of phosphoric acid to make 1:0, 1:1, 1:2, 1:3, and 1:4. The mixture was thoroughly mixed and then heated in the oven at 120 °C for 1 h. After activation, the activated carbon was washed with distilled water until the pH was 7.0. The washed AC samples were dried in the oven at 110 °C for 1 h to remove the moisture content.

Adsorption study of aqueous CV solution (sorbate) on varying samples of synthesized AC (sorbent) was carried out using 50 ml of CV sorbate at the constant initial concentration of 15 mg/l. The adsorption process was carried out by continuous mechanical shaking action of a laboratory shaker. The percentage sorbate uptake (%A) and the equilibrium adsorption capacity of the sorbent, q_e (mg/g) were determined by the following equations:

$$\%A = \frac{C_0 - C_e}{C_0} \times 100; \quad (1)$$

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

where C_0 – the initial concentration of the sorbate; C_e – equilibrium concentration of the sorbate; m – the weight of adsorbent, g; v – the volume of the sorbate, l.

An isotherm study of the adsorption of CV sorbate on the synthesized AC was carried out using Langmuir, Freundlich, and Temkin models. Graphical analysis of the linearized form of the various isotherm models was carried out using experimental laboratory data to establish the various model parameters.

The Langmuir isotherm mechanism is based on the monolayer adsorption model and depicts homogeneity in the adsorbent surface [17]. The Langmuir isotherm model is as follows:

$$q_e = \frac{q_\infty b C_e}{1 + b C_e}, \quad (3)$$

where q_∞ – the monolayer theoretical capacity of the adsorbent or the maximum achievable adsorption density (mg of adsorbate per 1 g of adsorbent); b – the Langmuir equilibrium constant, l/mg.

The linearized Langmuir isotherm model is as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_\infty} + \frac{1}{q_\infty b}. \quad (4)$$

The Freundlich isotherm mechanism is based on a multilayer adsorption model, and depicts heterogeneity in the adsorbent surface [11]. The Freundlich isotherm

mechanism is based on the multilayer heterogeneous adsorption model. The isotherm model is as follows:

$$q_e = K_f C_e^{1/n}, \quad (5)$$

where K_f – the Freundlich multilayer adsorption constant, related to bond strength and the dimensionless heterogeneity factor, l/g; n – adsorption intensity.

The linearized form of the Freundlich isotherm model is as follows [12]:

$$\log q_e = \log K_f + 1/n \log C_e. \quad (6)$$

The Temkin isotherm mechanism is based on the interaction between the adsorbent surface and the sorbate molecules/ions. The isotherm is developed on the assumption that the free energy of sorption is a function of the surface coverage [13, 14]. The Temkin isotherm model is as follows:

$$A_t C_e = e^{\frac{q_e b_t}{RT}}, \quad (7)$$

where C_e – concentration of the adsorbate at equilibrium, mg/l; q_e – the amount of adsorbate adsorbed at equilibrium, mg/g; T – the absolute temperature, K; R – the ideal gas constant, J/(mol · K); $\frac{RT}{b_t}$ – a measurement of heat of adsorption; $\frac{1}{b_t}$ – the adsorption potential of the adsorbent, mol/kJ.

A_t – Temkin constant as the equilibrium binding constant (l/min), corresponding to the maximum binding energy. Linearized Freundlich isotherm model is as follows:

$$q_e = \left(\frac{RT}{b_t}\right) \ln A_t + \left(\frac{RT}{b_t}\right) \ln C_e. \quad (8)$$

3 Results and Discussion

Table 1 presents the adsorption results using varying samples of the synthesized AC.

Table 1 – Percentage uptake of CV on the various samples of the synthesized AC

AC Sample	C_e , mg/l	%A
1:0	2.1942	85.37
1:1	0.9427	93.72
1:2	0.74089	95.06
1:3	0.9546	93.64
1:4	0.9974	93.35

It could be observed that the inactivated sample of the millet stover (1:0) had a sorbate uptake of 85.4%. However, the 1:1 AC sample gave 8.3% higher sorbate uptake, while a further increase of 1.3% was observed for the 1:2 AC sample. The sorbent uptake declined for the AC samples having a higher dosage of an activating agent. Therefore, the 1:2 AC sample was considered the optimum synthesized AC sample with an equilibrium sorbent concentration of 0.74 mg/l and sorbate uptake of 95.1%.

For the adsorption carried out using the 1:2 sample, Table 2 presents the equilibrium sorbate concentration at varying adsorption times.

Table 2 – Equilibrium sorbate concentration and adsorption capacity at varying adsorption time

Time, min	C_e , mg/l	q_e , mg/g
30	6.01	15.00
60	3.50	19.20
90	2.86	20.20
120	2.51	20.82
150	1.68	22.20
180	1.94	21.76
240	1.77	22.06
270	1.62	22.30

Starting with the initial sorbate concentration of 15 mg/l, the equilibrium sorbate concentration dropped by 60% after 30 min to attain a value of 6.01 mg/l.

Using equation (1), the equilibrium adsorption capacity after 30 min was 15.0 ml/l. With a further increase in the adsorption time, the equilibrium sorbate concentration dropped until no substantial decrease was observed after 240 min.

Figure 1 shows the Freundlich isotherm graph for the adsorption of CV sorbate on the sorbent synthesized from millet stover.

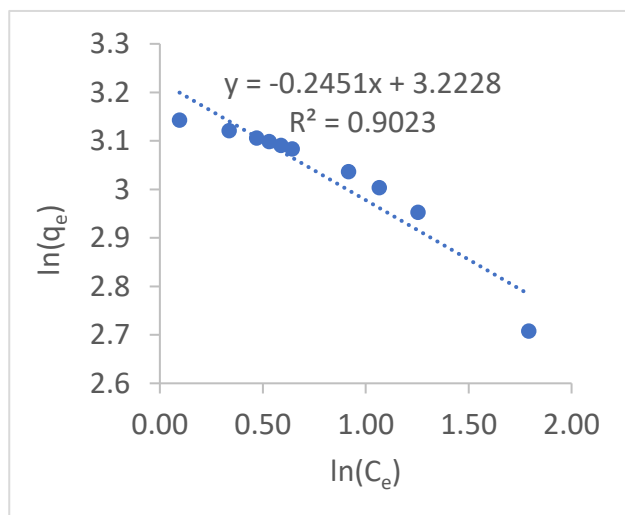


Figure 1 – Freundlich isotherm graph of the adsorption process

The Freundlich model properly fits the adsorption mechanism with an R^2 of 0.90. The graph had a negative slope of -0.2451 and a positive intercept of 3.2. Therefore, the Freundlich multilayer adsorption constant, K_f was 1,584.9 l/g, and the dimensionless heterogeneity factor, n was -4.08 .

Figure 2 shows the Langmuir isotherm chart of the adsorption of the sorbate on the sorbent.

The high coefficient of determination, R^2 of 0.99 showed that the Langmuir model fitted the adsorption mechanism perfectly. The graph's slope was 0.0715 g/mg, and the intercept was -0.0471 . Therefore, the maximum adsorption capacity of the sorbent was 14.0 mg/g. Langmuir constant, b was determined as -1.52 l/mg.

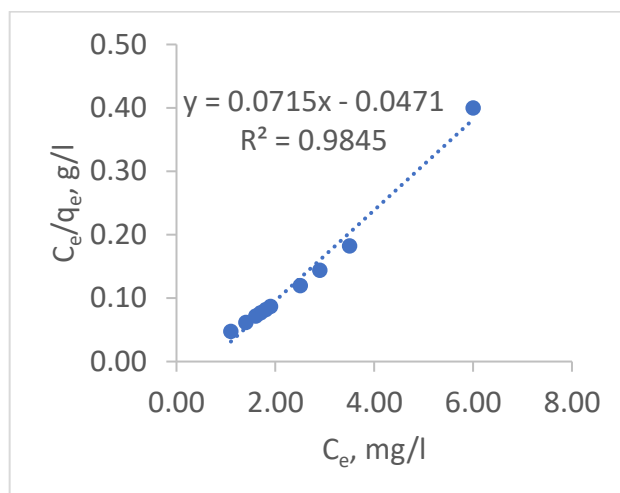


Figure 2 – Langmuir isotherm graph of the adsorption process

Figure 3 shows the Temkin graph for the adsorption of CV sorbate on the synthesized sorbent.

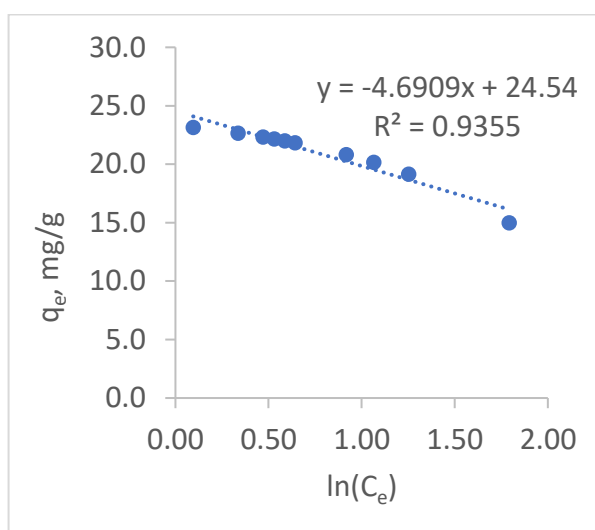


Figure 3 – Temkin isotherm graph of the adsorption process

The Temkin model also gave a good fit of the adsorption mechanism with a fairly R^2 of 0.94. The graph had a negative slope of -4.69 and a positive intercept of 24.54. The adsorption process was conducted at 298 K, using the gas constant of 8.314 J/(mol·K), the adsorption potential of the adsorbent $\frac{1}{b_t}$ was -0.002 mol/kJ, and the maximum binding energy A_t was 0.005 l/min.

Table 3 presents a summary of the various adsorption parameters determined for the adsorption of CV on the AC synthesized from millet stover.

Table 3 – Summary of the various isotherm parameters

Langmuir		Freundlich		Temkin	
R^2	0.99	R^2	0.90	R^2	0.94
q_e , mg/g	14.0	K_f , l/g	1,584.9	$\frac{1}{b_t}$, mol/kJ	-
b , l/mg	-1.52	n	-4.08	A_t , l/min	0.005

It could be observed that Langmuir was the best fit based on the R^2 value.

The Langmuir isotherm had the highest R^2 value of 0.99. This implied that the adsorption process was homogeneous monolayer adsorption [15, 16].

The equilibrium adsorption capacity was 14.0 mg/g, and the Langmuir constant was negative, having a value of -1.52 l/mg. This further implied that the sorbate molecules had a negative binding affinity to the site of the sorbent [17].

Although the Freundlich isotherm gave a reasonably high R^2 value of 0.90, the isotherm model was unsuitable for the adsorption mechanism as the Freundlich constant, n representing the multilayer adsorption intensity, was negative [18].

The Temkin isotherm model also gave a reasonably high R^2 value of 0.94. It had a negative adsorption potential, implying that the Temkin model was not a good fit for the adsorption mechanism.

4 Conclusions

Adsorption isotherm study of crystal violet solution over activated carbon synthesized from millet stover at low temperature was carried out.

Activation of the stover millet was carried out at $120\text{ }^\circ\text{C}$ using phosphoric acid as the activating agent. Varying sorbent samples based on the activating agent's dosage were prepared. They were 1:0, 1:1, 1:2, 1:3, and 1:4 samples.

The Adsorption study showed that the 1:2 sample was the optimum, with an equilibrium sorbent concentration of 0.74 mg/l and sorbate uptake of 95.1 %. The adsorption isotherm study using Langmuir, Freundlich, and Temkin isotherm models showed Langmuir's coefficient of determination (R^2), Freundlich, and Temkin models were 0.99, 0.90, and 0.94, respectively. The adsorption process was homogeneous monolayer adsorption as the Langmuir isotherm model gave the best fit for the adsorption mechanism having a maximum equilibrium adsorption capacity of 14.0 mg/g and the Langmuir constant of -1.52 l/mg. The sorbate molecules had a negative binding affinity to the site of the sorbent, as suggested by the negative value of the Langmuir adsorption constant.

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