Adsorption of Crystal Violet on Rice Husk Activated Carbon

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Abstract. The need to develop effective technology for the treatment of liquid effluent of dye-intensive industries such as textile, rubber, paint, and printing is synonymous with the need to save the life-threatening risks posed by these carcinogenic and mutagenic pollutants on human and aquatic lives. Isotherms of adsorption of crystal violet (CV) on activated carbon (AC) synthesized from rice husk are presented herewith to elucidate the mechanism of the adsorption process of crystal violet dye contaminated water on rice husk activated carbon. AC was synthesized from rice husk via a phosphoric acid activating agent at low temperatures. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D-R) isotherm studies were employed. The mean square values for Langmuir, Freundlich, Temkin and D-R models were 0.98, 0.91, 0.94, and 0.63, respectively. Analysis of the isotherms of the adsorption of crystal violet sorbate on the synthesized rice husk sorbent suggested that the adsorption process proceeded via a homogeneous monolayer mechanism. Langmuir isotherm gave the best fit of the adsorption process. Langmuir isotherm constant was –1.40 l/mg, and the equilibrium adsorption capacity was 13.53 mg/g.

Keywords: process innovation, adsorption isotherm, rice husk, activated carbon, crystal violet, energy efficiency.

1 Introduction

Water, an essential lifeline to the survival of humanity and all organisms, is continually being polluted by the day-to-day polluting activities of man, majorly industrial activities. Industrial activities such as textile, rubber, printing, pulp, paper, paint, and cosmetics production employ large volumes of dyes that are eventually released as effluents into the water bodies that provide drinking water for human communities. To avoid or at best reduce the high health risk associated with consumption of the carcinogenic and mutagenic industrial dyes such as crystal violet, effective technology for the treatment of the liquid effluent from dye intensive industries must be given the attention deserves. Dyes are classified as either natural or synthetic. Crystal violet (CV) is one of the dyes used in the textile industry, and it is synthetic. As a synthetic cationic dye, CV is a toxic dye [1, 2].

Treatment of the textile industry's liquid effluent becomes very indispensable to remove dyes and ensure safe effluent discharge to water bodies. Different conventional treatments methods such as precipitation, photo-catalytic decolorization, coagulation, flocculation, membrane separation, adsorption, electrochemical and biological degradation have been examined with varying levels of success by researchers [3]. Of all these methods, the adsorption process has gained more interest in recent times due to its benefits of high efficacy and economic benefits over other methods [4]. Adsorption is a process that occurs when molecules of a gas or liquid solute (sorbate) accumulate on the surface of a solid (sorbent). The adsorption is achieved by the physical or chemical interaction of the sorbate molecules with the active sites presented onto the surface of the sorbent [5–7].

Activated carbon is porous, a carbonaceous material having significant surface area activities for the adsorption of sorbate molecules. Internal pore structure and active sites dominated surfaces of oxygenated functional groups [8–10]. Activated carbon is applied in most industrial water treatment processes such as water treatment plants and municipal waterworks stations. It is also applied to treat industrial liquid and gas effluents as a strategy for pollution control from the source. Activated carbon is also used in other industrial applications where its adsorption potential is exploited for decolorization and deodorization applications such as decolorization of and deodorization of vegetable oil. Activated carbon is synthesized by controlled thermal and acidification of carbonaceous materials such as wood chips, fly ash, and corn cobs rice husk [11–14]. A good choice of raw material for the

synthesis of activated carbon comes with the dual benefit of providing effective adsorption and converting waste to wealth. This work aimed to study the adsorption isotherm of adsorption of dye (CV) contaminated water over a low temperature synthesized activated carbon using rice husk as the raw material.

2 Research Methodology

Sample of rice husk was collected from Gidan Shinkafa Rice Milling Industry, Dakata Area, Kano State. Phosphoric acid and crystal violet powder were purchased, and distilled water was prepared from a water distiller. Equipment used include 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.

Dried raw millet stover collected from the farm was washed to remove debris and other impurities. The washed millet stover was sun-dried for two days, after which it was crushed and milled using a milling machine.

Synthesis of activated carbon was carried out at low temperatures using phosphoric acid as the activating agent. 1:2 weight of powdered rice husk and phosphoric acid was measured into a crucible and mixed, which means 5.0 g powdered rice husk plus 10.0 g phosphoric acid. The homogenized mixture was heated at 120 °C for 1 h. After the synthesis, washing to a pH of 7.0 with distilled water was carried out. The washed adsorbent was dried in an oven at 110 °C for 1 h.

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

$$\%A = \frac{C_o - C_e}{C_o} \cdot 100; \tag{1}$$

$$q_e = \frac{C_o - C_e}{m} v, \tag{2}$$

where C_O – 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.

Isotherm study of the adsorption of CV sorbate on the synthesized sorbent was carried out using Langmuir, Freundlich, Temkin, and Dubini–Radushkevich (D-R) models. Linearized isotherm models were employed. Graphical analysis of the various adsorption parameters of the models obtained from experimental data was carried out to establish the various model parameters.

The Langmuir isotherm mechanism is based on the monolayer adsorption model, and it depicts homogeneity in the adsorbent surface [15]. The Langmuir isotherm model is as given:

$$q_e = \frac{q_\infty b C_e}{1 + b C_e}, \tag{3}$$

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 presented:

$$\frac{C_e}{q_e} = \frac{C_e}{q_\infty} + \frac{1}{q_\infty b}. \tag{4}$$

The Freundlich isotherm mechanism is based on a multilayer adsorption model, and it depicts heterogeneity in the adsorbent surface [16]. The Freundlich isotherm mechanism is based on a multilayer heterogeneous adsorption model. The isotherm model is as given:

$$q_e = K_f C_e^{\frac{1}{n}}, \tag{5}$$

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

The linearized form of the Freundlich isotherm model is as given [17]:

$$log\ q_e = log\ K_f + \frac{1}{n} log\ C_e. \tag{6}$$

The Temkin isotherm mechanism is based on the interaction between the adsorbent surface and the sorbate molecules/ions. The isotherm is developed to assume that the free energy of sorption is a function of the surface coverage [18, 19].

The Temkin isotherm model is as given:

$$A_t C_e = e^{\frac{q_e b_t}{RT}}, \tag{7}$$

where C_e – concentration of the adsorbate at equilibrium, mg/l, q_e – the amount of adsorbate adsorbed at equilibrium, mg/g; T – the temperature, K; R – the ideal gas constant; RT/b_t – a measurement of heat of adsorption; $1/b_t$ – 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 presented:

$$q_e = \frac{RT}{b_t} ln A_t + \frac{RT}{b_t} ln C_e. \tag{8}$$

The D-R isotherm model is based on Gaussian energy distribution onto a heterogeneous surface. It attempts to estimate the heterogeneity of the surface energies of the adsorbent in an adsorption process. The D-R isotherm model is as given:

$$\frac{q_e}{q_m} = e^{-\beta \varepsilon^2}, \tag{9}$$

where q_m – the theoretical saturation capacity, mg/g; ε – the Polyani potential; β – the Dubinin-Rudushkevich isotherm constant related to the mean free energy of adsorption per mole of the adsorbate, mol²/kJ².

Unlike the other isotherm models, the D-R model makes provision to analyze the type of sorption taking place in an adsorption process. Value of the mean free

energy E, kJ/mol, of adsorption per molecule of the adsorbate approaching the adsorbent from infinity is used to interpret the type of sorption. E is related to β according to [18]:

$$E = \frac{1}{\sqrt{2\beta}}. \qquad (10)$$

For a chemisorption process, the value of E ranges between 8–16 kJ/mol, whereas for a purely physical sorption process $E < 8$ kJ/mol [18].

The linearized Dubinin-Redushkevich isotherm model is as presented:

$$ln q_e = ln q_m - \beta \varepsilon^2, \qquad (11)$$

where $\varepsilon = RT ln \left(1 + \frac{1}{c_e}\right)$.

3 Results

Figure 1 shows the spectrophotometer absorbance of crystal violet (at the wavelength of 565 nm) at varying concentrations of the aqueous crystal violet solution.
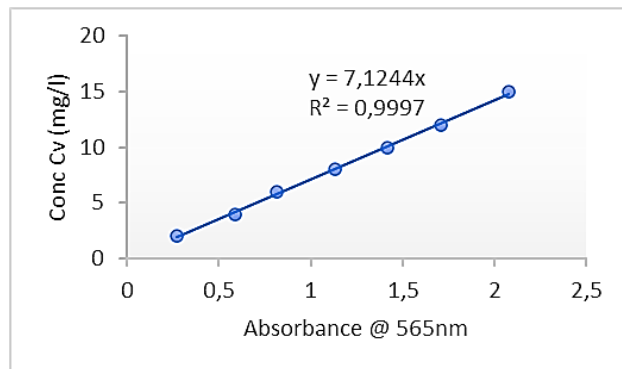

Figure 1 – Spectrophotometer absorbance
at a varying concentration of CV

The curve representing the sorbate concentration calibration curve shows a linear relationship between the sorbate concentration and the absorbance. This was used to determine concentrations of sorbate throughout the adsorption study.

Table 1 shows the adsorption equilibrium sorbate concentration at varying contact times.

Table 1 – Equilibrium concentration and adsorption capacity at varying contact time

Time, min	C_e, mg/l	q_e, ml/l
30	6.4	14.3
60	4.8	17.1
90	3.3	19.6
120	2.8	20.3
150	2.2	21.3
180	2.1	21.5
210	1.9	21.9
240	1.5	22.5
270	1.3	22.9
300	1.2	23.0

After starting with the initial sorbate concentration of 15 mg/l, the equilibrium sorbate concentration dropped by 57 % after 30 min to attain 6.4 mg/l. The equilibrium adsorption concentration and adsorption capacity after 30 min were 6.4 mg/l and 14.3 ml/l, respectively.

The equilibrium sorbate concentration value dropped continuously from 6.4 mg/l at 30 min until a relatively constant value of 1.2 mg/l was attained at 300 min. Conversely, the equilibrium adsorption capacity increased continuously from 14.3 ml/l at 30 min until a relatively constant value of 23 mg/l was attained at 300 min. Hence, the adsorption process tends to equilibrium in 300 min.

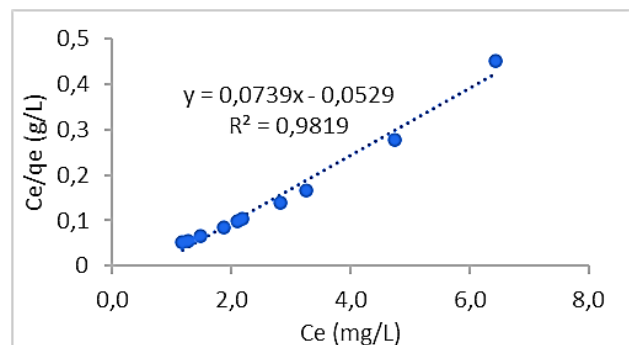Figure 2 shows the Langmuir isotherm chart of the adsorption process.

Figure 2 – Langmuir isotherm graph for the adsorption process

A high R^2 of 0.98 showed that the Langmuir model perfectly fit the adsorption mechanism. The graph's slope was 0.074 g/mg. The maximum adsorption capacity of the process was 13.53 mg/g. Langmuir constant b was determined as –1.40 l/mg.

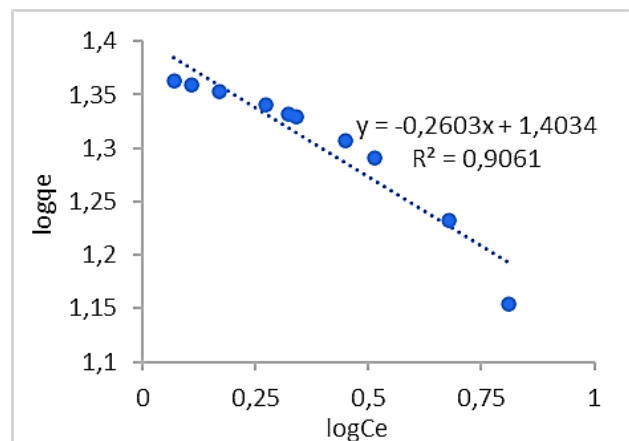Figure 3 shows the Freundlich isotherm graph for the adsorption of the process.

Figure 3 – Freundlich isotherm graph of the adsorption process

The Freundlich model was a fairly representing fit of the adsorption mechanism with a high R^2 of 0.91. The slope and intercept were –0.260 and 1.403, respectively. The Freundlich multilayer adsorption constant K_f was 25.3 l/g, and the dimensionless heterogeneity factor n was –3.84.

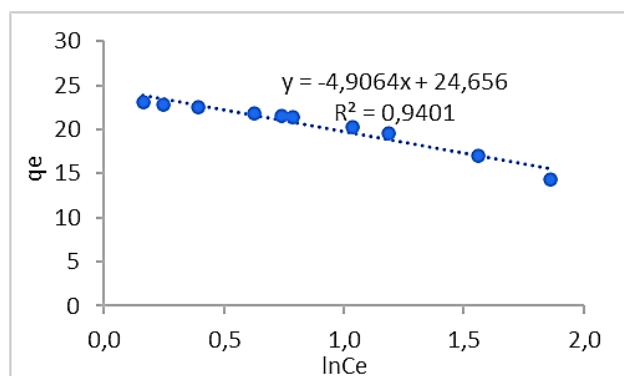Figure 4 presents the Temkin isotherm graph for the adsorption process.

Figure 4 – Temkin isotherm graph of the adsorption process

Figure 5 shows the D-R graph for the adsorption process.
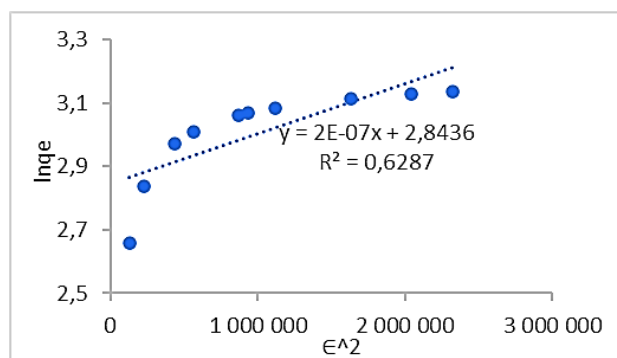
Figure 5 – D-R isotherm graph of the adsorption process

Freundlich model was also a good fit for the adsorption mechanism having an R^2 of 0.94. The slope and intercept were –4.906 and 24.656, respectively. The adsorption process was conducted at 298 K, using a constant gas value of 8.314 J/(mol·K), the adsorption potential of the adsorbent $1/b_t$ was –0.002 mol/kJ, and the maximum binding energy A_t was 0.007 l/min.

The D-R model did not fit the adsorption mechanism with a poor coefficient of determination, R^2 of 0.63. The slope and intercept were $2.0 \cdot 10^{-7}$ and 4.844, respectively. The theoretical saturation capacity q_m was 17.18 mg/g, and the mean free energy factor of adsorption per mole of the adsorbate β was $-7.0 \cdot 10^{-7}$ mol^2/kJ^2.

Table 2 summarizes the various adsorption parameters determined for the adsorption of CV on the synthesized rice husk AC.

Table 2 – Summary of the various isotherm parameters

Langmuir		Freundlich		Temkin		D-R	
R^2	0.98	R^2	0.91	R^2	0.94	R^2	0.63
q_e, mg/g	13.53	K_f, l/g	25.3	$1/b_t$, mol/kJ	–0.002	q_m, mg/g	17.18
b, l/mg	–1.40	n	–3.84	A_t, l/min	0.007	β, mol^2/kJ^2	$-7.0 \cdot 10^{-7}$

Therefore, the Langmuir isotherm model was the best fit for the adsorption mechanism based on its highest R^2 value of 0.98. Therefore, the adsorption process was homogeneous monolayer adsorption [7, 10]. The equilibrium adsorption capacity was 13.53 mg/g, and the Langmuir constant was negative with a value of –1.40 l/mg.

This implied that the sorbate molecules had a negative binding affinity to the site of the sorbent [15]. Although the Freundlich isotherm gave a high R^2 value of 0.91, the isotherm model was unsuitable for the adsorption mechanism as the Freundlich constant n representing the multilayer adsorption intensity was negative. Hence, the adsorption of CV sorbate molecules on the synthesized AC was not multilayer adsorption. The D-R isotherm representing non-homogenous multilayer adsorption [18] gave the poorest fit of the adsorption mechanism as the R^2 of D-R was the least, having the value of 0.63.

4 Conclusions

Isotherm study of aqueous crystal violet adsorption on activated carbon synthesized from rice husk was carried out using Freundlich, Temkin, Langmuir, and D-R isotherm models.

The R^2 values of the Langmuir, Freundlich, Temkin, and D-R models were 0.98, 0.91, 0.94, and 0.63, respectively. The Langmuir isotherm constant b was –1.40 l/mg. Freundlich isotherm constant n was –3.84. Temkin isotherm constant was 0.007 l/min, and D-R isotherm constant was $-7.0 \cdot 10^{-7}$ mol^2/kJ^2.

Analysis of the isotherms of the adsorption of crystal violet sorbate on the synthesized rice husk sorbent suggested that the adsorption process was homogeneous monolayer adsorption having Langmuir isotherm as the best fit of the adsorption mechanism. This result is consistent with the literature. Most adsorption studies of crystal violet and methyl blue dyes have been reported to fit well with the Langmuir isotherm model [10, 20, 21].

The equilibrium adsorption capacity was determined as 13.53 mg/g. A negative Langmuir constant obtained suggested that the sorbate molecules had a negative binding affinity to the site of the sorbent. The Temkin isotherm gave the second-best fit for the adsorption mechanism with an R^2 value of 0.94. The D-R model was the poorest fit of the adsorption mechanism of this study.

References

1. Hao, O. J., Kim, H., Chiang, P. C. (2000). Decolorization of waste water. *Critical Reviews in Environmental Science and Technology*, Vol. 30(4), pp. 449-505.
2. Bertolini, T. C. R., Izidoro, J. C., Magdalena, C. P., Fungaro, D. A. (2013). Adsorption of crystal violet dye from aqueous solution to zeolites from coal fly and bottom ashes. *Orbital: The Electronic Journal of Chemistry*, Vol. 5(3), pp. 179-191.
3. Ma, H. T., Ly, H. C., Pham, N. B., Nguyen, D. C., Vo, K. T. D., Tuan, P. D. (2017). Effect of the carbonization and activation process on the adsorption capacity of rice husk activated carbon. *Vietnam Journal of Science and Technology*, Vol. 55(4), pp. 494-494.
4. Parshetti, G. K., Parshetti, S. G., Telke, A. A., Kalyani, D. C., Doong, R. A., Govindwar, S. P. (2011). Biodegradation of crystal violet by Agro bacterium radiobacter. *Journal of Environmental Sciences*, Vol. 23(8), pp. 1384-1393.
5. Ojedokun, A. T., Bello, O. S. (2016). Sequestering heavy metals from wastewater using cow dung. *Water Resources and Industry*, Vol. 13, pp. 7-13.
6. Sarma, G. K., Gupta, S. S., Bhattacharyya, K. G. (2019). Nanomaterials as versatile adsorbents for heavy metal ions in water: A review. *Environ. Sci. Pollut. Control Ser.*, Vol. 26, pp. 6245-6278.
7. Somsesta, N., Sricharoenchaikul, V., Aht-Ong, D. (2020). Adsorption removal of methylene blue onto activated carbon/cellulose biocomposite films: equilibrium and kinetic studies. *Mater. Chem. Phys.*, Vol. 240, 122221.
8. Danish, M., Ahmad, M., T. (2018). A review on utilization of wood biomass as a sustainable precursor for activated carbon production and application. *Renew. Sustain. Energy Rev.*, Vol. 87, pp. 1-21.
9. Gonzalez-Garcia, P. (2018). Activated carbon from lignocellulosics precursors: A review of the synthesis methods, characterization techniques and applications. *Renew. Sustain. Energy Rev.*, Vol. 82; pp. 1393-1414.
10. Zakaria, R., Jamalluddin, N. A., Bakar, Z. M. A. (2021). Effect of impregnation ratio and activation temperature on the yield and adsorption performance of mangrove based activated carbon for methylene blue removal. *Results in Materials*, Vol. 10, 100183.
11. Canales-Flores, R. A., Prieto-García, F. (2020). Taguchi optimization for production of activated carbon from phosphoric acid impregnated agricultural waste by microwave heating for the removal of methylene blue. *Diam. Relat. Mater.*, Vol. 109, 108027.
12. Mandal, A., Bar, N., Das, S. K. (2020). Phenol removal from wastewater using low-cost natural bioadsorbent neem (Azadirachta Indica) leaves: Adsorption study and MLR modeling. *Sustainable Chemistry and Pharmacy*, Vol. 17, 100308.
13. Mansour, R. A., El Shahawy, A. Attia, A., Beheary, M. S. (2020). Brilliant green dye biosorption using activated carbon derived from guava tree wood. *Int. J. Chem. Eng.*, Vol. 20, 8053828.
14. Tang, S. H., Zaini, M. A. A. (2020). Development of activated carbon pellets using a facile low-cost binder for effective malachite green dye removal. *J. Clean. Prod.*, Vol. 253, 119970.
15. Islam, M. A., Chowdhury, M. A., Mozumder, M. S. I., Uddin, M. T. (2021). Langmuir adsorption kinetics in liquid media: Interface reaction model. *ACS Omega*, Vol. 6, pp. 14481-14492.
16. Sadegh, H., Ali, G.A.M., Gupta, V. K., Makhlouf, A. S. H., Shahryari-Ghoshekandi, R., Nadagouda, M. N., Sillanpaa, M., Megiel, E. (2017). The role of nanomaterials as effective adsorbents and their applications in wastewater treatment. *J. Nanostructure Chem.*, Vol. 7, pp. 1-14.
17. Salahudeen, N., Ahmed, A. S., Al-Muhtaseb, A. H., Dauda, M., Waziri, S. M., Jibril B. Y. and Al-Sabahi, J. (2015). Synthesis, characterization and adsorption study of nano-sized activated alumina synthesized from kaolin using novel method. *Powder Technology*, Vol. 280, pp. 266-272.
18. Das, B., Mondal, N. K., Bhaumik, R., Roy, P. (2014). Insight into adsorption equilibrium, kinetics and thermodynamics of lead onto alluvial soil. *Int. J. Environ. Sci. Technol.*, Vol. 11, pp. 1101-1114.
19. Said, K. A. M., Ismail, N. Z., Jama'in, R. L., Alipah, N. A. M., Sutan, N. M., Gadung, G. G., Baini, R., Zauzi, N. S. A. (2018). Application of Freundlich and Temkin Isotherm to Study the Removal of Pb(II) Via Adsorption on Activated Carbon Equipped Polysulfone Membrane. *International Journal of Engineering & Technology*, Vol. 7(3.18), pp. 91-93.
20. Senthilkumaar, S., Kalaamani, P., Subburaam, C. V. (2006). Liquid phase adsorption of Crystal violet onto activated carbons derived from male flowers of coconut tree. *Journal of Hazardous Materials*, Vol. B136, pp. 800-808.
21. Aydogmus, R., Depci, T., Sarikaya, M., Kul, A. R., Onal, Y. (2016). Adsorption of Crystal violet on activated carbon prepared from coal flotation concentrate. *IOP Conf. Series: Earth and Environmental Science*, Vol. 44, 052022.