

Removal of Crystal Violet Dye by Adsorption onto *Picrilima Nitida* Stem Bark Powder: Kinetics and Isotherm Studies

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Abstract: The removal of Crystal Violet (CV) dye with the powder of *picrilima nitida* stem bark (PNSBP) has been demonstrated based on adsorption parameters like contact time, initial dye concentration, adsorbent dose, pH, and temperature. The adsorbent was characterized by FTIR and SEM analysis. Equilibrium amount of CV dye adsorbed per unit mass of PNSBP adsorbent, q_e (mg/g), occurred after 60 min. contact time. The q_e values increased with increasing initial CV dye concentration from 25 mg/L to 125 mg/L, and with pH increasing from 2 to 10. However, the q_e value continuously decreased as temperature increased from 30 °C to 70 °C and PNSBP adsorbent dosage from 0.5 g to 4 g. Based on values of correlation coefficient (R^2), the Freundlich isotherm was more appropriate in explaining the mechanism of the CV adsorption onto PNSB. Kinetic studies showed that the CV dye adsorption onto PNSB adsorbent followed the pseudo second order reaction kinetics. Thermodynamic quantities were evaluated and the negative ΔG^0 values obtained indicated spontaneous adsorption process. The negative ΔH^0 and ΔS^0 values obtained indicate the exothermic nature and decrease in randomness during the adsorption process respectively.

Keywords: Adsorption, Crystal Violet, isotherm, Kinetics, *Picrilima Nitida*

I. Introduction

Dyes are heavily employed as coloration ingredients in many pharmaceutical, plastic, textile and food processing industries. One important dye, extensively used in textile dyeing and paper printing, is Crystal Violet also known as Basic Violet 3. A well-known cationic dye, Crystal Violet is usually employed for biological staining, as a dermatological agent, and as an additive to poultry feed to inhibit propagation of mold, intestinal parasites and fungus [1]. The discharge of dyes as constituents of the wastewaters from these industries, into several important water bodies, has become a major environmental concern. The adverse effects of the dyes include the reduction in the level of penetration of sunlight and oxygen necessary for the survival of water organisms and plants, as well as the formation of carcinogenic and toxic by-products during their natural degradation [2-4]. It is, therefore, very paramount to remove these dyes from the wastewaters before they are discharged into the water bodies. Compared with techniques like filtration, precipitation, coagulation and ozone treatment for the removal of dyes from wastewaters, adsorption technique has enjoyed greater application because of its simplicity and very low cost involvement.

Adsorbents obtained from plant materials are currently being researched as effective substitutes for conventional adsorbents like activated charcoal; since the plant materials are relatively cheaper, readily more available and effectively regenerated after use [5-9]. *Picralima nitida* is a plant material which has gained wide application in Nigeria tradomedicine as an agent for the treatment of various fevers, hypertension, jaundice, gastro-intestinal disorder, as well for malaria [10]. Similarly, the extracts from the seed, stem and roots of *Picralima nitida* have been reported to be effective for suppressing cough and as an aphrodisiac and hypoglycaemic agent in treatment of diabetes [11, 12]. Nevertheless, the application of the *picrilima nitida* plant parts as effective adsorbent for the removal of dyes has not been really considered. In view of this, the present study aims at investigating the removal of Crystal Violet dye from aqueous solution using *picrilima nitida* stem bark powder as a low cost adsorbent.

II. Experimental

1.1. Preparation of adsorbent

The *Picrilima nitida* stem barks (PNSB) were collected locally and identified at the Department of Crop Science at the Federal University of Technology Owerri, Nigeria. The stem barks were thoroughly washed with tap water and, thereafter, with distilled water until all dirt and sand were removed. The stem barks were then dried at 50 °C in an oven until moisture content was greatly negligible. The dried stem barks were then

grinded so that the particles could pass through 150 μm mesh sieve size, collected into air-tight containers and kept in air-tight desiccators to be used as adsorbent without further preparation.

1.2. Preparation of Crystal Violet (CV) dye solution

In order to prepare the stock solution of Crystal Violet (CV) dye solution, 1 g of commercially available CV (Fluka grade) was dissolved in 1 L of distilled water to obtain a stock concentration of 1000 mg/L. Experimental dye solutions of desired dye concentrations were prepared by appropriate dilution of stock solution.

1.3. Adsorbent Characterization

Fourier transform infra-red (FTIR) spectrophotometer was used to identify the different functional groups available on the adsorbent sites. The FTIR of the adsorbent was taken before and after adsorption of methyl red using FTIR spectrophotometer (Shimadzu-8400S). The adsorbent was encapsulated with KBr spectroscopy grade and by introducing the mix in a piston's cell of a hydraulic pump with compression pressure 15KPa/cm², the solid translucent disk was obtained. The FTIR spectrum was then recorded within the wave number range 4000 – 500cm⁻¹. In addition, surface morphology and texture of the adsorbent was analyzed using scanning electron microscope (SEM) (Model-PHENOM ProX). Prior to scanning, some quantity of the adsorbent was placed on a double adhesive sticker placed in a sputter machine for 5 sec; this gave the adsorbent a conductive property. Sample (adsorbent) stud was fixed on a charge reduction sample holder, and then was charged in the SEM machine.

1.4. Adsorption studies

All adsorption studies were carried out using 100 ml properly sealed flasks mounted on a rotary shaker operated at 100 rpm agitation speed. The effect of contact time on the adsorption capacity of the PNSB for CV was studied in the presence of 1 g of the adsorbent mixed with 50 mL of the dye solution and agitated separately at room temperature for 10, 20, 40, 60, 80, 100 and 120 min. The effect of initial dye concentration was studied at the optimum contact time in the presence of 1 g of the adsorbent with CV concentration varying as 25, 50, 75, 100 and 125 mg/L. The effect of adsorbent dosage was studied with 0.5, 1, 2, 3 and 4 g adsorbent dosage in the presence of 50 mg/L of the CV dye solution. In the presence of 1 g of adsorbent and 50 mg/L of the CV dye solution, the effect of temperature was studied at 30, 40, 50, 60 and 70 °C, while the effect of pH was studied at room temperature for pH 2, 4, 6, 8 and 10 (obtained by introducing 0.1 M HCl or NaOH solution into the dye solution and measuring with a DEEP VERSION model (EI) pH meter). After each adsorption experiment, the contents of each flask were centrifuged and the supernatant solutions carefully obtained and analyzed using a UV-Vis spectrophotometer. The adsorption capacity, q_e , which is the amount of the CV dye adsorbed per unit mass of the PNSB adsorbent, was calculated for each experimental variable according the equation (1); where C_0 and C_e (mg/L) are, respectively, the initial and equilibrium dye concentration in the liquid phase, V (L) is the volume of the dye solution and W (g) is the mass of the adsorbent

$$q_e = \frac{(C_0 - C_e)V}{w} \quad (1)$$

1.5. Adsorption isotherm and kinetics

In order to understand the mechanism by which the CV dye adsorbs onto the PNSB adsorbent, the experimental results were tested with the adsorption isotherms by fitting the values of C_e (concentration of dye at equilibrium (mg/L)) and q_e (amount of dye adsorbed per unit mass of adsorbent at equilibrium (mg/g)) obtained for the effect of initial dye concentration, into the Langmuir and Freundlich isotherms. The linear form of the Langmuir isotherm is represented in the Equation (2); where q_m and b are Langmuir constants which, respectively, can be calculated from the slope and intercept of the plot of C_e/q_e versus C_e , and are related to the adsorption efficiency and adsorption energy. The linear form of the Freundlich isotherm is expressed in Equation (3); where K is the Freundlich constant and $1/n$ is the empirical constant representing adsorption intensity, both of which are determined from the intercept and slope, respectively, of the plot of $\ln q_e$ versus $\ln C_e$.

$$\frac{C_e}{q_e} = \frac{i}{b} \left(\frac{1}{q_m} \right) + \frac{C_e}{q_m} \quad (2)$$

$$\ln q_e = \ln K + \left(\frac{1}{n} \right) \ln C_e \quad (3)$$

The kinetics of the adsorption of CV by PNSB was investigated, at 25 °C, by fitting into the first and second order of reaction based on the experimental values of q_e (amount of dye adsorbed per unit mass of adsorbent at equilibrium) and q_t (amount of dye adsorbed at a given time) for the varying contact time 20 min. to 120 min. A linearized form of the first order kinetics is given in Equation (4), whereby a plot of $\log(q_e - q_t)$ against contact time, t , would yield K_1 (the first order rate constant) as slope and the calculated q_e value (expressed as q_e') can be extracted from the intercept of the plot. The linearized form of a second order reaction

is provided in Equation (5), whereby a plot of t/q_t against t yields the second order reaction rate constant, as derived from the intercept of the plot.

$$\log(qe - qt) = \log(qe') - k_1(t) \tag{4}$$

$$\frac{t}{qt} = \frac{1}{K_2 qe^2} + t/qe \tag{5}$$

2.6 Adsorption Thermodynamics

The thermodynamic parameters such as change in Gibb's free energy (ΔG^0), change in enthalpy (ΔH^0) and change in entropy (ΔS^0) for the adsorption of CV onto PNSB have been determined using the following equations:

$$\Delta G = -RT \ln K_{ads} \tag{6}$$

The equilibrium constants (K_{ads}) were calculated according to the following equation:

$$K_{ads} = \frac{\text{Dye concentration on the solid (adsorbent) at equilibrium (q}_e^m)}{\text{Dye concentration in solution at equilibrium (C}_e)} \tag{7}$$

The Van't Hoff equation is expressed as follows:

$$\ln K_{ads} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{8}$$

Where R is gas constant, T is absolute temperature in Kelvin, ΔS^0 and ΔH^0 are entropy and enthalpy respectively. The plot of $\ln K_{ads}$ versus $1/T$ gives a linear relationship, which allows the computation of ΔH and ΔS values from the slope and intercept respectively.

III. Results And Discussion

3.1. Effect of contact time on CV adsorption onto PNSB

The effect of contact time on the adsorption capacity of PNSB for CV, q_e , is provided in Figure 1. The result shows that, as contact time increased from 10 min. to 120 min., the adsorption capacity sharply increased from 3.24 mg/g (10 min.) to 3.32 mg/g (40 min.) and, thereafter, only increased sluggishly and remained stable around 3.34 mg/g from 60 min. to 120 min. Based on the result, a rapid uptake of CV by the PNSB adsorbent occurs during early contact time due to an abundance of adsorption sites on the PNSB surface. This rapid uptake of the CV dye, however, leads to an early saturation of the adsorbent surface which is the reason for the insignificant change in the q_e values between 40 min. and 120 min. Such short time to reach equilibrium q_e value could strongly be related to a strong affinity between the CV and the PNSB surface. Nevertheless, the penetration of dye through the pores of the adsorbent apparently controls the adsorption process once the equilibrium is reached after 60 min., thus, the non-fluctuation of the q_e value beyond this contact time.

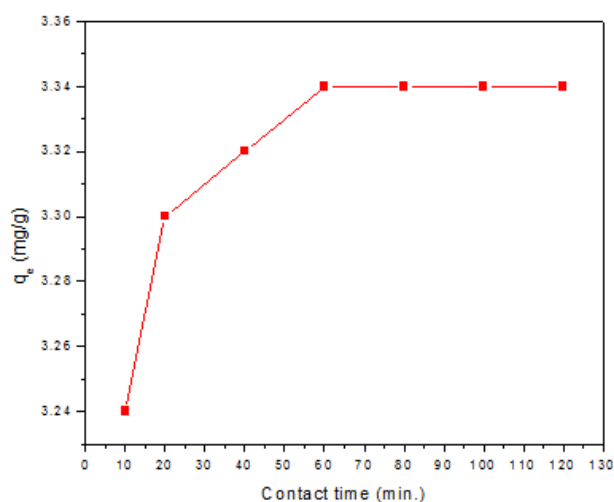


Fig. 1: Effect of contact time on the adsorption of CV onto PNSB

3.2. Effect of adsorbent dosage on CV adsorption onto PNSB

In Figure 2, the effect of adsorbent dosage on the adsorption capacity, q_e , of the PNSB for CV is presented. The result reveals a decrease in q_e from 8.30 mg/g to 1.11 mg/g as the amount of PNSB particles increased from 0.5 g to 4 g. Similar phenomenon was also reported for CV adsorption on carboxylate-functionalized sugarcane bagasse and on powdered mycelia biomass of *Ceriporia lacerata* [2, 7], as well as for methylene blue dye onto *Raphanus sativus* press cake adsorbent obtained by carbonization in a microwave oven

[4]. The authors concluded that, for a given adsorbate (CV) concentration, such increase in adsorbent (PNSB) dosage could lead to a decrease in the adsorbent/dye ratio as well as a splitting effect of concentration gradient between the adsorbent and the dye.

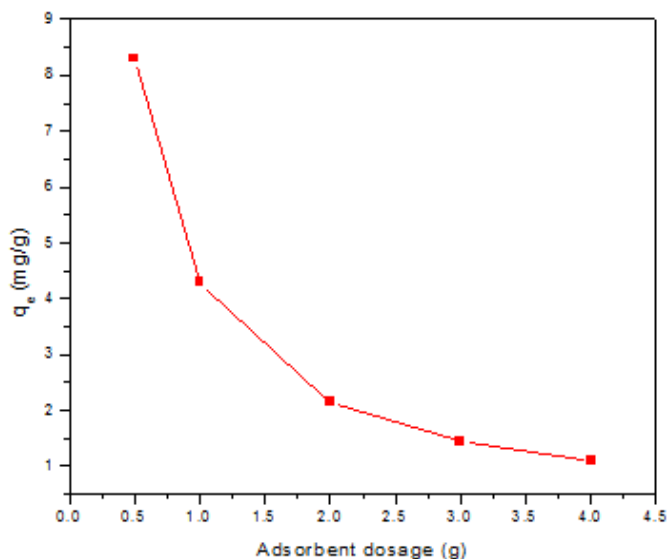


Fig. 2: Effect of adsorbent dosage on the adsorption of CV onto PNSB

Moreso, it is plausible that increased dosage could promote adsorbent particle agglomeration and overlapping of the active sites which, in turn, continuously blocks off the most preferred adsorption sites for an adsorbate molecule [5]. Assuming that a strong affinity exists between the CV and the PNSB adsorbent, as proposed from contact time experiment, such affinity could be disturbed due to the adsorbent/adsorbate distribution ratio and the particle agglomeration effects.

3.3. Effect of initial dye concentration on CV adsorption onto PNSB

Figure 3 shows the effect of initial dye concentration on the adsorption capacity, q_e , of PNSB for CV dye. Clearly, it could be observed that the q_e value continuously increased from 2.41 mg/g to 12.26 mg/g as CV dye concentration increased from 25 mg/L to 125 mg/L. Such can be well expected since higher dye concentration, for a given mass of adsorbent, would favor greater proximity between the dye molecules and the adsorbent surface. Thus, the barrier to mass transfer of dye from solution to adsorbent surface is greatly overcome and increased interaction between dye and adsorbent surface is favored, leading to greater dye uptake.

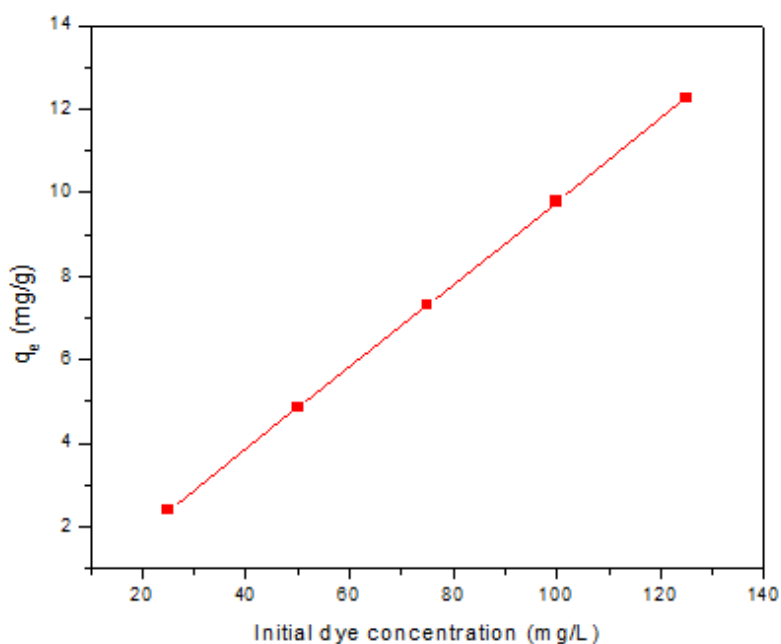


Fig. 3: Effect of initial dye concentration on the adsorption of CV onto PNSB

3.4. Effect of temperature on CV adsorption onto PNSB

The effect of increasing temperature from 30 °C to 70 °C on the adsorption capacity, q_e , of PNSB for CV dye is presented in Figure 4. The plot shows that q_e value decreased from 4.86 mg/g at 30 °C to 3.86 mg/g at 70 °C. It indicates that the adsorption of the CV dye onto the PNSB adsorbent must be exothermic in nature. Such decrease in adsorption capacity with increasing temperature has also been reported for CV dye [6]. The adsorption of CV onto PNSB adsorbent, therefore, is highly spontaneous at lower temperature and favors early saturation of the adsorbent surface. On the other hand, increasing temperature beyond the optimum value of 30 °C confers greater solubility on the CV dye, which causes the dye to remain more in solution rather than migrating to, and being adsorbed onto, the adsorbent.

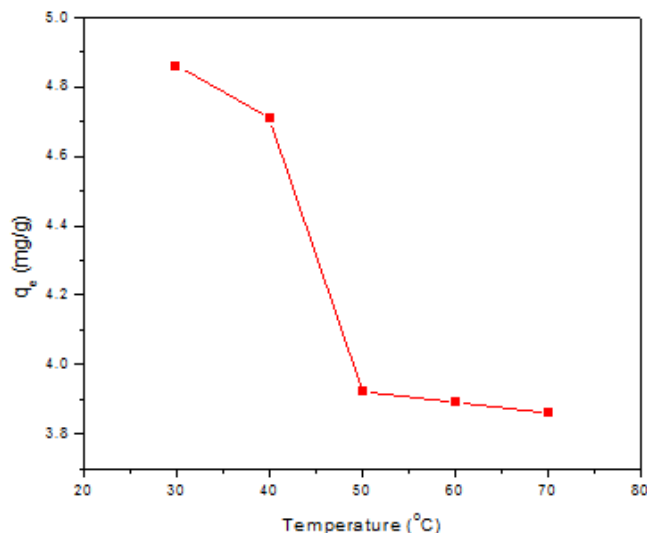


Fig. 4: Effect of temperature on the adsorption of CV onto PNSB

Moreover, increasing temperature could facilitate desorption of the already adsorbed CV dye molecules due to the kind of bonding at the CV-PNSB interface. The tendency that a salient agglomeration of the adsorbent particles could occur during temperature increase, which decreases the adsorption capacity of the PNSB adsorbent for the CV dye, cannot also be overlooked.

3.5. Effect of pH on CV adsorption onto PNSB

The effect of changing pH from 2 to 10 on the adsorption capacity of the PNSB adsorbent for the CV dye, q_e , is expressed in Figure 5. The result shows that the q_e value continued to increase from 4.40 mg/g at pH 2 to 4.58 mg/g at pH 10. It appears that a rise in the concentration of hydroxide ions in the solution (i.e. higher pH) favors increased attraction of the CV dye with the PNSB adsorbent. Similar effect of pH on the adsorption capacity of CV onto several other adsorbents has been reported [6, 8, 9].

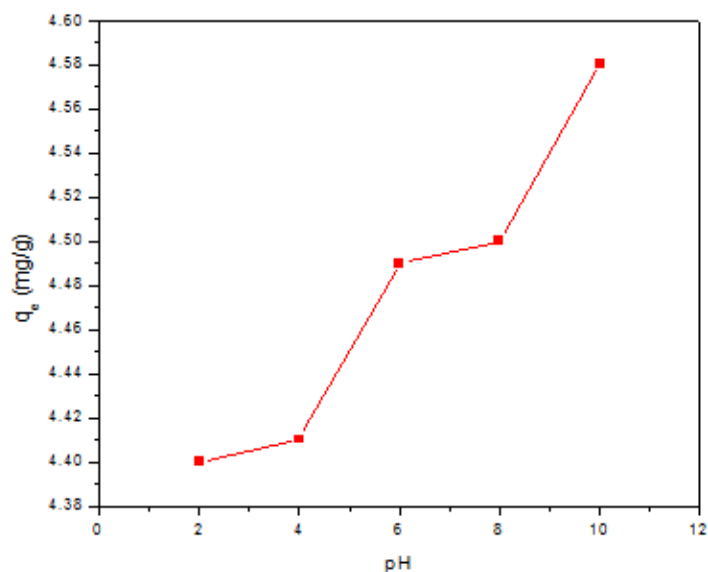


Fig. 5: Effect of pH on the adsorption of CV onto PNSB

The authors concluded that the CV molecule can maintain its positive charge up to pH 10, so that the increasing hydroxide ion concentration which confers a net negative charge on the PNSB adsorbent surface (as pH increases) would favor attraction and subsequent adsorption of the positively-charged CV molecule. It is also plausible that, assuming the adsorbent particles can agglomerate, as proposed from the effect of adsorbent dosage; increasing negative charges on the adsorbent surface (by increasing pH) could promote particle-particle repulsion and discourage such agglomeration which, in turn, favors increased CV adsorption.

3.6. Adsorption isotherm

By varying CV concentration from 25 mg/L to 125 mg/L in the presence of 1 g of PNSB at 27 °C after 60 min agitation at 100 rpm, the plot of C_e/q_e against C_e for the Langmuir isotherm is provided in Figure 6 while the plot of $\ln q_e$ versus $\ln C_e$ for the Freundlich isotherm is provided in Figure 7. The values of q_m and b (for the Langmuir isotherm) and the values of K and $1/n$ (for the Freundlich isotherm) are presented in Table 1. It can be inferred from the values of R^2 that the Freundlich isotherm ($R^2 = 0.9803$), more than the Langmuir ($R^2 = 0.9109$), could more adequately explain the mechanism by which the CV adsorbs onto the PNSB adsorbent. The greater agreement with the Freundlich isotherm implies that the PNSB adsorbent provides heterogeneous sites for the adsorption of the CV and that the CV adsorption onto PNSB is governed by physisorption process. The Freundlich isotherm can be applied to non-ideal adsorption on heterogeneous surfaces as well as multilayer adsorption. Furthermore, the value of $1/n > 1$ indicates that the adsorption of CV onto PNSB adsorbent is highly favorable. The mechanism of CV adsorption on many other adsorbents has also followed the Freundlich adsorption isotherm [13-15].

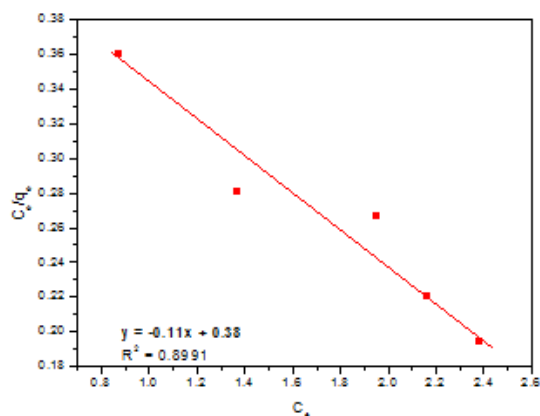


Fig. 6: Langmuir linear plot for the adsorption of CV onto PNSB at 25 °C

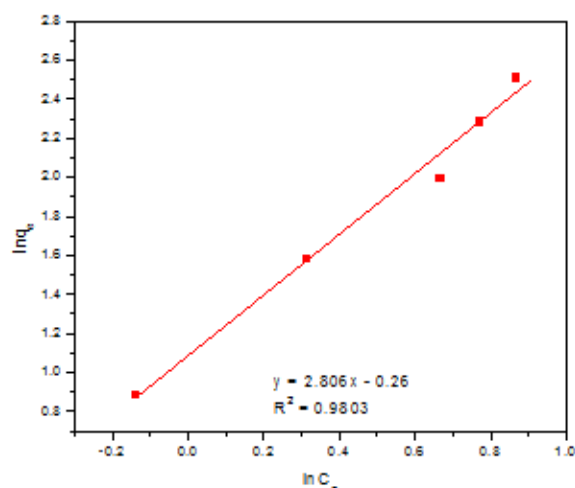


Fig. 7: Freundlich linear plot for the adsorption of CV onto PNSB at 25 °C

Table 1: Langmuir and Freundlich isotherm parameters for the adsorption of CV onto PNSB

Langmuir			Freundlich		
q_m (mg/g)	b	R^2	$1/n$	K (mg/g)(L/mg) ^{1/n}	R^2
9.993	0.228	0.9109	0.645	2.94	0.9803

3.7. Kinetics Studies

The plot of $\ln (q_e - q_t)$ against contact time, t , is provided in Figure 7, for the pseudo-first order reaction model. The values of K_1 , q_e and correlation coefficient (R^2) obtained from the plot are presented in Table 2. Based on the plot in Figure 7 and the values for in Table 2, it can concluded that there is a lack of correlation between the q_e value obtained from adsorption experiments (3.34 mg/g) and the q_e value obtained from the plot (0.08 mg/g) values, as well as a very low R^2 value (0.552). This indicates that the adsorption of CV onto PNSB does not follow a first order reaction kinetics. On the other hand, the plot of t/q_t versus contact time, t , is provided in Figure 8. The plot shows a straight line with positive slope and R^2 value up to 0.974, as well as more accurate correlation between the experimental q_e value (3.34 mg/g) and calculated q_e value (3.351 mg/g) obtained from the plot, as seen in Table 2. Thus, the adsorption of CV onto PNSB adsorbent actually follows a second order reaction kinetics. Similar second order kinetics has also been reported for CV adsorption onto several adsorbents [2, 16].

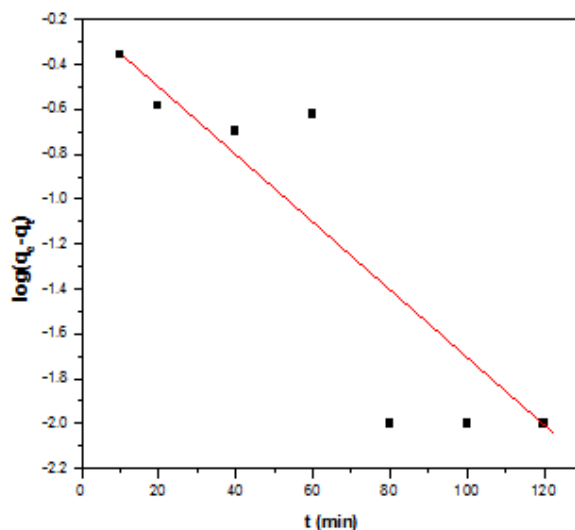


Fig. 7: First order reaction kinetics for the adsorption of CV onto PNSB

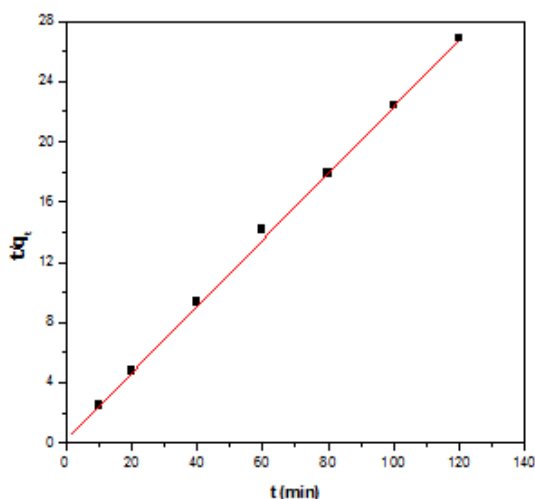


Fig. 8: Second order reaction kinetics plot for the adsorption of CV onto PNSB

Table 2: First order and second order parameters for the adsorption of CV onto PNSB

	Firstorder			Second order		
$q_{e(cal)}$ (mg/g)	K_1 (mg/g.min)	R^2	$q_{e(cal)}$ (mg/g)	K_2 (mg/g.min)	R^2	
0.08	0.015	0.552	3.351	0.103	0.974	

3.8 Thermodynamic Studies

The linear Van't Hoff equation plot for the adsorption of CV onto PNSB is provided in Figure 9. The thermodynamic parameters presented in Table 3. Negative ΔG^0 values obtained at all temperatures (Table 3) indicate the feasibility and the spontaneous nature of CV dyes adsorption onto PNSB.

The negative ΔH^0 values obtained for the adsorption of CV dye confirm the exothermic nature of the adsorption processes. While the negative value of ΔS^0 reveal decreased randomness during the adsorption process.

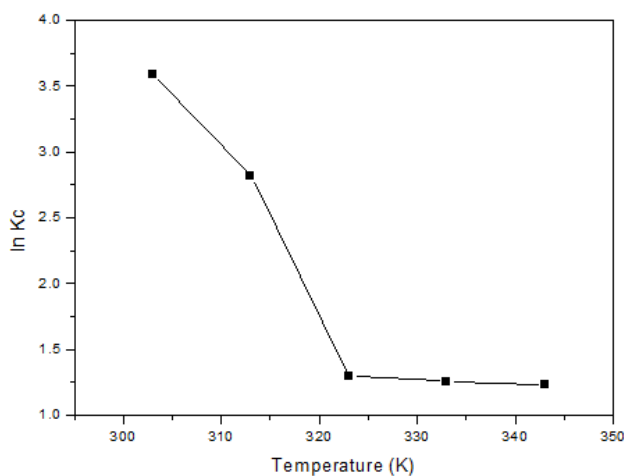


Fig. 9: Van't Hoff plot for the adsorption of CV onto PNSB

Table 3: Thermodynamic data and parameter for CV adsorption onto PNSB

T (K)	ΔG (KJ/mol.K)	ΔH (KJ/mol.K)	ΔS (J/mol.K)
303	-9640.06	-145.014	-52.245
313	-7333.07		
323	-3470.23		
333	-3480.04		
343	-3510.03		

3.9. Adsorbent Characterization

The FTIR spectra of PNSB before and after adsorption (Fig.10 & 11) of CV dye were analyzed to determine the vibration frequency changes in their functional groups. For PNSB before adsorption, various peaks are at 3630.91 cm^{-1} (O-H stretch, free hydroxyl), 3422.94 cm^{-1} (O-H stretch, H-bonded), 2926.71 cm^{-1} (C-H stretch from alkane), 1735.12 cm^{-1} (C=O stretch), 1654.31 cm^{-1} (C=C stretch), 1637.11 & 1559.87 cm^{-1} (N-H bend from 1^0 amines), 1508.47 cm^{-1} (C-C stretch in rings), 1458.51 cm^{-1} (C-H bend), 1425.14 cm^{-1} (CH_3), 1246.31 cm^{-1} (C-N), 1030.98 cm^{-1} (C-O stretch) and 668.55 cm^{-1} (C-Br stretch) [17]. After adsorption of CV dye it was found out that some of the functional groups were affected after the uptake process. This is judged from shifts in the position of some of the functional groups to lower frequency or band intensity before and after CV adsorption such as O-H, C=O, C=C and N-H from 3630.91 , 1735.12 , 1654.31 , and 1637.11 cm^{-1} to 3482.34 , 1718.15 , 1654.10 and 1636.80 cm^{-1} respectively. This indicates involvement of these groups for CV binding to PNSB [18]. Furthermore, Fig.12 shows the SEM images of PNSB powder. It can be observed from Fig. 12 that the external surface of PNSB powder is rough with irregular ridges. It also shows presence of pores.

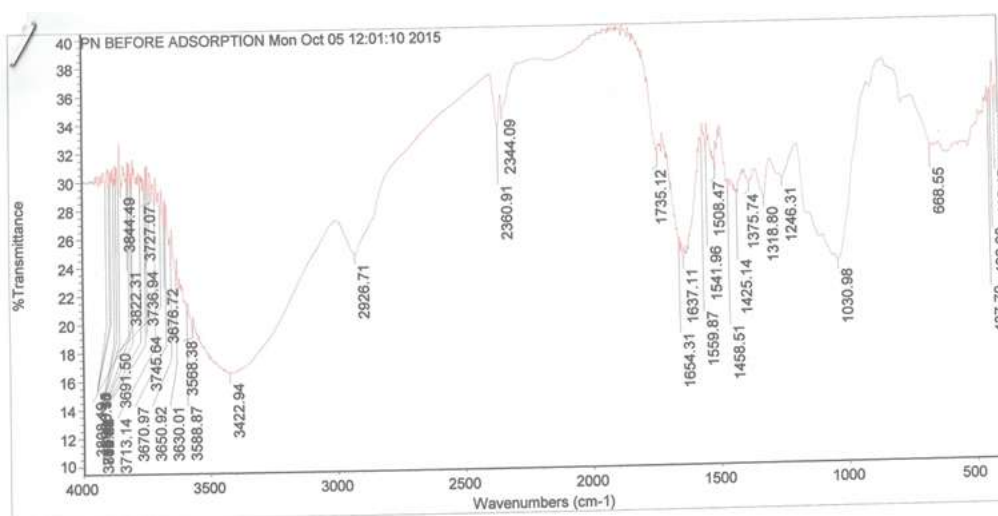


Fig. 10: FTIR Spectra of PNSB before adsorption

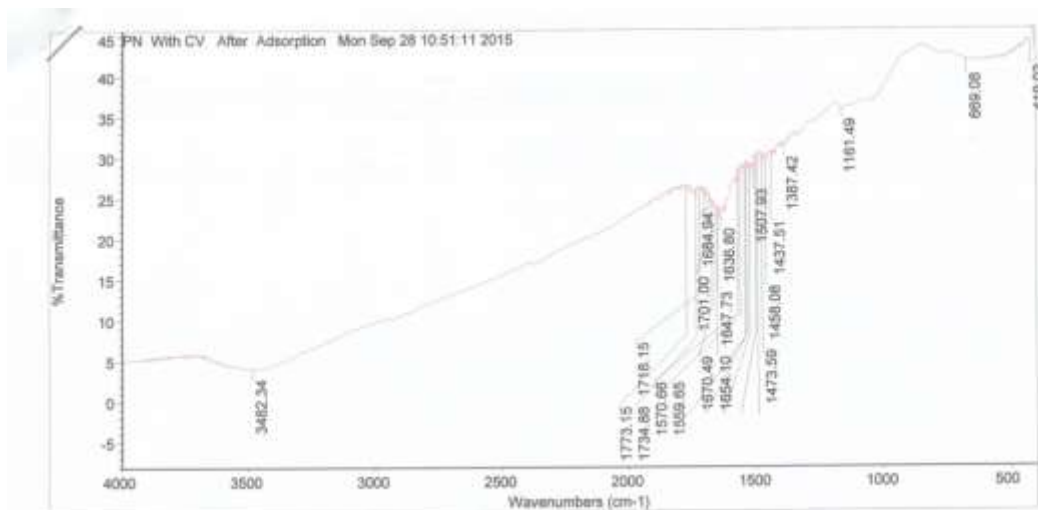


Fig. 11: FTIR Spectra of PNSB after adsorption

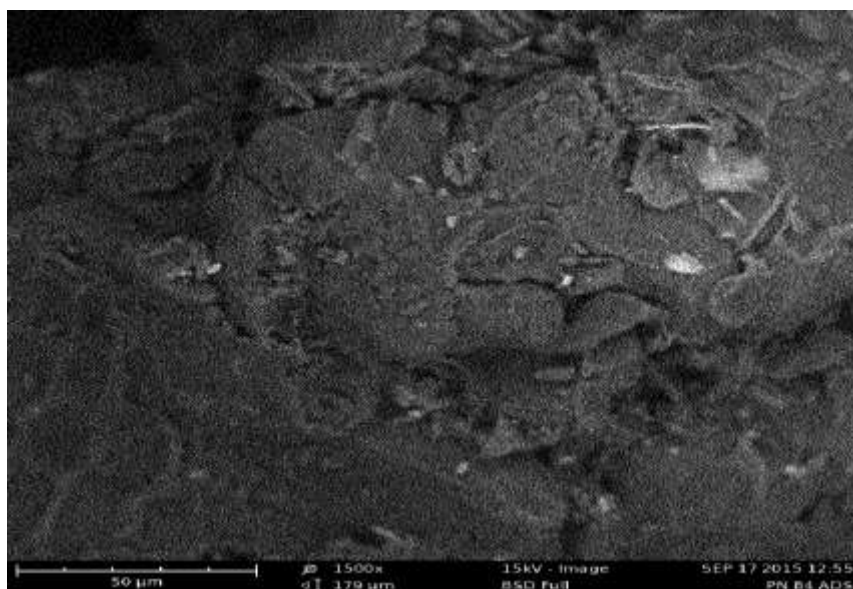


Fig.12. SEM micrographs of PNSB powder surface at magnification 1500×

IV. Conclusion

Picrilima nitida stem bark (PNSB) powder is an effective adsorbent for the removal of crystal violet (CV) from aqueous solution. An equilibrium contact time exists during which CV saturates the surface of the adsorbent. The removal of CV increases with increase in the initial dye concentration and pH, but decreases with increasing temperature and adsorbent dosage. The adsorption of CV onto PNSB follows a Freundlich isotherm and a second order reaction kinetics. The FTIR and SEM characterization indicates involvement of functional groups for CV binding to PNSB and the nature of the surface of the PNSBP adsorbent.

References

- [1]. A. Adak, M. Bandyopadhyay and A. Pal, Removal of crystal violet dye from wastewater by surfactant-modified alumina, *Sep. Purif. Technol.* 44(2), 2005, 139–144.
- [2]. B.C.S. Ferreira, F.S. Teodoro, A.B. Mageste, L.F. Gil, R.P. Freitas and L.V.A. Gurgel, Application of a new carboxylate-functionalized sugarcane bagasse for adsorptive removal of crystal violet from aqueous solution: Kinetic, equilibrium and thermodynamic studies, *Industrial Crops and Products*, 65, 2015, 521–534.
- [3]. L.F. Gil, R.P. Freitas and L.V.A. Gurgel, Application of a new carboxylate-functionalized sugarcane bagasse for adsorptive removal of crystal violet from aqueous solution: Kinetic, equilibrium and thermodynamic studies, *Industrial Crops and Products*, 65, 2015, 521–534.
- [4]. D.L. Nunes, A.S. Franca, and L.S. Oliveira, Use of raphanus sativus L. press cake, a solid residue from biodiesel processing, in the production of adsorbents by microwave activation, *Environ. Technol.* 32, 2011, 1073–1083.
- [5]. M. Shanthi, V. Kuzhalosai, Photocatalytic degradation of an azo dye, Acid Red 27, in aqueous solution using nano ZnO, *Indian Journal of Chemistry*, 51A, 2011, 428-434.

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- [6]. S. Chakraborty, S. Chowdhury and P.D. Saha, Adsorption of crystal violet from aqueous solution onto NaOH-modified rice husk, *Carbohydrate Polymers*, 86, 2011, 1533–1541.
- [7]. Y. Lin, X. He, G. Han, Q. Tian and W. Hu, Removal of crystal violet from aqueous solution using powdered mycelia biomass of *Ceriporia lacerata* P2, *Journal of Environmental Sciences*, 23(12), 2011, 2055–2062.
- [8]. P. Satish, D. Vaijanta, R. Sameer, and P. Naseema, Kinetics of adsorption of crystal violet from aqueous solutions using different natural materials, *International Journal of Environmental Sciences*, 1(6), 2011, 1-8.
- [9]. K.S. Bharathi, and S.T. Ramesh, Bioadsorption of crystal violet from aqueous solution by citrullus lanatus (watermelon) rind, *Journal of Environmental Research and Development*, 7(1A), 2012.
- [10]. C.K Nkere, and C.U. Iroegbu, Antibacterial screening of the root, seed and stem bark extracts of *Picralima nitida*, *African Journal of Biotechnology*, 4 (6), 2005, 522-526.
- [11]. E.S. Ayensu, *Medical plants in west africa* (Algonac, Michigan: Reference Publications Inc. 1978)
- [12]. B. Oliver, *Encyclopedia of medicinal plants*. (College of Arts, Science and Tech. Ibadan, 1960)
- [13]. L.K. Akinola and A.M Umar, Adsorption of crystal violet onto adsorbents derived from agricultural wastes: Kinetic and equilibrium studies, *J. Appl. Sci. Environ. Manage.* 19(2), 2015, 279- 288.
- [14]. T. Chinniagounder, M. Shanker, and S. Nageswaran, Adsorptive removal of crystal violet dye using agricultural waste cocoa (theobroma cacao) shell, *Research Journal of Chemical Sciences*, 1(7), 2011, 38 – 45.
- [15]. S. Patil, V. Deshmukh, S. Renukdas, and N. Patel, Kinetics of adsorption of crystal violet from aqueous solution using different natural materials, *International Journal of Environmental Sciences*, 1(6), 2011, 1116 – 1134.
- [16]. V.K. Verma, and A.K. Mishra, Kinetic and isotherm modeling of adsorption of dyes onto rice husk carbon, *Global Nest J.*, 12(2), 2010, 190-196.
- [17]. M.L Gary, L.P. Donald, S.K. George, and R.V. James, (2010). *Spectroscopy* (Bellingham, Washington: Brooks/Cole 2010) 15-87.
- [18]. N. Sharma, and B.K. Nnadi, Utilization of sugarcane baggase, an agricultural waste to remove malachite green dye from aqueous solution, *J. Mater. Environ. Sci.*, 4(6), 2013, 1052-1065.