https://dx.doi.org/10.4314/dujopas.v10i1b.29
ISSN (Print): 2476-8316
ISSN (Online): 2635-3490
Dutse Journal of Pure and Applied Sciences (DUJOPAS), *Vol. 10 No. 1b March 2024*

Adsorption Isotherms and Thermodynamics of *Thymol Blue* Removal from Aqueous Solution Using Native Pear *(Dacryodes edulis)* Seed Biomass

[1]Loretta Chukwudumebi Overah*, [1]Avwerosuo Ujor, and [1]Almond Anwuli

[1]Department of Chemistry,
Faculty of Science,
Delta State University,
Abraka.

Email: overah@delsu.edu.ng

Abstract

The release of dyes into watercourses not only upsets their beautiful nature but also hinders the transmission of sunlight into streams, reducing photosynthesis and resulting in the loss of aquatic life and reduction of water quality. Therefore, there is need to remove such colored substances. One of such dyes is thymol blue. This study was conducted with a view to removing thymol blue (TB) dye from an aqueous solution using a low-cost agricultural biomass, the African native pear (Dacryodes edulis), as the adsorbent. Batch experiments showed that the process was affected by pH, temperature, contact time, and initial thymol blue concentration. Optimum dye adsorption was achieved at pH 12. The data was analyzed using Langmuir and Freundlich isotherm models. The latter isotherm better described this process than the former. The thermodynamic quantities like free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were also evaluated. It was inferred from the results that the adsorption process was spontaneous, feasible, endothermic in nature, and occured by a physisorption mechanism. These findings indicate that the native peer seed is an efficient biosorbent for thymol blue removal from an aqueous environment.

Keywords: *Adsorbent, Thymol blue, Dacryodes edulis, Van't hoff, Isotherms, Thermodynamics*

INTRODUCTION

In recent years, environmental concerns and the need for sustainable solutions have driven research towards developing effective and eco-friendly methods for wastewater treatment (Mustapha and Halimoon., 2015). As a promising technique, adsorption has gained significant attention due to its versatility and potential for removing pollutants from aqueous solutions (Sud *et al.*, 2008; Overah, 2020). *Thymol Blue*, a widely used dye in various industries, poses environmental challenges as it can contaminate water sources and disrupt ecosystems (Hamad *et al.*, 2020).

This research examines the isotherms and thermodynamics of the adsorption of *Thymol blue* from aqueous solutions using *Dacryodes edulis* biomass. *Dacryodes edulis*, commonly known as Native Pear, is a tropical fruit tree whose biomass has shown remarkable adsorption properties in previous studies (Overah & Odiachi 2017; Overah, 2023). Thymol blue, $C_{27}H_{30}O_5S$, is classified as a triphenyl compound (Figure 1) with molar mass, 466.59 g.

**Author for Correspondence*

The choice of *Thymol Blue* (a water-insoluble dye) as a target pollutant is significant due to its prevalence in various industrial processes, such as in the textile and pharmaceutical industries (Hamad *et al.,* 2020). Its removal from wastewater is essential for environmental protection and ensuring the safety and sustainability of water resources.

By exploring the adsorption capacity of *Dacryodes edulis (DE)* biomass for *Thymol Blue*, this study aimed to contribute to the development of efficient and sustainable strategies for water purification. This study will delve into the adsorption isotherms and thermodynamics of *thymol blue* onto *Dacryodes edulis* biomass. Studying the interaction between *Thymol blue* molecules and *Dacryodes edulis* will provide valuable information about the process' feasibility and effectiveness of the *Dacryodes edulis* as an adsorbent for treating water contaminated with Thymol blue dye.

In addition, the investigation of *Thymol Blue* adsorption onto *Dacryodes edulis* biomass may provide a green and efficient solution for water pollution control. The findings of this study may have practical implications for industries seeking sustainable approaches to manage and mitigate the impact of dye pollutants in wastewater.

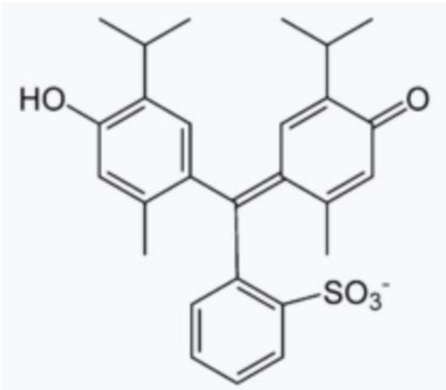

Figure 1: The Structure of *Thymol Blue*.

MATERIALS AND METHOD

Some of the materials and equipment used are UV-VIS Spectrophotometer N752 model, test tubes, test tube racks, pipettes, beaker, graduated cylinder, masking tape, syringe, conical flask, digital weighing balancer, speed governing multi-purpose oscillator (shaker), digital clock, water bath, and others. The reagents include *thymol blue* dye, Hydrochloric acid, distilled/deionized water and Sodium hydroxide.

Sample collection and preparation of biomass

African native pear seed (*Dacroydes edulis*) seeds were collected and prepared as reported by Overah *et al.,* (2023).

Preparation of stock solution of *Thymol blue*

In preparing a stock solution, 1g of *thymol blue* was dissolved in 1000 ml of distilled water to get a 1000 mg/L stock solution. The actual concentration of the TB in the prepared solution was measured using UV- Spectrophotometer and was used to carry out calculations for the serial dilutions.

Adsorption studies
In this study, adsorption experiments were employed in batches to study how the pH, TB concentration, and temperature affected the process following standard adsorption procedures (Overah, 2021).

Analysis of Dye Content
The ultraviolet spectrophotometer (UV) was used to determine the thymol blue concentration at the equilibrium by measuring the absorbance of TB at 595 nm. The calibration curve of the dye is a linear plot of concentrations and the correspondent absorbance. The displayed linear regression equation was used to estimate the concentrations of the dyes after each contact with the *Dacryodes edulis*. That is y = mx, takes the form of the Beer-Lambert law, A = ECl . The cell path length, I is unity, so that y, m (slope) and x are equivalent to the absorbance, A, molar absorptivity, E, and concentration, C, respectively.

Data Analysis.
The biomass performance was reported in terms of adsorption percentage using the equation (Aksu & Karabayir, 2008):

$$\%\ Dye\ Removal = \frac{C_a}{C_o} X\ 100 \qquad (1)$$

Also, the amount of *thymol blue* removed per unit mass adsorbent. q_e during the experiment was computed using the equation (Aksu & Karabayir, 2008):

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

Where; c_o= initial concentration (mg/L), c_a (concentration adsorbed) = C_o- C_e (mg/L),
V= volume of TB (L), *m*= mass of the dry DE (g).

Adsorption isotherm of *thymol blue* removal
The amount of dye adsorbed depends highly on the TB solution's initial concentration. The equilibrium adsorption Isotherm study was done by fitting the Langmuir and the Freundlich models with qe and Ce data obtained from the equilibrium adsorption Isotherm study.
The Langmuir model defines a single layer adsorption on a surface having a fixed number of binding sites. The linear form is (Aksu & Karabayir, 2008):

$$\frac{Ce}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \qquad (3)$$

A plot of Ce/qe against. Ce would be linear and qm and KL were deduced from the gradient and intercept, respectively.

The Freundlich equation describes the adsorption of target molecules on heterogeneous binding sites and is given in linear form(Aksu & Karabayir, 2008):

$$\text{Log } q_e = \log K_f + \frac{1}{n} \log C_e \qquad (4)$$

Where Kf represents adsorption capacity, it is the Freundlich constant, whereas n is adsorption intensity. A plot of log qe vs log Ce gives a straight line in which 1/n is the slope and log Kf is the intercept.

Thermodynamic Studies.
The thermodynamic parameters such as ΔG^0, ΔH^0, and entropy change (ΔS^0) were determined to predict the possibility or feasibility and nature of the biosorption process (Aksu & Karabayir, 2008). The ΔG^0 of the process relates to the equilibrium constant, Kc by the equation:

$$\Delta G^0 = -RT\ln K_C \qquad (5)$$

Where T is the temperature in Kelvin, and R is the universal gas constant having a value of

8.314 $Jmol^{-1}K^{-1}$, and K_c is thermodynamic equilibrium constant.
The thermodynamic equilibrium constant was determined as follows:

$$K_c = C_a/C_e \quad (6)$$

Also, ΔG^0 is related to ΔH^0 and ΔS^0 at constant temperature by the Van't Hoff equation (Aksu & Karabayir, 2008):

$$\ln K_C = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (7)$$

The values of ΔH° and ΔS° were derived from the slope and intercept, respectively, of Van't Hoff graph of $\ln K_c$ against $^1/_T$.

RESULTS AND DISCUSSION

Calibration Curve of *Thymol Blue*

Figure 2 is the calibration curve for *Thymol blue* at 595 nm on a UV-VIS spectrophotometer. The correlation coefficient depicts a very good linear relationship. The linear regression equation on Figure 2 was used to estimate the residual concentrations, as already described in the previous section in section 2.0.

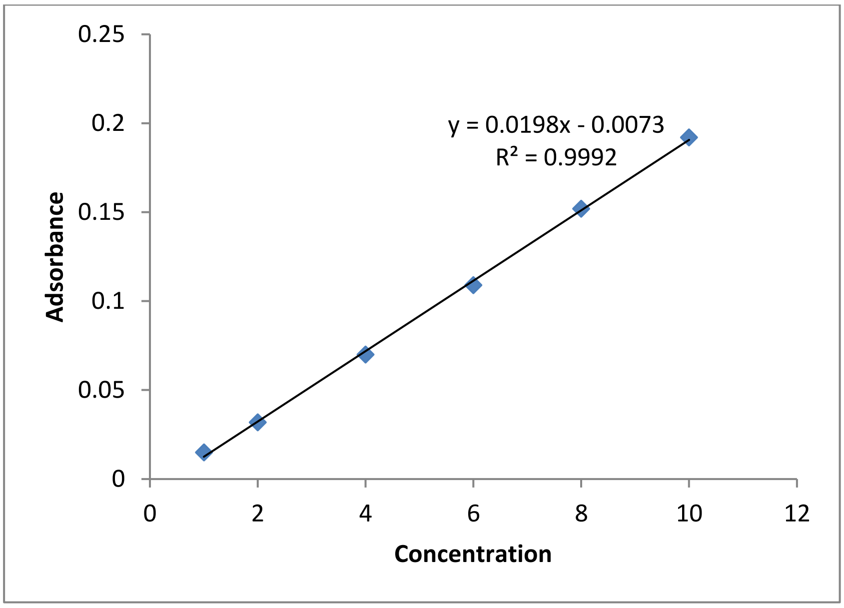

Figure 2: The calibration curve for *Thymol blue* adsorption @ 595nm.

Adsorption studies

The results of the adsorption studies carried out are discussed below:

pH Effect

The influence of pH was analyzed and presented in Figure 3. The available positively charged active centres decreased when the solution pH increased. On the other hand, there was an increase in the negatively charged sites. The surface of the *DE* became more negatively charged, which enhanced the interaction between the sorbents and the dye molecules. Therefore, the adsorption capacity of the *DE* increased at high pH values (Yu *et al.,* 2010). This result is displayed in Figure 3. The optimum pH was therefore taken as 12 and employed for the other studies.

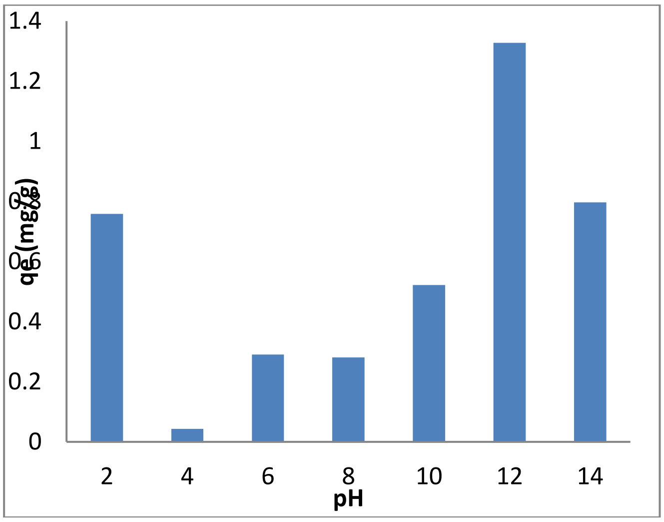

Figure 3: Effect of pH on uptake qe, of *thymol blue* onto *Dacryodes edulis* (dose 0.5 g, contact time 120 minutes, initial dye conc. 55 mg/L, temperature 35 °C)

Temperature Effect

The percentage of *thymol blue* adsorbed improved with a temperature increase from 15 °C to 35 °C (Figure 4). Mahmoud *et al.* (2020) reported using spent oil shale to adsorb methyl red from aqueous solutions at varied temperatures. They found out that as temperature increased, the percentage adsorbed also increased. Increasing the temperature led to more dye being removed from aqueous medium. This result can be ascribed to a reduction in the solution's viscosity with increasing temperature, which consequently boosts the diffusion rate of the dye to interior pores and exterior layers of spent oil shale (Gurses *et al.,* 2014). This outcome suggests that the adsorption process is endothermic.

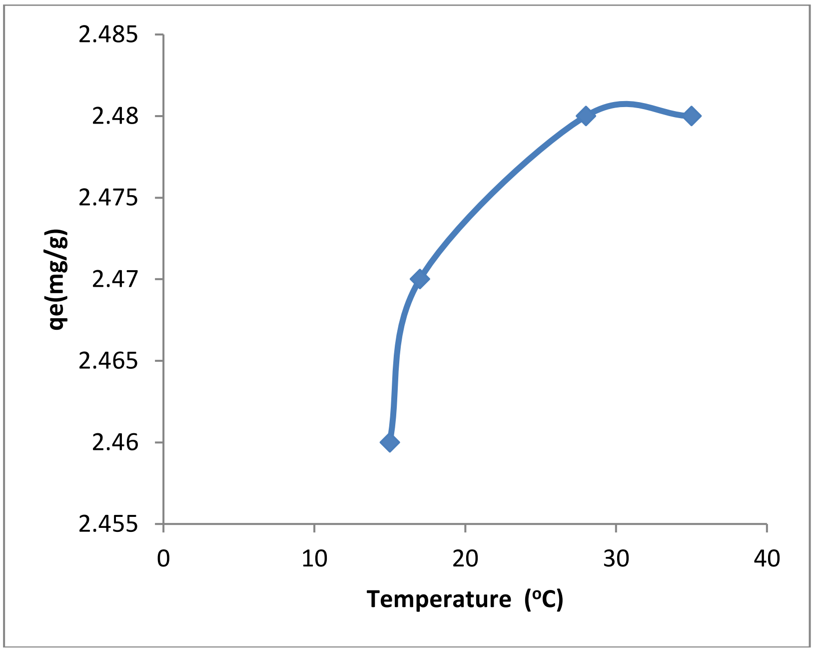

Figure 4: Effect of temperature on the adsorption capacity, qe of *Dacryodes edulis for thymol blue* (dose 0.5 g, contact time 240 minutes, initial dye concentration 50 mg/L).

Concentration effect

The experimental outcome shows that the adsorption of *thymol blue* dye increased with an increase in the concentration of the dye (Figure 5). This trend may be because the higher the concentration of dye, the lower the resistance to bulk movement of the dye molecules from the aqueous medium to the interface. Ashish *et al*. (2013) and Overah *et al*., 2023 reported similar results using *Limonia acidissima* and Dacryodes edulis to remove malachite green dye.

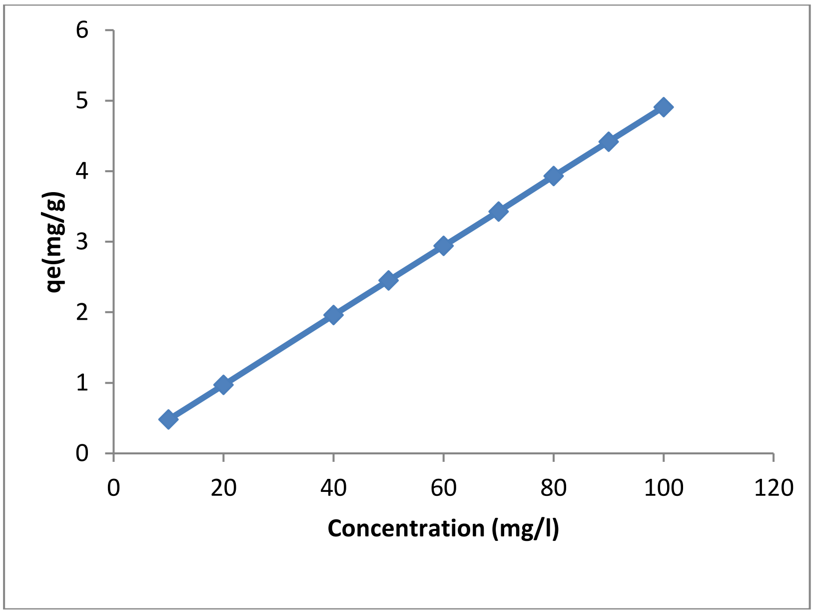

Figure 5: Effect of Concentration on the adsorption capacity, qe, of *thymol blue* onto *Dacryodes edulis* (dose 0.5 g, contact time of 120 minutes and at a temperature 35 ^{o}C).

Adsorption isotherms

Equilibrium isotherm parameters offer vital information about the adsorption mechanism, affinity of the adsorbent for the dye and the surface characteristics of the adsorbent. The Langmuir and Freundlich isotherms were employed for this study.

Langmuir Isotherm

The graph of Ce/qe against Ce, (Figure 6), with R^2 value of 0.521, suggests the poor compliance of *thymol blue adsorption* onto *Dacryodes edulis,* to the Langmuir isotherm. The implication is that the adsorption of *thymol blue* onto the *Dacryodes edulis* is not monolayer adsorption as assumed by Langmuir isotherm.

Freundlich Isotherm

The Freundlich model was also employed to calculate the adsorption intensity of thymol blue on the DE surface. From the plot of log qe versus log Ce, the R^2 value of 0.962 (Figure 7) reveals a good fit for the adsorption data. This is to show that the adsorption of *thymol blue* onto the *Dacryodes edulis* occured on heterogeneous binding sites. This result is in tandem with the report of Kuete *et al*., (2020) which reported TB adsorption of activated carbon prepared from Garcinia nut shells and impregnated with KOH and H_3PO_4. However, the Redlich–Peterson isotherm was the more suitable model to fit the process.

The corresponding Langmuir and Freundlich parameters are displayed in Table 1.

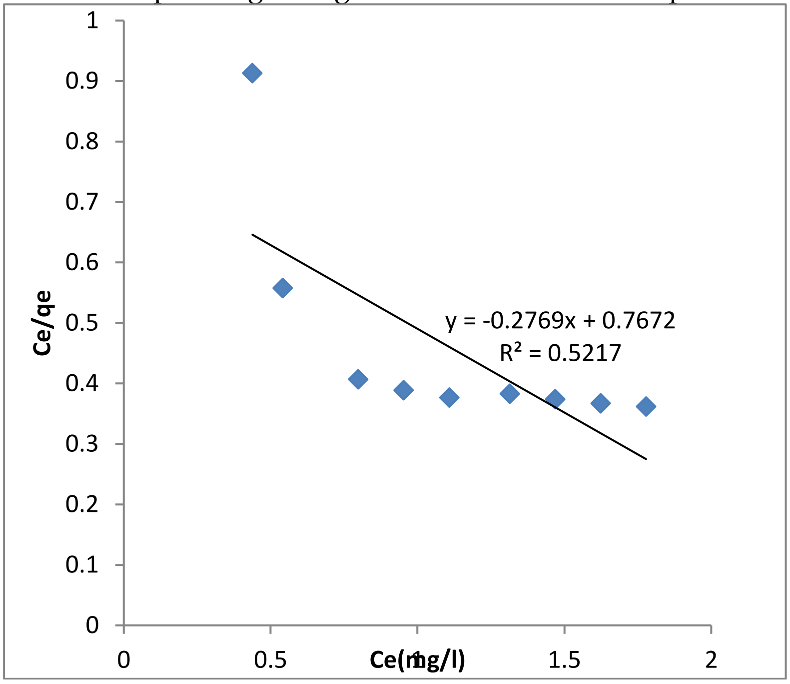

Figure 6: Langmuir Isotherm for *thymol blue* adsorption onto *Dacryodes edulis* (dose 0.5 g, contact time of 120 minutes, initial conc 50 mg/l and at a temperature 35 °C).

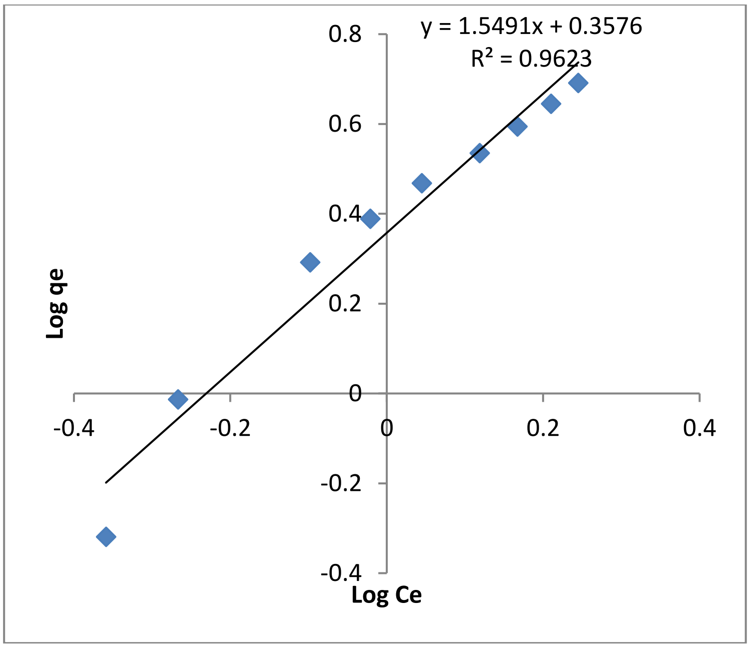

Figure 7: Freundlich isotherm for *thymol blue* adsorption onto *Dacryodes edulis* (dose 0.5 g, contact time of 120 minutes, initial conc 50 mg/l and at a temperature 35 °C).

Table 1: Langmuir and Freundlich Isotherms and Their Parameters

LANGMUIR ISOTHERM			FREUNDLICH ISOTHERM		
R^2	q_{max} (mg/g)	K_L	R^2	K_f	n
0.5210	3.623	0.3598	0.962	0.4473	0.6456

Thermodynamics Studies

The thermodynamic factors like ΔS° and ΔH° of the adsorption process, were deduced from the intercept and slope respectively, of the Van't Hoff plot (Figure 8) as described in the previous section. The ΔG° was estimated at the various temperatures studied. These results are displayed in Table 2.

The negative ΔG° values show the feasibility of the adsorption of *thymol blue* on *Dacryodes edulis* and the spontaneity of the adsorption process. The positive ΔH° depicts an endothermic process and the possibility of a physisorption mechanism. A positive ΔS° confirms the affinity of *Dacryodes edulis* for TB and increased disorderliness at the solid-liquid interface. These results concurred with the findings of Hajira *et al.,* (2008) reported the same observation in regards to the endothermic nature of the process. A similar study has been reported also by Hema and Arivoli (2008), on the adsorption of malachite green onto activated carbon from Pandanus leaves and Koyuncu *et al*., (2021), on the removal of TB from aqueous medium by natural and modified bentonite. Both researches reported an endothermic adsorption process which was temperature-dependent and thermodynamically practicable. Kuete *et al.*, (2020) also studied the sorption of thymol blue onto activated carbon prepared from the shells of *Garcinia cola nut* encapsulated with KOH and H_3PO_4. The process was also reported as endothermic, thermodynamically realistic and temperature dependent in keeping with our findings.

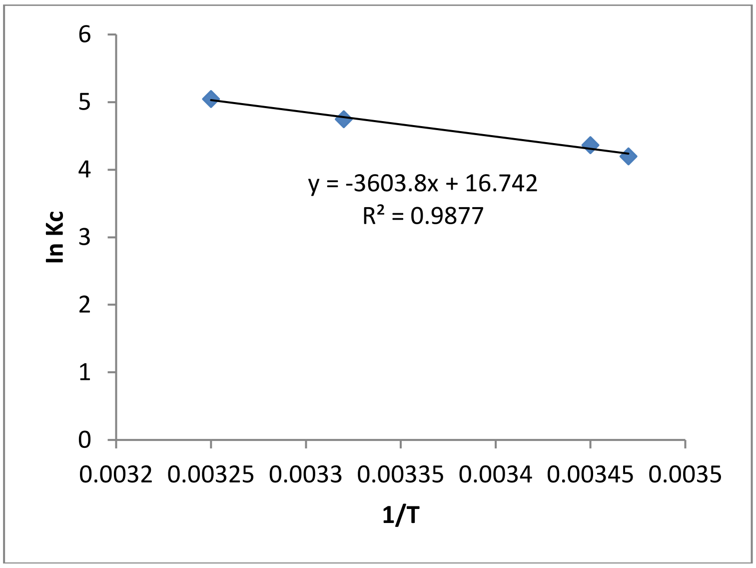

Figure 8: Van't Hoff plot of InKc vs 1/T

Table 2: Summary of the thermodynamic factors of Thymol blue adsorption onto Dacryodes edulis

ΔH° (KJ/mole)	ΔS° (J/K. mole)	ΔG °(KJ/mol)			
		288 K	293 K	301 K	308 K
29.96	139.2	-6.656	-7.332	-8.803	9.966

CONCLUSION

The removal of *thymol blue* dye onto *Dacryodes edulis* (African native pear occurred optimally at pH 12. The data fitted better to the Freundlich Isotherm meaning that multi-layer adsorption occurred at heterogeneous sites. Also from the thermodynamic studies, the process was endothermic, spontaneous, and therefore feasible for the removal of dyes from aqueous systems. Owing to the results obtained in this study, *Dacryodes edulis* biomass is therefore recommended for *thymol blue* removal from aqueous media.

Conflict of interest
The author and co-authors have no conflicting interest.

REFERENCES

Aksu, Z. and Karabayir, G. (2008). 'Comparison of biosorption properties of different kinds of fungi for the removal of Gryflan black RL metal-complex dye'. *Bioresource Technology,* 99:7730 – 7741.

Ashish, S.S., Aniruddha, M.M., Vikas, V.J., Prakash, D. R., Mansing, A.A., Sanjay, S.K., (2013). 'Removal of malachite green dye from aqueous solution with adsorption technique using Limonia acidissima (wood apple) shell as low cost adsorbent'. *Arabian Journal of Chemistry,* 2: 3229-3238.

Gurses, A., Hassani, A., and Kıranşan, M., (2014). 'Removal of methylene blue from aqueous solution using untreated lignite as potential low-cost adsorbent: kinetic, thermodynamic and equilibrium approach'. *Journal of Water Processing & Engineering,* 2: 10–21.

Hamad, M. I., Mohammed, H. and Alfutisi, M. (2021). 'Removing of *Thymol Blue* from aqueous solutions by pomegranate peel'. *EPH - International Journal of Applied Science,* 6 (3): 91 - 97.

Hema M. and Arivoli S. (2008). 'Adsorption kinetics and thermodynamics of malachite green dye unto acid activated low cost carbon.'*Journal of Applied Science and Environmental Management,* 12 (1): 43 – 51.

Koyuncu, H. Aldemir, A., Kul, A.R. and Canayaz, M. (2021). 'Removal of thymol blue from aqueous solution by natural and modified bentonite: comparative analysis of ANN and ANFIS models for the prediction of removal percentage.' *Pollution*, 7(4): 959-980.

Kuete I.T, Tchuifon D.R., Ndifor-Angwafor G.N., Kamdem A.T., Anagho S.G. (2020). 'Kinetic, isotherm and thermodynamic studies of the adsorption of thymol blue onto powdered activated carbons from *Garcinia cola nut* shells impregnated with H_3PO_4 and KOH: non-linear regression analysis. *Journal of Encapsulation and Adsorption Sciences,* 10 (1): 1-

Mustapha, M.U, and Halimoon, N. (2015). 'Micro-organism and biosorption of heavy metals in the environment'. *Journal of Microbial and Biochemical Technology*, Doi:10.4172/1948-5948.1000219.

Overah, L.C. (2021). 'Adsorption isotherms and kinetics studies of a cationic and anionic dye removal from aqueous solution onto *Raphia farinifera* Biomass'. *Nigeria Journal of Science and Environment,* 19(1):25-38.

Overah, L.C. and Odiachi J.I. (2017). 'Evaluation of *Dacryodes edulis* (native pear) seed for Pb(II) sorption from aqueous solution.' *Journal of Applied Science and Environmental Management,* 21 (1) 186-199.

Overah, L.C (2020) 'Nonlinear kinetic and equilibrium adsorption isotherm study of cadmium (II) Sorption by *Dacryodes edulis* Biomass'. *Nigerian Journal of Basic and Applied Sciences,* 28 (2):10 – 19.

Sarin, V., Singh T.S., Pant K.K. (2006) 'Thermodynamic and breakthrough column studies for the selective sorption of chromium from industrial effluent on activated eucalyptus bark'. *Bioresource Technology,* 97(16) 1986-1993.

Sud, D., Mahajan, G., Kau, M.P., (2008). 'Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions – a review'. *Bioresource Technology,* 99: 6017-6027.

Wu, X., Wu. D., Fu, R. (2007) 'Studies on the adsorption of reactive brilliant red X-3B dye on organic and carbon aerogels.' *Journal of Hazardous Materials*, 147(3):1028-1036.

Yu, J.X., Chi, R.A., Su, X.Z., He, Z.Y., Qi, Y.F., Zhang, Y.F. (2010). 'Desorption behavior of methylene *blue* on pyromellitic dianhydride modified biosorbent by a novel eluent: acid TiO_2 hydrosol'. *Journal of Hazardous Materials,* 177 (1-3): 222-227.