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MALACHITE GREEN SEQUESTRATION FROM AQUEOUS SYSTEM BY UNTREATED *DACRYODES EDULIS* SEED

***Overah, L.C.[1], Ebite, C.[2], and Ujor, A.[3]**
[1,2]Department of Chemistry, Faculty of Science, Delta State University, Abraka
[3]Department of Industrial Chemistry, School of Physical Science,
Federal University of Technology, Akure, Ondo State.
Corresponding author: overah@delsu.edu.ng

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ABSTRACT

This paper presents an assessment of the kinetics and thermodynamics of malachite green (MG) abstraction from an aqueous system onto untreated pear seed (Dacryodes edulis) biomass as an adsorbent at pH 12. The experiments were conducted in batches at 25 °C, with a biomass dose of 0.5 g, and at different durations (5 to 240 minutes) using a 50 mg/L malachite green dye solution. The kinetics data were examined using four models: pseudo-first-order, pseudo-second-order, intra-particle, and Elovich models. The fallouts indicated that the pseudo-second-order model represented the process' kinetics well, with R^2 values of 0.9998, rate constant, 0.346 g/mg/min, and a 90% adsorption efficiency. Thermodynamics study revealed a negative free energy change, ΔG^o, indicating a feasible and spontaneous process that is endothermic, having a positive ΔH^o. Comparing the findings with the findings of others reveals that malachite green adsorption onto various adsorbents is usually endothermic and follows the Pseudo-second-order mechanism most times. Overall, untreated pear seed biomass has the potential as an alternative to traditional adsorbents for extracting malachite green from an aqueous medium.

Keywords: Kinetics, thermodynamics, Pseudo-second-order, malachite green, Endothermic

INTRODUCTION

Malachite green is a hazardous chemical that is detrimental to a broad range of animals from the sea and land. It is known for being particularly deadly to freshwater fish, both in the short and long term (Babel *et al.*, 2015). Additionally, it can cause major health and environmental concerns, including decreased food consumption, growth, and fertility rates, and can harm organs such as the liver, spleen, kidney, heart, and bones, as well as results in skin lesions, eye, lung and bone problems (Babel *et al.*, 2015). Furthermore, malachite green is extremely harmful to mammalian cells and has been linked to the growth of tumours in the lungs, breasts, and ovary of rats that have been exposed to it (Yonar and Yonar, 2014). Malachite green, a water-soluble basic dye, has a controversial history in the aquaculture sector. Despite its popularity, the specific chemical composition of malachite green was not always specified, leading to potential toxic effects on fish (Banerjee *et al.*, 2016). The use of MG, both as a mono-component and in combination with other substances, has been widely documented in the scientific literature. However, due to concerns about human toxicity and environmental contamination, the EU outlawed the use of malachite green in fish food in the year 2000, and increased monitoring has since been implemented.

Adsorption is a technique that holds great potential for removing malachite green from water solutions (Gode and Pehlivan, 2015). There are various techniques for separating dyes from textile waste. For example, chemical oxidation, biodegradation, flotation, chemical coagulation, electro-dialysis, biodegradation, and adsorption. Out of these methods, adsorption has the greatest potential for complete treatment, as it is anticipated to be effective for an extensive variety of compounds (Overah *et al.*, 2011). However, because activated charcoal is so expensive, researchers are looking for a more cost-effective alternative.

Biosorption, which uses minimal adsorbents materials such as organic, agro-industrial, and chemical waste products, is appealing because it is both inexpensive and effective in removing colours from water solutions (Arivoli *et al.*, 2013; Chowdhury *et al.*, 2010). Biosorption investigations have been carried out with diverse biosorbents for the separation of MG from an aqueous setting such as rubber seed coats (Idris *et al.*, 2011: Hameed and Daud., 2008a), rambutan peels (Ahmad & Alrozi, 2011), ginger waste (Ahmad *et al.*, 2011), degreased coffee bean (Baek *et al.*, 2010), rice husks (Sharma and Uma, 2009), and rattan sawdust (Hameed and El-Khaiary, 2008).

Pear Seed (*Dacryodes edulis*) is a magnificent evergreen tree that may reach heights of 18-40 meters in forests, but typically reaches only 12 meters in plantations. It has a pale grey, rough bark with resin droplets and is characterized by its short trunk and dense crown (Kindt *et al.*, 2009). The tree's leaves are composed of 5-8 pairs of leaflets. The Pear Seed is a nutrient-rich source, containing a diverse array of carbohydrates, proteins, crude fibers, and essential minerals (*Deniz*, 2013). Physicochemical analysis has revealed that the seed holds useful functional properties that are of commercial interest. Studies have also reported its vasodilatory effects (Anyam *et al.*, 2016).

Dacryodes edulis seed waste has been reported in our earlier work as suitable for lead adsorption (Overah and Odiachi, 2017) as well as for the sorption of Cd(II) from an aqueous system (Overah, 2020). Also, Igwegbe *et al.*, 2020 tested *Dacryodes edulis* for the abstraction of Vat Yellow 4 and Congo red from aqueous solutions and found it more than 90 % efficient. Furthermore, activated carbon from *Dacryodes edulis* was applied to the sorption of MG and was found very useable and efficient (Igwegbe *et al.*, 2015).

In this study, a chemically untreated *Dacryodes edulis* (pear) seed shell was employed as a biosorbent for MG sorption, (a cationic dye), from water. It was untreated to reduce cost and induce an easy process while assessing its performance and comparing it with cases where it was chemically treated. By varying pH, temperature and time, the process's optimal conditions were determined. Further analyses were done to probe the Kinetic mechanism and thermodynamic description of the process.

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Figure 1. Pear Seed (*Dacryodes edulis*)

Source: Ekpa and Isaac, (2013).

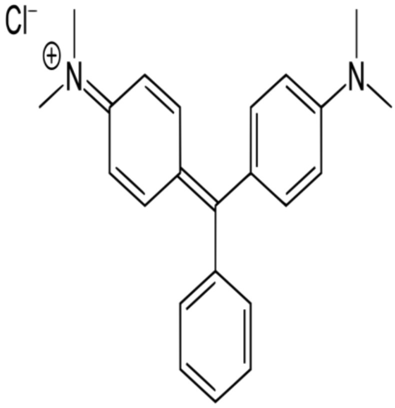

Figure 2. Malachite green Structure

Source: Banerjee *et al.*, (2016)

MATERIALS AND METHOD

Reagents and materials

The following materials and apparatus were utilized: pipettes, masking tape, syringe, test tube, testtube rack, conical flask, digital weighing balance, mechanical shaker, thermostat, ultraviolet spectroscopy 752 England-made, mortar, and sieve. The reagents used include malachite green, hydrochloric acid, deionized water, and NaOH. These were all analytical grades.

Dye solution preparation

In preparing MG stock solution, 1 g of the dye ($C_{23}H_{25}N_2$), molecular mass 364.911 g/mol, λ_{max} 617 nm) was accurately weighed and dissolved in 1 liter of deionized water. Working solutions of 50 mg/L were obtained by diluting the stock.

Adsorbent collection and preparation

The seeds of *Dacryodes edulis* were obtained from Agbor, Delta State, Nigeria and properly cleaned using de-ionized water to eliminate any impurities. They were then dried under sunlight for three days. The *Dacryodes edulis* were pulverized, screened and sieved to 1-2 mm particle size. The homogenized *Dacryodes edulis* biomass was soaked in 1 M HCl solution for 24 hours at *25 °C*. The soaked biomass was filtered and washed with de-ionized water severally till a neutral pH of 7 was attained. It was afterwards oven-dried at 50 °C for 6 hours. Allowing the dried biomass to cool, it was ground and sieved to various particle sizes before being kept in an air-tight container for sorption tests.

Adsorption studies

Adsorption tests were done in batches to get the optimum pH, time and temperature, using 50 mg/L MG solution diluted from the stock solution. For each study, to get the optimum, the factor under study was varied while keeping the other conditions constant as described by Overah (2011). In each case, 0.5 g of the *Dacryodes edulis* was contacted with a 25 ml aliquot of the MG solution and agitated for 24 hours. Each test set was done twice.

Measurement of Residual Dye Concentration

The procedure followed for the estimation of residual dye concentration after contact with the biomass is described by Overah 2020. The standard curve of MG at 617 nm wavelength was gotten as a straight-line plot of the concentrations which were prepared by serial dilution and corresponding absorbance. The displayed equation of the graph was used to calculate the subsequent residual concentrations of the dye after contact with the *Dacryodes edulis* biomass using the Beer-Lambert law.

Kinetic Treatment of Experimental Data

The adsorption kinetics depends on the physical properties and chemical make-up of the adsorbent material to a large extent (Berend *et al.*, 2014) and is usually describable by the four main models.

The Pseudo-first-order model expression was given by Langergren for the description of the kinetics of sorption by biological materials. It is linearly expressed as:

$$\log (q_e - q_t) = \log q_e - kt/2.303 \quad \ldots\ldots\ldots\ldots (1)$$

Where: q_e and qt are the masses of Malachite green adsorbed at equilibrium (mg/g), and at time t (mg/g and k is the rate constant. The graph of Iog (q_e-q_t) versus t being linear, certifies this model.

The pseudo-second-order model as developed by Ho *et al.*, (1996), is applicable to the adsorption system. This model was employed to investigate the extent it describes the mechanism of adsorption of MG from an aqueous system onto *Dacryodes edulis* as an adsorbent. The linear form:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad \ldots\ldots\ldots\ldots (2)$$

where qe and q_t are as already defined and k_2 is the rate constant (g/mg min). A linear outcome of the plot of t/qt against t, certifies this model.

In some cases, the kinetic mechanism may not be described by either of the two kinetics models (Radnia *et al.*, 2011). In such cases, the kinetics data can be evaluated on the intra-particle diffusion model which is described by Weber and Morris, (1963) and is expressed by Equation (3) (Demirbas *et al.*, 2004):

$$q_t = k_{id}(t)^{1/2} + C \quad \ldots\ldots\ldots\ldots (3)$$

where q_t is the milligram of MG adsorbed per gram of *Dacryodes edulis* at time *t*, *C* is the adsorption constant and k_{id} is the intra-particle diffusion rate constant. When intra-particle diffusion is the applicable model, q_t varies linearly with $t^{1/2}$.

The Elovich kinetics is another model which is used to analyze the gas sorption on solid surfaces, but can also be applied in aqueous phases and has been applied to metal and dye sorption from aqueous phases. The Elovich model can be expressed as:

$$q_t = \frac{1}{\beta} ln\, ln\, (\alpha\beta) + \frac{1}{\beta} lnt \quad \ldots\ldots\ldots\ldots (4)$$

where α (mg/g.min) is the initial chemisorption rate and β (g/mg) is the Elovich constant defined as the desorption constant. Plotting q_t against ln(t) would give a linear relationship with a gradient and intercept as ($1/\beta$) and ($1/\beta$)ln($\alpha\,\beta$) respectively.

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Thermodynamic Studies.

To test the viability and type of the sorption process, thermodynamic variables including Gibb's free energy change (ΔG^0), entropy change (ΔS^0), and enthalpy change (ΔH^0) were determined. The following equation relates the process's change in Gibb's free energy to the equilibrium (Sarin & Pant, 2006):

$\Delta G^0 = -RT\ln K_C$ ………………………….(4)
(Abrahim and Rassy, 2009)

Where K_C is the thermodynamic equilibrium constant, T is the Kelvin temperature, and R is the universal gas constant (8.314 $Jmol^{-1}K^{-1}$).

The equilibrium thermodynamic constant was obtained as follows:

$K_c = C_a/C_e$ ………………………. (5)
(Dubey and Gopal, 2009)

where C_e is the equilibrium concentration of the solution in milligrams per litre and C_a is the mass of adsorbate per liter (Dubey and Gopal, 2009). Based on thermodynamics, the Van't Hoff equation connects the change in Gibbs free energy to the changes in enthalpy (ΔH^0) and entropy (ΔS^0) at a constant temperature as:

$ln\, ln\, K_C = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}$ ……………………. (6)
(Dubey and Gokpal, 2009)

The ΔH^0 and ΔS^0 values were computed from the gradient and intercept respectively, of the Van't Hoff plot of $\ln K_C$ vs 1/T.

Data Analysis

The quantity of malachite green extracted from a solution per unit of mass adsorbent and percentage adsorbed were gotten as follows;

$q_e = \frac{(C_0 - C_e)V}{w}$ ………………… (7)

$\%\, Dye\, Removal = \frac{C_o - C_e}{C_o} X\, 100$ ….. (8)

where; C_o and C_e are the initial and final concentrations of the dye (mg/L), V is the volume (L) and m, the mass (g)

RESULTS AND DISCUSSION

Malachite Green Calibration Curve

The calibration curve of MG dye at 617 nm is a straight-line plot of absorbance against concentrations prepared through serial dilutions (shown in Table 1). The calibration curve (Figure 3) has a correlation coefficient of 0.99873. The equation of the graph is displayed on the plot and was used to calculate the subsequent residual concentrations (Ce) of the dye after contact with the *Dacryodes edulis seed* biomass.

That is, y = mx, (equation of linear graph) and since A= ECl (Beer-lambert's law) where l is cell path length taken as unity, then y is equivalent to A where A is the absorbance and m is the slope and is equivalent to E, the molar absorptivity, and x is the concentration, C.

However, in this case, the equation of the calibration curve has an intercept. Therefore, the subsequent concentrations were calculated by inserting the measured absorbance into the equation as y and solving for the concentration, x (Overah, 2020).

Table 1. Uv measurement of Absorbance vs concentration for Malachite Green at 617 nm

Conc. ppm	Abs
0	0
1	0.312
2	0.495
4	1.055

6	1.568
8	1.936
10	2.457

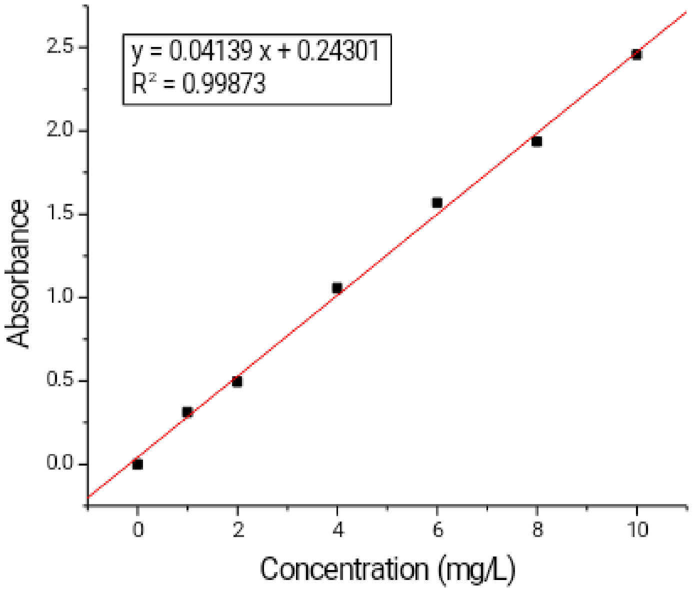

Figure 3. Calibration Curve of malachite green dye at 617 nm.

Batch Adsorption Experiments

The adsorption tests results are all presented in the following subheadings:

Impact of pH

The result of the impact of pH on the sorption of malachite green (MG) onto *Dacryodes edulis* seed biomass is shown in Figures 4a & b.

From the Figure, the optimum percentage adsorbed (Fig 4a) and uptake (Fig 4b) of malachite green by *Dacryodes edulis* was attained at pH 12. The observed increase in the adsorption percentage as the pH value increases towards alkalinity may be credited to the charge of the solution becoming progressively negative as the pH rises, causing an electrostatic attraction between adsorbent surface which is negatively charged and the positively charged adsorbate (cationic MG dye). This results in a large proportion of MG dye being adsorbed. This trend is similar to the reports of Igwegbe *et al.*, 2015 and Ahmad and Kumar, 2010.

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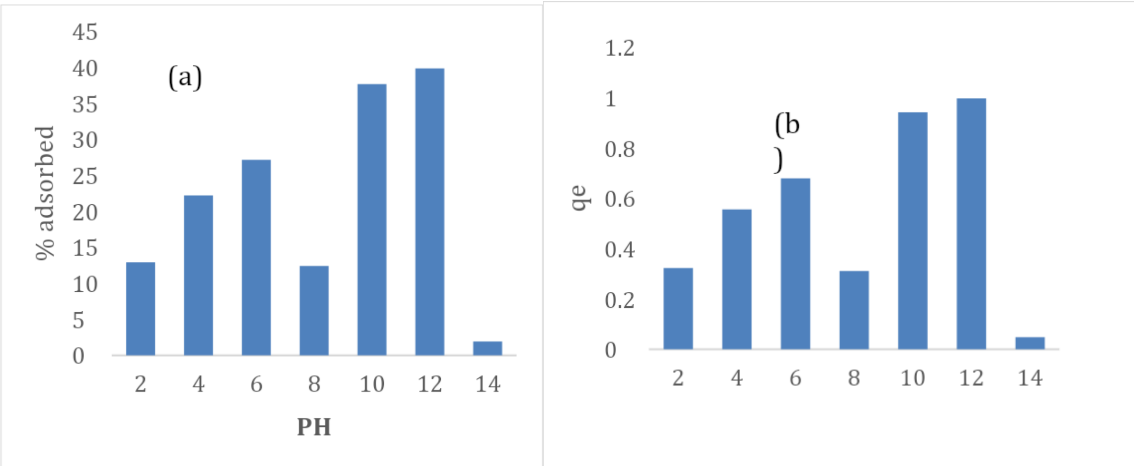

Figure 4: Impact of pH of malachite green on the (a) percentage adsorbed (b) uptake of dye onto *Dacryodes edulis* biomass

(Dose = 0.5 g, Time = 120 minutes, Concentration = 50mg/L)

Impact of Time of contact

Figure 5 shows that as time of contact increased from 5 to 240 minutes, the adsorption rate of the adsorbate also increased. Due to a large number of active sites readily available on the biomass surface, the dye ions quickly bound to the sites on the adsorbent surface at first (Igwegbe *et al.*, 2015). However, only a minor increase in adsorption occurred after a certain point. This behaviour conforms to expectations, because increasing contact time should result in the saturation of the binding sites on the biomass exterior, limiting further adsorption (Aqeela *et al.*, 2015).

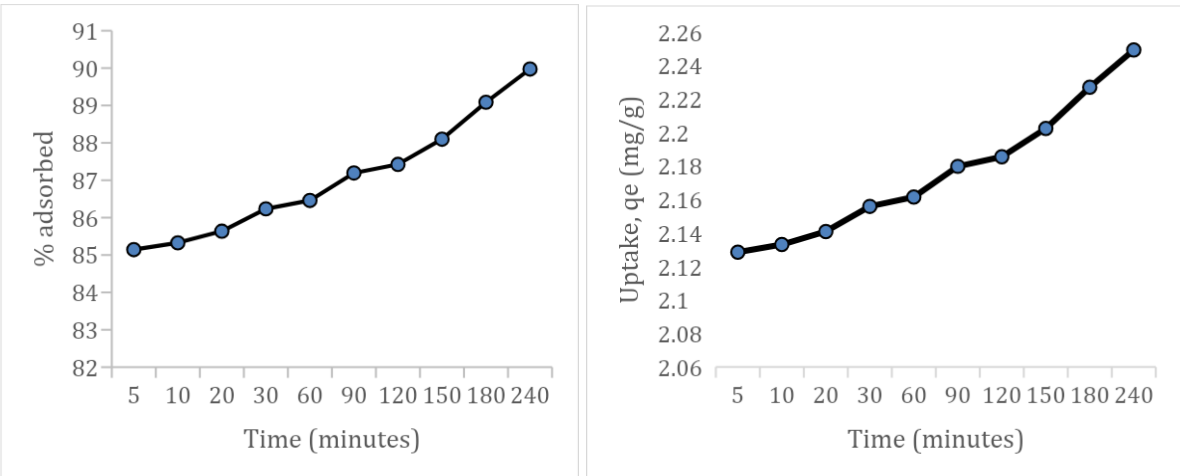

Figure 5: Impact of contact time on (a) percentage adsorbed and (b) Uptake of Malachite green dye onto *Dacryodes edulis*

(Dosage = 0.5 g, pH = 12, initial Concentration = 50 mg/L, volume of MG = 25 ml, Temperature = 308 K)

Impact of temperature

The study investigated the impact of temperature on malachite green adsorption onto *Dacryodes edulis*. The results revealed that as the temperature rose from 15-35 °C, more dye molecules were adsorbed, as depicted in Figure 6. The data also showed that raising the temperature increases the dye molecules' mobility, kinetic energy and amount of dye adsorbed (Ahmad and Kumar, 2010). This outcome leads to the conclusion that the process is endothermic. This finding is consistent with the report of Igwegbe *et al.*, (2015) for the adsorption of MG onto activated carbon from *Dacryodes edulis*. Moreover, the time-dependent experiment showed that 98% malachite green was adsorbed at the highest temperature of 35 °C. This trend supports the findings of Hema and Arivoli, (2008) and many others, who demonstrated that an increase in temperature enhances the adsorption capability.

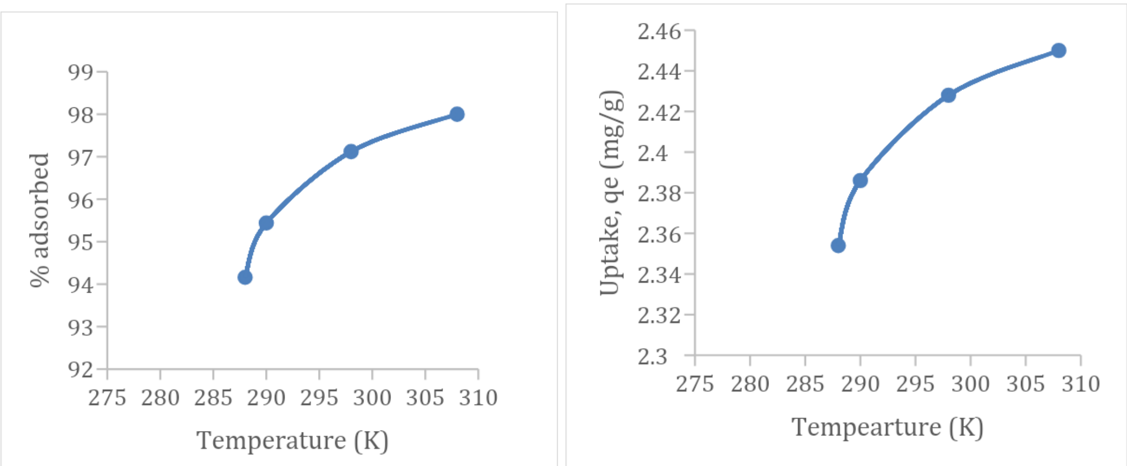

Figure 6: Impact of temperature on (a) Percentage Adsorbed (b) uptake of Malachite green onto *Dacryodes edulis* biomass

(Dosage = 0.5 g, pH = 12, Time = 240 minutes, Concentration = 50 mg/L)

Adsorption Kinetics

The kinetics of the adsorption process was investigated to predict the mechanism by which adsorption takes place.

Pseudo-first-order Kinetics

The pseudo-first-order kinetics model of malachite green removal by *Dacryodes edulis* biomass appears to be an inappropriate equation for the process, as indicated by the R^2 value of 0.7316. Therefore, this model was considered no further.

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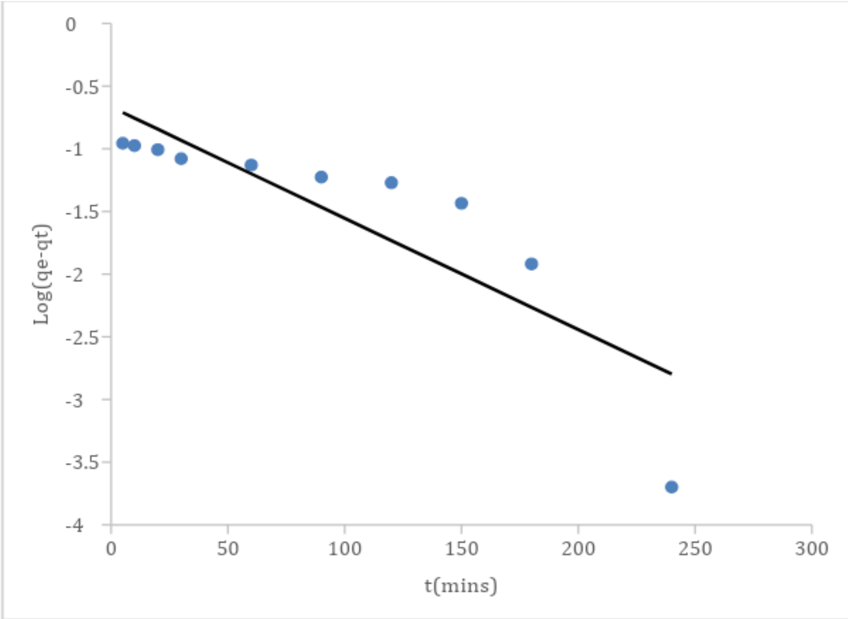

Figure 7: Pseudo-first order adsorption kinetics of the dye onto *Dacryodes edulis*

(Dosage 0.5g, pH 12, Time 240 minutes, Concentration 50 mg/L, Temperature 308K)

Pseudo-second-order Kinetics

Figure 8 shows a graph of t/qt vs t, from which K_2 and qe were obtained from the intercept and slope, respectively. The high coefficient of determination (R^2 = 0.999), which is close to unity, provides evidence that the pseudo-second-order mechanism accurately describes the adsorption of malachite green dye on *Dacryodes edulis*. This finding indicates that a chemical adsorption process is the rate-limiting step (Al-Ghouti *et al.*, 2005). This conclusion is consistent with the results obtained by Asiagwu (2012) and many others.

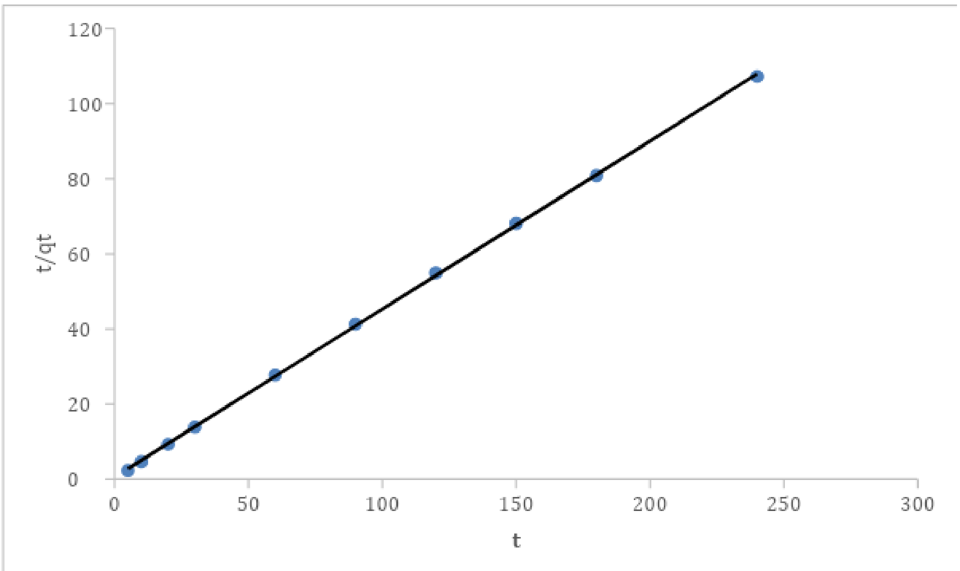

Figure 9: Pseudo-second order adsorption kinetics of Malachite Green onto *Dacryodes edulis* biomass

(Dosage 0.5 g, pH 12, Time 240 minutes, Concentration 50 mg/L, Temperature 308K)

Intra-particle Diffusion Model

Since the linear plot does not pass through the origin, the intra-particle diffusion is not the only variable affecting the sorption of malachite green by the adsorbent. This observation conforms with the discoveries of Igwegbe *et al.*, (2015).

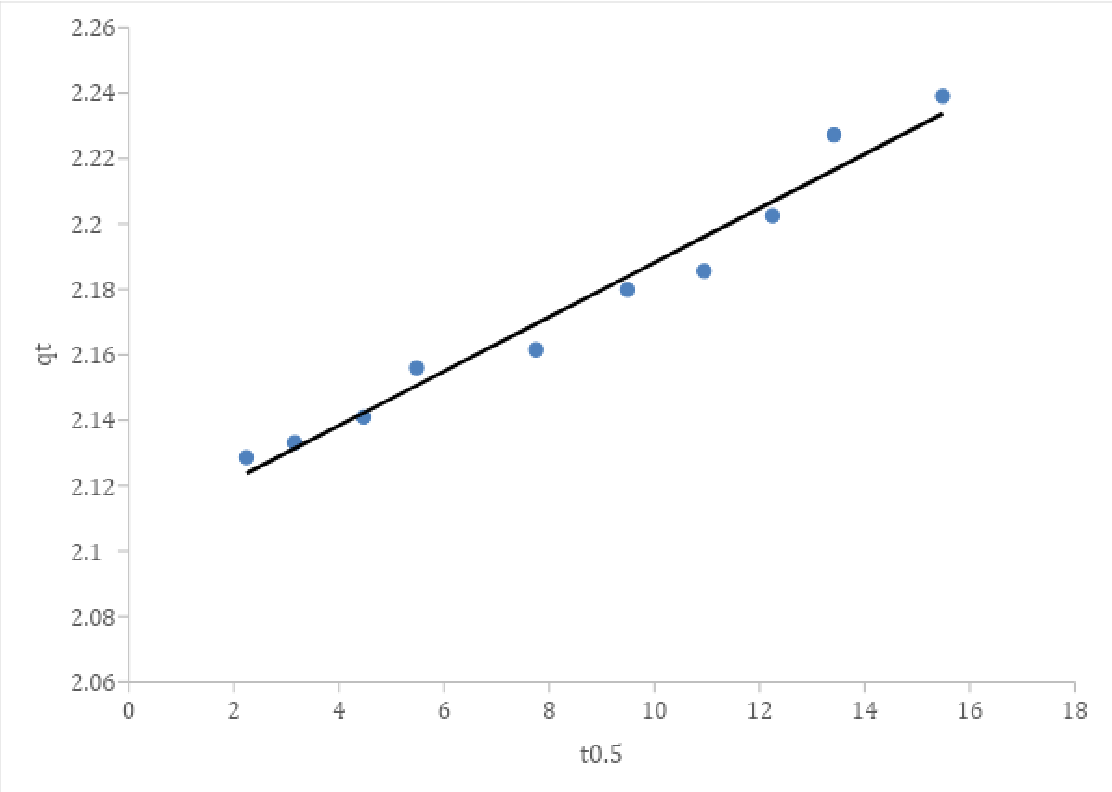

Figure **10**: The Intra particle Diffusion Kinetic of Malachite Green onto *Dacryodes edulis*

Elovich Model

The plot of qt vs lnt resulted in a fairly linear connection, as observed in Figure 11. Although the kinetics of MG adsorption was more suited to the intra-particle diffusion mechanism than the Elovich model, in the work of Igwegbe *et al.* (2015), the adsorption adheres to the Elovich model, as the value of R^2 was close to infinity. Hence both the Pseudo-second-order and intra-particle diffusion models adequately defined the kinetics of this process. The relevant calculated kinetic variables for both models are shown in Table 2.

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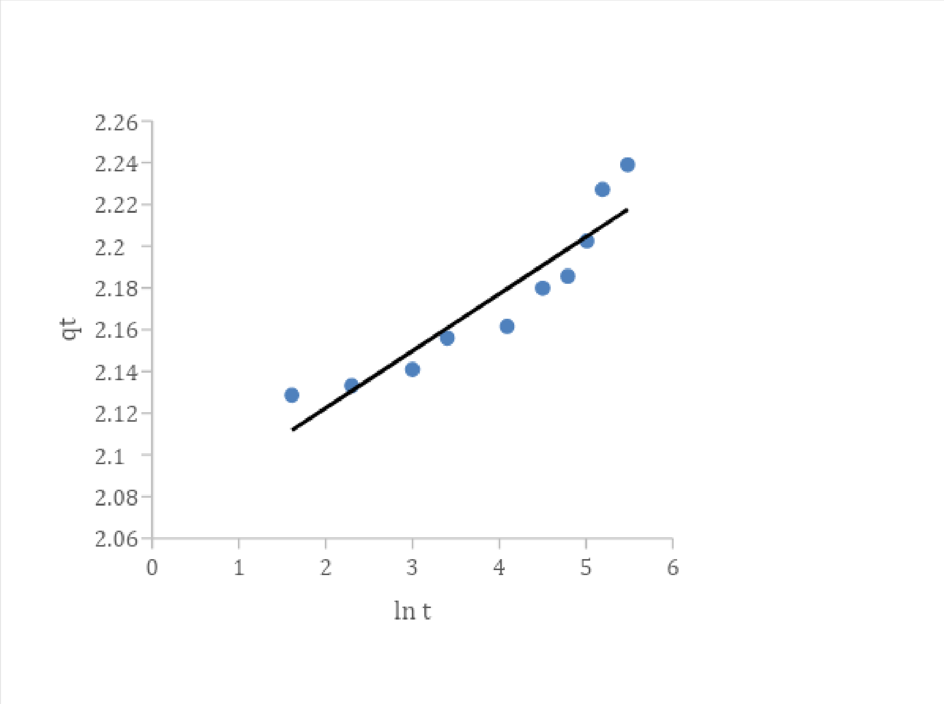

Figure 11: Elovich plot for malachite green sorption onto *Dacryodes edulis* biomass

Table 2: Estimated values of relevant kinetics factors for malachite green adsorption onto *Dacryodes edulis*

Kinetic model	Parameter	Values
Pseudo-Second-Order	K_2 (g/mg/min)	0.346
	qe (mg/g)	2.24
	R^2	0.9998
Intra-particle diffusion	C	2.1052
	K_{id} (mg/gmin$^{0.5}$)	0.008
	R^2	0.9695

Thermodynamics Studies

The thermodynamic factors, ΔG°, ΔH°, and ΔS°, were obtained for the sorption of malachite green onto the adsorbent material, *Dacryodes edulis* using the method earlier discussed and the result presented in Table 3. The results disclosed that ΔG° was negative at all the studied temperatures, meaning that the process is energetically favourable. Furthermore, the positive value of ΔH° signifies that the process is endothermic, requiring an input of energy to occur. Additionally, the positive ΔS° value suggests the increase in randomness at the solid-liquid interface due to the energy redistribution between the adsorbent and malachite green (Kothiyal and Sharma, 2013). Hema and Arivoli (2008) reported a similar observation.

Table 3. Calculated thermodynamics factors for malachite green abstraction onto *Dacryodes edulis* biomass

T	ΔH°(J/mol)	ΔS°(J/K.mol)	ΔG°(J/mol)
288k	40141.7	163.28	-6656.52
290k			-7329.62
298k			-8721.05
308k			-9961.17

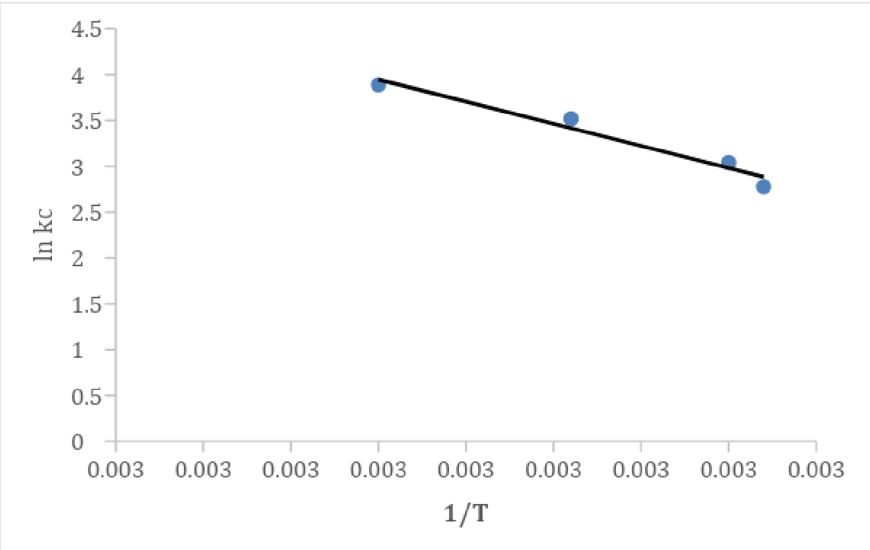

Figure 12. Van't Hoff plot for the adsorption of malachite green from aqueous solution.

The performance of untreated *Dacryodes edulis* biomass compared with other adsorbents for malachite green adsorption.

The uptake capacities, kinetics and thermodynamics mechanisms of malachite green adsorption onto various adsorbents are in this section compared with that of untreated *Dacryodes edulis* biomass and displayed in Table 4. Even though only 2.24 mg (from effect of time studies) of the MG dye was adsorbed, this corresponds to almost 90% adsorption. The difference in the amount of malachite green adsorbed by these different adsorbents may be due to the variance in their chemical makeup and experimental conditions like solution pH, initial concentration, time, and temperature.

Also, the kinetics of MG adsorption onto the various adsorbents are mostly compliant with the pseudo-second-order mechanism. Also, in all cases presented here, the reaction was endothermic.

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Table 4. Comparison of the adsorption characteristics of malachite green removal onto *Dacryodes edulis* and other adsorbents

Adsorbent	Maximum monolayer ads capacity(mg/g)	Adsorption isotherm	Kinetic mechanism	Thermodynamic process	Reference
Untreated *Dacryodes edulis*	Not determined	Not determined	Pseudo second order	Endothermic	This work
Phosphoric acid-treated Daryodes edulis	55.56	Langmuir, Freundlich, Temkin	Pseudo second order, Elovich and intraparticle diffusion	Endothermic	Igwebe *et al.*, 2015
Sodium Chloride-treated Dacryodes dulis	58.82	Langmuir, Freundlich, Temkin	Pseudo second order, Elovich and intraparticle diffusion	Endothermic	Igwebe *et al.*, 2015
Treated ginger waste	84.03	Langmuir and Freundlich	Pseudo second order	Endothermic	Ahmad and Kumar, 2010
Activated low-cost carbon	9.76	Langmuirr and Freundlich	Pseudo-first-order and intraparticle diffusion	Endothermic	Hema and Arivoli, 2008
Rattan saw dust	62.71	Langmuir	Pseudo-first-order and intraparticle diffusion	Not determined	Hameed and El-Khaiary, 2008
Acid treated rice husk	32.00	Freundlich	Pseudo second order	Endothermic	Elijah and Nwabanne, 2014

CONCLUSION

This study has thus far revealed that *Dacryodes edulis* can adsorb MG from an aqueous medium. The adsorption efficiency is affected by the pH, contact duration, and temperature.

The kinetic data support the pseudo-second-order model as the most suitable in describing the mechanism of MG separation from an aqueous medium using *Dacryodes edulis*. The negative ΔG° and positive ΔS° indicate the feasibility and spontaneous nature respectively of the process, while the positive ΔH° indicates an endothermic adsorption process.

These findings demonstrate that using chemically untreated *Dacryodes edulis* as waste biomass for removing malachite green from contaminated environments is an alternative to conventional methods. Its performance in terms of efficiency is quite comparable but less than the performance of chemically treated *Dacryodes edulis*. However, its benefits include low cost, ease of preparation and availability.

Competing Interests

The authors declare no competing interests.

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