PRINT ISSN 1119-8362
Electronic ISSN 2659-1499

Full-text Available Online at
https://www.ajol.info/index.php/jasem
https://www.bioline.org.br/ja

J. Appl. Sci. Environ. Manage.
Vol. 29 (2) 497-507 Feb. 2025

# Physico-Thermally Modified *Chrysophyllum albidum* Seed Shell Activated Carbon for Removal of Malachite Green Dye from Simulated Wastewater

***[1]AMUDA, OS; [1]YEKINI, BB; [1]OJO, DT; [1]OYEDIRAN, OF; [2]SALAM, KK**

**[1]Environmental Management and Protection Research Group (ENVIM-P), Department of Pure and Applied Chemistry, Ladoke Akintola University of Technology, Ogbomoso, 210001, Nigeria*
*[2]Environmental Management and Protection Research Group (ENVIM-P), Department of Chemical Engineering, Ladoke Akintola University of Technology, Ogbomoso, 210001, Nigeria*

**Corresponding Author Email: osamuda@lautech.edu.ng*
**ORCID: https://orcid.org/0000- 0003-2715-6526*
**Tel: +234 803 440 2907*

*Co-Author Email: yekinibasirat09@gmail.com; oluwadamilolaoladipo@gmail.com; olarikeoyediran@gmail.com; kksalam@lautech.edu.ng*

**ABSTRACT:** The objective of this paper was to physico-thermally modify *Chrysophyllum albidum* seed shell (CASS) to *Chrysophyllum albidum* seed shell activated carbon (CASSAC) for removal of malachite green dye from simulated wastewater using isotherm, kinetic, and thermodynamic models after applying appropriate standard techniques. The result of physico-thermal treatment of CASS to CASSAC showed that the modification of CASS increases total pore volume to 0.522 $cm^3/g$, average pore size to 24.22 Å and surface area to 1450.20 $m^2/g$. The maximum dye removal efficiency was 80.12% at experimental conditions of (initial dye concentration - 50 mg/L, CASSAC dosage - 0.30g, pH 8, and agitation time - 60 min). The Temkin and pseudo-first-order models best fit the data, indicating homogeneous monolayer adsorption driven by physisorption. Thermodynamic study showed adsorption is feasible, spontaneous, and endothermic. On the other hand, the reusability study was carried out and the adsorbent was utilized in three cycles with a drop in the removal efficiencies from 80.0 to 58.9% after the third cycle usage. This study concludes that CASSAC effectively removes malachite green dye from wastewater through adsorption, offering a cost-effective, sustainable, and environmentally friendly solution for textile wastewater treatment

**DOI: https://dx.doi.org/10.4314/jasem.v29i2.20**



**Cite this Article as:** AMUDA, O. S; YEKINI, B. B; OJO, D. T; OYEDIRAN, O. F; SALAM, K. K (2025). Physico-Thermally Modified *Chrysophyllum albidum* Seed Shell Activated Carbon for Removal of Malachite Green Dye from Simulated Wastewater. *J. Appl. Sci. Environ. Manage.* 29 (2) 497-507

**Dates:** Received: 23 December 2024; Revised: 27 January 2025; Accepted: 09 February 2025; Published: 28 February 2025

**Keywords:** Adsorption; *Chrysophyllum albidum* seed shell; Malachite green; Adsorption isotherms; Carbonization; Adsorbent.

*Abbreviations*: CASS = *Chrysophyllum albidum* seed shell; CASSAC = *Chrysophyllum albidum* seed shell activated cabon; MGD =Malachite green dye

Water pollution has emerged as a critical environmental issue worldwide due to the rapid growth of the global population and industrialization (Liu *et al.*, 2022). The presence of organic dyes in polluted water significantly threatens ecosystem biosafety and human health. Although various methods have been investigated for removing dyes and other toxic substances from water and the broader environment, researchers continue to explore novel, cost-effective, and eco-friendly biosorbents to

**Corresponding Author Email: osamuda@lautech.edu.ng*
**ORCID: https://orcid.org/0000- 0003-2715-6526*
**Tel: +234 803 440 2907*

efficiently remove these contaminants. One typical industrial dye and organic pollutant discovered in wastewater is malachite green (MG) dye. MG is used in the culinary and textile sectors as food coloring and dyeing agents, respectively (Oladoye *et al*., 2023). Malachite green (MG) is a toxic basic dye with carcinogenic and neurotoxic effects, linked to several human diseases (Al-Gheethi *et al*., 2022). Despite its dangers, MG is still widely used in various industries, including textiles, paper printing, and as an additive in poultry feeds, particularly in countries with less stringent regulations due to its low cost (Rout and Jena, 2021). Wastewater from such industry contains MG. In 2005, MG was found in fish imported from China and Taiwan, leading to the US FDA banning the import of certain seafood in 2007 (Khattri and Singh, 2009; Ismail *et al*., 2018). MG disrupts aquatic ecosystems by blocking sunlight, reducing dissolved oxygen levels, and harming marine life even at low concentrations (Al-Tohamy *et al.,* 2022). MGD has been identified as a cationic dye with wide applications in textile, leader, pharmaceutical industries and utilization comes generation of wastewater that are carcinogenic and mutagenic if not treated before its discharge to the water body (Oladoye *et al*., 2022). Adsorption has proven to be a good approach for the treatment of MGD due to success recorded from selection of this approach for wastewater treatment.

Several physical and chemical techniques, such as photocatalysis, coagulation-flocculation, and adsorption, have been employed to remove dyes and heavy metals from polluted water (Shabir *et al*., 2022). Among these methods, adsorption and photocatalysis are considered cost-effective and more efficient compared to other chemical and physical techniques (Fazal *et al.,* 2020). These methods are preferred due to their relatively simple design, ease of operation, cost-effectiveness, and energy efficiency. A variety of adsorbents, including activated carbons, enhanced biochars, nanoadsorbents, hybrid adsorbents, and others, have been used to remove emerging contaminants from wastewaters (Rathi and Kumar, 2021). However, synthetic adsorbent is expensive and indirectly introduces secondary pollutant (Dehghani *et al*., 2023).

Agricultural waste materials offer significant biosorption potential, with functional groups such as acetamido, alcoholic, carbonyl, phenolic, amino, and sulfhydryl groups (Ahmad *et al.,* 2021). Agricultural waste materials are highly efficient, low-cost, and renewable biomass sources that can be utilized for dye remediation (Bushra *et al.,* 2021). Biomaterials available in large quantities or specific agricultural waste products could be used as low-cost adsorbents, representing underutilized resources that are both widely available and environmentally friendly. Many studies have reported the processing of low-cost activated carbon adsorbents with sufficient densities and high porosity from pecan shells (Seffah *et al*., 2024), coconut shells (Kawalerczyk *et al*., 2024), and *Chrysophyllum albidum* seed shell wastes (Amuda *et al.,* 2013). Other low-cost, non-conventional adsorbents include agricultural by-products such as nut shells, wood, bone, peat, and coconut shells, which can be processed into activated carbons (Bushra *et al.,* 2021).

Residues or underutilized biomass have been successfully converted to adsorbents deplored for various wastewater of different pollutants with satisfactory results. There are lots of residues that have not been properly modified despite their availability. CASS is a waste generated from dash fruits. The quantity of this waste generated per year in Africa, Nigeria or even in the whole world was so enormous. There are some preliminary utilization routes presented in Amuda *et al.,* 2016, but there is need to modify the biomass for wide application. This is important because the source is a cheap and the process of producing activated carbon from cheap, renewable precursors, primarily agricultural waste and byproducts like *Chrysophyllum albidum* seed shells, is less harmful to consumers and is biodegradable and environmentally beneficial (Shuaib *et al*., 2024).

CASS is an underutilized biomass rich in carbon with little information on its application or its modification to value added products. This study introduces an environmentally friendly dye wastewater treatment technique using adsorbents derived from *Chrysophyllum albidum* seed shells. Therefore, the objective of this paper was to physico-thermally modify *Chrysophyllum albidum* seed shell (CASS) to *Chrysophyllum albidum* seed shell activated carbon (CASSAC) for removal of malachite green dye from simulated wastewater.

## MATERIALS AND METHODS

*Material***s:** The materials used in this study included CASS obtained from Araada Market in Ogbomoso, Oyo State, Nigeria, located at 8.11670° N and 4.24520° E. Additional materials included Malachite Green Dye (MGD) (Merck), HCl, NaOH, ethanol, and Whatman filter paper. All reagents used were of analytical grade.

*Preparation and activation of CASSAC used for the experiment***:** The methods of preparation and

activation of by Amuda *et al*., (2016) and Amer *et al*. (2017) were modified. The CASS obtained were crushed and thoroughly washed with distilled water until it was free from dirt and other impurities. The cleaned CASSs were then oven-dried (Model BOV-T50F) at 110°C for 24 hours and subsequently pulverized to particle size of 100 µm. The CASSs were carbonized using an electric muffle furnace at 300°C for 2 hours. The carbonized sample was physically activated using steam in a steam-activating reactor. The resultant steam-activated CASS Carbon was then oven-dried at 110°C for 2 hours and allowed to cool to room temperature to form CASS Activated Carbon (CASSAC). The dried CASSAC was ground, sieved to, and stored in an airtight container.

*Preparation of simulated wastewater solution and Calibration Curve:* The stock solution of the dye was prepared by dissolving 1g of the dye in 1000 $cm^3$ ($1dm_{3)}$ in distilled water volumetric flask and then make it up to the mark with distilled water. This gives 1000 mg/L of the solution. Working solutions was prepared from the stock solution by serial dilution. The pH of the dye solution was adjusted with 0.1M NaOH or HCl using a pH meter. The dye used for preparing the stock solution was of analytical grade and hence does not require further purification (Olowonyo *et al*., 2024).

*Adsorption experiments:* The batch removal of MGD from aqueous solution by CASSAC was studied by modifying the investigations of Shetty *et al*. (2023). 50 mL of MG solution with an initial concentration of 50 ppm was measured into a conical flask and 0.1 g of CASSAC was weighed into the conical flask. The mixture of CASSAC and MGD solution was agitated at 160 rpm for 1 hour at 30 $^oC$ using an environmental orbital shaker (Deneb Instruments). The mixture was filtered using Whatman No. 1 filter paper and the final concentration of MGD was determined by UVS (ASUV-6300PC) at an absorbance of 617 nm.

For optimization, several parameters were studied, including adsorbent dose (0.1-0.3 g/L), initial dye concentration (50-200 mg/L), pH (2-12) using a bench pH meter (PHS-26C) with 0.1M HCl and 0.1M NaOH, and contact time (10-60 minutes). The equations (1) and (2) were used to determine the equilibrium biosorption capacity and the removal efficiency (%R) of MGD using CASSAC The procedure and formulae used are reported in the literature (Olowonyo *et al.,* 2024) are presented in equation 1 and 2.

$$q_e = \frac{(c_o - c_e)}{m} \times V \qquad (1)$$

$$\%R = \frac{(c_o - c_e)}{c_o} \times 100 \times V \qquad (2)$$

Where m is the mass of CASSAC (g),$c_o$is the MGD initial concentration, $c_e$ is the MGD adsorbed by CASSAC and V is the volume of MG solution in L.

*Adsorption Isotherms, Kinetics, and Thermodynamics Models:* Isotherm study models explain the relationship between adsorbates and adsorbents during adsorption experiments (Kalam *et al.,* 2021). In this study, three isotherm models—Langmuir, Freundlich, and Temkin—were applied to the adsorption data to determine which model best fit the uptake (equation 3-5). The adsorption data were subjected to the isotherm models to ascertain which provided the best fit.

$$\frac{c_e}{qe} = \frac{1}{KLqm} + \frac{ce}{qm} \quad (3)$$

$$\log q_e = \log K_F + \frac{1}{n}\log c_e \quad (4)$$

$$q_e = \beta \ln K_T + \beta \ln c_e \quad (5)$$

Additionally, adsorption kinetics data were analyzed using three kinetic models: Pseudo-First-Order, Pseudo-Second-Order, and Intra-particle Diffusion models, as described in equation 6-8 (Bayode *et al.,* 2020; Obayomi *et al.,* 2023). By utilizing adsorption kinetics models, the mechanism of adsorbate uptake by the biosorbent was determined and the contact time data was used to examine the kinetic model. The performance evaluation of the kinetic and isotherm models fitted with the obtained adsorption data for the removal of MGD was conducted with coefficient of determination ($R^2$) and expressed in equation 3 above (Agarry *et al.* 2024).

$$\ln(q_e - q_t) = \ln q_e \quad (6)$$

$$\frac{1}{qt} = \frac{1}{k_2 qe^2} + \frac{1}{qe}t \quad (7)$$

$$Q_t = k\ difft^{0.5} + C \quad (8)$$

Change in energy that takes place in adsorption is showed through thermodynamics parameters. Three basic parameters are used for the evaluation of adsorption process; which are standard enthalpy change (ΔH°), standard entropy change (ΔS°) and standard free energy change (ΔG°) (Shetty *et al*., 2023).

*Characterization:* The produced CASSAC was characterized using applicable American Standards for Testing and Measurements (ASTM)s. The morphology of CASSAC was imaged by Scanning Electron Microscope-Electron Dispersion X-ray (SEM-EDX) (Hitachi SU 3500, Tokyo, Japan)(ASTM F1372-93 2020), functional groups were determined by Fourier-transform infrared spectroscopy (FTIR)(ASTM E1252-98 2021), surface area of CASSAC was analyzed by Emmett teller (BET) analysis (Tristar 3000V4.02)(ASTM D3663-20 2020), and crystallographic structure information was studied by x-ray dispersive (XRD, Inspect F50)(ASTM D3906-19 2019).

*Reusability study:* The reusability potential of the CASSAC was conducted by using a fixed concentration of 50 ppm of the MGD solution. The MGD solution was prepared in triplicate and the optimized mass of the CASSAC was weighed into each of the MGD solutions. The procedure for adsorption study in section 2.2 was followed. The removal efficiency was determined while the residue was dried at 70 $^{o}$C for 2 hours. The used CASSACs were treated with three solvents 0.1M HCl, 0.1M NaOH, and distilled water. The used CASSACs were mixed with the three solvents. The treated used CASSACs were dried in the oven at 70 $^{o}$C for 3 hours. This is the completion of a regenerated cycle. The regenerated CASSACs were subjected to removal of MGD in simulated aqueous solution and regenerated cycle is repeated for the cycles.

The percentage desorption of the recycled CASAC Bhatti *et al*. (2020) as shown in equation (3).

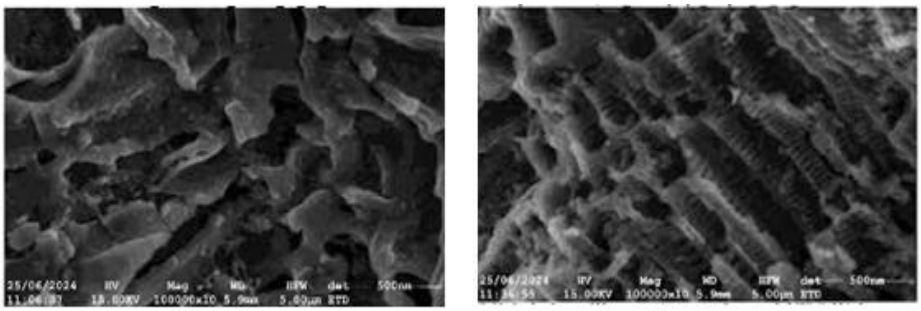
$$\%\, Desorption = \frac{C_{des}}{C_{ads}}\, x\, 100\% \qquad (9)$$

Where $C_{ads}$ (mg/L) is the concentration of MG adsorbed on the CASSAC and $C_{des}$ (mg/L) is the concentration of MG desorbed from the CASSAC.

## RESULTS AND DISCUSSION

*Characterization of CASSAC*

*SEM/EDX analysis:* The SEM images of CASSAC before and after adsorption are presented in Figure 3 (a and b). It is observed from Figure 3(a) that before adsorption, the surface of CASSAC has a large pore size, which facilitates the adsorption process, it was also well dispersible, there were no impurities on the surface of CASSAC. In contrast, Figure 3(b) shows that after adsorption, the surface of CASSAC is covered with dye molecules. This indicates that the activation process was effective in creating well-developed pores on the surface of the precursor, resulting in CASSAC with a large surface area and porous structure.



(a) (b)

**Fig. 1:** SEM images of CASSAC (a) before adsorption and (b) after adsorption of malachite green dye (magnification 500x)

Additionally, as shown in Figure 3(b), the dye attaches to the adsorbent on both the outer and interior surfaces of the pores, suggesting that the dye has bonded to the biosorbent's surface and pores, similar to other adsorption studies (Sen *et al.,* 2011; Hevira *et al.,* 2021; Zein *et al.,* 2022). The surface chemical composition of CASSAC was investigated using EDX (Figure 4). It is seen from Figure 3 that carbon, oxygen and iron elements were detected at weight percentages of 76.96%, 20.70% and 2.34% respectively. *BET analysis:* BET analysis confirmed the presence of pores on the surface of the biosorbent. These pores and cavities serve as adsorption sites for MGD, reducing the dye concentration in the solution. The surface area of the CASSAC, as estimated by BET measurements, was 1450.20 m²/g, with a total pore volume of 0.522 cm³/g and an average pore size of 24.22 Å, indicating a significantly large surface area. According to Azaman *et al*. (2018), high surface area is likely to enhance the adsorption capacity. Table 3 summarizes the BET analysis of the adsorbent. This result aligns with the work of Banerjee *et al*. (2019), who reported

BET surface areas in the range of 800–1200 m²/g for activated carbon prepared from agricultural waste.

*XRD analysis:* X-ray diffraction patterns of the activated CASSAC are represented in Fig. 5. The broad peak observed in the carbonized CASSAC between 17 and ~30° is assigned to amorphous carbon.

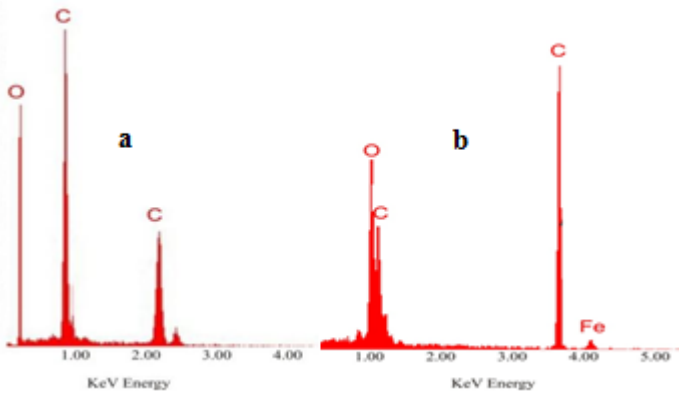



**Fig. 2:** EDX spectrum of CASSAC (a) before adsorption and (b) after adsorption of malachite green dye

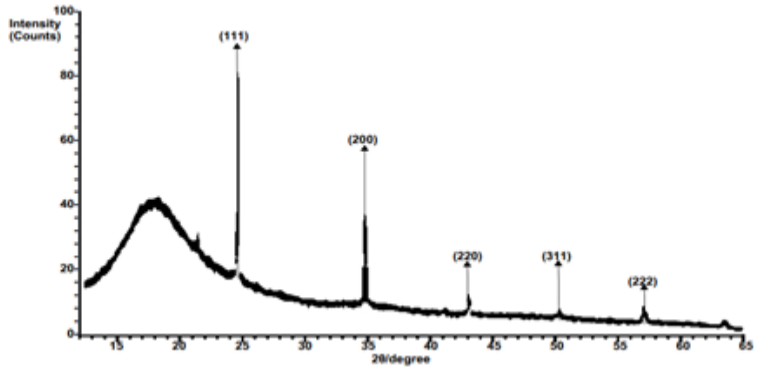



**Fig. 3:** XRD spectrum of CASSAC

Other peaks seen revealed a wide peak, attributed to the 2$\theta$ region 42–47° due to high broadening and low intensity. Low-intensity additional peaks on the adsorbent diffraction spectrum refer to the FeO impurity arising from the synthesis process. This aligns with Azaman *et al*. (2018).

*FTIR analysis:* To confirm the type of functional groups on the CASSACs before and after adsorption, FTIR spectra were performed and shown in Figure 6 (a and b). In the wave number 3298.63 $cm^{-1}$, there was a relatively wide strong peak, which was the stretching vibration of the –OH and –NH. This result is similar to Azaman *et al*. (2018) FTIR result on removal of malachite green from aqueous phase using coconut shell activated carbon. The strong peak at 2,672.26 and 2581.51 $cm^{-1}$ was the vibration peak of $–CH_3$ and $–CH_2$. The additional absorption peaks at 1,797.92 $cm^{-1}$ and 1,568.54 $cm^{-1}$ observed after adsorption was due to the stretching vibration of C=O and C–N vibration respectively. Absorption at 1,000 – 1,200 $cm^{-1}$ was from vibration of C–O existed predominantly before adsorption than after. The main difference between the infrared spectra of CASSAC before and after adsorption in the Figure 5 was that the peak at 2581.51 $cm^{-1}$ from vibration of $-CH_2$ became very weak and the peak at 3298.63 $cm^{-1}$ was enhanced from N–H stretching vibration, which indicated that a large number of amino groups were deposited on the CASSACs surface. Therefore, it can be concluded that organic substances were successfully adsorbed on the surface of the adsorbent.

*The effect of pH on adsorption*: The pH of the solution affects the charge on the surface of the adsorbent and the chemical structure and stability of the dye surface. The effect of solution pH on MGD adsorption is showed in Figure 7. The effect of pH on the removal of MGD was examined over a pH range of 2 to 12, while keeping other factors constant, including temperature, initial concentration, contact time, and the amount of CASSAC. As shown in

Figure 7a, the maximum sorption of MG by CASSAC was 65.29% at pH 8. At this pH, the negatively charged functional groups on the reactive dyes are attracted to the adsorbent surface, thereby increasing the adsorption capacity. But the adsorption capacity decreased significantly when the pH value was more and less than 8, so the pH of the working solution was adjusted to 8 in the following experiments. The similar results about effect of pH were also observed in the study (Gu *et al.*, 2019) of adsorption of light green anionic dye from solution using polyethyleneimine-modified carbon nanotubes.

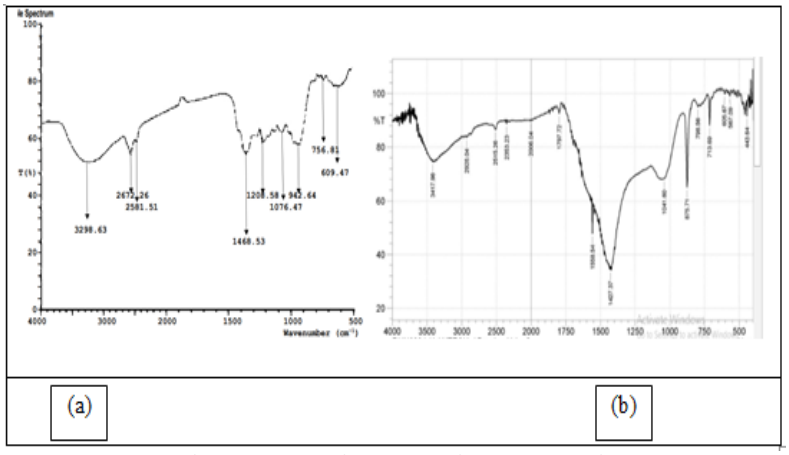



**Fig. 4:** FTIR Images of CASSAC (a) before and (b) after adsorption of Malachite Green Dye

*The effect of contact time on adsorption:* The effect of contact time on MGD adsorption onto CASSAC is illustrated inFigure 8. A 65% removal was achieved within 20 minutes. Initially, the adsorption process proceeded rapidly due to the availability of numerous interactive groups on the adsorbent surface. However, after 50 minutes, the adsorption reached equilibrium as the available active sites on CASSAC became saturated. This behavior is similar to the adsorption of malachite green dye from liquid phase using hydrophilic thiourea-modified poly (acrylonitrile-*co*-acrylic acid) observed and reported by Adeyi *et al.*, 2019.

*The effect of adsorbent dosage on adsorption:* A range of 0.1 to 0.3 g of adsorbent was used, with all other parameters kept constant. As shown in Figure 9, increasing the adsorbent dose led to a greater removal of MG from the solution. The removal percentage increased from 72.47% to 80.12%, which can be attributed to the increase in available adsorption sites, consistent with the ion exchange mechanism. Using an adsorbent dosage of 0.3 g, 80.12% of the MG present in the 50ppm solution was successfully removed. These findings suggest that the increase in exchangeable sites and contact surface area provided by a larger quantity of adsorbent results in a higher percentage of dye removal. This finding was on agreement with Azaman *et al.* (2018)'s report.

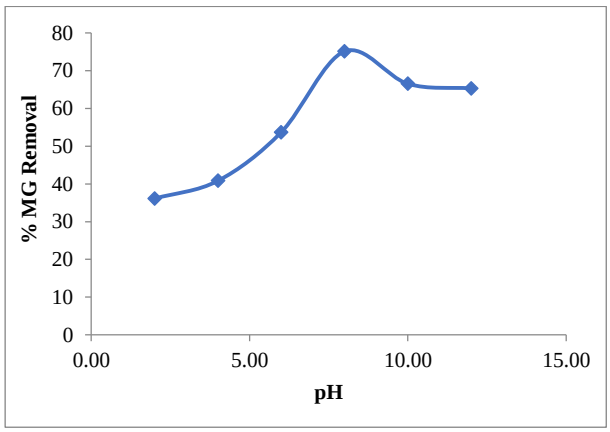



**Fig. 5:** Effect of pH on MG removal

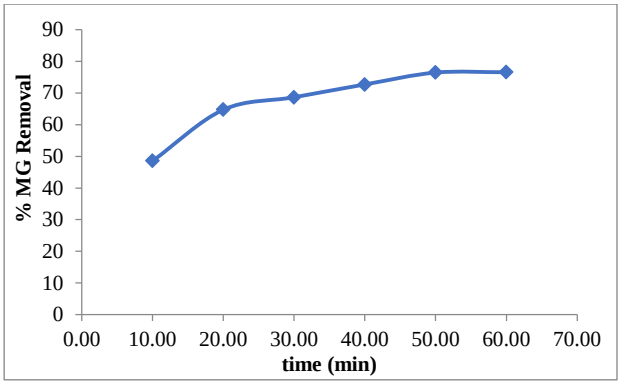



**Fig. 6:** Effect of contact time on MG removal

*The effect of initial concentration on adsorption*: The effect of the equilibrium concentration of MG in the solutions on adsorption is shown in Figure 10. The adsorption was investigated at constant pH 8, dose 0.1 g, agitation time 60 min and temperature 30 °C. The removal percentage decreased from 78.69% to 55.24%. As observed in Figure 8, percentage removal decreases as the concentration of MG in the solution increases. According to Azaman *et al.* (2018)'s report, the main reason for the drop in the removal (%) under study is a reduction in the number of available active spots on fixed CASSAC.

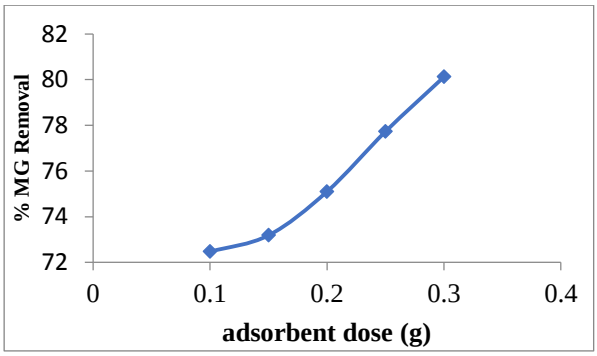



**Fig. 7:** Effect of CASSAC dosage on MG removal

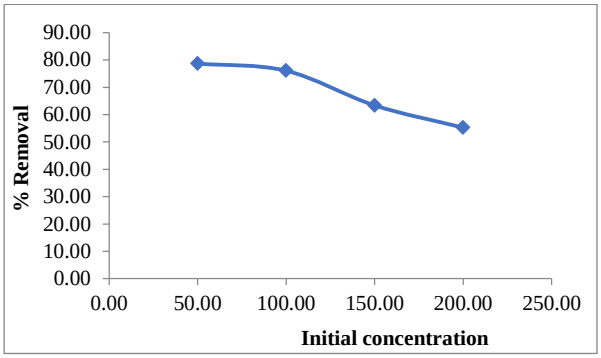



**Fig. 8:** Effect of initial concentration on MG removal

*Adsorption isotherms:* As shown in Figure 9 (a -c) and detailed in Table 4 below, the $R^2$ value for the Temkin isotherm model was near one, suggesting that the adsorption process is most consistent with the Temkin isotherm model.

**Table 1:** Isotherm model parameters for adsorption of MG onto CASSAC

| | Langmuir | | Freundlich | | | Temkin | | |
|---|---|---|---|---|---|---|---|---|
| Qm(mg/g) | $K_L$(L/mg) | $R^2$ | N | KF(mg/g) | $R^2$ | Bt | KT | $R^2$ |
| 10.989 | 0.200 | 0.9929 | 2.134 | 1.7811 | 0.9856 | 112.32 | 0.125 | 0.9937 |

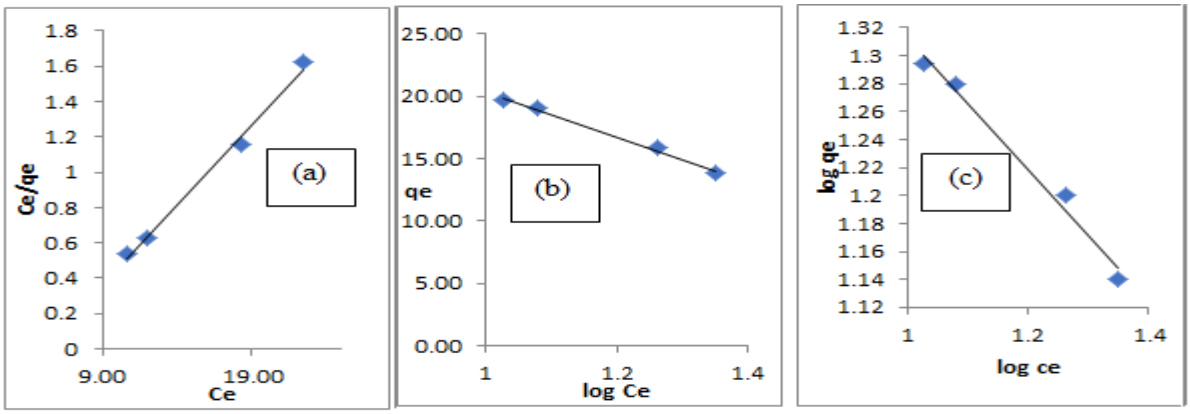



**Fig. 9:** (a-c) Isotherm of Malachite Green Dye onto CASSAC by (a) Langmuir, (b) Freunlich, and (c) Temkin

*Adsorption kinetics:* As shown in Figures 11 (a-c), Table 5 and 6**,** the pseudo-second-order kinetic model provided the best fit for the adsorption of MG by CASSAC, with a coefficient of determination ($R^2$) close to 1 and sum of square error (SSE) closer to zero when compared with the value obtained for pseudo-first order kinetic order. The $R^2$ values for the CASSAC model indicated that the pseudo-second-order kinetic model was more appropriate than the pseudo-first-order models for describing MGD adsorption kinetics. This suggests that CASSAC adsorbs MG dye primarily through chemical interactions, or chemisorptions (Muniyasamy *et al.*, 2020).

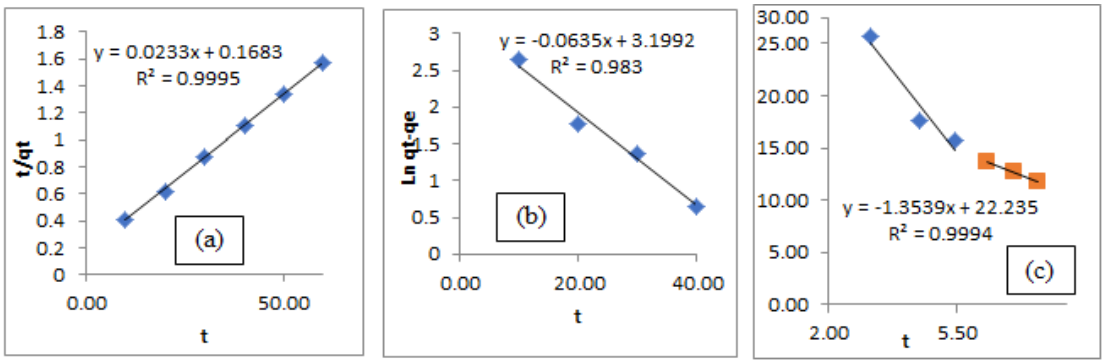



**Fig. 10:** (a-c) The kinetics of malachite green dye onto CASSAC by pseudo-first-order (a), pseudo-second-order (b) and intraparticle diffusion (c)

**Table 2:** Parameters of the Pseudo-first-order and Pseudo-second-order kinetic models together with their correlation coefficients of MG dye onto CASSAC.

| Adsorbents | $q_e$exp(mgg$^{-1}$) | $q_e$cal(mgg$^{-1}$) | β (gmg$^{-1}$) | $k_1$ (min$^{-1}$) | $R^2$ | SSE |
|---|---|---|---|---|---|---|
| Pseudo-First Order | 38.270 | 24.510 | - | 0.0635 | 0.9995 | 3.290 |
| Pseudo-Second Order | 38.270 | 42.918 | - | 0.0238 | 0.9830 | 0.543 |

**Table 3:** Parameters of the Intra-particle diffusion kinetic models together with their correlation coefficients of MG dye onto CASSAC.

| **Intra-particle diffusion** | **Adsorption process 1** | **Adsorption process 2** |
|---|---|---|
| $K_{id}$ (mg/g/min$^{1/2}$) | 7.431 | 1.3539 |
| C (mgg$^{-1}$) | 4.400 | 22.235 |
| $R^2$ | 0.928 | 0.9934 |

*Adsorption thermodynamic studies:* Thermodynamic parameters were evaluated to study the nature, feasibility, and spontaneity of the removal of MGD using CASSAC. The monitored parameters in thermodynamic studies reveal the various energy changes that occur during the adsorption experiment. In this study, the standard enthalpy change (ΔH°), standard free energy change (ΔG°), and standard entropy change (ΔS°) were the three thermodynamic parameters evaluated, as described in Table 7.

The enthalpy (ΔH°) expresses whether the adsorption process is endothermic or exothermic. Adsorption occurs exothermically or releases energy if the enthalpy value is negative, but if it is positive, adsorption consumes energy. Entropy (ΔS°) describes

the randomness or orderliness of the adsorption reaction. If the value is negative, the uncertainty or disorder decreases; if it is positive, the disorder increases (Agarry *et al*., 2024); Dada *et al*., 2020)

.

**Table 4:** Thermodynamic parameters for MG on CASSAC adsorbent

| Temperature (K) | ΔG (kJ/mol) | ΔH (kJ/mol) | ΔS (kJ/mol.K) |
|---|---|---|---|
| 303 | -2.14 | | |
| 313 | -3.77 | 21.94 | 84.76 |
| 323 | -5.12 | | |
| 333 | -7.52 | | |

*Adsorbent reusability:* The reusability of an adsorbent is a crucial factor in ensuring the economic viability of an adsorption process (Adeyi *et al*., 2019; Shetty *et al*., 2023). To reduce costs and minimize waste production, regeneration tests were conducted to assess the reusability of the adsorbent. Three different solvents—distilled water, 0.1 M HCl, and 0.1 M NaOH—were used to recover the adsorbent and evaluate its effectiveness after regeneration. Initially, 80% of the MGD was removed from simulated wastewater solution using CASSAC. However, the adsorption efficiency of CASSAC gradually decreased with each regeneration cycle, regardless of the solvent used. During the first cycle, 69% of the MGD was removed after washing with distilled water, while 72% and 79% of MGD were removed following washing with HCl and NaOH, respectively. In the second cycle, the removal efficiencies were 62%, 67%, and 71% for distilled water, HCl, and NaOH washing, respectively.

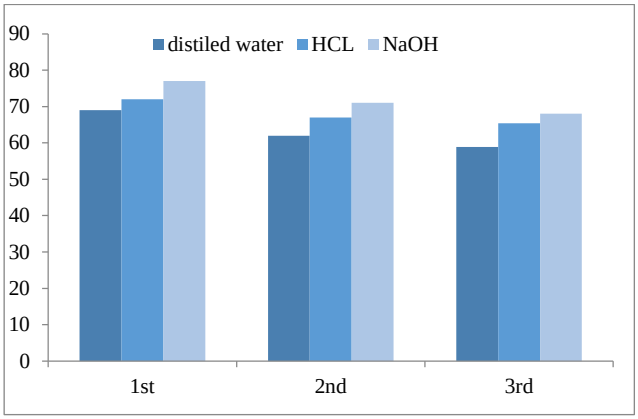



**Fig. 11:** The MG cycle of adsorption and desorption of CASC (Co; 50 ppm: V =50 ml; m=0.1g; T=60 min: T=25 $^{O}$C; Agitation Time=160 rpm)

At the end of the third cycle, the removal efficiencies further decreased to 58.9%, 65.3%, and 68% for the three respective solvents. The observed decline in removal efficiency of MGD using regenerated CASSAC over successive cycles may be attributed to several factors, including a reduction in available adsorption sites, blockage of pores, and loss of adsorbent material after ea1h regeneration cycle.

*Conclusion:* This study evaluated the efficacy of *C. albidum* seed shell, physically activated, for the adsorption of malachite green (MG) dye. The optimal conditions for MG adsorption on CASSAC were determined to be 0.10 g of adsorbent at pH 8. The adsorption isotherm study indicated that the Temkin model had the highest $R^2$ value compared to the Langmuir and Freundlich models, confirming that chemisorption is the primary mechanism involved in the adsorption process. Kinetic analysis showed that the pseudo-second-order model provided a higher $R^2$ value (0.973) compared to the pseudo-first-order model, with the experimentally and theoretically obtained values of $q_e$ in perfect agreement. This further supports the conclusion that the adsorption of MG by CASSAC follows a physisorption process.

*Declaration of Conflict of Interest:* The authors declare no conflict of interest regarding the publication of this paper.

*Data Availability:* Data are available upon request from the second author.

## REFERENCES

Agarry, SE; Kazeem, KS; Abass, OA; Micheal AO (2024). "Adsorptive Desulfurization of Diesel with Modified Pig Dung: Experimental Design with Optimization, Kinetics, Isotherms and Thermodynamics Studies." *D. Appl. Sci.* 6(8).

DOI: https://doi.org/10.1007/s42452-024-05859-5.

Ahmad, AA; Al-Raggad M; Shareef, N (2021). Production of activated carbon derived from agricultural by-products via microwave-induced chemical activation: a review. *Carbon Letter. 31*(5), 957-971.

Al-Gheethi, AA; Azhar, QM; Kumar, PS; Yusuf, AA; Al-Buriahi, AK; Mohamed, RMSR; Al-Shaibani, MM (2022). Sustainable approaches for removing Rhodamine B dye using agricultural waste adsorbents: A review. *Chemosphere. 287:* 132080.

Al-Tohamy, R; Ali, SS; Li, F; Okasha, KM; Mahmoud, YAG; Elsamahy, T; Jiao, H; Fu, Y; Sun, J (2022). A critical review on the treatment of dye-containing wastewater: Ecotoxicological and health concerns of textile dyes and possible remediation approaches for environmental safety. *Ecotoxic. Environ. Safety*, *231*, 113160.

Amuda, OS; Edewor, TI; Afolabi, TJ; Hung, YT (2013). Steam-activated carbon prepared from *Chrysophyllum albidum* seed shell for the adsorption of cadmium in wastewater: kinetics, equilibrium and thermodynamic studies. *Intl. J. Environ. Waste Manage*, *12*(2), 213-229.

ASTM D3663-20. 2020. Standard Test Method for Surface Area of Catalysts and Catalyst Carriers.

ASTM D3906-19. 2019. Standard Test Method for Determination of Relative X-Ray Diffraction Intensities of Faujasite-Type Zeolite-Containing Materials.

ASTM E1252-98. 2021. Standard Practice for General Techniques for Obtaining Infrared Spectra for Qualitative Analysis.

ASTM F1372-93. (2020). Standard Test Method for Scanning Electron Microscope (SEM) Analysis of Metallic Surface Condition for Gas Distribution System Components.

Azaman, SH; Afandi, A; Hameed, BH; Din, AM (2018). Removal of malachite green from aqueous phase using coconut shell activated carbon: Adsorption, desorption, and reusability studies. *J. Appl. Sci. Engine.*, *21*(3), 317-330.

Bushra, R; Mohamad, S; Alias, Y; Jin, Y; Ahmad, M (2021). Current approaches and methodologies to explore the perceptive adsorption mechanism of dyes on low-cost agricultural waste: A review. *Microporous and Mesoporous Materials*, *319*, 111040.

Cyril, A; Ibeabuchi, A; Romanus, O (2023). Phytochemical Screening and Antibacterial Activity of *Chrysophyllum albidum* Collected in Nsukka, South East Nigeria. *European J. Med. Plants. 34*(6), 13-22.

Dave, S; Das, J; Varshney, B; Sharma, VP (2022). Dyes and pigments: Interventions and how safe and sustainable are colors of life. In *Trends and Contemporary Technologies for Photocatalytic Degradation of Dyes*, 1-20. Cham: Springer International Publishing.

Dehghani, MH; Ahmadi, S; Ghosh, S; Othmani, A; Osagie, C; Meskini, M; Alkafaas, SS; Malloum, A; Khanday, WA; Jacob, AO; Gökkuş, Ö (2023). Recent advances on sustainable adsorbents for the remediation of noxious pollutants from water and wastewater: A critical review. *Arab. J. Chem.*, S105303.

Fazal, T; Razzaq, A; Javed, F; Hafeez, A; Rashid, N; Amjad, US; Rehman, F (2020). Integrating adsorption and photocatalysis: A cost-effective strategy for textile wastewater treatment using hybrid biochar-$TiO_2$ composite. *J. Hazard. Mat.*, *390*, 121623.

Ismail, A; Gonçalves, BL; de Neeff, DV; Ponzilacqua, B; Coppa, CF; Hintzsche, H; Oliveira, CA (2018). Aflatoxin in foodstuffs: Occurrence and recent advances in decontamination. *Food Res. Intern. 113*, 74-85.

Kalam, S; Abu-Khamsin, SA; Kamal, MS; Patil, S (2021). Surfactant adsorption isotherms: A review. *ACS Omega*, *6*(48), 32342-32348.

Khattri, SD; Singh, MK. (2009). Removal of malachite green from dye wastewater using neem sawdust by adsorption. *J. Hazard. Mat.*, *167*(1-3), 1089-1094.

Muniyasamy, A; Sivaporul, G; Gopinath, A; Lakshmanan, R; Altaee, A; Achary, A; Chellam, PV (2020). Process development for the degradation of textile azo dyes (mono-, di-, poly-) by advanced oxidation process-Ozonation: Experimental & partial derivative modelling approach. *J. Environ Manage*, *265*, 110397.

Oladoye, PO; Ajiboye, TO; Omotola, EO; Oyewola, OJ (2022). Methylene blue dye: Toxicity and potential elimination technology from wastewater.*Results. Enginee. 16*, 100678.

Oladoye, PO; Ajiboye, TO; Wanyonyi, WC; Omotola, EO; Oladipo, ME (2023). Insights into remediation technology for malachite green wastewater treatment. *Water Sci. Engine*, *16*(3), 261-270.

Olowonyo, IA; Salam, KK; Omolara, AM; Agbaje, L(2024). Synthesis, Characterization, and Adsorptive Performance of Titanium Dioxide Nanoparticles Modified Groundnut Shell Activated Carbon on Ibuprofen Removal from Pharmaceutical Wastewater. *Waste Manage. Bulletin* 1(4): 217–33. DOI: https://doi.org/10.1016/j.wmb.2023.11.003.

Rathi, BS; Kumar, PS (2021). Application of adsorption process for effective removal of emerging contaminants from water and wastewater. *Environ. Pollution*, *280*, 116995.

Reddy, PMK; Verma, P; Subrahmanyam, C (2016). Bio-waste derived adsorbent material for methylene blue adsorption. *J. Taiwan Institute. Chem. Engineers*, *58*, 500-508.

Rout, DR; Jena, HM (2021). Removal of malachite green dye from aqueous solution using reduced graphene oxide as an adsorbent. *Materials Today: Proceedings*, *47*, 1173-1182.

Seffah, K; Lakehal, I; Ouriache, H; Sadoun, L; Badis, D; Khenchali, K; Bendhina, A; Nadji, H. Ghernaout, D (2024). Pecan shells-based activated carbon for the removal of copper metal ions: optimization of the adsorption process using a full factorial design. *Intl J. Environ. Analy. Chem.*, 1-20.

Shabir, M; Yasin, M; Hussain, M; Shafiq, I; Akhter, P; Nizami, AS; Jeon, BH; Park, YK (2022). A review on recent advances in the treatment of dye-polluted wastewater. *J. Indus. Engine. Chem*, *112*, 1-19.

Shuaib, MM; Musah, M; Mathew, JT (2024). Preparation and Characterization of Activated Carbon from Africa Star Apple (*Chrysophyllum Albidum*) Seed Shell. *Fudma J. Sci. 8*(3), 194-199.

Tkaczyk, A; Mitrowska, K; Posyniak, A (2020). Synthetic organic dyes as contaminants of the aquatic environment and their implications for ecosystems: A review. *Sci. Total Environ. 717*, 137222.

Wong, S; AbdGhafar, N; Ngadi, N; Razmi, FA; Inuwa, IM; Mat, R; Amin, NAS (2020). Effective removal of anionic textile dyes using adsorbent synthesised from 2020). Effective removal of anionic textile dyes using adsorbent synthesised from coffee waste. *Sci. Reports* 10 (1), 1–13.