Mechanism and isotherm modeling of effective adsorption of malachite green as endocrine disruptive dye using Acid Functionalized Maize Cob (AFMC)

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Cationic Malachite green has been identified as a candidate for the endocrine disruptive compound found in the environment. In this study, the mechanism and isotherm modeling of effective adsorption of cationic malachite green dye onto acid-functionalized maize cob (AFMC) was investigated by batch technique. The operational parameters such as initial concentration (100–600 mg/L); contact time (10–120 min) and pH (3–10) influenced the removal efficiency and quantity adsorbed. A maximum of 99.3% removal efficiency was obtained at optimum conditions. AFMC physicochemical properties (surface area 1329 m²/g and particle size 300 μm < φ < 250 μm) enhanced its efficiency. Based on R² > 0.97 and consistently low values of adsorption statistical error functions (ASEF), equilibrium data were best fitted to Freundlich isotherm. Kinetic data were best described by a pseudo-second-order model with consistent R² > 0.98 and validated by ASEF. The mechanism of the process was better described by intraparticle diffusion. Evidence of the adsorption process was confirmed by the change in morphology via Scanning Electron Microscopy (SEM) and surface chemistry by Fourier Transform infrared (FTIR). The performance of AFMC enlisted it as a sustainable and promising low-cost adsorbent from agro-residue for treatment of endocrine disruptive dye polluted water.

A healthy environment is a necessity for the actualization and realization of Sustainable Development Goals (SDG). However, the global release of Endocrine Disruptive Chemicals (EDC) through unregulated anthropogenic activities is troublesome. This Endocrine Disruptive Chemicals (EDC) have been identified as emerging contaminants that can hamper the hormonal system at little doses leading to the following hazardous effects: cancerous tumors, birth defects, and developmental disorders12. EDC can cause hormonal dysfunction, deficit brain disorder, body deformation, breast, prostate, and thyroid cancers, many cases of sexual development problems. The hazardous effects of EDC are not alien to some of the negative effects of some dyes and antibiotics released into the environment. Malachite green dyes3–7.

The cationic dye of interest in this study is Malachite Green (MG) because of its versatility. It has found application in leather industries and in aquaculture as antiparasitic. It is used as a coloring agent in wool, silk, paper, etc.9. However, MG has been reported to be toxic, carcinogenic, and mutagenic. Malachite green could cause damage to humans and animals through direct inhalation and ingestion contact leading to various negative effects such as carcinogenesis, mutagenesis, teratogenesis, respiratory toxicity, and reduced fertility10,11. Systems and sensory organs of the body have been reported to be adversely affected by malachite green dyes12,13. MG does

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not biodegrade easily; it is known to be resilient to fading on exposure to light and water. More so, its removal from contaminated water via common conventional techniques (biological and chemical precipitation) is tough. However, its affinity for dissociation in solution makes it prone to liquid–solid adsorption. A cleaner environment and sustainable cities as part of the sustainable development goals would be difficult to achieve if the problem arising from endocrine disruptive chemicals are not combated. Some of the explored methods of wastewater treatment are advanced oxidation, adsorption, photocatalytic degradation, and biodegradation14,15. Exceptional among this treatment technique is adsorption owing to its ease of operation, low cost, adaptation to a broad range of dyes, and design flexibility16–18. Adsorption of pollutant using biomass such as agrowaste materials have attracted attention of researchers. Biomass-based adsorbents are sustainable materials derived among others from agricultural residues, forest, animal manures, food processing wastes and municipal wastes and they have found relevance in adsorption studies19,20. They are low cost, readily available and researchers have leveraged on their functionalization and modification potentials in order to increase their efficiency. Numerous biomass have been used in adsorption studies. Among agrowaste and biomass reported to be efficient are Sugarcane bagasse21, bio-material & chelating agent (Chitosan)22, Palm oil shell activated biomass23,24. Several sorbents have been reported effective in uptake of this EDC dye (MG Dye): Ocimum gratissimum4, magnetic biochar25, Opuntia ficus-indica activated carbon26, almond gum2, Carica papaya wood27, MOF nanocomposites28 Silico–manganese fume (SMF) waste29 para-aminobenzoic acid modified activated carbon3. Strength of selectivity and increase in the capacity of the sorbent with high removal efficiency could be enhanced by biomass functionalization. This has necessitated our interest in the modification of our sustainable low-cost agro-residue, maize cob. As a result, in this study, orthophosphoric acid has been used to functionalized and modified maize cob as low-cost agro-waste with the focus of achieving better sequestration. In this study, Acid Functionalized Maize Cob (AFMC) was developed purposely to effectively biosorb malachite green cationic dye as a candidate of endocrine disruptive chemical. Its range of dyes, and design flexibility16–18. Adsorption of pollutant using biomass such as agrowaste materials have attracted attention of researchers. Biomass-based adsorbents are sustainable materials derived among others from agricultural residues, forest, animal manures, food processing wastes and municipal wastes and they have found relevance in adsorption studies19,20. They are low cost, readily available and researchers have leveraged on their functionalization and modification potentials in order to increase their efficiency. Numerous biomass have been used in adsorption studies. Among agrowaste and biomass reported to be efficient are Sugarcane bagasse21, bio-material & chelating agent (Chitosan)22, Palm oil shell activated biomass23,24. Several sorbents have been reported effective in uptake of this EDC dye (MG Dye): Ocimum gratissimum4, magnetic biochar25, Opuntia ficus-indica activated carbon26, almond gum2, Carica papaya wood27, MOF nanocomposites28 Silico–manganese fume (SMF) waste29 para-aminobenzoic acid modified activated carbon3. Strength of selectivity and increase in the capacity of the sorbent with high removal efficiency could be enhanced by biomass functionalization. This has necessitated our interest in the modification of our sustainable low-cost agro-residue, maize cob. As a result, in this study, orthophosphoric acid has been used to functionalized and modified maize cob as low-cost agro-waste with the focus of achieving better sequestration. In this study, Acid Functionalized Maize Cob (AFMC) was developed purposely to effectively biosorb malachite green cationic dye as a candidate of endocrine disruptive chemical. Its mechanistic and isotherm modeling of biosorption were explored. The statistical validity of the models using different error models was also investigated. Pre- and post- adsorption characterization by surface morphology using Scanning Electron Microscopy (SEM) and surface chemistry by FTIR.

Materials and methods
All chemicals used are of analytical grade. Orthophosphoric acid, H₃PO₄ (Loba Chemie), Hydrochloric acid, HCl (Loba Chemie CAS No: 7647–01–0, 37% purity), Sodium hydroxide, NaOH (Reckland Scientific Ec No: 215–185–5, 97% purity), Sodium Chloride, NaCl (Loba Chemie 99.5%, CAS: 7647–14–5), Malachite Green dye (CAS No.: 569–64–2; C₂₃H₂₅ClN₂ (chloride); molar mass 364.911 g mol⁻¹). Acid Functionalized Maize Cob (AFMC) as low-cost adsorbent. Purposive and simple random sampling technique which is the best time saving technique was used for the collection of the maize cob agro-waste from the dumpsite of the University being an Agricultural-based University. Maize cobs obtained from Landmark University (Agro-based University) were screened and cleaned there after dried at 105 °C for 5 h in Gen lab oven, crushed, grounded, and screened to 106 µm. Acid activation was carried out following the procedure in our previous study30 and elsewhere in other literature31 using 0.5 M ortho-phosphoric acid (H₃PO₄). A detailed typical procedure for the preparation of Acid Functionalized Maize Cob (AFMC) was explicitly presented in the supplementary material (SI).

Physicochemical and spectroscopic characterization of AFMC. Determination of pH of AFMC. pH determination of AFMC was done by boiling 1 g AFMC in 100 mL distilled water for a period of 5 min. This was allowed to cool and its pH value was measured using an ATP-6 pH meter.

Determination of AFMC bulk density. Weight difference divided by the volume as depicted in Archimedes’ principle was used for bulk density determination as depicted in Eq. (1)42

\[
\text{Bulk density} = \frac{W_2 - W_1}{V}
\]

\(W_1\) = Weight of empty measuring cylinder, \(W_2\) = combination of AFMC mass and the crucible, \(V\) = volume.

Determination of AFMC moisture content. Moisture content was determined typically by introducing 5 g AFMC into the initially weighed crucible and heated for 1 h at 105 °C. Evaluation of the moisture content was done using Eq. (2)42

\[
\% \text{ Moisture content} = \frac{W_2 - W_1}{W_2 - W_3} \times 100
\]

\(W_1\) = Weight of crucible, \(W_2\) = Initial weight of crucible with sample, \(W_3\) = Final weight of crucible with sample.

Determination of AFMC surface area by Saer’s method. The AFMC surface area was determined using Sear’s method. This involves acidifying 0.5 g of each adsorbent with 0.1 M HCl to a pH of 3–3.5. The volume was made up to 50 mL with distilled water after the addition of 1 g of NaCl. The titration was carried out with standard 0.1 M NaOH at 298 K to pH 4, and then to pH 9.0 following the procedure reported in the literature35,34. The volume needed to raise the pH from 4 to 9 was noted and surface area evaluated using Eq. (3):
Batch biosorption studies. Preparation of malachite green adsorbate. Analytical grade reagents were used all through the study. Stock solution of 1000 mg/L MG dye (Fig. 1) solution was prepared by dissolving 1 g MG salt in 1000 mL distilled water. A lower working concentration was prepared (100–600 mg/L) by serial dilution.

Biosorption operational parameters. Various Operational parameters relevant to this study were carried out following reported method. The effect of pH was determined by varying the pH values between 3 and 10 via dropwise addition of 1 M HCl or NaOH where applicable. The effect of initial MG concentration was investigated by the introduction of 1 g AFMC into different concentrations of MG dye (100–600 mg/L). Variation of time as done to investigate the effect of contact time from 10 to 120 min. All through the study, the adsorbate-adsorbent system was agitated on the Orbital shaker to increase effective collision in the system. Measurement of residual concentration at maximum wavelength of 617 nm was done using double beam Libra Biochrom 5505 v1.0.4 PCB 1500 coupled with water Peltier system UV–Vis spectrophotometer.

Theory. Biosorption isotherm and kinetic modeling and statistical error validity. Equilibrium biosorption data obtained from the study of were analyzed using six of two-parameter models (Freundlich, Langmuir, Temkin, Dubinin–Raduskevich, Halsey, and Jovanovic). Similarly, both kinetics and mechanism models were fitted to Pseudo first-order, Pseudo-second-order, Elovich, Fractional power, Intraparticle, and liquid film diffusion models. Estimation of the quantity adsorbed and percentage removal efficiency was done using Eqs. (4) and (5).

Presented in Tables 1 and 2 are the descriptions of both isotherm, kinetics, and mechanism models used in this study.

Adsorption statistical error function (ASRF) models. In most cases, determination of best fitting relationship and finalizing the best isotherm and kinetics model have always been through the use of linear correlation coefficient ($R^2$) values. However, owing to inherent bias from this transformation, the following four rigorous statistical error function models were used: Sum of square error (SSE); Hybrid fractional error function (HYBRID); Nonlinear chi-square test ($\chi^2$); Marquardt’s Percent Standard Deviation (MPSD). Presented in Table 2 are the equation of the Adsorption Statistical Error Function (ASRF) Models from Eqs. (24)–(27).

$$S(m^2/g) = 32V - 25$$  (3)
The Langmuir equation is:

$$Q_e = \frac{Q_{\text{max}} K_a C_e}{1 + K_a C_e}$$

Where:
- $Q_e$ is the amount of adsorbate adsorbed at any time (mg/g).
- $Q_{\text{max}}$ is the maximum monolayer coverage capacity (mg/g).
- $K_a$ is the Langmuir isotherm constant (L/mg).

The Freundlich equation is:

$$Q_e = K_f C_e^{1/n_F}$$

Where:
- $Q_e$ is the amount of adsorbate adsorbed at any time (mg/g).
- $K_f$ is the Freundlich isotherm constant (L/g).
- $n_F$ is the Freundlich isotherm exponent.

The Temkin equation is:

$$Q_e = \frac{B T}{R} \ln(A T C_e)$$

Where:
- $Q_e$ is the amount of adsorbate adsorbed at any time (mg/g).
- $A$ is the Temkin isotherm equilibrium binding constant (L/g).
- $B$ is the Temkin isotherm constant related to the heat of adsorption and $A_T$ is the Temkin isotherm constant related to the heat of adsorption.

The DKR equation is:

$$Q_e = Q_{\text{D-R}} \exp^{-A_\text{D-R} \cdot \epsilon x}$$

Where:
- $Q_{\text{D-R}}$ is the theoretical adsorption saturation capacity (mg/g).
- $A_\text{D-R}$ is the D-R isotherm constant (mol^2/kJ^2).
- $\epsilon$ is the mean adsorption free energy helpful in determining the adsorption nature (physiosorption or chemisorption of the adsorption process).

The Halsey equation is:

$$Q_e = \exp \left[ \ln[q_e] \ln[q_e] \right]$$

Where:
- $Q_e$ is the amount of adsorbate adsorbed at any time (mg/g).
- $K_H$ is the Halsey isotherm constant.

The Jovanovic equation is:

$$Q_e = Q_f \left[ 1 - \exp[k_i C_i] \right]$$

Where:
- $Q_e$ is the amount of adsorbate adsorbed at any time (mg/g).
- $K_J$ is the Jovanovic isotherm constant (L/g).
- $Q_{\text{max}}$ is the maximum monolayer coverage capacity (mg/g).
- $k_i$ is the pseudo-second-order rate constant (min^{-1}).

### Table 1. Adsorption Isotherm Models (Non-linear and linear models with the description of parameters)

| Types of adsorption models | Non-linear expression | Linear expression | Parameters nomenclature and description |
|----------------------------|-----------------------|------------------|----------------------------------------|
| Langmuir                  | $Q_e = \frac{Q_{\text{max}} K_a C_e}{1 + K_a C_e}$ | $\frac{1}{Q_e} = \frac{1}{Q_{\text{max}}} + \frac{1}{Q_{\text{max}} K_a C_e}$ | $K_a$ is the Langmuir isotherm constant (L/mg) related to the binding energy of adsorption. $Q_{\text{max}}$ is the maximum monolayer coverage capacity (mg/g). $R_L$ dimensionless separation factor indicating the nature and favourability of adsorption process. From slope and intercept of linear plot of $Ce/Qe$ vs 1/Ce, $Q_{\text{max}}$ and $K_a$ were determined. |
| Freundlich                | $Q_e = K_f C_e^{1/n_F}$ | $\log Q_e = \log K_f + \frac{1}{n_F} \log C_e$ | $C_e$ equilibrium concentration of the MG dye adsorbate (mg.L^{-1}); $Q_e$ amount of MG dye adsorbed at equilibrium per unit weight of AFMC (mg g^{-1}); $K_f$ Freundlich indicator of adsorption capacity. $1/n_F$ Intensity of the adsorption indicating the surface heterogeneity and favourability of the adsorption process. $K_f$ and $1/n_F$ were determined from slope and intercept of linear plot of $\log Q_e$ vs $\log C_e$. |
| Temkin                    | $Q_e = \frac{B T}{R} \ln(A T C_e)$ | $Q_e = \frac{B T}{R} \ln A_T + \frac{B T}{R} \ln C_e$ | $B$ is the Temkin isotherm constant related to the heat of adsorption and $A_T$ is the Temkin isotherm equilibrium binding constant (L/g). $R$ is universal gas constant (8.314 J/mol.K). $T$ is absolute Temperature in Kelvin. $R = RT/b_T$, $b_T$ is constant related to heat of sorption (J/mol) obtained either from intercept or slope. |
| DKR                       | $Q_e = Q_{\text{D-R}} \exp^{-A_\text{D-R} \cdot \epsilon x}$ | $\ln q_e = \ln Q_{\text{D-R}} - A_\text{D-R} \cdot \epsilon x$ | $Q_{\text{D-R}}$ is the theoretical adsorption saturation capacity (mg/g) obtained from intercept. $A_\text{D-R}$ is the D-R isotherm constant (mol^2/kJ^2) related to free sorption energy obtained from the slope. $\epsilon$ is Polanyi potential determined by the expression: $\epsilon = RT \ln (1 + 1/C_e)$. $E$ is the mean adsorption free energy helpful in determining the adsorption nature (physiosorption or chemisorption of the adsorption process). $Q_{\text{D-R}}$ and $A_\text{D-R}$ were determined from intercept and slope of linear plot of $\ln q_e$ vs $E_x$. |
| Halsey                    | $Q_e = \exp \left[ \ln[q_e] \ln[q_e] \right]$ | $\log Q_e = \left( \frac{1}{n_H} \right) \ln K_H - \left( \frac{1}{n_H} \right) \ln C_e$ | $K_H = 6.62607 \times 10^{-19}$ is the Halsey isotherm constant; $n_H$ is the Halsey isotherm exponent. Both were determined from linear plot of $\log Q_e$ vs $1/C_e$. |
| Jovanovic                 | $Q_e = Q_f \left[ 1 - \exp[k_i C_i] \right]$ | $\ln q_e = \ln Q_{\text{max}} - K_i C_i$ | $K_J = 6.62607 \times 10^{-19}$ is the Jovanovic isotherm constant (L/g) determined from the slope of plot of $\ln q_e$ against $C_i$. |

### Table 2. Kinetics and mechanism modeling of adsorption

| Kinetic and mechanism models | Linear expression | Parameters nomenclature and description |
|-----------------------------|------------------|----------------------------------------|
| Pseudo first order (PFO)    | $\log (q_t - q) = \log q_e - \frac{K_i}{q_e}$ | $q_e$ is the quantity of adsorbate at equilibrium per unit weight of the adsorbent (mg/g). $q_t$ is the amount of adsorbed at any time (mg/g). $K_i$ is the pseudo first-order rate constant (min^{-1}). $h_i$ is the initial pseudo first-order rate constant (mg/g.min). $q_e$ and $K_i$ were determined respectively from intercept and slope of the linear plot of $\log q_e$ vs $t$. |
| Pseudo second-order (PSO)   | $\frac{1}{q_t} = \frac{1}{q_e} + \frac{1}{q_e} t$ | $k_2$ is the pseudo second-order rate constant (min^{-1}). $h_2$ is the initial pseudo second-order adsorption rate constant (mg/g.min). $q_e$ and $k_2$ were determined respectively from slope and intercept of the linear plot of $1/q_t$ vs $t$. |
| Elovich                     | $q_t = \frac{1}{n_F} \ln (a \beta) + \frac{1}{n_F} \ln (t)$ | $q_t$ is the amount of adsorbate per unit mass of adsorbate at time (t), and $a$ and $\beta$ are the constants slope and intercept of the determined from the linear plot of $q_t$ versus $t$. $\alpha$ is the initial adsorption rate (mg/g.min). $\beta$ is the desorption constant (g/mg) during any one experiment. The slope is $1/\beta$ while the intercept is $a/\beta \ln(a/\beta)$. |
| Fractional power (power function) | $\log (q_t) = \log(k) + v \log(t)$ | $q_t$ is the amount of adsorbate per unit mass of adsorbate, $k$ is a constant. $t$ is time, and $v$ is a positive constant ($< 1$). The parameters $v$ and $k$ are obtainable from slope and intercept of a linear plot of $\log (q_t)$ versus $\log (t)$. |
| Intraparticle diffusion (IPD) | $q_t = k_{\text{cal}} t^{0.5} + C$ | $k_{\text{cal}}$ is the intraparticle diffusion rate constant (mg. g^{-1}. min^{-0.5}). $C$ is the thickness of the adsorbent determined from slope and intercept of linear plot of $q_t$ vs $t^{0.5}$. |
| Liquid film diffusion (LFD) | $\ln (1 - F) = -K_{LFD} t + C$ | $F$ is fractional attainment to equilibrium and $K_{LFD}$ is the rate coefficient for particle-diffusion controlled process corresponding to the particle size of the adsorbent. $K_{LFD}$ was determined from the linear plot of $\ln (1 - F)$ vs $t$. |

Non-linear - chi - square test

$$\chi^2 = \sum_{i=1}^{n} \frac{(q_{\text{cal}} - q_{\text{exp}})^2}{q_{\text{cal}}})$$

Hybrid fractional error functions

$$HYBRID = \sum_{i=1}^{n} \left[ \frac{(q_{\text{exp}} - q_{\text{cal}})^2}{q_{\text{exp}}} \right]$$

Marquardt’s Percent Standard Deviation (MPSD)

$$MPSD = \sum_{i=1}^{n} \left[ \frac{(q_{\text{exp}} - q_{\text{cal}})^2}{q_{\text{exp}}} \right]$$

Both isotherm and kinetics data were tested with the statistical error validity models.
Results and discussion
Physicochemical characterization. Figure 1 shows the structure of Malachite green as a cationic dye. Presented in Table S1 of the supplementary document is the physicochemical characteristics of Malachite Green (MG) indicating that it is a cationic dye having vast application. The unique physicochemical properties of AFMC were determined and summarized in Table S2. The pH determined was 6.75, surface area (1329 m²/g), 12% moisture content, 0.386 g/cm³ bulk density, and approximated particle size 300 μm < D < 250 μm. It has been reported that for applicability, activated carbon in the range of pH 6 to 8 is acceptable. The pH of AFMC determined as 6.75 is suitable for activated carbon (AC). The amount of water bound to activated carbon is determined via the moisture content. Lower moisture content is desirable for active activated carbon because of the competition of the water vapor with the pores of AC. The moisture content of AFMC lower than commercial activated carbon (CAC)39 is suitable. The filterability of activated carbon is determined from the bulk density.

Effect of pH. Shown in Fig. S1 is the effect of pH on biosorption of MG cationic dye onto AFMC. Ionic mobility and degree of ionization as well as the surface chemistry was influence by this operational parameter. Protonation, as well as ionic competition between H⁺ and MG⁺ zwitterion in aqueous solution for available sites, was observed between pH 2–5 at the acidic region. Higher quantity adsorbed and removal efficiency observed between pH 6 and 8 was due to deprotonation, low competition, and a higher aggregate of MG⁺. 7.425 mg/g quantity of MG was adsorbed at 100 ppm as observed at pH 6. Beyond pH 6, no further increase was observed, therefore pH 6 was chosen as an optimum pH similar to the finding of Alqadami et al. where MOF was used for adsorption of both Malachite green and methylene blue and optimum pH for highest adsorption capacity of MG was at 6.838.

Effect of initial concentration. Figure S2 of the supplementary document shows the result of the effect on initial concentration on effective removal of EDC cationic MG dye using AFMC. Lower transport of the MG dye at lower concentrations led to lower adsorption due to low driving force. However, the percentage of the percentage removal efficiency increased with increase in concentration. The concentration gradient developed on initial concentration on effective removal of EDC cationic MG dye using AFMC. Lower transport of the MG dye at lower concentrations led to lower adsorption due to low driving force. However, the percentage of the percentage removal efficiency increased with increase in concentration. The concentration gradient developed was due to bombardment of the MG⁺ surrounding the active sites. It is obvious from Fig. S2 that rapid adsorption was observed at low concentration as a result of an increase in the active sites as compared to MG molecules in the bulk. Thereafter, diffusion, convection, and migration of MG molecules as a result of mass transport from the bulk lead to an increase in removal efficiency until a saturated point was reached. All the active sites were filled up at equilibrium and thereafter, no significant percentage removal efficiency observed. Similar finding was observed by Khan et al. and in the literature54,55.

Biosorption Isotherm modeling and statistical validity. Understanding of the binding interaction between AFMC and MG dye solution is enhances by the study of the isotherm models. Equilibrium data were fitted to six isotherm models namely; Freundlich (Fig. 2A), Langmuir (Fig. 2B), Temkin (Fig. 2D), Dubinin–Raduskevich (Fig. 2E), Halsey (Fig. 2F), and Jovanovic (Fig. 2G). Portrayed in Fig. 2A–G are the isotherm models’ linear plots. Better fit with R² > 0.97 were observed in Table 3a for Freundlich, Temkin, Dubinin–Raduskevich (D–R), Halsey. Equilibrium data did not fit well to Langmuir and Jovanovic considering their R² value less than 0.92 (Table 3). Both Freundlich and Halsey isotherm models describe the adsorption characteristic for the heterogeneous surface. The characteristics parameters of Freundlich isotherm models are KF (adsorption capacity) and 1/nF and nF (adsorption intensity) obtained from the linear plot of log Qe against log Ce. The function of the strength of adsorption of MG onto AFMC is determined from the parameter 1/nF. The value of 1/nF (2.1372) being above unity is an indication of a cooperative adsorption54,55. The favourability of the adsorption process of MG onto AFMC could be affirmed from the Langmuir dimensionless and separation factor (RL). The RL value indicates the adsorption nature to either unfavorable or unfavorable. It is unfavourable if RL > 1, linear if RL = 1, favourable if 0 < RL < 1 and irreversible if Rl = 0. The value of RL ranges between 0.00377 and 0.0744 and being less than one indicated favorable adsorption. There are many studies carried out on the adsorption of MG onto different adsorbents. Comparison of the Qmax monolayer capacities of adsorption of MG onto various adsorbents was presented in Table 4. Qmax of AFMC surpassed all those adsorbents compared indicating that AFMC is a better adsorbent for MG adsorption.

The Dubinin–Kaganer–Raduskevich is generally applied to determine the mechanism of the MG-dye and AFMC system with a Gaussian energy distribution onto a heterogeneous surface. The R² > 0.98 is an indication of a better description of equilibrium data by The DKR mean energy (E) value being less than 8 kJ indicated that the mechanism is physisorption. Studies from Bello et al. on scavenging of MG onto Citrus grandis peels further supported these findings38,39.

Statistical error validity on isotherm model. Studies have shown that the determination of the best isotherm model does not only depend on the R² value. Statistical validity model has been introduced to further justify the suitability of the best isotherm model to describe the adsorption process49,50. Table 5 has shown the values of the experimental and calculated quantity adsorbed, Qe, exp and Qe, cal, respectively. The four most used statistical validity models in adsorption studies explored are SSE, HYBRID, X², and MPSD. Adsorption Statistical Error Function (ASRF) has always been the most reliable validity parameter in justifying the best isotherm model for the equilibrium studies. To determine the isotherm best model, coupled with the higher R² value, there must be closeness between the data of the Qe, cal, and Qe, exp alongside a low value of the ASRF50,61. Considering Table 5, Freundlich, Temkin, and Halsey isotherm models fit well into these conditions for fitness. From Table 4, the R² values (0.9726 for Freundlich, 0.9726 for Halsey and 0.9846 for Temkin) are closer to one indicating a very close fit.
Figure 2. (A–G) Plots of: (A) Freundlich isotherm model, (B) Langmuir isotherm model, (C) Separation Factor on sorption of MG onto AFMC, (D) Temkin isotherm model, (E) D–R isotherm model, (F) Halsey isotherm model, (G) Jovanovic isotherm model for sorption of MG dye onto AFMC.
to unity with consistent agreement between $Q_e, \ exp$ and $Q_e, \ cal$ (254.13 mg/g and 293.43 mg/g for Freundlich; 254.13 mg/g and 243.75 mg/g for Temkin; 254.13 mg/g and 293.51 mg/g for Hasley).

Effect of contact time at various initial concentrations. Importance relevant parameter that controls the transfer and build-up of charges from the bulk to the pore active site in all transfer media is the contact time. Effect of contact time was studied from 10 to 120 min at six different initial concentrations from 100 to 600 mg/L as depicted in Fig. S3 of the supplementary document. Based on the results, rapid adsorption was observed in the first 30 min due to increase attractive forces between the active sites and MG molecules as a result of van der Waals forces and electrostatic attractions. Between 60 and 90 min not significant increase in adsorption capacity and removal, efficiency was observed due to attainment of saturation and equilibrium. A fast diffusion onto the external surface of AFMC was followed by fast pore diffusion into the intraparticle matrix as a result of the par-

| Type of isotherm | Model parameters | Evaluated value |
|-----------------|-----------------|-----------------|
| Freundlich      | $k_f$           | 2.1373          |
|                 | $\frac{1}{n_f}$ | 2.1373          |
|                 | $n_f$           | 0.4679          |
|                 | $R^2$           | 0.9726          |
| Langmuir        | Parameters      | Values          |
|                 | $Q_{max}$ (mg/g) | 64.5161         |
|                 | $K_L$ (L/mg)    | 0.01023         |
|                 | $R_L$           | 0.140–0.494     |
|                 | $R^2$           | 0.9149          |
| Temkin          | Parameters      | Values          |
|                 | $b_T$ (L/mol)   | 10.555          |
|                 | $\beta$ (L/g)  | 234.72          |
|                 | $A_T$ (L/g)     | 0.03078         |
|                 | $R^2$           | 0.9846          |
| D–R             | Parameters      | Values          |
|                 | $Q_d$           | 330.135         |
|                 | $A_{DKR}$       | $5 \times 10^{-4}$ |
|                 | $E$ (J/mol)     | $3.163 \times 10^4$ |
|                 | $R^2$           | 0.989           |
| Halsey          | Parameters      | Values          |
|                 | $1/n_H$         | $-2.1373$       |
|                 | $n_H$           | $-0.4679$       |
|                 | $K_H$           | 6.4286          |
|                 | $R^2$           | 0.9726          |
| Jovanovic       | Parameters      | values          |
|                 | $Q_{max}$       | 13.1615         |
|                 | $R^2$           | 0.9082          |

Table 3. Isotherm models’ parameters and for adsorption of malachite green onto AFMC.

| S/N | Adsorbents                              | Maximum monolayer capacity | References |
|-----|-----------------------------------------|-----------------------------|------------|
| 1   | Chitosan–zinc oxide composite           | 11                          | 10         |
| 2   | SSB/Fe–Cu                               | 63.5                        | 15         |
| 3   | Carica papaya wood                     | 52.63                       | 27         |
| 4   | Native shells of Peltophorum pterocarpum| 40                          | 40         |
| 5   | NaOH activated shells of Peltophorum pterocarpum| 62.5                       | 40         |
| 6   | Carbonized pomegranate peel            | 31.45                       | 58         |
| 7   | Fe$_2$O$_3$ by ODH                     | 15.72                       | 65         |
| 8   | Fe$_2$O$_3$ by PEG                     | 16                          | 65         |
| 9   | AFMC                                    | 64.52                       | This study |

Table 4. Comparison of the Qmax monolayer capacity of MG adsorption with other adsorbents.
gested a rapid kinetic process. The close agreement between $Q_e^{\text{exp}}$ and $Q_e^{\text{cal}}$ are indications of the best fitting the parameters $v$ and $k$ being positive, greater than unity, and increase with the increase in concentration sug-

The evaluated parameters are presented in Table 7. Both the rate-controlling step and the diffusion mechanism 

Table 5. Adsorption statistical error function (ASRF) data on adsorption isotherm models.

| ASRF models | Freundlich | Langmuir | Temkin | D–R | Halsey | Jovanovic |
|-------------|------------|----------|--------|-----|--------|-----------|
| $q_{e,\text{cal}}$ (mg/g) | 254.13 | 254.13 | 254.13 | 254.13 | 254.13 | 254.13 |
| $q_{e,\text{exp}}$ (mg/g) | 293.43 | 36.37 | 243.75 | 29.81 | 293.51 | 326.7 |
| $R^2$ | 0.9726 | 0.9149 | 0.9846 | 0.989 | 0.9726 | 0.9082 |
| SSE | 1544.49 | 47.419.29 | 107.744 | 50.319.46 | 1550.784 | 4431.565 |
| HYBRID | 6.077559 | 186.5496 | 0.429794 | 198.0068 | 6.102327 | 17.43818 |
| $X^2$ | 5.263572 | 130.791 | 0.442028 | 1668.006 | 5.283583 | 13.81841 |
| MPSD | 0.023915 | 0.734249 | 0.001668 | 0.779155 | 0.024013 | 0.068619 |

Kinetics and mechanism model of MG sequestration. The rate of binding of MG onto AFMC was determined by the adsorption kinetics which also helps in gaining insight into the mechanism of the sorption process. Across various concentrations from 100 to 600 mg/L, the kinetic data were fitted to the following kinetics and mechanism models: Pseudo first-order (PFO) (Fig. 3A), Pseudo second-order (PSO) (Fig. 3B), Elovich (Fig. 3C), Fractional power (power function) (Fig. 3D); Intraparticle Diffusion (Fig. 3E) and Liquid film diffusion (Fig. 3E). Based on the evaluated data presented in Table 6, correlation coefficient $R^2$ of pseudo-second-order (> 0.99) is highest among all the kinetics models explored. The $R^2$ value is consistently higher and increases as the concentration increases. The $h_1$ initial pseudo-second-order adsorption rate constant increases from 23.92 to 105.26 mg/g/min suggesting a rapid kinetic process. The error bars on the kinetic plots from Fig. 3A–D showed that the kinetic models were validated using statistical error functions. The consistency of 

The reaction was allowed to proceed till 90 min beyond which to increase was observed as depicted in Fig. 5. This finding is supported by the report of Hamdaoui et al. as well as Figen and Bayrak.

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Figure 3. (A) Pseudo first-order kinetics model (Conditions: pH 6, AFMC dose = 100 mg, contact time: 90 min; concentrations: 100–600 mg/L). (B) Pseudo second-order kinetics model (Conditions: pH 6, AFMC dose = 100 mg, contact time: 90 min; concentrations: 100–600 mg/L). (C) Elovich kinetics model (Conditions: pH 6, AFMC dose = 100 mg, contact time: 90 min; concentrations: 100–600 mg/L). (D) Fractional power kinetics model (Conditions: pH 6, AFMC dose = 100 mg, contact time: 90 min; concentrations: 100–600 mg/L). (E) Intraparticle diffusion model (Conditions: pH 6, AFMC dose = 100 mg, contact time: 90 min; concentrations: 100–600 mg/L). (F) Liquid film diffusion mechanism model (Conditions: pH 6, AFMC dose = 100 mg, contact time: 90 min; concentrations: 100–600 mg/L). (G) Schematic diagram of the adsorption of MG dye onto AFMC (AFMC is depicted by its AFMC SEM morphology).
fications as portrayed in Fig. 4A,B. However, after adsorption as depicted in Fig. 4C,D, there was the disappearance of crakes, impregnated pores with MG dye solution, and robustness of AFMC adsorbent are morphology evidence of the adsorption process.

Depicted in Fig. 5A,B are the FTIR spectra of AFMC before and after adsorption. The surface chemistry of AFMC before and after adsorption was investigated using FTIR. Broadband at 3390.70 cm⁻¹ is attributed to O–H stretching of the hydrogen bonding which disappeared after adsorption as evidence of its participation in the adsorption process⁶⁶. Aliphatic C–H stretching band at 2920.98 cm⁻¹ was also found to decrease after adsorption. Carbonyl group, –C=O stretching vibration attributed to the lignin aromatic groups was assigned to 1714.28 cm⁻¹ and 1667.29 cm⁻¹. Ascribed to –C=C– bending of the aromatic ring are the signals observed between 1515.10 and 1427.71 cm⁻¹ while –CH₃ bands as a result of deformation are observed at 1372.37 cm⁻¹. Several bands between 1200 and 800 cm⁻¹ are ascribed to characteristic carbohydrate bands while at 1049.93 cm⁻¹, C–O vibrational band assigned to cellulose is observed at 1049.93 cm⁻¹. The shift in bands and disappearance of functional groups confirmed their participation in the adsorption process⁶⁷.

Conclusion
This study has investigated the efficacy of Acid Functionalized Maize Cob (AFMC) as a sustainable, cost-effective, easy, unique, efficient adsorbent utilizing adsorption as a low-cost technique for effective removal of malachite green (cationic dye). Unique physicochemical properties of AFMC vis-à-vis high surface area (1329 m²/g), moisture content (12%), bulk density (0.386) enhanced the adsorptive capacity. Adsorption of malachite green onto AFMC before and after was confirmed SEM and FTIR. Effective removal of malachite green was achieved at pH 6, 10–120 min contact time, six different initial concentrations from 100 to 600 mg/L concentrations at ambient temperature. A rapid and fast kinetics was attained at 90 min with 93% removal efficiency. Based on higher R² > 0.97 and lower suitable statistical validity models (SSE, HYBRID, X², and MSPD), the equilibrium data were best described by Freundlich and Halsey isotherm models. The Langmuir adsorption monolayer capacity (Qmax) of AFMC being 66.52 mg/g surpassed several adsorbents previously used for adsorption of MG. Free energy value being less than 8 kJ from DRK supported a physisorption mechanism. Based on R² values and statistical error validity models, the kinetic and mechanism data were best fitted to Pseudo second order and supported by intraparticle diffusion. Subsequently, consideration could be given to AFMC as propitious material for environmental remediation.
Table 6. Parameters of kinetics models with associated Statistical Validity Data.

| Kinetics model parameters | Various concentrations |
|---------------------------|------------------------|
|                           | 100 mg/L  | 200 mg/L  | 300 mg/L  | 400 mg/L  | 500 mg/L  | 600 mg/L  |
| Pseudo first-order        |           |           |           |           |           |           |
| $q_e, \text{exp} (\text{mg/g})$ | 34.243   | 84        | 132.3     | 181.02    | 230.3     | 279.3     |
| $q_e, \text{cal} (\text{mg/g})$ | 13.9284  | 38.256    | 34.546    | 101.555   | 83.483    | 124.48    |
| $k_1 (\text{min}^{-1})$   | 0.0621    | 0.0506    | 0.0414    | 0.05      | 0.0407    | 0.5269    |
| $h_1 (\text{mg/g/min})$   | 0.864954  | 1.935754  | 1.430204  | 5.07775   | 3.397758  | 65.58851  |
| $R^2$                     | 0.5443    | 0.5827    | 0.7156    | 0.6609    | 0.6989    | 0.689     |
| $SSE$                     | 412.683   | 2092.514  | 9555.845  | 6314.687  | 21,555.23 | 23,969.23 |
| HYBRID                    | 12.0516   | 24.91088  | 72.22861  | 34.88392  | 93.59631  | 85.81895  |
| $X^2$                     | 29.6289   | 54.69767  | 276.6122  | 62.17997  | 258.199   | 192.5549  |
| MPSD                      | 0.351943  | 0.296558  | 0.545946  | 0.192708  | 0.40641   | 0.307264  |
| Pseudo Second-order       |           |           |           |           |           |           |
| $q_e, \text{exp} (\text{mg/g})$ | 34.243   | 84        | 132.3     | 181.02    | 230.3     | 279.3     |
| $q_e, \text{cal} (\text{mg/g})$ | 34.1296  | 84.746    | 133.333   | 181.812   | 232.5581  | 285.7143  |
| $k_2 (\text{g/mg/min})$   | 0.02054   | 0.00276   | 0.003583  | 0.00318   | 0.00174   | 0.00123   |
| $h_2 (\text{mg/g/min})$   | 23.9234   | 19.8412   | 63.694    | 105.263   | 94.339    | 101.0101  |
| $R^2$                     | 0.9986    | 0.9833    | 0.9992    | 0.9996    | 0.9989    | 0.9983    |
| $SSE$                     | 0.01286   | 0.556516  | 1.067089  | 0.637123  | 5.099016  | 41.14324  |
| HYBRID                    | 0.000376  | 0.006625  | 0.008066  | 0.00352   | 0.022141  | 0.147308  |
| $X^2$                     | 0.000377  | 0.006567  | 0.008003  | 0.003504  | 0.021926  | 0.144001  |
| MPSD                      | 1.1 × 10−5 | 7.89 × 10−5 | 6.1 × 10−5 | 1.94 × 10−5 | 9.61 × 10−5 | 5.27 × 10−4 |
| Elovich                   |           |           |           |           |           |           |
| $q_e, \text{exp} (\text{mg/g})$ | 34.243   | 84        | 132.3     | 181.02    | 230.3     | 279.3     |
| $q_e, \text{cal} (\text{mg/g})$ | 33.468   | 79.753    | 130.269   | 179.519   | 226.119   | 273.279   |
| $\alpha (\text{g/min}^2/\text{mg})$ | 8.95 × 10−7 | 10.3 × 10−7 | 9.26 × 10−7 | 2.42 × 10−7 | 1.93 × 10−7 | 0.494 × 10−7 |
| $\beta (\text{g/min}/\text{mg})$ | 2.0881   | 0.5732    | 0.2555    | 0.1758    | 0.1375    | 0.1079    |
| $R^2$                     | 0.4294    | 0.0791    | 0.8596    | 0.9643    | 0.7837    | 0.699     |
| $SSE$                     | 0.600625  | 18.03701  | 4.124961  | 2.253001  | 17.48076  | 36.25244  |
| HYBRID                    | 0.01754   | 0.214726  | 0.031179  | 0.012446  | 0.075904  | 0.129797  |
| $X^2$                     | 0.017946  | 0.226161  | 0.031665  | 0.01255   | 0.077308  | 0.132657  |
| MPSD                      | 0.000512  | 0.002556  | 0.000236  | 6.88E−05  | 0.00033   | 0.000465  |
| Fractional power          |           |           |           |           |           |           |
| $q_e, \text{exp} (\text{mg/g})$ | 34.243   | 84        | 132.3     | 181.02    | 230.3     | 279.3     |
| $q_e, \text{cal} (\text{mg/g})$ | 33.461   | 79.463    | 130.303   | 179.558   | 226.059   | 273.189   |
| $v(\text{min}^{-1})$      | 0.0144    | 0.021     | 0.031     | 0.0329    | 0.0331    | 0.0349    |
| $k_3 (\text{mg/g})$       | 31.232    | 71.8621   | 112.331   | 153.391   | 192.93    | 231.153   |
| $k_3v(\text{mg/g/min})$   | 0.449741  | 1.509104  | 3.482261  | 5.046564  | 6.385983  | 8.06724   |
| $R^2$                     | 0.4325    | 0.0791    | 0.8596    | 0.9643    | 0.7837    | 0.699     |
| $SSE$                     | 1118.675  | 6311.031  | 16,970.79 | 32,229.26 | 51,087.71 | 74,613.16 |
| HYBRID                    | 33.43221  | 79.42101  | 130.241   | 179.4922  | 225.9928  | 273.1192  |
| $X^2$                     | 77.685.77 | 300.525.3 | 547.445   | 979.6128  | 1,543.435 | 2,137.913  |
| MPSD                      | 0.999139  | 0.999472  | 0.999524  | 0.999634  | 0.999707  | 0.999745  |
Table 7. Mechanism model parameters of adsorption of MG onto AFMC.

| Mechanism models | Parameters | 100 mg/L | 200 mg/L | 300 mg/L | 400 mg/L | 500 mg/L | 600 mg/L |
|------------------|-----------|----------|----------|----------|----------|----------|----------|
| Intraparticle diffusion | $k_p (mg/g/min^{0.5})$ | 0.1671 | 0.7151 | 1.3105 | 1.8328 | 2.481 | 3.209 |
| | $C$ | 31.772 | 72.793 | 116.82 | 160.5 | 200.79 | 240.6 |
| | $R^2$ | 0.513 | 0.1304 | 0.945 | 0.9823 | 0.8944 | 0.822 |
| Liquid film diffusion | $K$ | 0.0628 | 0.0506 | 0.0421 | 0.0679 | 0.0487 | 0.0521 |
| | $C$ | 0.899 | 0.814 | 1.343 | 0.578 | 1.015 | 0.808 |
| | $R^2$ | 0.544 | 0.583 | 0.716 | 0.661 | 0.699 | 0.689 |

Figure 4. (A, B) SEM morphology of AFMC before adsorption at 1000 μm and 2000 μm magnifications. (C, D): SEM morphology of AFMC after adsorption at 1000 μm and 2000 μm magnifications.
Data availability
All data generated or analyzed during this study are included in this manuscript (and its Supplementary Information files).

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Author contributions
Author contributions. J.O. Ojediran and A.O. Dada conceived the idea, supervised the experiments, analyses the results and wrote the manuscript. S.O. Aniyi conceived the experiments and co-supervised the project, R.O. David carried out the experiment and also participated in analyzing the results. A.D. Adewumi also participated in data evaluation and statistical validity. All authors reviewed the manuscript.

Competing interests
The authors declare no competing interests.

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