

# Application of Sustainable Agricultural Solid Wastes for the Adsorption Removal of Malachite Green from Wastewater

Melkamu Biyana Regasa\*, Agesa Abdisa Hambisa

Department of Chemistry, College of Natural and Computational Sciences, Wollega University, Nekemte, Ethiopia

## Research Article

**Received:** 09-Nov-2023, Manuscript No. JEAES-23-119692; **Editor assigned:** 13-Nov-2023, Pre QC No. JEAES-23-119692(PQ); **Reviewed:** 27-Nov-2023, QC No. JEAES-23-112958; **Revised:** 04-Dec-2023, Manuscript No. JEAES-23-119692(R); **Published:** 11-Dec-2023, DOI: 10.4172/2347-7830.11.4.007

**\*For Correspondence:**

Melkamu Biyana Regasa,  
Department of Chemistry, College of  
Natural and Computational Sciences,  
Wollega University, Nekemte,  
Ethiopia

**E-mail:** malkako2011@gmail.com

**Citation:** Regasa MB, et al.  
Application of Sustainable  
Agricultural Solid Wastes for the  
Adsorption Removal of Malachite  
Green from Wastewater. RRJ Ecol  
Environ Sci.2023;11:007

**Copyright:** © 2023, Regasa MB, et al.  
This is an open-access article  
distributed under the terms of the  
Creative Commons Attribution  
License, which permits unrestricted  
use, distribution, and reproduction in  
any medium, provided the original  
author and source are credited.

## ABSTRACT

Water and wastewater treatment using adsorption technology based on agricultural solid wastes which are cheap and locally available have confirmed outstanding adsorption capabilities for removal of Malachite Green (MG) dye pollutant. Thus, this work reports low-cost and locally available Anchote Peel (AP) and Coffee Husk (CH) untreated adsorbents for the removal of MG from model wastewater. After characterizing the adsorbents by using Fourier infrared and x-ray powder diffraction spectrophotometers, the maximum dye removal efficiency at optimal experimental conditions: Solution pH, equilibrium contact time, amount of adsorbent, dye initial concentration and temperature) was determined to be 98.33% for AP and 98.11% for CH, respectively. The experimental results best agree with the Langmuir adsorption isotherms and pseudo-second-order kinetic model confirming that the uptake of MG involves of chemical processes to form monolayer followed by multilayer on the heterogeneous surface of the AP and CH adsorbents. Furthermore, the MG adsorption onto AP and CH is thermodynamically feasible, spontaneous, and non-uniform showing that there was surface change during adsorption. These adsorbents are cheap, abundant, environment benign and biodegradable. Finally, it was concluded that the AP and CH agricultural solid wastes based adsorbents are promising sustainable functional materials with due adsorption capabilities for removal of MG dye from aqueous solution.

**Keywords:** Malachite green; Anchote peel; Coffee husk; Adsorption; Water treatment

## INTRODUCTION

Malachite Green (MG) is an organic compound first synthesized in 1877 and commonly used as a dyestuff and antimicrobial in aquaculture industries. MG is a cationic dye commonly used in the industries for coloring and healing agent [1-3]. Apart from its wider applications, MG is persistent in the environment and acutely toxic to many living organisms. Thus, due to its public health risk and environmental issues, MG was grouped as a class II health hazard [4]. Many studies confirmed that MG is persistent in the environment, carcinogenesis, mutagenesis, teratogenesis, and show respiratory toxicity [3,5,6]. Consequently, it becomes compulsory to remove or degrade MG from environmental segments such as water bodies using suitable techniques.

There are various analytical methods employed for the elimination of MG dye removal from water and wastewater including photocatalytic degradation, combined photo-Fenton and biological oxidation, advanced oxidation processes, aerobic degradation, nanofiltration membranes, ozonation, coagulation, fluid extraction, solid phase extraction, and adsorption [7-10]. However, adsorption based on sustainable adsorbent materials becomes economically feasible to eliminate MG dye. This is accounted to the high efficiency, low operation cost, flexibility, simplicity, reusability, and capability to remove multiple pollutants from wastewaters [11]. Recently, low-cost and locally available adsorbents become promising to remove different organic dyes including MG and can replace the expensive commercially available materials. Such kinds of adsorbents are interesting since they are cheap, good in removing different dyes from aqueous media, biodegradable, and environmentally safe [12,13]. Therefore, the removal of MG from water and wastewater by using locally available and low-cost adsorbents is very important. Previous literature reports reveal that different biomass materials such as Chlorella-based biomass, Limoniaacidissima (wood apple) shell, pulverized teak leaf litter, chitosan, wheat bran, tamarind fruit shell, pomelo (*Citrus grandis*) peels, banana peel, rice husk and bamboo leaves biomass and soil have been successfully used to remove MG from water and wastewater [3,12-21]. In the adsorption technology, the applications of agri-wastes as adsorption materials in the removal of organic dyes from water and wastewater bodies become promising due to dual advantages namely environmental benign and biodegradability. On the other hand, MG water soluble cationic dye that persist in the environment to cause damage to nervous system, cancer, damage liver, spleen, kidney, lungs and bones and cytotoxic to mammalian cells. Therefore, due to its wide applications and toxic effects, MG dye removal from water bodies using suitable and sustainable technology is extremely important [6,10]. Thus, the aim of this work was to investigate Anchote Peel (AP) and Coffee Husk (CH) as low-cost and locally available abundant sustainable materials for the removal of MG organic dye from water bodies by adsorption method. The removal efficiency of the AP and CH was evaluated after careful optimization of different experimental parameters.

## MATERIALS AND METHODS

### Experimental part

**Chemicals and reagents:** Analytical standards of Malachite green dye was obtained from (Loba Chemie and Qualigens, India). Analytical grade reagent each (37%) hydrochloric acid (Merck, Germany) (97%), sodium hydroxide (CDH, India) were used in the present investigation. Stock solution of MG was prepared by dissolving a certain amount of dye in distilled water. These solutions were used for optimization of effective parameters and also for planning calibration curve in order to calculate the dye removal efficiency.

**Apparatus and instruments:** Chopping board and Teflon knife were used to cut Anchote peel (*Coccinia abyssinica*) into pieces while air circulating oven were used for drying. Porcelain mortar, pestle and crucibles were used during pounding of the samples. Analytical balance was used to weigh the Anchote peel and coffee husk samples. Round

bottom flasks with ground glass joint fitted with reflux condenser used for digesting the samples on block digester heating apparatus. Dyes concentration was measured by with ultraviolet visible (UV Vis) spectrophotometer (Shimadzu, DU 8800D), Fourier Transform Infrared Spectrophotometry (FTIR, Shimadzu FTIR 8400S spectrophotometer) spectra of the adsorbents, malachite green-load adsorbent and methyl orange-load adsorbent were recorded in the spectral range of 4000–400 cm. X ray powder diffraction (XRD) (model Xpert MPD, Philips,) spectrometry was used for characterization of the crystal nature of the adsorbents.

**Preparation of adsorbents:** Waste Coffee Husk (CH) and Anchote Peel (AP) were collected from agricultural product and local markets in the Nekemte City (latitude and longitude of 9°5'N 36°33'E and an elevation of 2,088 meters), suspended impurities were removed through extensive washing with tap water, cut into small pieces and then sun dries for four days. It was then dried in the oven at 105 °C for 24 hours until the peels become crispy. The dried peels were pulverized into the fine powder by a mechanical grinder and sieved through 1 mm siever. The AP powder obtained was used for experimental purposes.

**Batch adsorption experiments:** Adsorption equilibrium tests were conducted for the removal of MG in aqueous solution using AP and CH adsorbents. In order to estimate the biosorption characteristics of AP and CH on MG, batch sorption studies were carried out in 250 mL Erlenmeyer flasks containing a fixed amount (1.0 g) of adsorbent with 100 mL of 20 mg/L dye solution. Then the flask was then shaken at 200 rpm for 5 min and MG dye samples withdrawn at regular time intervals to measure the dye in the supernatant absorbance at 620 nm using UV-Vis spectrophotometer.

To determine the quantity of MG,  $q_e$  (mg/g), removed from aqueous solution at equilibrium and the efficiency of dye removing capacity or percentage removal (% R) of AP and CH were calculated from the following relationships [22]:

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

$$\%R = \frac{(C_0 - C_e) \times 100}{C_0} \dots\dots\dots (2)$$

where,  $C_0$  and  $C_e$  (mg/l) are the initial and equilibrium concentration of MG, respectively; V(L) is the volume of the dye, w (g) is the mass of AP or CH used;  $q_e$  (mg/g) and %R is the quantity of MG removed from aqueous solution. Except for the evaluation of the effect of temperature, all measurements were conducted at room temperature except for the study of the effect of temperature on the adsorption process and all measurements were made in triplicate to consider the average values for report. The effects of AP and CH adsorbents dose, equilibrium contact time, initial MG concentration, pH and temperature were studied together by adding 100 ml of dye solution to 1 g of AP and CH in 250 ml Erlenmeyer flask.

**Adsorption isotherms:** The design and selection of suitable adsorbents and the evaluation of their performances mostly rely on the adsorption isotherms. There is various adsorption isotherm used to describe the adsorption of dyes onto the surface of adsorbents. Here, the two most common isotherms Langmuir, and Freundlich were used to determine the adsorption capacity and heterogeneity of the system.

**Adsorption kinetics:** The adsorption kinetics experiments were conducted using initial MG concentrations of 200, 400 and 800 mg/l. In this work, pseudo-first-order and pseudo-second-order model have been used for testing the

experimental data in order to determine the rate at which the MG was adsorbed, to predict the adsorption mechanism and the rate-determining steps.

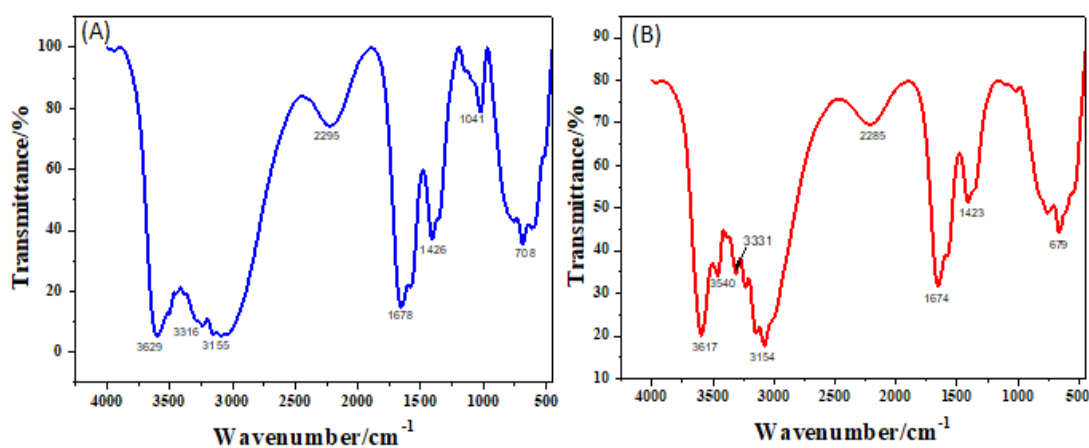
**Adsorption thermodynamics:** The effect of temperature on the adsorption of MG onto AP and CH adsorbents were investigated at various temperature ranges from 20 to 80°C using batch adsorption experiment described before. The initial concentration and volume of the MG dye solution were fixed at 500 mg/l and 100 ml, respectively; the initial pH of dye solution was adjusted to 6.0 while the mass of AP and CH used was fixed at 0.5 g to determine the amount of the residual MG ( $q_e$ ) in solution.

## RESULTS AND DISCUSSION

### Chemical characterization of adsorbents

The characterization of adsorbent materials is very important to better understand the nature of the materials. Thus, characterization of Coffee Husk (CH) and Anchote Peel (AP) were carried out by using FTIR and XRD. Thus, information obtained from the characteristic of adsorbents is necessary as their physical and chemical properties can influence the adsorption behavior. FTIR spectra was employed to ascertain the bond types, structures and functional groups in the AP and CH adsorption. Figures 1A and 1B showed the FTIR spectra of AP and CH powder respectively. The band between 3800-2700  $\text{cm}^{-1}$  stretching are Hydrogen region which consists -C-H, =C-H, hydroxyl group (O-H group) and alkyne group. Therefore, the bands at 3316  $\text{cm}^{-1}$  stretching and 2296  $\text{cm}^{-1}$  stretching for the spectrum of AP powder and the bands 3617, 3540, 3331, 3154 and 2285  $\text{cm}^{-1}$  for CH powder indicated they consist of -C-H, =C-H, and alkyne functional group.

**Figure 1.** FTIR spectrums of (A) AP powder and (B) CH powder.



The presence of C=C bond and C=O bond in AP and CH powders is accountable for the appearances of absorption bands at 1678  $\text{cm}^{-1}$  and 1674  $\text{cm}^{-1}$  respectively. Furthermore, the existence of amides in both adsorbents is evidenced from the presence of double peaks with equivalent halves near 3629-3315  $\text{cm}^{-1}$  that belongs to the primary amines ( $\text{NH}_2$ ) symmetric stretching. Similarly, the amide functional units can be confirmed from the absence of single broad peak at about 3400-3300  $\text{cm}^{-1}$  and the presence of C-N stretching near 1300-1000  $\text{cm}^{-1}$ . The peak at 2295  $\text{cm}^{-1}$ , 1678  $\text{cm}^{-1}$  and 1441  $\text{cm}^{-1}$  are due to the C≡N, C=O and N-H groups stretching vibrations. Moreover, the peak at 708  $\text{cm}^{-1}$  corresponds to NH out-of-plane bending. Thus, the biomaterial mainly consists of long chain amine compounds containing carbonyl functional units (Table 1). The presence of functional units such

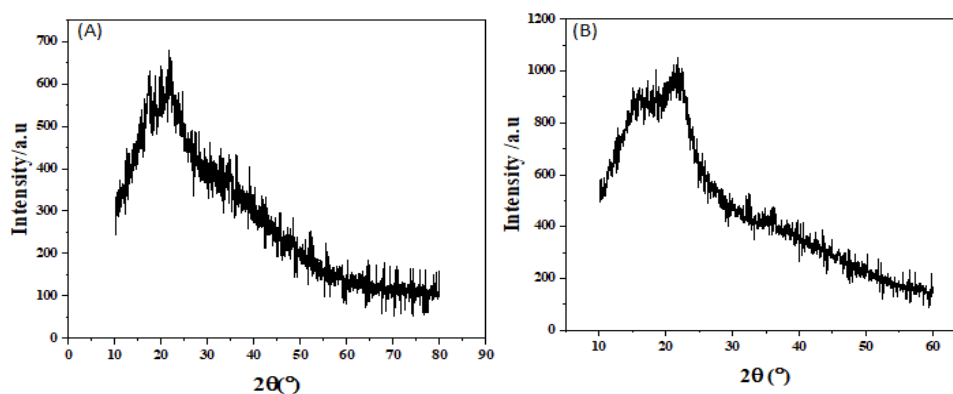
as amine and carbonyl groups in the bionanomaterials make them suitable for the adsorption of various adsorbates.

**Table 1.** Assignment of FTIR band positions of AP and CH adsorption in wave number (cm<sup>-1</sup>).

Assignment	AP powder	CH powder
O-H stretching	3316 cm <sup>-1</sup>	3617, 3540, 3331 and 3154 cm <sup>-1</sup>
C-H stretching	3316 and 2296 cm <sup>-1</sup>	3617, 3540, 3331 and 3154 cm <sup>-1</sup>
C=C stretching	1678 cm <sup>-1</sup>	1674 cm <sup>-1</sup>
C-O, C-N and C-C single bond stretch	708 cm <sup>-1</sup>	679 cm <sup>-1</sup>
C=O stretching	1426 and 1678 cm <sup>-1</sup>	1424 and 1674 cm <sup>-1</sup>
C-N stretching	1426 cm <sup>-1</sup>	1424 cm <sup>-1</sup>
C≡N stretching	2295 cm <sup>-1</sup>	2285 cm <sup>-1</sup>
N-H stretching(amines and amides)	3316 cm <sup>-1</sup>	3331 cm <sup>-1</sup>

X-ray powder diffraction (XRD) was used to study the surface properties, crystallinity or the amorphous nature of the AP and CH powders. As illustrated in Figures 2A and 2B, it was observed that the intensities are increased with increasing in angle up to certain transition angle and anomaly decreased further. The broad diffraction spectrum with a major semi-crystalline peaks was observed at 2θ=20° for AP powder and at 2θ=16.3° and 20° for CH powder respectively. For both samples the broad spectrums at about 2θ=20° indicates the materials are highly amorphous and porous in nature that is the characteristic of plant based natural polymers resulted from the diffusion scattering of biomaterial fibers [23].

**Figure 2.** XRD spectrum of AP powder (A) and CH powder (B).



**Adsorption studies**

The MG dye removal efficiency of the adsorbents was evaluated using the batch equilibrium experiment. The removal efficiency (percent removal, % R) and adsorption capacity (q<sub>e</sub>) for each adsorbent was employed to study the extent of dye adsorption. For both AP and CH adsorbents, the adsorption capacity at any t time (q<sub>t</sub>) was determined using the following equation [24]:

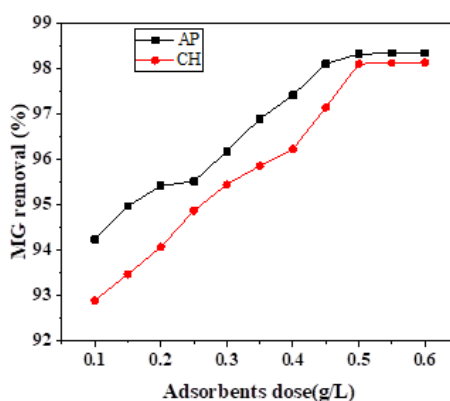
$$q_t = \frac{V(C_o - C_e)}{W} \dots\dots\dots (3)$$

Where  $C_o$  and  $C_e$  are the initial and the equilibrium MG dye concentrations (mg/L),  $V$  is the volume of solution (mL) and  $W$  is the amount of adsorbent used (g). The removal of MG from aqueous solution was examined by taking into account different experimental parameters which affect the efficiency. These parameters include adsorbent dose, pH, equilibrium contact time, initial concentration and temperature.

**Effect of adsorbents dose**

The efficiency of adsorption mainly depends on the number of active adsorption sites available on the adsorbent. This implies the amount of adsorbent used in adsorption process is particularly important because it determines the sorbent-adsorbent equilibrium in the system [25]. Thus the quantity of AP and CH powders were increased from 0.1 to 0.6 g/L at 100 mg/L dye concentration on equilibrium time of 3.00 h with agitation speed of 200 rpm at 25°C. The removal efficiency was determined in percentage as depicted in Figure 3. The maximum percentage removal of MG of 98.33% for AP and 98.11 % for CH was observed. For both adsorbents the removal efficiency was gradually increased as the adsorbents dose increased from 0.1 to 0.5 g/L and almost remains unchanged indicating that the equilibrium condition is maintained. The increase in the adsorption of the dye is clearly dependent on the increase in the binding sites on the surfaces of the adsorbent upon increases its quantities. The adsorbent quantity of 0.5 g/L is known to have sufficient available binding sites to accommodate more MG molecules thus giving high adsorption of MG dye. On the other hand, at lower and higher doses, the adsorption capacity seems low which might be due to the presence of very small vacant binding sites, overlapping of adsorption sites and the difficulty of the dye molecules to diffuse into the inner sites for adsorption [26-28]. Furthermore, the decreases in the adsorption capacity at high AP and CH to MG concentration ratio might be the creation of artificial adsorption process that does not favor optimum uptake of the MG dye molecules by the adsorbents [14].

**Figure 3.** Effect of adsorbents dose on the dye removal efficiency.

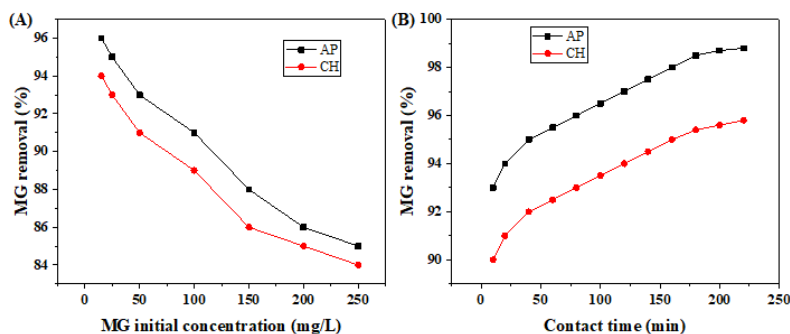


**Effect of contact time and initial dye concentration**

The effects of initial MG concentration and contact time on the adsorption capacity of AP and CH were investigated as shown in Figure 4. The variation of adsorption capacity with time for the adsorption of MG onto AP and CH decrease with increase in the amount of MG and slows down after 100 mg/L. Thus the equilibrium time for the MG-adsorbents at higher concentration relatively small this might be accounted for the increase in the diffusion path length in the adsorbents. Thus lower concentration of MG favors high removal efficiency. Furthermore, the adsorption capacity increases with contact time and reaches to equilibrium after an average time of 180 min. The

presence of available binding sites at the surface of AP and CH adsorbents is responsible for the rapid increase in the adsorption of MG at the beginning. Then after the rate of diffusion becomes slow indicating that the MG molecules takes relatively long time to penetrate into the inner part of the adsorbents once the surface attained saturation. Generally, the MG adsorption increases with increasing the dye initial concentration only until it attains an equilibrium condition. The overall decrease in the adsorption capacity at high MG initial concentration accounts that the repulsion between the adsorbed and new coming MG molecules as well as the decrease in the number of vacant surface sites available for binding the dye [14,29].

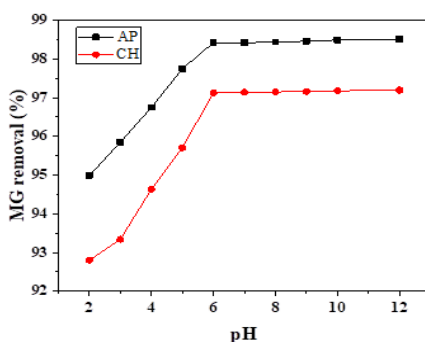
**Figure 4.** Removal efficiency of AP and CH adsorbents (A) Effect of MG initial concentration; (B) contact time



**Effect of pH**

The uptake of dye molecules onto the surface of adsorbents is highly dependent on the Initial pH of dye solution. To investigate the effect of initial pH of a dye solution on the adsorption efficiency, pH 2-12 was employed using MG initial concentration of 100 mg/L with 500 mg as adsorbent dosage, agitation time 180 min with agitating speed 200 rpm at 25°C (Figure 5). The high percentage removal was observed from 6-8 pH ranges with about 98.58% for AP and 97.21 % for CH removal of MG dye. At pH less than 6.0, percentage removal is low because the surface of the adsorbents repels the dye molecules due to the formation of positively charged surface on the adsorbent surfaces and the protonation of carboxylic groups of MG to form positive charges [30]. Above pH 6.0, the percentage removal was increased due to the increase in the electrostatic interactions between the cationic MG dye and the negatively charged surface of the adsorbents. Therefore, the removal efficiency is increased due to the increase in the adsorption of MG onto the surface of adsorbents which is in agreement with the previously reported adsorption systems [4,14,31]. Thus, the adsorbent introduced here work best in the pH range of 6.0-8.0 without treatment.

**Figure 5.** Effect of pH on the MG removal efficiency of AP and CH adsorbents.





### Adsorption isotherm studies

In the removal of contaminants from water bodies, the ratio of the amount adsorbed by adsorbents and that remains in solution at fixed temperature at equilibrium is very important in adsorption isotherm studies. The adsorption performance of a given adsorbent can be described Langmuir isotherm and Freundlich isotherm models using adsorption equation [32]. The experimental values of Langmuir isotherm and Freundlich isotherm constants for the adsorption of MG onto AP and CH at 25°C are listed in Table 2. As such the relatively high values of correlation coefficients (R<sup>2</sup>) (0.996 and 0.994) for AP and CH confirms that the isotherm data for MG best fit the Langmuir adsorption isotherm model equation:

$$q_e = q_{max} \frac{K_L C_e}{1 + C_e K_L} \dots\dots\dots (4)$$

where C<sub>e</sub> (mg/L) is the concentration of MG adsorbed at equilibrium, q<sub>e</sub> (mg/g) is the mass of MG adsorbed at equilibrium per unit mass of AP and CH, q<sub>max</sub> (mg/g) is the adsorption capacity of biosorbent toward specific dye pollutants, and K<sub>L</sub> (L/mg) is the adsorption rate constant. A straight-line plot of C<sub>e</sub>/q<sub>e</sub> versus C<sub>e</sub> where slope equal to C<sub>e</sub>/q<sub>e</sub> and intercept equals (1/q<sub>m</sub>)(1/K<sub>L</sub>) is presented in Figure 6. The calculated values of K<sub>L</sub>, q<sub>m</sub>, R<sub>L</sub> and the linear correlation coefficient, R<sup>2</sup>, are presented in Table 2. A separation factor (R<sub>L</sub>= 1/(1+K<sub>L</sub>C<sub>0</sub>)) which is a dimensionless is important to clarify the important characteristics of Langmuir equation in adsorption system. The R<sup>2</sup> value is 0.996 and 0.994 while the R<sub>L</sub> values are 0.409 and 0.649 for AP and CH, respectively indicating the adsorption process is favorable through molecular layer formation and reversible.

Table 2 indicates that the best model representing the adsorption of MG onto AP and CH is Freundlich isotherm which exhibits good linearity with an R<sup>2</sup> of 0.996 and 0.994 for AP and CH, respectively. This suggests that the surfaces of AP and CH are heterogeneous and favors the multilayer adsorption of MG dye. The solution of Freundlich equation generated from the following equation [33]:

$$q_e = K_f C_e^{1/n} \dots\dots\dots (5)$$

Where, the parameters K<sub>f</sub> and n represent Freundlich adsorption capacity and heterogeneity of the system, respectively. The value of R<sup>2</sup> is 0.983 (AP) and 0.981 (CH) while the value of n is 1.438 and 1.610 for AP and CH, respectively confirming that MG dye molecules adsorption onto the adsorbents surface is favorable.

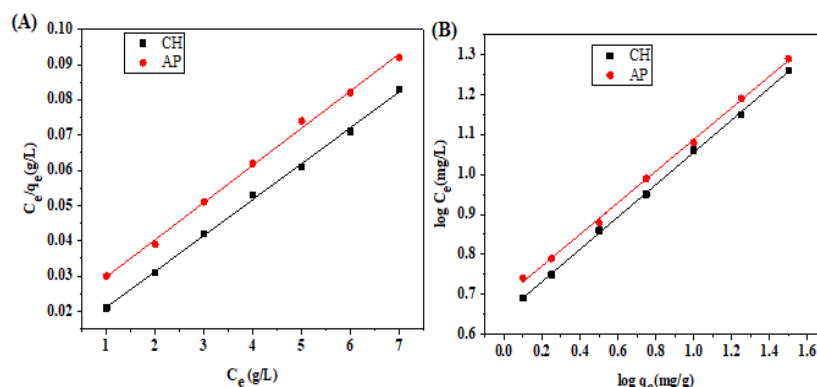
**Table 2.** Isotherm models results for the adsorption of MG on to AP and CH adsorbent at 25°C.

Adsorption isotherms	Constants	Adsorbent	
		AP	CH
Langmuir	Q <sub>m</sub>	227.3	17.783
	K <sub>L</sub>	0.029	0.025
	R <sup>2</sup>	0.996	0.994
Freundlich	K <sub>f</sub>	8.023	0.154
	n	1.438	1.61
	R <sup>2</sup>	0.983	0.981
R <sub>L</sub> at 50 mg/L		0.409	0.649

Based on the values of n, CH surface adsorption is more heterogeneous than that of AP. The strong correlation of the adsorption data with the Freundlich adsorption isotherm indicates the adsorption of MG onto AP and CH forms the multilayer and heterogeneous adsorption of molecules to the adsorbent surface.



Figure 6. Adsorption plot of MG onto AP and CH adsorbents (A) Linearized Langmuir; (B) Freundlich.



### Study of AP and CH adsorption kinetics

The efficient uptake of the adsorbate by the adsorbent with respect to time and quantity is the crucial step in the design of efficient and effective low-cost adsorbents. Thus, the adsorption kinetics can be studied using the pseudo-first-order and pseudo-second-order models by assuming the surface chemistry of the adsorbent [34]. In line with this, the pseudo-first-order and pseudo-second-order models were employed to investigate the adsorption kinetics of MG onto AP and CH adsorbents to generate different parameters (Table 3).

The pseudo-first-order equation has the following mathematical form:

$$q_t = q_e(1 - \exp(-k_1 t)) \dots\dots\dots (6)$$

where  $q_t$  is the amount of dye adsorbed by biosorbent at time  $t$ , while  $q_e$  and  $k_1$  are the parameters of the pseudo-first-order which indicate the amount adsorbed at equilibrium condition and time scaling factor. The kinetic parameter  $k_1$  is usually dependent on the pH of the solution, temperature, as well as the initial concentration of the solution.

The pseudo-second-order equation for the adsorption kinetics can be determined by using the following equation [35]:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \dots\dots\dots (7)$$

Similar to the parameter  $k_1$  in pseudo-first order, the parameter  $k_2$  is also a time scaling factor.

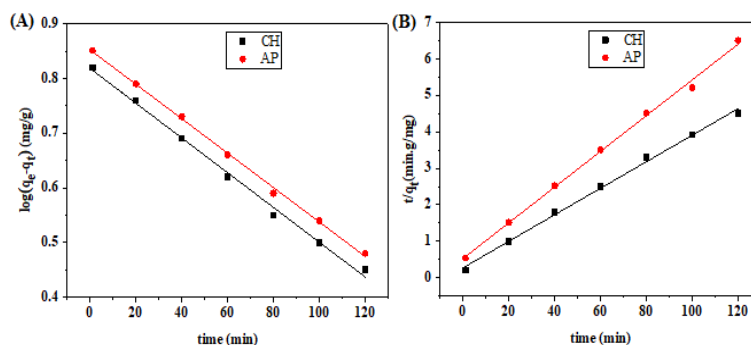
From Table 3, it is observed that the correlation coefficients for the pseudo-second-order kinetic model ( $R^2=0.9982$ ) is greater than that of pseudo-first order (0.9023). This is considered as the confirmatory check for the kinetic data as it best fits the pseudo-second-order kinetic model. The plots of pseudo-second-order kinetic for the adsorption of MG onto AP and CH adsorbents are presented in Figure 7.

Table 3. Adsorption kinetic parameters results for the adsorption of MG onto AP and CH adsorbents at 25 °C.

Adsorption kinetics	Constants	Adsorbent	
		AP	CH
Pseudo-first-order	$K_1$	0.0131	0.0995
	$q_e$	1.0921	10.093
	$R^2$	0.9023	0.915
Pseudo-second-order	$K_2$	0.0571	0.0148
	$q_e$	23.255	21.459

	R <sup>2</sup>	0.9982	0.9972
--	----------------	--------	--------

Figure 7. Plots for the adsorption of MG onto AP and CH adsorbents (A) Pseudo-first-order; (B) pseudo-second-order.



Based on the kinetic data R<sup>2</sup>, the adsorption data for the adsorption of MG onto AP and CH best fit with the pseudo-second-order than the pseudo-first-order kinetic model. The higher K<sub>2</sub> values indicate the fast adsorption of the MG to attain equilibrium condition. Overall, pseudo-second-order equation is relatively free random experimental errors; therefore, this equation gives better prediction for the various adsorption systems than the pseudo-first-order equation [36-38].

**Study of AP and CH adsorption thermodynamics**

The quantity of adsorbate taken up by the adsorbent directly depends on the temperature used during the experimental work and the functional groups available. The increase in temperature will lessen the adsorption capacity and even removed the adsorbate already adsorbed onto the surface of the adsorbent [39]. It is interlinked to the solubility of the adsorbate species that increase with a rise in temperature, while decreases in chemical potential [40]. The temperature effect on the adsorption can presented using the adsorption thermodynamic data and Vant Hoff equation which relates linear sorption distribution coefficient (K<sub>D</sub>) with the standards of entropy (ΔS°) and enthalpy change (ΔH°):

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \dots\dots\dots (8)$$

The value of ΔH was calculated from the slope of the linear regression of lnK<sub>D</sub> versus 1/T (Figure 8) while K<sub>D</sub> value was determined using the relation: K<sub>D</sub>=q<sub>e</sub>/C<sub>e</sub>, where q<sub>e</sub> represents the amount of MG adsorbed on AP and CH at equilibrium (mg/L).

The spontaneity and feasibility of adsorption processes of MG by both AP and CH adsorbents was evaluated by using Gibb’s free energy change (ΔG°):

$$\Delta G^\circ = -RT \ln K_D \dots\dots\dots (9)$$

Where R is gas constant and T is temperature (K).

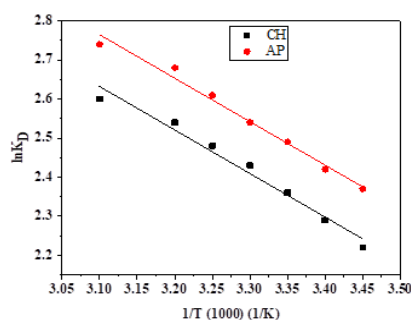
Thermodynamic parameters such as ΔH°, ΔS° and ΔG° for the adsorption of MG by both AP and CH are presented in Table 4.

**Table 4.** Adsorption thermodynamic parameters determined for the adsorption of MG onto AP and CH adsorbents at different temperatures.

Adsorbent	ΔH	ΔS	ΔG(KJ/mol)					
	(KJ/mol)		(KJ/mol.K)	20°C	25°C	30°C	35°C	40°C
AP	35.13	14.69	-7.87	-9.38	-10.49	-12.41	-13.58	-14.16
CH	26	70.4	-5.42	-6.64	-7.03	-8.87	-9.13	-10.64

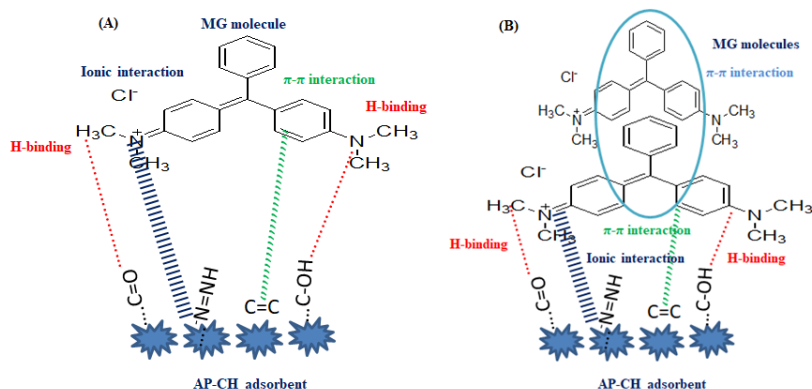
The negative value of  $\Delta G^\circ$  in this work indicates that the MG adsorption process onto AP and CH is spontaneous in nature and favorable thermodynamically [41]. The uptake of MG by AP and CH adsorbents has positive  $\Delta H$  values showing that the adsorption process is endothermic. Furthermore, the positive values  $\Delta S$  indicate that the adsorption system becomes more unsystematic and MG molecules showed strong affinity toward the active sites of the AP and CH adsorbents.

**Figure 8.** Plot of  $\ln K_D$  vs  $1/T$  for the adsorption of MG onto AP and CH.



### Adsorption mechanism

Organic pollutants like organic dyes have various chemical structure and its adsorption is affected by molecular size, charge, solubility, hydrophobicity, and reactivity and the nature of adsorbent [7,42]. The adsorption of MG dye onto agricultural wastes involves absorption, physical adsorption, ion-exchange, surface complexing, precipitation process and chemical sorption that are not related to metabolism. Based on the FTIR results (Figure 1), there are carboxylic, hydroxyl, amine, conjugate bonds and amide functional units. Thus, these units interact with those in MG through hydrogen bonding (H-bonding),  $\pi$ - $\pi$  interactions, ionic interactions and van der Waals forces [6,43]. MG adsorption occurs by physical adsorption in the form of monolayer formation followed by multilayer due the presence of two amine groups and positive charge on the nitrogen atom present in it [44,45]. The net interactions of these forces greatly assisted the MG by both AP and CH adsorbents. Generally, the adsorption of MG on to AP and CH can be grouped into monolayer and multilayer processes (Figure 9). The adsorption of MG onto AP and CH adsorbents through the formation of multilayer on the heterogeneous surface of adsorbents is dominating the system and reasonable because the experimental data best fitted with Freundlich adsorption isotherm [33]. Furthermore, the mechanism of the MG adsorption by the proposed adsorbents involves a chemical process mainly based on cation-exchange and electron sharing processes between the dye and the adsorbents [46].

**Figure 9.** (A) Proposed MG adsorption mechanism as monolayer; (B) multilayer by AP and CH adsorbents.

## CONCLUSION

Low-cost and locally available Anchote Peel (AP) and Coffee Husk (CH) adsorbents were designed and employed successfully as a water or wastewater treatment to minimize the severe problems for humans and aquatic biota due to dyestuffs water contamination. The AP and CH adsorbents were found to contain different functional units which help them to bind the Malachite Green (MG) dye molecules. The performance of AP and CH adsorbents to uptake the MG dye evaluated after careful optimization of experimental parameters such as adsorbent dose, equilibrium contact time, dye initial concentration, and pH. Under optimum experimental operation, the AP and CH were able to achieve the adsorption capacities of 98.33% for AP and 98.11% for CH, respectively. The experimental data showed best correlation with the pseudo-second-order kinetic model and Langmuir adsorption isotherm indicating the adsorption of MG involves chemical processes to form monolayer followed by multilayer on the heterogeneous surface of the AP and CH adsorbents. Furthermore, the adsorption of MG onto AP and CH was thermodynamically feasible and non-uniform. From the results of the present study, it seems the utilization of AP and CH as the low-cost, green and environment benign adsorbents is promising in the future for real applications.

## ACKNOWLEDGEMENTS

This work was supported by the School of Graduate Studies and Department of Chemistry of Wollega University, Ethiopia

## AUTHOR CONTRIBUTION STATEMENT

The authors are fully informed to participate in the project and have full knowledge of the nature of the project as well as to publish the work. M.B. Regasa has initiated the study conception and design as well as supervising the work, preparing and finalizing the manuscript. Experimental works were done by A.H. Abdisa and the first draft of the results and discussion were performed by same. All authors read and approved the final manuscript.

## FUNDING

The authors received no fund for this project.

## AVAILABILITY OF DATA AND MATERIALS

The supporting data will be available based on request.

## REFERENCES

1. Srivastava S, et al. Review: Toxicological effects of malachite green. *Aquat Toxicol.* 2004;66:319-329.

2. El-Zahhar, et al. Removal of malachite green dye from aqueous solutions using organically modified hydroxyapatite. *J Environ Chem Eng*. 2016;4:633–638.
3. Gan L, et al. Burkholderiacepacia immobilized on eucalyptus leaves used to simultaneously remove Malachite Green (MG) and Cr(VI). *Colloid Surf B Biointerfaces*. 2018;172:526–531.
4. Sartape AS, et al. Removal of malachite green dye from aqueous solution with adsorption technique using *Limonia acidissima* (wood apple) shell as low cost adsorbent. *Arab J Chem*. 2017;10:3229–3238.
5. Srivastava SJ, et al. Acute toxicity of malachite green and its effects on certain blood parameters of a catfish, *Heteropneustes fossilis*. *Aquat Toxicol*. 1995;31:241–247.
6. Ahmad AA, et al. Adsorption of malachite green by activated carbon derived from gasified *Hevea brasiliensis* root. *Arab J Chem*. 2021;14.
7. Tewari K, et al. Adsorption removal of malachite green dye from aqueous solution. *Rev Chem Eng*. 2017;34:1–27.
8. Kumar R. Removal of malachite green dye from waste water by using natural and synthetic adsorbents: a review. *Int J Adv Tech Eng and Sci*. 2015;3:304–309.
9. Getaye M, et al. Removal of malachite green from contaminated water using electro-coagulation technique. *J Anal Pharm Res*. 2017;6:00184.
10. Raval NP, et al. Malachite green a cationic dye and its removal from aqueous solution by adsorption. *Appl Water Sci*. 2017;7:3407–3445.
11. Tran NH, et al. Insight into the adsorption mechanism of cationic dye onto biosorbents derived from agricultural wastes. *Chem Eng Comm*. 2017;204:1020–1036.
12. Saha P, et al. Assessment on the removal of malachite green using tamarind fruit shell as biosorbent. *Clean Soil Air Water*. 2010;38.
13. Tsai WT, et al. Removal of malachite green from aqueous solution using low-cost chlorella-based biomass. *J Hazard Mater*. 2010;175:844–849.
14. Oyelude EO, et al. Removal of malachite green from aqueous solution using pulverized teak leaf litter: equilibrium, kinetic and thermodynamic studies. *Chem Central J*. 2018;12:81.
15. Subramani SE, et al. Isotherm, kinetic and thermodynamic studies on the adsorption behaviour of textile dyes onto chitosan. *Process Safety and Environ Protec*. 2017;106:1–10.
16. Papinutti L, et al. Removal and degradation of the fungicide dye malachite green from aqueous solution using the system wheat bran–*fomes sclerodermeus*. *Enzyme Microb Technol*. 2006;39:848.
17. Bello OS, et al. Scavenging malachite green dye from aqueous solutions using pomelo (*Citrus grandis*) peels: kinetic, equilibrium and thermodynamic studies. *Desal Water Treat*. 2015;56:521–535.
18. Balan K, et al. Decolorization of malachite green by laccase: optimization by response surface methodology. *J Taiwan Inst Chem Eng*. 2012;43:776–782.
19. Chowdhury S, et al. Scale-up of a dye adsorption process using chemically modified rice husk: optimization using response surface methodology. *Desalin Water Treat*. 2012;37:331–336.
20. Chen H, et al. Adsorption behavior of malachite green from aqueous solution onto bamboo leaves biomass. *Asian J Chem*. 2014;26:6579–6582.
21. Sundararaman TR, et al. Adsorptive removal of malachite green dye onto coal-associated soil and conditions optimization. *Adsorption Scie & Tech*. 2021.

22. Shaban M, et al. Removal of ammonia from aqueous solutions, ground water and wastewater using mechanically activated clinoptilolite and synthetic zeolite-A; kinetic and equilibrium studies. *Water, Air, Soil Pollut.* 2017;228:450–466.
23. Romo-Valera C, et al. Cytocompatibility and suitability of protein-based biomaterials as potential candidates for corneal tissue engineering. *Int J Mol Sci.* 2021;22.
24. Sarojini G, et al. Performance evaluation of polymer-marine biomass based bionanocomposite for the adsorptive removal of malachite green from synthetic wastewater. *Environ Res.* 2022;204.
25. Wanyonyi WC, et al. Adsorption of congo red dye from aqueous solutions using roots of *Eichhornia crassipes*: Kinetic and Equilibrium Studies. *Energy.* 2014;10:862-869.
26. Garg VK, et al. Removal of malachite green dye from aqueous solution by adsorption using agro-industry waste: a case study of *Prosopis cineraria*. *Dyes Pigm.* 2004;62:1-10.
27. Hamdaoui O, et al. Sorption of malachite green by a novel sorbent, dead leaves of plane tree: equilibrium and kinetic modeling. *Che Eng J.* 2008;143:73–84.
28. Oyelude EO, et al. Studies on the removal of basic fuchsin dye from aqueous solution by HCl treated malted sorghum mash. *J Mater Environ Sci.* 2015;6:1126–1136.
29. Ahmad, MA, et al. Removal of malachite green dye from aqueous solution using rambutan peel-based activated carbon: equilibrium, kinetic and thermodynamic studies. *Chem Eng J.* 2011;171:510–516.
30. Garg VK, et al. Dye removal from aqueous solution by adsorption on treated sawdust. *Bioresour. Tech.* 2003;89:121-124.
31. Baek MH, et al. Removal of malachite green from aqueous solution using degreased coffee bean. *J Hazard Mater.* 2010;176:820-828.
32. Igwe JC, et al. Adsorption isotherm studies of Cd (II), Pb (II) and Zn (II) ions bioremediation from aqueous solution using unmodified and EDTA-modified maize cob. *EcléticaQuímica.* 2017;32:33-42.
33. Freundlich HMF. On adsorption in solutions. *J Phys Chem.* 1906;57:385-470. [Google Scholar]
34. Putro JN, et al. Biosorption of dyes: In advances in green and sustainable chemistry, green chemistry and water remediation: Research and applications. 2021;99-133.
35. Blanchard G, et al. Removal of heavy metals from waters by means of natural zeolites. *Water Res.* 1984;18:1501-1507.
36. Plazinski W, et al. Theoretical models of sorption kinetics including a surface reaction mechanism: a review. *Adv. Colloid Interface Sci.* 2009;152:2-13.
37. Modenes AN, et al. A new alternative to use soybean hulls on the adsorptive removal of aqueous dyestuff. *Biores Technol Rep.* 2019;6:175-182.
38. Moghazy RM, et al. Eco-friendly complementary biosorption process of methylene blue using micro-sized dried biosorbents of two macro-algal species (*Ulva fasciata* and *Sargassum dentifolium*): full factorial design, equilibrium, and kinetic studies. *Int J Biol Macromol.* 2019;134:330-343.
39. Hajjaligol S, et al. Optimization of biosorption potential of nano biomass derived from walnut shell for the removal of malachite green from liquids solution: experimental design approaches. *J Mol Liq.* 2019;286.
40. Gunduz F, et al. Biosorption of malachite green from an aqueous solution using pomegranate peel: equilibrium modeling, kinetic and thermodynamic studies. *J Mol Liq.* 2017;243:790-798.

41. Daneshvar E, et al. Biosorption of three acid dyes by the brown macroalga *Stoechospermum marginatum*: isotherm, kinetic and thermodynamic studies. *Che Eng J.* 2012;195-196:297-306.
42. Fomina M, et al. Biosorption: Current perspectives on concept, definition and application. *Bio resource Tech.* 2014;160:3-14.
43. Cheung WH, et al. Intraparticle diffusion processes during acid dye adsorption onto chitosan. *Bioresour Tech.* 2007;98:2897–2904.
44. Azad FN, et al. Enhanced simultaneous removal of malachite green and safranin O by ZnO nanorod-loaded activated carbon: modeling, optimization and adsorption isotherms. *N J Chem.* 2015;39:7998–8005.
45. Banu SUN, et al. Synthesis and characterisation of nanocrystallite embedded activated carbon from *Eichornia crassipes* and its use in the removal of malachite green. *Int J ChemTech Res.* 2015;8:158–169.
46. Shaban M, et al. Photocatalytic removal of congo red dye using MCM48/Ni<sub>2</sub>O<sub>3</sub> composite synthesized based on silica gel extracted from rice husk ash; fabrication and application. *J Environ Manag.* 2017;204:1989–1999.