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Valorization of Lignocellulosic Wastes Material for Efficient Adsorption of a Cationic Azo Dye and Sludge Recycling as a Reinforcement of Thermoplastic Composite

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Abstract: This work explored the adsorption of Malachite Green (MG) dye by Acorn Pericarp (AP) in the context of biomass valorization. The Acorn Pericarp was analyzed by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction. The adsorption capacity under optimal experimental conditions was studied at different adsorbent doses, the initial concentration times of the dye and pH. The results presented in this work on the adsorption kinetics of MG showed that the pseudo-first-order model (R^2 = 0.9971) better described the adsorption kinetics at 10^{-5} M. The experimental isotherms showed that Acorn Pericarp adsorption followed the Langmuir isotherm model (R^2 = 0.9889). The thermodynamic study showed that MG adsorption is endothermic ($\Delta H^\circ > 0$) and spontaneous ($\Delta G^\circ < 0$). For a sustainable industry, the sludge was converted into reinforcement of polystyrene using in-situ polymerization with 10% by weight of filler. A morphological and structural analysis was performed using SEM and FTIR, the results of characterization showed that the AP sludge was incorporated well into the PS matrix.

Keywords: Acorn Pericarp; Malachite Green; adsorption; sludge; polystyrene; composite

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Citation: Jabri, M.; Dehmani, Y.; Loulidi, I.; Kali, A.; Amar, A.; Lgaz, H.; Hadey, C.; Boukhlifi, F. Valorization of Lignocellulosic Wastes Material for Efficient Adsorption of a Cationic Azo Dye and Sludge Recycling as a Reinforcement of Thermoplastic Composite. *Fluids* **2023**, *8*, 37. https://doi.org/10.3390/fluids8020037

Academic Editors: Carlos A. Nieto De Castro and Mehrdad Massoudi

Received: 7 October 2022
Revised: 4 January 2023
Accepted: 15 January 2023
Published: 18 January 2023

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1. Introduction

A multitude of chemicals are continuously discharged into water resources; these products degrade very slowly and have a strong impact on the environment. Humans are not the only ones affected by the danger of this chemical pollution, which produces a perceptible impact obviously destructing fauna and flora, eutrophication and the appearance of green tides or hormonal disturbances of the fauna. The wide use of synthetic dyes produces wastewater containing organic matter of a complex molecular structure characterized by high stability, which constitutes a serious environmental danger [1]. Malachite Green (MG) is a cationic triphenylmethane dye that is used to color cotton, tissue, paper, and leather, as well as to process paints and printing ink [1]. In the aquaculture business, MG is used as a fungicide and antiseptic to prevent parasites and illnesses in fish [2]. MG, on the other hand, is extremely harmful to mammalian cells. They can also have an impact on the food chain and produce human carcinogenic, mutagenic, and teratogenic effects.

The treatment of effluents including MG contaminants is critical in this situation. Adsorption is a technique for the treatment of wastewater containing dyes, and it is characterized by its simplicity and high performance. This technique, however, is limited by the commercial cost. Faced with this limitation, the adsorbents have been developed from low-cost sources such as agricultural and food wastes. Several researchers are increasingly focusing on the removal of Malachite Green. Kundu et al. [3] used Cu-doped Titania intercalated with Na in layers as an adsorbent for MG. For highly efficient MG

adsorption, Guo et al. [4] studied the synthesis of MgO/Fe_3O_4 nanoparticles incorporated into activated carbon from biomass. Qu et al. [5] also used activated carbon to study its effect on Malachite Green adsorption, while Dehmani and his co-workers [6] used iron nanoparticles as adsorbents for this dye.

Finding renewable raw materials for the production of fine chemicals, materials, and fuels has become an important goal [7,8]. Lignocellulosic biomass is a promising alternative to fossil resources due to its abundance, renewability, and versatility [7]. Lignocellulosic biomass is one of the most abundant renewable resources on Earth and its use does not increase net CO_2 emissions [9]. It is expected that sustainable and environmentally friendly bio-based industries using biomass as the main raw material will replace the current bio-based industries that cause serious environmental problems [10]. A biorefinery is a refinery that converts biomass into energy and other beneficial by-products such as chemicals. A biorefinery is the sustainable conversion of biomass into a range of biobased products (food, feed, chemicals (materials), and bioenergy (biofuels, electricity and/or heat)) [9]. In contrast to a refinery, a biorefinery can supply multiple chemicals by breaking down the initial raw material (biomass) into several intermediates (carbohydrates, proteins, triglycerides), which can then be broken down into value-added products [11].

The acorn is an alkene that contains a single seed (rarely two) and is surrounded by a cup at its base. Large forest areas in Morocco are set aside for acorns, and acorn pericarp are still thrown as solid waste, despite the fact that they have an unusual composition that can be transformed into a good adsorbent. However, the adsorption process also poses another issue that must be handled from the perspective of the circular economy. The sludge has led to an accumulation less tolerant in the environment, so as a solution there is the recycling of the sludge.

For several years, the apparition of some concepts, such as sustainable development, industrial ecology and green chemistry, has been accompanied by the development of new generations of materials. Among these materials, composites are constantly developing into high-performance and less expensive products while meeting environmental constraints and regulatory requirements for recycling.

Cellulosic biomass granulates as a reinforcement in polymers bring the possibility to gain many applications of multidisciplinary interests. Polystyrene (PS), with an annual production of 3.12 million tons, ranks fifth among the different plastics [12] lead the attention of several researchers for years to the use of natural fillers from agricultural biomass (Bio-fillers) that offers an alternative to the replacement of conventional fillers such as synthetic fillers. PS has been reinforced with sisal fibers [13], with date palms [14] and until now the bio-composite PS has an important place in the research topics; the results of PS reinforced with banana fibers is a good example [15]. In continuation of these efforts, a new composite material of a PS matrix incorporated by particles of acorn pericarp sludge (AP) is proposed in the present work by in situ polymerization.

The objective of this research work is to explore the possibility of using Acorn Pericarp (AP) to remove MG from wastewater by studying adsorption parameters such as concentration, temperature and time, acorn pericarp mass, as well as pH to determine the adsorbent's performance and then recycling the sludge by incorporation into the Polystyrene (PS) matrix. The PS is one of the most common plastic materials thanks to its very interesting properties. In the context of a sustainable industry, PS/AP sludge composites were prepared by in situ polymerization, with a mass percentage of 10% by weight of the reinforcement particles. The effect of adding AP sludge as reinforcement material on the structural and morphological properties was also examined by FTIR analysis and SEM.

2. Materials and Methods

2.1. Chemicals

All chemicals were analytical grade and used directly without further purification. Malachite Green-phenyl-d5 oxalate salt ($C_{52}D_5H_{49}N_4O_{12}$, 99%), sodium hydroxide (NaOH,

99%), and hydrochloric acid (HCl, 99%) were purchased from Sigma-Aldrich (Saint-Quentin-Fallavier, France).

2.2. Preparation and Characterization of Adsorbent

The acorn samples were obtained in the holm oak forest of El-Hajeb, Morocco. The AP was washed, dried in an oven for 24 h at 110 °C, crushed, and sieved to get fine, homogenous samples (<65 µm). AP was characterized, prior to the removal of Malachite Green, using various techniques. Fourier-transform infrared (FTIR) spectra were collected from 4000 to 400 cm^{-1} with a spectrometer (Shimadzu, JASCO 4100, Japan). X-ray diffraction (XRD) patterns of the adsorbent were obtained using an X'PERT MPD-PRO wide-angle powder diffractometer equipped with a diffracted beam monochromator and a Ni-filtered CuKa source (λ = 1.5418 Å). The surface morphology of the sample was visualized by a scanning electron microscope (SEM, Topcon model EM200B) equipped with energy-dispersive X-ray (EDX) analysis.

2.3. Isotherm and Kinetic Studies

Malachite Green adsorption studies were carried out at temperatures ranging from 25 to 55 °C. They were made by swirling an MG solution (20 mL) at 400 rpm with an adsorbate concentration ranging from 10^{-5} M to 10^{-4} M and 0.1 g of AP. Under various experimental circumstances, the kinetics and adsorption isotherm of Malachite Green were measured. The MG concentrations were determined using a Shimadzu UV-1240 spectrophotometer and a calibration curve established at = 618 nm.

The kinetic and isothermal adsorption capacities of malachite green were determined using Equation (1). Adsorption kinetics and isotherm data were modeled using the models shown in Table 1.

$$Qe\left(\frac{mg}{g}\right) = \frac{C_0 - C_e}{m_{adsorbent}} * V_{solution} \quad (1)$$

where Q is the adsorption capacity (mg/g), C_0 is the initial concentration of the MG solution (mg/L), C_e is the equilibrium MG concentration (mg/L), the adsorbent is the AP mass (g), and V_{sol} is the volume of the Malachite Green solution (L), respectively.

Table 1. The equations of the adsorption kinetic and isothermal models.

Isotherm	Equation	Parameter
Freundlich	$q_e = K_F C_e^{1/n}$	$K_F, 1/n$
Langmuir	$q_e = \frac{q_{max} K_L C_e}{1+K_L C_e}$	q_{max}, K_L
Pseudo-first-order (PFO)	$q_t = q_e[1 - exp(-k_1 t)]$	q_e, k_1
Pseudo-second-order (PSO)	$q_t = \frac{k_2 q_e^2 t}{1+k_2 q_e t}$	q_e, k_2

2.4. Preparation of Polystyrene Composite

The polystyrene composites were synthesized by in situ polymerization of styrene in the presence of benzoyl peroxide and toluene and the AP sludge particles. First, the sludge was dried for 12 h at 105 °C in an oven, ground to particle size (<65 µm) and used as reinforcement with 10% by weight. The reaction mixture was heated to 80 °C and the temperature was maintained constant for 1 h. Then, the resin was allowed to cool to room temperature for 15 min, washed with ethanol, filtered and transferred to silicone molds [16].

3. Results and Discussions

3.1. Characterization of Adsorbent

The diffractograms of the AP before adsorption are shown in Figure 1A. Two slightly narrow peaks are detected at 2θ values around 16° and 22°. Due to the crystalline structure of the cellulose in the adsorbent, the large band at about 22° justifies some crystalline

phases of the substance. In effect, lignocellulosic materials have a structural deficiency which makes it possible to obtain single crystals called whiskers [2]. A FTIR spectrum illustrating the functional groups of the Acorn pericarp samples is shown in Figure 1 (B). We noticed that the AP samples have similar aromatic and aliphatic functional groups. These groups come from the three main components of the studied adsorbents, namely cellulose, hemicellulose, and lignin. In fact, these three components are mainly composed of olefins, esters, ketones, aromatic rings, and alcohols, with different oxygen-containing functional groups such as O-H (3400–3200 cm^{-1}), C=O (1765–1715 cm^{-1}), C-O-C (1270 cm^{-1}), and C-O-H (~1050 cm^{-1}); the band at 1640 cm^{-1} is characteristic of the elongation of the C=C bonds of aromatic compounds. The morphology and structure of the AP were discussed by using the SEM. We can observe from Figure 1C that AP has a characteristic of a material with an elongated appearance and a more intact and firm structure.

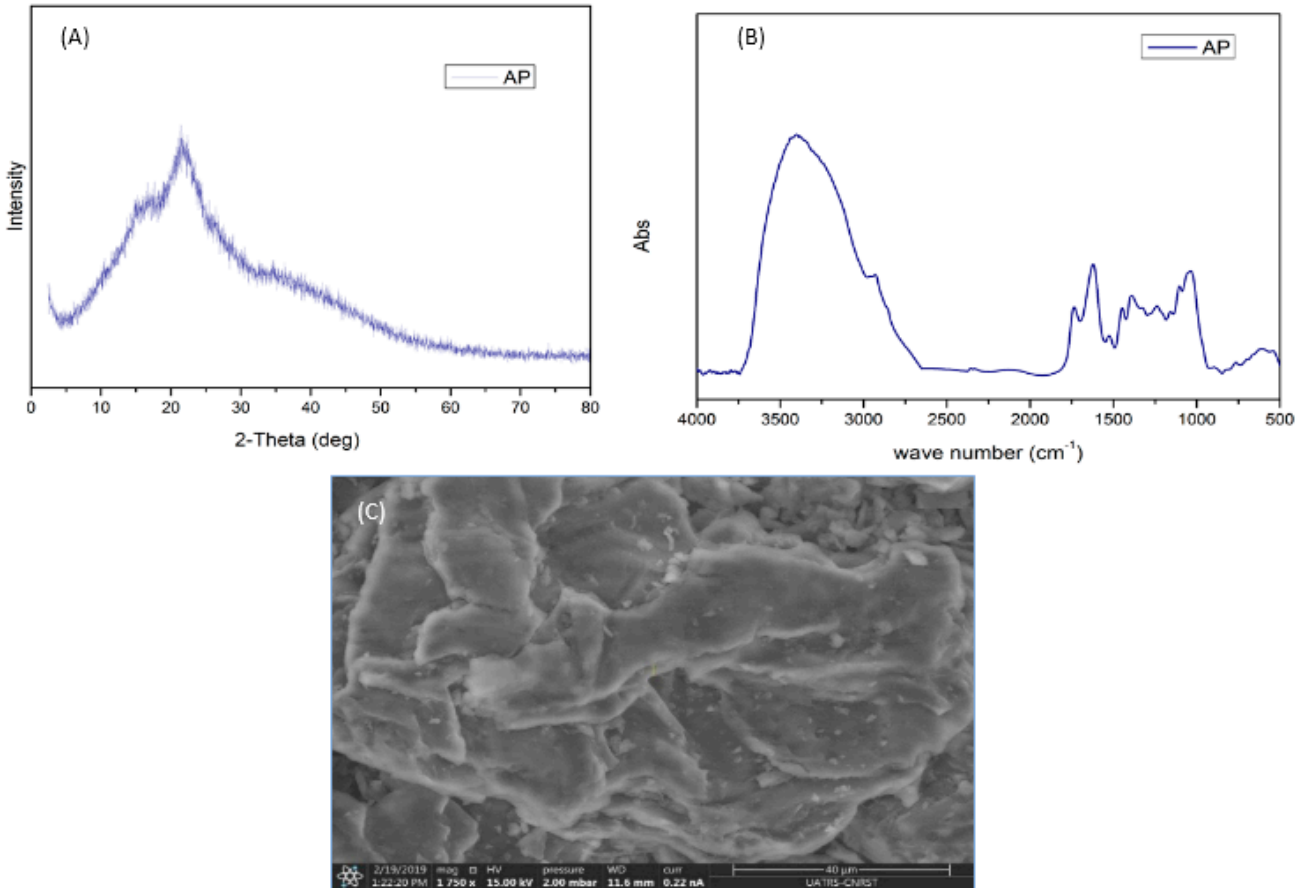


Figure 1. (**A**) X-ray diffraction patterns of AP; (**B**) FTIR spectrum of AP; (**C**) SEM image of AP.

3.2. Adsorption of Malachite Green: Influencing Factors

Figure 2 indicates the effect of adsorbent mass on the percentage removal of MG. It can be seen that the percentage removal of MG increases sharply and then reaches an almost constant value when the adsorbent dose increases from 0.04 to 0.14 g. This is because there are more binding sites of the adsorbent and a larger adsorption surface. When the dose was increased from 0.40 g to 1.4 g, no significant improvement in MG removal percentage was observed; therefore, the adsorbent dose of 0.1 g was identified as the preferred amount of adsorbent for further research [17,18].

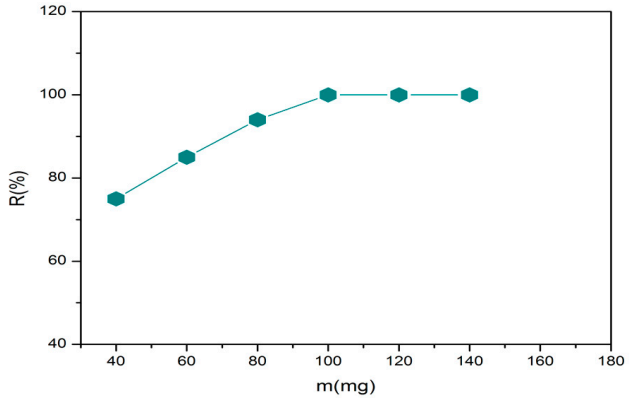


Figure 2. Effect of mass on the MG adsorption using AP from aqueous solution (Ci = 5 × 10^{-5} M, T = 303 K).

Malachite Green is a triphenylmethane dye whose molecular structure changes according to the pH value of the solution. Under acidic conditions, this dye contains cations and has excellent solubility in water. However, under basic conditions (pH = 11), changing the dye to a methanol base will result in a loss of color. Therefore, the study was conducted in the pH range of 2 to 10 with an initial concentration of 5 × 10^{-5} M. Figure 3 shows that the pH variations did not noticeably impact the overall removal efficiency of the dyes in aqueous media.

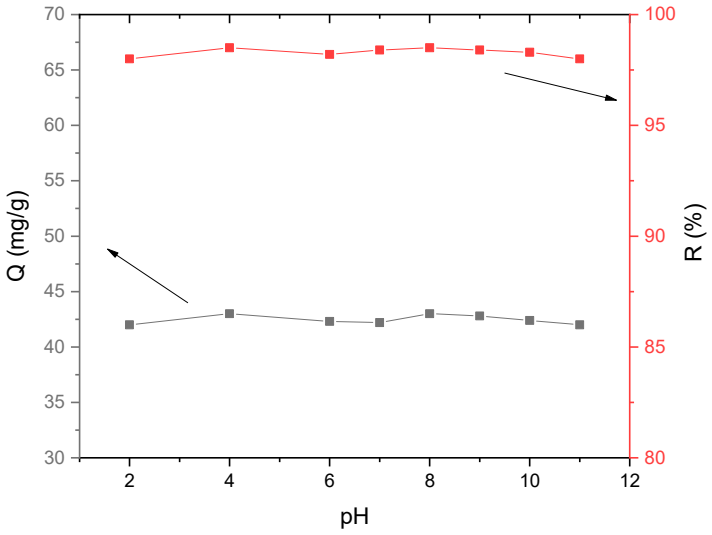


Figure 3. Effect of pH on the MG adsorption using AP from aqueous solution (m = 0.1 mg, Ci = 5 × 10^{-5} M, T = 303 K).

The efficiency of the removal of Malachite Green at different pH values is related to the dominant charge on the solid surface. The electrostatic mechanism is suggested to be the dominant adsorption mechanism under acidic and basic conditions, while chemical binding seems to have a limited contribution in the present case [19,20].

In summary, the AP samples showed an adsorption efficiency of almost 100% at all pH values (Figure 3) which gives a better chance of use in the field of industrial liquid waste treatment.

Figure 4 presents the influence of various temperatures on AP removal efficiency. Considering each temperature (25, 35, 45, and 55 °C), AP shows an excellent removal effect on MG dye. At all temperatures, the removal efficiency is between 90% and 98.44%, indicating that Acorn Pericarp is very stable and can retain its efficiency under a variety of challenging conditions. The increase in the amount of adsorption with temperature shows

that the processes are endothermic [21], an increase in temperature leads to an increase in the heat thus an increase in the space between the solid particles, all of which promote the adsorption of the Malachite Green molecule [22].

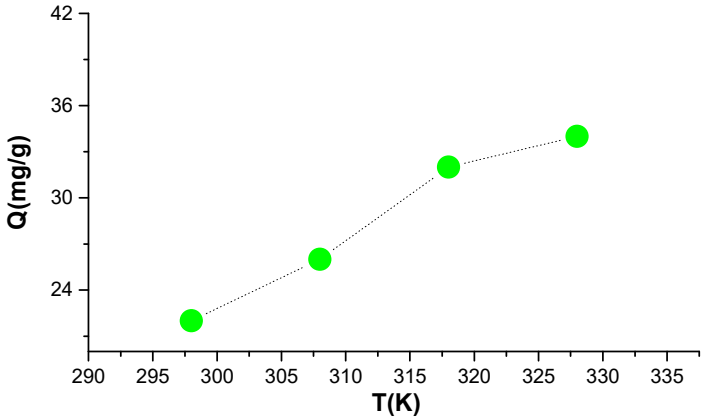


Figure 4. Impact of temperatures on the MG adsorption using AP.

Figure 5 shows the adsorption and removal of Malachite Green on AP between contact time and different MG dye concentrations. The results show that the best adsorption time for 10^{-5} M is 15 min, and the best adsorption time for 5×10^{-5} M is 40 min. As the contact time increases, the percentage removal decreases. Based on an adsorption time of 60 min, the percentage removal is greater than 99.4% at 10^{-5} M, 98.52% at 5×10^{-5} M, 94 at 10^{-4} M. For most initial dye concentrations, a consistent percentage removal is immediately achieved. Several investigators have explained similar patterns of dye concentration changes during biosorbent adsorption. The adsorption capacity of methylene blue by corn husks decreased as the concentration increased from 20 mg/L to 100 mg/L [23]. When the MG concentration was increased from 600 to 1500 mg/L, the % adsorption of acorn shells decreased from 76% to 67% [24].

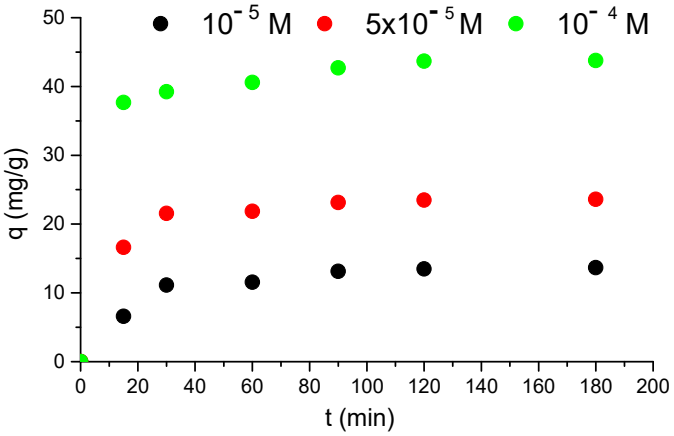


Figure 5. Impact of solution concentration on the MG adsorption using AP from aqueous solution.

3.3. Adsorption Kinetics and Isotherm Study

3.3.1. Adsorption Kinetics

The adsorption kinetics of MG by AP is studied using two models, namely the pseudo-first-order PFO and the pseudo-second-order PSO. A constant amount of AP (100 mg) was used to compare the adsorption kinetics at different MG concentrations (5×10^{-5} M) (Figure 6). Although the PSO model shows a good fit ($R^2 = 0.9853$), the PFO model ($R^2 = 0.9971$) better describes the adsorption kinetics at 10^{-5} M. At higher concentrations, the adsorption kinetics followed the PSO model (Table 2), indicating the

concentration-dependent adsorption of MG by AP, and surface adsorption is the rate-controlling step [25].

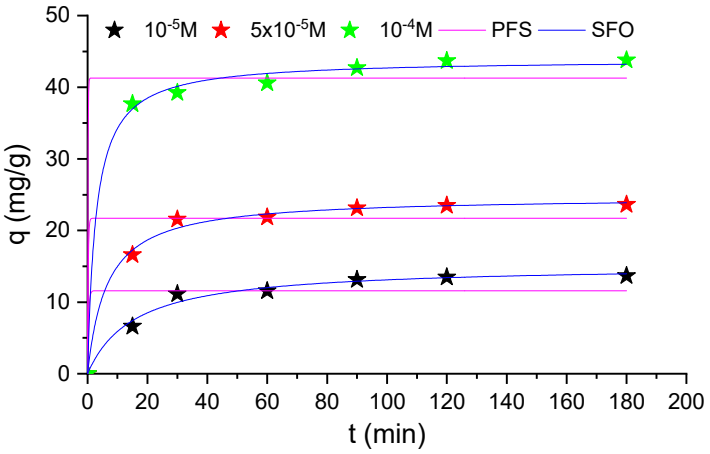


Figure 6. Adsorption kinetics of MG using AP from aqueous solution.

Table 2. Kinetic parameters for the MG adsorption on AP at different concentrations.

Ci (M)	Qe (exp)	Pseudo-First-Order (PFO)			Pseudo-Second-Order (PSO)		
		K_1	R^2	Qe	K_2	R^2	Qe
10^{-5}	12	3.09	0.71	11.795	0.004	0.99	15.16
5×10^{-5}	22	4.92	0.90	21.708	0.006	0.99	24.72
10^{-4}	42	8.48	0.97	41.28	0.008	0.99	43.89

3.3.2. Adsorption Isotherms

The equilibrium adsorption data of MG by AP was modeled by Freundlich and Langmuir isotherm models (Figure 7) (Table 3). Among the two isotherms tested, the adsorption of Malachite Green by AP was best described by the Langmuir isotherm (R^2 = 0.9889) indicating that MG is adsorbed on the homogeneous surface of AP as a monolayer [26,27]. It has been reported that most adsorption processes involving MG follow the Langmuir isotherm [28]. The present results are coherent with the findings of the kinetic studies. The value of the Langmuir constant (K_L) was observed to be 0.008 L/mg, which was comparable to reports in the literature [29].

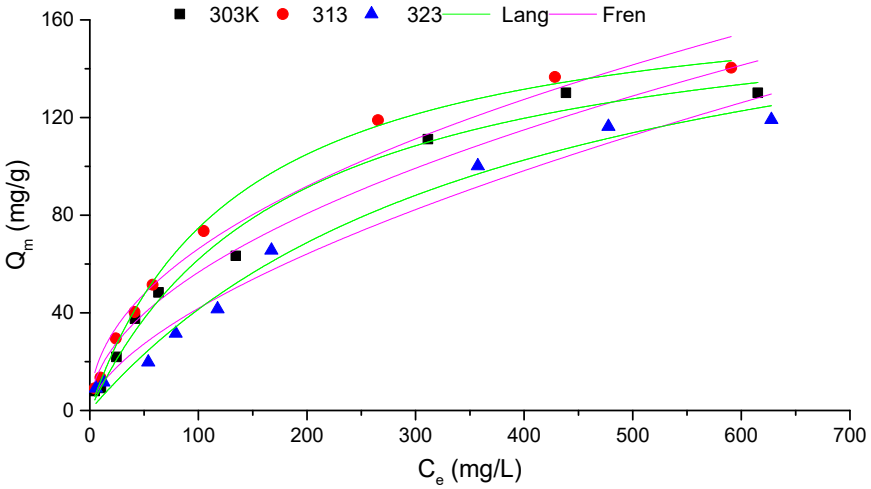


Figure 7. Adsorption isotherms of MG on AP from aqueous solution.

Table 3. Model parameters for the adsorption of MG on AP from aqueous solution.

Temperature (°C)	Modeled of Langmuir			Modeled of Frendlich		
	K_L	Qm	R^2	K_F	N	R^2
30	0.003	173	0.99	2.45	1.64	0.96
40	0.005	176	0.99	5.37	1.96	0.97
50	0.008	201	0.98	7.53	2.17	0.97

For the determination of thermodynamic parameters such as the variation of free energy (ΔG°), the variation of enthalpy (ΔH°) and the variation of entropy (ΔS°), The following equation was used. By plotting the Van't Hoff equation, ln (Ke) in terms of 1/T (Figure 8), the values of the preceding quantities are determined and are listed in Table 4.

$$Ln(K_e) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

The enthalpy variation, ΔH° achieved here is 122 kJ/mol (Table 4). The positive value of enthalpy variation confirms the endothermic nature of the adsorption process. The positive value of entropy, ΔS° corresponds to an increase in the degree of freedom of the adsorbed species. The positive value of ΔS° also signifies that some changes occur in the internal structure of palm oil fuel ash during the adsorption process. Similar types of observations have been reported by other researchers for the removal of lead and chromium from wastewater. The magnitude of the Gibbs free energy change, ΔG° obtained, is negative, suggesting that the adsorption is quick and spontaneous. The negative value of ΔG° confirms the feasibility of the adsorption process [30,31].

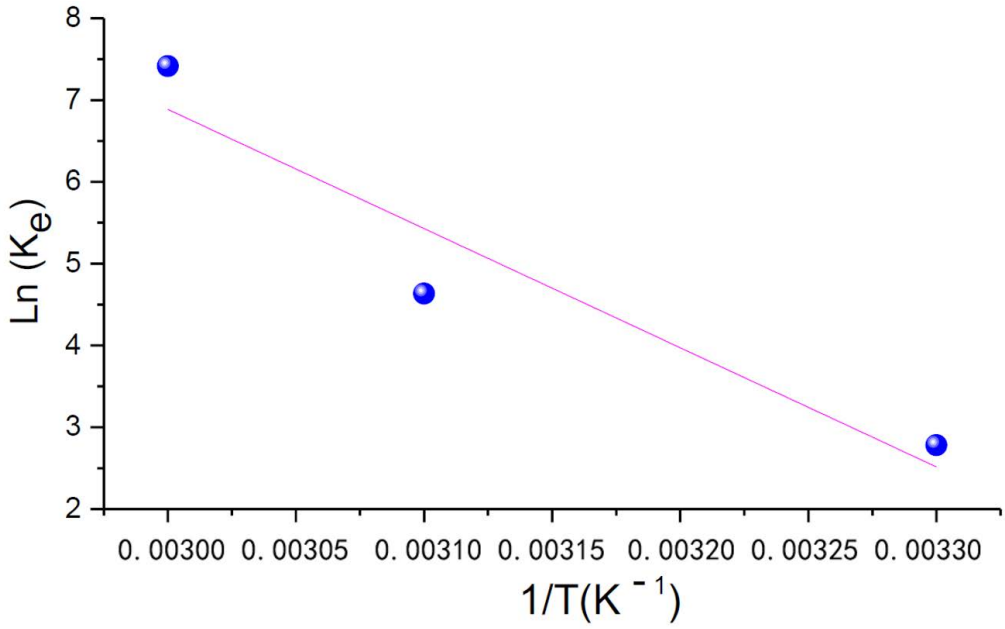


Figure 8. Van 't Hoff plot for the adsorption of MG from aqueous solution using AP.

Table 4. Thermodynamic parameters calculated for the MG adsorption from aqueous solution on AP.

T (°C)	ΔH° (kJ/mol)	ΔS° (J/Kmol)	ΔG° (kJ/mol)
30	121.085	415.5	−4.81
40			−8.966
50			−13.121

3.3.3. Mechanism of Adsorption

The adsorption of cationic dyes on the adsorbent's surface depends on several conditions and it is related to the chemical properties of both the adsorbent and adsorbate. Investigating the type of adsorption mechanism is crucial for the further development of adsorbents with outstanding characteristics. The MG is a cationic dye because its chemical properties are greatly influenced by experimental conditions such as pH. On the other hand, the PA has several functional groups in its composition, which would act as active adsorption sites when interacting with cationic dyes. Therefore, it is very suitable for application in dye removal as shown and confirmed in the present work. The adsorption of MG on the surface of the PA can be performed following these steps [32,33]:

- Diffusion of the dye from the bulk solution to the boundary layer.
- Through the boundary layer, dye molecules can be diffused into the surface of the adsorbent.

The adsorption of the MG is most probably dominated by electrostatic attraction. The PA composition, such as cellulose, would easily get negatively charged in contact with an aqueous solution, leading to increasing contact and attraction with the MG molecule. Other interactions, such as hydrogen bonds, are possible between the adsorbent's functional groups and the dye's molecule. In addition, the potential diffusion of dye molecules into the inner pores of the adsorbent is also highly probable.

It has been shown from experimental studies that the adsorption of MG is a spontaneous process, and it is thermodynamically favorable at all tested temperatures. Therefore, AP can be used as an effective and inexpensive adsorbent for the removal of Malachite Green in industrial processes [34].

3.3.4. Comparison of Other Studies

The adsorption process can be influenced by experimental conditions; thus, the comparison of the adsorption capacity of the same adsorbate or adsorbent is a very challenging task. Adsorbent's chemical characteristics are very different and influenced by the experimental conditions and the interacting molecule. Bearing this in mind, it would be interesting to get some insights into the difference between different adsorbent materials in removing a specific dye. It would open ways for further exploration and improvement in the case of high adsorption capacity and vice versa. In the case of MG, it can be seen from Table 5 that among several low-cost adsorbent materials, AP shows outstanding adsorption characteristics, which is demonstrated by its high adsorption capacity compared to other low-cost adsorbents. Therefore, the adsorbent material investigated in the present study can be an excellent choice for further exploration and development. In particular, the simple and inexpensive preparation of AP would favor its application to obtain an effective adsorption process for MG removal.

Table 5. Adsorption capacity of MG using different adsorbents reported in literature.

Adsorbent	Qm (mg/g)	Isotherm Model	Reference
Ntural red clay	84	Langumir	[35]
Activated sludge	250	Freundlich	[36]
Rambutan peel-based activated carbon	388	Langmuir	[37]
Neem sawdust	4.3	Langmuir	[38]
Activated carbon derived from Borassus aethiopum flower biomass	20.46	Langmuir	[39]
Bio-polymer	0.4768	Langmuir	[40]
Acorn pericarp	200	Langmuir	

3.4. Preparation of Polystyrene/AP Sludge Composites

The incineration of sludge can be accompanied by energy recovery in the form of heat; other alternatives are storage or burial. Waste is increasingly taxed and their incineration sometimes poses environmental problems (toxic emissions, etc.) that are costly or dangerous. Therefore, the reuse of sludge leads us to develop bio-composites, by incorporating biomass polluting and without market value (the AP sludge) in polystyrene to reduce their harmful environmental impact by reducing the accumulation of waste. A 10% by weight of AP has been used for the synthesis of polystyrene/AP sludge (Figure 9) using in situ polymerization of styrene with benzoyl peroxide and toluene. The mixture is subjected to heating under 80 °C for 1 h, then allowed to cool for 10 min at ambient temperature. The obtained material is rinsed with ethanol and filtered before being transferred into silicone molds [16]. In this way polystyrene is reinforced by cellulosic biomass colored by MG, eliminating the MG in the wastewater and then incorporating the particles as reinforcement for the polystyrene matrix and minimizing the petroleum carbon percentage.



Figure 9. Polystyrene/AP Sludge composites.

3.4.1. Morphological Analysis of Composite

SEM-EDS was used to examine the morphological and qualitative elemental information of polystyrene composites (Figure 10), the polystyrene has a compact and smooth morphology [16]. After the insertion of AP sludge, we observed noticeable changes in the morphology, from a compact polystyrene to a material which adopts a laminate morphology, for the qualitative elemental information, we observe the nitrogen of MG in AP sludge.

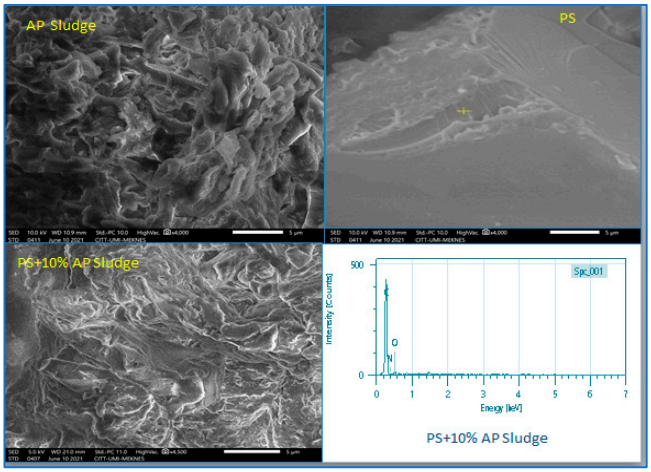


Figure 10. SEM-EDS of AP sludge, PS, and of PS/10%wt AP sludge.

3.4.2. Analyses Structural of Polystyrene Composite

The diffractograms of PS, Acorn pericarp, and PS reinforced by the Acorn pericarp sludge are presented in Figure 11a. A broad halo XRD diffraction pattern is shown in the

range of 7–30° for PS. The peaks located at 15° and 21° are associated with (2 0 0) and (1 1 0) crystallographic planes of cellulose [41]. In comparison with reinforced PS, we can see a very clear transition of curves including the peaks at 16° and 7° to the highest angles, namely to the right angles of the AC sludge (21° et 10°). The structural properties are also changed after the incorporation of AC sludge, which can be confirmed by the decrease in intensity. This indicates that cellulose is well incorporated into the PS.

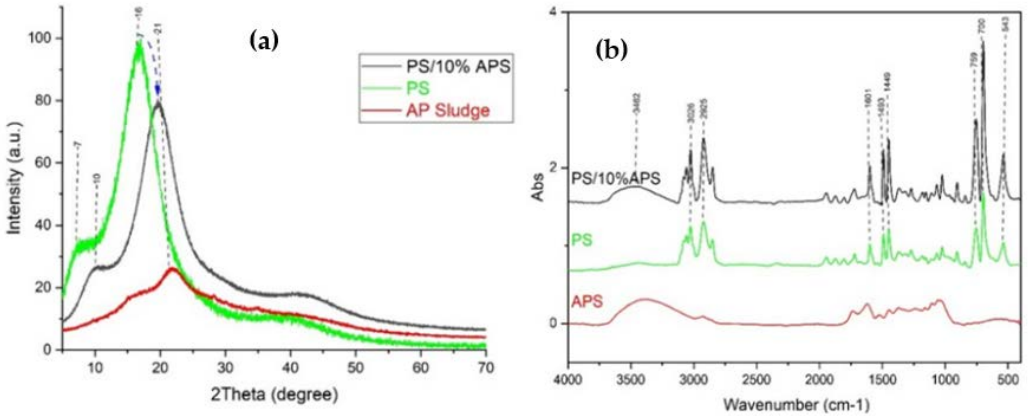


Figure 11. (**a**) X-ray of PS, AP sludge, and PS/AP sludge, (**b**) FTIR spectra of PS AP; sludge, and PS/AP sludge.

Figure 11b shows the FTIR spectra of PS, Acorn pericarp sludge (APS), and PS reinforced with Acorn pericarp sludge PS/10%wt APS. The medium bands about 1400 cm^{-1} are attributed to the C-C-H and C-H and C-C of the ring. The peaks at about 759–543 cm^{-1} are purely attributed to the ring [42]. We can note the intensification of all peaks for AP sludge, also we can see the appearance of the band about 3500 cm^{-1} attributed to the stretching vibration of hydroxyl Groupement (OH) of cellulose of AP.

4. Conclusions

This research work showed that Acorn Pericarp, as an available and economical material, can be effectively used to remove the malachite green. In addition, the AP sludge was converted into reinforcements of polystyrene in order to improve the performance of the composites and specially to reduce the risk of sludge accumulation into the environment. Acorn Pericarp showed excellent removal efficiency at all pH values, as well as the adsorbent dose of 0.1 g was chosen as the optimal adsorbent mass. The removal efficiency at all temperatures is $\geq$98.44%, which means that AP is very stable and can maintain its efficiency under various robust conditions. The adsorption kinetics of MG by AP is studied by two models, namely PFO and PSO. Although the PSO model showed a good fit (R^2 = 0.9853), the PFO model (R^2 = 0.9971) describes better the adsorption kinetics at 10^{-5} M. The equilibrium adsorption data of MG by AP were modeled by Freundlich and Langmuir isotherms. The adsorption of Malachite Green by the Acorn pericarp was best described by Langmuir isotherm (R^2 = 0.9889), indicating that MG is adsorbed on the homogeneous surface of the Acorn pericarp as a monolayer. It can be concluded that AP is a better alternative for the removal of MG dye from the aqueous solution. The polystyrene/AP sludge composite showed good matrix/reinforcement interactions. The present work would open interesting options for the valorization and recycling of local waste materials towards the implementation of a sustainable economic cycle on the local level.

Author Contributions: Conceptualization, methodology, resources, supervision, validation, writing—review and editing, H.L., M.J. and F.B.; formal analysis, data curation, writing—original draft preparation, M.J. and Y.D.; investigation, writing—review and editing, A.K., I.L., A.A. and C.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Some or all data, models, or code that support the findings of this study are available from the corresponding author upon reasonable request (List items).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Dhami, D.; Homagai, P.L. Adsorptive Removal of Malachite Green Dye from Aqueous Solution Using Chemically Modified Charred and Xanthated Wheat Bran. *J. Nepal Chem. Soc.* **2020**, *41*, 103–109. [CrossRef]
2. Loulidi, I.; Boukhlifi, F.; Ouchabi, M.; Amar, A.; Jabri, M.; Kali, A.; Chraibi, S.; Hadey, C.; Aziz, F. Adsorption of Crystal Violand onto an Agricultural Waste Residue: Kinetics, Isotherm, Thermodynamics, and Mechanism of Adsorption. *Sci. World J.* **2020**, *2020*, 5873521. [CrossRef] [PubMed]
3. Kundu, A.; Mondal, A. Kinetics, isotherm, and thermodynamic studies of methylene blue selective adsorption and photocatalysis of malachite green from aqueous solution using layered Na-intercalated Cu-doped Titania. *Appl. Clay Sci.* **2019**, *183*, 105323. [CrossRef]
4. Guo, F.; Jiang, X.; Li, X.; Jia, X.; Liang, S.; Qian, L. Synthesis of MgO/Fe_3O_4 nanoparticles embedded activated carbon from biomass for high-efficient adsorption of malachite green. *Mater. Chem. Phys.* **2020**, *240*, 122240. [CrossRef]
5. Mkrtchyan, E.; Burakov, A.; Burakova, I. The Adsorption of Malachite Green on Graphene Nanocomposites: A Study on Kinetics under Dynamic Conditions. *Mater. Today: Proc.* **2019**, *11*, 404–409. [CrossRef]
6. Dehbi, A.; Dehmani, Y.; Omari, H.; Lammini, A.; Elazhari, K.; Abouarnadasse, S.; Abdallaoui, A. Comparative study of malachite green and phenol adsorption on synthetic hematite iron oxide nanoparticles (α-Fe_2O_3). *Surf. Interfaces* **2020**, *21*, 100637. [CrossRef]
7. Iwaszczuk, N.; Szyba, M.; Iwaszczuk, A.; Yakubiv, V. Production of agricultural biogas from waste—An element of socially responsible actions in the food sector. *Acta Innov.* **2019**, *33*, 52–62. [CrossRef]
8. Rodríguez, H. Ionic liquids in the pretreatment of lignocellulosic biomass. *Acta Innov.* **2021**, *38*, 23–36. [CrossRef]
9. Gschwend, F.J.V.; Hennequin, L.M.; Brandt-Talbot, A.; Bedoya-Lora, F.E.; Kelsall, G.H.; Polizzi, K.; Fennell, P.S.; Hallett, J.P. Towards an environmentally and economically sustainable biorefinery: Heavy metal contaminated waste wood as a low-cost feedstock in a low-cost ionic liquid process. *Green Chem.* **2020**, *22*, 5032–5041. [CrossRef]
10. Usmani, Z.; Sharma, M.; Gupta, P.; Karpichev, Y.; Gathergood, N.; Bhat, R.; Gupta, V.K. Ionic liquid based pretreatment of lignocellulosic biomass for enhanced bioconversion. *Bioresour. Technol.* **2020**, *304*, 123003. [CrossRef]
11. Lopes, T.F.; Łukasik, R.M. Economic, social and environmental impacts attained by the use of the effluents generated within a small-scale biorefinery concept. *Acta Innov.* **2020**, *36*, 57–63. [CrossRef]
12. Plastics-the-facts-2021.pdf. Consulté le: 17 janvier 2023. [En ligne]. Available online: https://dein-kunststoff.de/wp-content/uploads/2022/08/Plastics-the-facts-2021.pdf (accessed on 6 October 2022).
13. Nair, K.C.M.; Diwan, S.M.; Thomas, S. Tensile Properties of Short Sisal Fiber Reinforced Polystyrene Composites. *J. Appl. Polym. Sci.* **1996**, *60*, 1483–1497. [CrossRef]
14. Masri, T.; Ounis, H.; Sedira, L.; Kaci, A.; Benchabane, A. Characterization of new composite material based on date palm leaflets and expanded polystyrene wastes. *Constr. Build. Mater.* **2018**, *164*, 410–418. [CrossRef]
15. Adeniyi, A.G.; Adeoye, A.S.; Ighalo, J.O.; Onifade, D.V. FEA of effective elastic properties of banana fiber-reinforced polystyrene composite. *Mech. Adv. Mater. Struct.* **2021**, *28*, 1869–1877. [CrossRef]
16. Jabri, M.; Oulidi, O.; Loulidi, I.; Amar, A.; Kali, A.; Boukhlifi, F. Acorn Waste Valorization as Reinforcement in Polystyrene Composite: A Comparative Study. In *Artificial Intelligence of Things for Smart Green Energy Management*; El Himer, S., Ouaissa, M., Emhemed, A.A.A., Ouaissa, M., Boulouard, Z., Eds.; Springer International Publishing: Cham, Switzerland, 2022; pp. 213–224. [CrossRef]
17. Hijab, M.; Parthasarathy, P.; Mackey, H.R.; Al-Ansari, T.; McKay, G. Minimizing adsorbent requirements using multi-stage batch adsorption for malachite green removal using microwave date-stone activated carbons. *Chem. Eng. Process.-Process Intensif.* **2021**, *167*, 108318. [CrossRef]
18. Fan, X.; Deng, L.; Li, K.; Lu, H.; Wang, R.; Li, W. Adsorption of malachite green in aqueous solution using sugarcane bagasse-barium carbonate composite. *Colloid Interface Sci. Commun.* **2021**, *44*, 100485. [CrossRef]
19. Giri, B.S.; Sonwani, R.K.; Varjani, S.; Chaurasia, D.; Varadavenkatesan, T.; Chaturvedi, P.; Yadav, S.; Katiyar, V.; Singh, R.S.; Pandey, A. Highly efficient bio-adsorption of Malachite green using Chinese Fan-Palm Biochar (*Livistona chinensis*). *Chemosphere* **2022**, *287*, 132282. [CrossRef]
20. Ruihao, T.; Wei, H.; Srinivasakannan, C.; Xuelin, L.; Xin, W.; Xinhui, D. A novel mesoporous Fe-silica aerogel composite with phenomenal adsorption capacity for malachite green. *Sep. Purif. Technol.* **2021**, *281*, 119950. [CrossRef]
21. Asnaoui, H.; Dehmani, Y.; Khalis, M.; Hachem, E.-K. Adsorption of phenol from aqueous solutions by Na–bentonite: Kinetic, equilibrium and thermodynamic studies. *Int. J. Environ. Anal. Chem.* **2022**, *102*, 3043–3057. [CrossRef]

22. Thiruchelvi, R.; Venkataraghavan, R.; Sharmila, D. Optimization of environmental parameters by Plackett-Burman design and response surface methodology for the adsorption of Malachite green onto Gracilaria edulis. *Mater. Today Proc.* **2021**, *37*, 1859–1864. [CrossRef]
23. Kim, M.; Sharma, N.; Chung, J.; Yun, K. Activated graphene with fractal structure for the adsorption of malachite green with high removal rate. *Microporous Mesoporous Mater.* **2021**, *322*, 111166. [CrossRef]
24. Ojediran, J.O.; Dada, A.O.; Aniyi, S.O.; David, R.O. Functionalized Zea Mays Cob (FZMC) as low-cost agrowaste for effective adsorption of malachite green dyes data set. *Chem. Data Collect.* **2020**, *30*, 100563. [CrossRef]
25. Baskaran, P.K.; Venkatraman, B.R.; Arivoli, S. Adsorption of Malachite Green Dye by Acid Activated Carbon—Kinetic, Thermodynamic and Equilibrium Studies. *J. Chem.* **2011**, *8*, 9–18. [CrossRef]
26. Sundararaman, T.R.; Saravanan, A.; Kumar, P.S.; Mabel, M.M.; Hemavathy, R.V.; Karishma, S.; Jeevanantham, S.; Hemavathi, R.; Ishwariya, A.; Kowsalya, S. Adsorptive Removal of Malachite Green Dye onto Coal-Associated Soil and Conditions Optimization. *Adsorpt. Sci. Technol.* **2021**, *2021*, 1–11. [CrossRef]
27. Gebreslassie, Y.T. Equilibrium, Kinetics, and Thermodynamic Studies of Malachite Green Adsorption onto Fig (*Ficus cartia*) Leaves. *J. Anal. Methods Chem.* **2020**, *2020*, 1–11. [CrossRef]
28. Miyar, H.K.; Pai, A.; Goveas, L.C. Adsorption of Malachite Green by extracellular polymeric substance of Lysinibacillus sSS1: Kinetics and isotherms. *Heliyon* **2021**, *7*, e07169. [CrossRef]
29. Li, W.; Xie, Z.; Xue, S.; Ye, H.; Liu, M.; Shi, W.; Liu, Y. Studies on the adsorption of dyes, Methylene blue, Safranin T, and Malachite green onto Polystyrene foam. *Sep. Purif. Technol.* **2021**, *276*, 119435. [CrossRef]
30. Rubio-Clemente, A.; Gutiérrez, J.; Henao, H.; Melo, A.M.; Pérez, J.F.; Chica, E. Adsorption capacity of the biochar obtained from Pinus patula wood micro-gasification for the treatment of polluted water containing malachite green dye. *J. King Saud Univ.-Eng. Sci.* **2021**, S1018363921000982. [CrossRef]
31. Bathla, A.; Singla, D.; Pal, B. Highly efficient CaCO3-CaO extracted from tap water distillation for effective adsorption and photocatalytic degradation of malachite green dye. *Mater. Res. Bull.* **2019**, *116*, 1–7. [CrossRef]
32. Ahmad, A.A.; Ahmad, M.A.; Yahaya, N.K.E.M.; Karim, J. Adsorption of malachite green by activated carbon derived from gasified Hevea brasiliensis root. *Arab. J. Chem.* **2021**, *14*, 103104. [CrossRef]
33. Lin, L.; Tang, S.; Wang, X.; Sun, X.; Yu, A. Adsorption of malachite green from aqueous solution by nylon microplastics: Reaction mechanism and the optimum conditions by response surface methodology. *Process Saf. Environ. Prot.* **2020**, *140*, 339–347. [CrossRef]
34. Alorabi, A.Q. Effective Removal of Malachite Green from Aqueous Solutions Using Magnetic Nanocomposite: Synthesis, Characterization, and Equilibrium Study. *Adsorpt. Sci. Technol.* **2021**, *2021*, 1–15. [CrossRef]
35. Sevim, F.; Lacin, O.; Ediz, E.F.; Demir, F. Adsorption capacity, isotherm, kinetic, and thermodynamic studies on adsorption behavior of malachite green onto natural red clay. *Environ. Prog. Sustain. Energy* **2021**, *40*, e13471. [CrossRef]
36. Aksu, Z. Biosorption of reactive dyes by dried activated sludge: Equilibrium and kinetic modelling. *Biochem. Eng. J.* **2001**, *7*, 79–84. [CrossRef]
37. Ahmad, M.A.; Alrozi, R. 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. [CrossRef]
38. Khattri, S.D.; Singh, M.K. Removal of malachite green from dye wastewater using neem sawdust by adsorption. *J. Hazard. Mater.* **2009**, *167*, 1089–1094. [CrossRef]
39. Nethaji, S.; Sivasamy, A.; Thennarasu, G.; Saravanan, S. Adsorption of Malachite Green dye onto activated carbon derived from Borassus aethiopum flower biomass. *J. Hazard. Mater.* **2010**, *181*, 271–280. [CrossRef]
40. Sekhar, C.P.; Kalidhasan, S.; Rajesh, V.; Rajesh, N. Bio-polymer adsorbent for the removal of malachite green from aqueous solution. *Chemosphere* **2009**, *77*, 842–847. [CrossRef]
41. Mulinari, D.R.; Baptista, C.A.R.P.; Souza, J.V.C.; Voorwald, H.J.C. Mechanical properties of coconut fibers reinforced polyester composites. *Procedia Eng.* **2011**, *10*, 2074–2079. [CrossRef]
42. Albunia, A.R.; Musto, P.; Guerra, G. FTIR spectra of pure helical crystalline phases of syndiotactic polystyrene. *Polymer* **2006**, *47*, 234–242. [CrossRef]

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