

Article

Removal of Dye (Methylene Blue) from Wastewater Using Bio-Char Derived from Agricultural Residues in Palestine: Performance and Isotherm Analysis

Hassan Sawalha ^{1,*}, Aseel Bader ¹, Jinan Sarsour ¹, Maher Al-Jabari ¹  and Eldon R. Rene ²

¹ Center of Excellence in Water, Energy and Environment Research and Services, Mechanical Engineering Department, Palestine Polytechnic University, Wadi Al-Haria, Hebron P.O. Box 198, Palestine

² Department of Water Supply, Sanitation and Environmental Engineering, IHE Delft Institute for Water Education, P.O. Box 3015, 2601 DA Delft, The Netherlands

* Correspondence: hsawalha@ppu.edu; Tel.: +972-569-1818-61

Abstract: The main aim of this study was to perform a parametric study for treating a model dye containing wastewater (i.e., methylene blue, MB) using locally available biomass wastes in Palestine as the adsorbent. Eight different types of biomasses were investigated in batch adsorption tests, including coffee grains, almond shells, pistachio shells, date pits, jute sticks, sunflower shells, peanut shells, and grapevine sticks. The experiments were conducted on three different phases of processing for these materials: as natural adsorbents, biochar, and activated carbon. The biochar was prepared by pyrolysis, while ZnCl₂ was used to chemically activate the materials for obtaining activated carbon. The influences of pH, initial MB concentration, and adsorbent dosage on the adsorption capacity and kinetics were investigated for activated carbon obtained from sunflower shells. The results indicate that the adsorption efficiency of natural adsorbents and biochar is highly dependent on the biomass type. As a natural adsorbent, peanut hulls demonstrated the maximum efficiency (>95%) for removing MB, whereas date pits showed the lowest efficiency (20%). In terms of biochar, jute sticks provide the highest removal efficiency. After activation with ZnCl₂, a considerable increase in their adsorption efficiency (>95%) was obtained for most of the adsorbents, with sunflower shells being the most efficient adsorbent. The results confirm the technical feasibility of the adsorption technology to treat dye containing wastewater using locally available biomass wastes.

Keywords: pyrolysis; lignocellulosic biomass; biochar; activated carbon; adsorption; equilibrium; kinetics; methylene blue



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1. Introduction

Within the last decade, the treatment of wastewater using resilient ecotechnologies has been proven to be effective in several developing countries [1]. Plant-based biomass wastes form a major component of municipal solid wastes and the municipalities have been striving to reduce and manage solid waste more efficiently, economically, and safely, by considering the prevailing conditions. The abundance of organic waste and biomass has prompted scientists to develop innovative methods that enable useful re-use wastes derived from biomass rather than direct disposal. This manifests itself in the conversion of waste to various forms such as gas, liquid, heat, and energy, as well as other possibilities such as biochar (which is rich in carbon) that can be utilized as an adsorbent in (waste) remediation procedures [2]. The term “biomass,” which is the subject of this study, refers to plant-derived materials or animal manures; it also refers to by-products of agricultural activities, food waste, and the wood processing business, among others. It generates no greenhouse emissions during the conversion process, as the CO₂ emitted is equivalent to the CO₂ produced by photosynthesis in the lifetime of plants [3]. Conventionally, thermal, physical, or biological methods are used to convert the biomass to useful products.

Choosing one of these technologies is dependent on the process's or application's desired outcomes. Thermal processing methods include combustion, gasification, liquefaction [4]. The primary focus of this study is using pyrolysis to obtain biochar from biomass wastes for wastewater treatment applications.

Pyrolysis is a type of thermal degradation that occurs when a biomass is heated in the absence of oxygen [5]. It operates in three modes according to the applied temperature and the period of the residence time. Each operation mode generates solid, liquid, or gaseous products in response to specific process conditions in the pyrolysis unit. To obtain the desired amount of a product, for example, a high percentage of liquid product such as bio-oil and a low percentage of chars and gas, a fast pyrolysis at a moderate temperature and a short residence time is used, whereas carbonization at a low temperature and a very long residence time is used to produce a char coal. Furthermore, a gas is produced through the process of gasification at elevated temperatures and lengthy residence times [3]. Pyrolysis of waste or biomass residues to activated carbon (AC) is carried out in two main steps. The first step involves carbonization of the solid materials in an inert atmosphere to produce biochar (slow pyrolysis). In the second step, the biochar is activated using appropriate oxidizing chemicals to produce AC with different surface characteristics and functional groups [6]. The AC is a carbon rich material that has micro- and mesoporous structure and it offers high internal surface area and porosity; it is employed as an adsorbent to treat pollutants in both the gaseous and liquid phases [6]. For instance, AC has been used in wastewater treatment to remove some heavy metals, dyes, and phenol [5,7]. Although char has a high capacity for adsorption, the relevance of activation to produce AC is in expanding the micro-porous structure of the existing char and removing undesired components to yield the best adsorbent material with the desired functional groups. Biochar adsorbents obtained from other biomass materials such as lychee seed, reed, municipal sewage sludge, tea waste, palm bark, eucalyptus, rice husk and cow dung have been applied for wastewater treatment [7–11]. In a previous work [12], AC was produced from the pyrolysis of teak sawdust under two different conditions: vacuum and ambient. The teak sawdust was chosen due to its high carbon and low ash content, which are desirable characteristics for producing activated carbon. The results from that study indicated that AC obtained from vacuum pyrolysis char has a greater surface area and pore volume than char prepared via atmospheric pyrolysis [12]. Coffee residues bound to clay were examined for their efficiency for using as adsorbents (CC-adsorbents) for solutions containing a high concentration of heavy metal ions [13], the investigated parameters included pyrolysis temperature, particle size diameter, adsorbent dose, etc. Previous research has also established the technological feasibility of lignocellulosic biomass as a source of carbonaceous adsorbents for the removal of organic and inorganic pollutants in wastewater, including some pharmaceutical chemicals [14].

This study aims at determining the technological viability of utilizing diverse biomass wastes, abundant in Palestine, as natural adsorbents for wastewater treatment, specifically the removal of methylene blue (MB). The study responds to the environmental concern that the concentration of colored compounds (e.g., dye molecules) in the effluent poses a major challenge in Palestine as it causes groundwater and surface-water pollution.

Utilizing abundant adsorbents offer a number of benefits, including high adsorption capacity for the pollutants, low regeneration costs, long-term and stable operation in batch and continuous reactors, and it does not involve hazardous issues while handling. In this experimental work, eight types of biomass-based adsorbents were investigated in this study. These included coffee grains, almond shells, pistachio shells, date pits, jute sticks, sunflower shells, peanut shells, and grape vine sticks. Batch adsorption tests were performed to determine the adsorption efficiency and kinetics under the influence of different process parameters.

2. Materials and Methods

2.1. Sampling Plant-Based Waste Biomass and Chemicals Used

Jute leaf sticks were provided by a local grocery store in Hebron (Palestine), whereas grapevine wood sticks were randomly sampled from a nearby planted area. Additionally, pistachio, date, almond, peanut, sunflower, and coffee grains were brought from a Hebron-based roasting factory. The model dye, methylene blue (MB) was purchased from LabChem, Inc. (Catalog number LC 16970; Pittsburgh, Zelienople, PA, USA). The activating reagents, $ZnCl_2$ (Product Number: 208086) was purchased from Sigma-Aldrich, Saint Louis, MO, USA. Lab grade HCl and NaOH were used for controlling the initial pH of the MB adsorption experiments at the required value.

2.2. Preparation of the Natural Adsorbents

Eight samples were generated from various types of waste biomass for direct testing as natural adsorbents. The samples were washed with distilled water in order to eliminate any residues or pollutants. Following that, samples were dried for 24 h at 104 °C in an oven (Daihan Labtech Co., Ltd., Gyeonggi-do, Korea). Following drying, materials were ground in a stainless-steel mill and then agitated for 15 min in an auto sieve shaker (MATEST, Treviolo (BG), Italy) and sieved to achieve a homogeneous particle size for the testing.

2.3. Production of Activated Carbon

Chemical activation was achieved by impregnating the raw materials with activating chemicals. A known quantity of each ground sample was mixed with a known quantity of an activation agent, $ZnCl_2$, in a glass beaker. The mixing ratio was 0.25 (weight of activating agent to the weight of the sample). The resultant mixture was diluted with distilled water to a concentration equivalent to ten times the weight of the sample and activating agent mixture [15]. The mixture was then agitated and heated to ~380 °C for 2 h, at an agitation speed of 90 rpm using a hotplate stirrer (LabTech International Ltd., East Sussex, UK) to become homogenized and heavily impregnated, until a thick, homogenous paste of the mixture was achieved. Finally, the mixture was dried for 30 h at 104 °C in an oven (Daihan Labtech Co., Ltd., Gyeonggi-do, Korea) until it was totally dry and ready to be pyrolyzed. To perform pyrolysis, porcelain crucibles with a volume of 40 mL were entirely filled with each type of impregnated raw materials; samples were slightly pressed to ensure the lowest possible oxygen levels with the voids. The weight of each substance prior and after pyrolysis were measured in order to determine the carbon and organic content of each sample. The crucibles were then completely wrapped in tinfoil and fitted with a lid. The crucibles were then placed in a muffle furnace (LabTech International Ltd., East Sussex, UK) for 1 h at a temperature of 700 °C. Then, the crucibles were allowed to cool. The weight of the crucibles after pyrolysis was measured in order to estimate its carbon (C) materials content [15]. The C content is usually obtained by elemental analysis. In the absence of oxygen, the residual solids in the materials, referred to as activated carbon, was also measured. The yield of activated carbon was determined using Equation (1):

$$\text{Yield, \%} = \frac{W_{AC}}{W_0} \times 100 \quad (1)$$

where, W_{AC} is the dry weight of final activated carbon (g), W_0 is the initial weight of the biomass samples (g).

The same procedure was followed to produce biochar from non-activated (impregnated) samples (i.e., without the addition of an activation agent). The morphologies of the natural and activated carbon of selected samples were visualized using a Quanta FEG Scanning Electron Microscope (SEM), FEI Company, Hillsboro, Oregon, USA. All used adsorbents: natural biomass, biochar and AC were washed with distilled water to remove any color residues before being used in the adsorption experiments.

2.4. Batch Adsorption Experiments

At ambient room temperature, a specified amount of each of the produced materials (5% weight/volume, w/v) was added to a specified volume of MB solution, (i.e., 5 g solid adsorbent/100 mL of MB solution containing 50 mg/L). Kinetic adsorption experiments were performed for each of the natural adsorbents. The mixture was agitated for 5 min using a magnetic stirrer, and thereafter allowed to settle for 10 min before being tested using a UV-vis Spectrophotometer to determine the absorbance of MB [8]. For the experiments involving MB adsorption on the AC and biochar, separate batches containing 5% w/v of the adsorbent, (i.e., 5 g solid adsorbent/100 mL of MB solution containing 50 mg/L) were prepared in separate plastic bottles, then samples were withdrawn at regular time intervals to determine the residual MB concentration. The collected samples were well mixed at 100 rpm for 5 min on a rotary shaker (ELMI Intelli-Mixer RM 2L, Riga, Latvia), and then allowed to settle. The amount of MB removed was calculated using Equation (2):

$$\text{Removal of MB, \%} = \frac{(C_i - C_e)}{C_i} \times 100 \quad (2)$$

where, C_i is the initial concentration of MB (mg/L) and C_e is the residual or equilibrium concentration of MB (mg/L).

2.5. Parametric Study

The effect of operating parameters namely the pH, initial MB concentration, and adsorbent's dosage were studied in order to identify the characteristics and the behavior of the adsorbents. The adsorbent dose was maintained constant at 0.5% w/v , i.e., 25 mg of the best adsorbent (sunflower shell) was added to 5 mL of 100 mg/L MB solution. The pH of the solution was measured using a pH meter (Mi150 pH meter, Milwaukee Instruments, Inc., Rocky Mount, NC, USA). Initial pH values of 2.0, 4.0, 7.0, 10.5 and 12.0 were chosen for these experiments. To investigate the effect of the initial MB concentration, solutions containing 25, 50, 75, 100, 150, 200, 250, and 300 mg/L were tested. In these experiments, the adsorption tests were conducted with an adsorbent dosage of 0.5% w/v , at a pH of 7.0 for an experimental time of 24 h. In order to investigate the effect of adsorbent dosage, different weights of the sunflower shell adsorbent (0.5, 1.0, 5.0 and 10% w/v) were added to 5 mL of 100 mg/L MB solutions, for a total experimental time of 24 h at 25 °C and pH 7.0.

2.6. Adsorption Isotherm

Adsorption experiments were conducted at ambient room temperature and at a pH = 7.0 by adding 0.025 g of the adsorbent to 5 mL of MB solutions at various concentrations. The mixtures were continuously mixed for 24 h. The concentrations (C_o and C_e) were measured to determine the adsorption capacity of the best activated carbon derived from the samples when they were at equilibrium conditions (Q_e). Q_e was calculated, from mass balance, using Equation (3) and plotted against C_e to obtain the adsorption isotherm that best fit the obtained data.

$$Q_e = \frac{(C_i - C_e) V}{m} \quad (3)$$

where, C_i is the initial MB concentration (mg/L), C_e is the residual or equilibrium MB concentration (mg/L), V is the volume of the liquid phase (mL), and m is the mass of the adsorbent (g). The equilibrium adsorption data were then fit to Langmuir isotherm equation as given by Equation (4):

$$\frac{1}{q_e} = \frac{1}{K_e} \frac{1}{C_e} + \frac{1}{q_{max}} \quad (4)$$

3. Results and Discussions

3.1. Adsorption Kinetics of the Natural, Unprocessed Biomass-Based Adsorbents

Figure 1 depicts the curves of adsorption kinetics of MB onto the different natural adsorbents during a period of 18 h of experiments. The obtained behaviors represent typical kinetic curves, in which the concentration of MB decreases with time due to its adsorption onto the adsorbents until approaching a plateau value that determines the adsorption capacity. The adsorption of MB on Grape Vines shows a different intermediate behavior possibly due to a release of materials after 2 h that increases the measured concentration (color change). It is clear that the adsorption capacity was greatly dependent on the type of biomass used. This is attributed to the variations in the shape, porosity, and carbon content of the different natural materials, which lead to large differences in the MB adsorption efficiency and capacity.

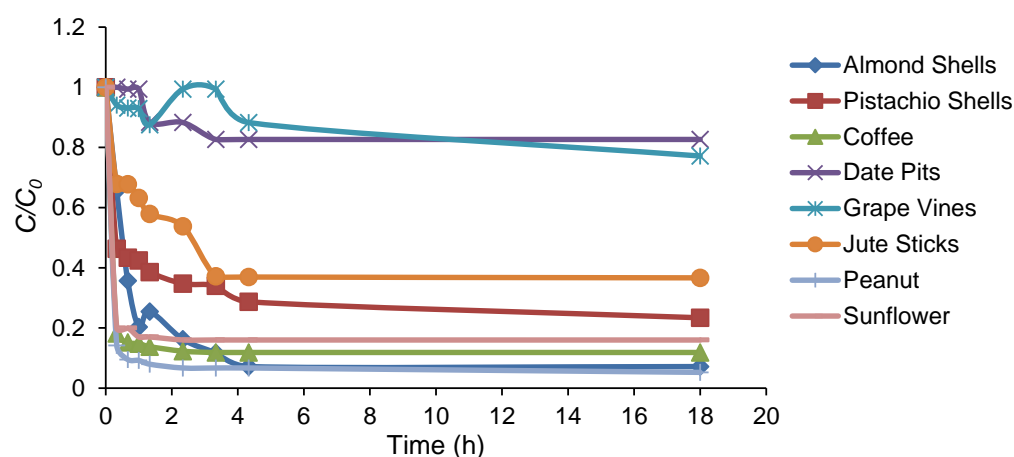


Figure 1. The curves of adsorption kinetics of MB onto the different natural adsorbents (adsorbent dose: 5% *w/v*; initial MB concentration: 50 mg/L; pH: 7.0).

The results show that peanut hulls and almond shells are the most effective natural adsorbents among the tested samples, yielding a removal efficiency of 93% and 92%, respectively. Coffee particles are also excellent adsorbents yielding a removal efficiency of 88%. One of the possible reasons for this is that the studied coffee sample had already been processed by heat when it was obtained from the roasting facility, which accounts for its relatively higher performance as an adsorbent. On the other hand, date pits are the least effective adsorbent, with a removal efficiency of 17.3%. This is attributed to their compacted structure that minimizes their porosity and reduces the available specific surface area for adsorptions. As reported in the literature [16,17], the molecular electrostatic potential, or MEP, is a technique that can be used to investigate the reactive sites on the tested adsorbate/adsorbents system and to envisage at the molecular level the electrophilic attack and the electrostatic potential zero regions that enable high adsorption characteristics for MB. Therefore, future studies in this research domain should also focus on MEP as a technique to investigate the multi-layer reactive sites present in the adsorbent [16].

3.2. Adsorption Tests Using Biochar and Activated Carbon

In this study, carbonization and activation methods were used to increase the adsorption performance of the natural plant-based biomass adsorbent. The yield of AC obtained after conducting pyrolysis on each sample is listed in Table 1. Table 1 shows that all investigated samples produce AC with a high to good yield ranging from 65% to 88%. The variations are attributed to structural changes in terms of the types of cellulosic compounds and lignin content as well as cell structure. The high carbon yields obtained from jute sticks and grape vine sticks (85% and 88%, respectively) are attributed to the presence of

lignin and cellulosic compounds in their structure, which contribute significantly in the production of carbon materials during the carbonization stage.

Table 1. Yield of activated carbon obtained after conducting pyrolysis on the biomass samples.

Biomass Samples	Yield (%)
Coffee	78
Date pits	74
Almond shells	73
Peanut hulls	80
Grape vine sticks	88
Pistachio shells	65
Jute sticks	85
Sunflower shells	80

Figure 2 depicts SEM images of the natural and AC of chosen biomass samples. Comparing the morphologies of the AC samples to those of the natural raw samples from the same source reveals a significant change in the porosity, micro and meso-porous structure. It is clear that the porosity of the AC samples is increased with the activation. Such an increase is associated with an increase in their adsorption capacity. As demonstrated in the literatures, different authors have tested both heat treatment and chemical treatment as an activation technique. According to Nguyen et al. [18] and Behloul et al. [19], there was a mass reduction of the adsorbent during heat treatment due to the decomposition of the cellulose component, particularly for methyl hydroxyl groups. The following aspects related to the surface morphology and its functions were highlighted by these authors: (i) the hemicellulose component decomposes between 200 and 270 °C, cellulose between 240 and 350 °C, and fine lignin between 280 and 550 °C; (ii) the presence of hydroxyl groups on the adsorbent surface is also apparent after heat treatment because it characterizes the carboxylic acids, alcohols, phenols, cellulose, pectin, and lignin; (iii) the weight loss due to ZnCl₂ based treatment was approximately 37% due to the thermal degradation of cellulose, (iv) ZnCl₂ plays a role in developing carbon matrix with high porosity, and (v) the formation of hydroxyl dichlorozincic acid during activation with ZnCl₂ creates a highly porous channel structure via its etching effect (Figure 2).

The performances of the natural, biochar and AC adsorbents for the MB removal are depicted in Figures 3 and 4 for materials prepared from coffee and date pits, respectively. The adsorption rate is much faster for the case with AC. Table 2 lists maximum rates of adsorption in (1/min), as obtained from the kinetic curves, and the obtained adsorption efficiencies. These results reveal that the adsorption capacity of the majority of biomass adsorbents can be significantly increased by pyrolysis and by activation using ZnCl₂. The level of enhancement depends on the type of the starting biomass material. In a recent study, Li et al. [20] prepared a novel hierarchically porous carbon adsorbent derived from starch (i.e., Starbon) and conducted MB adsorption experiments. According to the authors, the Starbon material's high adsorption capacities correlate well with its BET surface area and micropore volume. At a dye concentration of 600 mg/L, this Starbon material exhibited the highest adsorption capacity of 890 mg/g, with a removal efficiency of 75%. Xue et al. [21] conducted adsorption experiments for the removal of methylbenzene (MB) from polluted water using activated carbon and composite materials prepared from agricultural waste biomass. The mechanism was primarily attributed to endothermic and exothermic adsorption processes, electrostatic interactions, van der Waals forces, and hydrogen bonding. Besides, the authors also demonstrated that activated carbon functionalized with sodium dodecyl sulfate had the highest MB adsorption capacity.

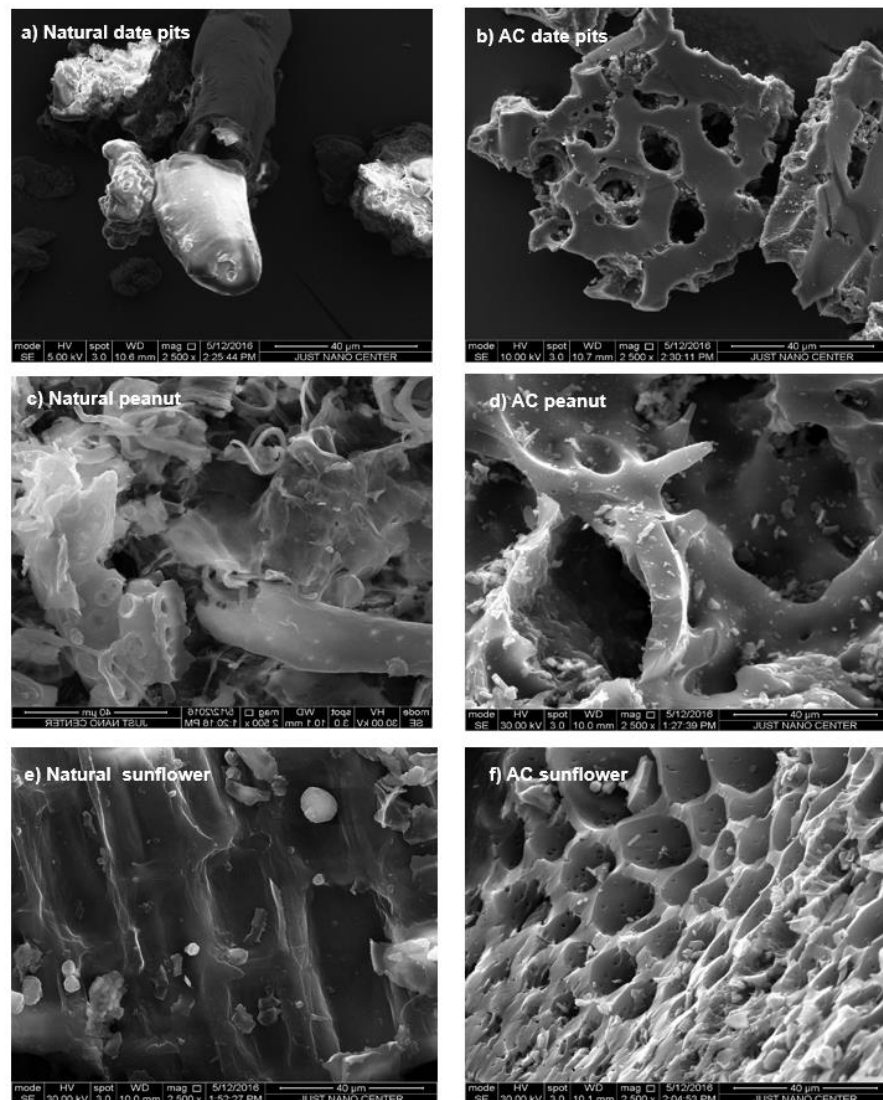


Figure 2. SEM micrographs of natural and AC biomass materials: (a) natural date pits, (b) AC date pits, (c) natural peanuts, (d) AC peanuts, (e) natural sunflower and (f) AC sunflower.

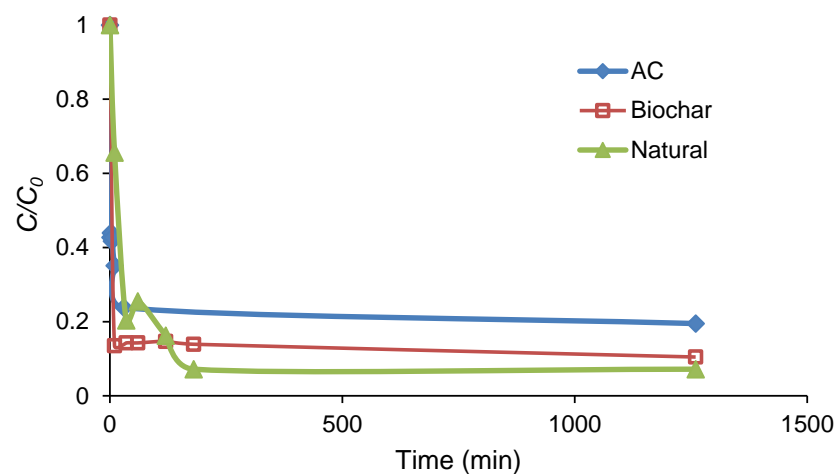


Figure 3. The curves of adsorption kinetics of MB onto coffee particles as a natural adsorbent, biochar and activated carbon (adsorbent dose: 5% w/v; initial MB concentration: 50 mg/L; pH: 7.0).

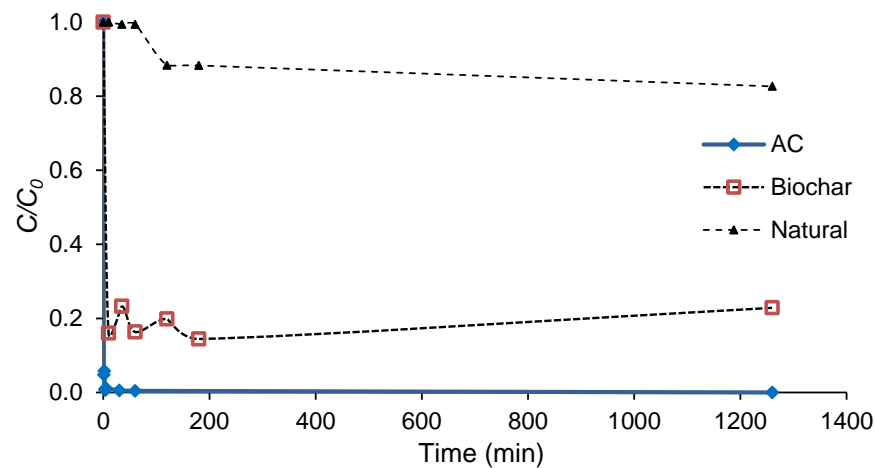


Figure 4. The curves of adsorption kinetics of MB onto date pits particles as a natural adsorbent, biochar and activated carbon (adsorbent dose: 5% *w/v*; initial MB concentration: 50 mg/L; pH: 7.0).

Table 2. Adsorption efficiency and maximum rate of adsorption for biochar and activated carbon prepared from different natural plant-based wastes.

Type of Adsorbent	Biochar		Activated Carbon	
	Removal Efficiency (%)	Rate of Adsorption (L/min)	Removal Efficiency (%)	Rate of Adsorption (L/min)
Coffee	90	0.0865	80	0.572
Date pits	77.2	0.084	100	0.951
Almond shells	89	0.0836	100	0.8503
Peanut hulls	99.6	0.0944	100	0.9911
Grape vine sticks	99.6	0.0988	100	0.9994
Pistachio shells	98.9	0.0978	100	0.9956
Jute sticks	99.94	0.099	100	0.9945
Sunflower shells	99.64	0.094	100	0.996

In this study, the adsorption efficiency of coffee, which already has a very good adsorption efficiency as a natural adsorbent, can be enhanced by only 2% (increases from 88% to 90%) from the enhancement of the porosity of its structure after carbonization. This is attributed to the relatively high carbon content yield (78%) by pyrolysis. On the other hand, an opposite trend is obtained with activation with $ZnCl_2$; the adsorption efficiency drops from 88% to 80% by activation. This is explained by the lack of chemical affinity between coffee particles and $ZnCl_2$, which indicates little or no tendency for coffee particles to combine with the activating agent via any chemical reaction. It is worth noting that previous studies have clearly shown that KOH was an effective activating agent for coffee compared with other activating agents (i.e., carbon dioxide) [22]. The coffee AC impregnated with KOH gave a pore volume and surface area up to $0.43 \text{ cm}^3/\text{g}$ and $893 \text{ m}^2/\text{g}$, respectively. In that study, however, impregnation with carbon dioxide reduced the pore volume and surface to approximately half of the values obtained with KOH [22].

Figure 4 depicts a noticeable improvement in the porous structure of the date pits after thermal treatment with both biochar and activated carbon. The removal of MB was increased from 17% for natural date pits to 77% using biochar and nearly 100% using activated carbon. Furthermore, the adsorption rate increases faster when the date pits are treated by pyrolysis, and it increases further by activation. The chemical activation of date pits with $ZnCl_2$ increases the removal efficiency by 23%. This is associated with a carbon yield of 74%. This is explained by the chemical reagent's capability in the degradation of the organic/lignocellulosic materials present in the sample, as well as preventing the

formation of tars and other unwanted materials/residues that can block the pores during the carbonization stage.

Table 2 indicates that the pyrolysis of the almond shells reduces the removal efficiency of biochar by 3% below its capacity as natural adsorbents (from 92% to 89%). This is expected to be due to the formation of undesirable charring outcomes that prevent the development of porosity, and possibly due to the narrowing of pore volume during heat treatment. However, in addition to oxidizing organics, the role of the activating agent is to occupy some pore volume that prevents such a narrowing effect in order to maintain and improve its porous structure. This is confirmed with the behavior of activated carbon with a removal efficiency of 100% and a relatively high rate of adsorption of 0.85 L/min.

The peanut hulls sample demonstrated excellent adsorption efficiency for both biochar and activated carbon, as well as the highest removal efficiency as a natural adsorbent (93%). The effect of activation with $ZnCl_2$ is rather minor, (improving the efficiency by <1%), however, the activation step increases the removal (adsorption) rate from 0.0944 to 0.99 (1/min). Hence, for this case of peanut hulls, the carbonization stage may be sufficient to produce a high porous char with a good adsorption efficiency. It is worth noting that the carbon yield of carbonized peanut hulls is relatively high, reaching ~80%.

In general, the grape vine sticks, pistachio shells, sunflower shells, and jute sticks have similar behaviors of significant increase in the adsorption efficiency by pyrolysis and a significant increase in the adsorption rate by activation as peanut hulls as shown in Table 2. In this study, the AC prepared from sunflower shells present a high adsorption capacity with a rate of adsorption (0.996 L/min) and high removal efficiency (>99%).

In previous literature, several researchers attempted to link the properties and adsorption capacity of AC or biochar produced after carbonization to the amount of cellulose or lignin in the biomass matrix. The relevant published data show that lignin-based carbon has more pore volume than cellulosic carbon, which explains the high adsorption efficiency of biochar derived from pistachio shells, peanut hulls, and sunflower shells, which are known to have a higher lignin content in their structure [6]. Besides, the char obtained from a biomass with a higher cellulosic content was easier to prepare than char obtained from biomass with a higher lignin polymer content, which primarily imparts density or hardness to the biomass matrix. This is consistent with the AC yields of jute sticks and grape vine sticks, which are 85% and 88%, respectively, given that the cellulosic content in these samples ranges from 40 to 65% [14]. These structural characteristics explain the excellent performance of these plant-based waste biomass, i.e., as adsorbents, to remove MB from wastewater.

3.3. Effect of Adsorption Parameters on the Removal of MB and Kinetic Constants

Figure 5 shows the effect of initial MB concentration on the efficiency of AC obtained from sunflower shell at concentrations of 25, 50, 75, 100, 150, 200, 250, and 300 mg/L. The results show that for low concentrations ranging from 20–100 mg/L, the removal efficiency reaches about 99%, since the adsorbate amount can be collected onto the surface of the adsorbent before reaching its saturation limit. On the other hand, for higher concentrations, e.g., >250 mg/L, the removal efficiency drops below 80%. These results are reasonable because the surface-active sites of AC will not be able to adsorb all the MB at high concentrations after saturation [23]. Yilmaz et al. [24] investigated the effect of initial MB concentration (5 to 100 mg/L) and reported that, when the concentration of MB was increased from 5 to 55 mg/L, there was a correlation between the rise in MB removal and the increase in MB concentration. However, the authors also reported that the high levels of MB in the wastewater limits the driving force for adsorption by increasing the intermolecular competition on the adsorbent, which in turn slowed down the MB adsorption/uptake rate and efficiency.

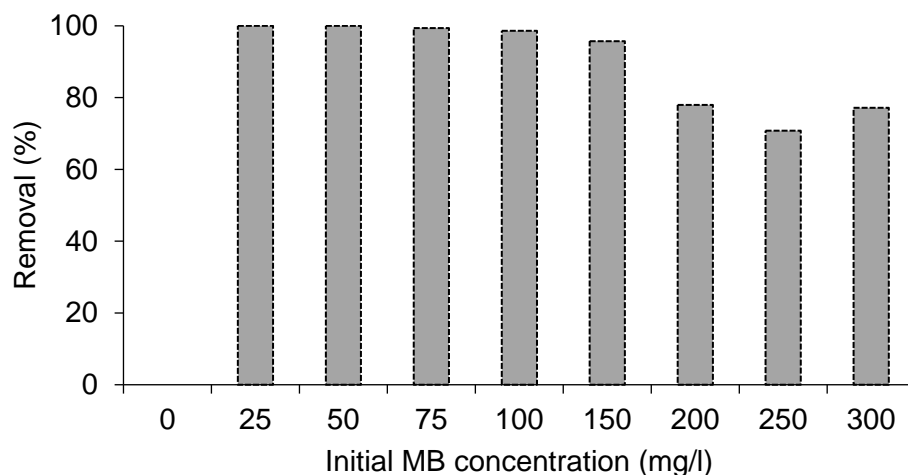


Figure 5. Effect of initial MB concentration on the adsorption efficiency of AC obtained from sunflower shell (pH: 7.0; adsorbent dose: 0.5% *w/v*; contact time: 24 h).

Figure 6 depicts the effect of adsorbent dosage of AC obtained from sunflower shell, i.e., 0.5, 1, 5, and 10% *w/v* on the MB removal efficiency. It is clear that, at low dosages, increasing the dosage increases the removal (adsorption) efficiency, as theoretically known. This is due to the increasing number of active sites that adsorb the solute, the removal efficiency increased from 98% for 0.5% *w/v* adsorbent dose to >99% for 5 and 10% *w/v* adsorbent dosages, respectively [25]. Gupta et al. [26] investigated the effect of adsorbent dose at a constant MB concentration of 100 mg/L, pH of 11.0, contact period of 60 min, temperature of 60 °C and a stirring speed of 150 rpm. According to the authors, the adsorbent dosage ranged between 0.2 and 1.0 g/L and the removal efficiency of MB increased with increasing adsorbent concentrations. The MB removals increased from 41% to 96% as the adsorbent dosage increased from 0.2 g/L to 1.0 g/L and this increase was attributed to the greater number of active sites being available at a higher adsorbent concentration/dose. However, in this study and as reported in the literature, after a certain dosage, the level of enhancement in the removal efficiency becomes minor since the extra available adsorbent will not contribute further to the removal of MB.

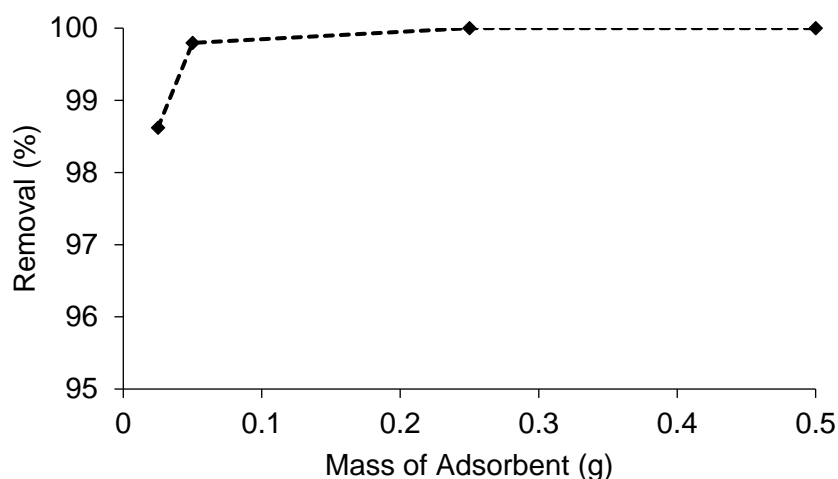


Figure 6. Effect of adsorbent dose on the removal of MB by AC obtained from sunflower shell (pH: 7.0; initial MB concentration: 100 mg/L; contact time: 24 h).

Figure 7 depicts the effect of pH on MB removal efficiency of AC obtained from sunflower shell. It is clear that the adsorption process is highly favorable at extreme pH ranges (both acidic and alkaline conditions) and it becomes less favorable close to neutral

conditions. These findings can be explained by the effect of pH on the surface charge of the adsorbent, high pH values or low pH values lead to increased attraction between the AC and the MB molecules (e.g., due to the replacement of the hydrogen ions on the adsorbents surface) [23]. Ramutshatsha-Makhwedzha et al. [27] investigated the influence of various process parameters on the removal of methyl orange (MO) and MB: 50 mL of model wastewater solution with initial dye concentration 50–200 mg/L, pH 2.0–10.0, adsorbent dose 0.010–0.8, and contact time 5–180 min. The authors reported that MO and MB had maximum adsorption capacities of 33 and 38 mg/g, respectively.

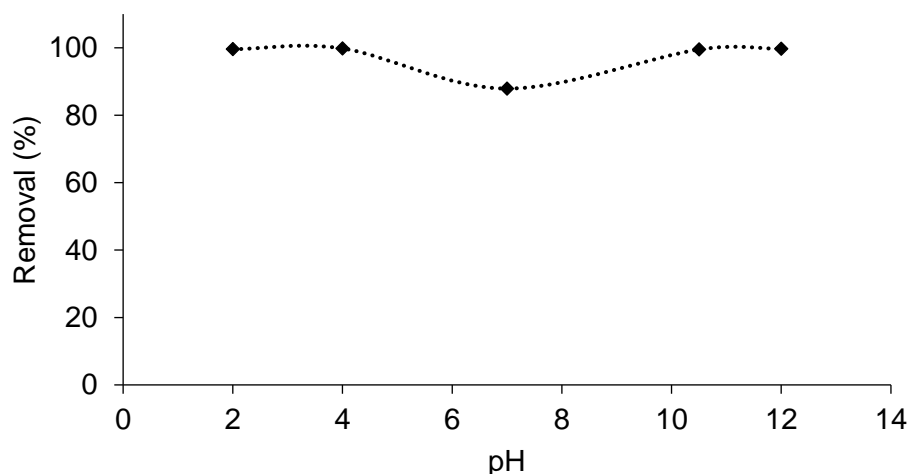


Figure 7. Effect of pH on the removal of MB on AC obtained from sunflower shell (initial MB concentration: 100 mg/L; AC dose: 0.5% *w/v*; contact time: 24 h).

However, when considering the effect of pH, the authors found that the removal efficiency of MO was at the greatest value (94%) at pH 2.0, while that of MB was at the greatest value (93%) at pH 5.0. This behavior was attributed to the following factors: (i) the transfer/removal of protons from the different functional groups present on the adsorbent's surface, and (ii) the anionic and cationic nature of MO and MB, respectively. In another study, using *Citrus limetta* peel as the adsorbent, Rani and Chaudhary [28] conducted adsorption experiments to remove MB and crystal violet (CV) from wastewater. Following optimization experiments, maximum removals of 83% for MB and 90% for CV, respectively, were observed at an adsorbent dose of 0.1 g, a contact time of 120 min, and a pH of 7.0. Intriguingly, the authors found that the removal of MB and CV dyes increased as the pH values increased, i.e., from acidic to basic pH conditions.

Figure 8 shows the experimental adsorption data fit for sunflower shells-based AC (i.e., the best AC in this study) using the Langmuir isotherm model, while Figure 9 shows the linearized plot of $1/q_e$ with $1/c_e$ as given by Equation (4) [29]. It is clear that a linear relationship is obtained confirming the Langmuir isotherm's validity for the obtained results. The maximum adsorption capacity was obtained ($q_{max} = 29.8$ mg solute/g adsorbent), and the equilibrium constant $K_e = 6.7 \times 10^{-7}$ g/mL.

Future research in this field should focus on the following aspects: (i) characterization of the adsorbents (i.e., before and after activation) using FTIR, SEM, Boehm titration, EDX, iodine adsorption, pHpzc, nano-CT, XPS, Raman, and XANES techniques in order to reveal their important physical and chemical properties and elucidate the adsorption mechanism [30,31], (ii) test the adsorption efficiency for different pollutants (e.g., dyes and heavy metals) through fixed bed column experiments, determination of the breakthrough curves and fit the data to well-known Thomas, Yoon–Nelson, Bohart–Adams, and Yan models [32]. Besides, as a phenothiazine derivative, MB is colorless under reducing conditions, but it turns blue under oxidizing conditions. Depending on the process and environmental conditions, biochar and AC may release some adsorbed MB into the solution under real field conditions. In order to estimate the true MB removal efficiency in adsorption

columns, it is recommended to conduct blank tests and make an appropriate correction of the residual MB concentration.

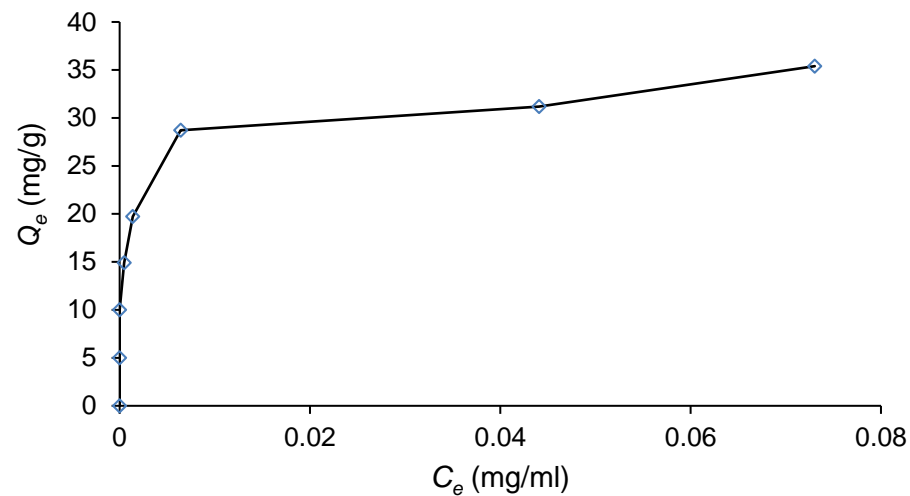


Figure 8. The equilibrium isotherm, Q_e as a function of the C_e of MB on AC obtained from sunflower shell.

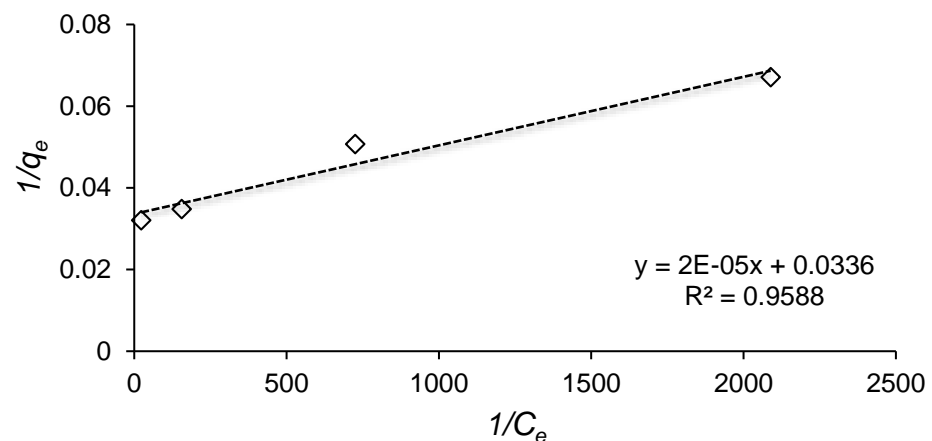


Figure 9. Linearized fit of the Langmuir isotherm of MB on AC obtained from sunflower shell: $1/q_e$ as a function of $1/C_e$ (Equation (4)).

4. Conclusions

The novelty of this study was to determine the viability of removing MB from polluted water using locally available biomass-based wastes in Palestine, including coffee grains, almond shells, pistachio shells, date pits, jute sticks, sunflower shells, peanut shells, and grape vine sticks. This is the first regional study to screen, select, and determine the kinetics of a high-performing adsorbent (natural and modified) for dye removal. In terms of natural adsorbents, the peanut hulls were found to be the most efficient natural adsorbent, whereas date pits were observed to be the least efficient natural adsorbent. The removal efficiency of MB improved significantly by pyrolysis and activation for the majority of the biochar and AC. In terms of biochar, jute sticks exhibited the highest removal efficiency and rate of adsorption under the tested conditions, whereas the adsorption efficiency of coffee grains decreases slightly after pyrolysis. Most of the biomass-based AC tested in this study demonstrated high removal of MB (>95%). Sunflower shells were found to be the most effective AC-based adsorbent, achieving MB removal >99%.

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