

Article

Valorization of Peanut and Walnut Shells through Utilisation as Biosorbents for the Removal of Textile Dyes from Water

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Abstract: The present research focuses on the application of peanut and walnut shells, in their natural state, for the removal of methylene blue (MB) from water solutions in batch and dynamic (flow-through) conditions. Under batch conditions, at a 100 mg/L MB concentration of aqueous solution, the optimum dose of the studied biosorbents was determined to be 2.5 g/L, reaching about 95–97% efficiency of MB removal for both materials. Langmuir and Freundlich isotherms were used to model and evaluate the experimental data under different initial concentrations of MB (25 to 100 mg/L). The determined maximum adsorption capacities are 41.50 mg/g for walnut shells and 46.80 mg/g for peanut shells. Under flow-through conditions, breakthrough curves are determined for three sizes of fractions (<0.25 mm, 0.315–0.5 mm, and 0.8–1.6 mm). For peanut shells, the smaller the particle size, the higher the adsorption capacity and the column breakthrough time. For walnut shells, however, the particle size seems to have a more complex influence on the adsorption process parameters, and this phenomenon deserves future investigation. The adsorption capacity for one and the same fraction size of 0.315–0.5 mm and initial MB concentration of 50 mg/L is higher under dynamic flow conditions, i.e., 51 mg/g compared to 20 mg/g for walnut shells and 46 mg/g compared to 17.5 mg/g for peanut shells.

Keywords: biosorbents; peanut shells; walnut shells; adsorption kinetics; methylene blue; dye removal



Citation: Lazarova, S.; Tonev, R.; Dimitrova, S.; Dimova, G.; Mihailova, I. Valorization of Peanut and Walnut Shells through Utilisation as Biosorbents for the Removal of Textile Dyes from Water. *Processes* **2023**, *11*, 2291. <https://doi.org/10.3390/pr11082291>

Academic Editor: Andrea Petrella

Received: 28 June 2023

Revised: 24 July 2023

Accepted: 26 July 2023

Published: 31 July 2023



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1. Introduction

Dyes used in the industrial sector are mainly synthetic and serve to colour various products, such as textiles, paper, rubber, plastic, and others. Most of them are organic compounds with multiple aromatic rings fused or linked together by covalent bonds and modified by various hydrophilic functional groups. Currently, thousands of structurally diverse synthetic dyes such as azo, diazo, acid, basic, reactive, disperse, metal complex, and anthraquinone are available on the market. After use, they end up in wastewater, and even in low concentrations, they are dangerous pollutants that affect aquatic life and the food web in water bodies [1,2].

While many synthetic dyes are relatively non-toxic, some of their degradation byproducts, such as anilines, are often more toxic than the parent compounds and can even be carcinogenic [3]. Due to their complex chemical structure, these dyes are often resistant to biodegradation in wastewater treatment processes as well as in natural aquatic environments [4]. In addition to toxicity, residual organic dyes can expose the aquatic ecosystem to various hazards by depleting dissolved oxygen, blocking the penetration of sunlight, and inhibiting photosynthesis and the growth of aquatic organisms. The treatment of industrial waters from the textile, lignin-cellulose, and paper industries might be further aggravated

due to the high content of dissolved solids, high concentrations of BOD and COD, bright colour, or the presence of toxic heavy metals [5].

In engineering practice, no universal technology is suitable for dye removal from wastewater. Usually, a combination of methods is used, including physical, chemical, and biological treatment, depending on the number of contaminants in the wastewater stream. Conventional methods are coagulation and flocculation, reverse osmosis, and adsorption with activated carbon [6,7]. Adsorption has been proven to be effective for the removal of different types of dyes, as activated carbon is a commonly used adsorbent. Its wider application in wastewater treatment technology is, however, still limited by its high cost and several requirements concerning the quality of treated wastewater.

A relatively new trend in wastewater treatment is biosorption. In the literature, the term “biosorbent” includes natural products of biological origin, such as bacteria, viruses, fungi, algae, agricultural products, or waste biomass from industrial processing. It is essentially a physicochemical and metabolically independent process based on various mechanisms, including absorption, adsorption, ion exchange, surface complexation, and precipitation [8]. Biosorbents based on agricultural plant residues or waste plant biomass in their natural state or after appropriate physicochemical treatment are the subject of intense research as low-cost alternative adsorbents, both for heavy metal ions and for the treatment of textile industry wastewater [9–13]. Recycling agricultural waste into useful products is an innovative approach in biotechnology that is fully in line with the European Circular Economy Action Plan [14].

Some of the analytical techniques commonly used in analyses of the dye adsorption process and characterisation of solid adsorbents are scanning electron microscopy (SEM), infrared spectroscopy or Fourier transform infrared spectroscopy (FTIR), and the Brunauer–Emmett–Teller (BET) method [15]. The adsorption capacity represents the maximum amount of the dye methylene blue (MB) adsorbed by 1.0 g of adsorbent [16,17]. It is calculated by:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m}, \quad (1)$$

where q_e —adsorption capacity (mg/g); C_0 —initial concentration of MB (mg/L); C_e —concentration of MB at equilibrium (mg/L); V —the volume of the sample (L); and m —adsorbent mass (g).

It is usually assumed that MB forms a monolayer of adsorbed molecules on the surface of sorbent particles. It is possible to determine the specific surface area of MB coverage (S_{MB} , m^2/g) from the q_e values determined in solution with high concentrations of MB, enough time for adsorption, and a constant temperature [16]:

$$S_{MB} = \frac{q_e \cdot S \cdot N_a}{M_{MB}}, \quad (2)$$

where N_a —Avogadro’s number (6.02×10^{23} molecules per mol); S —cross-sectional area, which is taken as 1.20×10^{-18} m^2 per molecule for MB [17]; and M_{MB} —molar mass of MB (319.86×10^3 mg/mol), given by the producer—Sigma-Aldrich Chemie GmbH, St. Louis, MO, USA.

The efficiency of MB removal from the solution due to adsorption processes is given by:

$$E\% = \frac{C_0 - C_e}{C_0} \cdot 100, \quad (3)$$

where E (%) is the MB removal percentage from the initial concentration (C_0 —mg/L).

Usually, the adsorption equilibrium is described by Langmuir and Freundlich isotherms [18]. The Langmuir model is given by:

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

where K_L is the Langmuir constant and $q_{\max}$ is the maximum adsorption capacity of the biosorbent (mg/g). To establish the main characteristics— K_L and $q_{\max}$ —the linearised form is used:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} \cdot K_L} + \frac{C_e}{q_{\max}}, \quad (5)$$

The Langmuir isotherm refers to adsorption on completely homogeneous surfaces with negligible interaction between the adsorbed molecules [19].

The Freundlich model follows:

$$q_e = K_F \cdot C_e^{\frac{1}{n}}, \quad (6)$$

where K_F and n are empirical constants that are characteristics of the system indicating the adsorption capacity and adsorption intensity, respectively, and other parameters are the same as in Equation (4). The linearised form is written as Equation (7):

$$\ln(q_e) = \ln(K_F) + \frac{1}{n} \cdot \ln(C_e). \quad (7)$$

In practice, the treatment of dye-contaminated waters is most often a continuous, dynamic process characterised by dynamic curves. Their determination can be carried out in a column with a fixed bed. For analysis of the results, mathematical models are most frequently applied. The most common ones are those of Thomas and Yoon–Nelson [20,21].

The Thomas model is based on the Langmuir isotherm and second-order reaction kinetics. This model is generally suitable for systems where the outflow rate is constant with no axial dissipation (chemical reaction) conditions:

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp\left(\frac{K_{Th} \cdot q_e \cdot m}{Q} - K_{Th} \cdot C_0 \cdot t\right)}, \quad (8)$$

where C_t is the solution concentration at time t (mg/L); K_{Th} is the Thomas constant (mL/min.mg); Q is the sample flow (mL/min); and m is the mass of the adsorbent (g). The linearised form is given by:

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{K_{Th} \cdot q_e \cdot m}{Q} - K_{Th} \cdot C_0 \cdot t. \quad (9)$$

Compared to other models, the Yoon–Nelson model does not require information on the physicochemical characteristics of the adsorbate, the type of adsorbent, or the properties of the adsorption layer. It is expressed by the following equation:

$$\frac{C_t}{C_0 - C_t} = \exp(K_{YN} \cdot t - \tau \cdot K_{YN}), \quad (10)$$

where K_{YN} is the rate constant (min^{-1}) and τ is the time required for 50% adsorbate breakthrough (min). In linearised form, the model is written as follows:

$$\ln \frac{C_t}{C_0 - C_t} = K_{YN} \cdot t - \tau \cdot K_{YN}, \quad (11)$$

The constants K_{YN} and τ can be determined by the slope and the intercept of the plot $C_t/C_0 - C_t$ vs. t . The adsorption capacity can be determined by:

$$q_e = \frac{C_0 \cdot Q \cdot t}{1000 \cdot W}, \quad (12)$$

where W is the total volume of sample passed through the column (L) and Q is the flow rate (mL/min).

Peanuts and walnuts are typical crops in Bulgaria. Their shells are a by-product of the food industry or their processing into oils and other products. The plant biomass from shells is a natural resource and could be utilised as a biosorbent for the removal of toxic pollutants in wastewater treatment processes [22], construction additives [23], energy, and soil fertilisation [24].

The applicability of new adsorptive materials includes the investigation of column equilibria to define the kinetic mechanism of adsorption and predict process performance.

This work aimed to investigate and model the removal of methylene blue dye from aqueous solutions with natural peanut and walnut shells in conditions similar to commercial water treatment technologies.

2. Materials and Methods

Peanut shells (PS) from the peanut plant known as *Arachis hypogaea* and walnut shells (WS) from the walnut tree known as *Juglans regia* were used in this study.

2.1. Adsorbent Preparation

The PS and WS were washed with warm tap water (45 ± 5 °C). Then, the material was dried at room temperature and ground in a rotary mill to a maximum particle size of 2 mm. Subsequently, the particles were fractionated using a laboratory sieve machine with individual sieve sizes <0.250 mm, 0.315–0.5 mm, 0.5–0.8 mm, and 0.8–1.6 mm.

2.2. Model Water Preparation

The tests were performed with a methylene blue ($C_{16}H_{18}ClN_3S \cdot xH_2O$, Sigma-Aldrich Chemie GmbH, >97%) solution prepared with distilled water. To determine its concentration, a calibration curve was constructed based on solutions with a previously known concentration. A UV-VIS spectrophotometer was used, and the absorbance in the range $\lambda = 400\text{--}700$ nm was checked. Optimal results are achieved at $\lambda = 664$ nm.

2.3. Shell Surface Characterisation

Standard FTIR, SEM, and BET analyses were performed for further characterisation of the PS and WS samples before and after saturation in terms of functional groups, the morphological and surface structure of the material, as well as the pore size. The studied fraction was 0.315–0.500 mm.

The IR spectra were recorded in the $4000\text{--}400$ cm^{-1} range by using an FTIR spectrometer, the Varian 600-IR, with a spectral resolution no worse than 0.07 cm^{-1} . The disc-shaped samples for these measurements were prepared by mixing the powdered samples with KBr. The precision in determining the absorption maxima positions was ± 3 cm^{-1} .

The NOVA 1200e apparatus (Quantachrome Instruments, Beach, FL, USA) was used for BET surface analysis and pore distribution analysis. Prior to the adsorption measurements, the samples (1 g) were degassed at 105 °C under vacuum. The analysis was carried out at 77 K with N_2 . Surface area and pore volumes were determined using the Brunauer–Emmett–Teller (BET) equation.

Scanning electron microscopy (SEM) images of the tested samples were taken on an SEM/FIB LYRA I XMU microscope (TESCAN) having the following characteristics: electron source—wolfram-heated fibre; resolution— 3.5 nm at 30 kV; and acceleration voltage— 200 V $\div$ 30 kV.

2.4. Adsorption Experiments in a Batch Study

Batch studies for the determination of S_{MB} were performed following the procedure described by Idris-Hermann et al. [17]. In 50 mL of MB solution with a concentration of 150 mg/L, 0.1 g of the processed materials were added. The samples were placed in a shaking machine for 24 h at room temperature.

Additional studies, also with a shaking machine, were performed to determine the optimum dose of adsorbent. In 50 mL of MB solutions with a concentration of 100 mg/L,

different doses of PS and WS were added (fraction 0.315–0.500 mm), ranging from 1 to 4 g/L. All the tests were performed at constant room temperature (around 20 °C) and a pH of around 4.8. The duration of each test was 6 h at 200 rpm on the shaking machine. The series was repeated with a constant dose (2.5 g/L) at different initial concentrations of MB (25–100 mg/L) to determine the parameters of the Langmuir and Freundlich models.

2.5. Fixed-Bed Column Experiments

To determine the effectiveness of PS and WS samples in a natural state for the removal of MB from an aqueous solution, fixed-bed column adsorption studies were performed (Figure 1). The experimental setup included a tank, a peristaltic pump, and a transparent acrylic column with a diameter of 2.4 cm. A layer of glass wool (approximately 5.5 cm) was placed at the bottom of the column to prevent the carryover of fine adsorbent particles. The tests were performed with 10 g of three different size fractions (powder $d < 0.25$ mm, medium size $d = 0.315$ –0.5 mm, and large size $d = 0.8$ –1.6 mm). The MB solution was fed in a top-down direction at a constant flow rate of 36 mL/min. The initial concentration (C_0) was kept relatively constant at 48 (± 2) mg/L. At certain time intervals at the outlet of the column, samples were taken to determine the residual concentration of MB. The duration of each experiment was until the residual MB concentration at the outlet reached about 90% of the initial concentration. The pH of the effluent sample was around 4.9 (± 0.2), and all the tests were carried out at room temperature (18 °C $\pm$ 2.0).

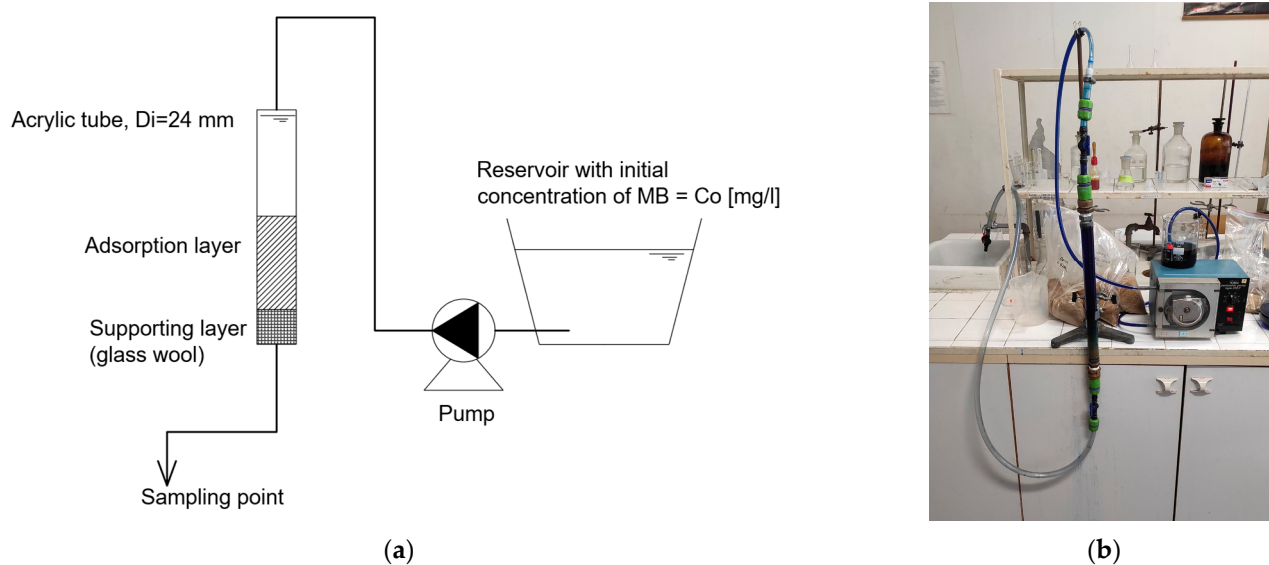


Figure 1. Scheme of the experimental fixed-bed column (a) and photo (b).

3. Results

3.1. Characterisation of the Samples

3.1.1. BET Analysis

The surface area of WS was found to be 0.7 m²/g, which is twice as small as the PS surface area—1.4 m²/g. The determined pore volume of both materials was 0.003 cm³/g. Both materials have mesopores in the range of 2–50 nm, as the average pore diameter of WS is larger (17.5 nm) than that of PS (8.5 nm).

3.1.2. SEM Analysis

In the morphological and surface examination of both types of samples, layers of pores in a close arrangement were observed. The SEM pictures before the adsorption with MB show a mostly homogeneous, hollow, and hard surface with significant porosity for both materials (Figure 2). This suggests that the surfaces of the PS and WS were able to adsorb the positively charged dye in the pores and cracks.

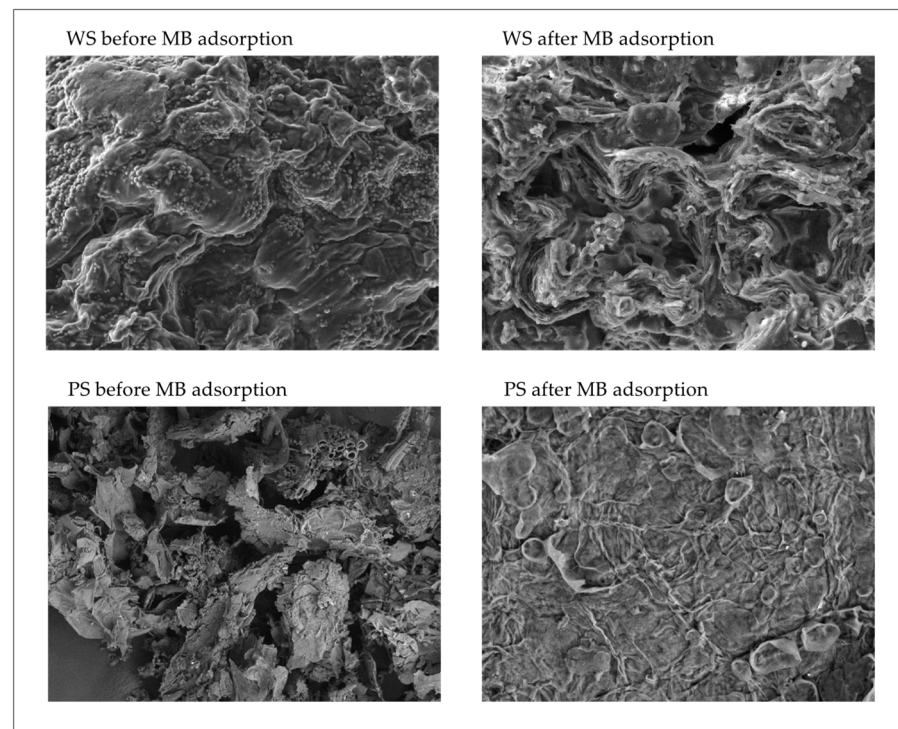


Figure 2. SEM analysis of PS and WS in their natural states before and after MB adsorption.

3.1.3. FTIR Analysis

The analysis performed for both materials showed several bands related to different functional groups. The deep peak around 3347 cm^{-1} , observed in the spectra of both WS and PS, corresponds to the presence of -OH groups, and the peak around 2925 cm^{-1} can be attributed to the C-H bond. The peaks at 1740 cm^{-1} , 1648 cm^{-1} , 1629 cm^{-1} , and 1512 cm^{-1} are due to vibrational fluctuations of the C=O bond, and those at 1268 cm^{-1} and 1163 cm^{-1} represent C-H deformation vibrations. The characteristic peak at $1056\text{--}1033\text{ cm}^{-1}$ corresponds to the C-O bond (Figure 3).

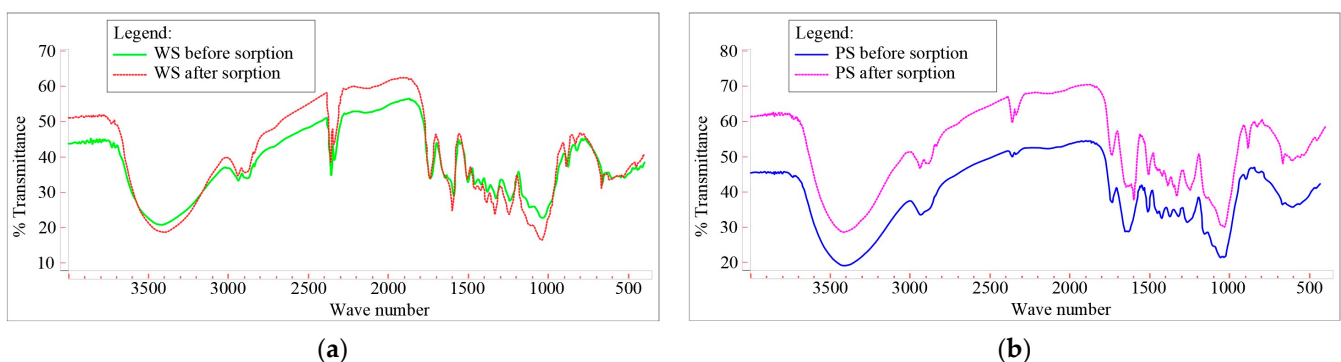


Figure 3. Results from FTIR analysis (a) PS and (b) WS.

3.2. Adsorption Experiments

3.2.1. Specific Surface Area of MB Coverage

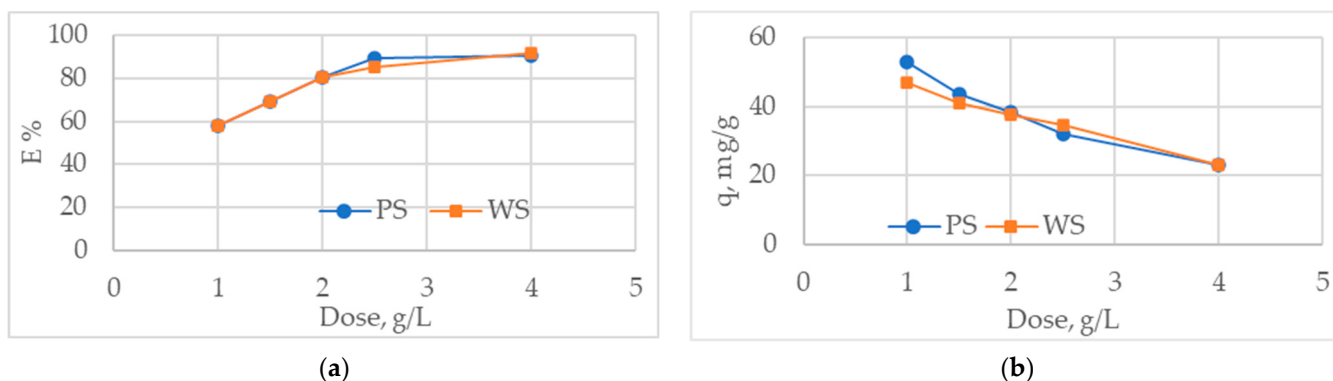
The results for the MB-specific area, based on Equation (2), are shown in Table 1. They are compared with other studies.

Table 1. Results from methylene number tests, fraction 0.315–0.500 mm.

Material and Modification	q_e [mg/g]	S_{MB} [m ² /g]	Reference
WS—natural state	46.60	105.28	Current work
PS—natural state	50.04	113.06	Current work
Garcinia kola nutshell (H ₃ PO ₄)	72.86	147.96	[17]
Garcinia kola nutshell (KOH)	73.18	148.61	[17]
Garcinia kola nutshell (ZnCl ₂)	72.59	147.41	[17]

3.2.2. Adsorbent Dosage

The effect of the dosage of PS and WS (1.0–4.0 g/L) on MB removal and the adsorption capacity of the materials is shown in Figure 4.

**Figure 4.** Effect of adsorbent dose on (a) removal efficiency and (b) adsorption capacity.

Due to the smooth increase in efficiency and smooth decrease in adsorption capacity, the optimal dose for subsequent analysis in the current study is set at 2.5 g/L.

3.2.3. Adsorption Capacity Relative to the Initial MB Concentration

The results from the tests conducted for the establishment of Langmuir and Freundlich model parameters are presented in Tables 2 and 3.

Table 2. Results from the tests with different initial MB concentrations.

Test Parameters	C_0 (mg/L)	WS q_e (mg/g)	PS q_e (mg/g)
Fraction = 0.315–0.5 mm Dose = 2.5 g/L Solution volume = 50 mL	25	9.67	9.40
	50	20.05	17.41
	75	28.44	25.28
	100	34.80	31.30

Table 3. Estimated parameters of Langmuir and Freundlich models.

Material	Langmuir Model			Freundlich Model		
	q_{max} mg/g	K_L	r^2	$1/n$	K_F	r^2
WS	41.5	0.337	0.998	0.452	11.2	0.927
PS	46.8	0.163	0.997	0.578	7.7	0.991

3.3. Fixed-Bed Column Tests

The main goal of fixed-bed column studies is most often related to the determination of specific characteristics of the material in laboratory conditions with a view to its applicability in the purification of water contaminated with dyes. The main parameters that are the subject of research are most often the initial concentration of the pollutant, the rate of

passage of the solution through the adsorption medium, the height of the layer, as well as other indicators like pH and temperature [20,25]. In the current study, the focus is on particle size.

To achieve conditions close to those of the adsorption column used in practice, a backwash of the material is performed before each test series. Afterwards, a few minutes are allowed for the adsorbent particles to settle down. Only then was the test started, feeding the MB solutions from top to bottom. Table 4 presents the characteristics of each fixed bed, containing 10 g of the material, after settling.

Table 4. Characteristics of the fixed-bed tests, each containing 10 g of material.

Material	Fraction	Bed Height	Bed Volume	Cross-Section	Velocity
		H [cm]	BV [cm ³]	F [cm ²]	v [cm/min]
WS	1.600–0.800	4.2	19.0	4.52	8.0
	0.500–0.315	6.5	29.4		
	<0.250	6.2	28.0		
PS	1.600–0.800	10.5	47.5	4.52	8.0
	0.500–0.315	10.3	46.6		
	<0.250	9.2	41.6		

The obtained results of effluent concentrations vs. elapsed time are given in Figure 5. For both materials, there is an immediate breakthrough in the largest fraction of 1.6–0.8 mm. This is a probable reason for the lack of the typical S shape in the curve, observed usually in fixed-bed adsorption studies [26], which is also observed for the smaller fractions. However, for the medium fraction of WS, the shape of the curve differs compared to other WS fractions (Figure 5b). The elapsed time until the breakthrough in the fixed bed, the time for reaching 90% of the initial MB concentration, and the layer saturation time are summarised in Table 5.

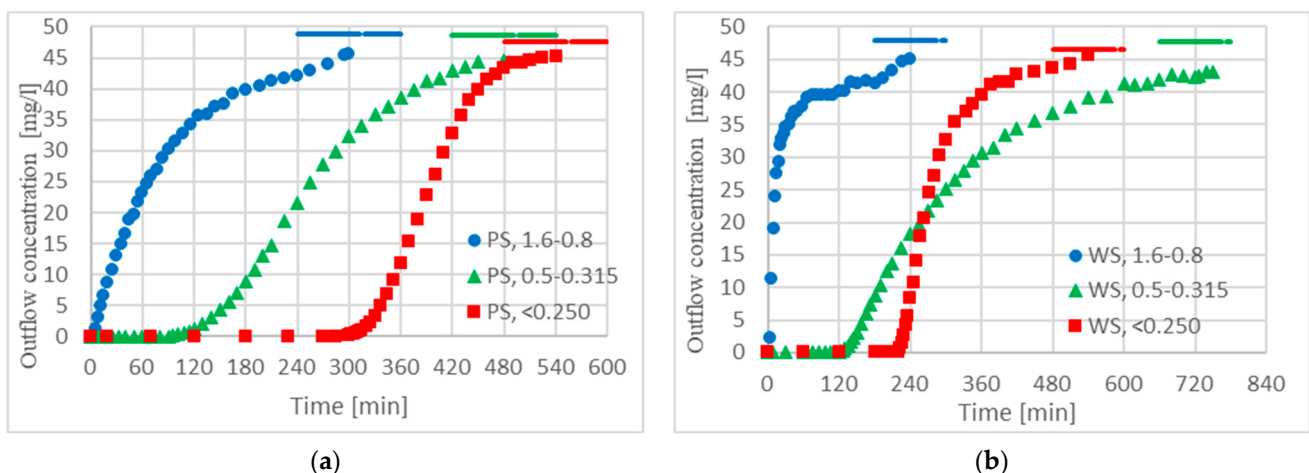


Figure 5. Fixed-bed outflow concentrations of (a) PS and (b) WS for different fractions.

Table 5. Characteristic time ranges of the fixed-bed column tests.

Material	Fraction	Breakthrough Time [min]	Time to Reach 90% of C ₀ [min]	Difference between Breakthrough and Saturation [min]
PS	1.600–0.800	3	275	272
	0.500–0.315	91	435	344
	<0.250	300	480	180
WS	1.600–0.800	3	210	207
	0.500–0.315	120	660	540
	<0.250	220	450	230

The results obtained from the Thomas and Yoon–Nelson models are presented in Table 6.

Table 6. Characteristic time ranges of the fixed-bed column tests for the Thomas and Yoon–Nelson models.

Peanut Shells (PS)				Walnut Shells (WS)			
Fraction	Model Parameters	q_e [mg/g]	R^2	Fraction	Model Parameters	q_e [mg/g]	R^2
Thomas model							
1.600–0.800	$K_{Th} = 0.50$	14	0.67	1.600–0.800	$K_{Th} = 0.39$	0.06	0.50
0.500–0.315	$K_{Th} = 0.47$	46	0.89	0.500–0.315	$K_{Th} = 0.30$	51	0.76
<0.250	$K_{Th} = 0.90$	68	0.95	<0.250	$K_{Th} = 0.62$	49	0.73
Yoon–Nelson model							
1.600–0.800	$K_{yn} = 0.025$; $\tau = 79.3$	14	0.67	1.600–0.800	$K_{yn} = 0.019$; $\tau = 0.4$	0.06	0.50
0.500–0.315	$K_{yn} = 0.023$; $\tau = 264.6$	46	0.89	0.500–0.315	$K_{yn} = 0.014$; $\tau = 306.0$	51	0.76
<0.250	$K_{yn} = 0.041$; $\tau = 395.4$	68	0.95	<0.250	$K_{yn} = 0.030$; $\tau = 284.8$	49	0.73

To examine more closely the observed fixed-bed column behaviour with WS medium and small fractions, additional tests were conducted with increased flow—39, 60, and 91 mL/min, respectively. This led to decreased contact times of around 8%, 67%, and 152% compared to the first tests. After applying the Thomas and Yoon–Nelson models, it was established that the total adsorption capacity decreased (Figure 6), and for 60 and 91 mL/min, the capacity of the small fraction was slightly bigger than the medium fraction.

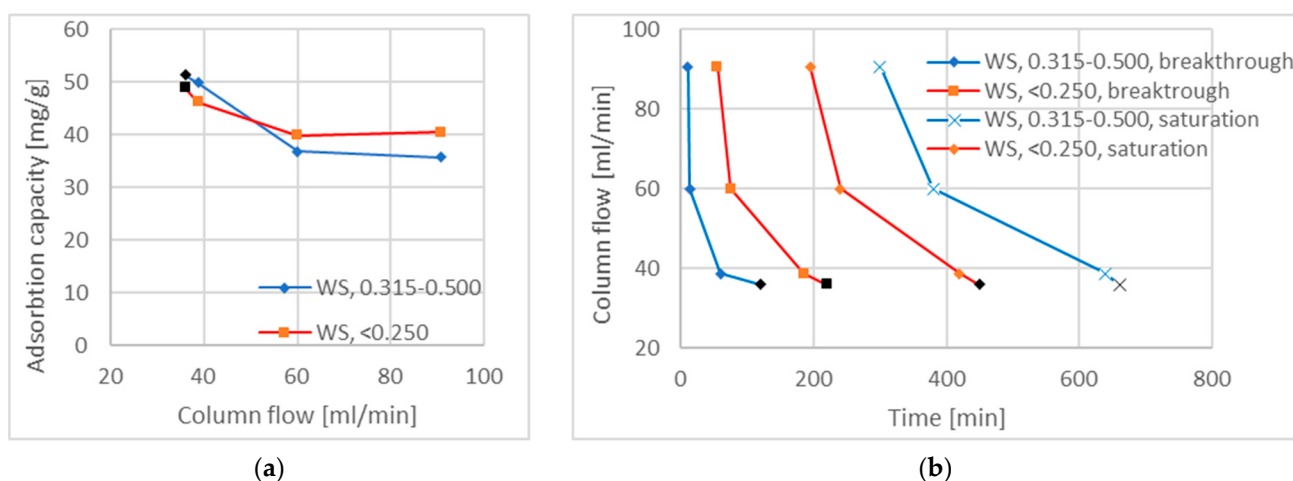


Figure 6. WS fixed-bed small and medium fractions—(a) capacity, and (b) characteristic times.

4. Discussion

4.1. Characterisation of the Samples

The results of the BET analysis show that PS and WS, in their natural states, have a relatively small surface area. The comparison of the pictures before and after the adsorption of MB dye in SEM analyses (Figure 2) corresponds to a smoothing of the porous structure of the samples and a more uniform morphology, which suggests the formation of a coating on the surface of the materials. An MB molecule covering the surface of PS and WS can also be observed as an accumulated spherical shape on the material, which is a prerequisite for successful dye adsorption. Similar observations are made by other authors [27,28].

The FTIR spectra have typical characteristics of lignocellulosic materials (cellulose, hemicellulose, and lignin) and are close to the results published in the literature for peanut and walnut shells [18,29,30]. Similar results of the FTIR spectrum for both PS and WS prove the presence of hydroxyl, amino, ester, and carbonyl groups, which contribute to

the negative charge of the surfaces. This is a favourable prerequisite for the binding of cationic MB dye molecules. It can be suggested that the adsorption takes place through the functional groups present on the surfaces of both materials. Similar conclusions are drawn by other authors [29,30].

4.2. Adsorption Experiments

4.2.1. Batch Studies for Estimation of the Relative Surface Area of MB

The results presented in Table 1 for PS and WS show that the q_e and S_{MB} of these shells in their natural state are comparable with the published results for other biosorbents from nut shells, but in a modified state [17]. Usually, the modifications increase the capacity of biosorbents, and similar results could also be expected for PS and WS in a modified state. This will be subject to future research. The presented results should be regarded as background for evaluating the potential of PS and WS as biosorbents without incurring additional costs for modification.

4.2.2. Adsorbent Dosage

A general trend of increasing adsorption efficiency (%) and decreasing adsorption capacity (q_e) with the increase of the dose of added adsorbent is observed for both materials. Such results are commonly reported for adsorption systems since the increase in dosage creates more vacancies (pores) [21]. The highest adsorption efficiency (about 90%) is at the dosage of WS and PS of 4 g/L, however, the difference between a dose of 2.5 g/L and a dose of 4 g/L is not significant. The highest observed adsorption capacity is 46.90 mg/g for WS; and 53.14 mg/g for PS at a dose of 1 g/L. In their study on walnut shells as a low-cost adsorbent for MB dye removal, Uddin and Nasar also found the same tendency [27]. Similar results were also observed by Boumchita et al. for peanut shells [31].

4.2.3. Langmuir and Freundlich Models

The obtained results show that the proposed mathematical models describe the experimental adsorption data of MB on walnut and peanut shells with almost equal accuracy. Based on the higher values of the correlation coefficients (r^2) obtained with the Langmuir equations compared to those of Freundlich (Table 3), it can be assumed that the active sites are rather homogeneously distributed on the surface of the adsorbents, confirming monolayer adsorption of the physical type. Our previous studies of PS produced similar results [32].

Boumchita et al. also concluded that there are rather homogeneously distributed sites on the surface of peanut shells with a maximum monolayer adsorption capacity [31]. Farch et al. confirmed the physical-type monolayer adsorption, reaching the maximum removal of MB dye with WS as an adsorbent [33]. In their study, they reached a maximum adsorption capacity of $q_{max} = 21.25$ mg/g at a dye concentration of 10–50 mg/L (20.05 mg/g in the current study—Table 2). The comparison of the obtained results regarding Langmuir maximum adsorption capacity (q_{max}) with other biosorbents is summarised in Table 7.

Table 7. The adsorption capacity of different biosorbents.

Adsorbent	Dye	q_e (mg/g)	Reference
Peanut hull	MB	68.03	[34]
Brazil nut shells	MB	7.81	[35]
Walnut shell	MB	51.55	[29]
Cyanthilium cinereum	MB	76.34	[36]
Paspalum maritimum		56.18	
Walnut shell	MB	41.5	This work
Peanut shell	MB	46.8	This work

4.3. Fixed-Bed Column Tests

Although the granulated fractions are widely used for active carbon adsorption columns, it seems that for peanut and walnut shells in their natural state, smaller diameters will be more beneficial for practical purposes if they are used as biosorbents. Obviously, with the decrease in particle size, the time before breakthrough increases at the same hydraulic conditions, adsorbent mass in the column, and initial MB concentration. This is a logical result because the smaller fractions should have more surface area, so the adsorption capacity should be greater. On the other hand, the small number of vacancies on the surface of the fraction 1.6–0.8 mm can be the reason for the fast breakthrough. However, it is interesting that the needed time for full saturation of the medium fraction for both materials (0.5–0.315 mm) is much bigger compared to the large (1.6–0.8 mm) and small (<0.250 mm) fractions, especially for the WS.

The BET, FTIR, and SEM analyses show that there are two sorption mechanisms for MB—due to functional groups and due to physical adsorption over the mesopores on the surface. It seems that the needed time for the full formation of the coating over the particle size is related not only to the number of distributed sites (i.e., with the surface area) but also to the type of the sites, whose ratio may differ with the change in particle size. This can partly explain the obtained results from the Thomas and Yoon–Nelson models that the total adsorption capacity of the medium fraction WS is slightly higher than that of one of the small fractions (Table 6). Tang et al. also observed that the effectiveness of walnut shells for removing MB from aqueous solutions is not proportionally related to their surface area [29]. The removal efficiency of particles with sizes of 0.841 mm and 0.25 mm and a surface area of 1.01 m²/g and 1.24 m²/g, respectively (estimated with BET analysis), increases from around 45% to around 80%. However, the increase in removal efficiency of particles 0.177 mm and 0.125 mm, or 2.82 m²/g and 3.12 m²/g, respectively, is negligible—97% to 99%.

However, no significant differences in the behaviour are observed for both powdered and medium fractions by changing the flow velocity, which also signifies that the total surface area is not the only factor for the determination of the adsorption capacity for the WS. Changes in the flow did not affect the shape of the S curves for small and medium-sized WS, and the described tendency stayed the same. Overall, it can be said that particle size plays an important role in the rate of adsorption in the fixed-bed column because for a smaller fraction, the breakthrough time is longer.

5. Conclusions

Peanut and walnut shells exhibit adsorption properties towards cationic dyes, particularly methylene blue. It could be concluded that two parallel mechanisms occur at the surface of the particles: adsorption due to functional groups and a physical one over the mesopores. In almost all the tests conducted, PS showed a higher adsorption capacity than WS. Most probably, this is a consequence of the larger surface area of particles of the same size. The analysis shows that the total volume of the mesopores and the types of functional groups are almost the same for both materials, so the higher adsorption capacity of PS can be attributed to the larger number of functional groups on the surface.

From a practical point of view, the adsorbents can be added as reagents to the flow during the water treatment process or used as a fixed bed through which water passes. For the same initial concentration of MB (50 mg/L), fixed-bed treatment led to a higher total adsorption capacity for both materials: 51 mg/g compared to 20 mg/g for WS and 46 mg/g compared to 17.5 mg/g for PS. This can be explained by the fact that, in fixed-bed columns, diffusion does not play as much of a role in the adsorption process.

For peanut shells, it is observed that there is a clear inversely proportional tendency between particle size on the one hand and adsorption capacity and column breakthrough time on the other hand. An interesting observation for walnut shells was the difference in the shape of the S curve for different fractions and almost the same adsorption capacity for small (<0.25 mm) and medium (0.315–0.5 mm) particle sizes in a fixed-bed column.

Although it is not clear what the reason for that is, it seems that from one point on, the particle size of the WS does not have much influence over the adsorption capacity but rather over the rate of adsorption. For a full understanding of this observation, further studies need to be conducted.

Author Contributions: Conceptualization, S.L., R.T. and S.D.; Methodology, S.L., R.T. and S.D.; Validation, S.D.; Formal analysis, S.L., R.T. and I.M.; Investigation, S.L., R.T. and I.M.; Data curation, S.L., R.T. and I.M.; Writing—original draft, S.L. and R.T.; Writing—review & editing, S.D. and G.D.; Visualization, S.L. and R.T.; Supervision, S.D. and G.D.; Project administration, S.D. and G.D.; Funding acquisition, S.D. and G.D. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Project BG05M2OP001-1.002-0019: “Clean technologies for sustainable environment—water, waste, and energy for circular economy”, financed by the Operational Programme “Science and Education for Smart Growth” 2014–2020, co-financed by the European Union through the European structural and investment funds. Some of the data and analysis are developed under contract BN-242/20, financially supported by the Centre for Scientific Research and Design at the UACEG. Part of the article processing charges were covered by the University of Architecture, Civil Engineering, and Geodesy.

Data Availability Statement: The data that support the findings of this study are available from the corresponding author upon reasonable request.

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

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