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Utilization of Biomass Waste at Water Treatment

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Abstract: This work presents some preliminary results on the direct use of untreated biomass from agricultural activities as adsorbents for water treatment. Waste was also used to produce activated carbons (ACs) by chemical activation with KOH. The efficacy of agricultural waste such as stubble, sawdust from Teak (*Tectona Grandis*), fibers from Imbondeiro (*Adansonia digitata* L.), bamboo flowers, and other regional plants were tested on methylene blue (MB) removal from the aqueous phase. Adsorption studies were conducted in a batch system and the influence of kinetics, pH, and temperature was evaluated. The adsorption performance of the natural adsorbents was significantly high concerning MB. In particular, Imbondeiro presented a maximum removal capacity of 188.3 mg per gram. This amount was similar to or even higher than the values obtained on ACs produced by their predecessors at 873 K. The studies were finished by constructing slow filters containing natural adsorbents or ACs. The maximum amounts of MB removed on a continuous flux were lower than those obtained for a diversity of untreated biomass types on a batch system. However, these amounts were comparable to the published results obtained on a diversity of untreated biomasses in batch mode.

Keywords: biomass utilization; natural adsorbents; dyes removal; water treatment

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1. Introduction

Water is a crucial resource for the development and survival of plants and animals. Since 1980, freshwater consumption has increased by about 1% per year [1]. While industrialized countries have observed a decline in water use, developing and undeveloped countries have seen the opposite trend. Worldwide, more than 69% of freshwater is used for agricultural activities, which, together with the increase in urbanization and industrialization, has led to a massive water contamination [1–3]. In the water supply overview provided by the World Bank [2], it is noted that two billion people around the world do not have access to drinking water of adequate quality [2] or basic sanitation, which leads to the deaths of almost 829,000 people per year [3,4].

In Mozambique, in 2011, 90% of deaths from cancer, malaria, and diarrheal diseases were attributed to the ingestion of contaminated water. Approximately 65% of people living in rural areas treat drinking water at their own homes using only a rudimentary leachate system [5].

To reduce the global burden of diseases, it is essential to implement appropriate treatment methods before water consumption. Based on the advantages and disadvantages

of different methods tested to treat water, adsorption, particularly on activated carbons (ACs), has been highlighted [6–10]. The ease of use, low implementation costs, potential for multiple reuse of the adsorbent materials, and the recuperation of the adsorbate are the main benefits of the adsorption process [11]. However, the production costs of ACs, combined with the difficulty of supplying remote and isolated areas and the need for sustainable management of saturated adsorbents, restrict their application [12,13]. To replace ACs, various types of biosorbents and biomasses, without any treatment, have been used as alternative adsorbents to remove organic pollutants from liquid effluents [13–21]. Srivinasan et al. (2010) examined the performance of various biosorbents (fungi, bacteria, algae, chitosan, and peat) and other low-cost adsorbents (peat, bentonite, steel-plant slag, fly ash, China clay, maize cob, wood shavings, and silica) on the removal of dyes from wastewater [19]. Mohammed et al. (2014) presented a list of studies focused on the use of natural adsorbents in the removal of MB, tested between 2003 and 2013 [13]. Katubi et al. (2021) presented a list of published results concerning the use of biomass as a natural adsorbent or coagulant for the removal of dyes and metals from aqueous solutions [14]. In 2020, Mohammed et al. presented a list of studies concerning the use of ACs prepared from agricultural wastes on the removal of methylene blue, methyl orange, and methyl red dyes from the aqueous phase [15].

Table 1 presents some findings related to using natural adsorbents, without any treatment, in eliminating MB from the aqueous phase.

Table 1. Optimal conditions used for MB removal from the aqueous phase using natural adsorbents.

Adsorbents	Q_{ads} mg g^{-1}	pH	Equilibrium Time h	Reference
Barley bran	63.2	5.07	4	[9]
Enset midrib leaf	35.5	5.66	1	[9]
Sugarcane bagasse	9.4		24	[18]
Chlorella vulgaris microalgae	275	--	72	[20]
Corn husk	30.3	6.2	0.25	[21]
Ficus carica bast treated with H_2SO_4	55.56	7.8	1.33	[22]
Natural adsorbents (review)	--	--	--	[12,13]
Potato peel	48.7	--	1.0	[23]
Date palm leaves	43.1	6.5	2.7	[16]
Modified zeolites	133.1			[24]
Hylocereus undatus (dragon fruit peels)	192.31	5.6	0.15–2	[25]

MB has become increasingly important in the field of water treatment because it is environmentally persistent, toxic, carcinogenic, and mutagenic [26–36]. These effects are quite similar to the side effects caused by the majority of organic pollutants present in water used for household activities by rural populations in developed countries. The presence of MB effluents discharged from industries has recently been associated with decreasing the amount of useful water [33].

This work investigated the application of new alternative low-cost adsorbents to replace ACs for methylene blue (MB) removal from the aqueous phase. The adsorbents were waste materials from agricultural and forestry activities, which are easily readily available in Mozambique's rural areas and can be used locally by the residents to treat water before consumption.

2. Materials and Methods

Various types of waste materials from agricultural activities (biomass fractions) have been tested as adsorbents for MB removal from the aqueous phase. The selection of biomass materials was based on their availability in Mozambique. Sawdust from *Teak* (T), wood from *Adansonia digitata* L. (I), trunks and flowers of bamboo (FB), trunks and flowers of Mayan (FM), and stubble (S) were used as adsorbents, collected directly from the field. Figure 1 shows the low-cost natural adsorbents employed in the removal of MB from the aqueous phase. For comparative purposes, the natural biomass materials were also converted into activated carbons (ACs). The precursors were only submitted to a chemical activation with KOH in a ratio of 1:1 (w/w) at 873 K. The yield of the process that allowed the production of ACs ranged from 17 to 21%.

(**a**) Tectona Grandis (T) (**b**) Imbondeiro (Imb) (**c**) Stubble (S) (**d**) Bamboo flowers (BF) (**e**) Maia flowers (FM)

Figure 1. Low-cost adsorbents used on MB removal from the aqueous phase. Photos are the authors' own.

2.1. Pre-Treatment of Natural Adsorbents

The different types of biomass were dried using sunlight (303 K) for a week and then in an oven at 353 K until the mass remained constant. After drying, the natural adsorbents (FB, S, FM, T, and I) were reduced to smaller sizes and subsequently crushed. These were washed with 2 L of distilled water at 353 K for 2 h to remove impurities. The adsorbents were screened in fractions smaller than 2.5 and 1.25 mm before being used in the following studies.

2.2. Activated Carbon Production

For comparative purposes, the natural adsorbents were also converted into activated carbon (AC). The precursors were mixed with KOH, purchased from VWR, Portugal, in a ratio of 1:1 (w/w) and subjected to a heating ramp of 10 K min^{-1} until 873 or 973 K, then remained at this temperature for 30 min. The AC production took place in a semi-industrial rotary horizontal tubular furnace. ACs were produced and cooled always under a flow of 70 mL min^{-1} of nitrogen. The ACs were washed with distilled water until the pH of the washing water was close to 7, and then dried at 363 K.

2.3. Adsorbent Characterization

All natural adsorbents and their respective ACs were characterized by elemental analysis (EA), scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX), attenuated total reflectance-Fourier transform infrared (ATR-FTIR) analysis, and through the determination of the pH at the point of zero charge (pHpzc); the procedures are detailed in a previous work [8]. CHNS-O analysis was carried out, in triplicate, using a Eurovector EuroEA elemental analyzer. The morphology of the adsorbent was examined using a Phenom ProX Desktop Scanning Electron Microscope (SEM) instrument with an accelerating voltage set from 5 to 15 kV. The surface of the adsorbents was scanned by ATR-FTIR spectroscopy analysis between 400 and 4000 cm^{-1}. The analysis was performed on a PerkinElmer Spectrum Two IR spectrophotometer with an attenuated total reflection accessory. The pHpzc was determined by the mass titration technique using 7% mass/volume suspensions of adsorbent material in a solution of sodium nitrate

(0.1 mol L^{-1}). The suspensions were left in a bath under agitation (20 rpm) for 48 h, and then the pH of the supernatant was measured.

2.4. Dyes Adsorption

To address the various colorless contaminants present in the well waters serving rural populations of Mozambique, methylene blue (MB), a cationic dye, was used. MB ($C_{16}H_{18}ClN_3S$) with a purity higher than 85% was purchased from Sigma Aldrich, Madrid, Spain. The influence of the pH of the medium on pollutant removal was evaluated by adjusting the pH to values ranging from 3 to 11 using HCl or NaOH (0.1 mol L^{-1}) as necessary. MB kinetic studies were conducted up to 168 h at T = 298 K and pH 6.

To obtain the adsorption isotherms, a fixed amount of adsorbent (natural materials—25.0 mg, ACs—10.0 mg) was added to a series of Erlenmeyer flasks. A fixed volume (25.0 mL) of aqueous solution, with concentrations ranging from 0 to 400 mg L^{-1} of MB, was added to each. The suspensions were agitated at 20 rpm in a shaking bath, a Linear model—Grant, at 298 K, for a period of 24 h. After this time, the suspensions were filtered and diluted if necessary, and the residual concentrations of MB were determined by UV–Vis spectrophotometry using a Nicolet Evolution 300 Spectrophotometer from Thermo Electron Corporation. The amount of MB present in the solution was evaluated by measuring the absorbance at its characteristic wavelengths (i.e., 668 nm). The quantity of dye retained by the adsorbents, Q_{ads}, was determined from the difference between the initial and remaining MB amounts in solution, considering the volume of the solution and the mass of the adsorbent, using Equation (1).

$$Qads = \frac{(Ci - Ceq)}{m} \times V \quad (1)$$

The percentage of removal of MB removal was evaluated using Equation (2).

$$R\ (\%) = \frac{(Ci - Ceq)}{Ci} \times 100 \quad (2)$$

In Equations (1) and (2), Q_{ads} is the amount of dye adsorbed by the mass of adsorbent (mg g^{-1}), R (%) is the percentage removal, C_i and C_{eq} represent the initial and equilibrium dye concentrations (mg L^{-1}), V is the volume of dye solution (L), and m represents the mass of the adsorbent (g).

2.5. Preparation of Filters Containing Natural Adsorbents or ACs

Filters containing natural adsorbents or ACs were prepared as illustrated in Figure 2. PET bottles were used, and in the narrowest part (with an inner diameter of 2.5 cm), a layer of cotton, followed by successive layers of 2 cm each of gravel, coarse, and fine sand, and the adsorbent under study. The filter ended with another layer of 2 cm of fine sand to prevent the adsorbent from floating during filtration.

A total of 250 mL of a solution containing 50 mg L^{-1} of MB was passed through the filter at a flux varying between 25 and 30 mL per minute. The filtrate was filtered again until the amount of MB in the filtrate remained under the limit quantification of the equipment. In this situation, 250 mL of the initial solution (50 mg L^{-1}) was used for a new cycle. The passage of the solution through the filter continued until the pollutant concentration in the filtrate reached zero or remained constant. The amount of MB present in the filtrate after each passage through the filter was evaluated by spectrophotometry.

Figure 2. Preparation of filters containing sand and low-cost adsorbents. Different steps in the filtration process (Photo is the authors' own).

3. Results

3.1. Adsorbent Characterization

Biomass materials (as collected from the field) and their respective ACs were characterized through Fourier transform infrared spectroscopy by ATR-FTIR analysis. Representative spectra of the natural adsorbents (Imbondeiro (Imb)), Imbondeiro saturated with MB (Im + MB)), and its respective AC (AC-Imb-KOH-873) are included in Figure 3.

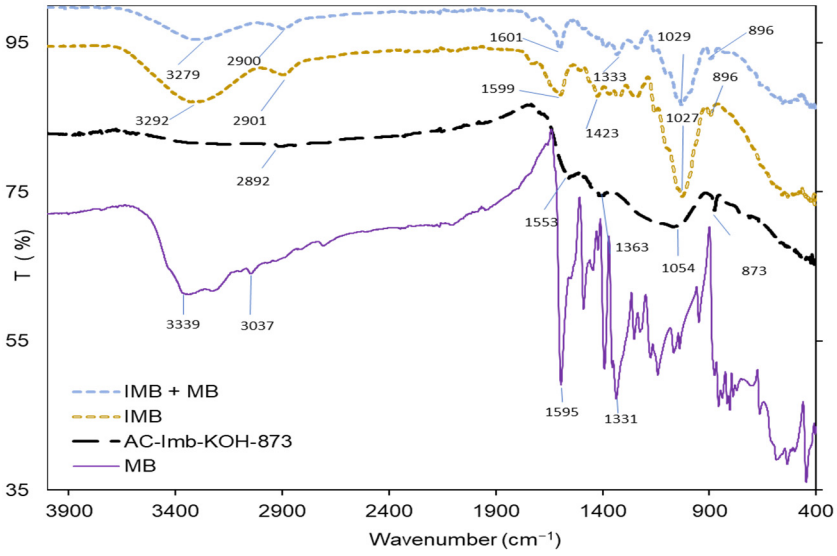


Figure 3. FTIR spectra obtained on Imb saturated with MB; Imb and AC prepared from Imb and MB.

The predominant functional groups in biomass materials are phenolics, carbonyls, esters, ethers, and hydroxyl, separately or combined in different proportions. The natural adsorbents, even after being saturated with MB, exhibited a wide and well-defined band at 3292 and 3279 cm^{-1}, respectively. The band observed may be caused by the vibrations of O-H or NH groups in stretch mode. The bands with a lower intensity, around 2900 cm^{-1}, corresponded to the C-H stretching in the methyl and methylene groups in symmetrical and asymmetric modes. Both bands were less expressed in the spectra of the ACs. The bands around 1600 cm^{-1} corresponded to C=C stretching mode in a ring structure This band was

also present on the ACs, but at a lower wavenumber (1553 cm^{-1}). The bands between 1330, 1363, and 1423 corresponded to a C-OH bending mode. The band at 1029 and 1027 cm^{-1} can be attributed to vibrations of the C-O bond in a primary or secondary C-OH group. These bands were less intense in the spectra of their respective ACs. The band at 896 cm $^{-1}$ corresponded to a C=C bending in an alkene. On the ACs, this band was more intense, identifying the presence of aromatic structures. On the spent adsorbent, some small bands were shifted to a slightly lower wavenumber, which suggests the interactions of dye molecules with the functional groups of the biosorbent [27].

The chemical composition of the natural adsorbents and ACs was determined through elemental analysis and SEM-EDX. The point of zero charge (pHpzc) was also evaluated and the data are presented in Table 2. The natural adsorbents presented an acidic pHpzc, varying from 4.4 to 5.4. The ACs presented a more basic pHpzc, varying from 6.9 to 7.7. The surface morphology of the natural adsorbents and their respective ACs was examined by SEM, as shown in Figure 4a–j. The ACs retained the physical form of their precursors. In particular, in the ACs produced from stubble and Imbondeiro, the presence of elongated fibers was identified. According to the EDX data, the ACs had a lower oxygen and higher carbon content than their precursors. During the activation process, the most volatile organic compounds are released, leading to a reduction in oxygen and an increase in carbon content.

Table 2. Elemental composition of the natural adsorbents and ACs (expressed in % *w*/*w*) obtained by elemental analysis (EA) and EDX. AC-Imb-KOH−873—means AC prepared from Imbondeiro at 873 K.

Adsorbents	EA			EDX			pHpzc
	N	C	H	C	O	N	
Stubble (S)	--	--	--	34.4	66.6	3.5	4.4
Teak (T)	--	--	--	32.1	67.9	--	4.7
Imbondeiro (Imb)	--	--	--	34.1	65.9	--	5.4
Bamboo flower (FB)	--	--	--	27.1	66.6	6.3	5.1
Mayan flower (FM)	--	--	--	26.0	68.1	5.9	4.6
AC-S-KOH-873	0.7	69.3	0.1	41.7	58.3	--	7.4
AC-T-KOH-873	0.4	78.3	1.2	48.1	51.9	--	7.1
AC-Imb-KOH-873	0.6	72.1	--	44.4	55.6	--	6.9
AC-FB-KOH-873	1.3	70.5	0.1	42.8	57.2	--	6.7
AC-FM-KOH-873	2.7	70.5	0.9	46.4	53.6	--	7.7

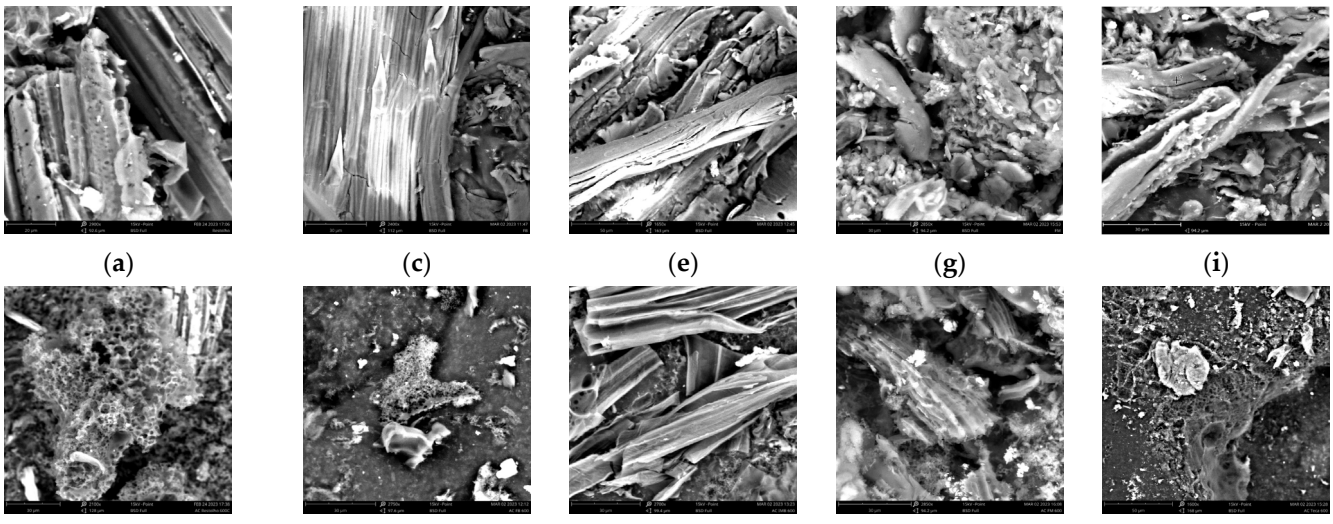


Figure 4. SEM images. (**a**) Stubble. (**b**) AC-S-KOH-700. (**c**) Bamboo flower. (**d**) AC-FB-KOH-700. (**e**) Imbondeiro. (**f**) AC-Imb-KOH-700. (**g**) Mayan flower. (**h**) AC-FM-KOH-700. (**i**) Teak. (**j**) AC-T-KOH-700.

ACs from Teak, which presented an excellent performance concerning pesticide removal from the aqueous phase, were also used for comparative purposes. These ACs were produced at 873 and 973 K through activation with KOH and K_2CO_3 in a ratio of 1:1 (*w*/*w*), and their textural features are shown in Table 3. The ACs prepared at 973 K presented a higher apparent surface area and microporous volume. Another noteworthy point is that ACs prepared at a lower temperature (873 K) presented a relatively narrow average pore size, which could limit the pollutant's access to the pores.

Table 3. Structural parameters of the ACs prepared from Teak by chemical activation at different temperatures (data were from [8]). In Table 3, η refers to the AC production yield (η was evaluated by the mass ratio between the AC and the precursor used), expressed in percentage; A_{BET} is the apparent surface area; V_s is the total volume; A_s is the external surface area (V_s and A_s were obtained using the alpha-s method proposed by Carrott et al. (1987) [26]); V_0 is the microporous volume; E_o is the energy of adsorption; L_0 is the mean pore size (V_0, E_0, and L_0 were obtained through the application of the Dubinin–Radushkevich equation) [27].

Samples	η	A_{BET}	α_s			DR	
	%	$m^2\ g^{-1}$	A_s $m^2\ g^{-1}$	V_s $cm^3\ g^{-1}$	V_0 $cm^3\ g^{-1}$	E_0 $kJ\ mol^{-1}$	L_0 nm
AC-T-KOH-1-1-873	20.4	581	21	0.20	0.15	25.40	0.77
AC-T-KOH-1-1-973	19.1	908	57	0.40	0.33	17.40	1.79
AC-T-K_2CO_3-1-1-873	16.0	554	32	0.23	0.14	21.7	1.17
AC-T-K_2CO_3-1-1-973	15.1	1736	27	0.79	0.44	19.0	1.43

3.2. MB Adsorption on Natural Low-Cost Adsorbents

Various types of biomass were selected to be tested in the removal of dyes from the aqueous phase. During this work, only *Adansonia digitata* L. (Imbondeiro), the sawdust of *Teak*, stubble, bamboo flower, and Mayan flower were kept to be tested for the removal of MB from the liquid phase. Methylene blue (MB) was used as a probe molecule to test natural adsorbents in the removal of colored organic compounds from the aqueous phase.

The effect of the contact time was evaluated initially using a dilute solution with 4 mg L^{-1} of MB on the natural adsorbents. For this concentration, the percentage removal reached more than 90% after a contact time of 2 h, as presented in Figure 5. In the *Teak* adsorbent, which is a hardwood, at a lower MB concentration (T—4 ppm), adsorption was slower when compared with Imb (I—4 ppm). As Imb showed a higher adsorption capacity when compared with S, T, FB, and FM, the following optimization conditions were conducted with it. Subsequently, the influence of contact time was reevaluated using a MB concentrated solution on selected adsorbents such as Imbondeiro and ACs prepared from Imbondeiro and *Teak* (AC-Imb-KOH-973 and AC-T-KOH-973). A solution with a MB concentration exceeding 200 mg L^{-1} at pH 6 was used and results are also included in Figure 5. From the concentrated solutions, the adsorption equilibrium was approached slower. For Imbondeiro and its respective AC, the adsorption equilibrium was attained after 48 h, while for AC-T-KOH-973, the adsorption equilibrium approach was even slower. Initially, the adsorption process was fast, before slowing down, until it reached a steady state.

To better understand the adsorption phenomenon, kinetic studies were examined based on the pseudo-first-order and pseudo-second-order reactions. Data obtained from the adjustment to the experimental results are included in Table 4 and Figure 6a,b. Both graphs present a good correlation with the experimental data.

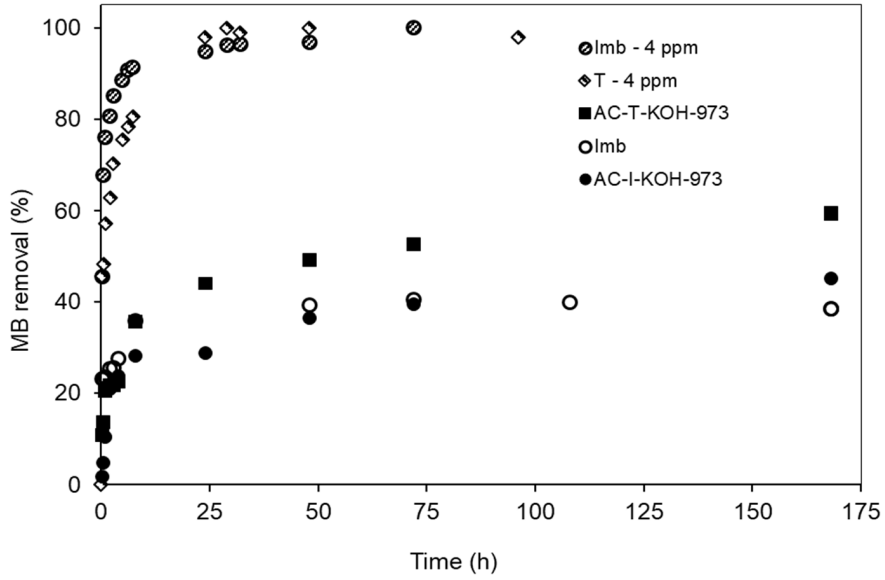
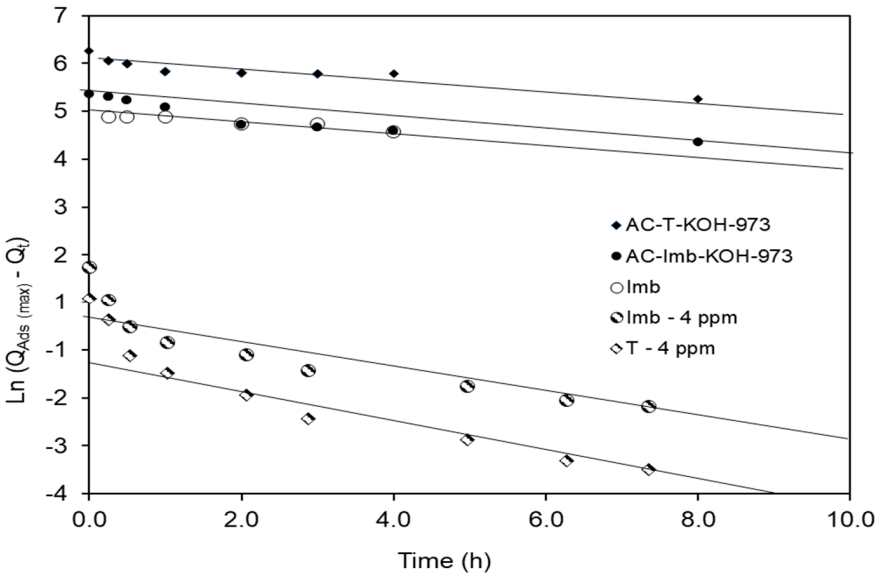


Figure 5. Kinetic study of the MB adsorption on the Imb natural material, AC-Imb-KOH-973 K, and AC-T-KOH-973 K.

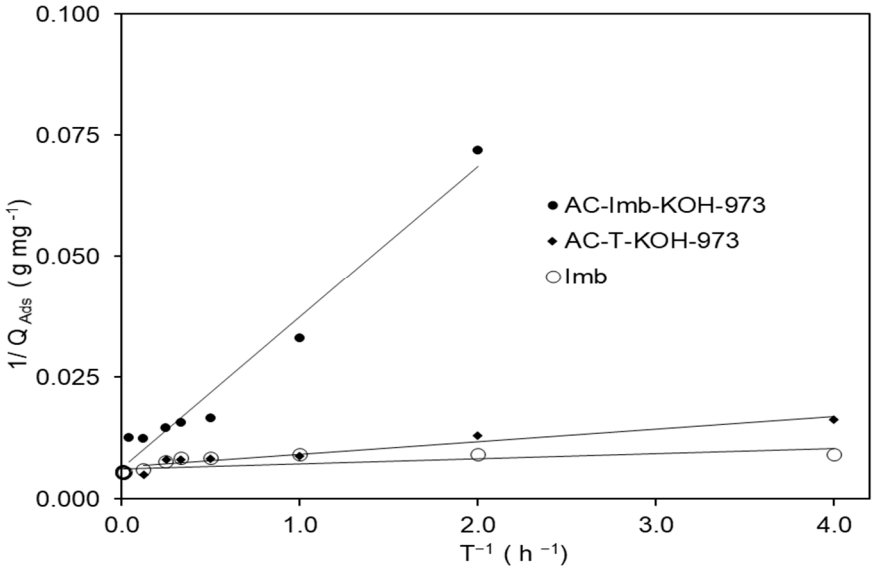
Table 4. Parameters of the application of the pseudo-first-order and pseudo-second-order models. The kinetic studies were conducted from diluted (4 mg L^{-1}) on Imb (Imb—4 ppm) and T (T—4 ppm) and on Imb, AC-T-KOH-973, and AC-Imb-KOH-973 from concentrated solutions (250 mg L^{-1}).

Adsorbents	$Q_{max,\ exp}$ $Q_{max\ (Exp)}$ mg g^{-1}	Pseudo-First-Order Model			Pseudo-Second-Order Model			
		$Q_{max1,\ cal1}$ mg g^{-1}	K_1 h^{-1}	R^2	$Q_{max,\ cal2}$ mg g^{-1}	V_0 mg g^{-1} h^{-1}	K_2 h^{-1}	R^2
Imb—4 ppm	3.3	1.27	0.34	0.89	3.2	14.2	1.23	0.97
T—4 ppm	3.2	0.54	0.36	0.96	3.2	3.2	0.32	0.97
Imb	188.3	83.3	0.0792	0.92	175.5	227.3	0.007	0.83
AC-Imb-KOH-973	123.4	120.7	0.0209	0.91	142.9	32.7	0.020	0.92
AC-T-KOH-973	156.1	249.1	0.0924	0.85	149.3	400	0.018	0.97



(**a**)

Figure 6. *Cont.*



(**b**)

Figure 6. (**a**) Linearization plot of pseudo-first-order for the MB adsorption kinetics from diluted and concentrated solutions. (**b**) Linearization plot of pseudo-second-order for the MB adsorption kinetics.

3.3. The Sevond Figure Has a Minus Signal

The maximum amount of MB adsorbed, calculated from the pseudo-second-order model, was closer to the maximum amount of MB obtained experimentally. Therefore, it can be inferred that the MB adsorption onto the different adsorbents follows a pseudo-second-order reaction, agreeing with Jahan et al. (2023) [31].

From the diluted solutions, the MB adsorption velocity was higher on the Imb when compared with other natural adsorbents, mainly with T. However, MB adsorption presented a higher velocity when obtained from the MB-concentrated solutions.

The effects of the solution pH on MB adsorption by the five natural adsorbents are presented in Figure 7. MB adsorption exhibited significant favorability at a pH higher than 6.0. The amount of MB adsorbed at pH 10.0 was only slightly higher than that obtained at pH 6. Since all natural adsorbents had pH_{pzc} values in the range of 4.4 to 5.4, (Table 2), their behaviors were virtually identical. When the surfaces of the natural adsorbents were negatively charged at pH 6 (pH > 5.4), MB adsorption was favorable. At a pH lower than 4.6, the adsorbents were positively charged (pH 3.0), leading to increased electrostatic repulsion.

Subsequent MB adsorption assays were conducted at a pH 6, which is close to the pH of some industrial effluents, in agreement with Kong et al. (2013) [17] and Selmi et al. (2020) [30]. However, Fito et al. (2020) reported the optimum conditions for MB adsorption from the liquid effluent on ACs (initial concentration of MB = 100 mg L^{-1}, pH 9, contact time of 60 min; adsorbent dosage of 60 mg/100 mL). The maximum adsorption capacity achieved was 322 mg g^{-1} on an AC prepared from the Rumex Abyssinicus plant, which has a surface area of 2522 m^2 g^{-1} [32].

Additionally, the effect of temperature on the MB adsorption using the natural adsorbents was assessed. After an extensive contact time (>6 h), the rise in temperature did not appear to have any appreciable impact, as shown in Figure 8. However, for shorter contact times, less than 3 h, the MB adsorption was favored at high temperatures.

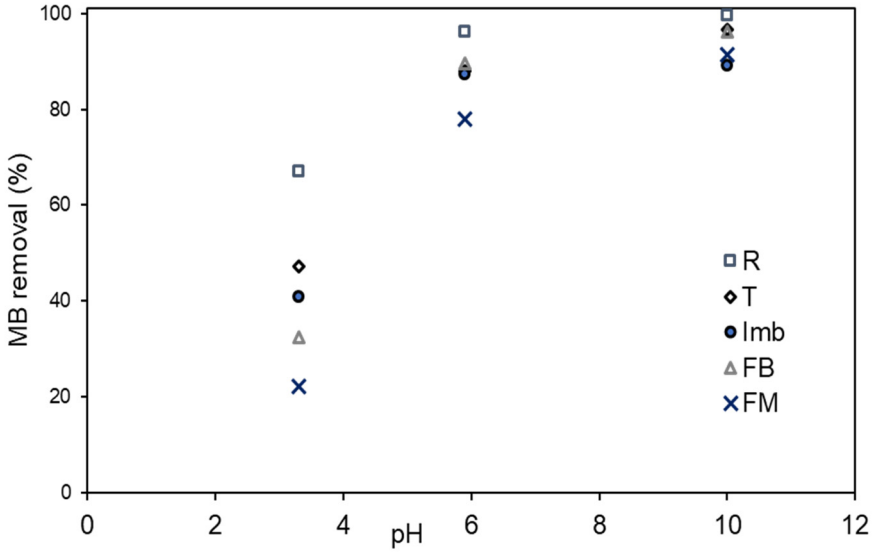


Figure 7. Influence of the pH of the solution on MB adsorption on natural adsorbents (data were obtained from a MB solution with 8 mg L^{-1}. When using a solution with 200 mg L^{-1} on Imb and AC-T-KOH-973, the percentage removal was lower, but the tendency was the same).

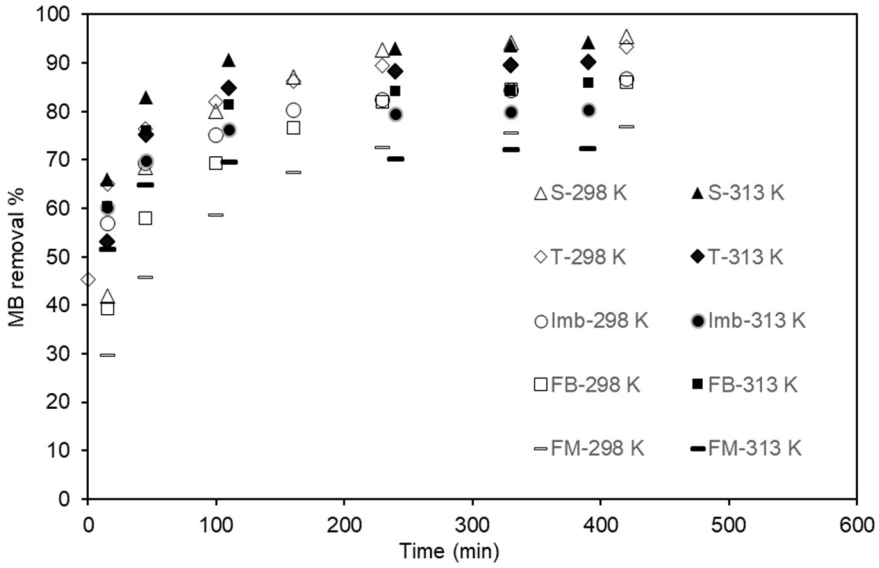


Figure 8. Temperature influence on MB adsorption on natural adsorbents. Open symbols refer to data obtained at 298 K and filled symbols to data obtained at 313 K.

The mechanism of MB adsorption was evaluated based on the change in Gibbs free energy (ΔG°), enthalpy change (ΔH°), and change in entropy (ΔS°). The thermodynamic equilibrium constants K_d ($K_d = Q_{ads}/C_{eq}$) were calculated by the ratio between the amount of MB adsorbed (Q_{ads}) and the MB amount in solution (C_{eq}) [36].

ΔG° was correlated to K_d throughout the following equation, $\Delta G^\circ = -RT \ln K_d$ (T is the temperature and R is the gas constant R = 8.3145 J K^{-1} mol^{-1}). A plot of ΔG° versus T allows for obtaining ΔS° from the slope and ΔH° from the intercept. The thermodynamic parameters obtained on Imb and FB are included in Table 5.

Table 5. Thermodynamic parameters calculated for the MB adsorption on Imb and FB.

Samples	T (K)	K_d	ΔG° (KJ mol^{-1})	ΔH° (KJ mol^{-1})	ΔS° (J K mol^{-1})	R^2
Imb	298.15	6.80	−4.76	−18.83	−46.67	0.75
	303.15	7.02	−4.93			
	313.15	4.89	−5.22			
FB	298.15	7.76	−5.08	12.76	60.05	0.98
	303.15	8.88	−5.51			
	313.15	10.03	−6.01			

On FB and S, it was found that K_d increased with T and a positive value of ΔH°, which indicates an endothermic process. On FM, T, and Imb, the Kd value was more irregular, but the general trend was a decrease with the increase in T. The negative values of ΔH° indicate an exothermic process. The low values of ΔH° indicate that MB adsorption mainly occurs by physical interactions. The negative values of ΔG° confirm that MB adsorption is a spontaneous process.

MB adsorption isotherms were obtained on natural adsorbents and are presented in Figure 9. Imb performed very well when compared with the other natural adsorbents. On particles with granulometry between 1.25 and 2.5 mm, Imb was adsorbed at a maximum of 156.7 mg MB g^{-1}, which was more than double the amount adsorbed on the other natural adsorbents. For comparative purposes, ACs prepared from the five types of biomass (Imb, T, S, FB, and FM) were also tested on MB removal from the aqueous phase. However, the amount of ACs produced from the five types of biomass was small and the production conditions of the ACs were not optimized. For these reasons, only a few assays from the MB concentrated solutions were performed, and the data are presented in Table 6.

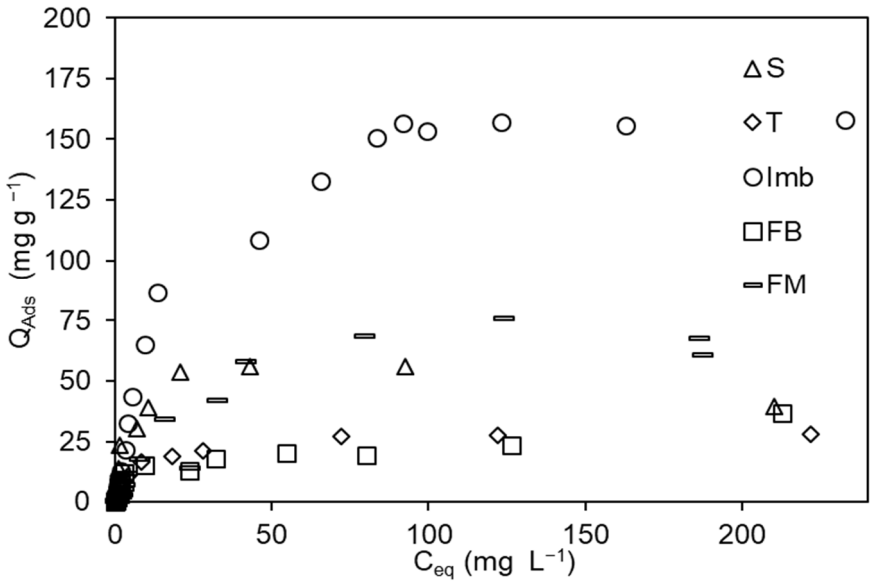


Figure 9. MB adsorption isotherms obtained on the original biomass.

Based on data presented in Table 5 and Figure 9, Imb always adsorbed more MB than other natural adsorbents. The maximum amount of MB adsorbed on S, T, FB, and FM (27.9 to 69.8 mg g^{-1}) was quite similar to the published results. Results available for when biomass was used directly on MB removal are as presented in Table 1 [9,11,15,17] or after being transformed into biochar or ACs [30–32]. More relevant still is that Imb adsorbed a similar or greater amount of MB when compared to its respective ACs. As shown in Table 5, for the same experimental conditions (MB = 250 mg L^{-1}, pH 6, T = 298.0 K, and agitation = 20 rpm), the MB amount adsorbed was 156.8, 123.3, and 156.9 mg g^{-1} for Imb, AC-Imb-KOH−873, and AC-Imb-KOH-973, respectively.

Table 6. Maximum MB amount adsorbed on natural adsorbents and their respective ACs, produced by chemical activation with KOH using a mass ratio of 1:1 at 873 K and 973 K (data were obtained at 298 K from a solution of 250 mg L^{-1} or even 400 mg L^{-1} of MB after a contact time of 24 h).

Adsorbents	MB at pH 6.0 mg g^{-1}	Adsorbents	MB at pH 6.0 g g^{-1}
S	63.7	AC-S-KOH-873	110.4
T	27.9	AC-T-KOH-873	82.7
Imb	156.8	AC-Imb-KOH-873	123.3
FB	42.8	AC-FB-KOH-873	118.0
FM	69.8	AC-FM-KOH-873	95.7
---	---	AC-Imb-KOH-973	156.9
---	---	AC-T-KOH-973	159.7
---	---	AC-T-K_2CO_3-973	248.4

The isotherms presented in Figure 9 were obtained on adsorbents with a particle size less than 2.5 mm. However, the maximum adsorption capacity on Imb was obtained with particles smaller than 1.25 mm, which allowed us to obtain a maximum adsorption capacity of 188.3 mg g^{-1}. The decrease in particle size increased the contact surface area, which favored MB adsorption. The fact that Imbondeiro presented a higher MB adsorption capacity than the ACs prepared at 873 K from the five types of biomass is even more astounding. The data were confirmed by six trials. However, this comparison may reverse if the experimental conditions used to produce the ACs were optimized. Optimizing the activation temperature and the proportion of the precursor to the activating agent would enable the creation of ACs with greater porosity and surface area. It must be highlighted that the ACs produced from Teak and Imbondeiro at 973 K have been found to have superior performance in MB removal from the liquid phase when compared with the Imb and with ACs produced at 873 K, as shown in Table 5.

ACs previously prepared from Teak at 973 K with KOH and K_2CO_3 were tested on MB removal from the aqueous phase. The assays were conducted in triplicate and surprisingly, in similar experimental conditions, the MB removed by the untreated Imb was similar to the amount adsorbed by AC-T-KOH-973. AC-T-KOH-973 was previously identified as presenting a good performance concerning MCPA and the removal of other pesticides from the liquid phase [8]. MB adsorption isotherms obtained on AC-T-KOH-973, AC-T-K_2CO_3-973, AC-Imb-KOH-973, and on the original Imb are presented in Figure 10. The isotherms were modeled using Langmuir and Freundlich equations and the parameters obtained are presented in Table 7. Based on these, the Langmuir equation provided more accurate estimates for MB adsorption than the Freundlich equation.

Table 7. Parameters obtained by fitting the Langmuir and Freundlich equations to the experimental isotherms obtained on Imb, AC-Imb-KOH-973, AC-T-KOH-973, and AC-T-K_2CO_3-973.

Adsorbents	n_{max} mg g^{-1}	n_{mL} mg g^{-1}	K_L L $mmol^{-1}$	R^2	K_F mmolg^{-1} [L $mmol^{-1}]^{1/n_F}$	n_F	R^2
Imb	156.8	153.8	14.1	0.99	1.01	1.69	0.94
AC-Imb-KOH-973	156.9	169.5	12.3	0.97	0.84	3.36	0.94
AC-T-KOH-973	159.7	147.1	4.93	0.95	0.84	2.91	0.94
AC-T-K_2CO_3-973	248.4	250.2	7.65	0.99	0.97	3.09	0.97

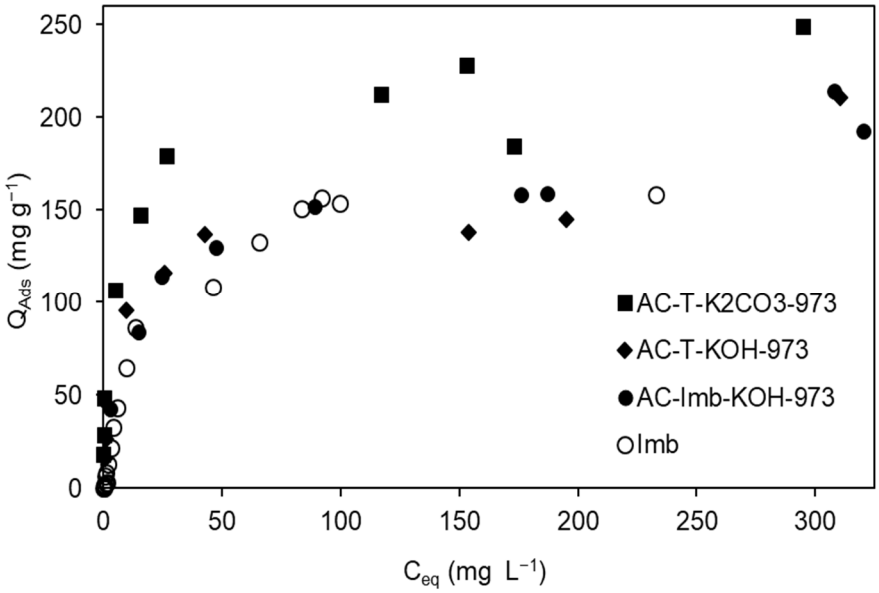


Figure 10. MB adsorption isotherms were obtained on AC-T-KOH-973, AC-T-KO_2CO_3-973, AC-Imb-KOH-973, and Imb after a contact time of 24 h.

Filters containing untreated adsorbents or ACs, as illustrated in Figure 3, which can be used to treat water in rural areas of underdeveloped countries, were tested for MB removal from the aqueous phase. Imbondeiro, bamboo flower, sawdust from Tectona Grandis, stubble, and AC-T-KOH-973 acted as adsorbents for MB removal in continuous mode. The results obtained under continuous flow were less reproducible than those obtained in a batch system. The flow rate of the solution through the filter ranged between 25 and 30 mL min^{-1}, which corresponded to a contact time between the adsorbent and MB of less than 10 min (the contact time in a batch mode was 24 h). However, the prepared filters performed well in removing MB from the aqueous phase, as shown in Table 8. In continuous flow, Imb and AC-T-973 presented a similar maximum amount of MB adsorbed (49.8 mg g^{-1} and 49.1 mg g^{-1}, respectively). The results followed the same trend as those obtained on the batch systems.

Table 8. Maximum MB amount adsorbed on natural adsorbents and AC prepared from Teak by chemical activation with KOH with a ratio of 1:1 at 973 K.

Adsorbent	Methylene Blue at pH 6.0 (Batch Mode) mg g^{-1}	Methylene Blue at pH 6.0 (Continuous Mode) g g^{-1}
S	63.7	24.7
T	27.9	18.2
Imb	156.8	49.8
AC-T-KOH -973	159.7	49.1

With the conditions tested, Imb presented a maximum MB adsorption capacity similar to or even higher than the results obtained on a batch mode with different untreated peels, as shown in the data presented in Table 1 and as reported by Jawada et al. (2018) [35] or on ACs as reported by the same author in 2016 [36].

4. Conclusions

In this study, the adsorption of methylene blue (MB) from the aqueous phase was investigated by a set of natural biomass wastes used as adsorbents. The adsorption process showed significant improvement at a pH > 6 and at a temperature of 298 K. The five untreated biomaterials tested exhibited a considerable adsorption capacity for MB in both batch and continuous systems, presenting a maximum adsorption capacity compared to

the published values. Imbondeiro is a low-cost adsorbent for the effective removal of MB, which presented a maximum removal capacity of 188.3 mg MB per g, which is a higher value than those obtained with their respective ACs. The values of ΔH° were, in all cases, lower than 40 kJ mol^{-1}, which indicates the presence of MB physical adsorption.

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