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Comparative Study of Adsorption of Methylene Blue and Basic Red 9 Using Rice Husks of Different Origins

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Abstract: Methylene blue (MB) and basic red 9 (BR9) are cationic dyes that are commonly used in the dye industry and negatively affect humans and other living organisms. This study compares the performance of Indonesian rice husk (IRH) and Hungarian rice husk (HRH) as bio-adsorbents for removing MB and BR9 from aqueous solutions. Chemical content, zeta potential, and Fourier-transform infrared spectroscopy analyses were used to characterize the rice husks (RHs). Adsorption studies were performed through batch experiments involving several parameters, namely, pH, adsorbent dose, initial dye concentration, contact time, and temperature to observe the self-association (aggregation) of MB and BR9. Adsorption kinetic studies showed that maximum dye removal was achieved at a contact time of 120 min. MB and BR9 adsorption followed a pseudo-second order kinetic model, and the BET multilayer isotherm model provided a better fit to the experimental data of MB and BR9 adsorption. The IRH adsorption capacities were 15.0 mg/g for MB and 7.2 mg/g for BR9, whereas those of HRH were 24.4 mg/g for MB and 8.3 mg/g for BR9. Therefore, these RHs are potential bio-adsorbents for removing MB and BR9 from aqueous solutions.

Keywords: adsorption; basic red 9; bio-adsorbent; methylene blue; rice husk



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1. Introduction

The textile industry is continuously developing and contributing to the world economy. However, this industry is a major global polluter and uses large amounts of water, chemicals, and fuels, which are transformed into highly loaded wastewater [1,2]. These chemicals include cationic dyes such as methylene blue (MB) and basic red 9 (BR9).

MB is mostly used in paper, pharmaceutical, textile, rubber, plastic, food, leather, and cosmetic industries [3,4]. It is also an environmental contaminant that harms humans and other living species. Although it is not highly toxic, it has negative effects, such as heart rate increase, neuronal apoptosis, nausea, inflammation of the leptomeninges, vomiting, and water pollution [3,5].

BR9 is a triamino derivative of triphenylmethane and has the largest dye group within the triarylmethane dye class. It is commonly used in the textile, paper, leather, and ink industries because of its bright color, low energy consumption, and high solubility [6–8]. Under anaerobic conditions, BR9 decomposes into carcinogenic aromatic amines and its release into the environment in the form of wastewater can cause hazardous effects such as cancer, skin irritation, mutations, and allergic dermatitis [8]. According to the European Textile Ecology standard and the International Agency for Research on Cancer (IARC), BR9

is a carcinogenic dye because it endangers the health of humans and other organisms, and biodegrades poorly [6,9].

Wastewater treatment technologies are needed to remove pollutants from dye wastewater, and dye recycling is required to achieve sustainability. Current wastewater treatment technologies include membrane technology, ultrasonication, biological techniques, coagulation/flocculation, photocatalysis, and adsorption [10]. Adsorption is an excellent method for removing dyes from wastewater because of its low processing cost and simple design [11]. Several studies have been conducted on the adsorption of cationic dyes using bio-adsorbents such as date seeds, orange peels, dragon fruit peels, spent *Ganoderma lucidum* substrates, black tea leaves, and wood apple shells [12–17]. These studies show that adsorption is an efficient and the most effective method for the removal of cationic dyes.

Adsorbent materials from natural resources are being developed, and agricultural waste is a prospective resource. Agricultural waste can be a new, inexpensive, efficient, and environmentally friendly material for wastewater treatment. Rice husk (RH), an agricultural waste material, can be used for wastewater treatment because it is water-insoluble and has a granular morphology, good mechanical qualities, and chemical stability. RH has excellent adsorption ability because it is rich in active functional groups such as carboxyl and phenolic groups [18,19]. In general, raw RHs of different origins have good physical properties, including a Brunauer–Emmett–Teller (BET) specific surface area of 0.65–2.56 m²/g and a pore diameter of 6.1–7.0 nm [5,20–22]. Therefore, RH can serve as an alternative to chemical materials in wastewater treatment and pollution mitigation solutions.

Indonesia is the fourth largest rice producer in the world. In 2021/2022, its rice production reached 35 million tons [23]. Its dry grain production in 2022 was 54.75 million tons, but this was $\pm 64\%$ rice and $\pm 36\%$ by-product. The by-products of rice milling processes include RH (15–20%), bran (8–12%), and rice groats ($\pm 5\%$) [24]. Approximately ± 10.95 million tons of RH was produced in 2022. The utilization of RH from the rice milling process remains limited; it sometimes becomes waste, and thus a source of environmental pollution [25].

The role of RH as a good bio-adsorbent for removing cationic dyes from aqueous solutions has been studied intensively. The adsorption of malachite green (MG) was studied by Saha et al. [26] and Zou et al. [27]. Bayrak Tezcan et al. [28] reported the removal of basic yellow 51 (BY51), whereas Quansah et al. [29] studied the adsorption of crystal violet (CV). MB and BR9 are widely studied because they are cationic dyes commonly used as coloring agents and in dye adsorption experiments; furthermore, they are nonbiodegradable and are toxic and carcinogenic upon short-time exposure [30–33]. However, to the best of our knowledge, no study has been published on dye adsorption using RHs of different origins. Whether differences in chemical composition affect adsorption capacity is also unclear.

To achieve environmental sustainability and solutions to global challenges, adsorption was performed in this study according to the reduce–reuse–recycle principle. In particular, the goals were reducing pollutants from dyes, reusing water and agricultural waste, and recycling dyes for sustainable dyeing (Figure 1). This study was performed to investigate the adsorption of MB and BR9 from aqueous solutions using Indonesian rice husk (IRH) and Hungarian rice husk (HRH) as bio-adsorbents.

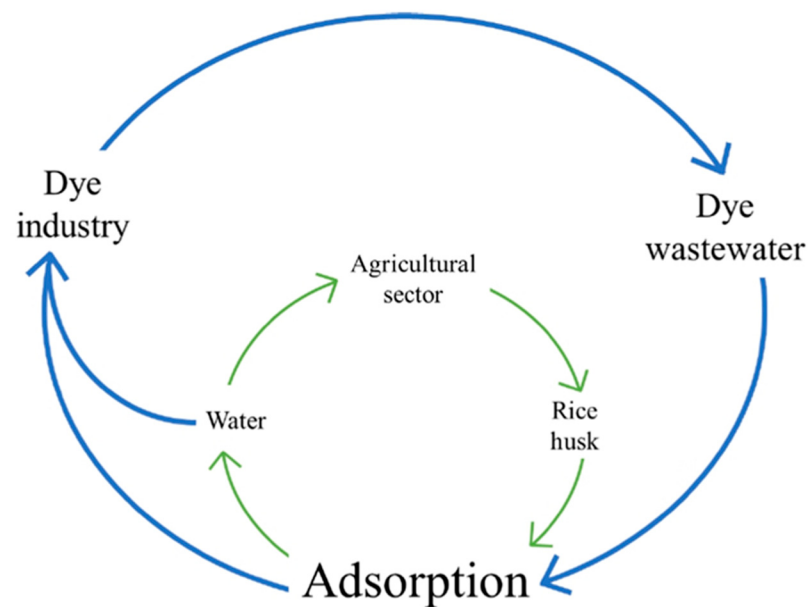


Figure 1. Adsorption process using the sustainable dyeing concept.

2. Results and Discussion

2.1. Chemical Content Analysis

RH is a lignocellulosic material that can be utilized as an adsorbent for dye removal. The chemical content of RH can be analyzed through various treatment methods, including acid pretreatment. Sulfuric and hydrochloric acid solvents are commonly used for this treatment. Acid pretreatment is suitable for lignocellulosic materials due to its ability to break down the rigid structure of lignocellulosic materials into cellulose and lignin [34,35]. The chemical content of RH was investigated and is shown in Figure 2. IRH has higher cellulose and ash contents than HRH, but HRH has higher lignin content. The higher ash content in IRH may influence its adsorption capacity [28,29]. In general, RH contains 28.6–43.3 cellulose, 19.2–24.4 lignin, and 11.3–20 ash [30,31]. Cellulose contains β -glucose monomers, whereas lignin contains polymeric aromatic structures that involve the oxidative coupling of 4-hydroxyphenylpropanoids and the three primary monolignols (coniferyl, sinapyl, and p-coumaryl alcohols) [32].

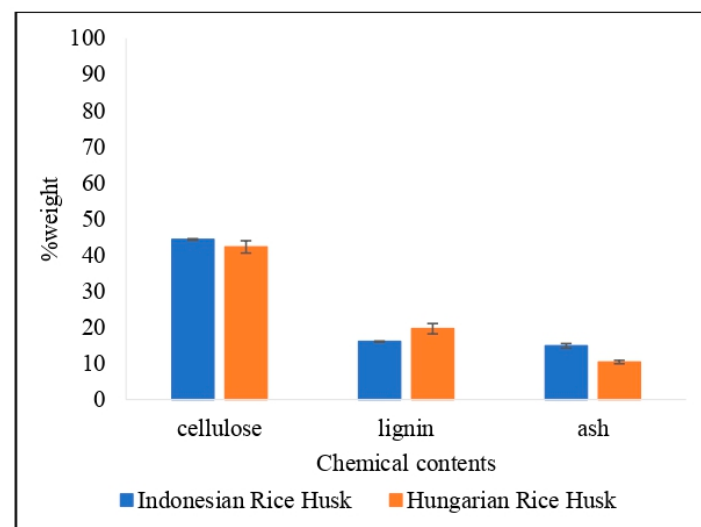


Figure 2. Chemical content of RHs.

2.2. Zeta Potential Measurement

The zeta potential is an essential tool for understanding the charge characteristics of particles. Zeta potential measurement is also known as electrokinetic potential measurement, which is conducted to analyze particle charges and predict the stability of nanoparticles in a colloidal dispersion [36]. The zeta potential values of the RHs are shown in Figure 3a,b.

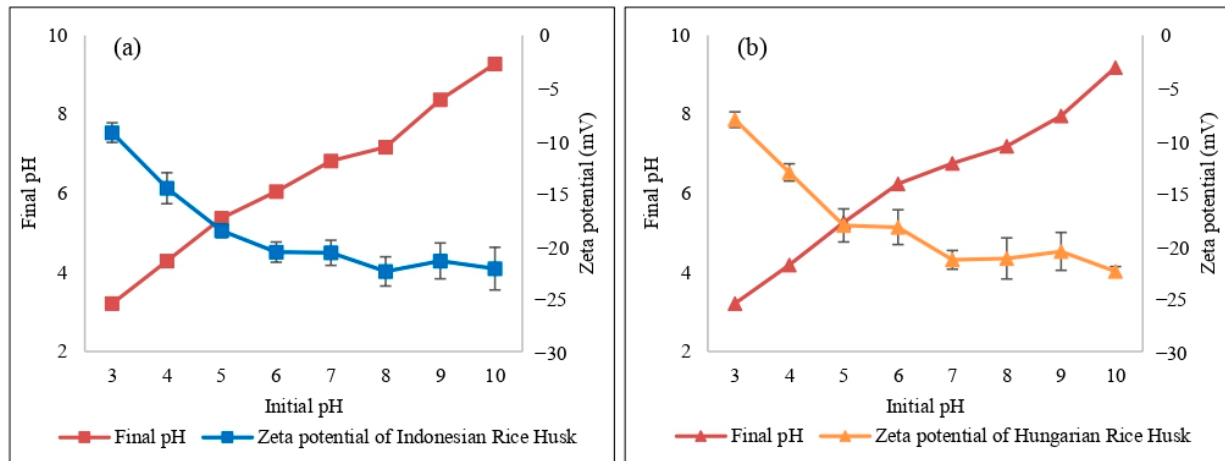


Figure 3. Zeta potentials of (a) IRH and (b) HRH.

There is a lack of zeta potential measurement where environmental changes, such as changes in pH and ion strength, occur [37]. The zeta potential sign is negative at all studied pH values. An increase in pH can decrease the zeta potential value, thus increasing the negative charges on the RH surface. RH functional groups, such as carboxyl and phenolic groups, contribute significantly to the RH surface charge. The increasing pH can enhance the deprotonation of the surface groups because of the weakening interaction between the surface functional groups and H^+ . Meanwhile, at more acidic pH values, the RH surface shows high protonation of the surface due to the association between the surface functional groups and H^+ [38,39]. The negative surface contributes to the RH functional group's ability to adsorb positive ions [40].

2.3. Effect of pH

The solution pH affects the ability of hydrogen ions (H^+ or protons) to bind to functional groups on an adsorbent surface, for example, carboxyl (COOH), amine (NH), phenolic hydroxyl (OH), and metal ions [41]. The MB removal percentages at pH 5–10 are shown in Figure 4a. IRH and HRH achieve a maximum MB removal percentage of 96% at pH 10. This result is supported by the zeta potentials of IRH and HRH, which are equal at pH 10. These findings agree with those of Labaran et al. [42], where MB removal occurred under alkali conditions.

The BR9 removal percentages at pH 3–7 are shown in Figure 4b. IRH and HRH achieve maximum BR9 removal percentages of 82% and 87%, respectively, at pH 7. This result is confirmed by the zeta potential of HRH, which is higher than that of IRH at pH 7. These findings agree with those reported in a previous study on the use of activated *Gossypium hirsutum* seeds for BR9 removal [8].

The dye removal percentage increases under alkali conditions for MB and neutral conditions for BR9 but decreases under acidic conditions. This is because of the protonation and deprotonation of the functional groups on the adsorbent surface and the dye molecules. At low (acidic) pH values, the number of hydrogen ions (H^+ or protons) in the solution increases and more functional groups on the RH surface are protonated. This competition with H^+ ions for surface sites reduces the probability of cationic MB adsorption on the RH surface. However, increasing the pH toward alkali conditions reduces the number of

hydrogen ions (H^+ or protons) near the surface. Thus, the functional groups on the RH surface become more deprotonated, thereby affecting the charge density and strengthening the Coulomb interaction between the negative charge of the adsorbent and the positive charge of the dye molecules [43,44].

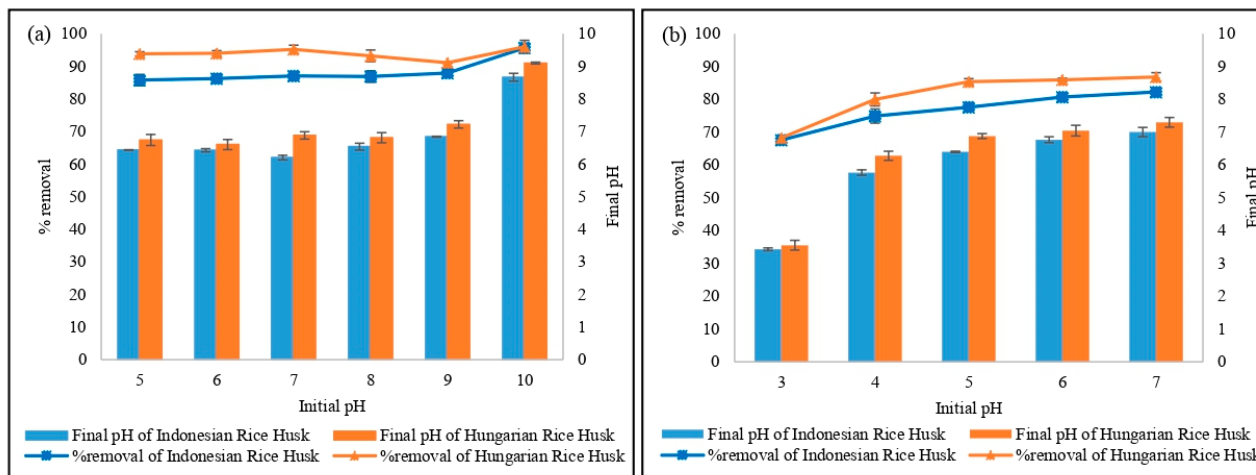


Figure 4. Effect of pH on MB (a) and BR9 (b) removal by rice husks of different origins (adsorbent dose: 500 mg; initial concentration of dyes: 30 mg/L; temperature (T°): 25 °C; time (t): 120 min).

2.4. Effect of Initial Dye Concentration

The effects of various initial dye concentrations (30, 60, 90, and 120 mg/L) on MB and BR9 removal by IRH and HRH at room temperature were studied, as shown in Figure 5a,b. The amounts of MB (120 mg/L) adsorbed using IRH and HRH in the aqueous solutions are 55.6 mg/g and 55.7 mg/g, respectively. The amounts of BR9 (120 mg/L) adsorbed using IRH and HRH are 53.9 mg/g and 54.3 mg/g, respectively.

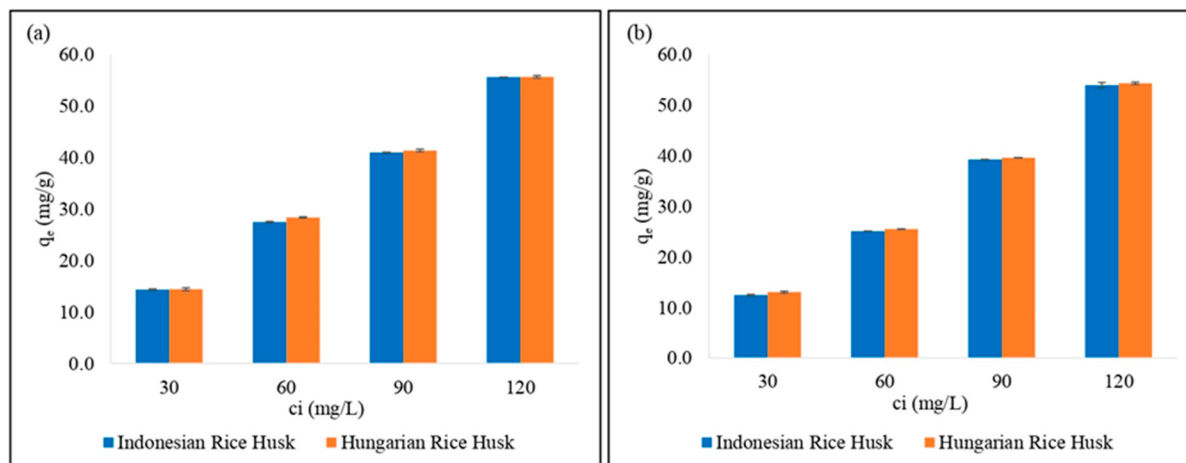


Figure 5. Effect of initial concentration on MB (a) and BR9 (b) removal by rice husks of different origins (pH: 10 for MB, 7 for BR; adsorbent dose: 500 mg; temperature (T°): 25 °C; time (t): 120 min).

As the initial dye concentration increases, the dye removal percentage decreases, and the amount adsorbed (mg/g) at equilibrium (q_e) increases. At higher initial concentrations, the driving forces increase and the RH surface is saturated because the number of unoccupied active sites on the adsorbent decreases. The mass transfer of dyes from the solutions to the RH surface reduces, reducing the adsorption rate [45–47]. Therefore, adsorption depends on the initial dye concentration. In general, no significant differences are observed between the use of IRH or HRH at various initial dye concentrations.

2.5. Effect of Adsorbent Dose

The effects of different adsorbent doses (125, 250, and 500 mg) on adsorption were studied using 250 mL of each dye solution. The adsorbent dose is an important parameter for determining optimal adsorption conditions because the adsorbent capacity is affected by the initial dye concentration [48]. The maximum MB removal percentage of IRH and HRH at 500 mg is 96%. An increase in the adsorbent dose from 0.5 g/L to 2 g/L can improve the removal percentage. The effects of the doses of the two adsorbents are shown in Figure 6a,b.

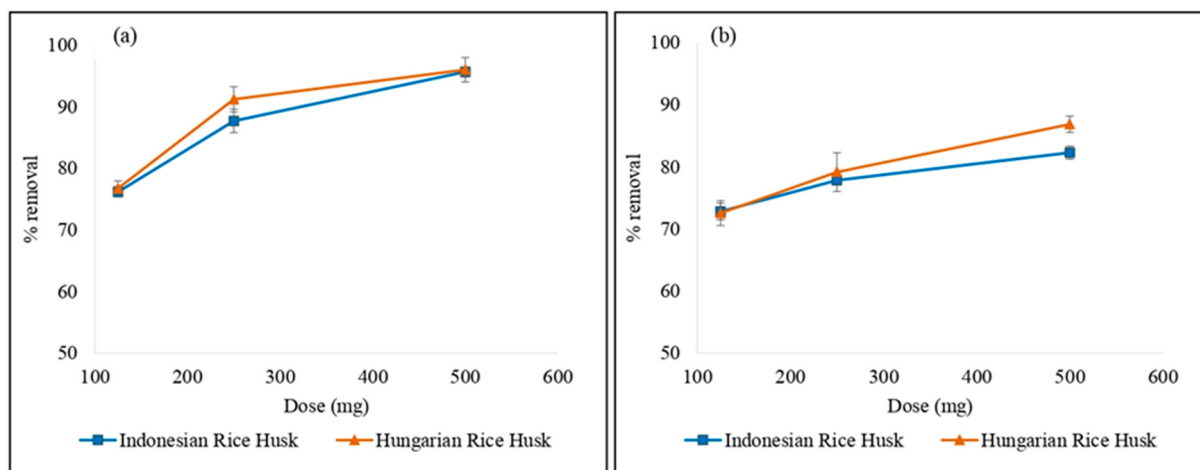


Figure 6. Effect of adsorbent dose on MB (a) and BR9 (b) removal by rice husks of different origins (pH: 10 for MB, 7 for BR9; initial concentration of dyes: 30 mg/L; temperature (T°): 25 $^\circ$ C; time (t): 120 min).

The maximum BR9 removal percentages of IRH and HRH are 82% and 87%, respectively. The removal patterns for both dyes are similar—the removal percentage improves with the adsorbent dose. Increasing the adsorbent dose can enhance the removal capacity by increasing the active adsorption sites and surface areas [49,50], thus increasing the available active sites for the adsorption of dyes.

2.6. Effect of Contact Time

The contact time parameter is used to determine the equilibrium time. Depending on the adsorbent material and the adsorbate, the adsorption process requires a certain period to achieve equilibrium [51]. Here, the adsorption was conducted from 5 min to 120 min to understand the effect of contact time. Every 5 min during the adsorption process, samples are taken to obtain removal percentages. The effects of contact on the adsorption performance of the two adsorbents are shown in Figure 7a,b.

The adsorption process consists of three phases: initial, intermediate, and equilibrium [52,53]. The adsorption process starts in the initial phase, which is fast and has high removal rates. The MB and BR9 removal percentages of HRH within 5 min are 89% and 73%, respectively, whereas those of IRH are 90% and 71%, respectively. In the intermediate phase, the removal rate gradually slows down. The removal rate becomes constant (equilibrium phase) within 120 min, at which the MB and BR9 removal rates of HRH (IRH) are 96% (96%) and 87% (82%), respectively. HRH generally exhibits a higher removal percentage than IRH.

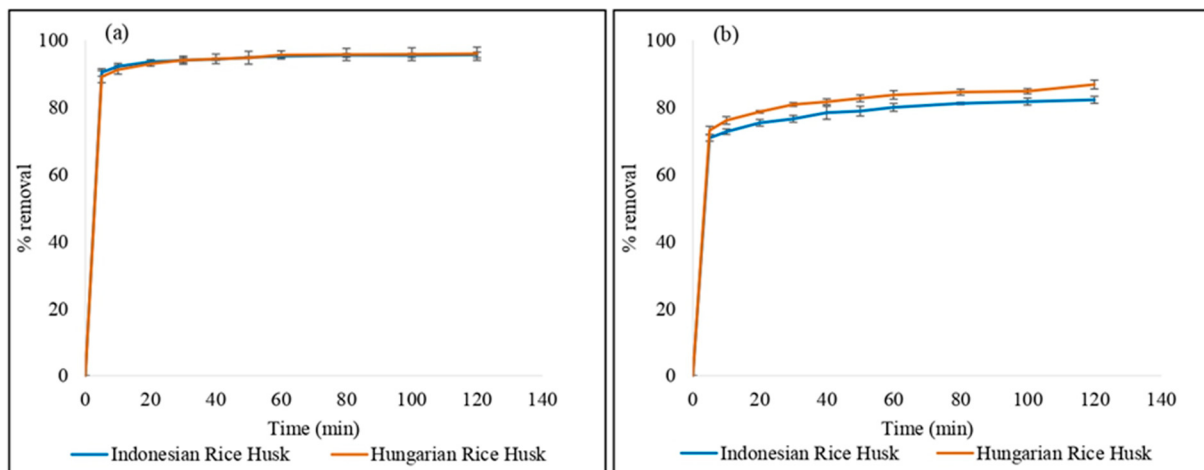


Figure 7. Effect of contact time on MB (a) and BR9 (b) removal by rice husks of different origins (pH: 10 for MB, 7 for BR9; adsorbent dose: 500 mg; initial concentration of dyes: 30 mg/L; temperature (T°): 25 $^\circ$ C).

2.7. Effect of Temperature

The physicochemical reactions in the adsorption process are influenced by temperature. An increase in temperature typically increases the dye molecule's mobility from a solution to an adsorbent surface [54]. The effect of temperature (25 $^\circ$ C, 35 $^\circ$ C, and 45 $^\circ$ C) was examined, as shown in Figure 8a,b. The MB removal percentages of IRH at 25 $^\circ$ C, 35 $^\circ$ C, and 45 $^\circ$ C are 96%, 96%, and 96%, respectively, whereas those of HRH at 25 $^\circ$ C, 35 $^\circ$ C, and 45 $^\circ$ C are 96%, 96%, and 97%, respectively. MB adsorption is independent of temperature. In particular, this parameter is not always beneficial to the process and thus can be neglected in some cases [55].

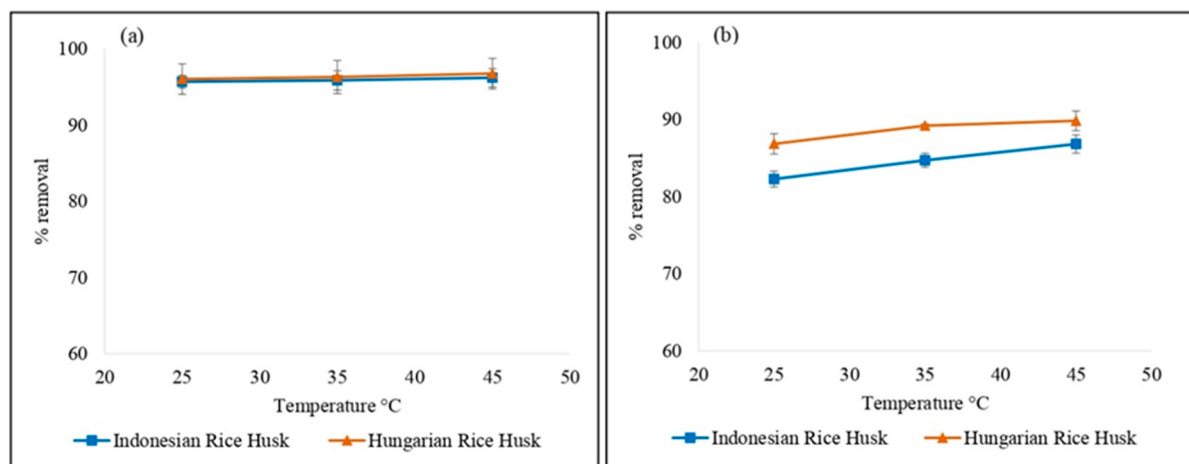


Figure 8. Effect of temperature on MB (a) and BR9 (b) removal by rice husks of different origins (pH: 10 for MB, 7 for BR9; adsorbent dose: 500 mg; initial concentration of dyes: 30 mg/L; time (t): 120 min).

BR9 removal using IRH and HRH gave similar results. The removal percentages of IRH at 25 $^\circ$ C, 35 $^\circ$ C, and 45 $^\circ$ C are 82%, 85%, and 87%, respectively, and those of HRH at 25 $^\circ$ C, 35 $^\circ$ C, and 45 $^\circ$ C are 87%, 89%, and 90%, respectively. The same results were obtained by Zhao et al. [56]. However, the effect of temperature is not highly significant in this study; the associated differences in removal percentage are relatively small. The effect of temperature is strongly dependent on the adsorbent surface nature (energetically homogeneous or heterogeneous) for adsorption from aqueous solutions [57].

2.8. FT-IR Analysis

The FT-IR analysis results for the RHs before and after dye adsorption are displayed in Figure 9a,b. The dye adsorption conditions were as follows: pH: 10 for MB, 7 for BR9; adsorbent dose: 500 mg; initial dye concentration: 30 mg/L; temperature (T°): 25 $^\circ\text{C}$; time (t): 120 min. The analysis results in Table 1 indicate the functional groups present on the RH surfaces and the interactions before and after dye adsorption by the RHs. The observed peaks in the RHs are similar to those obtained by Genieva et al. [58] in their FT-IR study.

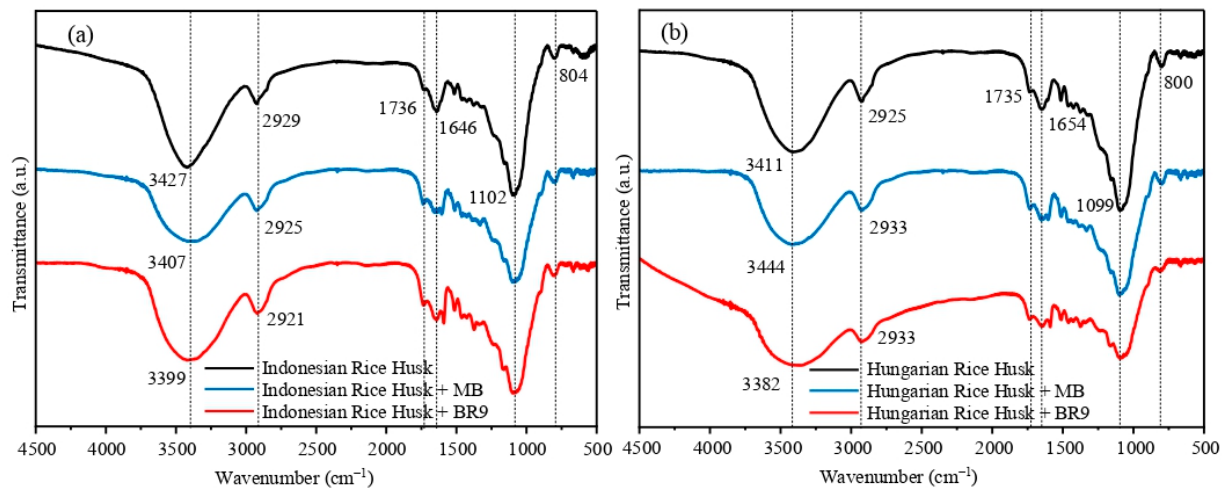


Figure 9. FT-IR absorption spectra for (a) IRH (before and after adsorption of MB and BR9), and (b) HRH (before and after adsorption of MB and BR9).

Table 1. FT-IR analysis results for RHs before and after adsorption of MB and BR9.

Absorption Peak (cm^{-1})						Assignment
IRH	HRH	IRH + MB	HRH + MB	IRH + BR9	HRH + BR9	
3427	3411	3407	3444	3399	3382	O–H and N–H
2929	2925	2925	2933	2921	2933	C–H, $-\text{CH}_3$ or $-\text{CH}_2$
1736	1735	-	-	-	-	C=O
1646	1654	-	-	-	-	O–H
-	-	1605	1605	1593	1519	C=N and C=O
-	-	1335	1331	-	-	C–N
-	-	-	-	1164	1168	C–N
1102	1099	-	-	-	-	Si–O–Si
804	800	-	-	-	-	Si–O

The peaks at 3427 cm^{-1} and 3411 cm^{-1} are due to the stretching vibrations of the O–H bonds in the structures of cellulose, hemicellulose, and lignin. The peaks at 2929 cm^{-1} and 2925 cm^{-1} are due to the symmetric and asymmetric stretching vibration of the aliphatic C–H bonds in $-\text{CH}_3$ and $-\text{CH}_2$ groups. In addition, the peaks at 1736 cm^{-1} and 1735 cm^{-1} are ascribed to stretching vibrations of the C=O bonds in aldehyde groups of hemicellulose. Strong hydrogen bonding is indicated by the peaks at 1646 cm^{-1} and 1654 cm^{-1} . The peaks at 1102 cm^{-1} and 1099 cm^{-1} are attributed to Si–O–Si stretching vibrations. The peaks at 804 cm^{-1} and 800 cm^{-1} are due to the symmetric and asymmetric vibrations of Si–O bonds.

The peaks shift after MB adsorption. The peaks at 3407 cm^{-1} and 3444 cm^{-1} are due to the O–H bonding interaction between MB and RH. The peaks at 2925 cm^{-1} and 2933 cm^{-1} indicate the stretching vibration of the $-\text{CH}_3$ in the dimethylamino groups. The peak at 1605 cm^{-1} is attributed to the heterocyclic stretching vibration of C=N. The peaks at 1335 cm^{-1} and 1331 cm^{-1} are ascribed to the stretching vibrations of the C–N bonds in the dimethylamino groups [59].

After BR9 adsorption, the peaks shift to 3399 cm^{-1} and 3382 cm^{-1} due to the stretching vibrations of O–H and N–H bonds. The peaks at 2921 cm^{-1} and 2933 cm^{-1} are due to the symmetric and asymmetric stretching vibrations of the C–H bonds in the $-\text{CH}_3$ and CH_2 groups. The peaks at 1593 cm^{-1} and 1519 cm^{-1} are ascribed to the stretching vibrations of C=N and C=O bonds, respectively. The peaks at 1164 cm^{-1} and 1168 cm^{-1} indicate the stretching vibrations of C–N bonds.

2.9. Adsorption Isotherm

The adsorption isotherm describes the relationship between the amount of adsorbate adsorbed by the adsorbent (q_e) and the equilibrium concentration of adsorbate (c_e) at a constant temperature. The parameters obtained from adsorption equilibrium models provide helpful information about surface properties, adsorption mechanisms, and the adsorbent–adsorbate relationship [52].

The capacities of IRH and HRH to adsorb MB and BR9 were investigated via batch adsorption experiments at different initial dye concentrations and constant adsorbent doses at a given temperature. The adsorption equilibrium data for MB and BR9 were studied using the Harkins–Jura and Brunauer–Emmett–Teller (BET) multilayer isotherm models. The experimental data and isotherm models are compared in Figure 10a–d.

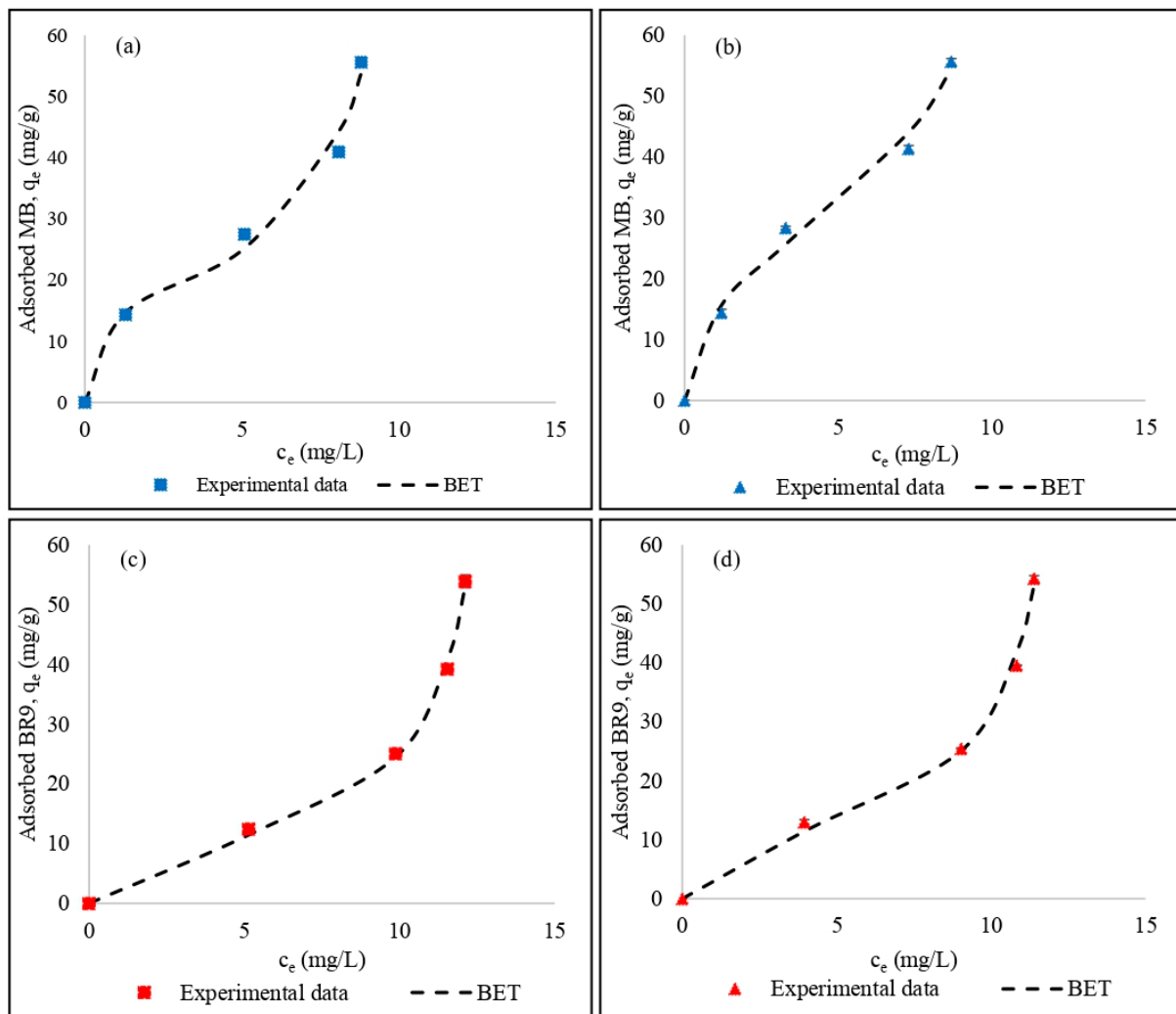


Figure 10. Experimental data and BET model fitting for (a) MB adsorbed using Indonesian rice husk, (b) MB adsorbed using Hungarian rice husk, (c) BR9 adsorbed using Indonesian rice husk, and (d) BR9 adsorbed using Hungarian rice husk.

In this experiment, the isotherm shape can be described as a C-type isotherm. A C-type (constant partition) isotherm is a partition of solutes that takes place between the aqueous phase and the interfacial layer of a solid [60]. Therefore, the BET multilayer model is more appropriate for the adsorption isotherm in this study. MB and BR9 aggregated in the adsorption experiment; the self-association of these dyes in aqueous solutions has been reported in the literature [61]. Organic dyes in aqueous solutions frequently self-aggregate into dimers, trimers, and higher-order aggregates based on concentration [62].

Fujita et al. [63] found that MB exists as dimers in an aqueous solution or as aggregates on the surface. A monomer–dimer can exist in the concentration range of 10^{-3} – 10^{-6} M [64]. According to Fernández-Pérez et al. [65] and Fernández-Pérez and Marban [66], the aggregation of MB molecules in a solution forms dimers at concentrations below 3.4×10^{-5} M, monomers at a concentration of 1.1×10^{-6} M, and tetramers at a concentration of 3.5×10^{-3} M. The monomer–dimer equilibrium for MB has been investigated at concentrations of 2×10^{-6} – 5×10^{-5} M [67]. Pathrose et al. [68] found that BR9 can form dimers and aggregates at concentrations of 10^{-2} – 10^{-5} M. According to Figure 10a–d, MB concentrations of 2.8×10^{-5} M (~9 mg/L) and BR9 concentrations of 4.1×10^{-5} (~12 mg/L) tend to increase to infinity, since the aggregation is perceptible in the aqueous solution and on the surface.

Table 2 shows the isotherm parameters of the Harkins–Jura and the BET multilayer models obtained via nonlinear fitting. Based on the correlation coefficient (R^2) and the nonlinear chi-square (χ^2) (Table 2), the BET multilayer adsorption isotherm fits the experimental adsorption data better. Equation (1) presents the Harkins–Jura equation form for determining the isotherm parameter [69]:

$$q_e = \left(\frac{A}{B - \log C_e} \right)^{1/2} \quad (1)$$

Table 2. Isotherm parameters for MB and BR9 adsorption.

Isotherm Model	Parameter	IRH		HRH	
		MB	BR9	MB	BR9
Harkins–Jura	A	26.38	10.32	39.37	12.85
	B	1.20	1.18	1.30	1.18
	R^2	0.960	0.974	0.970	0.963
	χ^2	0.28	0.18	0.20	0.25
BET	Q_m (mg/g)	15.02	7.27	24.50	8.32
	K_L	0.08	0.07	0.07	0.07
	K_S	4.78	983.02	1.10	114.40
	R^2	0.979	0.995	0.981	0.989
	χ^2	0.14	0.04	0.13	0.08

C_e is the equilibrium concentration of adsorbate, A is the Harkins–Jura isotherm parameter, and B is the Harkins–Jura isotherm constant. The Harkins–Jura adsorption isotherm describes heterogeneous pore distribution and multilayer adsorption [70].

The BET multilayer isotherm is a theoretical model commonly used in gas–solid equilibrium systems [71,72]. However, the classical BET equation can be modified for liquid phase adsorption and has three degrees of freedom (Q_m , K_S , and K_L) [73]. The BET equation for liquid phase adsorption [73] is expressed using Equation (2):

$$q_e = Q_m \frac{K_S C_e}{(1 - K_L C_e)(1 - K_L C_e + K_S C_e)} \quad (2)$$

Q_m is the amount adsorbed during complete monolayer adsorption, K_S is the equilibrium constant of adsorption of the first layer, and K_L is the equilibrium constant of adsorption of the upper layers of the adsorbate on the adsorbent.

In the BET multilayer isotherm model, the maximum adsorption capacity can reach infinity [73]. The isotherm modeling in this study is similar to that of Vargas et al. [74], who used sisal fibers (*Agave sisalana*) for MB removal, and that of Côrtes et al. [75], who used fish scales for BR9 removal.

A comparison of the adsorption capacities of IRH and HRH for MB removal is given in Table 3. In the literature, the highest adsorption capacity for MB removal is 1346.7 mg/g [76], while the lowest is 1.6 mg/g [77]. Particle size has a vital role in adsorption capacity, and a varying adsorbent particle size correlates directly with particle diffusion into pores [78].

Table 3. Comparison of the adsorption capacity of raw RH for MB removal.

No	Origins	Adsorption Capacity (mg/g)	Particle Size	pH	References
1	India	1347.7	400–841 μm	7	[76]
2	China	19.7	0.425–0.850 mm	7	[27]
3	Malaysia	1.6	NA	5.8	[77]
4	Iran	24.7	<250 μm	10	[79]
5	Brazil	52.2	5 mm	11	[80]
6	Thailand	21.9	<400 μm	5.7–6.2	[5]
7	Nigeria	13.5	NA	10	[42]
8	Korea	25.4	0.075–1.16 mm	7	[29]
9	Indonesia	15.0	<250 μm	10	This study
10	Hungary	24.5	<250 μm	10	This study

The chemical composition of RH, which includes lignin and silica, can affect the adsorption capacity of RH. The chemical composition of an adsorbent can affect the bonding strength between the adsorbate and the functional groups on the adsorbent surface [29]. The use of chemical fertilizers and the composition of soil chemistry in a paddy field can vary the chemical composition of RH [81]. Therefore, the wide range of RH chemical compositions reveals their dependence on, among others, RH origin, farm climate, and crop technology. Based on studies of MB adsorption using RHs of different origins, RH origin is a factor that influences MB adsorption capacities.

In our study, the adsorption capacities of IRH and HRH for MB removal are 15.0 mg/g and 24.5 mg/g, respectively. According to the results, HRH has a higher adsorption capacity because it contains less ash. However, IRH and HRH have better adsorption capacities compared with other RHs. As a bio-adsorbent, RH can also be used for wastewater treatment because it is abundant and environmentally friendly. Other advantages, such as simplicity and low costs, can be achieved using raw RH.

The adsorption capacities of various adsorbents for BR9 removal have been investigated and compared (Table 4). The highest adsorption capacity for BR9 removal was reported by Kong et al. [82], while the lowest was obtained by Zhao et al. [56]. In the current study, the IRH and HRH adsorption capacities for BR9 removal are 7.2 mg/g and 8.3 mg/g, respectively. HRH has a higher adsorption capacity for BR9 removal than IRH.

Many agricultural and waste materials have been utilized as adsorbents to remove BR; however, to the best of our knowledge, raw RH has not been used. From environmental and economic points of view, RH can be utilized as an alternative adsorbent to elucidate BR9 adsorption.

Table 4. Comparison of adsorption capacities of various adsorbents for BR9 removal.

No	Adsorbent	Adsorption Capacity (mg/g)	pH	References
1	Fish Bones	14.8	7	[83]
2	Activated <i>Gossypium Hirsutum</i> Seeds	67.1	8	[8]
3	Leather Activated Carbon	139.3	8	[82]
4	Malted Sorghum Mash	58.5	4–9	[84]
5	Triptycene-Based Porous Polymer	586.2	2–9	[85]
6	Multi-Walled Carbon Nanotubes	55.5	8	[86]
7	Pistachio Nut Shells	118.2	12	[87]
8	Alkali-Activated Diatomite	9.8	9	[56]
9	Eggshell Membrane	48.0	6	[88]
10	<i>Astragalus</i> Root	20.2	10	[89]
11	Indonesian Rice Husk	7.2	7	This study
12	Hungarian Rice Husk	8.3	7	This study

2.10. Adsorption Kinetics

A kinetic model can describe adsorption processes and possible rate-controlling steps such as mass transport and chemical reaction processes [90]. Two kinetic equations, namely, pseudo-first-order (PFO) [91] and pseudo-second order (PSO) [92], were used to investigate the MB and BR9 adsorption kinetics. Their nonlinear forms are expressed as Equations (3) and (4):

$$q_t = q_e \left(1 - e^{-k_1 t}\right) \quad (3)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + k_2 q_e t} \quad (4)$$

where q_e and q_t represent the adsorption capacities (mg/g) of the adsorbent at equilibrium and at time t (min), respectively. k_1 is the first-order rate constant and k_2 is the second-order rate constant.

The PFO kinetic model describes the adsorption process as controlled by the diffusion step; it follows a physical adsorption mechanism (physisorption kinetics). By contrast, the PSO kinetic model describes the adsorption rate as affected by the chemical interaction between the adsorbate and the adsorbent; it follows a chemical adsorption mechanism (chemisorption kinetics) [93,94]. The kinetic parameters for MB and BR9 adsorption are shown in Table 5.

Table 5. Kinetic parameters for MB and BR9 adsorption.

Kinetic Model	Parameter	IRH		HRH	
		MB	BR9	MB	BR9
Pseudo-first order	q_e (mg/g)	14.19	11.83	14.20	12.38
	k_1	0.61	0.43	0.54	0.41
	R^2	0.637	0.474	0.666	0.736
	χ^2	0.001	0.01	0.003	0.01
Pseudo-second order	q_e (mg/g)	14.32	12.13	14.38	12.71
	k_2	0.23	0.1	0.16	0.08
	R^2	0.945	0.825	0.956	0.921
	χ^2	0.0002	0.005	0.0004	0.004

Based on the correlation coefficient (R^2) and the nonlinear chi-square (χ^2) result in Table 5, all the experimental data fit the PSO kinetic model better than the PFO kinetic model. Thus, chemisorption controls the MB and BR9 adsorption processes, where functional groups play a central role [95,96]. Chemisorption occurs through the sharing or exchange of electrons between the negatively charged RH functional groups, as evidenced

by the zeta potential measurement, and the positively charged cationic dyes [97]. The initial concentration selected during the adsorption kinetic process affects the kinetic model. A relatively high initial concentration tends to be relatively stable during the adsorption process and better fits a PFO kinetic model. Conversely, a PSO kinetic model fits better when the initial concentration is relatively low and changes significantly during the adsorption process [98].

In addition, the PSO kinetic rate k_2 for MB adsorption (0.16–0.23 g/mg/h) is higher than the PSO kinetic rate k_2 for BR9 adsorption (0.08–0.1 g/mg/h). This result suggests the formation of covalent bonds between the MB molecules and the RH surface [99]. The experimental data and calculated (PSO kinetic model) adsorption kinetics are represented by plotting time (min) against q_e (mg/g) in Figure 11a–d. The experimental q_e data closely match the calculated q_e data from the PSO kinetic model.

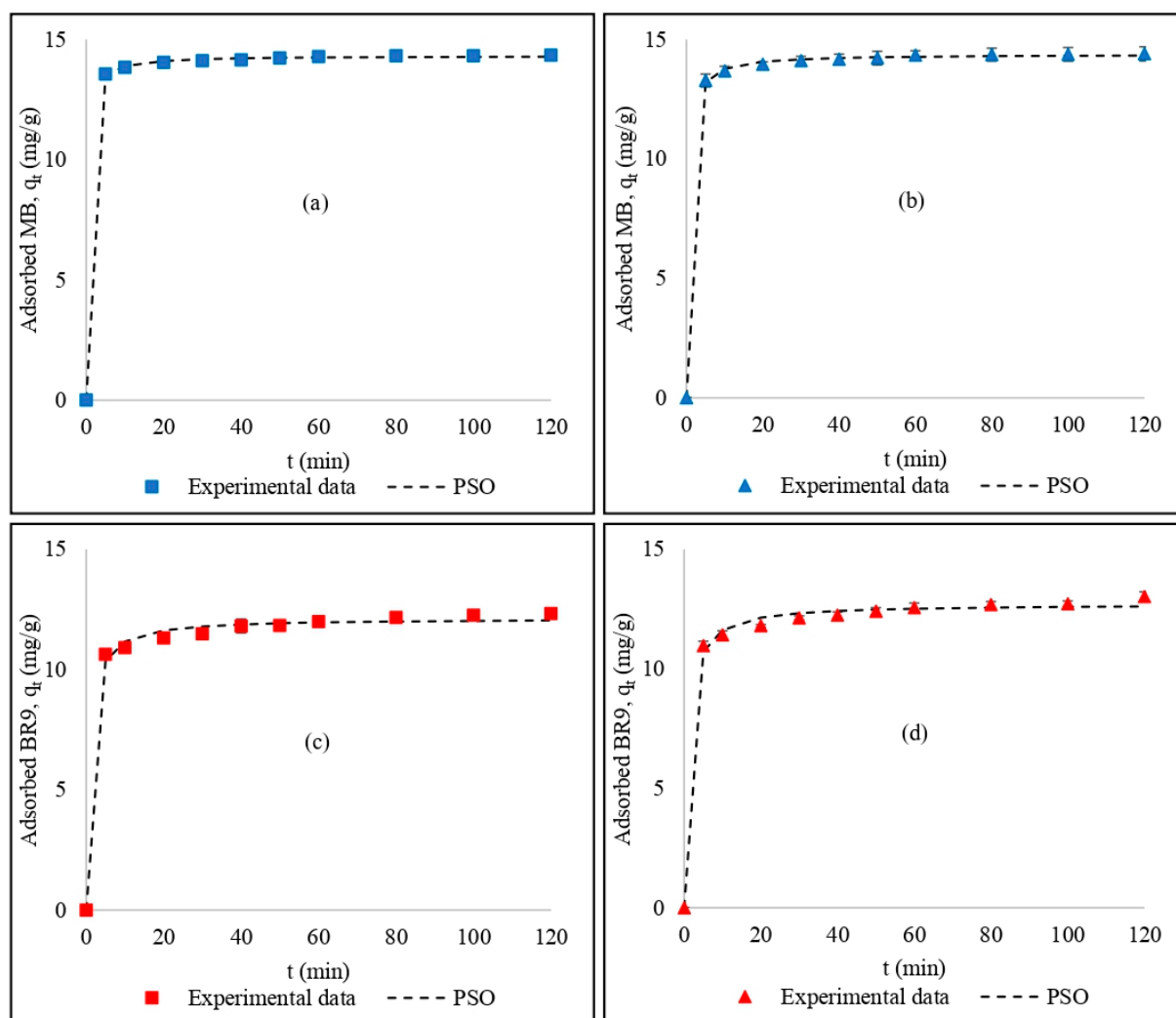


Figure 11. Experimental data and PSO model fitting for (a) MB adsorbed using Indonesian rice husk, (b) MB adsorbed using Hungarian rice husk, (c) BR9 adsorbed using Indonesian rice husk, and (d) BR9 adsorbed using Hungarian rice husk.

3. Materials and Methods

3.1. Preparation of Dye Solutions

MB and BR9 solutions were prepared by dissolving 1 g of the dye (MB from Molar Chemical, Halásztelek, Hungary and BR9 from Sigma–Aldrich, St. Louis, MI, USA) in 1 L of deionized water. The mixture was diluted with distilled water to obtain the target concentration. The chemical diagrams of MB and BR9 are depicted in Figure 12a,b. Sodium

hydroxide (NaOH) and hydrochloric acid (HCl) solutions were used to modulate the pH levels of the dye solutions. All the substances utilized in the experiments, including MB, BR9, NaOH, and HCl, were of analytical reagent quality.

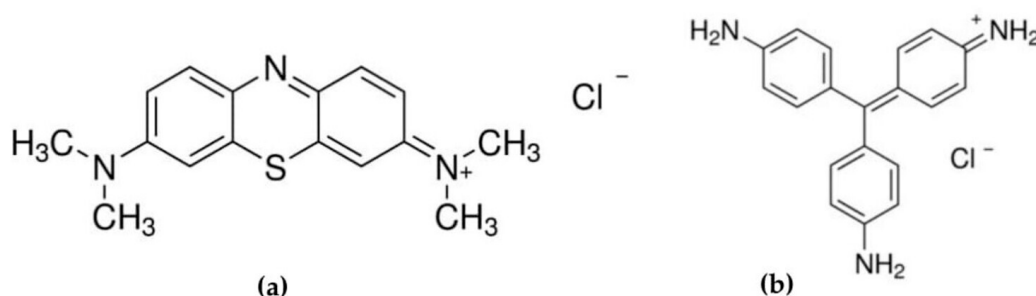


Figure 12. Chemical diagrams of (a) MB and (b) BR9.

3.2. Preparation of Adsorbents

The raw materials (RHs) for the experiments were obtained from Indonesia and Hungary. Indonesian rice or *Oryza sativa* subsp. *Javanica* (tropical *japonica*) rice was harvested in the 2020 cropping season in Cianjur City, Indonesia, by smallholder farmers in a rainfed rice field where the irrigation source was rainwater and a small amount of fertilizer was used. Hungarian rice or *Oryza sativa* subsp. *Japonica* var.M488 (Hungarian Plant Breeding) was harvested in the 2020 cropping season in Kisújszállás City, Hungary. It was produced by Nagykun 2000 Mezőgazdasági Zrt using Kubani technology, namely, seedbed preparation, sowing in warm weather (20 April and 10 May), and germination in flooded troughs. At the beginning of sowing, the area was watered constantly, with one-third of each plant in water. Each RH sample was washed using distilled water until the pH was constant and then vacuum-dried in an oven at 105 °C for 120 min without inert gases. Finally, the dried material was crushed and ground to the desired size (<250 µm) for the adsorption experiments.

3.3. Characterization of Adsorbents

3.3.1. Chemical Content Analysis

Lignin and cellulose analyses were conducted according to the method of Cheson [100]. A mixture containing 1 g of dried sample (a) and 150 mL of distilled water was heated in a water bath at 90–100 °C for 1 h. The mixture was filtered and the residue washed using 300 mL of hot water. The residue was dried in an oven until the weight was constant (b). The residue was mixed with 150 mL of 0.5 M sulfuric acid (H₂SO₄) and heated in the water bath at 90–100 °C for 1 h. The mixture was filtered, washed using 300 mL of distilled water, and the residue dried (c). The dried residue was soaked in 10 mL of 72% H₂SO₄ at room temperature for 4 h. Afterwards, 150 mL of 0.5 M H₂SO₄ was added to the mixture, which was refluxed in the water bath for 1 h. The solid was washed using 400 mL of distilled water, heated in the oven at 105 °C, and weighed until a constant weight (d) was reached. Finally, the solid was heated until it became ash, which was then weighed (e). The percentages of cellulose, lignin, and ash were calculated using Equations (5)–(7):

$$\% \text{ Cellulose} = \frac{c - d}{a} 100 \quad (5)$$

$$\% \text{ Lignin} = \frac{d - e}{a} 100 \quad (6)$$

$$\% \text{ Ash} = \frac{e}{a} 100 \quad (7)$$

3.3.2. Zeta Potential and Fourier Transform Infrared Spectroscopy (FT-IR) Analyses

A zeta sizer Nano ZS dynamic light scattering (Malvern, UK) with a 4 mW He–Ne laser source ($\lambda = 633$ nm) was used for zeta potential measurement at 25 °C, where a disposable zeta cell (DTS1070) was filled with each RH suspension. Preparation of each suspension: 10 mg of the RH was mixed with 10 mL of 0.01 M NaCl at different pH values. To modulate the pH values, 0.1 M hydrochloric acid or 0.1 M sodium hydroxide solutions were used and rechecked after the study.

FT-IR analysis was performed using a Bruker Vertex 70 spectrophotometer (Ettlingen, Germany) with a spectral resolution of 4 cm^{-1} . Each spectrum was recorded from 500 to 4500 cm^{-1} and composed from the average of 16 scans. After grinding the sample, 100 mg potassium bromide (KBr) pellets were prepared with 1 $w/w\%$ of sample content and measured in transmission mode.

3.4. Batch Adsorption Experiments

IRH and HRH were used to remove MB and BR9 in batch adsorption experiments. Batch adsorption was performed to determine the effects of certain parameters—pH, contact time, initial dye concentration, adsorbent dose, and temperature—on their adsorption performance. The influence of various pH values on MB and BR9 adsorption was investigated (pH 5–10 for MB and pH 3–7 for BR9) by adjusting the initial pH of the solutions using 0.1 M HCl or 0.1 M NaOH. The influence of the initial dye concentration (30, 60, 90, and 120 mg/L), adsorbent dose (125, 250, and 500 mg), contact time (5–120 min), and temperature (25 °C, 35 °C, and 45 °C) were investigated to obtain the optimal MB and BR9 adsorption conditions. In batch adsorption experiments, 250 mL of each aqueous dye solution was used, with a stirring speed of 100 rpm.

After the adsorption process, the solution was centrifuged at 4000 rpm for 15 min using a Heraeus Megafuge 16R centrifuge (Thermo Scientific, Waltham, MA, USA). The dye concentration in the solution was measured spectrophotometrically using a Biochrom WPA Lightwave II UV/visible Spectrophotometer (Cambridge, UK) at 664 and 545 nm (λ_{max}) for MB and BR9, respectively. The dye removal percentage was calculated using Equation (8):

$$\% \text{ Removal} = \frac{c_i - c_f}{c_i} 100 \quad (8)$$

where c_i (mg/L) and c_f (mg/L) are the initial and final dye concentrations, respectively, in the aqueous solution. The amount of adsorbed dye in the aqueous solution was estimated using Equation (9):

$$q_e = (c_i - c_e) \frac{V}{m} \quad (9)$$

where q_e is the amount of adsorbate adsorbed by the adsorbent; c_i (mg/L) and c_e (mg/L) are the initial and equilibrium dye concentrations, respectively, in the aqueous solution; V (L) is the solution volume; and m (g) is the mass of the adsorbent in volume (V). Each reported experimental result is the average of three replicate measurements, and error bars represent the standard error of the average.

3.5. Isotherm and Kinetic Studies

Isotherm studies were conducted using 500 mg of the adsorbent and 250 mL of the dye solution (30–120 mg/L concentrations) at pH 10 for MB and pH 7 for BR9. Adsorption was conducted for a contact time of 2 h at room temperature. Two nonlinear isotherm models, namely, Harkins–Jura and Brunauer–Emmett–Teller (BET) multilayer were used to evaluate the adsorption isotherms of MB and BR9.

Kinetic studies were performed by adding 500 mg of the adsorbent to the 250 mL dye solution at a fixed concentration (30 mg/L) at room temperature and the optimum pH (10 for MB and 7 for BR9). The amount of adsorbed dye was recorded from 5 min to 120 min. The adsorption kinetics for MB and BR9 were examined using two nonlinear kinetic models: pseudo-first-order (PFO) and pseudo-second order (PSO).

4. Conclusions

This study used raw IRH and HRH as bio-adsorbents to remove MB and BR9 from aqueous solutions. Findings showed that pH, adsorbent dose, initial dye concentration, and contact time significantly affected adsorption, but temperature did not. The MB removal percentage of IRH and HRH at pH 10 was 96%, while BR9 removal percentages at pH 7 were 82% and 87%, respectively. The optimal adsorbent dose for adsorbing MB and BR9 using IRH and HRH from a 250 mL aqueous solution was 500 mg. The isotherm data agreed with the BET multilayer adsorption isotherm model. The kinetic data indicated that MB and BR9 adsorption follow the pseudo-second order kinetic model. IRH and HRH exhibited different MB and BR9 adsorption capacities because of their different chemical compositions. Moreover, the chemical composition of RH depended on the RH location, farm climate, and crop technology, among others. The adsorption of MB and BR9 using a simple solution could help elucidate the general aspects of the adsorption process. Therefore, binary solutions and real wastewater should be used in further studies to get a better understanding of the interaction between adsorbent and adsorbate. Furthermore, dye recycling during adsorption should be explored to achieve sustainable dyeing and help address global challenges. Finally, both RHs in this study were rich in functional groups and have potential as efficient bio-adsorbents for dye removal from water and wastewater due to their low cost, simplicity, and environmental friendliness.

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