Rice Husk as Bioadsorbent for Dyes Removal and Recovery from Aqueous Solutions

<u>Thesis Booklet</u>

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INTRODUCTION AND OBJECTIVES

The dye industry is continuously developing and contributing to the world economy. The widespread use of dyes, with more than 100,000 kinds accessible for commercial purposes and an annual production of 1.6 million tons. However, this industry is a major global polluter and uses large amounts of water, chemicals, and fuels, which are transformed into highly loaded wastewater.

Wastewater treatment technologies are needed to remove pollutants from dye wastewater, and dye recycling is required to achieve sustainability. Multiple studies have verified that adsorption is a highly effective method for removing dyes, demonstrating its superior ability to remove pollutants compared with other conventional techniques.

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.

Indonesia is the fourth largest rice producer in the world. In 2023/2024, its rice production reached 31 million tons. Approximately ± 10.79 million tons of RH was produced in 2023. The utilization of RH from the rice milling process remains limited; it sometimes becomes waste and, thus, a source of environmental pollution. Besides, Hungarian rice husks are used for composting, brick, and animal feed. Reusing rice husks as bioadsorbents can reduce waste generation in the agricultural sector.

The role of RH as a good bioadsorbent for removing cationic dyes from aqueous solutions has been studied intensively. Methylene Blue (MB) and Basic Red 9 (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. 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 rice husk, and recycling dyes for sustainable dyeing. Moreover, desorption and regeneration studies were carried out to investigate the recovery efficiencies and adsorption–desorption cycles, thus evaluating the sustainability and cost-effectiveness of RH as a bioadsorbents. The adsorption experiments were carried out taking into account the principles of circular economy to assess the environmental sustainability of RH.

To achieve this overarching goal, the following specific objectives have been delineated:

1. Characterization of the physicochemical properties of the Hungarian rice husk (HRH) and Indonesian rice

husk (IRH) utilizing appropriate analytical techniques and methodologies.

2. Examination of the influential parameters governing the adsorption of MB and BR9 adsorption from single dye solution by the HRH and IRH using batch adsorption experiments.
3. Determination of kinetic and isotherm models that properly describe the mechanisms and properties of MB and BR9 adsorption from single dye solution by the HRH and IRH.
4. Examination of the influential factors affecting the adsorption of MB and BR9 adsorption from binary dyes solution by the HRH and IRH using batch adsorption experiments.
5. Determination of kinetic and isotherm models that properly describe the mechanisms and properties involved in the adsorption of MB and BR9 from binary dyes solution by the HRH and IRH.
6. Verify the efficiency of the HRH and IRH in removing MB from real wastewater using batch adsorption experiments.

7. Identification of the influential parameters affecting the adsorption of MB from real wastewater by the HRH and IRH.
8. Determination of kinetic and isotherm models that properly describe the mechanisms and properties of MB adsorption from real wastewater by the HRH and IRH.
9. Implementation of the hydrogen carbonization method to enhance the adsorptive properties of the RH for MB removal.
10. Exploration of the novel physicochemical properties of the RH Hydrochar.
11. Comparison of the contact time parameters for MB adsorption from real wastewater between the RH Hydrochar and raw RH.
12. Investigation of the desorption and regeneration studies of HRH and IRH.
13. Investigation on the recovered of MB dye for cotton fabrics.

MATERIALS AND METHODES

Dyes Preparation: A single solution was made using MB, and BR9 solutions were prepared by dissolving 1 g of the dye in 1 L of distilled water and mixing them for binary solutions. A wastewater stock solution containing MB (1000 mg/L) was prepared to imitate the composition of dye-containing wastewater originating from textile industries. The solution was prepared by dissolving 1 g of MB (Molar Chemical, Hungary), 22.5 g of Na_2SO_4, and 5 g of Na_2CO_3 in 1 L of distilled water, which was maintained at a temperature of 80 °C for 1 h.

Bioadsorbent Preparation: Rice husks (RH) from Indonesia (*Oryza sativa subsp. Javanica* (tropical *japonica*)) and Hungary (*Oryza sativa subsp. Japonica* var.M488) were washed, vacuum-dried, and ground to the desired size. Hydrothermal carbonization (Hydrochar) was performed in a 2 dm^3 batch reactor. The reactor was equipped with an electric heater and a stirrer controlled by a Parr 4842 microprocessor control unit, was loaded with 100 g of material and 400 g of distilled water. The experiment was performed at a temperature of 250 °C.

Characterization of RH: Chemical content analysis determined the lignin, cellulose, and ash, while zeta potential and Fourier Transform Infrared Spectroscopy (FT-IR) analysis assessed surface properties. Scanning Electron Microscopic (SEM) analysis was performed to examine the morphology of the adsorbent surface.

Batch Adsorption Studies: Single adsorption experiment was performed to determine the effects of certain parameters—pH, contact time, initial dye concentration, adsorbent dose, and temperature. Binary adsorption experiment was conducted to assess the effect of pH, adsorbent dose, contact time, and initial concentration. Important factors were identified using 23 factorial designs in Minitab® 20 statistical software. In addition, the MB model wastewater experiment examined the impact of various factors, including the pH, initial concentration, adsorbent dose, particle size, and contact time. Isotherm and kinetic studies were performed to model adsorption behavior.

Desorption and Regeneration: To assess the feasibility of adsorbent regeneration, we selected two potential solvents for desorption: 1 M HCl and 1 M NaOH solutions. To evaluate the regeneration of the adsorbent, we performed a minimum of four successive adsorption/desorption cycles.

Application on Textile Fabric: Finally, 150 mL filtrate was used for dyeing cotton fabrics at 80 °C for 60 min. The cotton fabric was dried at room temperature followed by color measurements.

SCIENTIFIC RESULTS

1. Characterization of RH

Acid pretreatment is suitable for lignocellulosic materials due to its ability to break down the rigid structure of lignocellulosic materials into cellulose and lignin. 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. In general, RH contains 28.6–43.3 cellulose, 19.2–24.4 lignin, and 11.3–20 ash.

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.

FT-IR analysis identified various functional groups in RH, such as O–H, N–H, C–H, C=O, and Si–O bonds. After dye adsorption, the original band positions shifted, and new bands appeared. Further, the IR spectra of RHs change after hydrogen carbonization, affecting its adsorption properties.

The surface morphology of RH and its hydrochar can be analyzed by SEM. The micrographs show that the surfaces were highly irregular and could not be characterized by any well-defined morphology, containing only a few fine particles. After hydrothermal carbonization, the RH is transformed into smaller particles with rough surfaces and porous structures.

2. Adsorption of cationic dyes using RH from aqueous solution

The study used raw Indonesian rice husk (IRH) and Hungarian rice husk (HRH) as bioadsorbents 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.

3. Binary adsorption of cationic dyes using RH from aqueous solution

Removal of MB and BR9 in binary adsorption was investigated also. Maximum removal percentages for MB and BR9 using HRH were 91.7% and 88.8%, respectively, and 83.8% and 78.2% using IRH, respectively. A BET multilayer isotherm best fit experimental data for binary adsorption. Binary adsorption of dyes followed the Elovich Equation based on kinetic data. A factorial design analysis indicated that interactions among adsorbent type*pH*dose for both dyes were insignificant. Interactions between main factors (adsorbent type, pH, and dose) were significant for MB and BR9, except for two-way interactions (adsorbent type*dose) for BR9.

4. Adsorption of methylene blue using rice husk from model wastewater

This study examines the effectiveness of using raw RHs as bioadsorbents to remove MB from wastewater. The impact of pH, adsorbent dose, initial dye concentration, particle size, and contact time on adsorption was investigated. The removal percentages of MB by HRH, IRH, HRH hydrochar, and IRH hydrochar at pH 12 were 92%, 88%, 94%, and 92%, respectively. MB removal was most effective at an adsorbent dose of 600 mg, achieved within a contact time of 60 minutes. In addition, the BET multilayer adsorption model characterized the isotherm data well, whereas the kinetic results were in good agreement with the Elovich model.

5. Desorption and regeneration of rice husk

After we investigated the applicability of HCl and NaOH as regenerating solutions, we found that the 1.0 M HCl solution produced the best result for the desorption of MB. After carrying out four adsorption–desorption cycles

(Figure 42), we found that the adsorption and desorption efficiencies of MB by HRH and IRH decreased from 92% to 87% and from 88% to 83%, respectively. Moreover, the RHs were effectively recycled for four consecutive adsorption/desorption cycles, demonstrating their exceptional reusability. Thus, it has been demonstrated that RH is both environmentally friendly and cost-effective as an adsorbent.

6. Reusing dye for cotton fabrics

After desorption, the MB was recovered, and the solutions were used for dyeing cotton fabrics. After four cycles, the recovered MB was still capable of dyeing the cotton fabrics. Based on the results, the acceptable tolerance for this investigation was considered $\Delta E^* < 5$. Based on the literature, the acceptable range for ΔE^* tolerance is between 2 and 6, beyond which differences are highly discernible.

NEW SCIENTIFIC RESULTS

1. Rice Husk (RH) is proven to be a bioadsorbent for MB and BR9 removal from aqueous solution:

a. Removal percentages for MB using HRH and IRH were 96%, respectively, and for BR9 using HRH and IRH were 83.8% and 78.2%, respectively.
b. The optimal condition for MB and BR9 removal was achieved at a contact time of 120 min using concentration value is 2 g/L, initial dye concentration of 30 mg/L at pH 10 (MB) and pH 7 (BR9) and a stirring rate of 100 rpm.
c. 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.
d. The adsorption of MB and BR9 is governed by chemisorption, a process characterized by the sharing or exchange of electrons between the negatively charged functional groups on the RH bioadsorbent and the positively charged cationic dye molecules.

2. HRH and IRH exhibited different MB and BR9 adsorption capacities because of their different chemical compositions. The HRH adsorption capacities were 24.4 mg/g for MB and 8.3 mg/g for BR9, whereas those of IRH were 15.0 mg/g for MB and 7.2 mg/g for BR9.

3. Rice husk can be considered as bioadsorbent for binary adsorption of tested cationic dyes from aqueous solution as well:

a. Removal percentages for MB and BR9 using HRH were 91.7% and 88.8%, respectively, and 83.8% and 78.2% using IRH, respectively.
b. The adsorption capacity of HRH was 10.4 mg/g for MB and 10 mg/g for BR9; values for IRH were 9.3 mg/g and 9.6 mg/g, respectively.
c. Adsorption is controlled by chemisorption, as evidenced by the application of the Elovich equation in describing the adsorption kinetics of MB and BR9.
d. A factorial design analysis indicated that interactions among adsorbent type*pH*dose for both dyes were insignificant. Interactions between main factors (adsorbent type, pH, and dose) were significant for

MB and BR9, except for two-way interactions (adsorbent type*dose) for BR9.

4. Rice husk was an effective bioadsorbent for Methylene Blue removal from model wastewater:

a. Removal percentages for MB using HRH and IRH were 92% and 88%, respectively.
b. The optimal condition for MB removal was achieved at a contact time of 60 min using 600 mg of adsorbent dose in 250 mL aqueous solution, initial dye concentration of 60 mg/L at pH 12 and a stirring rate of 100 rpm.
c. The HRH and IRH adsorption capacities were 52.23 mg/g and 47.92 mg/g.
d. The chemisorption took place during the adsorption process, as indicated by the Elovich model. This model assumes that adsorption involves chemical interactions between the MB and the RH biodsorbent.

5. Rice husk was successfully modified by hydrothermal carbonization method for efficient Methylene Blue adsorption:

a. The hydrothermal carbonization changed the previously smooth surface of the raw RH,the RH is transformed into smaller particles with rough surfaces and porous structures.
b. The removal percentage for hydrochar RH was slightly greater than that for raw RH; however, the difference was insignificant. Consequently, raw RH is cheaper and more effective for MB removal from wastewater than RH hydrochar.

6. Rice husk was successfully utilized for desorption and regeneration processes, aligning with the principles of the circular economy to evaluate the environmental sustainability of this bioadsorbent:

a. 1.0 M HCl was the most effective desorbing solution in the desorption of MB from model wastewater.
b. The RH was effectively recycled for four consecutive adsorption-desorption cycles and can be reused with a 5% reduction in adsorption percentages.

7. The MB solution recovered by desorption can be used for dyeing cotton fabrics:

a. After four processing cycles, the recovered MB was still capable of dyeing the cotton fabrics.
b. Reusing dye for cotton fabrics after the adsorption-desorption process demonstrated an acceptable range for ΔE^* value of 0 to 5 or below.

PUBLICATIONS

MTMT Author ID: 10081549

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