

Potential Indonesian Rice Husk for Wastewater Treatment: Agricultural Waste Preparation and Dye Removal Application

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Abstract

This study used a novel method to transform rice husk waste into a highly effective and specific adsorbent for several dyes, including malachite green, direct yellow, congo red, and rodhamine B. The rice husk was analyzed and used for the purpose of eliminating these colors from water-based solutions. The adsorbent exhibited excellent heat stability, and the sample retained the functional groups of lignin. The parameters pertaining to kinetics were also examined. The adsorption exhibited a time-dependent rise and reached its peak after 100 minutes. In the kinetics tests, the most suitable model to characterize the behavior was found to be the pseudo-first order, with a regression value near to one. The rice husk shown significant potential and selectivity in the removal of malachite green and rodhamine B, particularly in the presence of direct yellow and congo red, from aqueous solutions.

Keywords

Agricultural Waste, Rice Husk, Wastewater Treatment

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1. INTRODUCTION

Rice as one of the most widely consumed cereal crops shows regional characteristics in its geographical distribution. This is largely concentrated in Asia where more than 90% of rice worldwide is produced (Varela Milla et al., 2013). There are more than 75 countries that cultivate rice, while Indonesia is the third largest rice producer after China and India. As an unavoidable byproduct of the rice industry, such as rice husks have traditionally had a low utilization rate especially in Indonesia (Foo and Hameed, 2009). The general practice of disposing of agricultural waste is by piling and/or stockpiling on empty land. In some cases, efforts have been made to recover energy from rice husks through combustion and gasification, producing heat, electricity and biogas. However, insufficient burning of carbon particles in rice husks will cause the release of toxic gases. As a result, the current rice husk disposal methods not only cause safety problems, waste resources, but also cause serious pollution to the environment. Therefore, utilizing this enormous rice husk resource in an environmentally friendly and sustainable manner has become one of Indonesia major environmental challenges (Malik et al., 2020).

When population expansion and the resulting rise in consumption are taken into account, proper waste management

becomes a critical challenge. Numerous wastes have been examined, put to the test, and altered (da Rosa et al., 2019). Researchers are working to increase our understanding of waste management. In the same way, there should be a growing need to develop novel approaches to managing this issue. Consequently, it is critical to draw attention to the wastes produced by the agroindustry, such as rice husk (Ahmad et al., 2020), bamboo (Li et al., 2019), wasted olive oil, palm shell, etc. (Naushad et al., 2019) Natural polymers like cellulose, hemicellulose, and lignin as well as trace amounts of inorganics like silica are present in all of these components. It is noteworthy to mention that silica is a highly significant inorganic material found in rice husk, with a level that can approach 20% w w-1 (da Rosa et al., 2019).

Conversely, the issue of environmental difficulties caused by the existence of dyes in water-based systems is not a recent one and poses challenges in finding effective remedies due to their limited ability to break down and dissolve in water (Amalina et al., 2022). In 2003, it was estimated that there were over 100,000 different types of commercial dyes in existence. These materials find application in several industries such as textiles, leather, paper, plastics, and more. The global production of these compounds exceeds 700,000 tons per year, with a projected growth rate of approximately

3 to 4% in comparison to traditional dye businesses. This equates to an additional 30,000 tons per year (Rahayu et al., 2021).

Furthermore, it is approximated that the textile industry alone is accountable for the discharge of 280,000 tons of dyes into wastewater (Sharma et al., 2023). The loss of dye in applications other than textiles might reach up to 50%, depending on the dye class and fixing procedure employed. Even trace amounts of dyes in water can be hazardous to aquatic life. The existence of pigmented waste substances leads to issues concerning the diminished diffusion of oxygen in water and disrupted photosynthesis in aquatic organisms as a result of decreased light permeability. The persistence of dyes' aromatic structure is likely the cause of their carcinogenic and mutagenic effects in nature (Ahmad et al., 2023b). Dyes, such as malachite green, congo red, rodhamine B and direct yellow, play a crucial role in various industrial sectors, including textiles (for cotton and polyamide fibers), printing (requiring high-purity reactive dyes), leather (where cationic dyes were the first synthetic dyes used), and plastics (utilizing fat and oil-soluble colors) (Ahmad et al., 2023a). These dyes have detrimental impacts on the health of both humans and animals. Several symptoms may manifest if consumed, including a burning feeling, cognitive disorientation, nausea, excessive perspiration, vomiting, diarrhea, and gastritis. Recently, effective methods for eliminating dyes from water have been employed, such as quantum dots based photocatalysis and magnetic nanoparticles based adsorption (Sharma et al., 2023). Nevertheless, these techniques have many disadvantages, including exorbitant expenses, substantial reagent usage, and the creation of unwanted or poisonous byproducts (da Rosa et al., 2019). Consequently, the use of this technology in industries remains challenging. Adsorption operation is a significant process among the known procedures because of its high efficiency, low cost, and ease of operation (Agarwal et al., 2016; Amalina et al., 2022; Huang et al., 2019).

This study presents a novel methodology consisting of two stages to assess the potential of rice husk, an agro-industrial waste, for use as an adsorbent material. The objective is to develop a rice husk adsorbent that can rapidly and effectively remove colors from water-based solutions. The rice husk adsorbent was subjected to characterization in order to assess its functional groups and surface area properties. Studying the kinetics and equilibrium assays provides optimal conditions for dye removal. This method facilitated the creation of a solution to address two environmental issues: the conversion of a plentiful agricultural waste, such as rice husk, into a rapid and effective adsorbent, and the potential for using adsorption processes to remove colors and recover wastewater.

2. EXPERIMENTAL SECTION

2.1 Materials and Instrumentations

the rice husk is by-product of rice processing with 20% of paddy produced. Rice husk was obtained in local paddy field in Ogan Ilir Regency, South Sumatera. They are highly rich in silica with about 75–90% organic matter content. Rice husk obtained by paddy produced in Indonesia. Dyes including rhodamine-B (Rh-B), congo red (CR), malachite green (MG) and direct yellow (DY) purchased by Merck. Instruments used XRD Rigaku SmartLab; FTIR Jasco 4200 by implementing the KBr pellet method; SEM Hitachi SU8010, specific surface area and porosity of the materials was determined with N₂ adsorption-desorption analysis in a Quantachrome Nova 4200e instrument; UV-Visible spectrophotometer Biobase.

2.2 Adsorption Experiments

To investigate the adsorption parameters, several factors were considered including the mass of adsorbents, adsorption time, concentration, and temperature. The adsorption experiments were conducted using 0.05 g adsorbent; concentration of adsorbate 50 mg/L and volume 50 mL; contact periods varying from 0 to 200 minutes. After adsorption, the concentration of the filtrate was measured at a wavelength of 400-700 nm using a UV-Visible spectrophotometer in specific wavelength of dyes.

3. RESULT AND DISCUSSION

Rice husk is a byproduct of rice milling and is often considered an agricultural waste. According to Ahmad et al. (2023a), rice husk can be appropriate to reduce pollutants in wastewater such as dyes. Researchers also using rice husk for one of the potential uses for biochar and biomass energy. Indonesia is one of the largest producers of rice globally especially, in South Sumatera, Ogan Ilir Regency. Paddy fields are flooded fields used for cultivating rice, and they play a crucial role in Indonesia's agricultural landscape. As shown in Figure 1, the local paddy field show in Figure 1.A and Figure 1.B shows the Rice Husk. Without any chemical treatment, rice husk can be the alternative solution for dye treatment in waste water. Thus, the rice husk was heated in the oven for two days at 80 °C to reduce the water. then, the rice husks that have been in the oven are crushed and sifted using an 80 Mesh sieve. After the rice husks have become fine grain, put them back in the oven at 60 °C for a day, then they are ready to be characterize (XRD, FTIR, BET, SEM) and use as adsorbent.

The results of rice husk xrd pattern was shown in Figure 2. Based on Figure 2. the XRD pattern of rice husk typically shows diffraction peaks at specific angles that correspond to the amorphous structure of the material. Rice husk primarily consists of cellulose, hemicellulose, lignin, and various inorganic minerals, such as silica. The XRD pattern of rice husk is characterized by the presence of sharp diffraction



Figure 1. Local Paddy Field in Ogan Ilir Regency, South Sumatera

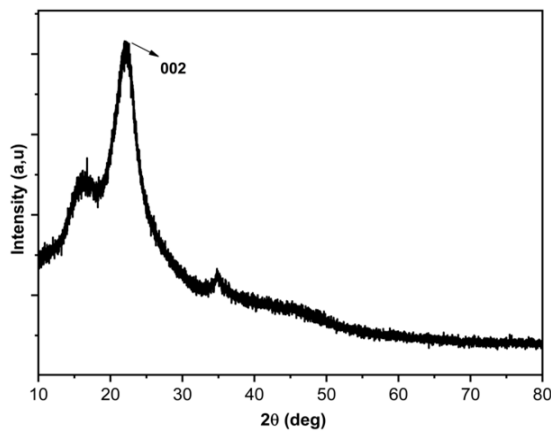


Figure 2. XRD Pattern of Rice Husk

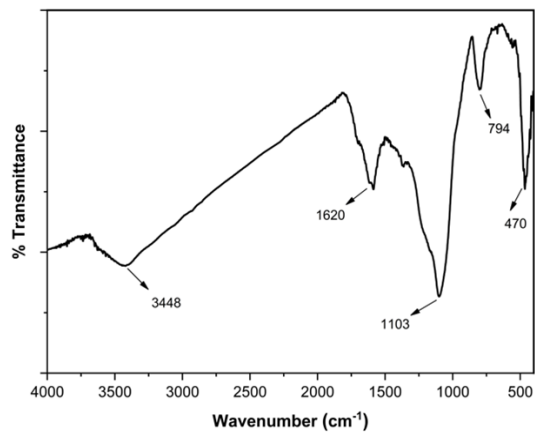


Figure 3. FTIR Spectra of Rice Husk

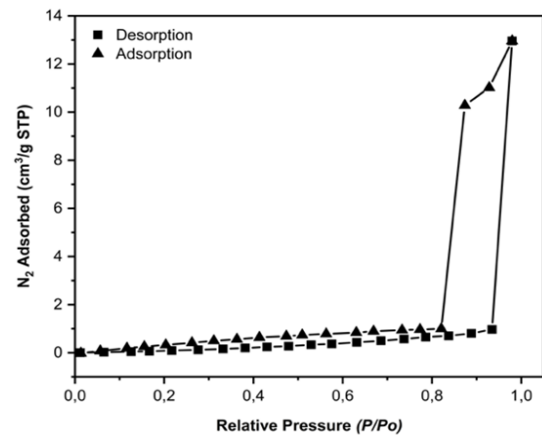


Figure 4. The Nitrogen Adsorption-Desorption Isotherm of Rice Husk

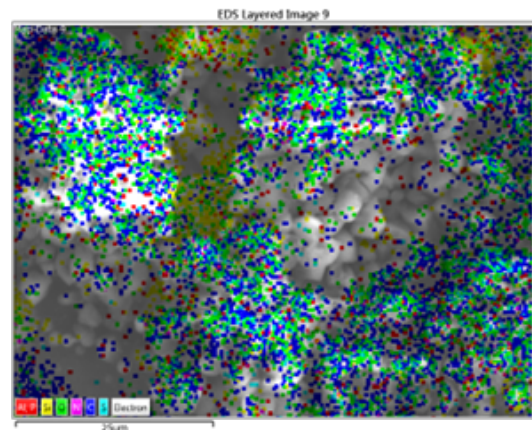


Figure 5. Morphology of SEM-EDS of Rice Husk

peaks at specific angles, primarily associated with the silica corresponds to the (002) plane of silica (SiO_2) at 26° . Rice husk contains cellulose, which may exhibit wide and overlap XRD peaks at around 2θ angles of 16° , and 22° . Furthermore, rice husk was determined by FTIR characterization as shown in Figure 3. FTIR spectra of rice husk showed charac-

teristic peaks associated with its various components O–H stretching with broad peak around 3448 cm^{-1} . The sharp peak under 1000 cm^{-1} indicate the reflection of Si–O–Si bond. O–H bending in water molecule was reflect at 1620 cm^{-1} and overlap with C–H stretching at 1600 cm^{-1} . Thus,

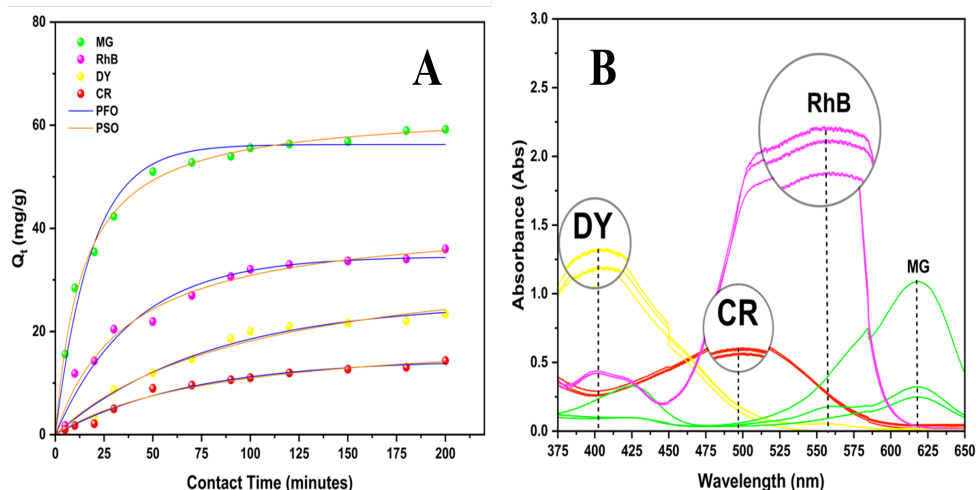


Figure 6. Kinetics and Selectivity Dyes Adsorption by Rice Husk

Table 1. Typical Properties of Rice Husk

Property	Range
Surface Area	7.085 m ² /g
Bulk Density	96-160 Kg/m ³
O	42.5 %
C	40 %
Si	9.3 %
N	3.7 %
P	2.9 %
Al	1.0 %
S	0.7 %

the sharp peak at 1103 cm⁻¹ C–O–C stretching (glycosidic linkages) from cellulose and hemicellulose.

The Brunauer-Emmett-Teller (BET) method is a widely used technique for determining the specific surface area of porous materials. The surface area of rice husk was determined using BET method as shown in Figure 4. This type of isotherm is typically used to characterize the surface area and porosity of rice husk. The shape of the isotherm provides valuable information about the pore structure of the material. Type of nitrogen adsorption-desorption isotherm of rice husk indicated type II isotherm (Gibbs type). This type indicates a rice husk with mesoporous characteristics. It typically exhibits a steep initial rise at low relative pressures, indicating the presence of micropores, followed by a hysteresis loop at higher relative pressures, indicating the presence of mesopores. Based on BET calculated, the surface area of rice husk 7.085 m²/g as listed in Table 1. Table 1. Showed the compositions of rice husk, identified by EDS. According to Table 1, the most component of rice husk is carbon 40% and oxygen 42.5%. The oxygen content of 42.5%

in the rice husk indicates that the characterized rice husk still contains a lot of water molecules and sugar molecule, so the active site of carbon is still not effective. However, 40% of the carbon component contained is sufficient to be used as an active site in the adsorption process.

Thus, the morphology of rice husk was indicated by SEM as shown in Figure 5. The surface of the rice husk is uniform and the surface is covered with a lot of carbon and oxygen which is indicated to come from sugar and cellulose molecules which make the rice husk have micropores.

After the materials characterized well, rice husk was prepared to adsorption process. the adsorption process was conducted by time adsorption and selectivity dye adsorption. The silica content in rice husk ash is one of the key factors contributing to its adsorption capabilities. The time adsorption was investigate the kinetics of the adsorption process to understand how quickly the dye molecules are taken up by the adsorbent. The kinetics of adsorption can be described by various models. One of the commonly used models is the pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetics models (Yuan et al., 2023). The best fitted regression depends on the experimental data can be expressed the models fit. According to Figure 6 A, the effect of adsorbent contact time is one of the essential key for adsorption experiments, which can offer the lowest time required for the maximum adsorption capacity. The plot indicates that all dyes adsorption rises as contact time increase. Adsorption was fast during the 10 minute until 100 min, and thereafter a steady increase until equilibrium was established after 200 min. Nonlinear regression was used to estimate the parameters of both models. The values of regression showed PSO better than PFO. The computed equilibrium values (qcal) of PSO model agree with the experimental results. This finding shows that the retention and adsorbed capacity of MG on rice husk was correlated by PSO and more adsorbed

than others dyes.

The results of adsorption selectivity (Figure 6B) also support that MG is more adsorbed compared to other dyes such as RhB, DY, and CR. MG has a small molecular structure and size so it is more easily adsorbed (Lin et al., 2018; Jaffari et al., 2023; Zhang et al., 2019). Apart from that, the cationic groups of MG and RhB dyes make them more easily adsorbed compared to anionic dyes such as DY and CR. Based on the results above, it can be concluded that rice husks can be used as an alternative waste utilization for waste management.

4. CONCLUSION

In this work, rice husk was prepared without chemical treatment, rice husk was analyzed by XRD, FTIR, BET and SEM/EDX. According to the experimental results, the MG more selective than RhB, DY and CR by the rice husk during MG has small molecule and surface of rice husk demonstrates that the adsorption phenomenon using cationic dye MG and RhB more efficient than anionic dye. The adsorption kinetic was described with a pseudo-second-order model. It can be concluded that rice husks can be used as an alternative agriculture waste for dye removal in wastewater.

5. ACKNOWLEDGEMENT

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