Simultaneous Methylene Blue Adsorption and pH Neutralization of Contaminated Water by Rice Husk Ash

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ABSTRACT: In this study, the potential of rice husk ash (RHA) to act as an adsorbent for treating dye-containing wastewater was demonstrated. The RHA used in this study contained 91.7% silica, which was composed of crystalline (cristobalite and tridymite) and amorphous phases. The mechanochemical treatment of RHA led to an increase in its specific surface area from 6.2 to 14.6 m²/g in 15 min and dramatically improved its methylene blue (MB) adsorption ability. Langmuir adsorption isotherms revealed that the maximum adsorption capacity of the treated RHA was 8.59 mg/g, which is 2.45 times higher than that of raw RHA. pH-dependent adsorption studies on the RHA revealed that MB was adsorbed on the deprotonated Q³ silanol through electrostatic interactions. Moreover, the RHA adsorbent showed pH buffering at a pH value of approximately 7; thus, the pH of the solution could be neutralized simultaneously with the adsorptive removal of MB.

1. INTRODUCTION

Treatment of contaminated water is essential for sustainable development. Water treatments and related topics have been actively researched.¹⁻¹⁴ Wastewater-containing synthetic organic dyes are discharged from several plants, such as in the food, cosmetics, paper, printing, plastics, and textile industries, into water bodies. These dyes adversely affect the environment and ecosystems by increasing the chemical and biochemical oxygen demand (COD and BOD, respectively), hampering the photosynthesis process and leading to bioaccumulation.¹⁵ Therefore, their removal from industrial wastewater is of major environmental concern. Several techniques to remove organic dyes from wastewater are available, including membrane separation, photocatalytic degradation, enzymatic degradation, biodegradation, Fenton treatment, and adsorption.¹⁶⁻²² Among these, adsorption is the most widely used approach for removing organic dyes from wastewater because it is inexpensive, easy, safe, and eco-friendly. In addition, it does not require large-scale equipment. However, wastewater from the different industries utilizing dyes typically covers a wide pH range.²³ This characteristic necessitates the study of the behavior of the adsorbent over a wide pH range.

Rice husk is an agricultural byproduct that is abundantly available and is a potential biomass source in rice-producing countries. Due to its high calorific power, rice husk has been used for decades as fuel in power plants.²⁴⁻²⁶ Rice husk ash (RHA) is produced during the combustion of rice husk. RHA consists of 85–98% silica,²⁷ and its low density and bulky form make its disposal a challenge. In some areas, RHA is treated as waste and disposed at landfill sites, causing air and water pollution. Airborne RHA particles have been linked to respiratory diseases in humans.²⁸ If RHA is not used further, there may be large-scale waste accumulation, disposal problems, and environmental pollution. Therefore, it is imperative to recycle RHA.

Various studies have been conducted on the effective utilization of RHA as a silica source or as an alternative to silica because the main component of RHA is silica. For example, RHA has been used as a construction material to produce concrete²⁹,³⁰ and silicon-based materials such as silicon carbide, zeolite, and mesoporous silica.³¹⁻³³ Researchers have reported the use of RHA to adsorb toxic metal ions, such as cadmium(II), lead(II), mercury(II), zinc(II), selenium(IV), and chromium(VI) ions.³⁴⁻³⁸ Other classes of compounds such as organic matter and volatile organic compounds, including phenol, benzene, styrene, bisphenol-A, and ammonia, can be adsorbed by RHA.³⁸⁻⁴¹ Furthermore, studies on the adsorption of organic dyes such as rhodamine B and remazol red by RHA have also been reported.⁴²,⁴³

Received: May 31, 2021
Accepted: August 11, 2021
Published: August 16, 2021
For crystalline inorganic materials, mechanochemical treatment decreases their crystallinity and increases the surface energy and reactivity, causing an increase in chemical activity.\textsuperscript{44,45} Mechanochemical treatment has been studied for the activation of materials, and its effect on adsorbents has been reported.\textsuperscript{46−48} It has been shown to increase the adsorption capacity and rate of coal fly ash for phenol.\textsuperscript{46} Thus, mechanochemical treatment is expected to enhance the adsorption capacity of RHA. However, the finer details of the effect of mechanochemical treatment on the physicochemical properties of RHA have not been clarified, and the effect on the adsorption reaction has not been elucidated.

In this study, RHA obtained from a rice husk power plant in Myanmar was subjected to mechanochemical treatment in a planetary ball mill. The physicochemical properties of the obtained products were characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FE-SEM), and the N\textsubscript{2} adsorption method to investigate the effect of the treatment on the RHA. The adsorption kinetics and equilibrium studies of raw and treated RHA were conducted using methylene blue (MB) dye. The effect of the pH value of the MB aqueous solution on the adsorption of MB onto RHA was investigated since the properties of RHA adsorbents over a wide pH range have not been determined before, to the best of our knowledge.

2. RESULTS AND DISCUSSION

2.1. Material Characterization. Figure 1 shows the XRD patterns of the raw and mechanochemically treated RHA samples. The XRD pattern of the raw RHA confirmed the presence of diffraction peaks corresponding to the cristobalite (ICDD no. 39-1425) and tridymite (ICDD no. 18-1170) phases. There was also a broad halo peak typical of amorphous silica at $2\theta = 23^\circ$.\textsuperscript{49} As the treatment progressed, the diffraction peaks became broader, and their intensities decreased. After 60 min of mechanochemical treatment, the diffraction peaks became negligible. In contrast, the halo peak attributed to amorphous silica was clearly observed after the mechanochemical treatment. These results indicate that the crystalline silica in the raw RHA transformed into amorphous silica after the mechanochemical treatment. In the mechanochemically treated samples, tungsten carbide (ICDD no. 73-0471) contamination from the tungsten carbide container and grinding medium was detected. The intensities of the peaks increased as the treatment progressed.

Figure 2 shows the FTIR spectra of the raw and mechanochemically treated RHA samples. The band assignments of the FTIR spectra were based on previous studies.\textsuperscript{50,51} The bands at 470 and 795 cm$^{-1}$ are assigned to the Si–O–Si bending and Si–O–Si symmetrical stretching vibrations, respectively. No major changes were observed in these bands due to the mechanochemical treatment. A strong broad band at 1100 cm$^{-1}$ was assigned to the Si–O–Si asymmetric stretching vibration and was accompanied by a shoulder band at 1215 cm$^{-1}$ assigned to the Si–O–Si vibration in amorphous SiO$_2$. The intensity of the shoulder band increased with increasing mechanochemical treatment time. The band at 1630 cm$^{-1}$ and wide broad band around 3480 cm$^{-1}$ arose due to the mechanochemical treatment, and they were assigned to both the Si–OH vibration and the O–H vibration of physically adsorbed water.

![Figure 1. XRD patterns of raw and mechanochemically treated RHA samples (treatment times: 15, 30, and 60 min).](https://doi.org/10.1021/acsomega.1c02833)

![Figure 2. FTIR spectra of raw and mechanochemically treated RHA samples (treatment times: 15, 30, and 60 min).](https://doi.org/10.1021/acsomega.1c02833)
Figure 3 shows the FE-SEM images of the raw RHA (a) and RHA samples treated mechanochemically for 15 (b), 30 (c), and 60 min (d).

The nitrogen adsorption–desorption isotherms (a) and BJH pore-size distribution plots (b) of the raw and mechanochemically treated (for 15, 30, and 60 min) RHA samples are shown in Figure 4.

Table 1. Physicochemical Properties of the Samples

| sample             | BET specific surface area (m²/g) | average pore diameter (nm) |
|--------------------|----------------------------------|----------------------------|
| raw RHA            | 6.2                              | 27.1                       |
| 15 min-treated RHA | 14.6                             | 17.1                       |
| 30 min-treated RHA | 10.8                             | 18.7                       |
| 60 min-treated RHA | 11.3                             | 18.3                       |

The isotherms of the raw RHA sample revealed that a large amount of nitrogen was adsorbed, and a hysteresis loop was observed at $P/P_0 > 0.8$, indicating the presence of large mesopores and macropores. The specific surface area was found to be 6.2 m²/g. The BJH pore-size distribution plot revealed the existence of a variety of meso- and macropores in the raw RHA sample. Hysteresis loops were also observed in the mechanochemically treated samples. The treated samples showed higher nitrogen adsorbed.
adsorption than the raw RHA sample. There was a significant increase in the number of pores, smaller than 40 nm in size, for the mecanochemically treated samples as indicated by the BJH pore-size distribution plots. We believe that these pores formed between the small particles that formed aggregates. The specific surface areas of the samples treated for 15, 30, and 60 min were 14.6, 10.8, and 11.3 m²/g, respectively. The mecanochemical treatment increased the specific surface area of the RHA samples with the maximum value being attained after 15 min of treatment. The reduction in the specific surface area due to the prolonged treatment is attributed to the aggregation of particles because of the high energy generated during the treatment.

2.2. Adsorption Kinetics. The ability of the treated samples to absorb MB was compared with that of the raw RHA sample. The treated sample, which had the highest specific surface area (treated for 15 min), was used for this comparison. The quantity of MB adsorbed on the samples, \( q_m \) (mg/g), was calculated from the initial and final concentrations according to the following equation:

\[
q_m = \frac{V(C_0 - C_e)}{m}
\]

where \( C_0 \) is the initial concentration (mg/L), \( C_e \) is the final concentration (mg/L), \( V \) is the volume of the solution (L), and \( m \) is the mass of sample (g). Figure 5 shows the percentage removal of MB via adsorption as a function of time and Figure 6 shows the solution pH of the RHA samples as a function of time during the adsorption experiments. When raw RHA was used as the adsorbent, the adsorption removal percentage increased to more than 40% within 30 min and almost reached equilibrium in 3 h. The adsorption removal percentage after 6 h was 50.2%. For the treated sample, the adsorption removal percentage increased to 88.9% within the first 30 min, after which the concentration slightly decreased until 3 h. After 6 h, the adsorption removal percentage was 83.6%. The quantities of MB adsorbed over a 6 h period by the raw and treated RHA samples were 3.01 and 5.02 mg/g, respectively. These results indicate that the treated sample had a higher adsorption rate and capacity than the raw RHA sample. The pH of the solution increased in the first 30 min but decreased thereafter and became almost constant after 3 h. The final pH values of both samples were almost the same, that is, slightly above the neutral point. It should be noted that the time required for the MB concentration to reach the equilibrium value was the same as that required for the pH to reach the equilibrium state, that is, 3 h. This indicates that there was a correlation between the MB adsorption and solution pH. This correlation was elucidated by conducting pH-dependent adsorption experiments for MB adsorption, as discussed in the following section.

2.3. Adsorption Isotherms. Figure 7a,b shows the MB adsorption isotherms of the raw and treated (15 min) RHA samples, respectively. The isotherms were assessed using the Langmuir and Freundlich models. The Langmuir equation is expressed as

\[
\frac{q_e}{q_m} = \frac{1}{K_L C_e} + \frac{1}{q_m}
\]

where \( q_e \) (mg/g) is the amount of MB adsorbed under the equilibrium concentration in the aqueous phase at \( C_e \) (mg/L), and \( q_m \) (mg/g) and \( K_L \) (L/mg) are the maximum adsorption capacity and Langmuir constant, respectively. The Freundlich equation is expressed as

\[
q_e = K_F C_e^{1/n}
\]

where \( K_F \) and \( 1/n \) are the Freundlich constants. The parameter values determined using eqs 2 and 3 are listed in Table 2. According to the correlation coefficient \( R^2 \), the Langmuir model is more appropriate for use. The maximum adsorption capacities calculated by the Langmuir model of the raw and treated RHA samples were 3.51 and 8.59 mg/L, respectively. The adsorption capacity of the treated sample was approximately 2.45 times higher than that of the raw RHA sample (Figure 7a,b). After mecanochemical treatment for 15 min, the specific surface area of the raw RHA sample increased from 6.2 to 14.6 m²/g (by approximately 2.35 times), Table 1). The magnitude of the increase in the adsorption capacity of the treated sample was almost the same as that of the specific surface area. This was due to the adsorption of MB onto the adsorbent surface. These results demonstrate that the ability of RHA to absorb MB can be dramatically improved by employing a mecanochemical treatment. The MB adsorption capacities of the raw and treated RHA were compared with those of various adsorbents derived from wastes (Table 3). The adsorption capacities of the RHA adsorbents prepared in this study were within the range of the values.

2.4. pH-Dependent Adsorption. In general, the solution pH is considered as an important parameter that influences the adsorption at water–adsorbent interfaces. Therefore, the
adsorption of MB on the raw and treated (15 min) RHA samples was investigated at different solution pH values ranging from 3.0 to 11.0. The effect of the initial pH on the MB adsorption removal percentage of the raw and treated RHA samples is shown in Figure 8a,b, respectively. For the raw RHA sample, at an initial pH of 3.0, the adsorption removal percentage increased sharply from 0.0% to 27.3% after 30 min. Thereafter, the adsorption removal percentage continued to increase gradually and reached 34.3% after 6 h. It was found that the MB adsorption ability of the raw RHA sample increased with an increase in the initial pH. When the initial pH was 11.0, the MB adsorption removal percentage increased to 76.7% in the first 30 min and then to 82.7% after 6 h. At an initial pH of 5.0−9.0, the adsorption removal percentage rose above 80% in the first 30 min, and there was almost no change thereafter. For the treated sample, when the initial pH was 3.0, the adsorption removal percentage increased sharply from 0.0% to 48.7% after 30 min. Thereafter, the adsorption removal percentage continued to increase gradually and reached 57.3% after 6 h. At an initial pH of 5.0−11.0, almost the same trend in the adsorption removal percentage was observed, that is, the adsorption removal percentage rose above 80% in the first 30 min, and there was almost no change thereafter. For the raw RHA sample, the MB adsorption ability at pH = 5−9 was significantly different from that at pH = 11. However, in the case of the treated sample,
the MB adsorption ability remained almost constant over the initial pH range of 5−11.

The pH values of the solutions containing the raw and treated RHA samples as a function of time are shown in Figure 9a,b, respectively. Notably, both the raw and treated RHA samples exhibited a pH-buffering ability. When the initial pH was 5−9, the solution pH changed as time progressed and almost reached stability (approximately pH 7). This is a characteristic property of RHA, because silica materials generally do not exhibit such pH-buffering ability. This increase in pH can be attributed to the dissolution of alkaline components (such as Na and K) present in the RHA. In the treated sample, the pH increased in the first 30 min when the initial pH was 5.0 and 7.0. This is because the dissolution of the alkaline component was promoted by the reduction in particle size of RHA and an increase in its specific surface area by mechanochemical treatment. The decrease in pH was due to the deprotonation of the surface silanol groups. The raw and treated RHA samples showed a slight increase in the solution pH at an initial pH of 3.0 and a slight decrease in the solution pH at an initial pH of 11.0.

At an initial pH of 5−9, the final MB adsorption removal percentages were almost the same in both samples. The final pH values of the samples were also almost the same. This indicates that the pH of the aqueous solution significantly affected the MB adsorption ability of the samples. Figure 10 shows the proposed adsorption mechanism of MB on RHA. The main component of RHA is silica, and the silica surface comprises mainly two types of silanol groups: Q₃ for the \( (\text{SiO})_3 \)−SiOH structure and Q₂ for the \( (\text{SiO})_2 \)−Si−(OH)₂ structure with each group having a different \( pK_a \) value.

Figure 9. Changes in solution pH with time during adsorption experiments with raw (a) and 15 min-treated RHA samples (b) at an initial pH of 3−11 (25 °C, adsorbent dosage = 500 mg, and \( C_0 = 5.0 \text{mg/L} \) for raw RHA sample and 10.0 mg/L for 15 min-treated RHA sample). Small and large dotted lines denote pH values of 4.5 and 8.5, respectively.

Figure 10. Illustration of the proposed mechanism of MB adsorption on RHA.

3. CONCLUSIONS

In this study, RHA discharged from a rice husk power plant in Myanmar was used as an adsorbent for MB. The main component of RHA is silica (crystalline and amorphous). The mechanochemical treatment of the RHA resulted in the transformation of the crystalline silica into amorphous silica, and the specific surface area of the RHA increased from 6.2 to 14.6 m²/g within 15 min. The MB adsorption ability of RHA improved significantly after mechanochemical treatment. The adsorption equilibrium was attained after approximately 3 h. The maximum adsorption capacity of the treated RHA sample 21609

https://doi.org/10.1021/acsomega.1c02833
ACS Omega 2021, 6, 21604−21612
was calculated by fitting the Langmuir equation to the adsorption isotherm and was found to be 8.59 mg/L, which is 2.45 times higher than that of the raw RHA sample. The adsorption of MB onto the RHA was mainly due to its electrostatic interaction with the deprotonated Q$^+$ silanol present on the surface of the RHA. Notably, the RHA adsorbent showed pH-buffering ability, that is, the neutralization of the solution pH and the adsorption of MB occurred simultaneously.

4. EXPERIMENTAL METHODS

4.1. Sample Preparation and Characterization. RHA obtained from a rice husk power plant in Myanmar was used as the starting material. The chemical composition of the raw RHA was 91.7% SiO$_2$, 0.8% Al$_2$O$_3$, 0.1% Na$_2$O, 1.8% K$_2$O, 0.4% CaO, 0.5% Fe$_2$O$_3$, 0.5% MgO, and 1.2% P$_2$O$_5$. The ignition loss was 2.9%. Figure 11 shows the preparation process of the RHA adsorbent. The raw RHA was subjected to mechanochemical treatment using a planetary ball mill (Fritsch P7), a tungsten carbide container, and a tungsten carbide grinding medium. The raw RHA samples (2.5 g) were placed in a ball milling container and subjected to mechanochemical treatment at a rotation speed of 500 rpm for 15, 30, and 60 min.

The powder XRD patterns of the samples were obtained using Cu Kα radiation with a diffractometer (Rigaku, RINT 2000). FTIR spectra were recorded on a FTIR-4100 spectrometer (JASCO, Japan). The particle morphologies of the samples were examined using FE-SEM (Hitachi, S-4700). FTIR spectra were recorded on an FTIR-4100 spectrometer (JASCO, V-750) at the wavelength corresponding to the maximum absorbance (664.5 nm).

To determine the equilibrium adsorption capacities of the RHA samples, a predetermined amount of sample (100 mg to 1.00 g) was added to 100 mL of the MB solution (10.0–50.0 mg/L), and the resulting mixture was stirred with a magnetic stirrer at 300 rpm for 6 h at 25 °C. Solid particles were separated from the solution by filtration with a 0.20 μm PTFE filter, and the concentration of the residual MB in the filtrate was measured using a UV–vis spectrophotometer.

The pH-dependent experiments on the RHA samples were carried out by adjusting the initial pH (3–11) of the 5.0 mg/L MB solution for the raw RHA and the 10.0 mg/L MB solution for the treated RHA sample using nitric acid or sodium hydrate solutions, respectively. The RHA samples (500 mg) were added to 300 mL of the MB solution, and the resulting mixture was stirred with a magnetic stirrer at 300 rpm for 6 h at 25 °C. The pH of the mixture was measured intermittently using a pH meter. The solutions were sampled intermittently through a 0.20 μm PTFE filter, and the concentration of the residual MB in the filtrates was measured using a UV–vis spectrophotometer.

4.2. MB Adsorption. The adsorption abilities of the mechanochemically treated RHA samples were compared to those of the raw RHA. Aqueous solutions were prepared by dissolving a predetermined amount of MB (Wako Pure Chemical Industries, Ltd.) in distilled water. All of the experiments were performed at 25 °C.

The kinetics of MB adsorption on the RHA samples were investigated according to the following method. The RHA samples (500 mg) were added to 300 mL of MB solution (10.0 mg/L) and stirred with a magnetic stirrer at 300 rpm for 6 h at 25 °C. The pH of the resulting mixture was measured intermittently using a pH meter (Horiba, D-71). The solutions were sampled intermittently through a 0.20 μm PTFE filter, and the concentration of the residual MB in the filtrates was measured using a UV–vis spectrophotometer.

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by the Cooperative Research Project Foundation of the Advanced Science Research Laboratory, Saitama Institute of Technology. The authors would like to thank Editage (www.editage.com) for English language editing.

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