

Rice Husk Ash: A Promising Heavy Metal Adsorbent For Wastewater Treatment

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Abstract

The primary polluter of the environment is liquid waste. Silica is one substance that can be utilized to minimize water pollution. Silica can be produced from agricultural biomass waste, such as rice husk ash. This study investigated the preparation of rice husk ash and the optimal synthesis method for producing bio-silica. A literature review of studies on rice husk ash, heavy metals, and adsorbents was conducted. The findings indicated that boiling rice husk at 800°C and washing with HCl produced high-purity silica. XRD (X-ray diffraction), FT-IR (Fourier transform infrared) spectrophotometers, and ED-XRF (Energy Dispersive X-ray fluorescence) were employed to characterize the rice husk ash. The precipitation, sol-gel, acidification, and hydrothermal methods were compared for bio-silica synthesis. The synthesized bio-silica can be used as a heavy metal adsorbent for various metal ions, including Pb²⁺, Zn²⁺, Mn²⁺, Cu²⁺, As³⁺, As⁵⁺, and Cd²⁺.

Keywords: adsorbent, bio-silica, heavy metal, rice husk silica, rice husk ash

Introduction

Indonesia has experienced rapid industrial growth in various sectors, which has harmed the environment. The expansion of industries has increased production waste. The waste generated can be liquid, solid, or gas. The most high-risk industrial waste that pollutes the environment is liquid waste. Industrial liquid waste generally contains significant levels of dangerous heavy metals. Industrial liquid waste is indicated to contain heavy metals such as lead (Pb), chromium (Cr), cadmium (Cd), copper (Cu), and so on

(Halim et al., 2021). High levels of heavy metals in liquid waste can pollute the water environment if not treated first. The maximum lead (Pb) level in water is 0.05 ppm, chromium (Cr) level is 0.05 ppm, and cadmium (Cd) level is 0.005 ppm, as specified in Minister of Health Regulation No. 32 of 2017. Arsenic can also be found in liquid waste as arsenate (As(V)) and arsenite (As(III)). Because arsenic is poisonous and carcinogenic, its presence in water is strictly prohibited (Bui et al., 2021). Heavy metal content in the water that exceeds the permissible limit is generally harmful to

aquatic life because metal ions are complex for water microbes to break down.

Adsorbents are a modern innovation that can be used in industrial wastewater treatment. Adsorption is frequently used in the industry since it is less expensive, safer, and absorbs organic compounds. The process of accumulating an adsorbate on an adsorbent due to the attraction interactions between molecules is known as adsorption. Because of the chemical nature of each component, interactions can occur in multiple (Halim et al., 2021). Nano-sized adsorbents with pore surfaces ranging from 30-100 nm are helpful for wastewater filtering (Nguyen et al., 2019). Bio-silica, an adsorbent manufactured from agricultural biomass waste such as sugarcane, wheat, and rice husk, is being produced in large quantities. Biomass is a renewable raw material from agriculture, plantations, forests, and animal waste (Steven et al., 2021). The advantage of using agricultural biomass over traditional silica is that it is less expensive and can aid in waste management and treatment (Moayed et al., 2019). Agricultural biomass waste can also be converted into a readily available natural raw material with a high silica concentration.

The rice husk is a hard coating that protects the rice grains. The husk is removed from the rice grains during rice milling and becomes agricultural biomass waste (Wardalia, 2017). Rice husk contains 32.24% cellulose, 21.44% lignin, and 21.34% hemicellulose, respectively (Homagai et al., 2022). When rice husk is burned at high temperatures, rice husk ash with a silica content greater than 90% is produced (F. Hincapié Rojas et al., 2019; Farhan & Ebrahim, 2021; Jyoti et al., 2021). With less than 1% content, rice husk ash contains potassium oxide, sodium oxide, magnesium oxide, lime, aluminum oxide, manganese oxide, and iron oxide (Shen, 2017; Steven et al., 2021). These components can be transformed into soluble ions by washing with acid, resulting in silica-rich rice husk ash (F. Hincapié Rojas et al., 2019).

Rice husk contains silica as an amorphous phase, which is highly reactive

and extremely comparable to that found in nature (Shen, 2017; Steven et al., 2021). If the rice husk is exposed to high temperatures and long burning duration, this phase can change into crystalline form. When burned at temperatures below 700°C for less than 2 hours, the silica in rice husk ash remains amorphous in some situations. When burned at temperatures above 700°C for a more extended time, the amount of crystalline silica generated increases (Steven et al., 2021). The properties of rice husk can be seen in Table 1.

Table 1. Typical properties of rice husk (Okoro et al., 2022)

Property	Range
Bulk density	96-160 (kg/m ³)
Hardness	5-6 (Mohr's scale)
Ash	22-29%
Carbon	~35%
Hydrogen	4-5%
Oxygen	31-37%
Nitrogen	0.23-0.32%
Sulfur	0.04-0.08%
Moisture	8-9%

Silica is a common mineral in the Earth's crust, and so far, pure silica is primarily obtained by mining quartz sand (Steven et al., 2021). The quartz sand is then heated with sodium carbonate at 1300°C. The result is sodium silicate, which will be acidified to produce pure silica (Liu et al., 2016). The manufacture of silica necessitates a lot of energy and significant production costs and is not environmentally friendly. In contrast, silica can be found in agricultural biomass waste ash, notably rice husks, referred to as bio-silica. As a result, using rice husks for manufacturing bio-silica may replace synthetic silica production since it is more cost-effective and has higher purity (Rusdianasari et al., 2020; Steven et al., 2021).

Previous research has found that silica in rice husk ash is stable and insoluble in water and in the form of particles that can speed up the absorption of a chemical. Silica derived from rice husk ash can be formed into nanoparticles of various sizes. Rice husk ash silica is composed of two significant atoms, Si and C, and has a vast surface area and high

porosity, making it an excellent adsorbent. Because bio-silica adsorbents do not react chemically with other chemicals, they can be utilized as absorbent media to separate wastewater components.

Methodology

The literature review (LR) method was used in this study. The literature review collects data or sources about rice husk ash as an adsorbent. The research articles were obtained throughout the previous eight years from the PubMed, Web of Science, and ScienceDirect databases. The search used the terms rice husk silica, rice husk ash, and heavy metal adsorbent. The methodology of the study included the following steps: (1) topic selection for review; (2) identification and selection of relevant publications; (3) article analysis; and (4) review of manuscript organization.

Result and Discussion

The silica content of rice husk ash is affected by rice variety, soil conditions, fertilizers, location, and weather. Furthermore, the silica content and forms of rice husk ash can be affected by the temperature, chemical treatment, and methods (Suryana et al., 2018). Rice husk-rich silica could be made by heating treatment at high temperatures to produce ash as a silica synthesis material. Alternatively, it can be extracted from rice husk as sodium silicate using solvent extraction. The ash from heating rice husk contains various metal ions and unburned carbon, influencing its purity and colour. The heating aims to eliminate the ions or metallic impurities that accelerate the hydrolysis of cellulose and hemicellulose in rice husk, resulting in raw materials for producing high-purity amorphous or crystalline bio-silica (El-Sakhawy et al., 2022; Hafez, 2022).

The preparation and manufacture of rice husk ash are divided into two steps. The

first stage involves carbonizing biomass at temperatures below 800°C in an oxygen-free environment. The product is then chemically or physically activated in the second stage. Physical activation is accomplished by carbonizing the raw material and heating it at high temperatures by adding steam, CO₂, or O₂. Steam and CO₂ are mild oxidants and, at high temperatures, gasify the carbon atoms from the char, releasing CO or CO + H₂. CO₂ is employed because it is conveniently accessible, controlled, and environmentally friendly. Chemical activation is accomplished by the addition of oxidizing or dehydrating chemicals. KOH, ZnCl₂, H₃PO₄, and K₂CO₃ can be added (Moayedi et al., 2019).

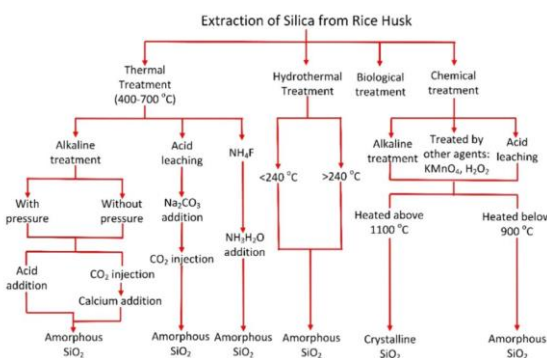


Figure 1. Various methods for producing different structural silica from rice husk (Shen, 2017)

The typical processes for manufacturing silica from rice husk are outlined in Fig. 1, along with the removal of contaminants before and after heating processes. The chemical process, which consists of simple acid leaching and post-annealing, is one of the easiest and most effective ways to create ultrafine silica nanoparticles from rice husk ash. Leaching of rice husk with different chemical solutions (e.g., HCl, H₂SO₄, H₃PO₄, HNO₃, HF, NH₄OH, and NaOH) before thermal processes under different conditions (e.g., temperature, time) can be so compelling to enhance the hydrolysis of cellulose and hemicelluloses in

rice husk and removing most of the metallic impurities, which allows producing white-colour silica altogether, with high surface area (Shen, 2017).

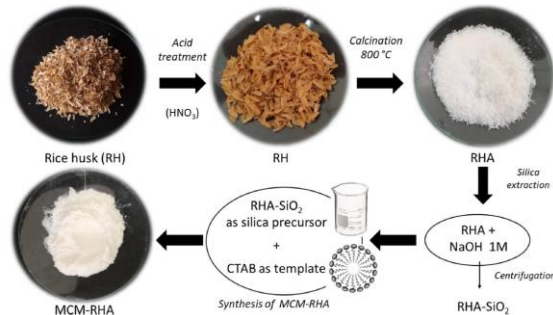


Figure 2. The preparation procedure of rice husk (Carraro et al., 2021)

Carraro et al. (2021) prepared rice husk silica by acid treatment shown with HNO_3 . Rice husk was washed with distilled water several times to remove the adhered soil, dust, and impurities (Fig. 2). Then, it was dried at 100°C overnight. The clean rice husk was stirred with nitric acid (HNO_3) at room temperature to decrease all metallic impurities. Then, it was repeatedly washed and filtered with distilled water at pH 7. The treated sample was then dried at 100°C for 24 hours. The acid-leached sample was calcined

at 800°C for 6 hours. The white rice husk ash (RHA) obtained was ground to powder. In order to extract the silica as sodium silicate, the resulting powder was stirred with sodium hydroxide (NaOH) at 80°C for 18 hours. The resulting mixture was then centrifuged to separate the supernatant and sediment. Finally, the supernatant was filtered and labeled as RHA-SiO_2 (Carraro et al., 2021)

Amorphous silica is formed at temperatures ranging from 550 to 800°C , while crystalline silica is formed at temperatures over 800°C (Shen, 2017). According to MAKhedr et al. (2022), burning rice husks at 450°C and 600°C yields rice husk ash with amorphous silica contents of 89.2% and 91.8%, respectively. Another study discovered that burning at 700°C produced silica with a 90.5% (Khan Bangwar et al., 2017). Suryana et al. (2018) discovered that burning rice husks at 800°C yielded rice husk ash with 94.9% silica concentration in the form of amorphous silica. This research means that the best temperature for burning rice husks with the maximum silica concentration is 800°C . The silica content at different temperatures can be observed in Table 2.

Table 2. Silica content at different burning temperatures

Temperature ($^\circ\text{C}$)	Silica Structure	SiO_2 (%)	Reference
450	amorphous	89.2	(MAKhedr et al., 2022)
600	amorphous	91.8	(MAKhedr et al., 2022)
700	amorphous	90.5	(Khan Bangwar et al., 2017)
800	amorphous	94.9 – 99,6	(Carraro et al., 2021; Lee et al., 2017; Suryana et al., 2018)

Lee et al. (2017) developed a chemical activation technique for preparing rice husk silica. Sulfuric acid (H_2SO_4), hydrochloric acid (HCl), oxalic acid, and ionic liquids (1-butyl-3-methylimidazolium hydrogen sulfate) were used in the experiment. These chemicals were used to wash the rice husk, reducing contaminants and obtaining high-purity silica. Rice husk was pyrolyzed at the temperature of 800°C . When pyrolysis results with HCl or ionic liquids were compared to those without any chemicals, the mass of ash

obtained increased. The purity of the amorphous structured silica obtained after treatment with HCl or ionic solutions was also high, reaching 99.6% and 99.5%, respectively (Lee et al., 2017).

Azat et al. (2019) studied leaching with HCl in silica preparation. Silica extraction was performed by applying HCl before calcination at 600°C . According to the results, the obtained silica exhibited a high purity (98.2 - 99.7%) and a surface area of $120 - 980 \text{ m}^2\text{g}^{-1}$. The silica structure is amorphous, with pore

diameters of 0.9 nm and pore volumes of 1.2 cm³g⁻¹ (Azat, Sartova, et al., 2019). HNO₃ can also be used to leach rice husk ash. Dried rice husk was roasted at 550°C for 1 hour to eliminate organic compounds. The residual carbon compounds were reduced by heating them to 700°C subsequently. After leaching

with HNO₃, the recovered ash yielded silica with a purity of 98.48%. The silica particles were spherical and had a diameter of 14-28 nm (F. Hincapié Rojas et al., 2019). Table 3 shows the silica concentration of several activation compounds.

Table 3. Silica content in different chemical activation

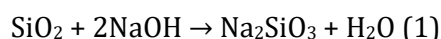
Temperature (°C)	Chemical Activation	Silica Structure	SiO ₂ (%)	Reference
600	HCl	amorphous	98.2-99.7	(Azat, Korobeinyk, et al., 2019; Azat, Sartova, et al., 2019)
700	HNO ₃	amorphous; spherical	98.48	(F. Hincapié Rojas et al., 2019; Suryana et al., 2018)
800	HCl	amorphous	99.6	(Lee et al., 2017; MAKhedr et al., 2022)
800	Ionic liquid	amorphous	99.5	(Lee et al., 2017)

Silica Synthesis Method

There are several methods for producing silica from rice husk ash into bio-silica. The synthesis process determines the structure and properties of silica. The temperature or chemical treatment influences the production of amorphous and crystalline bio-silica. Precipitation, sol-gel, acidification, and hydrothermal methods can all be employed to create bio-silica. The synthesis methods are detailed in greater detail in the following subsections.

- The Precipitation Method

Precipitation is a popular method for generating silica from rice husk ash. This method involves extracting rice husk ash using HCl, adding a sodium hydroxide (NaOH) solution, and stirring with a magnetic stirrer to produce pores. Silica can dissolve in an alkaline solution and, due to its high solubility, produce sodium silicate (Na₂SiO₃) (Qomariyah et al., 2019), resulting in the chemical reaction (Nguyen et al., 2019):



According to the previous chemical equation, stirring in sulfuric acid (H₂SO₄) attempts to bind the sodium in Na₂SiO₄. The following is the chemical reaction equation of sodium silicate (Na₂SiO₃) with sulfuric acid (H₂SO₄) (Nguyen et al., 2019):



Based on the following chemical equation, adding sodium silicate (Na₂SiO₃) to sulfuric acid (H₂SO₄) results in pure silica precipitate (SiO₂). The precipitate is then heated at 110°C for 24 hours. The dried product will be white powder SiO₂, with a size of 50 nm, that can be utilized as an adsorbent.

- The Sol-Gel Method

The sol-gel method is the second method for synthesizing silica from rice husk ash. The sol-gel technique of synthesis of bio-silica consists of two stages: hydrolysis and condensation (Farhan & Ebrahim, 2021). This

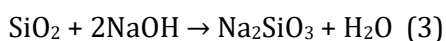
technology offers various advantages, including an effortless procedure, the ability to synthesize at low temperatures, and the production of materials with high purity and homogeneity (Huljana & Rodiah, 2019).

The sol-gel method transforms rice husk ash into sodium silicate by adding NaOH and converting it into bio-silica. The HCl solution is applied during the chemical treatment to transform the sodium silicate phase into a gel. Dry silica gel (Xerogel) can be made by removing the Cl ions from the gel with aquades and heating it in an oven at 110°C. FTIR spectroscopy can be used to characterize the obtained silica. The results demonstrate that silica may absorb at 1056.99 cm⁻¹ and 784.38 cm⁻¹ wavelengths. The particle size of silica generated by the sol-gel technique ranges between 15 and 90 nm (Huljana & Rodiah, 2019).

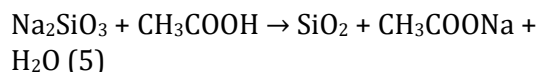
Meliyana et al. (2019) used the sol-gel method to synthesize bio-silica by adding 1 N HCl. Based on the results of the Particle Size Analyzer (PSA) examination, bio-silica with a size of 92-98 nm was obtained. Farhan and Ebrahim (2021) effectively fabricated bio-silica from rice husk ash using 2 N HCl and 2.5 N NaOH. The resulting crystal shape is amorphous, with a particle diameter of 52.83 nm.

- The Acidification Method

The acidification procedure involves extracting an alkali solution via reflux and acidification steps. The reflux process involves the addition of a NaOH solution, whereas the acidification process involves the addition of HCl and acetic acid (CH₃COOH) solutions. The addition of acid solutions is intended to produce silica gel. The following chemical reaction occurs when NaOH solution is added (Dhaneswara et al., 2020):



The acidification reaction of sodium silicate using HCl and CH₃COOH are described in equations 4 and 5, respectively.



The research results show that the best purity of silica produced by the acid washing method is 98-99 wt% using 1 M CH₃COOH and 10% NaOH. Bio-silica manufactured with 10% NaOH and 1 M HCl has a pore diameter of 9 nm, whereas bio-silica synthesized with 1 M CH₃COOH and 10% NaOH has a pore diameter of 8.4 nm. Pore sizes less than 50 nm imply that the final synthesis is a mesoporous bio-silica (Dhaneswara et al., 2020). Sharifnasab, H., and M. Y. Alamooti (2017) also synthesized bio-silica using acid leaching. The rice husk ash solution was combined with NaOH after leaching with HCl. The process yields bio-silica with a particle size of 60 nm.

- The Hydrothermal Method

The hydrothermal process has various advantages, including low cost and simple stages in manufacturing bio-silica material. Three methods exist for creating nanoparticles in hydrothermal processes: temperature difference, temperature reduction, and metastable phase approaches. The hydrothermal process takes 4 hours and uses temperatures of 150°C, 200°C, and 250°C.

According to the research results, all bio-silica was in the amorphous form. The particle size ranged from 0.16 to 13.49 nm, with a more uniform size distribution at 200°C and 250°C than at 150°C. With increasing temperature and frequency, all three bio-silica were classified as semiconductors. The optimum treatment for synthesizing rice husk bio-silica was a temperature of 200°C for 4 hours and a pressure of 2 atm (Irzaman et al., 2022). Different sizes of bio-silica were obtained based on the synthesis process, as shown in Table 3.

Table 3. The size and diameter particles of bio-silica synthesized using various methods

The Synthesized Method	Particle Sizes (nm)	Particle Diameter (nm)	Reference
Precipitation	50	-	(Nguyen et al., 2019)
Sol-Gel	15 - 98	-	(Huljana & Rodiah, 2019; Rodiah et al., 2021)
	92-98	-	(Meliyana et al., 2019)
Acidification	-	52.83	(Farhan & Ebrahim, 2021)
	-	9	[(Dhaneswara et al., 2020)
	60	-	(Sharifnasab & Alamooti, 2017)
Hydrothermal	0.16 -13.49	-	(Irzaman et al., 2022)

Analysis Of Bio-Silica

XRD (X-ray diffraction), FT-IR (Fourier transform infrared) spectrophotometers, and ED-XRF (Energy Dispersive X-Ray Fluorescence) can be used to characterize bio-silica. Crystallinity is measured via XRD analysis. Broad and non-sharp peaks indicate amorphous silica at diffraction angles of 20-22°. As crystalline silica polymorphism, narrow and sharp peaks at diffraction angles of 19°, 22°, 26°, 31°, and 33° are related to cristobalite, tridymite, and quartz. Other oxides, such as aluminum oxide at roughly 17° and iron oxide, potassium oxide, and calcium oxide at 32°, 45°, and 57° may also be reported as impurities (Steven et al., 2021).

The FTIR analysis is used to determine the bio-silica bonding groups. Amorphous silica's primary functional groups are siloxane (Si-O-Si), silanol (Si-O-H), and Si-H bonds. A 1044-1100 cm⁻¹ peak distinguishes the asymmetric siloxane bond. Peaks for the symmetric siloxane bond are located at 438-475 cm⁻¹ and 796-900 cm⁻¹. Peaks at wavenumbers 2500-3800 cm⁻¹ represent the stretching and bending of H-O-H silanol bonds, whereas a peak at 2100 cm⁻¹ indicates the Si-H bond. At wavenumber 621 cm⁻¹, crystalline bio-silica is observed (Steven et al., 2021).

XRF characterization assesses the amount or purity of mineral elements with high peaks. Peaks are located at different energy ranges, namely 1.7-1.8 keV for silicon,

potassium at 3.2-3.4 keV, sodium marked by a peak at 1.0-1.2 keV, calcium at 3.6-3.8 keV, 1.2-1.4 keV for magnesium, oxygen at an energy range of 0.4-0.6 keV, aluminum at 1.5-1.6 keV, carbon at 0.1-0.2 keV, 2.0-2.1 keV for platinum, chlorine peak is observed at 2.3-2.4 keV, and 2.2-2.3 keV for sulfur (Steven et al., 2021).

Application Of Bio-Silica As Heavy Metal Adsorbent

Processed rice husk ash as an adsorbent for industrial liquid waste can be accomplished through temperature and technique modifications. Wardalia (2017) researched the adsorption ability of rice husk ash. Several parameters, including rice husk ash mass and absorption duration, can influence the adsorption ability of rice husk ash on liquid waste. In general, a heavier amount of rice husk ash will increase the number of particles, making the liquid waste more straightforward to absorb. The mass of rice husk ash is also related to the absorption time process. Because of the large number of particles in rice husk ash, it will be easier to absorb a large amount of liquid waste (Wardalia, 2017).

Wardalia (2017) carried out three weighings to determine the mass of rice husk ash to be evaluated. The first mass of rice husk ash collected was 1.0 g, followed by 1.5 g, and 2.0 g. The three mass variations of rice husk ash produced various adsorption

capacity values. The 1.0 g mass of rice husk ash had an adsorption capacity of 675 kg Pb/Kg, the 1.5 g mass had an adsorption capacity of 867 kg Pb/Kg, and the 2.0 g mass had an adsorption capacity of 927 kg Pb/Kg. The research results show that the 2.0 g mass of rice husk ash has a higher adsorption capacity value than the 1.0 g and 1.5 g masses. The difference in adsorption capacity values obtained from different masses of rice husk ash indicates that the larger the adsorbent mass, the higher its capacity for adsorbate. The research also obtained the adsorption time from the different mass variations. The 2.0 g rice husk ash required 20 minutes of the 2-hour process. The greater the rice husk ash, the easier it is to absorb more heavy metal (Wardalia, 2017).

Another study found that differences in concentration change bio-silica's adsorption capacity. According to Rusdiana et al. (2020), the lower the Fe level in textile wastewater, the lower the concentration of KOH used in bio-silica synthesis. As a result, bio-silica can absorb more Fe metal. Adding 1.5 M KOH solvent can improve absorption efficiency by 75.06%, 75.24%, 80.38%, 85.21%, and 88.63%, respectively. However, when employing a 2.5 M KOH solvent, the efficiency values are only 18.22%, 23.41%, 24.94%, 25.43%, and 30.44% with the same contact time. The ideal contact time is 25 minutes of stirring. The longer the contact time between bio-silica and wastewater, the more colloidal Fe molecules interact with the adsorbent, thus increasing the adsorption capacity as the contact time increases (Rusdianasari et al., 2020).

Another heavy metal that has been studied is arsenic. The adsorbent used was a nanocomposite. Bui et al. (2021) synthesized an iron-manganese oxide-activated bio-silica nanocomposite using sodium silicate from rice husk ash. Sodium silicate was added to KMnO_4 and FeSO_4 to form the nanocomposite. The adsorption capacity of the nanocomposite for As(III) and As(V) was 19.1 and 20.3 mg g^{-1} at pH 7, respectively (Bui et al., 2021).

According to Erdoo Kukwa et al. (2020), in their study on silica adsorbent utilizing rice

husk for Cu^{2+} , Pb^{2+} , Mn^{2+} , and Zn^{2+} , temperature, pH, contact time, and adsorbent amount can all affect adsorption performance. The efficacy of heavy metal ion adsorption decreases as the temperature rises. This efficacy is owing to the tendency of metal ions to detach from the adsorbent surface to the solution phase, weakening the interaction between the adsorbent and the adsorbate. Adsorption capacity decreases with rising temperature, indicating that the adsorption process is exothermic. Based on the study's results, a temperature of 28°C is optimal for adsorption. The obtained order of heavy metal adsorption efficiency is $\text{Pb}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+} > \text{Cu}^{2+}$ (Erdoo Kukwa et al., 2020).

The effect of pH on Pb, Zn, Cu, and Mn adsorption was investigated for 8 hours at a temperature of 28°C. The percentage of heavy metal ion adsorption increased from acidic to pH eight and then decreased at pH 10. The surface of the adsorbent is saturated with hydronium ions (H_3O^+) at acidic pH, resulting in repulsive forces between the adsorbent and adsorbate. Increasing the pH of the adsorbent from pH 4 to 10 causes deprotonation on the surface of the adsorbent. The order of decreasing percentage of heavy metal ions adsorbed is $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+}$. Regarding contact time, the amount of metal adsorbed was shown to be precisely related to the adsorption time. The maximum adsorption percentage was 99.20%, while the lowest was 80.91%. $\text{Pb}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+} > \text{Cu}^{2+}$ was the order of percentage adsorption. The amount of adsorbent used determined the final observation. The higher the percentage of heavy metal adsorption, the more adsorbent is needed. This is due to the large mass of adsorbent exchange sites or the availability of a surface area. The results showed that the percentage adsorption of heavy metal ions was in the order $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+}$ (Erdoo Kukwa et al., 2020).

Conclusion

Rice husk ash is an agricultural biomass waste that can be utilized as a source of silica. With proper preparation, high-purity silica

can be obtained, which can be further synthesized and utilized as an adsorbent. Various synthesis methods can be applied, such as precipitation, acidification, sol-gel, and hydrothermal methods. The resulting synthesized material needs to be optimized for its adsorption capacity towards heavy metals, such as through studies on the effects of pH, temperature, contact time, amount of adsorbent used, and reactant concentration. The author hopes there will be more development of agricultural biomass-based adsorbents with high adsorption capacity.

References

- Azat, S., Korobeinyk, A. V., Moustakas, K., & Inglezakis, V. J. (2019). Sustainable production of pure silica from rice husk waste in Kazakhstan. *Journal of Cleaner Production*, 217, 352–359. <https://doi.org/10.1016/j.jclepro.2019.01.142>
- Azat, S., Sartova, Z., Bekseitova, K., & Askaruly, K. (2019). Extraction of high-purity silica from rice husk via hydrochloric acid leaching treatment. *Turkish Journal of Chemistry*, 43(5), 1258–1269. <https://doi.org/10.3906/kim-1903-53>
- Bui, T. H., Pham, V. S., Thanh-Nho, N., & Trieu, Q. A. (2021). Removal of Arsenic from Water Using a Composite of Iron-Manganese Oxide Incorporated Active Rice Husk Silica. *Clean - Soil, Air, Water*, 49(4). <https://doi.org/10.1002/clen.202000233>
- Carraro, P. M., Benzaquén, T. B., & Eimer, G. A. (2021). Eco-friendly synthesis of nanostructured mesoporous materials from natural source rice husk silica for environmental applications. *Environmental Science and Pollution Research*, 28(19), 23707–23719. <https://doi.org/10.1007/s11356-020-11043-0>
- Dhaneswara, D., Fatriansyah, J. F., Situmorang, F. W., & Haqoh, A. N. (2020). Synthesis of Amorphous Silica from Rice Husk Ash: Comparing HCl and CH₃COOH Acidification Methods and Various Alkaline Concentrations. *International Journal of Technology*, 11(1), 200–208. <https://doi.org/10.14716/ijtech.v11i1.3335>
- El-Sakhawy, M., Adel, A. M., Diab, M. A., & Al-Shemy, M. (2022). Facile methods for the preparation of micro- and mesoporous amorphous silica from rice husk. *Biomass Conversion and Biorefinery*, 12(10), 4709–4718. <https://doi.org/10.1007/s13399-020-01112-2>
- Erdoo Kukwa, R., Tyoker Kukwa, D., David Oklo, A., Thaddeus Ligom, T., Ishwah, B., & Ajegi Omenka, J. (2020). Adsorption Studies of Silica Adsorbent Using Rice Husk as a Base Material for Metal Ions Removal from Aqueous Solution. *American Journal of Chemical Engineering*, 8(2), 48. <https://doi.org/10.11648/j.ajche.20200802.12>
- F. Hincapié Rojas, D., Pineda Gómez, P., & Rosales Rivera, A. (2019). Production and characterization of silica nanoparticles from rice husk. *Advanced Materials Letters*, 10(1), 67–73. <https://doi.org/10.5185/amlett.2019.2142>
- Farhan, R. Z., & Ebrahim, S. E. (2021). Preparing nanosilica particles from rice husk using precipitation method. *Baghdad Science Journal*, 18(3), 494–500. <https://doi.org/10.21123/BSJ.2021.18.3.0494>
- Hafez, A. I. (2022). Synthesis of Silica and Silica Compounds Based on Rice Husk Ash: Article Review. *Water, Energy, Food and Environment Journal An International Journal*, 3(2), 76. <https://doi.org/10.18576/wefej/0302>

- Halim, A., Romadon, J., & Yinal Achyar, M. (2021). Pembuatan Adsorben Dari Sekam Padi Sebagai Penyerap Logam Berat Tembaga (Cu) Dan Timbal (Pb) Dalam Air Limbah Manufacturing Adsorbent From Rice Husk As An Absorption For Heavy Metal Copper (Cu) And Lead (Pb) In Waste Water. *Jurnal SEOI*, 3(2), 66–74.
- Homagai, P. L., Poudel, R., Poudel, S., & Bhattarai, A. (2022). Adsorption and removal of crystal violet dye from aqueous solution by modified rice husk. *Heliyon*, 8(4). <https://doi.org/10.1016/j.heliyon.2022.e09261>
- Huljana, M., & Rodiah, S. (2019). Sintesis Silika dari Abu Sekam Padi dengan Metode Sol-gel. *Prosiding Seminar Nasional Sains Dan Teknologi Terapan*.
- Irzaman, Irmansyah, Aisyah, S., Har, N. P., & Aminullah. (2022). Effect of Different Hydrothermal Temperatures on the Properties on Nano-Silica (SiO₂) of Rice Husk. *International Journal of Renewable Energy Development*, 11(3), 640–646. <https://doi.org/10.14710/ijred.2022.43904>
- Jyoti, A., Singh, R. K., Kumar, N., Aman, A. K., & Kar, M. (2021). 'Synthesis and properties of amorphous nanosilica from rice husk and its composites. *Materials Science and Engineering B: Solid-State Materials for Advanced Technology*, 263. <https://doi.org/10.1016/j.mseb.2020.114871>
- Khan Bangwar, D., Saand, A., Ali Keerio, M., Ali Soomro, M., & Bhatti, N.-K. (2017). Development of an Amorphous Silica from Rice Husk Waste. *Engineering, Technology & Applied Science Research*, 7(6), 2184–2188. www.etasr.com
- Lee, J. H., Kwon, J. H., Lee, J. W., Lee, H. sun, Chang, J. H., & Sang, B. I. (2017). Preparation of high purity silica originated from rice husks by chemically removing metallic impurities. *Journal of Industrial and Engineering Chemistry*, 50, 79–85. <https://doi.org/10.1016/j.jiec.2017.01.033>
- Liu, X., Chen, X., Yang, L., Chen, H., Tian, Y., & Wang, Z. (2016). A review on recent advances in the comprehensive application of rice husk ash. In *Research on Chemical Intermediates* (Vol. 42, Issue 2, pp. 893–913). Springer Netherlands. <https://doi.org/10.1007/s11164-015-2061-y>
- MAKhedr, M., Sabry, R. M., & MALi, H. (2022). Preparation and Characterization of Egyptian Rice Husk Ash. *Water, Energy, Food and Environment Journal An International Journal*, 3(1), 25. <https://doi.org/10.18576/wefej/030103>
- Meliyana, Rahmawati, C., & Handayani, L. (2019). Sintesis Nano Silika Dari Abu Sekam Padi Dengan Metode Sol Gel. "Peran Ilmu Pengetahuan Dalam Pembangunan Di Era Revolusi Industri 4.0 Berdasarkan Kearifan Lokal, 800–807.
- Moayed, H., Aghel, B., Abdullahi, M. M., Nguyen, H., & Safuan A Rashid, A. (2019). Applications of rice husk ash as green and sustainable biomass. In *Journal of Cleaner Production* (Vol. 237). Elsevier Ltd. <https://doi.org/10.1016/j.jclepro.2019.117851>
- Nguyen, H. X., Dao, N. T. T., Nguyen, H. T. T., & Le, A. Q. T. (2019). Nanosilica synthesis from rice husk and application for soaking seeds. *IOP Conference Series: Earth and Environmental Science*, 266(1). <https://doi.org/10.1088/1755-1315/266/1/012007>

- Okoro, H. K., Alao, S. M., Pandey, S., Jimoh, I., Basheeru, K. A., Caliphs, Z., & Ngila, J. C. (2022). Recent potential application of rice husk as an eco-friendly adsorbent for removal of heavy metals. *Applied Water Science*, 12(12), 1–8. <https://doi.org/10.1007/s13201-022-01778-1>
- Qomariyah, L., Widiyastuti, W., Winardi, S., Kusdianto, K., & Ogi, T. (2019). Volume fraction dependent morphological transition of silica particles derived from sodium silicate. *International Journal of Technology*, 10(3), 603–612. <https://doi.org/10.14716/ijtech.v10i3.2917>
- Rodiah, S., Huljana, M., Al Jabbar, J. L., Ichsan, C., & Marzuki, H. (2021). Silica-Rice Husk as Adsorbent of Cr (VI) Ions Prepared through Sol-Gel Method. *Walisongo Journal of Chemistry*, 4(1), 65–73. <https://doi.org/10.21580/wjc.v4i1.8045>
- Rusdianasari, R., Taufik, M., Bow, Y., & Fitri, M. S. (2020). Application of Nanosilica from Rice Husk Ash as Iron Metal (Fe) Adsorbent in Textile Wastewater. *Indonesian Journal of Fundamental and Applied Chemistry*, 5(1), 7–12. <https://doi.org/10.24845/ijfac.v5.i1.7>
- Sharifnasab, H., & Alamooti, M. Y. (2017). *Preparation of silica powder from rice husk* (Vol. 19, Issue 1). <http://www.cigrjournal.org>
- Shen, Y. (2017). Rice husk silica derived nanomaterials for sustainable applications. *Renewable and Sustainable Energy Reviews*, 80(February), 453–466. <https://doi.org/10.1016/j.rser.2017.05.115>
- Steven, S., Restiawaty, E., & Bindar, Y. (2021). Routes for energy and bio-silica production from rice husk: A comprehensive review and emerging prospect. *Renewable and Sustainable Energy Reviews*, 149. <https://doi.org/10.1016/j.rser.2021.11329>
- Suryana, R., Iriani, Y., Nurosyid, F., & Fasquelle, D. (2018). Characteristics of silica rice husk ash from Mojogedang Karanganyar Indonesia. *IOP Conference Series: Materials Science and Engineering*, 367(1). <https://doi.org/10.1088/1757-899X/367/1/012008>
- Wardalia. (2017). Pengaruh Massa Adsorben Limbah Sekam Padi Terhadap Penyerapan Konsentrasi Timbal. *Jurnal Teknik*, 13(1), 71–80.