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Effectiveness of Using Rice Husk as a Bioadsorbent on Amonia (NH3) and Nitrite (NO2-) Levels an Liquid Waste of the Tofu Industry

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ABSTRACT

Tofu industry liquid waste contains ammonia (NH_3) and nitrite (NO_2^-) compounds which can cause pollution if released into the environment without prior processing. Rice husks can be used to make active carbon which acts as a bioadsorbent against various contaminants which is cheap and easy to obtain. The research aims to test the effectiveness of using rice husks in doses of 5 grams, 10 grams and 15 grams as a bioadsorbent on NH_3 and NO_2^- levels in liquid waste at the Rina Tofu Factory. This type of quasi-experimental research with a Completely Randomized Design (CRD) approach. Determination of NH_3 and NO_2^- levels using the spectrophotometric method with three replications. Data were analyzed using the One-Way ANOVA test ($\alpha = 5\%$). The research results showed that the initial concentration of NH_3 was 0.16 mg/L and fluctuated after contact with rice husks (5 gram dose: R_I = 0.13 mg/L, R_{II} = 0.15 mg/L, R_{III} = 0.25 mg/L; 10 gram dose: R_I = 0.21 mg/L, R_{II} = 0.27 mg/L, R_{III} = 0.12 mg/L dose 15 grams: R_I = 0.32 mg/L, R_{II} = 0.26 mg/L, R_{III} = 0.30 mg/L). Meanwhile, the initial concentration of NO_2^- was 0.043 mg/L and increased after contact with rice husks (5 gram dose: R_I = 0.091mg/L, R_{II} = 0.138 mg/L, R_{III} = 0.125 mg/L; 10 gram dose: R_I = 0.117 mg/L, R_{II} = 0.151 mg/L, R_{III} = 0.122 mg/L; 15 gram dose: R_I = 0.112 mg/L, R_{II} = 0.137 mg/L, R_{III} = 0.126 mg/L). There is no difference in the effectiveness of using rice husks on NH_3 (ρ-value = 0.114) and NO_2^- (ρ-value = 0.750) levels in liquid waste from the tofu industry. Further research needs to be carried out regarding variations in contact time between rice husks and liquid waste from the tofu industry.

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INTRODUCTION

Developments in the industrial sector in Indonesia are currently quite rapid. As the industry increases, more and more waste is produced (1). Liquid waste, also known as waste water, is water that is no longer used and is the result of waste from various activities carried out by humans to fulfill daily living needs. As the population increases with all its needs, it is certain that the amount of waste water will increase. The emergence of waste is caused by the processing and handling of waste which is not a serious concern (2).

Liquid waste produced by industry is still a problem for the surrounding environment, because in general household industries channel their waste water directly into ditches or rivers without being treated first (3). Likewise, the tofu industry is generally a home industry that is widely spread in big cities and small towns (4).

Tofu production produces solid waste and liquid waste. Solid waste is waste produced from the filtering process and the clumping process of dregs from soybeans, while liquid waste is waste produced from the washing, boiling, pressing and molding processes. Tofu liquid waste is usually thrown directly into rivers or sewers, which causes environmental pollution. The liquid waste produced in the processing of 1 ton of tofu is around 3,000 to 5,000 liters of turbid and smelly waste (5).

Tofu industry liquid waste contains large amounts of carbohydrates, fats and proteins. Complex organic materials in the form of carbohydrates, fats and proteins are first converted into simpler compounds, namely glucose, glycerol, fatty acids and amino acids. Amino acids are the result of protein breakdown and will be oxidized to ammonia nitrogen (NH3) and carboxyl compounds. The NH3 compound will be oxidized again to become nitrite (NO2-). If oxygen is available it will be oxidized again to nitrate (NO3-) (6). The maximum level of ammonia permitted according to Minister of Environment Regulation Number 5 of 2014 concerning Waste Water Quality Standards is 5 mg/L. If ammonia levels exceed the applied limits, it can have an impact on human health such as damage to the kidneys, lungs, impaired brain function, and decreased blood values.

Nitrites in soil are naturally the result of microbial oxidation originating from organic materials and can also be formed from industrial waste. The nitrite content in water bodies greatly influences the quality of water bodies. In water bodies, when compared to the biochemical reactions that occur, the nitrogen cycle consumes the most dissolved oxygen (7). Referring to the Minister of Environment Regulation Number 5 of 2014 concerning Waste Water Quality Standards, the maximum level of nitrite is 1 mg/L.

Tofu waste processing aims to reduce and prevent negative impacts on the environment, especially water bodies. One method for handling waste is to reduce the levels of dangerous substances such as COD and Ammonia contained in tofu waste. Therefore, one alternative for processing liquid waste is the adsorption method (8). Adsorption is the process of absorbing certain materials, which occurs due to the attraction between the absorbent molecules and the active sites on the surface of the absorbent. With this absorption, the water becomes clear because the substances in it are bound by the absorbent. This system is effective for reducing color and eliminating odor and taste (3).

The use of conventional adsorbents requires relatively more expensive operational and regeneration costs. Conventional adsorbents that are often used in the adsorption process are alumina, activated carbon, silica gel, and zeolites. This adsorbent has good adsorption capacity but is not economical. Some raw materials that can be used include: wood, coconut shells, coal waste, wood processing waste and agricultural waste such as coffee husks, chocolate husks, rice husks, straw, corn cobs and fronds (1). The most popular and widely used adsorbent material for air waste treatment is activated carbon. Activated carbon comes in the form of a porous structure powder or granules; These interconnected pores increase the surface area of the carbon making it the best adsorbent (9).

Rice husks are the hard protective layer of rice grains. The husks are made of hard materials, including opaline silica and lignin to protect the seeds during the growing season. Most of the husks cannot be digested by humans. During the milling process, the husks are removed from the wheat to make brown rice; The brown rice is then ground again to remove the bran layer to become white rice. Rice husks are class “A” insulation. they are difficult to burn and less likely to let moisture in to spread mold or mildew. When burned, rice husks produce large amounts of the element silica. The very high content of amorphous silica of the husk gives it and its ash (SiO2 ~ 20 wt.%) after combustion are very valuable properties for excellent thermal insulation. Apart from that, rice husks contain lots of floral fiber, protein and several functional groups such as carboxyl and midogen (10).

Rice husks are a natural absorbent material that has the potential to remove various contaminants, and are also cheap and renewable. The chemical composition of rice husk consists of 32% cellulose, 20% hemicellulose, 21% lignin, and 20% other organic materials which play an important role in determining good absorption properties (11). Rice husks are rice husks that wrap rice, where the rice husks will be separated into waste or waste, where the waste resulting from rice production is now used as raw material for biopolymers needed to produce absorbent materials (12).

In recent years, several studies have been carried out regarding the use of rice husks (unmodified and modified) as an adsorbent to remove various contaminants. Rice husks, like other natural materials, may not absorb certain contaminants efficiently. Therefore, surface modification is usually applied to increase the adsorption efficiency and biomass capacity (13).

Based on initial observations made, the Rina Tofu Factory was established in 2008, located in Hulawa Village, Telaga District, Gorontalo Regency. This tofu factory's production hours start at 06.00 – 23.00 WITA, with a total of 6 employees. The average daily production amount is 400-500 kg/day. Preliminary test results on liquid waste at the Rina Tofu Factory showed ammonia levels of 0.51 mg/L and nitrite levels of 0.80 mg/L.

METHODOLOGY

The research was carried out in October 2024 at the Rina Tofu Factory. The production of rice husk carbon and the activation process were carried out at the Public Health Laboratory, Universitas Negeri Gorontalo. Testing for NH_3 and NO_2^- levels was carried out at the Regional Technical Implementation Unit (UPTD) of the Gorontalo Province Regional Health Laboratory using the spectrophotometric method. The type of research is a quasi experiment with a Completely Randomized Design (CRD) approach. The sample in this study was 675 ml of liquid waste from the Rina Tofu Factory, which was obtained using the grab sampling technique. Observations were carried out on the control group (without treatment), the treatment group was given rice husks in doses of 5 grams, 10 grams and 15 grams, which were carried out three times each (Figure 1). The data were then analyzed using the One Way-ANOVA test (α = 5%).

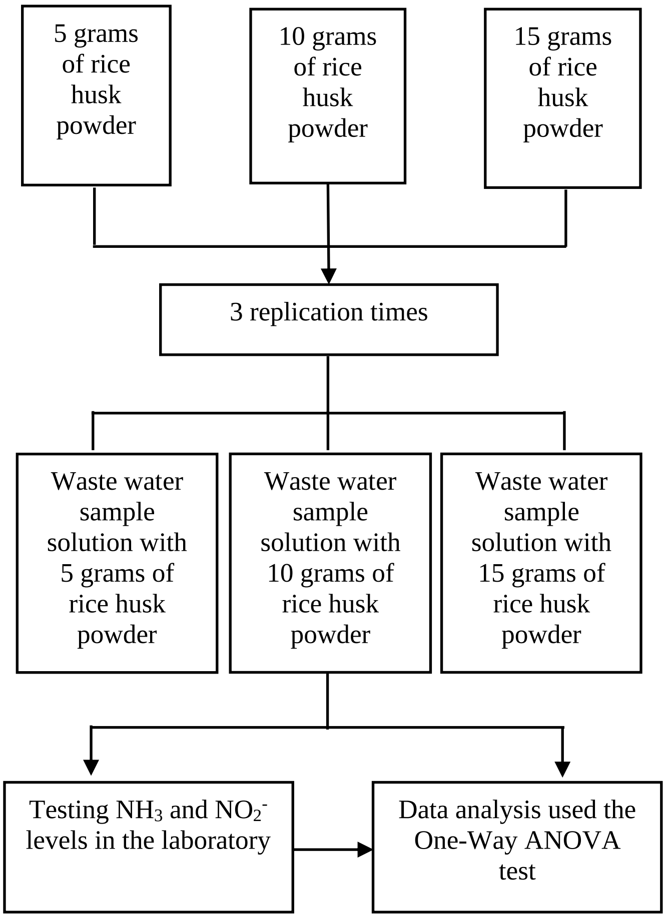

Figure 1. Research Design

RESULTS

NH_3 levels in liquid waste from the tofu industry with varying doses of rice husks of 5 grams, 10 grams and 15 grams

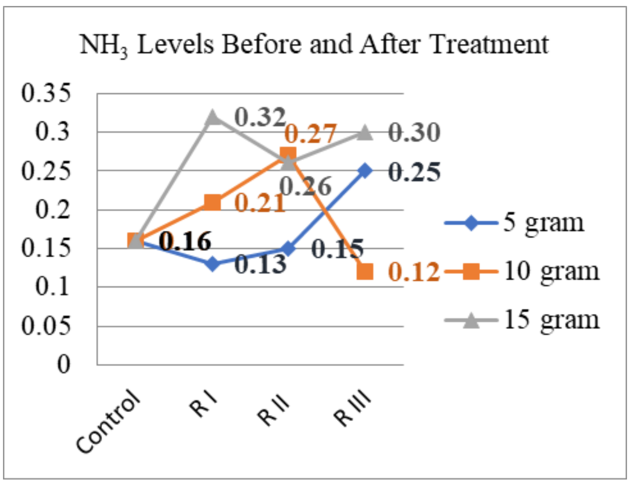

Figure 2. NH_3 levels before and after treatment

Figure 2 shows that after being treated with rice husks at doses of 5 grams, 10 grams and 15 grams, where stirring was carried out for 30 minutes at a speed of 130 rpm, the results obtained were that there was a decrease in NH_3 levels in the treatment with a dose of 5 grams, while in the treatment with a dose of 15 grams there was an increase in NH_3 levels.

NO_2^- levels in liquid waste from the tofu industry with varying doses of rice husks of 5 grams, 10 grams and 15 grams

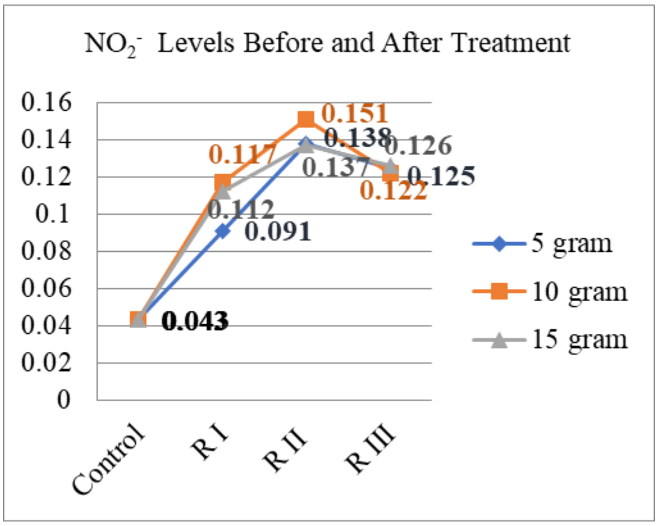

Figure 3. NO_2^- levels before and after treatment

Figure 3 shows that after being treated with rice husks in doses of 5 grams, 10 grams and 15 grams, which were stirred for 30 minutes at a speed of 130 rpm, the result was an increase in NO_2^- levels in the liquid waste of the tofu industry.

Differences in dosage (5 grams, 10 grams, and 15 grams) of rice husks on NH_3 levels in liquid waste from the tofu industry

Data Normality Test

Table 1. Data normality test

Test Parameters	Variations in rice husk dosage	ρ-value
Ammonia (NH_3)	Dosage 5 grams	0.298
	Dosage 10 grams	0.780
	Dosage 15 grams	0.637

Based on Table 1, it can be seen that the results of the data normality test using the Shapiro-Wilk test obtained ρ-value > 0.05, which means the data is normally distributed.

Test For Homogeneity Of Variance

Table 2. Homogeneity of variance test

Test Parameters	ρ-value
Ammonia (NH_3)	0.372

Based on Table 2, it can be seen that the results of the homogeneity of variance test using the Levene test obtained ρ-value = 0.372 > 0.05, meaning that the data has the same or homogeneous variance.

One-Way ANOVA Test

Tabel 3. Uji One-Way ANOVA

Test Parameters	Variations in rice husk dosage	ρ-value

Ammonia (NH_3)	Doses 5 grams, 10 grams, and 15 grams	0.114

Based on Table 3, it can be seen that the results of the One-Way ANOVA test show ρ-value = 0.114 > 0.05, meaning that there is no difference in the effectiveness of using rice husks on NH_3 levels in liquid waste from the tofu industry.

Differences in dosage (5 grams, 10 grams, and 15 grams) of rice husks on NO_2^- levels in liquid waste from the tofu industry

Data Nomality Test

Tabel 4. Data normality test

Param Test Parameters	Variations in rice husk dosage	ρ-value
Nitrite (NO_2^-)	Dosage 5 grams	0.518
	Dosage 10 grams	0.261
	Dosage 15 grams	0.868

Based on Table 4, it can be seen that the results of the data normality test using the Shapiro-Wilk test obtained ρ-value > 0.05, which means the data is normally distributed.

Test Homogeneity Of Variance

Table 5. Homogeneity of variance test

Test Parameters	ρ-value
Nitrite (NO_2^-)	0.410

Based on Table 5, it can be seen that the results of the homogeneity of variance test using the Levene test obtained ρ-value = 0.410 > 0.05, meaning that the data has the same or homogeneous variance.

One-Way ANOVA Test

Table 6. One-Way ANOVA Test

Test Parameters	Variations in rice husk dosage	ρ-value
Nitrit (NO_2^-)	Doses 5 grams, 10 grams, and 15 grams	0.750

Based on Table 6, it can be seen that the results of the One-Way ANOVA test show ρ-value = 0.750 > 0.05, meaning that there is no difference in the effectiveness of using rice husks on NO_2^- levels in liquid waste from the tofu industry.

DISCUSSION

NH3 levels in liquid waste from the tofu industry with rice husks in doses of 5 grams, 10 grams and 15 grams

The use of rice husks as a bioadsorbent at doses of 5 grams, 10 grams and 15 grams produces a fluctuating pattern of changes in NH3 (ammonia) levels. This fluctuation indicates an inconsistency in the ability of rice husks to absorb ammonia at various doses used. This is caused by several factors, namely the adsorption capacity of rice husks, the initial concentration of ammonia, and the desorption process. In addition, increasing the dose of rice husk is not always directly proportional to the effectiveness of ammonia absorption, indicating that a certain dose has exceeded the optimal capacity of rice husk as a bioadsorbent.

A dose of 5 grams of rice husks reduces ammonia levels in tofu liquid waste. At a dose of 5 grams, rice husks have sufficient capacity to function as an adsorbent, although this capacity is not optimal. This dosage allows rice husks to bind ammonia molecules in solution without saturation or desorption occurring, and utilizes a smaller amount of rice husks to distribute the material evenly in the solution so that the contact surface area increases without disturbing the stability of the system (1).

A dose of 10 grams of rice husks is the optimal point, because at this dose the rice husks have sufficient capacity to adsorb ammonia molecules without experiencing saturation or desorption. The optimal amount of rice husk allows efficient distribution in solution, maximizing the contact surface area for the adsorption process. This dose also maintains system balance, avoiding disturbances in ionic stability that can occur at doses that are too high, so that the absorption process runs effectively. The available active surface is sufficient to interact with ammonia molecules, thereby increasing the adsorption efficiency. However, doses that are too high can cause the adsorbent materials to block each other in the adsorption process, thereby reducing the efficiency of interaction with ammonia (14).

A dose of 15 grams of rice husk in this study showed an increase in ammonia levels after treatment, indicating that the rice husk had reached a saturation point in its adsorption capacity. The saturation point of all active sites on the surface of rice husks has been completely filled by ammonia molecules, so that the ability of rice husks to absorb ammonia becomes ineffective. Even at higher doses rice husks not only failed to bind ammonia but also contributed to the release of ammonia back into the solution. When the adsorbent material is excessive, the adsorption efficiency decreases because some rice husks do not have sufficient surface to interact with ammonia molecules (15).

NO2- levels in liquid waste from the tofu industry with rice husks in doses of 5 grams, 10 grams and 15 grams

The use of rice husks as a bioadsorbent at doses of 5 grams, 10 grams and 15 grams showed an increase in NO2- (nitrite) levels. The increase in nitrite levels is influenced by several factors that cause rice husks to become ineffective, namely, limited functional composition, contact time, organic content in waste, and environmental pH.

The dose of 5 grams of rice husk in this study was the lowest dose used so that the capacity of rice husk to absorb nitrogen compounds or induce biological reactions was limited. At this dose, undesirable reactions also occur between rice husks and other components in the waste which can trigger an increase in nitrite levels. This occurs because the decomposition process of rice husks produces other compounds that weaken the condition of the waste (16).

A dose of 10 grams of rice husks showed lower effectiveness compared to a dose of 5 grams in reducing nitrite levels. This increase in dosage increases the amount of adsorbent material and increases the surface area of rice husks for interaction with nitrite. However, even though the surface area increases, the affinity of rice husks for nitrite remains low. Other molecules that are more easily adsorbed such as organic compounds or ammonia can compete with nitrite to fill the active sites on the surface of rice husks, thereby significantly reducing the opportunity for nitrite to be adsorbed (17).

A dose of 15 grams of rice husks was not effective in reducing nitrite levels and even caused an increase in nitrite levels in tofu wastewater. This is caused by excess adsorbent material which results in uneven distribution of rice husks and the potential for clumping which reduces the active surface area for interaction with nitrite. High doses of organic matter can cause anaerobic or subaerobic conditions, which inhibit nitrification and can slow the conversion of ammonia to nitrite. In addition, the release of nitrogen compounds from rice husks into the solution can also worsen the condition by adding a source of nitrite through organic degradation processes. At high doses such as 15 grams, rice husks can also support the activity of nitrifying bacteria where ammonia is converted to nitrite, especially due to stirring for 30 minutes which increases the distribution of oxygen in the solution (18).

Differences in dosage (5 grams, 10 grams, and 15 grams) of rice husks on NH3 levels in liquid waste from the tofu industry

Based on the research results, there is no difference in the effectiveness of using rice husks as a bioadsorbent on NH3 (ammonia) levels in liquid waste from the tofu industry. This ineffectiveness is caused by several factors, namely the influence of manually burning the adsorbent, the limited absorption capacity of rice husks, the contact time of the adsorbent, the influence of pH and temperature of the waste. In the adsorption process, the most ammonia is adsorbed in the pores of rice husks compared to nitrite. The more bacteria there are in the waste, the more organic material in the liquid waste of the tofu industry will be decomposed so that ammonia and nitrite levels can be reduced.

Manual burning can affect the quality of the adsorbent material because manual burning tends to be less controlled and more variable in temperature and duration. In manual combustion, temperatures that are difficult to control can cause over or under combustion, thus affecting the quality and adsorption capacity of rice husks. In addition, manual burning often produces more combustion residue or unwanted residues that can contaminate the adsorbent material and reduce its quality (19).

Rice husks have less than optimal absorption capacity compared to other materials, for example wood shavings. Even though rice husks are able to absorb organic waste, their effectiveness in reducing ammonia levels is not as great as other materials. This is caused by the physical and chemical characteristics of rice husks which are less effective in binding nitrogen from organic waste. The structure of rice husks tends to be hard and has small and uneven pores. This reduces the ability of rice husks to absorb ammonia efficiently (20). Contact time influences the effectiveness of reducing pollutant levels in tofu liquid waste, whether using adsorbents such as rice husks or other processing methods. Sufficient contact time allows the adsorbent to effectively bind ammonia molecules with a decreasing rate that is fast in the initial phase and slows as it reaches equilibrium (5). Contact time greatly influences the reduction of pollutant levels. In the adsorption process, longer contact times allow more organic compounds to be absorbed by the adsorbent (21).

Environmental factors also contribute to the ineffectiveness of rice husks as a bioadsorbent. An environment with an unstable pH can inhibit the efficiency of ammonia absorption, because changes in the form of ammonia affect the level of chemical interaction with rice husks. Ammonia adsorption by rice husks is very sensitive to changes in pH. At high pH, ammonia is in the form of a free gas, which is difficult to absorb by materials such as rice husks. Vice versa, at low to neutral pH, ammonia tends to change into ammonium ions (NH_4^+) which are more easily bound by rice husks (22).

Tofu liquid waste usually has a high temperature because the tofu production process uses hot water. High temperatures can affect the ability of rice husks to absorb ammonia. In hot conditions, ammonia gas evaporates more easily, making it more difficult for rice husks to adsorb (23).

Differences in dosage (5 grams, 10 grams, and 15 grams) of rice husks on NO_2^- levels in liquid waste from the tofu industry

Based on the research results, there is no difference in the effectiveness of using rice husks as a bioadsorbent on NO_2^- (nitrite) levels in liquid waste from the tofu industry. Rice husks contain various components that have the potential to adsorb nitrite ions, but there are several factors that inhibit their effectiveness. Rice husks contain silica (SiO_2) which reaches 15 - 20%. Silica is an inert compound that does not interact directly with nitrite, thereby reducing the ability of nitrite adsorption on the surface of rice husks. Apart from that, rice husks also contain 20 – 30% lignin and 30 – 50% cellulose. Although this is good for the physical structure, the chemical properties of lignin and cellulose are not active towards nitrite, so physical adsorption of nitrite is less than optimal (5). Rice husk contains functional groups, such as hydroxyl (-OH), carboxyl (-COOH), and amine ($R-NH_2$), which can play a role in the adsorption of nitrite ions. However, the number and reactivity of these groups are limited (24).

The contact time between rice husks and tofu liquid waste can influence the results of nitrite adsorption. The longer the contact time, the better the adsorption process will be until the optimum time for the absorption process is obtained. Contact time is directly proportional to the increase in adsorbent mass, the more adsorbent mass, the higher the nitrite content. This is because the mass of rice husk activated charcoal given is too much so that the activated charcoal itself is crowded together and causes the interaction of rice husk activated charcoal with tofu liquid waste to be less effective (25).

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CONCLUSIONS

Based on the research results, it can be concluded that the use of rice husks as a bioadsorbent with varying doses of 5 grams, 10 grams and 15 grams shows a fluctuating pattern of changes in NH_3 levels, while NO_2^- levels show an increase in concentration. There was no difference in the levels of NH_3 and NO_2^- in varying doses of 5 grams, 10 grams and 15 grams of rice husks in liquid waste from the tofu industry. It is recommended for future researchers to study variations in contact time of rice husks on NH_3 and NO_2^- levels of liquid waste from the tofu industry.

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