

Removal Pollutants in Textile Wastewater Using Unmodified Rice Husk

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Abstract. The goal of this study was to evaluate rice husks potential to decrease both organic and inorganic contaminants from textile effluent. Rice husks are added in amounts up to 38% of the total adsorption bed volume. Using a submerged flow system with a three-day HRT, the native textile effluent (diluted to 75%) was constantly pumped at a rate of 15 ml/minute. In-situ and laboratory analyses of the water quality parameters were conducted. The treated water by rice husk has met the requirements for river ecosystems with parameter values such as pH and Temperature is normal, TSS 65 mg/L, TDS 400mg/L, DO 4 mg/L, COD 200 mg/L, TN 5 mg/L, and TP 2 mg/L. TSS, COD, Ammonium, TP, and TN efficiency of removal were 86.94%, 84.19%, 67.25%, 61.24%, and 48.72%, respectively. The difference in removal efficiency can be attributed to various factors such as the nature of the pollutant, the adsorption capacity of the adsorbent, the concentration of the pollutant, and the interaction between the adsorbent and the pollutant. The wastewater treatment with rice husk is a promising approach for industrial-scale applications due to its adsorption properties and cost-effectiveness.

1 Introduction

The textile industry uses millions of gallons of water every day, and typically, 200 liters of water are consumed to produce one kilogram of fabric. The textile industry is known as one of the industries that makes the most liquid waste. Water pollution by the textile industry can cause severe damage to aquatic ecosystems. Harmful chemical compounds like synthetic dyes, heavy metals, and other chemicals can damage aquatic life and disrupt food chains[1]. Textile dyes significantly degrade the aesthetic quality of water bodies, increase biochemical and chemical oxygen demand (BOD and COD), interfere with photosynthesis, and decrease light penetration[2].The textile industry needs environmentally friendly and sustainable purification technology is needed. Given limited natural resources and increased sustainability awareness, finding effective and economical alternatives has become crucial. Several technologies can be used to treat textile wastewater, namely adsorption, biological treatment, precipitation, coagulation/flocculation, and flotation. Adsorption effectively removes various pollutants, including dyes, heavy metals, and organic compounds. Other

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advantages are that it has high efficiency, low cost, and ease of operation. However, the disadvantages of adsorption include the need to replace adsorbent materials frequently and difficulties in regenerating adsorbent materials[3].

The use of agricultural waste is a topic that continues to be developed as an alternative adsorbent, one example is rice husk. In several previous studies, rice husk, which is a by-product of the rice milling process, is that waste that is available in large quantities and easily renewable has great potential as an adsorbent in removing pollutants from wastewater. Studies have shown that rice husk-based adsorbents are effective in removing dyes, heavy metals, and organic compounds from wastewater[3]. Fixed bed column studies have shown that raw rice husks, bottom treated rice husks, and thermally treated rice husks are superior to other adsorbents tested to remove pollutants from textile wastewater[4]. Activated carbon produced from rice husk has effectively removed dyes from textile wastewater because it has a high surface area and pore volume[5].

Recent research suggests that unmodified rice husks can be used as bio-based adsorbents to eliminate contaminant from textile effluent. Rice husks are cheap, renewable resource that has the potential to remove various pollutants from wastewater. The adsorption capacity of rice husks can be increased by pre-treatment methods, and chemical treatments have been found to be more effective than thermal treatments [6]. Rice husk adsorbents and adsorbed contaminants can be regenerated, and biocatalyst immobilization on rice husks is a promising approach. Other studies have also shown that rice husks can be used to remove contaminants such as arsenic, humic acids, phenols, and leachate of municipal solid waste landfills[7]. Rice husk biochar has been found to remove organic or inorganic toxins from waste, reducing environmental pollution. Modified rice husks with waste from alkaline scouring have been shown to improve the ability to remove dyes[8]. The cellulose-based agricultural waste rice husk has been shown to enhance the degradation of synthetic dyes by using several extremophile-producing enzymes. The newly born rice husk has also been proven to be effective in the removal of cationic dyes such as methylene blue and crystal violet from textile effluent[6]. The study shows that rice husks have great potential as a bio-based adsorbent for removing pollutants from textile wastewater.

The results of bibliometric analysis with the Vos Viewer device (Figure 1) also prove that rice husk research, especially rice husk ash, has been carried out. In the last 10 years the topic of rice husk ash research has been studied the most, indicated by large green circles. While the study of rice husks without modification is still very little which is shown by small circles and writing that is less sharp. The webs in Figure 1 show the interrelationships between each topic. Research related to rice husks, especially in ash and biochar in textile effluent is generally only on testing the reduction of dyes in textile wastewater. As for lowering other pollutants in textile wastewater, it is still not widely studied.

This study aims to examine the potential of using rice husk without additional chemical modification as an adsorbent to remove pollutants from textile wastewater, namely total suspended solids (TSS), Chemical Oxygen Demand (COD), Total Dissolved Solids (TDS), color, total nitrogen (TN), total phosphorus (TP), and ammonium. In this way, we can seek a more environmentally friendly and cost-effective treatment to solve the wastewater purification problem. This study provides information that unmodified rice husk can be an alternative source to reduce the negative impact of the textile industry on the environment and provides new insights into the use of natural materials for water purification in various other industrial applications.

2.2 Preparation of Experiment

Testing of pollutants removal was conducted in a laboratory scale using vertical bed adsorption. The flow scheme as seen in Figure 2. Textile effluent were placed in a storage tank and then flowed at a fixed flow rate of 15 ml /minute. Rice husks are inserted in bed that have a volume of 27 L and 38% are filled. Water sampling is carried out every 3 days at inlet and outlet. Observations were made for 33 days.

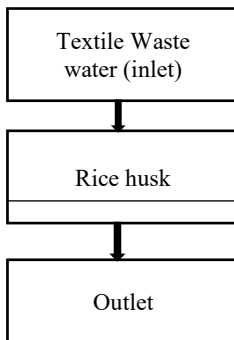


Fig. 2. Vertical flow schematic of the adsorption column

2.3 Water quality parameter analysis

The measured water quality parameters are dissolved oxygen (DO) and pH which control the adsorption process. Adsorbent performance was measured by calculating the removal efficiency of total suspended solids (TSS), color, total dissolved solids (TDS), total phosphorus (TP), total nitrogen (TN), and ammonium. All parameters have been analyzed according to APHA 2017 standard methods [10].

2.4 Calculation of efficiency and adsorption capacity

The values of removal efficiency and adsorption capacity (q , mg/kg) were calculated using equations (1) and (2) [11]:

$$RE (\%) = \frac{C_o - C_t}{C_o} \times 100\% \quad \dots\dots\dots (1)$$

$$q \left(\frac{mg}{g}\right) = \frac{C_o - C_t}{m} V \quad \dots\dots\dots (2)$$

Where C_o = inlet concentration, C_t = outlet concentration, m = adsorbent mass (kg) dan V = treated water volume (L).

3 Results and discussion

3.1 Results

3.1.1 Effect of Contact Time to Removal Efficiency

Unmodified rice husks still contain various compounds that can cause interference with the removal process, one of which is tannin. Tannins are a group of polyphenolic compounds that can dissolve in water. The dissolution of tannins in water causes the color of the water to turn brown which increase the concentration of color and total dissolved solids (TDS) [12], so that the concentration of color and TDS after passing through the husk bed is higher than the initial concentration of effluent (Figure 3). Therefore, out of the 7 parameters only 5 parameters are able to be eliminated properly by rice husks from textile waste namely Ammonium, TSS, TN, COD and TP as seen in Figure 4.

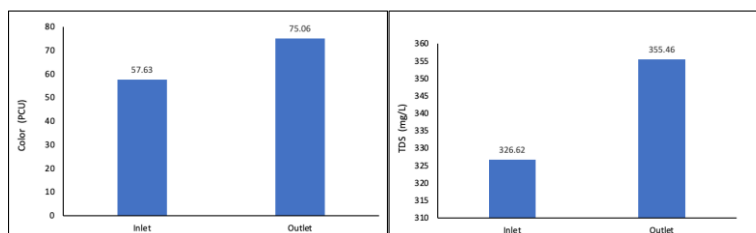


Fig. 3. Increasing of Color and TDS in effluent after passing rice husk bed.

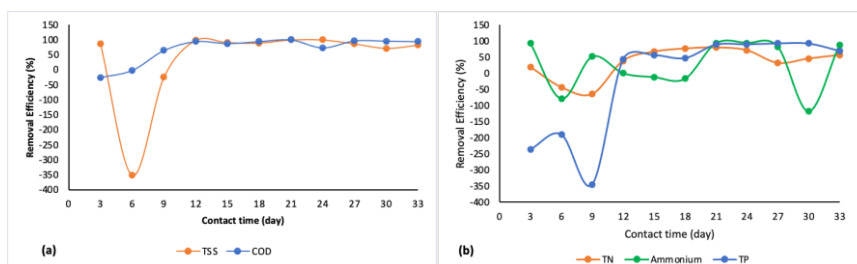


Fig.4. Effect of contact time to removal efficiency of (a) TSS and COD, (b) TN, Ammonium, and TP.

The adsorption of pollutants is only efficient starting from the tenth day, because rice husks need stabilization of compounds in them such as tannins that dissolve in water during the adsorption process. The maximum efficiency for each parameter occurs in the contact time range of 20 - 25 days, where the maximum efficiency of TSS is 99%, COD is 99%, TP is 92%, TN is 75% and ammonium is 93%. After the 25th day, the efficiency of each parameter began to decrease because of saturation in the rice husks. Therefore, averaging over 33 days of contact time, the average efficiency of each parameter is 86.94%; 84,19%; 61,24%; 48.72% and 67.25% for TSS, COD, TP, TN, Ammonium parameters respectively.

3.1.2 Effect of pH to Adsorption Capacity

Adsorption occurs when molecules or ions of a particular substance attach to the surface of a solid or liquid without undergoing chemical changes, the surface of the adsorbent material exerts a force of attraction on those molecules or ions, causing them to adhere to the surface. The amount of pollutants adsorbed is expressed by the adsorption capacity value. In figure 5

can be seen the value of adsorption capacity measured in mg/kg, which illustrates how much substance can be adsorbed by 1 kg of rice husk at the specified pH. Adsorption capacity is influenced by pH, where changes in pH values can affect the surface properties of the adsorbent and the behavior of the adsorbed compounds. This occurs as a result of the ionization of compounds with the liberation of H⁺ and OH⁻ ions thereby changing the surface charge of the adsorbent and the formation of ion complexes[13]. Rice husk has been able to eliminate pollutants from textile wastewater in the range of contact time of 20-25 days with a pH tends to be alkaline (pH value >7). The maximum adsorption capacity for each parameter is 7556.38 mg/kg; 62.88 mg/kg; 40.98 mg/kg; 5868 mg/kg and ammonium 21.82 mg/Kg.

3.1.3 Correlation between parameters

Correlation is used to measure the extent to which two parameters or variables are related to each other and also for validation to help test the validity of a hypothesis. Table 2 shows the correlation value a between variables in the adsorption process. Person correlation explains that values of $0.40 < r < 0.69$ indicate a moderate relationship; $0.70 < r < 0.89$ is a strong connection; and $0.90 < r < 1.00$ indicate a very strong connection. The correlation values shown in Table 2 are for correlations that have $r > 0.5$ values. A correlation of positive indicates one variable is rising, the other is also rising proportionally. Meanwhile, a negative correlation indicates that when one variable rises, the other falls proportionally. On the other hand, a correlation close to 0 indicated that there is no strong linear relationship between two variables[14].

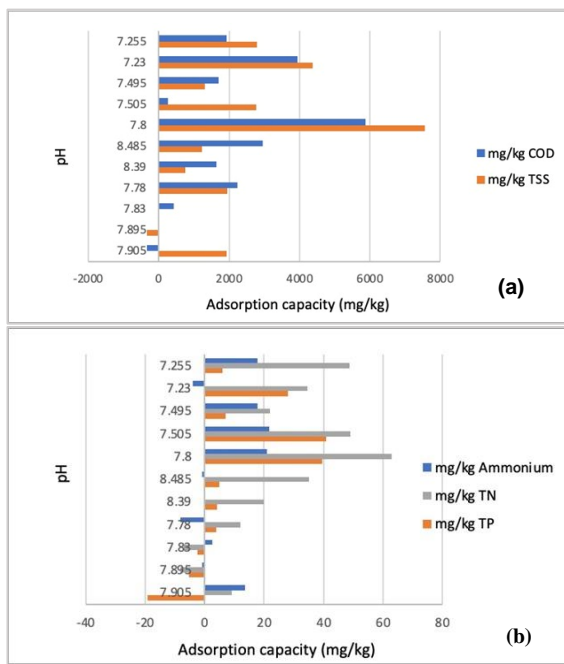


Fig. 5. The effect of pH on the adsorption capacity of rice husks in eliminating TSS and COD (a), and TN, TP, and ammonium (b).

Table 2. Correlation between variables in the adsorption process

Comparison	r
Contact time vs DO	0.753
Contact time vs TN	-0.748
Contact time vs TP	0.666
Contact time vs pH	-0.6
Contact time vs Color	-0.562
Contact time vs COD	-0.698
COD vs TP	0.922
Color vs TN	-0.748
Color vs pH	0.666
TSS vs Color	-0.506
TSS vs TN	0.561
TSS vs pH	-0.537

Based on table 2, the variability that has a strong correlation is COD with TP because the main source of pollution is organic materials. COD and TP reflect high levels of organic pollution so they are positively correlated. Furthermore, DO and contact time were also positively correlated with stronger relationships. A positive correlation between contact time and dissolved oxygen is an indication that water treatment or wastewater treatment can improve water quality by increasing the concentration of dissolved oxygen in the water. It is very important to ensure that organisms living in the water have enough oxygen to undergo their respiration process and to maintain the good quality of the aquatic ecosystem. The negative correlation between color and TN with a strong relationship suggests a reduction in the concentration of nitrogen compounds may contribute to the decrease in water color. This happens because textile liquid waste from the dyeing process is organic waste that contains nitrogen compounds (such as ammonia or nitrate) and compounds that give color to water (such as colored organic compounds). The negative correlation between TN and contact time indicates that the longer the contact time with a nitrogen reduction process (such as the nitrification-denitrification process), the more nitrogen can be removed from the water.

3.1.4 Classification of Water Quality

Based on Government Regulation No. 22 of 2021 regarding the implementation of environmental protection and management, river water quality is grouped into 4 classes, namely:

- Group A is class 1 water with excellent water quality, suitable for various purposes, including human consumption without further treatment.
- Group B is class 2 water with good water quality, suitable for human consumption after simple treatment.
- Group C is class 3 water with sufficient quality, suitable for human non-consumption purposes, such as irrigation, fisheries, and industrial purposes.
- Group D is class 4 water with poor quality, suitable only for human non-consumption purposes that do not require water treatment, such as industrial waste disposal and other activities that do not require high-quality water.

Table 3 Grouping of water classes based on the value of the treated water concentration after textile wastewater is treated with rice husks.

No	Parameter	Value	Group
1	pH	7.78	A
2	TSS	61.51 mg/L	C
3	COD	65.06 mg/L	D
4	DO	4.92 mg/L	A
5	Color	75.06 PtCo	C
6	TDS	343.63 mg/L	A
7	TN	4.93 mg/L	A
8	TP	1.142 mg/L	B

Treating textile wastewater with rice husk (Table 3) gives excellent water quality in terms of pH, DO, TDS, and total nitrogen, suitable for human consumption. However, the parameters of TSS, COD, and quality color of treated water are not suitable as a drinking water source but have reached the threshold of liquid waste into the river so as not to harm the ecosystem and life.

3.2 Discussion

Directly using rice husk without modification has been proven to reduce TSS, color, COD, TDS, TN and TP in wastewater. The performance is good but still needs improvement because the contact time is not working correctly initially. In the future, this can be avoided by first carrying out initial treatment, i.e. soaking and washing several times, then drying before using the rice husk as an adsorbent. This aims to reduce tannin compounds contained in rice husks which contribute to the increase in organic compounds in waste so that color absorption and COD have not been maximized.

Applying a vertical flow system in the adsorption bed brings convenience for operation because there is no need for an electric pump to push wastewater from the storage tank to the adsorption bed. This design helps reduce operating cost and energy[15]. This technology does not require particular operating expertise so it can be applied at various industrial scales, including small ones. This low-cost technological innovation encourages industrial companies to treat waste before being discharged into water bodies, because up to now, the processing operational cost factor has been one of the reasons that caused industrial companies to produce effluent from the production process directly into the river without being treated.

Searching for the latest research developments (last five years) through publish or perish (PoP) software[16] by selecting articles published in Scopus-indexed journals yielded results as shown in Table 4. The publications shown in Table 4 selected ten articles representing the research topic. Based on the data in the table, research related to natural and modified rice husks have focused on the removing dyes in textile wastewater, one of the primary sources of toxic pollutants in water. However, this study provides new information that, in addition to color, unmodified rice husks also can reduce COD, TSS, TN, TP, and ammonium. TN and TP concentrations demonstrate the availability of nutrients, the presence of which in excessive quantities can cause eutrophication of aquatic ecosystems. High concentrations of COD can reduce the amount of dissolved oxygen in water. Microbial decomposition of organic matter requires oxygen, and if COD is high, this can deplete oxygen in the water, negatively impacting aquatic life and causing “dead zone” in the water. TSS in water can

disrupt aquatic habitats by contaminating and reducing light reaching the water. This can damage algae and aquatic plants that require sunlight for photosynthesis. In addition to disrupting the life of aquatic organisms, pollutants found in textile effluent can also harm human health. Excessive ammonium content in water can be harmful to human health if the water is used for domestic or agricultural purposes. Ammonium in drinking water can result health problems such as digestive disorders and kidney problems.

Based on the above explanation, research related to the use of unmodified rice husk should continue to be developed because rice husks have the potential to become an adsorbent by adsorbing various types of pollutants present in textile wastewater. Overall, the results of this research can constitute an alternative for the development of industrial waste treatment because it is inexpensive, easily renewable, and environmentally friendly. The development of this research is part of the sustainable development goals related to the availability of clean water and the preservation of underwater ecosystem life.

Table 4. Development of recent research related to the use of rice husks in textile waste treatment

No	Adsorbent	Effluent	Pollutants removed	Year	Reference
1	Activated carbon from saw dust and rice husk	Synthetic and real textile effluent	azo dyes	2019	[17]
2	Activated carbon from rice husk	Synthetic and real textile effluent	color and metals	2020	[18]
3	Rice husk	Synthetic effluent	cationic dyes	2020	[19]
4	modification nanocrystalline using rice husk ash	Synthetic effluent	Color	2020	[20]
5	Silica from rice husk	Synthetic effluent	Color	2020	[21]
6	Sugarcane bagasse and Rice husk	Synthetic effluent	Color	2021	[22]
7	Torrefied rice husk	Synthetic effluent	Methylene blue	2022	[23]
8	Modification nanocomposite using rice husk	Synthetic effluent	dyes	2021	[24]
9	Rice husk biochar	Synthetic effluent	Remazol dyes	2023	[25]
10	Modification nanoparticle using rice husk	Synthetic effluent	dyes	2022	[26]

No	Adsorbent	Effluent	Pollutants removed	Year	Reference
11	Unmodified rice husk	Real textile effluent	TSS,COD, Ammonium, TN,TP	2023	This work

4 Conclusion

Unmodified rice husks with a vertical flow system are innovations in developing cheap and environmentally friendly textile wastewater treatment technology. The results showed that unmodified rice husks were able to reduce TSS, TN, TP, TDS, and ammonium in textile effluent to meet the threshold set in Government Regulation No. 22 of 2021. The contact time and pH influence the reduction efficiency and adsorption capacity. Contact time with maximum efficiency occurs between 20-25 days with pH conditions that tends to be alkaline. Adsorption of wastewater is often better at alkaline pH because alkaline conditions can increase adsorption efficiency.

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