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# Influence of Rice Husk Carbon Activation on the Adsorption Process of Fe and Mn Metals from Coal Wastewater

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**Abstract**

Liquid waste is the most common type of waste compared to solid or gas waste. The most significant issue with liquid waste is the liquid waste originating from coal washing, which can decrease the acidity level (pH) and increase the total suspended solids (TSS), Iron (Fe2+), and Manganese ($Mn^{2+}$) content. In this study, activated carbon adsorbents were produced from rice husk material. The research aims to obtain data on the characteristic quality of activated carbon made from rice husk with different concentrations of $ZnCl_2$ activator substance, to acquire data on the effectiveness of activated carbon, and to obtain data on the levels of Iron ($Fe^{2+}$) and Manganese ($Mn^{2+}$), TSS, and pH after the adsorption process. This research was conducted through several stages, including raw material preparation, carbonization, activation, and absorption of coal liquid waste content. Based on the research results, activated carbon from rice husk with a 15% $ZnCl_2$ activator concentration using heating method and a 15% $ZnCl_2$ activator concentration using soaking method, the initial TSS value of 911 mg/L decreased to 527 mg/L with a 15% $ZnCl_2$ activator concentration using heating method and 613 mg/L with a 15% activator concentration using soaking method. The Iron ($Fe^{2+}$) content decreased from 0.71 mg/L to 0.01 mg/L with a 15% activator concentration using heating method and 0.07 mg/L with a 15% activator concentration using soaking method. The Manganese ($Mn^{2+}$) content decreased from 0.63 mg/L to 0.15 mg/L with a 15% activator concentration using heating method and 0.08 mg/L with a 15% activator concentration using soaking method. The pH level increased from 6.56 to 7.36 with a 15% activator concentration using heating method and 7.24 with a 15% activator concentration using soaking method.

**Keywords:** Adsorption, Coal wastewater, Iron, Manganese, Rice Husk

## 1. Introduction

South Sumatra covers 109,254 km2, making it the largest region on the island of Sumatra. This area represents around 22.0% of Sumatra's total area, or roughly 5.4% of Indonesia's total area.

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The coal potential in South Sumatra Province accounts for about 85% of the total reserves on Sumatra Island, totaling approximately 22.24 billion tons. In the South Sumatra program for national energy, coal is seen as a feasible alternative to crude oil. Coal mines are located in Muara Enim, Banyuasin, Musi Rawas, Ogan Kumering Ulu, Ogan Kumering Ilir, and Lahat. Coal production in these areas totals 9,119,457 tons. Coal mining results in numerous significant environmental issues, with acid mine drainage (AMD) being the primary concern. Acid mine drainage is created through the hydrogeochemical weathering of sulfide-containing rocks (pyrite, arsenopyrite, and marcasite) when they react with water and oxygen [26,30]. This reaction is facilitated by iron and sulfur-oxidizing microorganisms (Fe) [5,9]. The presence of Al, Fe, Mn, and sulfate is a major concern besides Cu, Ni, Pb, Cd, Cr, and Zn [35]. Considering field data, there is no wastewater treatment at mining sites where the wastewater contains metal compounds such as Cu, Zn, Mn, Fe, Cd, Cr, Ni, and Pb [20]. The introduction of waste from coal mining activities into river streams can harm aquatic ecosystems by causing habitat destruction and degradation of water quality. This leads to a decrease in the biodiversity of specific aquatic ecosystems and their capacity to support life. The severity and extent of damage depend on various factors, including the frequency of water inflow, volume and chemical content of drainage, and the buffering capacity of the receiving river stream [17, 19, 21, 24, 25, 27, 34, 36]. Heavy metal pollution from coal wastewater can cause harmful health effects like kidney damage, liver failure, gastric disorders, mental retardation, and reproductive issues in humans. Heavy metals can also have carcinogenic effects on humans [11, 31]. Biosorption is the process of eliminating contaminants from water systems by utilizing biological materials. This method involves absorption, adsorption, ion exchange, surface complexation, and deposition. Biosorbents offer benefits in terms of accessibility, efficiency, and capacity. This process is easily accessible and can be regenerated easily, making it very advantageous [29,32]. Biosorption is a metabolic-independent method that relies on dead biomass and agricultural residues [13]. Different types of biomasses like rice husks, wheat husks, banana peels, and microbial biomass are utilized as biosorbents [8]. Rice husks are a type of agricultural biomass and are the primary by-product of the rice milling industry. Global rice production totals approximately 600 million tons annually. Rice husks make up over 100 million tons of this total, comprising 20% - 34% of the weight of rice[7]. Rice husks are composed of 50% cellulose, 30% lignin, and 20% organic compounds [28]. Rice husks possess a tough outer surface, a low volume density, and the greatest amount of amorphous silica compared to other types of grasses (37). The high carbon content in rice husks makes them suitable for conversion into activated carbon with high energy content via thermochemical treatment. Waste rice husk activated carbon is both cost-effective and eco-friendly. Rice husk activated carbon, which is high in silicon and alumina, can be used for creating zeolites, amorphous silica, and silica-based catalysts. Its organic components are also ideal for producing activated carbon, carbon-based catalysts, and porous carbon [3,18]. In addition, the rice husk activated carbon surface includes various acidic (carboxylate, lactonic, and phenolic), neutral (benzoquinone and others), and basic (quinonoid carbonyl groups, pyrone, and benzopyranil groups) functional groups. These functional groups play a key role in pollution remediation, allowing rice husk activated carbon to effectively adsorb heavy metals, organic substances, and other pollutants in water environments [12,15].

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Research conducted by Zhang et al, 2014, demonstrated that rice husk can effectively adsorb Cu. Abdel-Ghani et al, 2007, found that rice husk can achieve a removal efficiency of 98.15% for Pb at room temperature and is effective for adsorbing various metal ions[10].

## 2. Materials and Methods

*2.1. The materials used in this study :*

Rice husks as a carbon source, $ZnCl_2$ solution as an activator, and coal wastewater as the adsorption test solution.

*2.2. The research method was divided into several steps:*

*a)* Carbonization
Rice husks were washed thoroughly and dried. The dried rice husks were heated in a muffle furnace at 500℃ for approximately 2 hours until carbon was formed (indicated by the absence of smoke).

b) Carbon Activation
Method I. The carbon was heated in a $ZnCl_2$ solution at 100℃ for 1 hour. The concentration of the $ZnCl_2$ solution was varied at 5%, 10%, and 15%. The carbon was then filtered and washed thoroughly (indicated by a neutral wash solution) before being placed in a porcelain crucible and heated in a muffle furnace at 500℃ for about 2 hours.

c) Method II. The carbon was soaked in a $ZnCl_2$ solution for 1 day. The concentration of the $ZnCl_2$ solution was varied at 5%, 10%, and 15%. The carbon was then filtered and washed thoroughly (indicated by a neutral wash solution) before being placed in a porcelain crucible and heated in a muffle furnace at 500 ℃ for about 2 hours.

d) Adsorption Test 5 grams of activated carbon were added to 100 ml of coal wastewater and stirred. At regular intervals (5, 10, 15, 20, and 25 minutes), sample solutions were taken for TSS, pH analysis, and for the analysis of iron (Fe) and manganese (Mn) levels using ICP-OES.

## 3 Results and Discussion

*3.1. Optimal Quality Levels of Activated Carbon for Adsorption Testing*

Based on the measurements of water content, ash content, fixed carbon content, and methylene blue adsorption capacity, the best activated carbon according to SNI standards (1995) for conducting adsorption tests on coal wastewater was determined. The research findings are presented in Table 1:

**Table 1.** Research Findings based on Variation of $ZnCl_2$ Solution Concentration as Activator for Rice Husk Activated Carbon and Variation of Methods

| **Analysis Parameter** | **Quality Standard** | **Unit** | **Results and Samples** | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | **Heating % $ZnCl_2$** | | | **Soaking % $ZnCl_2$** | | |
| | | | 5 | 10 | 15 | 5 | 10 | 15 |
| Water Content | Max 15 | % | 8,7 | 4,3 | 5,6 | 9,3 | 5,9 | 3,6 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Ash Content | Max 10 | % | 0,82 | 1,72 | 1,2 | 1,32 | 1,88 | 1,19 |
| Fixed Carbon Content | Min 65 | % | 89,45 | 92,11 | 91,95 | 87,99 | 90,25 | 93,81 |
| Methylene Blue Adsorption Capacity | Max. 0,2-0,3 | ppm | 0,196 | 0,712 | 0,233 | 0,061 | 0,344 | 0,141 |

Rice husk possesses physical and biochemical properties suitable as a potential precursor in activated carbon production. It is a type of biomass known as lignocellulosic material, which is made up of lignin, cellulose, and hemicellulose. Cellulose and hemicellulose are fractions that are easily vaporized and lost during pyrolysis. The study conducted by Menya et al. in 2018 showed that rice husk treated with NaOH and citric acid, without carbonization, could eliminate 60-70% of humic substances from peat swamp runoff. Additionally, they found that rice husk carbon had similar effectiveness to commercially activated carbon [22]. The 2014 study by Nsaifabbas et al. found that raw rice husk, without activation, could eliminate 98.24% of humic acid from a solution[23].

*3.2. Morphology of Rice Husk Activated Carbon*

The surface morphology of rice husk activated carbon was analyzed with Scanning Electron Microscopy (SEM) to observe patterns and images of the surface treated with heating and soaking in 10% $ZnC_2$. See Figures 1a and 1b for details.

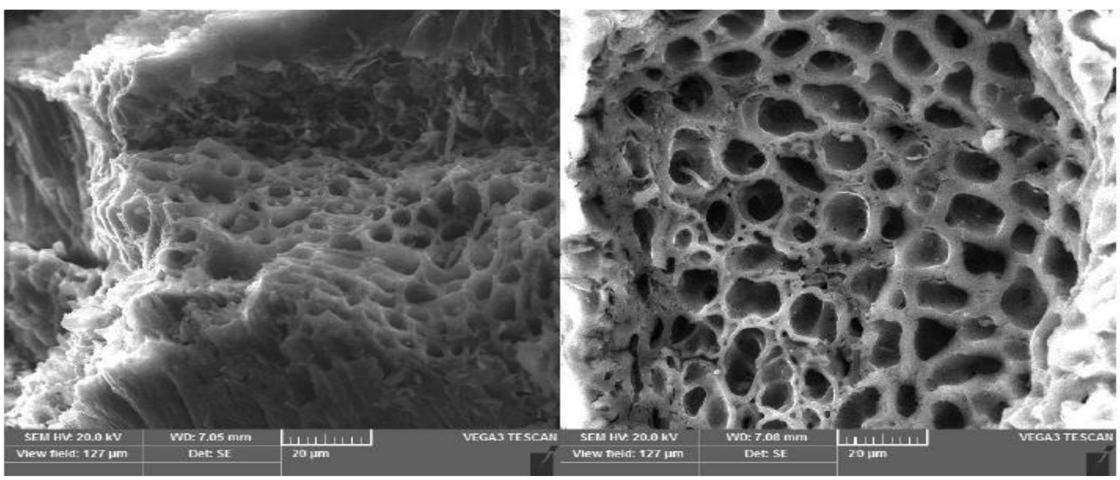


Figure 1. Rice Husk Activated Carbon at 10% ZnCl2 Concentration using Heating Method (a) and Soaking Method (b)

The surface morphology of rice husk activated carbon in Figure 1a, treated with heating, and Figure 1b, treated with soaking at a 10% $ZnCl_2$ activation concentration, exhibits heterogeneous, coarse morphology with grooves, and numerous pores on the rice husk surface, indicating its suitability for heavy metal adsorption and possessing high adsorption capacity.

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*3.3. The Influence of Agitation on the Quality of Coal Wastewater using Rice Husk Activated Carbon in the Heating Method*

The research results demonstrate that rice husk exhibits high efficiency in adsorbing $Fe^{2+}$, $Mn^{2+}$, TSS, and pH test substances under optimal working conditions. The strong interaction between metal ions and active groups within the rice husk is the reason for this. Procedures were optimized to obtain quantitative results for metal ions in rice husk. Analytical parameters such as contact time, pH, amount of rice husk, and initial heavy metal concentration were considered. This is presented in Tables 2 and 3.

**Table 2**. Research Findings based on Variation of Agitation Duration and Heating Method Variation of Rice Husk Activated Carbon

| **Analysis Parameter** | **Quality Standard** | **Unit** | **Results and Samples for Variation of Agitation Duration (Minutes) in Heating Activation Treatment** | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | **0** | **5** | **10** | **15** | **20** | **25** |
| pH Level | 6-9 | - | 6,36 | 7,08 | 7,23 | 7,28 | 7,31 | 7,36 |
| TSS Level | Max.200 | mg/L | 911 | 796 | 753 | 647 | 594 | 527 |
| Iron (Fe) Level | Max.7 | mg/L | 0,71 | 0,31 | 0,17 | 0,15 | 0,13 | 0,01 |
| Manganese (Mn) Level | Max.4 | mg/L | 0,63 | 0,48 | 0,39 | 0,26 | 0,19 | 0,15 |

**Table 3.** Research Findings based on Variation of Agitation Duration and Soaking Method Variation of Rice Husk Activated Carbon

| **Analysis Parameter** | **Quality Standards** | **Unit** | **Results and Samples for Variation of Agitation Duration (Minutes) in Soaking Activation Treatment** | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | **0** | **5** | **10** | **15** | **20** | **25** |
| pH Level | 6-9 | - | 6,56 | 7,09 | 7,12 | 7,14 | 7,20 | 7,24 |
| TSS Level | Max.200 | mg/L | 911 | 781 | 732 | 657 | 630 | 613 |
| Iron (Fe) Level | Max.7 | mg/L | 0,71 | 0,29 | 0,23 | 0,18 | 0,12 | 0,07 |
| Manganese (Mn) Level | Max.4 | mg/L | 0,63 | 0,45 | 0,30 | 0,20 | 0,15 | 0,08 |

a) pH Influence

pH is a critical factor that controls the adsorption of metal ions in wastewater. The impact of pH on the adsorption of $Fe^{2+}$ and $Mn^{2+}$ was examined within the initial pH range of 6.56. Table 2 displays the connection between the starting pH of the solution and the percentage of heavy metals removed using rice husk activated carbon in the heating process. Table 3 illustrates the same relationship for the soaking process of rice husk activated carbon treatment.

The pH of coal wastewater did not show significant changes during adsorption with rice husk activated carbon using heating and soaking methods. Using rice husk activated carbon through

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heating, the pH increased from 6.56 to 7.36.Using rice husk activated carbon through soaking, the pH increased from 6.56 to 7.24. At elevated pH levels, the release of Fe2+ and Mn2+ increases as a result of the electronic attraction between negatively charged sites on the surface of the rice husk adsorbent and each metal ion. Research conducted by Yefremova et al. (2023) suggests that the adsorption capacity of rice husk adsorbents is significantly influenced by the optimal pH level. Specifically, removal rates of 95.76% for Fe2+ and 100% for Pb2+ were observed at pH 8 [38].

b). The Effect of Contact Time

The influence of contact time on the adsorption rate using rice husk-based activated carbon is optimal, as evidenced by the removal of pH, TSS, $Fe^{2+}$, and $Mn^{2+}$ through adsorption, which increases with increasing time and reaches maximum values at around 20 minutes for pH, TSS, $Fe^{2+}$, and $Mn^{2+}$ (Tables 2 and 3). The reduction in TSS in coal wastewater through adsorption is observed using both rice husk activated carbon prepared via heating and soaking methods. With rice husk activated carbon prepared via heating, there is a decrease in TSS from 911 to 527 mg/L, and with rice husk activated carbon prepared via soaking, there is a decrease in TSS from 911 to 613 mg/L. The decreasing TSS values result in clearer water due to the close relationship between suspended solids and the turbidity level of water, thus making activated carbon more effective in reducing TSS values [4]. The decrease in $Fe^{2+}$ values in coal wastewater is observed through adsorption using both rice husk activated carbon prepared via heating and soaking methods. Rice husk activated carbon prepared via heating experiences a decrease in iron from 0.71 to 0.01 mg/L, and with rice husk activated carbon prepared via soaking, there is a decrease in iron from 0.71 to 0.07 mg/L. The rapid increase in $Fe^{2+}$ ion adsorption with increasing contact time can be attributed to the presence of vacant sites on the adsorbent surface until equilibrium is reached [6]. The decrease in $Mn^{2+}$ values in coal wastewater is observed through adsorption using both rice husk activated carbon prepared via heating and soaking methods. Rice husk activated carbon prepared via heating experiences a decrease in $Mn^{2+}$ from 0.63 to 0.15 mg/L, and with rice husk activated carbon prepared via soaking, there is a decrease in iron from 0.63 to 0.08 mg/L. Increasing the contact time improves the diffusion of adsorbates into the pores of the adsorbent from the outer to the inner part [2]. This is supported by the research findings of Lakshmana et al., 2023, where the removal of Cu and Ni ions using rice husk adsorbents reached 62.42 - 65.49% [16].

## 4. Conclusion

All activated carbons from rice husks, whether activated by heating or soaking methods, have met the quality standards for activated carbon according to SNI (1995).

The most optimal and adequate conditions for producing activated carbon from rice husks, both through heating and soaking activation methods, are at a 15% activator concentration.

The analysis results indicate that the effectiveness of activated carbon from rice husks, whether through heating or soaking activation methods, is nearly identical in terms of raising pH, reducing Iron ($Fe^{2+}$) and Manganese ($Mn^{2+}$) levels, and decreasing TSS levels. The best agitation

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time is 25 minutes among the range of 5 minutes to 25 minutes, indicating that the longer the agitation time, the better the adsorption results.

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