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The Role of Acid Catalysts in Optimizing Iron Adsorption: Mechanistic Insights and Applications

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Abstract – *This research aims to evaluate the influence of acid catalysts HCl and H_2SO_4, on the adsorption efficiency of Fe (Iron) using silica extracted from rice husk ash. The synthesis process employs the sol-gel method, including the initial treatment of rice husk ash, sodium silicate extraction, and the formation of silica gel with acid catalysts. The research results show that acid catalysts affect the structure and adsorption efficiency, with the highest efficiency obtained using the 0.5M HCl catalyst with an adsorption efficiency of 62.3% and the 0.5M H_2SO_4 catalyst with an adsorption efficiency of 24.85%. FTIR analysis to identify functional groups revealed siloxane (Si-O-Si) and silanol (Si-OH) contained in silica, which support the metal adsorption capability. The results of the morphological observation using SEM show that the amorphous silica structure has diverse pores based on the type of catalyst.*

Keywords: *silica; sol-gel method; HCl and H_2SO_4; FTIR; SEM*

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INTRODUCTION

Rice husk is an agricultural waste that is abundant in Indonesia, but its utilization is still limited. Direct burning of rice husk can increase carbon emissions in the atmosphere. To optimize the use of rice husk, it is important to find alternative innovative technologies that are more beneficial. Rice husk contains organic components such as protein, fat, nitrogen compounds, fiber, pentose, cellulose, and lignin, as well as inorganic components in the form of minerals needed for plant growth. When rice husk is burned, all organic components are converted into carbon dioxide (CO_2) and water (H_2O), while the inorganic components are transformed into ash. Rice husk ash contains silica ranging from 87% to 97%, which has the potential to be used as a raw material for silica production (Trivana et al., 2015).

Rice husk can be used as a primary material in the production of silica gel-based materials, because of high silica content. Rice husk ash contains sodium silicate, which can be synthesized into silica gel that can be used as an adsorbent medium. Synthesizing silica gel requires special treatment to obtain silica results, namely by using several methods such as the sol-gel process, gas phase process, co-precipitation method, plasma spraying & forging process, and emulsion techniques (Salman et al., 2015)

Silica gel is one of the synthetic silica compounds that has an amorphous structure and can be synthesized through the sol-gel process. This method involves the production of material using organic substances via a chemical reaction in a solution at low temperatures. The principle involves the hydrolysis and condensation of molecules from the precursor solution (Huljana & Rodiah, 2019).

The process of synthesizing silica gel from rice husk ash consists of two stages, namely the ashing process and making the silica gel itself. The process of making silica gel includes four steps: first, the formation of sodium silicate based on the reaction of silica contained in rice husk ash; second, melting at high temperatures (above the melting point of the base used); third, the hydrosol formation process through the reaction of sodium silicate with acid; and fourth, the reaction that produces silica hydrogel and heats the silica hydrogel to become sol gel (dry silica gel). The aim of the research was to make silica gel from rice husks as an Fe (iron metal) adsorbent in water with the help of HCl and H_2SO_4 catalysts and to find out the comparison of making silica gel with HCl and H_2SO_4.

Strong acid catalysts have a higher adsorption capacity than weak acids when used to produce silica gel. HCl and H_2SO_4 acid catalysts, which are frequently used in a variety of chemical processes and will aid in the creation of silica hydrogel, are utilized in this practical silica gel manufacture.

MATERIALS AND METHOD

Materials

The materials used were rice husks, (SiO_2), NaOH, H_2SO_4, HCl, and $FeSO_4$.

Rice Husk Ash Treatment

Treatment of rice husk ash follows the procedures established in the research by Huljana & Rodiah (2019). The process begins with cleaning the rice husks using running water and drying them under sunlight. Once the rice husks are completely dry, they are placed in a furnace at a temperature of 600°C for two hours, transforming them into ash which is then ground using a mortar to achieve a uniform size. The finely ground ash is afterward mixed with a 4M HCl solution and 100 mL of distilled water, and stirred using a magnetic stirrer for two hours at a temperature of 85°C. After the stirring process, the mixture is allowed to sit until it reaches room temperature, then filtered using filter paper to obtain the raffinate. This process concludes by rinsing the raffinate with distilled water and measuring the pH until it reaches a neutral value, before finally drying it in an oven at 105°C until white silica is produced.

Extraction of Rice Husk Ash

Production of silica acid refers to the research conducted by Yusuf et al (2023). The process begins by dissolving 50 grams of rice husk ash obtained from leaching using 1M NaOH in 100 mL of distilled water. The solution is then heated and mixed using a magnetic stirrer for one hour to ensure homogeneity. Afterward, the solution is allowed to stand for 18 hours to provide sufficient time for the reaction to occur. Next, the resulting solution is filtered and washed with hot water at a temperature of 85°C to remove any remaining insoluble materials. The result of this filtration process is a sodium silicate solution, which is an important step in the production of silica acid.

Silica Synthesis

Production of silica gel refers to the research conducted by Yusuf et al, (2023). The process begins with the addition of Na_2SiO_3 solution using HCl and H_2SO_4 catalysts according to a completely randomized design (RAL) with varying concentrations of HCl (0.5; 1; 1.5; 2; 2.5) M and H_2SO_4 (0.5; 1; 1.5; 2; 2.5) M. The addition is done slowly while continuously stirring until the mixture transforms into a gel with a neutral pH of 7. After the gel is formed, it is left for 12 hours before being filtered to separate the gel product. The filtered gel is then treated with distilled water until it reaches a pH of 7, after which it is weighed and dried in an oven at 120°C for 5 hours and then cooled in a desiccator. The final result is silica gel, which is then ground using a mortar and pestle to achieve a uniform size and produce a fine powder.

Adsorption of Fe Metal Ions

The process of testing the adsorption of Fe metal ions refers to the research conducted by Yusuf et al (2023). It begins with preparing a 1N $FeSO_4$ solid, which is then dissolved in a beaker using distilled water. Once the solution is formed, it is transferred to a volumetric flask and distilled water is added until reaching the marked line, followed by stirring until homogeneous. Next, the resulting silica gel is mixed with the $FeSO_4$ solution and stirred for 60 minutes to ensure interaction between the silica gel and the metal ions. After the stirring process, the mixture is placed in a centrifuge tube and spun for 30 minutes at a speed of 2000 rpm. This process produces a filtrate that will be tested using a Visible Spectrophotometer to determine the concentration of iron (Fe) metal, using a wavelength range of 350-450 nm (Khaira, 2013).

Functional Group Analysis with Fourier Transform Infra-Red Spectroscopy (FTIR)

Functional group analysis test from rice husk silica gel using Fourier Transform Infra-Red Spectroscopy (FTIR). In FTIR testing, you can find out which functional groups in Si-H (silanol) occur (Tarigan et al., 2022).

Morphological Analysis with Scanning Electron Microscope (SEM)

Morphological analysis of the surface or cross-section of the silica gel is conducted using a Scanning Electron Microscope (SEM), referring to the research carried out by Setiani et al (2013). The sample is placed on a set holder with double-sided adhesive and coated with a gold layer, after which the sample is inserted into the SEM sample compartment in a vacuum state. The topographical images are then observed at a magnification of 5000 times.

RESULTS AND DISCUSSION

Absorbance Measurement of Iron (Fe) Standard Solutions

Analysis of Iron (Fe) Standard Solutions with concentrations of 1.1 ppm, 2.2 ppm, 3.3 ppm, 4.4 ppm, and 5.5 ppm was conducted using UV-VIS spectrophotometry at a wavelength of 350 nm.

Solution	Wavelenght	Absorbance	Concentration (mg/l)
Fe (1,1 ppm)	350	0,186	0,000132857
Fe (2,2 ppm)	350	0,416	0,000297143
Fe (3,3 ppm)	350	0,64	0,000457143
Fe (4,4 ppm)	350	0,881	0,000629286
Fe (5,5 ppm)	350	0,929	0,000663571

Table 1. Absorbance Measurement Results of Iron (Fe) Standard Solutions

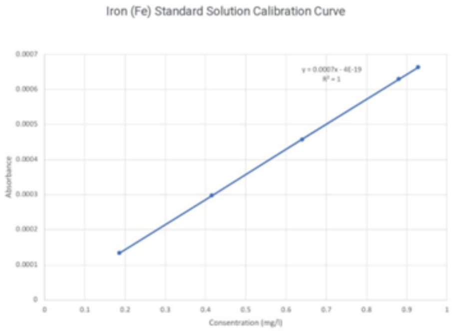

Figure 1. Calibration Curve of Iron (Fe) Standard Solutions

The absorbance measurement data from iron (Fe) standard solutions at various concentrations, visualized in the graph above, yielded the equation

$y = 0.0007x - 4E{-}19$ for the correlation between concentration and absorbance. The y-value represents the absorbance at the optimum wavelength, while the x-value denotes the absorbed iron (Fe) content, where $x=(y+4E{-}19)/0{,}0007$

The graphical visualization demonstrates that the iron (Fe) content exhibits a strong positive correlation with absorbance concentration, as evidenced by the coefficient of determination (R^2) value of 1, indicating 100% accuracy of the calibration curve in concentration determination.

Analysis of Iron (Fe) Adsorption Efficiency

Analysis results of iron (Fe) metal content in solutions following the adsorption process using silica gel as an adsorbent with HCl and H_2SO_4 catalysts. The adsorption efficiency of iron (Fe) metal is presented in Table 2.

Sample	Catalyst Concentration (M)	Iron (Fe) Concentration (mg/l)	Adsorption Efficiency (%)
1A	0,5	0,67	62,30
1B	1	1,12	37,16
1C	1,5	0,90	49,73
1D	2	1,12	37,16
1E	2,5	1,35	24,59
2A	0,5	1,34	24,85
2B	1	1,61	9,81
2C	1,5	1,61	9,81
2D	2	1,61	9,81
2E	2,5	1,61	9,81

Table 2. Analysis Results of Iron (Fe) Adsorption Efficiency

The adsorption efficiency measurements were obtained by measuring the iron (Fe) concentration before adsorption using silica gel, yielding a concentration of 1.79 mg/l. The highest adsorption efficiency of iron (Fe) metal by silica gel was observed in sample 1A using 0.5 M HCl catalyst, achieving an efficiency of 67.3%. For samples with H_2SO_4 catalyst, the maximum efficiency was obtained from sample 2A with a catalyst concentration of 0.5 M.

The addition of a catalyst significantly influences the adsorption efficiency of iron (Fe) metal by silica gel. The adsorption efficiency decreases with increasing concentrations of HCl and H_2SO_4 catalysts. This decrease in adsorption efficiency is attributed to the reduction in proton formation during the reaction. Protons function as formation agents for siloxane (Si-O-Si) and silanol (Si-OH) functional groups. Higher acid catalyst concentrations result in reduced proton generation, leading to impediments in functional group formation. Siloxane (Si-O-Si) and silanol (Si-OH) serve as absorbents by promoting enhanced interaction between the adsorbent and iron (Fe) metal.

Functional Group Analysis with FTIR

The synthesis's effectiveness is evaluated by FTIR analysis, which analyzes the functional groups in the silica that is generated. The purpose of this experiment was to compare the use of HCl and H_2SO_4 catalysts in the manufacture of silica from rice husk ash. The effective synthesis of silica xerogel from rice husk ash was followed by an integrated spectrum from the treatment after functional groups were identified using FTIR. This is indicated by the presence of silanol (Si-OH) and siloxane (Si-O-Si) groups, which are functional groups of silica.

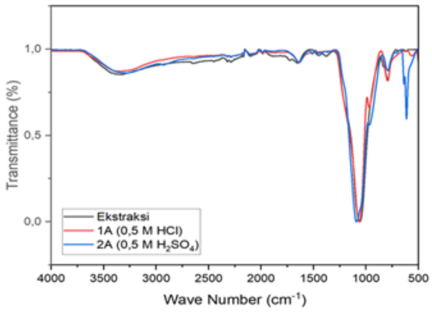

Figure 2. FTIR Analysis Results of Silica Extracted from Rice Husk Ash, 1A (0.5M HCl and 2B (0,5M H_2SO_4)

The results of the FTIR analysis are known from the spectrum shown in figure 2 In rice husk silica, there is an -OH bend group from Si-OH with a wavelength of 3351-3371 cm-1, a hydroxyl (-OH) bond from H_2O with a wavelength of 1639-1645 cm-1, at a wavelength of 1066-1094 cm-1 there is an asymmetric Si-O stretch vibration group from Si-O-Si. At a wavelength of 969-973 cm-1, it shows a symmetric Si-O stretch vibration from Si-OH. There is a symmetric Si-O stretch vibration group from Si-O-Si with a wavelength of 794-795 cm-1, and then there is a Si-O-Si group with a wavelength of 452-459 cm-1 (Trivana et al., 2015)

The FTIR results, one of the functional groups on rice husk silica that can interact with Fe metal will be shown. For example, the hydroxyl group can form bonds with Fe metal, which can then facilitate the absorption of metal by silica. The silica framework structure can provide stability and strength to the material, affecting silica's ability to absorb Fe metal.

From the analysis, the functional group that can interact with Fe metal is the hydroxyl group (-OH) in the wavelength range of 969-973 cm-1 and 3351 – 3371 cm-1. Therefore, in the interaction with Fe metal, the OH group on the silica surface is very relevant and important.

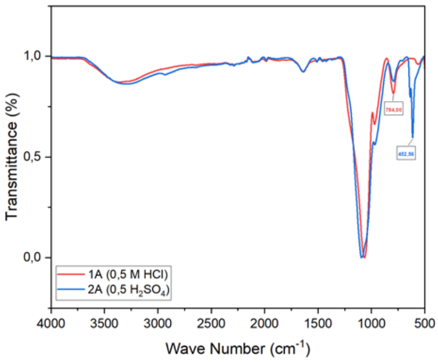

Figure 3. FTIR Analysis Results of Silica Rice Husk Ash 1A (0.5M HCl) and 2A (0,5M)

Figure 3 shows the FTIR results on Rice Husk Ash Silica samples 1A and 2A, which show differences. In sample 1A with a wavelength of 794 cm-1, the symmetric Si-O stretch vibration group from Si-O-Si is observed, while in sample 2B with a wavelength of 452, it indicates the formation of bonds between silicon (Si) and oxygen (O_2) atoms in the silica structure.

The FTIR analysis results for samples 1A and 2B do not show significant results, which is due to the composition of the samples being the same in terms of HCl and H_2SO_4, thus not having a major impact (Sujoto et al., 2023). As for the molecular changes that can affect the structure and pore characteristics of the ash or silica produced from the duration of combustion.

Morphology of Rice Husk Ash Silica Gel

To confirm the results of the conducted research, the morphology of the rice husk ash silica was observed using a Scanning Electron Microscope (SEM) by comparing the morphology of unmodified silica and treated silica. The surface of the unmodified silica and the silica with the best adsorption efficiency of 0.5M is shown in Figure xxx.

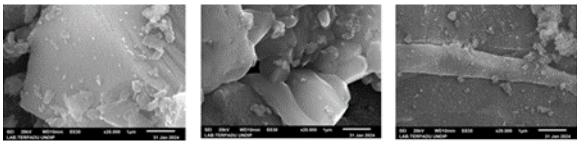

Figure 3. SEM images of rice husk ash silica samples at 20,000x magnification (a) without modification (b) H_2SO_4 modification (c) HCl modification

The results of SEM analysis show that the particles in the figure have an irregular shape, the surface of the sample is uneven and consists of slab-shaped clumps (clusters) which indicates the presence of uneven grain size on the surface of the sample. This is due to the sample being predominantly amorphous in structure, as shown by the research results of (Nayak et al., 2019). In Figure 3 (A and B), the morphology of the untreated sample and the sample pre-treated with acid using H_2SO_4 has a porous network structure of spherical particles. Whereas the sample with pretreatment using HCl has few voids and tends to be horizontally transverse elongated rod-shaped. The protrusions on the outer epidermis in the HCl modification appear softened but not yet destroyed. This indicates that the protrusions are likely composed of other inorganic compounds besides silica. It was confirmed that nano silica was successfully synthesized with the following results obtained on the size of its surface morphology.

No.	Sample Silica	Morphology Size (nm)
1	Unmodifiend Rice Husk Ash	861,7 nm
2	Modifield Rice Husk Ash Silica H_2SO_4	277,3 nm
3	Modifield Rice Husk Ash Silica HCl	129,9 nm

Table 3. Sample Morphology Size

CONCLUSION

The research results indicate that the use of HCl and H_2SO_4 acid catalysts can enhance the adsorption efficiency of Fe metal compared to without a catalyst, with the highest efficiency observed in the 0.5M HCl catalyst with an adsorption efficiency of 62.3% and the 0.5M H_2SO_4 catalyst with an adsorption efficiency of 24.85%. FTIR analysis on the siloxane (Si-O-Si) and silanol (Si-OH) functional groups in silica supports the metal adsorption capability. Morphological observations using SEM show that the amorphous silica structure has varied pore sizes based on the type of catalyst. Overall, the use of HCl and H_2SO_4 catalysts can enhance the adsorption efficiency of Fe metal with silica based on rice husk ash.

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