Potential of rice husk silica as a source of L-lysine modified silica for adsorption of Fe(III) ion

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Abstract. Iron metal (Fe) is one of the most harmful heavy metals for human health. The maximum content of Fe in drinking water allowed by Ministry of Health of the Republic of Indonesia (2010) is 0.3 mg/L. The objective of this study was to synthesize of silica from rice husk and modified with L-lysine for adsorption of iron. Commonly used method for detection of iron is FAAS which has range of detection at 2.5-10 ppm. Therefore preconcentration is needed. This research developed specific adsorbent for application in Solid Phase Extraction (SPE) using silica gel that come from rice husk. The silica then modified by reacted it with 3-aminopropyltrimethoxysilane and then L-lysine. The purpose of modification is to increase the active group on the silica gel surface, making it more selective in binding to Fe(III) ions. The results showed that conditions for the adsorption of Fe(III) by rice husk silica (SSP) and L-lysine modified silica (SLL) was pH 2, adsorbent mass was 10 mg and adsorption time was 30 minutes. The highest adsorption capacity of SSP and SLL were 39.7 mg/g and 46.6 mg/g. It can be concluded that rice husk silica and L-lysine modified silica have good potential as adsorbent of iron.

1. Introduction

Iron is one of the heavy metals that found in the environment, because its presence in large quantities comes from industrial water waste. Iron is also an important element in the human body, but excess iron can cause iron poisoning. The poisoning of iron includes nausea, vomiting, hypotension and shock [1]. Based on that, the Republic of Indonesia Ministry of Health issued regulations on the levels of Fe allowed in drinking water, which is a maximum of 0.3 mg/L [2].

The measurement of Fe content in water and wastewater based on the National Standardization (BSN) can used the Flame Atomic Absorption Spectrophotometer (FAAS) by adding nitric acid. The addition of nitric acid can dissolve metals, not only Fe metal but other metals such as copper, cobalt, zinc and lead. These metals can interfere with the measurement of the Fe signal. In addition, the range of iron measurement concentration using FAAS is higher than 0.3 ppm. Therefore, pre-concentration and separation steps are needed before Fe$^{3+}$ ion samples are measured using FAAS so that the sensitivity and selectivity of the
measurement increases. One of the most widely used pre-concentration and separation methods is Solid Phase Extraction (SPE).

The SPE method has many advantages such as easy to use, has high selectivity, is economical (requires a little solvent), and does not take long. Extraction media that are often used in solid phase extraction are silica gel [3]. Silica gel is an inorganic solid that has many active sites in the form of silanol (Si-OH) and siloxane (Si-O-Si). As an extracting medium, silica gel has the advantage of having a large surface area, high stability, no expansion, and easy modification [4]. Silica gel has weaknesses, low selectivity and effectiveness of the surface in interacting with heavy metals, so it is necessary to modify the surface of silica gel with organic functional groups.

Modifications can be made using organic ligands that have N, S, O and P like amino acids [5]. L-lysine is one type of amino acid which has carbonyl groups and amine groups. The used of L-lysine in silica provides an active group that can function as a donor atom and form a coordinate covalent bond with metal ions. The use of L-lysine as a silica modifier for metal adsorption has been reported, including for the adsorption of Sc metal [6]. Modification of chitosan with L-lysine as adsorbent of Pt (IV), Pd (II) and Au (III) ions has been reported by [7]. Therefore, in this study modification of silica gel with L-lysine was used to adsorb Fe(III) ions. The silica used is silica derived from rice husk charcoal as reported by [9] that rice husk charcoal contains 85-95% silica. Silica from rice husk charcoal has been successfully made through the process of ignoring rice husk charcoal, followed by dissolution of sodium silicate and silica formation through a sol-gel process [9]. The selection of rice husk as raw material is an effort to utilize agricultural waste.

2. Materials and Method

2.1. Synthesize of rice husk silica (SSP)
Rice husk charcoal was cleaned, then soaked in hot water for 2 hours and dried in an oven. Then as much as 50 g of rice husk charcoal were mashed and sieved with a 200 mesh sieve, then put into porcelain and placed into a furnace at 750° for 4 hours. 1 g of rice husk ash was mixed with 50 mL 2.5 M NaOH and then heated at 100°C for 1 hour. Then sodium silica solution was filtered with Whatman paper No. 42. The filtrate was added with ethanol and H\textsubscript{2}SO\textsubscript{4} to get pH 2. Then NH\textsubscript{3} was added. Silica gel was dried in an oven at 110°C for 24 hours. The final step was characterization using Fourier Transform Infrared (FTIR).

2.2. Modification of rice husk silica (SSP) with L-lysine (SLL)
A total of 2 g of activated SSP were mixed with aminopropyltrimethoxysilane (APTMS) (1% v/v in toluene). The mixture was agitated with reflux at a temperature of 110°C. Then the 3-aminopropylsilica (APS) that obtained was dried in an oven at 110°C for 12 hours. Next APS was reacted with glutaraldehyde under nitrogen conditions for 90 minutes at room temperature. The mixture was filtered, washed and dried in a desiccator. As much as 1 g of APS-glutaraldehyde was reacted with 25 mg/L L-lysine dissolved in 0.1 M phosphate buffer solution (pH 7.4), left for 48 hours at room temperature under nitrogen gas conditions. Modified L-lysine (SLL) silica was obtained and characterization was performed using FTIR.

2.3. Measurement of SSP and SLL adsorption capacity
The mechanism of adsorption capacity and isotherm of Fe(III) ion absorption was carried out at a temperature of 25°C, pH 2.0 and contact time of 30 minutes [10]. The effect of
concentration was done by adding silica rice husk (SSP) and L-lysine modified silica (SLL) adsorbents as much as 10 mg to 20 mL Fe(III) ion with a concentration range (5, 10, 25 and 40 mg/L). The initial concentration of Fe(III) ions and remains in the solution was determined using AAS.

3. Results and Discussion
3.1. Rice husk silica and L-lysine modified rice husk silica (SLL)
Decarbonization was a process of ash formation carried out at high temperatures. In this study the decarbonization process was carried out at 750°C for 4 hours [9]. The results of the process of burning rice husk charcoal and decarbonization process can be seen in Figure 1.

![Figure 1. Rice husk (a), charcoal (b), and ash of rice husk (c).](image)

The decarbonization process began with burning a sample of rice husk using a furnace to obtain rice husk charcoal. Washing rice husk charcoal used hot water for 2 hours in order to remove impurities such as rice husk that were not completely burned, and other unwanted impurities. The process of ashing was done at a temperature of 750°C for 4 hours. According to [11] the higher the ignition temperature, the more complete the ignition process, this was due to the loss of organic elements from the rice husk charcoal. The stage of washing rice husk ash using 6M HCL aims to remove impurities in rice husk ash to obtain pure silica [11].

Rice husk silica was obtained through the sol-gel process. Sodium silicate was obtained from the reaction of rice husk ash with NaOH at a temperature of 100°C for 1 hour. In this reaction process, the dissociation of NaOH to Na⁺ and OH⁻ occurred which facilitates the formation of Na₂SiO₃. The formation of silica through the reaction of sodium silicate with ethanol solvent and concentrated sulfuric acid can be seen in Equation 1.

\[
\begin{align*}
\text{SiO}_2 & + 2\text{NaOH} \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O} \\
\text{NaSiO}_3 & + \text{H}_2\text{SO}_4 \rightarrow \text{SiO}_2 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}
\end{align*}
\]

The important step before the adsorption process was to modify silica with amino acid of L-Lysine. The addition aims to add active groups (donor) that can absorb metals through the formation of coordinating covalent bonds, so as to increase the effectiveness of adsorption. The silanization process with silane reagent used APTMS and was carried out in a non-water atmosphere using toluene solvents. The APS obtained was reacted with glutaraldehyde in a
phosphate buffer solution (pH 8) under nitrogen conditions. The addition of glutaraldehyde was intended as a connecting bridge \(-\text{NH}_2\) in APS with L-lysine (Figure 2).

![Figure 2. APS-glutaraldehyde reaction mechanism [12].](image)

APS-glutaraldehyde was reacted with L-lysine in 0.1M phosphate buffer solution (pH 7.4) under nitrogen conditions, with the aim of keeping the reaction inert, and avoiding the oxidation process. The addition of L-lysine to silica aims to add active groups that function as donor atoms that will form a covalent bond coordinating with metal ions, so as to increase the effectiveness of adsorption. The expected reaction can be seen in Figure 3.

![Figure 3. L-lysine modified silica chemical reaction.](image)

3.2. Characterization of Rice Husk Silica (SSP) and L-lysine Modified Silica (SLL) Function Group

FTIR characterization was carried out to identify the rice husk silica (SSP) and L-lysine modified silica (SLL) function groups. This characterization aims to see the bonds and interactions formed on the rice husk silica (SSP) and silica that have been modified with L-lysine. The results of the functional group can be seen in Figure 4.
The result of FTIR analysis showed a difference in the spectrum pattern between rice husk silica and L-lysine modified silica. The SSP adsorption spectrum pattern shows the absorption at wave number 3449.25 cm\(^{-1}\) which showed the stretching of hydroxyl (\(-OH\)) groups on silanol (Si-OH) and water (H\(_2\)O) groups. Silanol and water vibrations are shown in areas 3200-3700 cm\(^{-1}\) [13]. The absorption band at wave number 2110.29 cm\(^{-1}\) was characteristic of the vibration of silica monohydrate (H-Si-Si-H) [14]. Wave number 617.06 cm\(^{-1}\) showed Si-O stretching vibration in siloxane [15]. In general, SSP shows a spectrum pattern with Si-OH and Si-O-Si functional groups.

Identification of the presence of L-lysine in rice husk silica as a modified result was shown in wave number 2941.14 cm\(^{-1}\) which was the Si-CH\(_2\) stretching vibration of the methylene group (-CH\(_2\)). This corresponds to the L-lysine spectrum in Figure 4 (black) that two absorption at wave numbers 2981 cm\(^{-1}\) and 2894 cm\(^{-1}\) were symmetrical and asymmetrical groups of –CH\(_2\) [12]. Identification of carboxyl (COO\(^{-}\)) and carbonyl (CO) groups was shown in wave number 1640.81 cm\(^{-1}\). The existence of wave numbers at 1409.94 cm\(^{-1}\) and 1090.12 cm\(^{-1}\) was stretching vibrations from N-H and CN amines. This approach the wave number identified in L-lysine with each wave number of 1414 cm\(^{-1}\) and 1140 cm\(^{-1}\) [13].

Modification of silica gel was related to changes in the active site on the surface which was to change the silanol group into another functional group. Modification of rice husk silica using L-lysine through silane reagent produced a new peak at wave numbers 2361.60 cm\(^{-1}\) and 694.83 cm\(^{-1}\). The formation of a new peak with wave numbers 2361.60 cm\(^{-1}\) and 694.83 cm\(^{-1}\) was respectively thought to originate from the vibration shift of monohydrate (H-Si-Si-H) and siloxane (Si-O-Si) stretches of silica due to modification using acid amino L-lysine. Changes in the characteristics of the silica gel surface through functional group modification is one of the modification functions with chemical treatment [16] In this study modification using the sol-gel method was carried out through the process of immobilizing silane reagents.

3.3. Characterization of rice husk silica (SSP) and L-lysine modified silica (SLL) function group
Capacity determination was carried out to determine the effect of the initial concentration of metal ions on the number of metal ions which were adsorbed by the adsorbent at optimum conditions and the interaction that occurred between the adsorbent and the adsorbate carried
out at a constant temperature. Determination of adsorption capacity and adsorption isotherm was carried out at pH 2, weight of 10 mg and contact time of 30 minutes [10] and various initial concentrations of 5-40 mg/L. This experiment was carried out at room temperature and obtained the maximum adsorption capacity of each silica rice husk (SSP) and L-lysine (SLL) of 39.65 mg/g and 46.56 mg/g. The maximum percentage of adsorption obtained for each adsorbent is 58.97% and 65.3%. Increased capacity and percent adsorption of SSP and SLL can be seen in Figure 5.

![Figure 5. Adsorption capacity (a) and adsorption percent (b) rice husk silica (SSP) and L-lysine modified silica (SLL).](image)

Figure 5 showed that the greater the concentration, the adsorption capacity and percent adsorption will increase. This was because the greater the concentration of adsorbate, the greater the number of Fe(III) metal ions so that more was absorbed. In this study the adsorption capacity of Fe(III) ions in L-lysine modified silica (SLL) was greater than rice husk silica (SSP). This was because the availability of the active group (-NH2) on the surface of the L-lysine modified silica. According to the Lewis acid base theory, the active side of the SLL surface acts as an electron pair donor that can bind Fe(III) ions. The low ability of rice husk silica (SSP) compared to L-lysine modified silica (SLL) in absorbing Fe(III) metal was due to O atoms in the SSP as donors bound directly to Si in the silica structure.

The data in this study were not in accordance with Langmuir's theory which explains that on the surface of the adsorbent there was an active site which was proportional to the surface area of the adsorbent. In this study the active site of adsorbent with a high concentration of 40 mg/L has been not shown a decrease in adsorption ability, this indicates that the optimum conditions in the study of [10] that used in this study has been not provided optimum results on L-lysine modified silica. Therefore, it was necessary to get optimum condition (pH, weight and contact time) of L-lysine modified silica in absorbing Fe(III) ions.

4. Conclusion
Rice husk waste has been successfully utilized for the synthesis of rice husk silica and L-lysine modified silica. Modification of silica rice husk with L-lysine bridged by silanization reaction using APTMS was successfully formed through functional group characterization (FTIR). The adsorption capacity of each rice husk silica and L-lysine modified silica on Fe(III) ion were 39.7 mg/g and 46.6 mg/g.
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