

L-Histidine-Modified Silica from Rice Husk and Optimization of Adsorption Condition for Extractive Concentration of Pb (II)

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ABSTRACT

A new chelating agent, L-histidine-modified silica from rice husk (LHSRH), was prepared as a selective adsorbent for Pb(II). LHSRH was synthesized by immobilizing L-histidine on silica from rice husk modified with 3-aminopropyltrimethoxysilane. The LHSRH was used to adsorb Pb(II) ion. The pH range, amount of the adsorbent, and adsorption time were optimized by response surface methodology. We found the optimum condition for the adsorption of Pb(II) was at pH 5, adsorbent amount about 0.1 g, and adsorption time about 15 minutes. The adsorption capacity for Pb(II) ion was found to be 62.5 mg/g. The adsorption behavior of the matrix followed the Langmuir's model.

Key word : L-histidine, silica, rice husk, extractive concentration, Pb(II)

INTRODUCTION

Lead (Pb) is one of the most hazardous heavy metals for human health because it is non-biodegradable, could accumulate within biological systems, and toxic even at low concentration. Poisoning of Pb can cause damage to the nervous system, encephalopathy, and decrease in the IQ. Lead can also damage the kidney, liver, reproduction system, brain function, and even mortality [1-3]. A guideline for drinking water issued by the Ministry of Health, Republic of Indonesia (2010) determines that the maximum Pb level is 0.01 ppm [4]. This low permissible concentration makes a direct determination of Pb difficult and requires a sensitive method or a pre-concentration step.

The method for determination of Pb in water and wastewater, which is used as a standard by the National Standardization Agency of Indonesia, is flame atomic absorption spectrophotometry (FAAS) which employs nitric acid as the solvent. However, nitric acid not only dissolves Pb, but also other metals such as copper, cobalt, zinc, iron and these metals could interfere with the measurement of Pb. Therefore, due to the complexity of the sample matrix and frequently low concentration of Pb exist in many samples, there is a crucial need for pre-concentrating Pb ions from the matrix before FAAS analysis to increase the sensitivity.

Conventional pre-concentration method for metal ions includes liquid-liquid extraction, co-precipitation, ion exchange, filtration membrane, etc. These methods are considered uneconomical because mostly require a significant amount of organic solvent causing

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environmental problems. Nowadays, solid phase extraction (SPE) is one of attractive choice and commonly used for pre-concentration technique due to many advantages, such as easy to use, high selectivity, lower cost (requires less solvent), and less time. One of the most common extractants used in SPE is silica gel [5-7].

Silica can be extracted from various silica sources in nature, one of which is from rice husk [8-10]. Rice husk contains 17%-20% silica in a complex form [10]. Since 2007, Department of Physics, Bogor Agricultural University (IPB) has been developed a rice husk stove utilizing rice husks as fuel as an alternative source of energy. Rice husk stove combustion will produce ash as a waste [11]. From the previous research, rice husk ash (RHA) will contain about 85%-95% amorphous silica [10]. Therefore with the high silica content of RHA generated from the rice husk stove makes this material is an economically promising raw material in the production of silica [11].

Silica gel as solid support has received significant attention because it possesses some definite advantages, such as large surface area, high thermal and mechanical stability, stable under acidic condition, non-swelling, and easy to modify with other chemicals [5-7]. However, silica gel has some disadvantages too, for example, low surface selectivity and effectivity that will result in weak interaction with heavy metal ions. This weak interaction is due to the low acidity of the silanol groups (fewer donor properties) resulting in adsorption that is not selective for a specific metal ion, such as Pb ion.

To solve this problem, addition of active groups to modify the silica surfaces to make silica more selective in binding the Pb ions is needed. So far, various modifications have been done to enhance the adsorption capacity and selectivity of silica gel, such as immobilization of organic ligands (organofunctionalization) having donor atoms (O, N, S, P) like amino acid [12]. The existence of donor atoms in amino acid side chains like an imidazole group in histidine, a thiol group in cysteine, and an indolyl group in tryptophan, can bind metals and have been demonstrated to work in the human body. For example, histidine in superoxide dismutase, where the nitrogens of the imidazole group bind two metal ions, i.e., Zn(II) coordinated at the δ nitrogen and Cu(II) at the ϵ nitrogen [13]. Metal binding of amino acids in the human body is very interesting considering that the metal ions exist as trace element yet they can bind these metal ions. In this study, immobilization of L-histidine onto silica synthesized from rice husk is expected to produce extractant with high adsorption capacity and selectivity for Pb (II) metal ions.

EXPERIMENT

Materials and Instrumentation

Rice husk charcoal (RHC) was obtained from the Department of Physics IPB, 3-aminopropyltrimethoxysilane and glutaraldehyde (Sigma Aldrich, St Louise, USA), L-Histidine (Merck, New Jersey, USA), hydrochloric acid (HCl), sodium hydroxide (NaOH), toluene, nitrogen gas, and standard solutions of Pb, Cd, and Zn (Merck, New Jersey, USA). Flame atomic absorption spectrophotometer (FAAS) AA-6800 (Shimadzu, Kyoto, Japan) was used for the determination of metal ions. The wavelength used for measuring Pb, Cd, and Zn was at 283.3, 324.8, and 213.4 nm, respectively. pH adjustment was performed using pH meter HM-20S (TOA, Tokyo, Japan). Batch adsorption test was done using a Unitronic OR P shaker water bath (JP Selecta, Barcelona, Spain). Infrared spectra were recorded using FTIR spectrophotometer 8400S (Shimadzu, Kyoto, Japan). XRD pattern was obtained using XRD 7000 diffractometer (Shimadzu, Kyoto, Japan). Drying and ashing were carried out using an oven (Mettler, Schwabach, Germany) and furnace (Nabertherm, Lilienthal, Germany), respectively.

Procedure

Rice Husk Charcoal (RHC) Ashing Process

The RHC were cleaned from dirt, soaked in hot water for 2 h, and then dried in an oven. The dried charcoal was sieved by using a 200-mesh sieve and ashing were performed in a furnace at 400°C for 2 h and then continued at 750°C for 4 h to produce rice husk ash (RHA) [11,14].

Preparation of Sodium silicate

Twenty grams of RHA was boiled in 150 mL of 6M HCl and stirred with a magnetic stirrer (250 rpm, 200°C for 2 h). The mixture was washed with hot distilled water to be acid-free at several times and dried in the oven. The cleaned RHA was mixed stoichiometrically with 158 mL of 4M NaOH solution then boiled with constant stirring until it was obtained the solution half of the initial volume in the hotplate. The mixture was melted in a furnace at 500°C for 30 min. Sodium silicate (Na₂SiO₃) solids were cooled to reach room temperature, after that it dissolved in 200 mL distilled water, homogenized with a magnetic stirrer, and left overnight. The solution was filtered through Whatman No.42 filter paper to obtain Na₂SiO₃ solution [8-9].

Synthesis of Silica from Rice Husk (SRH)

Na₂SiO₃ solution (20 mL) obtained from the previous step was titrated with 3M HCl solution with constant stirring until the gel was formed and then continued to age overnight. The gel was washed with hot distilled water several times to remove acid and dried in the oven at 120°C for 48 h. The pure silica powder was then characterized with FTIR and XRD [8,14].

Synthesis of 3-aminopropylsilica (APS)

An amine terminus was made on the silica surface using APTMS, a silylating agent. Two grams of activated SRH (heated at 160°C for 24 h) was mixed with 65 mL of 1% APTMS solution (in toluene) and under reflux (110°C), the mixture was agitated for 24 h. Separation of APS from the solution was performed using a centrifugation at 3000 rpm. The APS was washed three times with toluene to remove APTMS residue, after this, the APS dried at 110°C for 12 h and then characterized with FTIR [15].

Immobilization of L-histidine onto APS

APS was reacted with 50 mL of 5% glutaraldehyde in 0.01 M phosphate buffer (pH=8) under nitrogen for 90 min at room temperature. The APS-Glutaraldehyde mixture was filtered, rinsed with distilled water, and then dried in the desiccator. Glutaraldehyde serves as a linker between the amine terminus on the APS and L-histidine. Twenty milligrams of L-histidine was dissolved in 20 mL of 0.01 M phosphate buffer, pH 5.3 and then reacted with 1 g of APS-glutaraldehyde for 48 h at room temperature under nitrogen gas. The L-histidine-modified silica from rice husk (LHSRH) obtained was rinsed several times with distilled water and then filtered, dried, and characterized by FTIR [16].

Optimization of Adsorption Condition (pH, Adsorbent Weight, and Adsorption Time) Using Response Surface Methodology

Optimization of adsorption condition was performed at pH (4-8), the weight of adsorbent (0.1-0.5 g) and adsorption time (15-120 min). Response surface methodology (RSM) were used to find the optimum condition for adsorption of Pb(II). The RSM was

conducted in Minitab version 16 (Minitab, Inc., State College PA, USA).

Adsorption Capacity and Isotherm of LHSRH Using Batch Adsorption

About 0.5 g of LHSRH was mixed with 25 mL of Pb(II) solution with various concentrations (50; 100; 200; 300; and 400 ppm) in a shaker batch using the optimum condition found earlier. The remain Pb(II) ions in the solution was determined by FAAS [14,17]. Langmuir and Freundlich isotherm models was applied to find the isotherm of LHSRH.

Effect of Other Co-existing Metal Ion

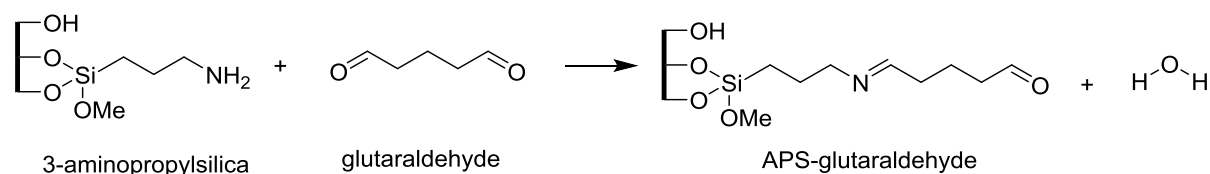
To investigate the selectivity of LHSRH in this study, about 0.5 g of LHSRH was shaken with a mixture of metal ions (Pb, Cd, and Zn) under optimum condition using a shaker batch. The mixture of metal ions were varied into three concentration proportions (1:1:1; 2:1:1; 1:2:2). Unadsorbed Pb, Cd, and Zn metal ions in the solution were determined by FAAS to evaluate the selectivity.

RESULT AND DISCUSSION

Synthesis of L-histidine Modified Silica from Rice Husk

In this study, we produced Na_2SiO_3 as a precursor for the synthesis of silica. Clean RHC was first ashed in a furnace in a gradual increase of temperature to 400°C for 2 h and continued at 750°C for 4 h to obtain a pure quality of silica [11]. To dissolve organic materials and reduce metal oxide impurities such as Fe_2O , MgO , Na_2O , K_2O , and CaO , the RHA was leached using 6M HCl [8]. Then 4M NaOH was then stoichiometrically added to the RHA. The solution was stirred and boiled until half of the initial volume to vaporize the water molecules generated in the reaction. Na_2SiO_3 in greenish white solid was produced after melting it at 500°C for 30 min [9]

Synthesis of silica was performed by titrating the Na_2SiO_3 solution with 3M HCl. Addition of HCl caused the siloxy group (Si-O-) protonated into silanol (Si-OH). Then the silanol group was attacked by siloxy group with the aid of acid catalyst to form a siloxane bond (Si-O-Si). This process occurs fast and continuously forming an amorphous silica network [12]. This stage is a crucial step before silica modification with L-histidine. Silica activation needs to be done to remove water because silica is an amorphous substance. Silylation was performed with silane reagent, 3-aminopropyltrimetoxysilane (APTMS), and conducted in a non-water environment using toluene. The mixture was refluxed for 24 h, and the resulting product then washed with toluene to dissolve unreacted APTMS. The obtained APS was reacted with glutaraldehyde in phosphate buffer (pH 8) under a nitrogen atmosphere. Glutaraldehyde is a connector for NH_2 group in APS and L-histidine [16]. Figure 1. showed the reaction scheme to produce LHSRH.



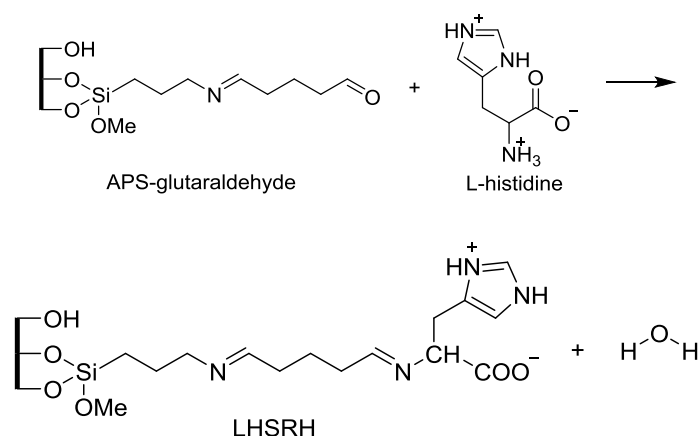


Figure 1. The reaction scheme to produce LHSRH

X-Ray Diffraction and FTIR Spectra Pattern

The silica obtained from rice husk was amorphous white powder, confirmed by X-Ray Diffraction pattern shown in Figure 2. The diffraction pattern of the SRH in Figure 2 showed a broad peak at the 2θ around $20.15 - 22.99^\circ$. The 2θ between $20-22^\circ$ with a broad peak was reported by Kalaphaty et al. [8] is amorphous silica.

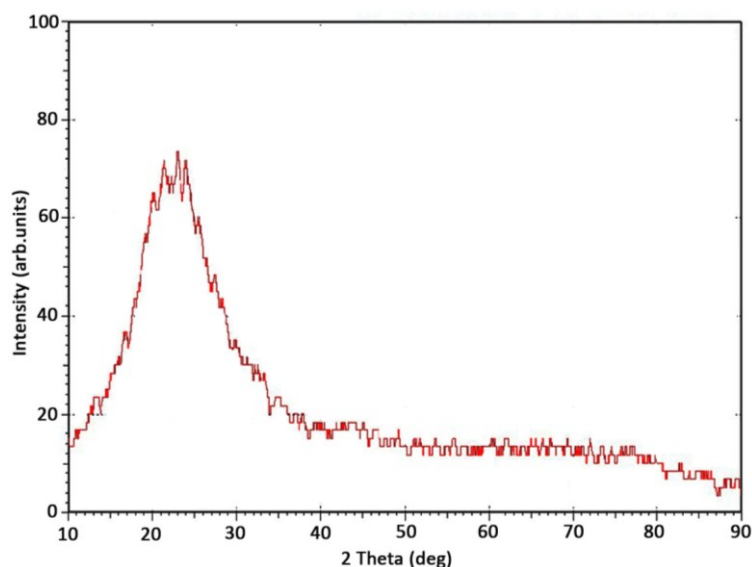


Figure 2. XRD pattern of silica from rice husk

FTIR was used to measure the spectra of SRH, APS, and LHSRH (Figure 3) to confirm the presence of specific and additionally functional groups. The absorption bands at 3448.49 and 1627.81 cm^{-1} correspond to the stretching and bending of hydroxyl groups (-OH) from silanol (Si-OH) and water, respectively. Intensive bands at $1043.42-1215.07$ cm^{-1} represent the asymmetric stretching of Si-O from siloxane group (Si-O-Si). Vibration at 956.63 cm^{-1} shows Si-O stretching from Si-O. Symmetric stretching of Si-O from Si-O-Si was reflected by vibration at 800.40 cm^{-1} . Generally, absorption bands appeared in SRH spectra demonstrated that the predominant functional groups of silica were silanols and siloxanes [17-19].

After reacting silica with APTMS in order to insert an amino group (-NH₂), the spectra of APS exhibit some new bands and band shifts compared to SRH spectra. The band at 3450 cm⁻¹ indicates that there is an overlap between the -OH group of Si-OH and -NH and -CH groups. Vibrations at 2956.67 and 1475.44 cm⁻¹ assigned as stretching and bending vibration of Si-CH₂, respectively. One of the most important sign that aminopropylsilica (APS) has been formed is the appearance of a band at 1525.59 cm⁻¹ indicating the stretching vibration of primary amine (-NH₂) [7, 15, 19].

Immobilization of L-histidine on the SRH leads to the appearance of new bands. Absorptions at 1712.67-1745.46 cm⁻¹ indicate the carboxylate group (-COO). Vibrations of cyclic C=C of imidazole group appear at 1645.17- 1677.95 cm⁻¹. There is shifts in the absorption of -NH₂ stretching at 1521.73 cm⁻¹ caused by overlapping with -C=N vibration. Bands at 1070.42-1128.28 cm⁻¹ indicate the vibration of -CO group. However, specific groups of silica and APS still appear in LHSRH spectra but the absorptions have shifted [19].

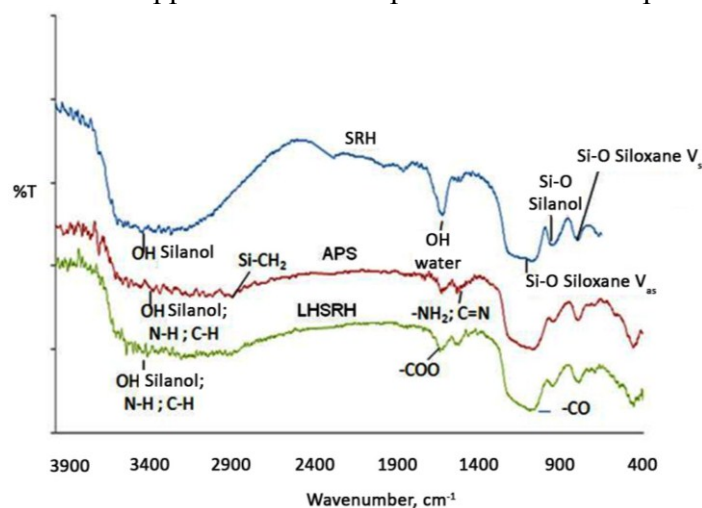


Figure 3. FTIR spectrums of silica from rice husk (SRH), aminopropylsilica (APS), and L-histidine-modified silica from rice husk (LHSRH)

Effect of pH, Adsorbent Weight, and Adsorption Time

To enhance the adsorption efficiency, RSM was used to develop a regression model to find out the optimum condition of pH, amount of adsorbent, and adsorption time. Central composite design (CCD) were successfully employed for batch experimental design. We performed the experiment with 20 runs consisted of 8 runs for full factorial, 6-star points, 6 replicates at the center point. The results showed that the adsorption efficiency of LHSRH around 87-99%. It was demonstrated that the adsorbent had a high potential to adsorb Pb(II) ions. Modification of the adsorbent with L-histidine gives more silica's active sites, namely imidazole and carboxylate groups. Determination of optimum condition by using RSM considered the relation between variables and response as can be seen in the estimated regression coefficients in Table 1. Adsorption efficiency was employed as the response to examine the effect of each variable and the interaction between them. Variables with a value of $p < 0.05$ indicate a significant effect to response. From the result showed in Table 1, the effects of pH, amount of adsorbent, and adsorption time can be explained by the empirical second order polynomial model equation: $Y = 99.25 + 1.77x_1 + 1.16x_2 - 3.02x_1x_2$, which represents adsorption efficiency of Pb(II) (Y) as a function of pH (x₁), amount of adsorbent (x₂), and adsorption time (x₃).

Table 1. Estimated regression coefficients for adsorption efficiency

Term	Coef.	SE Coef.	T	P
Constant	99.2451	0.5440	182.434	0.000
pH	1.7730	0.5004	3.543	0.005
Weight	1.6354	0.5004	3.268	0.008
Time	-0.8142	0.5004	-1.627	0.135
pH*pH	-1.4627	0.9543	-1.533	0.156
Weight*Weight	0.5752	0.9543	0.603	0.560
Time*Time	2.0376	0.9543	-2.135	0.059
pH*Weight	-3.0174	0.5595	-5.393	0.000
pH*Time	0.6828	0.5595	1.220	0.250
Weight*Time	0.5529	0.5595	0.988	0.346

*Analysis result by Minitab 16

Figure 4 showed the adsorption efficiency of LHSRH at optimum condition as the darkest green color from the contour plot. The optimum condition obtained was pH 5, weight of adsorbent 0.1 g, and adsorption time 15 minutes. At pH 4, the nitrogen of the imidazole group became partially positive and had weaker adsorption efficiency. At pH 8, the adsorption efficiency decreased due to precipitation of $Pb(OH)_2$. By using this optimum condition, we determined the adsorption capacity and isotherm adsorption of LHSRH to Pb(II) ions.

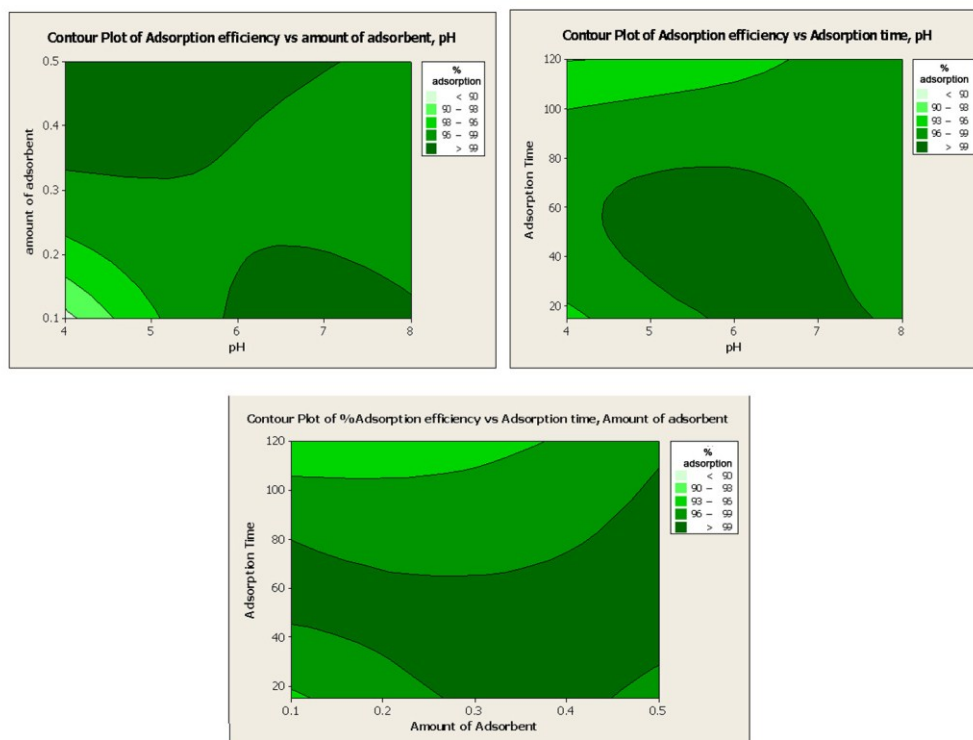


Figure 4. Contour plot of adsorption efficiency of Pb(II) by LHSRH in various pH, weight of adsorbent, and adsorption time

Adsorption Capacity and Isotherm Adsorption of LHSRH

Determination of adsorption capacity and isotherm adsorption of LHSRH were performed at the optimum condition with variation in the initial concentration of Pb(II) solution (50-400 ppm). We exclude thermodynamic factors as a parameter and measurement was conducted at room temperature. Table 2 showed the adsorption capacity and adsorption efficiency of LHSRH for each Pb(II) initial concentration. The amount of Pb(II) adsorbed per unit mass of LHSRH increases with the increase in the initial concentration of Pb(II). The initial concentration was raised until relatively stable values for adsorption capacity were obtained. There was a decrease in the adsorption capacity for concentration > 300 ppm, which is mainly due to the precipitation of Pb(II) ion into Pb(OH)^+ and Pb(OH)_2 specimens. Also, there might be the insufficiency in the availability of the adsorbent's active sites for the number of adsorbates. The adsorption capacity of LHSRH in adsorbing Pb(II) was 62.5 mg/g.

Table 2. Pb(II) concentration, adsorption efficiency, and adsorption capacity of LHSRH

[Pb(II)] (ppm)	Adsorption efficiency (%)	Adsorption capacity (mg/g)
50	98.14	8.46
100	63.68	15.12
200	91.91	48.06
300	72.52	67.08
400	51.22	59.27

The acidity of Pb(II) solution contributes to the adsorption process by LHSRH. Nitrogens on the imidazole group of histidine have a lone pair of electrons that will make coordinative bonds with Pb(II) ion (Figure 5). At pHs greater than pKa of histidine (~6.15), the pyridine nitrogens on the imidazole side chain are deprotonated so that there is no lone pair of electrons could bind Pb(II) [16]. At high acidic pH, nitrogens of imidazole are protonated. Thus they become partially positive. In this condition, LHSRH has a weaker adsorption capacity. On the other hand, the adsorption capacity at higher pH (pH=8) decreases due to the formation of Pb(OH)_2 precipitates.

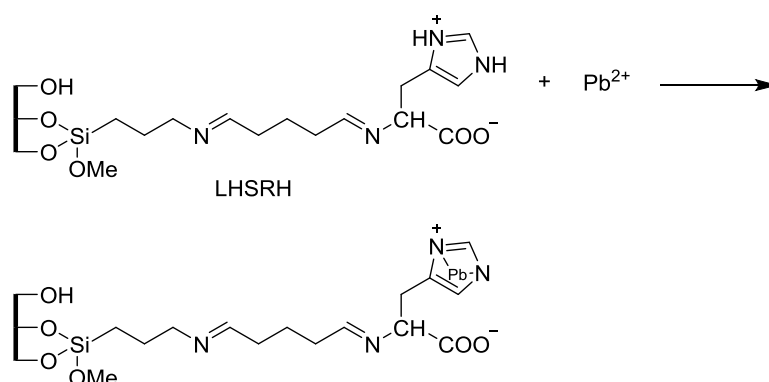


Figure 5. Adsorption Pb(II) on the LHSRH

Langmuir and Freundlich isotherm model were used to find the isotherm adsorption of LHSRH as shown in Figure 6. We found the isotherm adsorption of LHSRH followed the Langmuir model since the R^2 value is higher ($R^2=0.9955$) than using Freundlich equation ($R^2=0.9129$). Based on the result, the LHSRH adsorption process occurred in the same mechanism and formed the single layer during maximum adsorption.

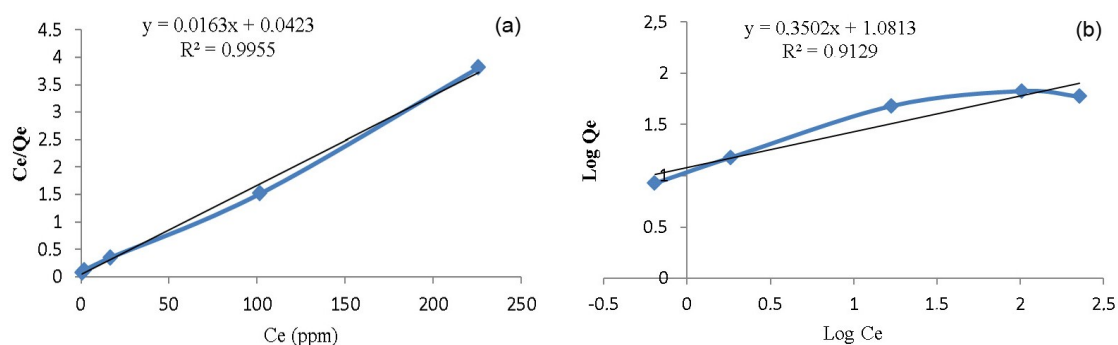


Figure 6. Isotherm adsorption model for Pb(II) by LHSRH (a) Langmuir (b) Freundlich

In order to find out the adsorption's energy, the adsorption's parameters of LHSRH to Pb (II) were also examined. From the calculation as shown in Table 3, it was found that the adsorption energy of LHSRH is -2.206 kJ/mol for Langmuir isotherm and 6.208 kJ/mol for Freundlich isotherm. Based on the energy adsorption value, it may be concluded that the type of adsorption of Pb(II) ion by LHSRH of this study is physical adsorption. Minus value (-) in Langmuir isotherm indicates that the adsorption process was spontaneous [20].

Table 3. Adsorption parameters of LHSRH

Langmuir				Freudlich				
Qm (mg/g)	b (mol/g)	K_L (mol/L)	E (Kj/mol)	R^2	n (mol/g)	Kf (mg/g)	E (Kj/mol)	R^2
62.5	0.302	3.8×10^{-11}	-19.64	0.995	0.0138	12.05	-24.33	0.912

Selectivity of LHSRH

Selectivity determination was performed to examine the selectivity of LHSRH to adsorb Pb(II) metal ion with other existing metal ions. Cadmium and zinc were used in this research with 3 comparison models as shown in Table 4. Table 4 showed the LHSRH could selectively adsorb Pb(II) ion with the existence of another ion such as Cd and Zn. The adsorption efficiency for Pb(II) was higher than Cd and Zn. Adsorption occurs through the binding of metal ions by the imidazole group in histidine. From the concept of Hard and Soft Acids and Bases (HSAB), it is indicated that the imidazole group is a borderline base as well as Pb and Zn are borderline acids while Cd is a soft acid [14], which is, therefore, Pb and Zn are more easily interacted with LHSRH compared to Cd. From the adsorption capacity results, it can be seen the following order of metal ion adsorption $Pb > Zn > Cd$.

Table 4. Selectivity of LHSRH in adsorbing Pb(II)

Metal Proportion	Metal	Adsorption Efficiency
(1:1:1)	Pb	55.413
	Cd	16.730
	Zn	55.581
(2:1:1)	Pb	99.853
	Cd	28.394
	Zn	57.583
(1:2:2)	Pb	99.816
	Cd	52.400
	Zn	33.619

CONCLUSION

Silica can be synthesized from rice husk. Immobilization of L-histidine adds more active sites to rice husk silica and gives higher adsorption efficiency of Pb(II) ion as well as the adsorption capacity. At optimum condition (pH 5; the weight of adsorbent 0.1 gram; and adsorption time 15 min), L-histidine-modified silica from rice husk is capable of adsorbing Pb(II) selectively in the existence of Zn and Cd. It is expected that the L-histidine-modified silica from rice husk could be developed as a Pb(II) ion extractant.

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