ALCHEMY Jurnal Penelitian Kimia
Laman resmi: https://jurnal.uns.ac.id/alchemy
ISSN 1412-4092
EISSN 2443-4183

Isolation of Silica-Lignin Composites from Rice Husk and Their Adsorption to Cr(VI)

Yati B. Yuliyati*, Seli Listiani, Solihudin Solihudin, Atiek Rostika Noviyanti

Department of Chemistry, University of Padjadjaran Jl. Raya Bandung-Sumedang Km. 21 Jatinangor, Sumedang, West Java Indonesia telp/fax: +62 227794391

** Corresponding author*

E-mail: yati.b.yuliyati@unpad.ac.id

DOI: 10.20961/alchemy.14.2.19818.267-276

Received 26 March 2018, Accepted 03 August 2018, Published Online 03 September 2018

ABSTRACT

Rice husk is the most abundant agricultural waste in Indonesia. It can be used as a precursor for multifunctional materials such as silica-lignin composite for adsorbents. Silica-lignin can reduce heavy metal content in an industrial waste, such as the content of Cr(VI). This study aims to isolate and characterize silica-lignin composite, and determines the isotherm type of silica-lignin for hexavalent chromium adsorption. The isolation from rice husk used an alkali extraction method. Confirmation of typical functional groups in the silica-lignin composite was characterized by FTIR, while the morphology was characterized by SEM, respectively. The results reveal that the silica-lignin isolation was successfully performed. FTIR spectra indicate a typical wavenumber of the silica-lignin. The SEM image of the composite showed homogeneous morphology. The silica-lignin adsorption process on hexavalent chromium followed a Brunauer–Emmett–Teller (BET) isotherm type indicated by multilayer adsorption with a surface area of 948.8421 mg. g^{-1}.

Keywords: alkali extraction, BET, rice husk, silica-lignin,

INTRODUCTION

Heavy metal waste is a serious problem due to its harmful effects on humans and animals. Some heavy metals are toxic, such as Cr(VI). Chromium is mostly found in the environment, in various valences, including bivalent, trivalent and hexavalent. Chromium is a heavy metal with a density of 7.19 g/cm^3 at 20 °C. Chromium is hard and shiny, and is typically applied as a coating for another metal because of its high melting point (1875 °C) and boiling point (2658 °C). For this reason, Cr is frequently used in various industries such as plastic, pigment, wood preservation, electricity layering, skin tanning, cement, mining, dye and manure. The tanning industry contributes the most chromium waste in the environment, including land and water (Sivakumar, 2015).

Many approaches have been applied to handle heavy metal waste in water environments, including adsorption (Guo *et al.*, 2008; Kravchenko *et al.*, 2009), chemical precipitation (Kravchenko *et al.*, 2009), ion switching (Dbrowski *et al.*, 2004), membrane filtration (Borbely and Nagy, 2009), flocculation (Bratskaya *et al.*, 2009), and soluble extraction (Donegan, 2006). Adsorption has several key advantages, and is considered as among the most effective and economical methods available. Natural products such as silica and lignin were reported as adsorbents (Qiu *et al.*, 2009; Wu *et al.*, 2008). Many studies have reported isolation of silica and lignin separately from rice husk ash, but no one has ever isolated the natural composite of silica and lignin simultaneously.

Silica-lignin can be applied as a heavy metal adsorbent for Ni (II) and Cd (II) (Klapiszewski *et al.*, 2015). Silica-lignin can be isolated from rice husk through a sol-gel process by using sodium hydroxide, because it contains 19.8% lignin and 18.7% silica. It is mesoporous, with a 60 nm diameter, and is 471.7 m^2/g higher in surface area compared to silica (Qu *et al.*, 2010). Many studies have reported isolation of silica and lignin separately from rice husk ash, however a report on simultaneous isolation of silica-lignin is not existed.

This research investigates and reports the isolation of silica-lignin composite from rice husks by using potassium carbonate in various conditions. Adsorption of Cr(VI) on silica-lignin includes equilibrium adsorption, kinetic adsorption and factors that influence adsorption of Cr(VI) on lignin such as influence of pH, adsorbent dosage, initial Cr(VI) concentration and determining the type of adsorbent also reported.

EXPERIMENTAL SECTION

Rice husks, HNO_3 (Merck), H_2SO_4 (Merck), diphenilcarbazide (Merck), Potassium dichromate (Merck) and potassium carbonate. FT-IR (PerkinElmer *Spectrum 100*), UV-Vis (Genesys 10 S) and SEM-EDX (MC1000 ion sputter Hitachi).

Isolation and characterization of Silica-Lignin

Silica-lignin composite was isolated in various mass ratios of rice husk and potassium carbonate solution (1:1; 1:2; 1:2,5; 1:3). The mixture was heated to 150 °C for 4 hours, while stirred continuously. Precipitate was filtered from the supernatant while the mixture was hot. The filtrate was reheated to 90 °C, then dripped with sulfuric acid, drop by drop, while continuously stirring until a certain pH was reached (2, 3 and 4; 3 variations of filtrate pH). They were then allowed to cool down to room temperature for 12 hours, for the establishment of sol. The established sol was then centrifuged. In order to obtain silica-lignin composite, precipitation was washed with distilled water until neutralized, and then dried at 100 ^{o}C for 12 hours. The content of lignin, cellulose and hemicellulose was carried out by the Chesson method. A silica-lignin sample, with 150 mL distilled water, was then heated to 90-100 °C for 1 hour. The mixture was filtered, and the residue was washed with hot distilled water. The residue was dried in an oven until it had a constant weight, and then mixed with 150 mL 1 N H_2SO_4, and heated to 90-100 °C for 1 hour. The mixture was then filtered and washed with distilled water, before being dried again. Dried residue was soaked with 10 mL H_2SO_4 72% at room temperature for 4 hours. After that, 150 mL 1 N H_2SO_4 was added to the mixture and heated for 1 hour. The mixture was filtered and washed with distilled water, and the residue was heated in an oven at 105 °C, before being weighed until a constant weight is obtained. Finally, precipitate was heated until it changed to ashes, and then weighed to obtain silica-lignin. The isolated silica-lignin composite was then analyzed by using FTIR, SEM and EDX.

Adsorption of Cr(VI) using the adsorbent

The determination of the silica-lignin composite with adsorption and the largest surface area is required before being used for Cr (VI) metal adsorption test, using the equation (1):

$$LPS = \frac{Xm \times N \times A}{M_{MB}} \quad (1)$$

where,

LPS: specific surface area (m^2 / g)

Xm : adsorption (mg /g)

N : Avogadro number ($6,023 \times 10^{23}$/mol)

A : cross-sectional area of Methylene Blue (1.3 × 10-16 m2)

M_{mb}: molecular weight of Methylene Blue (319.86 g / mol)

When a specific surface area is known, then the type of adsorbent, diameter and pore volume can be estimated.

Chromium (VI) in various concentrations (0,1; 0,25; 0,5; 0,75; 1; 1,5; and 2 ppm) was prepared from the solutions, and then placed in conical flasks, and the silica-lignin composite absorbent was added to the model solution respectively. In order to obtain a homogeneous mixture, the solution was mixed with the adsorbent using a magnetic stirrer. The mixture was left for 30 minutes, and then filtered with the addition of HNO_3 until it reached a pH of 2. Diphenyl carbazide was then added for the adsorption experiment, and the Cr (VI) was determined using a UV spectrophotometer. The adsorbed Cr (VI) concentration was calculated by subtracting the initial and final concentrations.

RESULTS AND DISCUSSION

Isolation of silica-lignin

The silica-lignin content were prepared in a variation of potassium carbonate and pH, which are shown in Figure 1. Isolated of silica-lignin content were tested by the Chesson method (Datta, 1981) (see Figure 1).

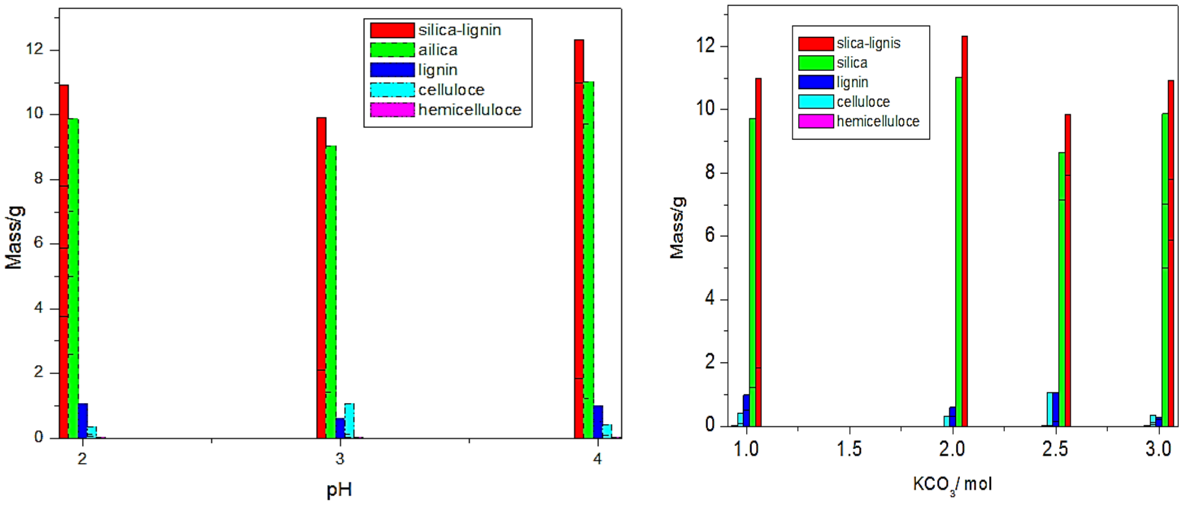

Figure 1. Content of Silica-lignin, silica, lignin cellulose and hemicellulose, isolated at various of pH levels and K_2CO_3 mole portions.

The largest silica-lignin content was obtained at pH 4 and 2 mole K_2CO_3 content. The pH and K_2CO_3 greatly affect the silica-lignin isolation from rice husks.

Characterization

The FTIR spectra of the samples are presented in Figure 2.

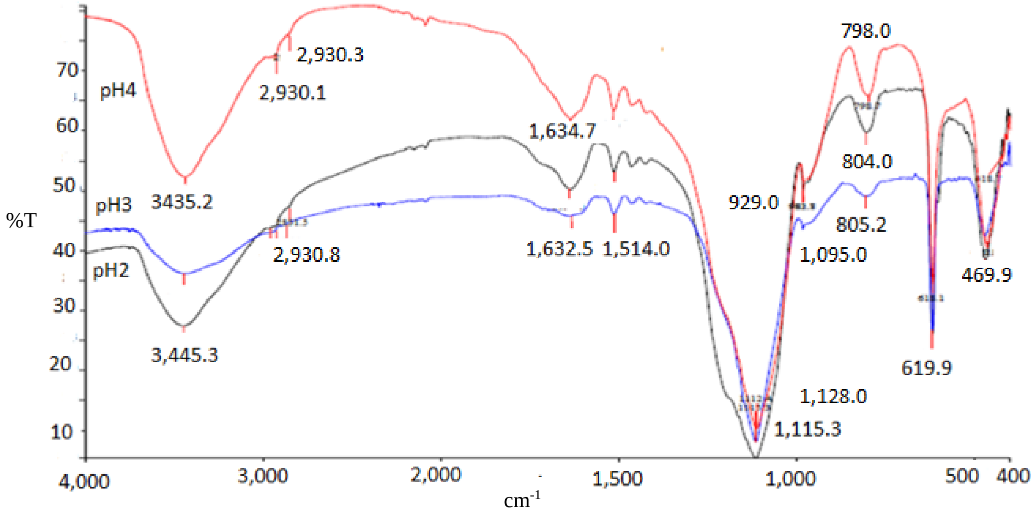

Figure 2. FTIR spectra of silica-lignin ware prepared at pH (a) 2, (b) 3 and (c) 4.

The absorption bands were ascribed O-H (3,435.2 cm^{-1}, and 3,445.3 cm^{-1} respectively), C-H of methyl and methylene (2,930.1 cm^{-1} and 2,930.8 cm^{-1}), C = C of alkene (1,632.5 cm^{-1}, 1,634.7 cm^{-1}, and 1,638.0 cm^{-1}), C = O and Si-OH (1,630.0 cm^{-1}), C-O group (1,115.3 cm^{-1} and 1,128.0 cm^{-1}), Si-O-Si (1,095 cm^{-1}), Si-OH (929.0 cm^{-1}), and benzene (798.0 cm^{-1}, 804.0 cm^{-1}, and 805.2 cm^{-1}). These functional groups are constituents of silica and lignin, and it is strongly suspected that silica-lignin composite are contained in the isolation product.

The SEM and EDAX characterization of silica-lignin prepared from rice husk and potassium carbonate and distilled water at a ratio of 1: 1:150 at pH 2, 3, and 4 is shown in Figure 3.

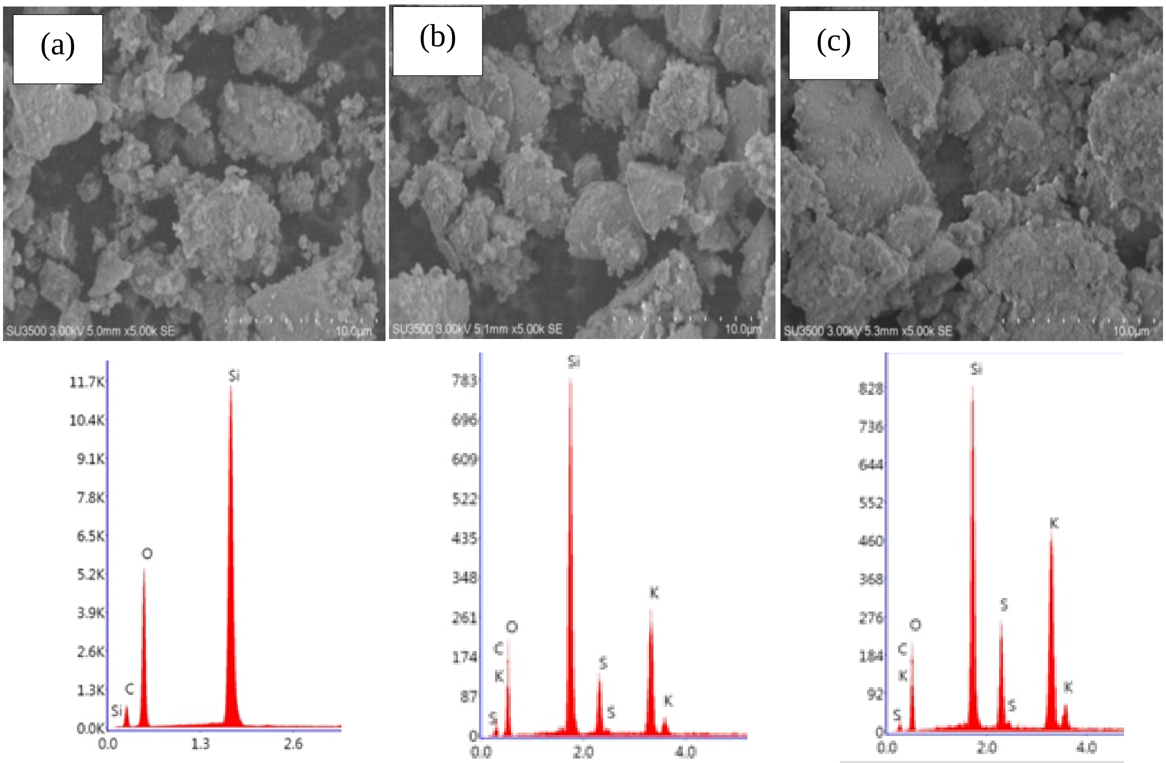

Figure 3. Micrograph SEM and EDAX analysis of silica-lignin prepared at a pH of (a) 2, (b) 3 and (c) 4.

The differences of pH in the silica-lignin isolation slightly cause differences in particle size and morphology. This difference is due to the differences in the silica-lignin composition (Figure 1). Usually, the silica surface is a porous grain that can form clusters of relatively similar size, whereas lignin tends to be non-porous (Hermiati *et al*., 2017). In silica-lignin composites, silica acts as a host and lignin as a filler (Klapiszewski *et al*., 2015). In addition, the differences may be caused by the presence of different elements (confirmed by EDAX) in each isolation with different treatments (pH and potassium carbonate concentration).

The EDAX result shows that the preparation of silica-lignin isolation with pH 2 has higher purity than the other result, in which the other result contains K and S supposedly derived from solvents in the isolation process, i.e., K from K_2CO_3, and S from H_2SO_4.

The absorption silica-lignin test on methylene blue uptake is shown in Table 1. The specific surface area is calculated by using the following equation (2):

$$S = \frac{Qe \times Av \times A_{MB}}{W \times 10^{20}} \qquad (2)$$

where S = specific surface area, m^2g^{-1}; Qe = amount of methylene blue (MB) adsorbed, mg. g^{-1}; W = molecular weight MB, mg/mole; AV = Avogadro’s number (6.02×10^{23} per mole); and AMB = area covered by one molecule of MB (130 Ǻ^2) (Ahiduzzaman and Sadrul, 2016). It can be seen that the adsorbent had a wide working pH range. For a pH of 2, the methylene blue uptake was almost higher than other any other condition. The results indicate that methylene blue adsorption by silica-lignin was highly pH-dependent. This test can measure the size of the specific surface area, and then predict the diameter of the pores. The highest specific surface area was obtained at a pH of 2 when the ratio of silica: potassium carbonate: distilled water was (1: 1: 150).

Table 1. The adsorption of silica-lignin in methylene blue and its specific surface area.

Mass ratio of Silica:lignin:water and pH	Absorption of methylene blue/ mg.g^{-1}	Specific surface area/m^2.g^{-1}
(1 : 1 : 150) pH 2	3.8761	948.8421
(1 : 2 : 150) pH 3	2.6534	649.5215
(1 : 3 : 150) pH 4	3.4197	837.1234

The silica-lignin absorption capacity of methylene blue is relatively small, indicating the size of the silica-lignin particle is smaller than the methylene blue, it can be ascertained that absorption only occurs on the surface.

Adsorption of Cr(III)

The time required to reach saturated adsorption is of great importance for evaluating the affinity of the adsorbent to the Cr(VI) ions. Therefore, the effect of stirring time on the adsorption at room temperature was investigated (Figure 4). It is shown that the optimum contact time of Cr(VI) with silica-lignin adsorbent was 30 minutes, and the adsorption capacity was 0.1459 mg/g, which then decreased. This indicates that a duration of 30 min was sufficient for adsorption of Cr(VI) using this adsorbent.

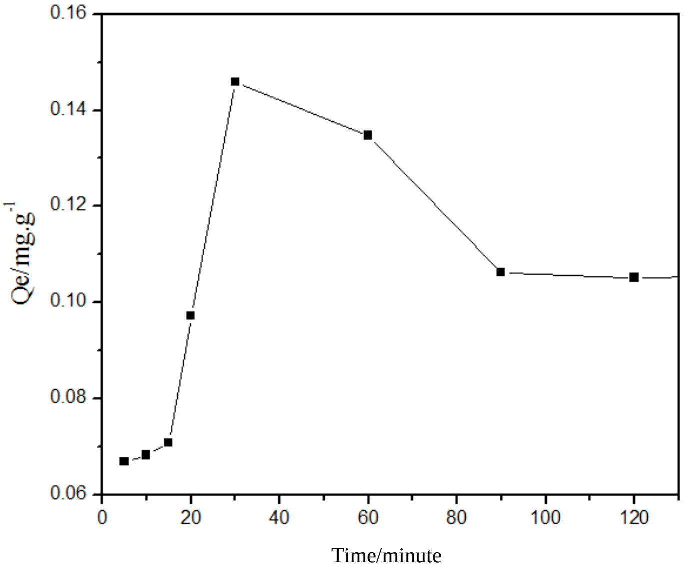

Figure 4. Adsorption capacity of silica-lignin versus variation time of adsorption of Cr (VI), a duration of 30 min was optimal time for adsorption.

The equilibrium relationship between the concentration of the adsorbent in the solid phase and the concentration of adsorbent in the liquid phase showed the adsorption isotherm type. The linear relation coefficient R^2 was also calculated. The high value of R^2 (0.9456) indicates the applicability of the BET isotherms model for the adsorption of Cr (III) by the adsorbent prepared in this work (Figure 5). It is also supported by the graphic shown in Figure 5, it appears that there is some saturation of adsorption (multilayer absorption), which is characteristic of BET.

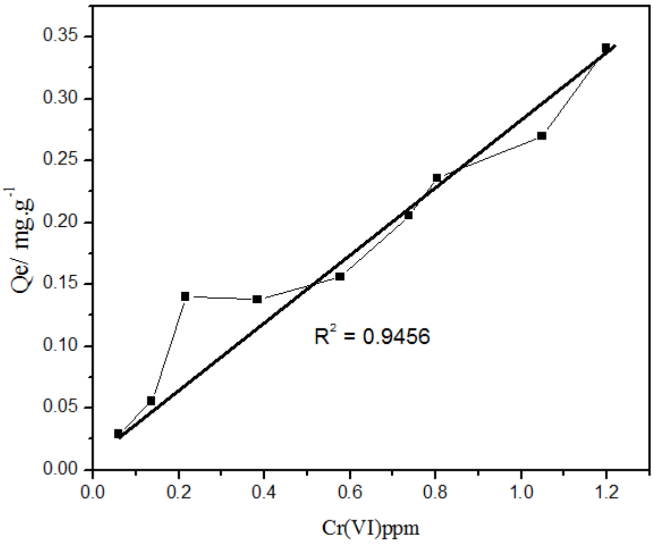

Figure 5. Multilayer adsorption of Cr(VI) by silica-lignin composites.

CONCLUSIONS

The degree of acidity (pH) and potassium carbonate concentration affects the silica-lignin ratio. This difference affects the composite morphology resulting in a consequence of the difference in absorption capacity to Cr (VI) and its specific surface area. The silica-lignin adsorption is a BET isotherm, indicated by multilayer absorption, with an adsorption capacity of 0.1459 mg/g.

ACKNOWLEDGEMENTS

The authors are grateful to Universitas Padjadjaran for research Grant of HIU 2017 no. 872/UN6.3.1/LT/2017.

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