

Silica-Rice Husk as Adsorbent of Cr (VI) Ions Prepared through Sol-Gel Method

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Abstrak

Salah satu logam berat yang terkandung dalam limbah cair industri tekstil adalah kromium (Cr). Ion kromium heksavalen (Cr^{6+}) bersifat sangat toksik dan penumpukannya di dalam tubuh manusia akan menimbulkan berbagai dampak negatif. Penelitian ini bertujuan untuk mengetahui karakteristik silika hasil sintesis dengan metode sol-gel untuk memperoleh homogenitas dan kemurnian tinggi. Sintesis silika dikalsinasi pada $700^{\circ}C$ selama 4 jam, kemudian diinvestigasi performanya dalam mengadsorpsi ion Cr^{6+} dalam air limbah tekstil. Adanya gugus -OH dari silanol (-Si-OH) terlihat pada bilangan gelombang $3367,70\text{ cm}^{-1}$, sedangkan gugus fungsi siloksan tercatat pada $1056,99\text{ cm}^{-1}$ dan $784,38\text{ cm}^{-1}$ akibat peregangan asimetris O-Si-O dan vibrasi regangan Si-O. Kondisi optimum silika untuk menyerap ion Cr^{6+} terjadi pada pH 2 dengan waktu kontak 90 menit dengan efisiensi penyerapan sebesar 75,65% dan mengikuti isotherm Freundlich.

Kata kunci: ion Cromium heksavalen; sekam padi; metode sol-gel; silika; limbah cair industri tekstil rumahan

Abstract

One of the heavy metals contained in the textile industry wastewater is chromium (Cr). Chromium hexavalent ions (Cr^{6+}) are highly toxic and its accumulation in the human body will cause various negative impacts. This study aimed to determine the characteristics of silica synthesized by the sol-gel method to gain homogeneity and high purity. Synthesized silica was calcined at $700^{\circ}C$ for 4 hours and its performance to adsorb Cr(VI) ions in textile wastewater was investigated. The presence of -OH group from silanol (-Si-OH) was appeared at wavenumber 3367.70 cm^{-1} , meanwhile siloxane functional groups were recorded at 1056.99 cm^{-1} and 784.38 cm^{-1} due to the O-Si-O asymmetric stretching and Si-O bending vibration. Optimum conditions of silica to adsorb Cr(VI) ions took place at pH 2 and contact time of 90 minutes by adsorption efficiency of 75,65% and followed the Freundlich isotherm.

Keywords: Chromium hexavalent ions; rice husk; sol-gel method; silica; textile home industrial wastewater

Introduction

The textile home industries not only have positive impact, but also give a negative impact in the form of increasing the frequency and quantity of industrial wastewater. Industrial wastewater is by product of coloring process used synthetic dyes. The use of synthetic dyes produced hazardous materials such as heavy metal ions.

One of the heavy metals contained in the textile industry wastewater is chromium (Cr) ions (Yadav, Jain and Malik, 2014). The chromium is widely used in the dyeing process, both as a color pigment and as a mordant or color binder (Fitria, 2015). Chromium is a very toxic heavy metal. This toxicity was determined by its oxidation number, where chromium in the oxidation state of 6+ (hexavalent) has higher toxicity than chromium 3+ (trivalent).

Hexavalent chromium ions contaminated in environment could harm organisms that lived in by inhalation of air or by ingesting contaminated drinking water. Hexavalent chromium ion is a strong carcinogen, there are many mechanisms by which chromium exposure causes cell damage and adverse health effects when accumulated directly or indirectly into the body of an organism (DesMarais and Costa, 2019).

Accumulation continued when organisms entered the human food chain. At high levels of Chromium(VI) ions accumulation could cause various health problems, such as respiratory inflammation, kidney and liver damage, lung cancer, etc. Therefore, an effort is needed to overcome the pollution of textile industrial wastewater containing Chromium(VI) ions.

Various methods have been carried out to overcome or reduce water pollution due to the presence of Chromium(VI) ions, one of them was adsorption method. Adsorption method was relatively simple process, more economical and environmentally friendly (did not produce a by-product in the form of

hazardous substances), so that widely used to reduce metal ion contamination. Adsorption process was influenced by the type of adsorbent used. One of the capable adsorbents to adsorb Cr(VI) ions is silica from rice husk. Silica has an active site in the adsorption process, catalysis, etc. To determine the properties of the adsorbent of silica can be observed from the preparation method (Nagaraju *et al.*, 2002). We focused on the preparation of silica through the sol gel method. According to de Lima, et al reported that silica from rice husk ash was synthesized using this method gained a high degree of purity and homogeneity (Lima *et al.*, 2011).

Rice husk contains 87-97% of silica (Umah, Prasetyo and Barroroh, 2012). The high silica content in rice husk ash was potential to be used as an adsorbent, because silica has an OH- functional group of silanol (Si-OH) bonds that could interact with metal ions. Performance of this adsorbent to Chromium(VI) ions had been investigated.

In this study, rice husk was calcined at 700°C for 4 hours. In addition, the presence of OH-functional group of silanol (Si-OH) bonds and other functional groups was characterized using FTIR spectrophotometer. The synthesized silica adsorbent applied to reduce Cr(VI) ions in textile home industrial wastewater. Adsorption of Cr(VI) ions was observed under different experimental conditions namely pH, contact time and adsorbate concentration. The research data obtained were then analyzed using the Langmuir and Freundlich adsorption isotherm models.

Experimental Section

Materials and Instruments

The materials used in this study were Ciharang rice husks collected from the village of Mulya Jaya, Lalan sub-district, Musi Banyuasin, while sample of textile industry wastewater collected from the Jumputan fabric craft center in Kertapati,

Palembang, South Sumatera. Potassium dichromate ($K_2Cr_2O_7$) was purchased from Merck Chemicals. All reagents and solvent are analytical grade.

The instruments used to confirm the silica adsorbent and to determine the adsorption capacity were Fourier Transform Infrared (FTIR) Bruker ALPHA II and Atomic Absorption Spectrometer (AAS) iCE 3000 Series, respectively.

Procedure

Synthesis of silica from rice husk.

Rice husk was calcined in a muffle furnace at 700 °C for 4 hours, then added to 1 M HCl (1:1 w/v) and stirred for 30 minutes. The 50 grams of rice husk ash was mixed with 1 M NaOH (60 mL/10 grams of silica) for 60 minutes, then filtered and washed with 100 mL of hot water. After aging for 18 hours, gel subsequently dried at 80 °C for 2 hours. Obtained silica was mashed using 200 mesh sieve to obtain silica with uniform particle size, then characterized using Bruker FTIR Spectrometer ALPHA II.

Determination of pH and contact time optimum. The 5 ppm chromium solution was prepared in five beakers and subsequently adjusted respectively at pH 2, 4, 6, 8, 10 by dropping a solution of HCl or NaOH. Then 0.5 grams of silica put into each beaker and stirred for 60 minutes. Then the filtrate was analyzed using Atomic Absorption Spectrometer (AAS) iCE 3000 Series. The highest adsorption capacity obtained as used to determine the contact time optimum.

Silica of 0.5 grams added into 5 ppm chromium solution at the optimum pH obtained, then each solution was stirring respectively for 30, 60, 90, and 120 minutes. Adsorption capacity was determined.

Determination of adsorption isotherms. Adsorption isotherms was determined in pH and contact time optimum with variations of concentration at

5, 10, 15, 20, and 25 ppm respectively. Adsorption capacity was determined using Eq 1.

$$Q = \frac{C_0 - C_e}{W} \times V \quad (1)$$

Applications in the textile home industrial wastewater.

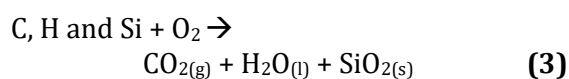
Wastewater samples were obtained from the *Songket* and *Jumputan* textile home industry located in the Kertapati, Palembang, South Sumatera. The procedures used refer to Indonesian National Standard (SNI) No. 6989.59: 2008 about sampling water and wastewater (BSN, 2008). Concentration of Cr(VI) ions in sample was determined at following conditions such as the acidity was adjusted at the optimum pH and then contacted with 0.5 grams of silica during the optimum time.

The efficiency of adsorption was calculated using Eq 2 (Sethy and Sahoo, 2019).

$$E (\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

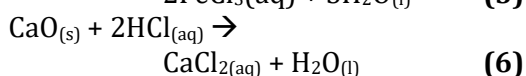
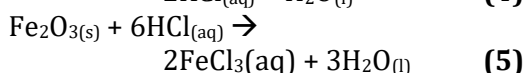
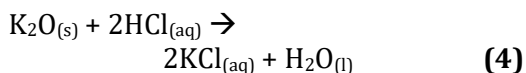
Results and Discussion

Synthesis of silica from rice husk. The agriculture waste such as rice husk ash had organic compounds and several extraneous components (trace amount metal ions)(Le, Thuc and Thuc, 2013). Decomposition reaction occurred in burning process of rice husks as shown in Eq 3 (Yusmaniar *et al.*, 2017).



Conventionally, silica powder was obtained by following acid precipitation method or using high energy inputs to the decomposition of rice husk ash (Yuvakkumar *et al.*, 2014). Hence, in this study a new development method was adopted to produce silica powder using decomposition of rice husk ash through the

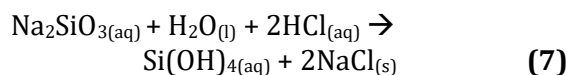
sol-gel route. The rice husk ash was pretreated with thermal and hydrochloric acid which was efficient to decompose of organic compounds such as cellulose, hemicellulose, and lignin, and almost reduction in trace of metal (K_2O , Fe_2O_3 , and CaO) as shown in **Eq 4**, **5**, and **6** which were soluble in water (Pratomo, Wardhani and Purwonugroho, 2013).



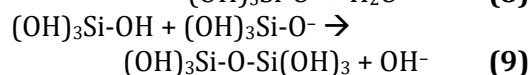
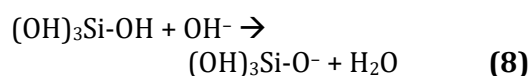
Another purpose behind thermal treatment was to get purity silica over $700^\circ C$. Previous study reported that calcination at $700^\circ C$ produced an amorphous silica through sol-gel method (S Wardiyati, W A Adi and Deswita, 2017), but in higher temperature over $800^\circ C$ obtained silica crystal other than amorphous silica (Bie *et al.*, 2015). Silica in crystalline structures more difficult to react because the structure was very stable. This condition was unfavorable to the reaction that confirmed by its performance to adsorb hexavalent chromium ions in waste water.

Silica in rice husk ash was converted into a solution of sodium silicate (Na_2SiO_3) by adding NaOH solution. Then sodium silicate used as a precursor for silica gel preparation. In principle, the route for obtaining silica gel was identical to the gelation process using inorganic acids or thermal treatment over boiling point of water. By using hydrochloric acid as gelation agent, the overall reaction could be

represented in **Eq 7** (S Wardiyati, W A Adi and Deswita, 2017). Formation gel at pH 7 was relatively faster because the covalent bond of Si-O-Si played a role in the formation of gel structure.



The addition of dropwise hydrochloric acid to reach pH 7 polymerized to form siloxane (Si-O-Si), the overall reaction may occurred through the following reactions (**Eq 8** and **Eq 9**) (Liou and Yang, 2011).



The OH ions played an important adsorptions role. The gel formation conditions were too sensitive in gelation pH rather than aging time due to porosity shape of the adsorbent (silica).

Free silicic acid was easily polymerized to form dimers, trimers and subsequently to form silicate acid polymers which then combined to form spheres of particles (primary silica particles) (S Wardiyati, W A Adi and Deswita, 2017). This polymerization continued until the solution thickens to form a soft gel. Sholika *et al.* stated that silanol groups from primary silica particles which were close to each other experienced condensation accompanied by the release of water molecules to form secondary particles with a relatively larger size than primary silica particles (Sholikha *et al.*, 2010).

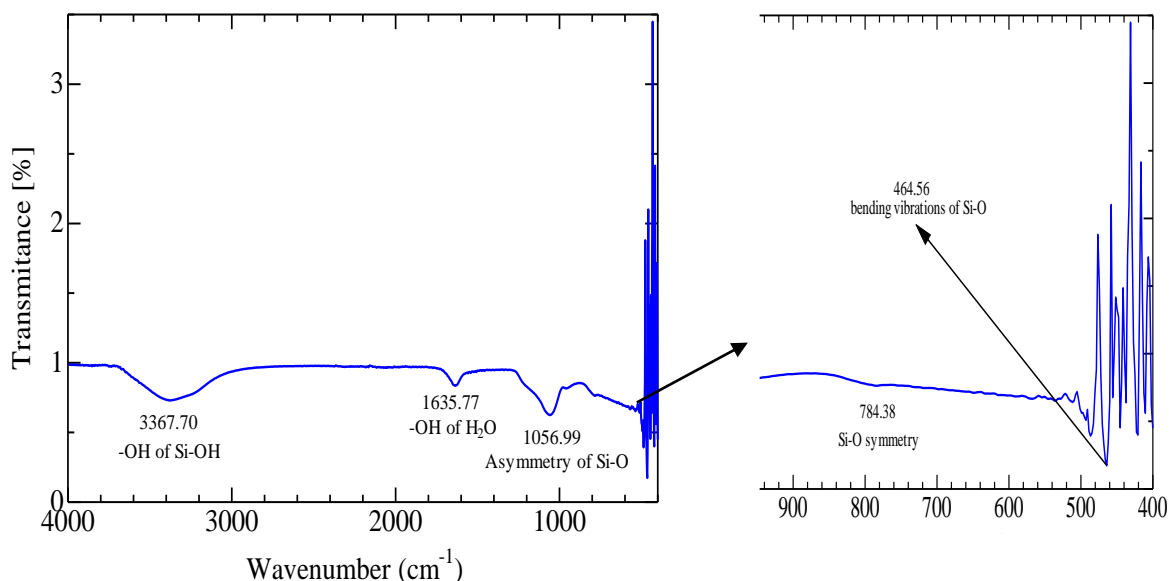


Figure 1 . FTIR spectra of silica

The infrared spectra of silica can be seen in Figure 1. As shown in Figure 1, there was spectra observed 3367.70 cm^{-1} . The characteristics of spectra were width and broad. This spectra indicates the presence of -OH group from silanol (-Si-OH) that observed in the range of wave numbers $3670\text{-}3000\text{ cm}^{-1}$ (Ananthi, Geetha and Ramesh, 2016). A similar width absorption also appeared at wave number 1635.77 cm^{-1} which showed the bending vibrations of the -OH group of water molecules.

The main absorbance peak appeared at the wavenumber $1200\text{-}1050\text{ cm}^{-1}$ was associated with the asymmetrical stretching vibration of the Si-O group from siloxane (Si-O-Si) (Ananthi, Geetha and Ramesh, 2016). The presence of silica was proved by appearing typical adsorption at wavenumbers 1056.99 cm^{-1} and 784.38 cm^{-1} due to the O-Si-O asymmetric stretching and Si-O bending vibration modes (Athinarayanan *et al.*, 2015) and symmetrical stretching vibrations of the Si-O group from siloxane. The peak in the adsorption region 464.56 cm^{-1} showed the bending vibrations of the Si-O group from

siloxane. These of spectra proved that Si (OH)₄ had been polymerized.

There were no characteristic adsorption peaks at wave numbers of 2800 cm^{-1} to 3000 cm^{-1} , indicating that the organic compounds previously contained in rice husk ash were completely decomposed after calcination and extraction.

Determination of pH and contact time optimum. Adsorption capacity of each solution at pH 2, 4, 6, 8, 10 shown in Figure 2 that had a downward trend. In Figure 2 showed that the higher the pH, more decrease the adsorption capacity.

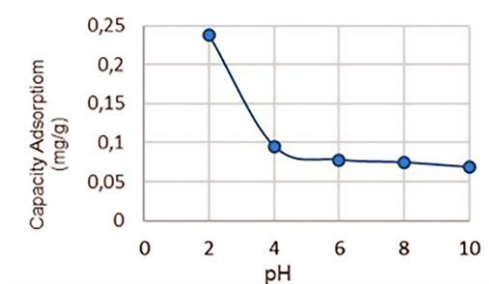


Figure 2. Effect of pH on adsorption of Cr (VI) metals

The optimum conditions were obtained at pH 2 with capacity adsorption of 0.23741 mg/g and an adsorption efficiency of 45.50% .

Silica acted as a Lewis base in this environment due to the ability to give up its electron pairs. Therefore, at low pH, the surface of the adsorbent was in positively charged because it was surrounded by H^+ ions. This causes an electrostatic force between the Cr^{6+} metal ion and the surface of the adsorbent so that the adsorption capacity decreased.

According to Nurhasni et al., at neutral pH the adsorption ability also decreased because metal ions undergo hydrolysis reaction in solution so that it was unstable in ionic form and decreased adsorption efficiency. Under alkaline conditions, metal ions tend to form hydroxide deposits which could cover the surface of the adsorbent, causing the

adsorption capacity to decrease (Nurhasni, Hendrawati and Sanniyah, 2014).

Contact time for silica and Cr^{6+} metal ions to reach adsorption equilibrium had been investigated. Determination of optimum contact time was done in variations of 30, 60, 90, and 120 minutes. The metal solution with a concentration of 5 ppm was adjusted to the optimum pH that had been obtained previously, namely pH 2. The filtrate of each solution was tested using AAS and obtained the contact time optimization chart in Figure 3.

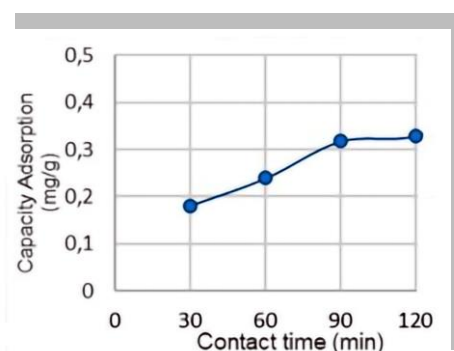


Figure 3. Effect of contact time on Cr (VI) metal adsorption

As shown in Figure 3, adsorption capacity of ions was linear to contact time. The optimum contact time was reached at 90 minutes, with an adsorption capacity (Q) value of 0.31037 mg/g and an adsorption efficiency ($E\%$) of 75.65% .

The adsorption capacity of metal ions continued to increase along with the length of time contact due to diffusion process. The longer contact time increased the concentration of attached Cr(VI) ions on the surface of adsorbent.

Determination of adsorption isotherms. The adsorption isotherm illustrated the process of adsorbate distribution between the liquid phase and the solid phase at different concentrations (Saadi et al., 2015). The adsorption isotherm could be determined by converting the

Langmuir and Freundlich equations into linear or straight-line equations.

Determination of the adsorption isotherm in this study was done by varying the concentration of the standard solution of the metal ion Cr(VI) which was then interacted with silica. The result obtained from the analysis using the Langmuir and Freundlich equations can be seen in Figure 4 and 5.

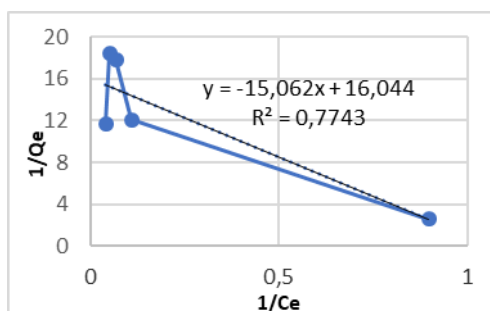


Figure 4. Langmuir Isotherm

Based on Figure 4 and 5, the coefficient of determination (R^2) on the Freundlich isotherm is greater than the value of R^2 in the Langmuir isotherm. In this case, the pattern of adsorption isotherms of Cr(VI) ions by silica followed the Freundlich isotherm model.

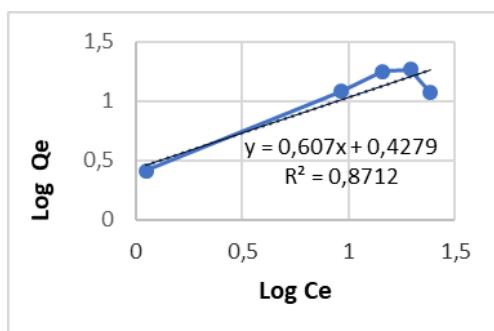


Figure 5. Freundlich isotherm

The Freundlich isotherm illustrated that adsorption between chromium hexavalent ions and silica occurs physically (physisorption). Physical adsorption occurred because metal ions have a relatively weak intermolecular force to an active site of the surface of silica, this intermolecular force called the van der

Waals force. This interaction caused the adsorbate to move from one part of the surface to others, and on the left surface will be replaced by other metal ions.

In the Freundlich isotherm model, adsorption of Cr(VI) ions occurred on heterogeneous silica surfaces, which means that each active group had different absorbing abilities. Besides, physical adsorption could form several layers (multilayer). The active site bound metal ions more strongly in the first layer than the adsorption energy decreased in the next layer and continued until the adsorption process completed or the equilibrium concentration had been reached (Saadi *et al.*, 2015).

Applications in the textile industry wastewater. contains in wastewater of dyeing process was investigated, before contacted with silica in optimum conditions. The results of chromium hexavalent adsorption in wastewater samples can be seen in Table 1.

Table 1. Adsorption results in wastewater

Initial Concentration (mg/L)	Final Concentration (mg/L)
0,4062	*not detected

As shown in Table 1, the concentration of Cr(VI) in the textile home industry wastewater meets the maximum standard Ministry of Environment and Forestry Regulation Number 3 in 2010. When wastewater was contacted with silica, adsorption occurred optimally because the final concentration obtained was that the Cr⁶⁺ metal ions were no longer detected. The undetectability of the metal in the sample indicated that the wastewater contained metal in such a small amount so that not detected by AAS which has a sensitivity of 0.001 mg/L.

Conclusion

Silica prepared through the sol gel method was confirmed to be able to adsorb Cr(VI) ions with E% by 75.65 at pH 2 in 90 minutes. Adsorption isotherms of Cr(VI) ions to the silica followed Freundlich

isotherm models. To get higher E%, silica may also be added with other metal oxides to improve the performance of silica in adsorption of trace elements, which is not conclusive, but needs further investigation.

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