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Cite as: AIP Conference Proceedings 1823, 020032 (2017); https://doi.org/10.1063/1.4978105
Published Online: 17 March 2017

Agung Purwanto, Yusmaniar, Fatmawati Ferdiani, and Rachma Damayanti

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Synthesis and Adsorption of Silica Gel Modified 3-aminopropyltriethoxysilane (APTS) from Corn Cobs against Cu(II) in Water

Agung Purwanto1,a, Yusmaniar2,b, Fatmawati Ferdiani3,c, Rachma Damayanti4,d

1,2,3,4 Program Studi Kimia, Fakultas Matematika dan Ilmu Pengetahuan Alam, Universitas Negeri Jakarta, Jl. Pemuda No.10, Rawamangun 13210, Jakarta, Indonesia

a) agungunj@yahoo.com
b) ys_maniar@yahoo.com
c) fanieferdiani@ymail.com
d) rachmadamai@gmail.com

Abstract. Silica gel modified APTS was synthesized from silica gel which was obtained from corn cobs via sol-gel process. Silica gel was synthesized from corn cobs and then chemically modified with silane coupling agent which has an amine group (NH2). This process resulting modified silica gel 3-aminopropyltriethoxysilane (APTS). Characterization of silica gel modified APTS by SEM-EDX showed that the size of the particles of silica gel modified APTS was 20μm with mass percentage of individual elements were nitrogen (N) 15.56%, silicon (Si) 50.69% and oxygen (O) 33.75%. In addition, silica gel modified APTS also showed absorption bands of functional groups silanol (Si-OH), siloxane (Si-O-Si), and an aliphatic chain (-CH2-), as well as amine (NH2) from FTIR spectra. Based on the characterization of XRD, silica gel 2θ of 21.094° and 21.32° respectively. It indicated that both material were amorphous. Determination of optimum pH and contact time on adsorption of silica gel 3-aminopropyltriethoxysilane (APTS) against Cu(II). The optimum pH and contact time was measured by using AAS. Optimum pH of adsorption silica gel modified APTS against metal Cu(II) could be obtained at pH 6 while optimum contact time was at 30 minutes, with the process of adsorption metal Cu(II) occurred based on the model Freundlich isotherm.

INTRODUCTION

Water is the most important need for the continuity of human activity. In other hands, toxic heavy metals have damaged water resources through various intermediaries, such as air, food, or heavy metals contained waste. Heavy metals can be distributed into human body and will be accumulated. If this situation continues for long time, it can be harmful to human health.

Essential heavy metals such as copper (Cu) is important and needed in human metabolism at non excessive amount. But at higher concentration it will lead to be toxic substances in body. The poison effect which is generated can be vomiting, a burning sensation in esophagus area and diarrhea. It also can be followed by hypotension, liver damage and coma [1]. Reducing the levels of heavy metals needs to be performed to improve water quality. Elimination of heavy metals contained from wastewater has been becoming an important subject for research. There are some methods to overcome the pollution and poisoning risks caused by heavy metals such as chemical precipitation, coagulation, complexation, solvent extraction, membrane separation, ion exchange and adsorption [2]. Adsorption of heavy metals is widely used in the industry because its several advantages: more economical, also do not cause toxic side effects and able to eliminate organic materials [3]. An adsorbent which is environmentally friendly from natural materials or materials from industrial waste is a potential material to be used. There are several terms as an adsorbent that is, have a broad surface area as indicated by the porosity [4].

Corncob is one potential agricultural waste to be converted to silica gel. This material is easily obtained with an abundant amount and also contains a SiO2 more than 60% [5]. There are weaknesses in the use of silica gel as
adsorbent, those are the low effectiveness of adsorption of silica to metal ions, and low capacity of oxygen (silanol and siloxane) as an electron-pair donor resulting weak bonding of metal ions on the surface of silica. In spite of that, modifications need to be done with the addition of active groups on the silica surface [2]. Making the silica adsorbent from the ash of corn cobs will be done in this study, which may be further modified using the reagent 3-aminopropyltriethoxysilane (APTS) to be able to adsorb Cu(II) in a water medium.

EXPERIMENTAL

Synthesis of Silica Gel from Corn Cob

The method used in the synthesis of silica gel from corn cob was sol-gel method. This method was adapted from Velmurugan (2015) [6]. Corn cobs were combusted and calcined at 600 °C for 5 hours. Ten grams of corn cob ash were dissolved in aqua DM 60 mL, then solution of 5 M HCl added until the pH became 1. Then the mixture was refluxed for 2 hours, then the solution was filtered with Whatman no.41 and the residue was washed with 100 mL aqua DM. The residue was mixed into 60 mL of 1M NaOH, and refluxed for 1 hour to dissolve silica contain and obtained a solution of Sodium Silicate. The solution was filtered with Whatman no.41 and the residue was washed with 100 mL boiled aqua DM. Then solution of 1 M HCl added into filtrate until the pH 7 with constant stirring, and incubated to form gel. The time required to form a gel lasted for 18 hours. Gel then filtered and washed with aqua DM to remove Cl-. After that, the gel was transferred to plate evaporator for drying at 100 °C for 18 hours in order to obtain silica gel. Then silica gel was characterized by using Fourier Transform Infra Red (FTIR), Scanning Electron Microscopy (SEM)-Electron Diffraction X-Rays (EDX), and X-Rays Diffraction (XRD).

Synthesis of Silica Gel Modified 3-aminopropyltriethoxysilane (APTS)

Twenty grams of silica gel was suspended in 200 mL of toluene, then followed by addition of 10 mL 3-aminopropyltriethoxysilane (APTS). The mixture was refluxed for 20 hours. After reflux, the mixture was filtered and washed with 25 mL ethanol (2 times washing). Furthermore, the resulting modified silica gel APTS was obtained white solid and then dried in a desiccator (at room temperature). Silica gel modified APTS was characterized by using Scanning Electron Microscopy (SEM)-Electron Diffraction X-Rays (EDX), Fourier Transform Infra Red (FTIR), and X-Rays Diffraction (XRD).

Adsorption of Silica Gel Modified 3-aminopropyltriethoxysilane (APTS) Against Metal Cu(II)

A total of 0.10 grams of silica gel modified APTS mixed with 10 ppm of Cu(NO₃)₂ solution and stirred at 150 rpm in various pH and contact times. pH 2, 3, 4, 5, 6 and 7 were used to determine the optimum pH and 10, 20, 30 and 40 minutes were used to determine the optimum contact time of the adsorption silica gel modified APTS against metal Cu. Then the solution was filtered and its adsorption capacity against Cu(NO₃)₂ had been measured using Atomic Absorption Spectroscopy (AAS). Data from AAS processed in Microsoft Excel.

Determining Isotherm Adsorption of Silica Gel Modified 3-aminopropyltriethoxysilane (APTS) against Metal Cu(II)

Isotherm adsorption was determined at optimum pH and contact time. A total of 50 mL of Cu(NO₃)₂ solution at multiple concentrations, 30, 60, 90, 120, 180 ppm were put in 250 mL Erlenmeyer flasks. This mixture were stirred, the solution was filtered with filter paper. Filtrate was analyzed using Atomic Absorption Spectroscopy (AAS). Data from Microsoft Excel AAS processed in the form of a chart to determine the isotherm adsorption.
RESULTS AND DISCUSSION

Scanning Electron Microscopy-Electron Diffraction X-Rays (SEM-EDX)

Besides aiming to determine the size of the silica gel, characterizing with SEM-EDX also aimed to determine the amounts of silicon (Si) and oxygen (O) which are main constituents of silica (SiO$_2$) and also determine the amounts of nitrogen (N) in silica gel modified APTS. Figure 1 shows the size and morphology of the silica gel which was synthesized from corn cobs. The figure shows that the surface of the silica gel was ununiform and consists of clumps (clusters). It is indicating the grain size was quite diverse with an uneven distribution on the surface of silica gel [7]. From this result, the size particle of silica gel was 20 μm. SEM results also indicated that the particle size of silica gel modified APTS was 20 μm. This result showed that the addition of silane coupling agent on silica gel did not affect the size of the silica gel. Percentage mass of silicon (Si) and oxygen (O) which is a constituent element of silica was also shown in Fig. 1. The content of silica gel from corn cob contained elements of oxygen (O) was 38.91% and the element silicon (Si) was 61.09%.

EDX results of silica gel with silica gel modified APTS had a difference results because silica gel modified APTS contained mass percentage of nitrogen (N). This indicated that silica gel modified APTS could be synthesized. The element nitrogen (N) was obtained from 3-amino propyltriethoxysilane which containing amine groups. EDX results of silica gel modified APTS see Fig. 1d, it shows that there was a mass percentage of nitrogen (N) 15.56%, mass percentage of silicon (Si) 50.69% and a mass presentation of oxygen (O) 33.75%.

Fourier Transform Infra Red (FTIR)

Spectra FTIR of silica gel, silica gel modified APTS and the comparison between those two showed in Fig. 2. Silica gel modified APTS showed absorption band at wave number 469.37 cm$^{-1}$ which corresponds to bending vibration of Si-O-Si, while the silica gel absorption band at wave number 472.94 cm$^{-1}$ showed the bending vibration of Si-O-Si from SiO$_4$ [8]. Silica gel modified APTS also showed absorption band at wave number 800.81 cm$^{-1}$ was a symmetric stretching vibration of Si-O from Si-O-Si, while the silica gel absorption band at wave number 803.96
Silica gel absorption band at wave number 969.22 cm\(^{-1}\) showed the Si-O stretching vibration of Si-OH, but in the FTIR spectra of silica gel modified APTS an absorption band at wave number 900 cm\(^{-1}\) (Si-O stretching vibration of Si-OH) not found. This was due to the reduced number of silanol result of condensation with the amine compound [10]. Moreover, silica gel modified APTS absorption band at wave number 1097.91 cm\(^{-1}\) was a asymmetric stretching vibration of Si-O from Si-O-Si. While in silica gel, vibrations from oxygen atoms join silicon atoms were contiguous when the Si-O-Si stretching appears at wave number 1099.73 cm\(^{-1}\) showed a asymmetric stretching vibration of Si-O from Si-O-Si [11].

Absorption band at wave number 1521.53 cm\(^{-1}\) was only detected in FTIR spectra results that indicated a bending vibration amine (N-H primer) on silica gel modified APTS while absorption band at wave number 1649.59 cm\(^{-1}\) was only detected in FTIR spectra of silica gel, it was a bending vibration of water molecules trapped within a silica matrix [12]. Moreover, in FTIR spectra of silica gel modified APTS, emerging new absorption band in 2938.02 cm\(^{-1}\) which was stretching vibration of CH\(_2\) groups [2]. Wide absorption band at wave number 3445.68 cm\(^{-1}\) was the stretching vibration of O-H bond of silanol (Si-OH) and based on adsorption of water molecules on surface of silica gel from corn cobs [13]. Silica gel modified APTS absorption band at wave number 3650.42 cm\(^{-1}\) was a stretching vibration of group N-H and O-H, O-H group of the Si-OH absorption intensity decreased comparing to spectra of silica gel. Decreasing in absorption intensity indicated a reduced number of silanol was a result of condensation with APTS [9].

**X-Rays Diffraction (XRD)**

Based on the results of characterizing by XRD, it was found that the silica gel was synthesized to have \(2\theta = 21.094^\circ\). The results showed that the silica gel synthesis product had an amorphous structure [14]. The XRD results of silica gel are shown in Fig. 3. The addition of silane coupling agent on silica gel had not changed the structure of the silica gel modified APTS. The XRD results of silica gel modified APTS showed that \(2\theta = 21.32^\circ\) and according
to previous studies, silica gel modified with peak APTS showed an amorphous structure [15]. The XRD results silica gel modified APTS is shown in Fig. 3.

FIGURE 3. Results of Characterization Using XRD (a). Silica Gel, (b). Silica Gel Modified APTS.

**Determination Optimum pH of Adsorption Cu(II)**

Based on the results the optimum pH of adsorption of Cu(II) using adsorbents silica gel modified APTS in a water was at pH 6 with ion metal Cu\(^{2+}\) which could be adsorbed was 4.24335 mg / g. Figure 4 and Table 1 shows the adsorption continued to increase at a pH of 2-5, there were optimum at pH 6, and the graph down at pH 7. The adsorption process of metal Cu(II) in acidic condition was not optimal. It was caused by surface of the adsorbent has positively charged so the adsorbent surface rejected to bind metal ions which also had positively charged in acidic pH. This phenomena caused the low adsorption of Cu(II) [16]. The absorption of the metal ion Cu\(^{2+}\) at pH 7 decreased, it was because at pH 7 Cu\(^{2+}\) was beginning to precipitate so that the adsorbent's ability to adsorb being dropped [17]. The amount of metal ions adsorbed Cu\(^{2+}\) is maximal at pH 6 because at pH 6 the active sites on adsorbent was in the form of neutral, so it had a function as an electron-pair donor [2].

**TABLE 1.** Number of Metal Ions Cu\(^{2+}\) Adsorbed on Variation pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>Abs</th>
<th>Co (mg/L)</th>
<th>Ce (mg/L)</th>
<th>q (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.3027</td>
<td>10</td>
<td>7.9201</td>
<td>1.03995</td>
</tr>
<tr>
<td>3</td>
<td>0.292</td>
<td>10</td>
<td>7.5944</td>
<td>1.2028</td>
</tr>
<tr>
<td>4</td>
<td>0.2668</td>
<td>10</td>
<td>6.4957</td>
<td>1.75215</td>
</tr>
<tr>
<td>5</td>
<td>0.2559</td>
<td>10</td>
<td>2.937</td>
<td>3.5315</td>
</tr>
<tr>
<td>6</td>
<td>0.2566</td>
<td>10</td>
<td>1.3033</td>
<td>4.34835</td>
</tr>
<tr>
<td>7</td>
<td>0.2566</td>
<td>10</td>
<td>1.3035</td>
<td>4.34825</td>
</tr>
</tbody>
</table>

FIGURE 4. Effect of pH on Adsorption Cu(II) with Silica Gel Modified APTS Adsorbent.
Determination Optimum Contact Time of Adsorption Cu(II)

Figure 5 and Table 2 shows the optimum contact time of adsorption metal Cu(II) using silica gel modified APTS in water was at 30 minutes. Seen from the graph when the contact time of 10, 20 and 30 minutes, the amount of metal ions adsorbed metal Cu$^{2+}$ increased, and the amount of metal ions adsorbed down when the contact time at 40 minutes. When adsorption process had reached the optimum point, then the metals which could be adsorbed were decreasing. The amount of metal ions adsorbed by the adsorbent of silica gel modified 3-aminopropyltriethoxysilane (APTS) at 30 minutes was 4.41735 mg/g.

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>Abs Co (mg/L)</th>
<th>Ce (mg/L)</th>
<th>q (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.2140</td>
<td>10</td>
<td>1.5662</td>
</tr>
<tr>
<td>20</td>
<td>0.1868</td>
<td>10</td>
<td>1.3178</td>
</tr>
<tr>
<td>30</td>
<td>0.1701</td>
<td>10</td>
<td>1.1653</td>
</tr>
<tr>
<td>40</td>
<td>0.1917</td>
<td>10</td>
<td>1.3626</td>
</tr>
</tbody>
</table>

Freundlich isotherm equation had $R^2$ value which was close to 1, $R^2 = 0.9444$. Freundlich isotherm assumed that the adsorbent had a heterogeneous surface and each molecule had the potential of different adsorption [18].
TABLE 3. Results of Adsorption Metal Cu(II) for Determining Isotherm Adsorption Model.

<table>
<thead>
<tr>
<th>Abs</th>
<th>Co (mg/L)</th>
<th>Ce (mg/L)</th>
<th>q (mg/g)</th>
<th>Ce/q</th>
<th>log Ce</th>
<th>log q</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1512</td>
<td>30</td>
<td>0.9928</td>
<td>14.503</td>
<td>0.068452</td>
<td>-0.00314</td>
<td>1.1614</td>
</tr>
<tr>
<td>0.1785</td>
<td>60</td>
<td>1.2420</td>
<td>29.379</td>
<td>0.042275</td>
<td>0.094122</td>
<td>1.4680</td>
</tr>
<tr>
<td>0.2023</td>
<td>90</td>
<td>1.4593</td>
<td>44.270</td>
<td>0.032963</td>
<td>0.164145</td>
<td>1.6461</td>
</tr>
<tr>
<td>0.2659</td>
<td>120</td>
<td>2.0400</td>
<td>58.98</td>
<td>0.034588</td>
<td>0.30963</td>
<td>1.7707</td>
</tr>
<tr>
<td>0.2912</td>
<td>180</td>
<td>2.271</td>
<td>88.8645</td>
<td>0.025556</td>
<td>0.356217</td>
<td>1.9487</td>
</tr>
</tbody>
</table>


![Isotherm Langmuir](image)

FIGURE 7. Curve of Isotherm Freundlich.

![Isotherm Freundlich](image)

CONCLUSION

Silica gel modified APTS was successfully synthesized from silica gel which was obtained from corn cobs. Peak absorption band of silica gel modified APTS contained silanol functional groups (Si-OH), a siloxane (Si-O-Si), amines (NH₂) and aliphatic chains (-CH₂-). The particle size of silica gel modified APTS was 20 μm. XRD diffraction patterns of modified silica gel 2θ = 21.3254°. Modification of silica gel using APTS did not change the amorphous structure. The process of adsorption of Cu(II) using silica gel modified APTS on research had optimum...
at pH 6 and contact time at 30 minutes. Isotherm models prevailing in this study was Freundlich isotherm with $R^2$ was 0.9444.

REFERENCES