Modified Silica Adsorbent from Volcanic Ash for Cr(VI) Anionic Removal

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ABSTRACT

In the present research, cetyltrimethyl ammonium bromide (CTAB)-modified silica from Kelud’s volcanic ash has been prepared and examined as adsorbent for removal of the hazardous Cr(VI) anion. The research was initiated with purification of SiO$_2$ from the volcanic ash that was carried out by reacting the volcanic ash with NaOH powder at 900 °C for 2 h, followed by dissolving the ash to water at 100 °C, and then was acidified with HCl 1 M to form hydrogel. By calcination of the hydrogel, silica (SiO$_2$) gel was obtained. The next step was modification of the silica with CTAB, that was performed by interacting the CTAB solution with the gel, in which the concentration of the CTAB was varied. Then the CTAB-modified silica samples were characterized by using FTIR, XRD, and SEM machines. The activity of the adsorbent was examined for adsorption of CrO$_{4}^{2-}$ in the solution. The results of the research demonstrate that the amorphous silica gel and the amorphous CTAB-modified silica have been obtained. The CTAB-modified silica was found to possess much higher ability in the adsorption of CrO$_{4}^{2-}$ anion, that was 48.90 mg/g, compared to that of the unmodified silica gel, as much 5.68 mg/g. These findings strongly prove that the negative surface of the CTAB-modified silica adsorbent has been successfully formed. Furthermore, it is also observed that increasing concentration of CTAB in SiO$_2$-CTA can promote more effective adsorption of the CrO$_{4}^{2-}$ from the solution, but the further enlargement of the CTAB concentration leads to the adsorption decreased, and the highest adsorption was shown by CTAB-modified silica prepared with 0.10 mole of CTAB/1 mole SiO$_2$.

Keywords: volcanic ash; silica; modification; CTAB; adsorbent; Cr(VI)

INTRODUCTION

Volcanic ash from eruption of Merapi (Yogyakarta) and Kelud (East Java) mountains in high quantity is still left in the environment that can create air and water pollutions. The major component in volcanic ash is silica (SiO$_2$) that has electron rich surface [1], enabling the volcanic ash to be an adsorbent for removing some hazardous heavy metals from the solution [2]. Silica has been reported as an effective adsorbent to remove several heavy cationic metals in the solution [3]. Silica has also high hydrophilic surface, motivating Sayari et al. [3], Parida et al. [4] and Koner et al. [5] to use the silica as adsorbent for removing...
polar organic pollutant. In addition to be prepared from tetra ethyl ortho silane (TEOS) [3-5], silica has also been synthesized from natural materials such as siliceous sand [6], or even from the agricultural waste including bottom ash from sugar industry [7], black rice husk ash [8], and rice husk ash [9]. So far the use of silica purified from the volcanic ash as an adsorbent has not been paid of attention.

Silica has been reported as a good adsorbent for polar toxic organic molecules and hazardous heavy catiionic metals [3-5], however silica was not effective to adsorb the anion metal, such as CrO$_{4}^{2-}$ [10]. In fact, the hazardous metals can be also found as anionic form, such as AsO$_{4}^{3-}$, CrO$_{4}^{2-}$, and [Ag(S$_{2}$O$_{3}$)$_{2}$]$^{2-}$. Among the anions, CrO$_{4}^{2-}$ gets more attention due to the high toxicity, and contamination by CrO$_{4}^{2-}$ can lead to the serious environmental and health problems [11]. The diminish of anionic Cr(VI) concentration has been carried out by using activated alumina and charcoal [12] and activated carbon [13] adsorbents, but the less effective adsorption was observed. The low adsorption is caused by the same negative charge belonged to both the surfactants and CrO$_{4}^{2-}$ that inhibit their mutual interaction.

To remove the toxic Cr(VI) anions, positive surfaced adsorbents are required, which are rarely found compared to the negative surfaced adsorbents [14]. Accordingly, modifications of materials to form positive surfaced adsorbents are essential to be carried out. The modification of an adsorbent can be performed by attaching a cationic surfactant that is organic molecule with the long carbon chain giving hydrophobic character as a tail and hydrophilic amine with positive charge as a head that is compensated by bromide ion. In the aqueous solution, the bromide is released while leaving positive charge [15]. The positive charge allows the surfactant-modified adsorbent to adsorb the anionic heavy metals.

Cationic surfactants that have been attached on the silica surface are polyaniline [16], and cetyl-trimethyl ammonium bromide (CTAB) [17-23]. Compared to polyaniline, as surface modifiers, CTAB seems to be favored. CTAB molecule for surface modification to create positive charge has been incorporated into zeolite [24], bentonite type clay [25], and silica [17-23]. The most silica modified with CTAB [17-23] was prepared from commercial material of tetra ethyl ortho silane (TEOS). In fact, silica extracted from the low cost natural materials has been frequently reported [7-9], but less CTAB modified-silica from natural materials was studied [26]. The other low cost natural material that is potential as silica source is volcanic ash, but up to now the volcanic ash has not been explored yet. In fact, in Yogyakarta and Kediri (Indonesia), the volcanic ash left from the volcano eruption is still found in abundant pale.

Accordingly, in this research, CTAB-modified silica that was purified from volcanic ash of Kelud Mt. is addressed. The modified silica adsorbent then was examined for removing Cr(VI) anionic in the solution.

**EXPERIMENTAL SECTION**

**Chemicals and Instruments**

NaOH, HCl, K$_2$CrO$_4$ and Cetyltrimmonium Bromide (CTAB) that were analytical grade, were used without any purification, and the volcanic ash from Kelud eruption collected from the area around Yogyakarta. The instruments used were AAS, FTIR, and XRD as well as SEM machines.

**Procedure**

**Silica gel preparation**

Silica gel from the volcanic ash was obtained by melting the ash with NaOH powder at 900 °C for 4 h. The solid obtained then was dissolved in water accompanied by heating at 100 °C for 20 min, and the solution of silicate was formed. The solution then was acidified with HCl 2 M up to reach pH 7, to form hydrogel. The hydrogel then was heated at 110 °C to get silica gel.

**Modification of silica gel by using CTAB**

The CTAB-modified silica gel was prepared by following procedure as reported previously [6]. 10 mole of silica gel was added with a series of 500 mL CTAB solution giving variation of mole amount, that were 0.25, 0.50, 1.00, 2.00, and 3.00 moles. The mixtures were stirred magnetically for 12 h. The solids were separated from the mixtures by filtration, and were rinsed with deionized water until the filtrate was free from Cl ion, which was tested by AgNO$_3$ solution. The solids of CTAB-modified silica gel were dried at 110 °C for 3 h. The CTAB-modified silica samples obtained were noted as SiO$_2$-CTAB$_{0.25}$, SiO$_2$-CTAB$_{0.50}$, SiO$_2$-CTAB$_{1.0}$, SiO$_2$-CTAB$_{2.0}$, and SiO$_2$-CTAB$_{3.0}$ that are in accordance with the CTAB concentrations. Characterization of SiO$_2$ and CTAB-modified silica were performed by means of XRD to check the structure, FTIR to identify the interaction between CTAB and SiO$_2$, and SEM to observe the morphology. The CTAB-modified silica adsorbent characterized was only CTAB-modified silica 1.0 representing the others.

**The adsorption activity of the CTAB-modified silica gel**

The activity of the CTAB-modified silica gel as adsorbent was examined for taking out CrO$_{4}^{2-}$ ions from the solution. The adsorption was proceeded by batch
system. For that purpose, 50 mL of the solutions containing 10 mg/L of CrO$_4^{2-}$ was added with 50 mg of the CTAB-modified silica gel, and then it was magnetically stirred for 3 h. The mixture was filtered and the clear solution was obtained. The clear solution was analyzed by AAS to find out the concentration of CrO$_4^{2-}$ that was not adsorbed. By subtracting the initial concentration of CrO$_4^{2-}$ by the unadsorbed one, the adsorbed CrO$_4^{2-}$ can be calculated. The adsorption process was carried out by employing CTAB-modified silica with various content of CTAB noted as SiO$_2$-CTA$_{0.25}$, SiO$_2$-CTA$_{0.5}$, SiO$_2$-CTA$_{1.0}$, and SiO$_2$-CTA$_{3.0}$.

RESULT AND DISCUSSION

Characterization Results of CTAB-Modified Silica Adsorbent

XRD data

Characterization of SiO$_2$-CTA$_{1.0}$, representing the other SiO$_2$-CTA adsorbents, by using XRD method gives a pattern as illustrated by Fig. 1.

The patterns show that both SiO$_2$ gel and SiO$_2$-CTA are in the amorphous phase, which were also reported previously [7-9]. The amorphous gel was formed because in the SiO$_2$ gel preparation, the hydrogel was heated at 110 °C to release the water, that inhibits it to form the crystalline phase, as also reported in previous papers [9]. The amorphous SiO$_2$-CTA also implies that the impregnation of CTA on to SiO$_2$ structure does not influence the structure of the SiO$_2$ gel [18,21-22].

FTIR data

To identify the possible interaction between SiO$_2$ with CTA in SiO$_2$-CTA adsorbents, their infrared spectra have been recorded, as seen in Fig. 2. Several absorptions appear at the various wavelengths as summarized in Table 1.

The wavelengths of 468.33, 956.69, and 1635.14 cm$^{-1}$ belonged to silanol group [6-9] are observed in the spectra of the silica gel, and the absorbance shifts into higher wavelengths when silica

![Fig 1. The XRD pattern of (a) SiO$_2$ gel and (b) SiO$_2$-CTA$_{1.0}$](image1)

![Fig 2. The Infrared spectra of (a) SiO$_2$, (b) CTAB, (c) SiO$_2$/CTA$_{0.25}$, (d) SiO$_2$/CTA$_{0.5}$, (e) SiO$_2$/CTA$_{1.0}$, and (f) SiO$_2$/CTA$_{3.0}$](image2)

**Table 1.** The summary of the absorption appeared at several wavelengths

<table>
<thead>
<tr>
<th>The typical bond</th>
<th>The wavelength of the absorptions of SiO$_2$</th>
<th>The wavelength of the absorptions of SiO$<em>2$/CTA$</em>{1.0}$ with various mole ratio of SiO$_2$ : CTAB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-O bend at silanol</td>
<td>462.92</td>
<td>468.33, 470.63, 470.63, 470.63, 470.63</td>
</tr>
<tr>
<td>Si-O bend at silanol</td>
<td>956.69</td>
<td>960.69, 960.69, 960.69, 964.41, 964.1</td>
</tr>
<tr>
<td>Si-O asymmetric bend at siloxane group</td>
<td>1080.14</td>
<td>1087.85, 1087.85, 1095.35, 1095.35</td>
</tr>
<tr>
<td>O-H bend at silanol group</td>
<td>1635.64</td>
<td>1627.92, 1627.92, 1627.92, 1627.92</td>
</tr>
<tr>
<td>O-H asymmetric bend at siloxane group</td>
<td>3448.72</td>
<td>3400.28, 3400.28, 3400.28, 3400.28</td>
</tr>
<tr>
<td>N of tertiary amine</td>
<td>3425.58</td>
<td>3400.28, 3400.28, 3400.28, 3400.28</td>
</tr>
<tr>
<td>C-H bend in alkane</td>
<td>1481.33</td>
<td>1475.33, 1475.33, 1465.33, 1453.62</td>
</tr>
<tr>
<td>C-H bend in carbon chain in CTAB</td>
<td>2916.37</td>
<td>2916.37, 2916.37, 2916.37, 2916.37</td>
</tr>
</tbody>
</table>
The surface area of SiO$_2$ gel is modified becomes SiO$_2$-CTA. The shifts may suggest the presence of the strong interaction between N- atoms of CTAB with O atoms of the silanol group from the silica gel [18,20-21] that may represent the stable SiO$_2$-CTA adsorbent.

The wavelength shift is also observed in SiO$_2$-CTA spectra that is from 3425.58 into 3400.28 cm$^{-1}$ of tertiary amine or $–N\cdot R_2$, that was similar data reported previously gel [18,20-21]. This shift strongly supports of the interaction between N- atoms of CTAB with O atoms of the silanol group from the silica gel. From the spectra it is also seen that the intensity of the shifts increases with the raise of the CTAB concentrations, implying the strength of the interaction [17].

**SEM data**

The other tool to characterize SiO$_2$/CTA adsorbents was SEM that provide the images as presented as Fig. 3. The figure illustrates that both SiO$_2$ gel and SiO$_2$/CTA adsorbents possess the featureless images. Such images reveal that the adsorbents are in amorphous forms [7,20-22], which are consistent with their XRD data.

The difference seen is that the surface of SiO$_2$ looks rough, meanwhile SiO$_2$/CTA has smoother surface. It is implied that the CTA covers the SiO$_2$ surface and may provide larger surface area than the unmodified SiO$_2$ [18,21].

In addition the surface characters of the adsorbents, including surface area and porosity have also been determined, as presented in Table 2.

*Table 2. The surface characters of the adsorbents*

<table>
<thead>
<tr>
<th>Character</th>
<th>SiO$_2$ gel</th>
<th>SiO$<em>2$–CTA$</em>{1.0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area (m$^2$/g)</td>
<td>40.670</td>
<td>92.571</td>
</tr>
<tr>
<td>Pore Volume (cc/g)</td>
<td>$3.07 \times 10^{-1}$</td>
<td>$4.26 \times 10^{-1}$</td>
</tr>
<tr>
<td>Pore radii (Å)</td>
<td>$1.50973 \times 10^{2}$</td>
<td>$0.920143 \times 10^{2}$</td>
</tr>
</tbody>
</table>

The activity of the adsorbents was examined to take the CrO$_4^{2-}$ out from the solution, and the results are presented in Fig. 4. From the figure it is seen that SiO$_2$/CTA can promote more anion adsorption compared to SiO$_2$, that is same result as obtained by Bryleva et al. [18]. The CrO$_4^{2-}$ anion adsorption degree of SiO$_2$ was found as 5.68 mg/g, which is higher than that of activated carbon, which was 3.46 mg/g [13]. The surface of silica containing silanol (Si-OH) groups enables it to adsorb the chromate anion, may be through hydrogen bonding [18]. In contrast, the activated carbon has hydrophobic surface that prevents the CrO$_4^{2-}$ adsorption [13].

The higher adsorption degree of anion Cr(VI) by SiO$_2$/CTA is due to the availability of the positive surface contributed by CTAB$^+$ on the SiO$_2$ surface [22]. Further, the enhancement of the anion adsorption was
observed, when the CTAB concentration was increased. With low CTAB concentration that is below its CMC, the tail or the hydrophobic part outside of the surface of SiO\textsubscript{2}/CTA existed as hydrophobic character \[18,22\], as displayed by Fig. 5.

Increasing CTAB concentration on SiO\textsubscript{2} can form bilayer resulting in the positive surface \[18,22\], as also illustrated by Fig. 5b. In addition, more CTA level in SiO\textsubscript{2} also provides more surface active for adsorption. However, much CTA level can decrease the adsorption that is caused by the disorder of bilayer that decrease the positive surface, as illustrated by Fig. 5c. It is clearly observed that 1.0 mmole of CTA /10 mmole of SiO\textsubscript{2} can reach the highest adsorption degree of CrO\textsubscript{4}\textsuperscript{2-} by SiO\textsubscript{2}/CTA that is 48.90 mg/g. The adsorption degree is in the same order as obtained by Venditti et al. \[21\], which was 46 mg/g, although the adsorption degree is still lower than the adsorption degree of SiO\textsubscript{2}/Polyaniline \[16\] that was as much as 63.42 mg/g.

CONCLUSION

It can be concluded that the silica extracted from the Kelud’s volcanic ash has been successfully incorporated by CTAB to form SiO\textsubscript{2}/CTA having positive charge surface, the SiO\textsubscript{2}/CTA adsorbent was also found to have larger active surface and smaller pore volume. Such characters belonged to SiO\textsubscript{2}/CTA adsorbent promotes more anionic CrO\textsubscript{4}\textsuperscript{2-} adsorption. Furthermore, the adsorption capacity of SiO\textsubscript{2}/CTA is found to be controlled by CTA loaded and the highest adsorption degree that is about 48.9 mg/g, which is demonstrated by SiO\textsubscript{2}/CTA prepared by introducing 0.1 mole CTAB in each mole of SiO\textsubscript{2}.

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