Adsorption of Metal Cr(III) On Amino-Silica Hybrid From Rice Hull Ash

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ABSTRACT
In this research, adsorption of Cr(III) on amino-silica hybrid (ASH) from rice hull ash has been investigated. Synthesis amino-silica hybrid (ASH) was carried out by adding HCl 3 M to the mixture of (3-aminopropyl)-trimethoxysilane and sodium silicate solution was obtained from destruction of rice hull ash with NaOH. The adsorbents were characterized by infrared spectrophotometer (FTIR) and X-ray diffraction (XRD). Adsorption of Cr(III) on ASH was conducted in a batch system for one hour by varying concentration of metal ion. The adsorbed metal ion was calculated based and after adsorption that was analyzed by AAS method. Characterization with FTIR showed that ASH has been synthesized which was indicated by appearing the absorbance of functional groups Si-OH (silanol), Si-O-Si (siloxane), and -NH$_2$ (amino). The XRD data showed the structure of ASH was amorphous. The research showed that hybridization increases the adsorption capacity for metal ions Cr(III).

Key words: rice hull ash, amino-silica hybrid, adsorption

INTRODUCTION
Use of heavy Metal in industry often generate problem because dismissal of his waste can contaminate environment of vicinity and cause ugly to life if his existence in environment have abysmal float certain boundary. Heavy metals such as silver (Ag), cadmium (Cd), lead (Pb), cobalt (Co), copper (Cu), iron (Fe), mercury (Hg), molybdenum (Mo), nickel (Ni), tin (Sn), zinc (Zn) and elements such as lighter aluminum (Al), arsenic (as) and selenium (Se) could potentially result in toxic effects to the organism (Freedman, 1995). Effects of heavy metals toxic to living things, especially humans. Indonesia reports in the form of pollution in Buyat Bay, North Sulawesi. The Gulf of metal contaminated arsenic result in a strange disease on the population surrounding a result of consuming marine life around the bay Buyat. In the case of this pollution, shows how important the efforts of heavy metals from sewage treatment industry in order to avoid cases of environmental pollution that endanger life forms.

Cr(Kromium) representing one of heavy metal of pollute the environmental. Waste of Cr can come from industry of metal veneering, paint and the ink. accumulation of Metal of Cr if exceeding concentration required by body hence will cause cancer of hul and exhalation channel (Mertz Dkk, 1974). Handling heavy metal waste has done much to address the risks of pollution and toxicity to living things. Adsorption process is expected to take heavy metal ions from water. According to Blais et al. in Alex (2005), this technique has advantages over other techniques, such as low cost and no toxic side effects. Now being developed processing techniques rice hull ash as adsorbent to help overcome the problem of heavy metal waste. Rice hull ash is an agricultural waste are very abundant in Indonesia, especially in East Halmahera, North Maluku Subaim. Centered rice mill, rice hull ash is an agricultural waste has been a problem and not maximum utilization of rice hull ash. Therefore, it is necessary to attempt to cultivate rice hull ash ash as a natural source of sufficient potential to be an effective adsorbent material and selective (Narsito et al., 2004).

Silica gel is one of the inorganic solids that can be used for the adsorption of heavy metals. Various efforts have been done for example by immobilization mercapto or thiol groups (-SH) via sol gel process (Narsito et al. 2004). Based on this background, this research study studied the adsorption properties of Cr(III) on amino-silica hybrid through a batch technique. Amino-silica hybrid materials were synthesized by a solution of sodium silicate base hull ash processing results and active organic compounds (3-aminopropyl)-trimethoxysilane through sol-gel process.

RESEARCH METHOD
Material
The chemicals used in this study include: rice hull ash is taken from a brick kiln in the village Subaim East Halmahera of North Maluku as a source of silica. For the manufacture of adsorbents include: distilled water, NaOH 4M, 3M HCl; 6M HCl obtained from 37% (3-aminopropyl)-trimethoxysilane (Mercck), universal pH indicator paper, aluminum foil, filter paper Whatman no. 42. The process of adsorption of Cr(III) with a static technique (batch) include the manufacture of metal solution using Cr(NO$_3$)$_3$.9H$_2$O.
Tools

Tools of analysis include atomic absorption spectrophotometer (AAS), X-ray diffraction and infrared spectrophotometer (FTIR).

Research Procedures

Preparation and Characterization of Adsorbent

Weighing 20 g samples of rice hull ash ash was washed with 120 mL of 6 M HCl and dried in an oven. Then diluted with 4 M NaOH, in order to obtain a solution of sodium silicate filtrate. Next, take 20 mL solution of sodium silikat (Na$_2$SiO$_3$) and added 2 mL compound (3-aminopropyl)-trimetoksilan (APS), and then add dropwise 3 M HCl while stirring, stirring to form the gel to a neutral pH. The results obtained oven dried and crushed and the gel formed sifter. The resulting solid was in the form of Amino-silica hybrid (HAS). The same work was also carried out without the addition of APS. The result obtained are called silica gel (SG) used as adsorbent comparison. HAS and SG further characterized by FTIR and XRD

Adsorption of Cr (III) on the adsorbent

Created a solution of Cr(III) with each concentration series. To a solution of Cr(III) made the series a concentration of 20, 60, 100, 140, 180 and 220 mg / L. Solution of Cr(III) that have been made, each 50 mL were taken and put into a plastic cup and 0.5 grams of adsorbent (HAS and SG) of different added to each plastic cup. The mixture was stirred and centrifuged with a speed of 2000 rpm and the results are analyzed by AAS.

RESULTS AND SOLUTION

Characteristics of silica gel and amino-silica hybrid

Characterization of synthesized solids were calculated using an infrared spectrophotometer (FTIR). Every functional groups on silica gel (SG) and amino-silica hybrid (HAS) has a characteristic absorption at certain wave numbers. This characterization is used as a qualitative indication of the success of the synthesis of SG and HAS through the emergence or change absorption characteristics to functional groups on the adsorbent. Characterization results are presented in Figure 1.

![Figure 1 FTIR spectra of silica gel (A) and amino-silica hybrid (B)](image)

Figure 1 (A) which is the characteristic absorption spectra of SG showed the wavenumber 470.6 cm$^{-1}$ is the Si-O bending vibrations of the siloxane groups (Si-O-Si). Absorption band at 952.8 cm$^{-1}$ shows the Si-O stretching vibration of silanol (Si-OH). Strong absorption band at wavenumber 1099.3 cm$^{-1}$ is the asymmetric stretching vibration of Si-O of siloxane(Si-O-Si)(Sastrohamidjojo,1992).

From Figure 1 (B) shows that the process of modification of SG using compound (3-aminopropyl)-trimetoksilan (APS) results in an amino-silica hybrid (HAS) resulted in a change and the emergence of specific infrared absorption band for the group of the APS. Gelomang absorption band at a lower number is 948,9 cm$^{-1}$ shows Si-O stretching vibration of Si-OH absorption intensity decreased indicating reduced amount due to the condensation of silanol groups with APS compounds. Absorption band at 3444.6 cm$^{-1}$ region which are believed to be widened absorption-OH groups of silanol experiencing overlap with NH group of compounds APS diimobilisasikan in SG.
Adsorption of Cr(III)

Thermodynamics of adsorption. In this discussion than the thermodynamic properties and adsorption SG HAS batch techniques for metal ions Cr(III). Adsorption done by mixing a solution of metal Cr(III) on the variation of the concentration with 0.5 grams of adsorbent (SG and HAS) for 1 hour at room temperature (25°C). Determining the capacity of the Langmuir adsorption isotherm model based on the adsorption isotherm curve connecting the equilibrium metal ion concentration (µmol / L) on the adsorbent (SG and HAS) with the amount of metal ions adsorbed (µmol / g) and is presented in Figure 2.

![Graph](image)

Figure 2 curve relationship equilibrium concentration (µmol / L) on the adsorbent with the amount of metal adsorbed (µmol / g) of metal ions: (a) SG.Cr(III) and HAS.Cr(III).

Figure 2 shows that the adsorption isotherms of metal Cr(III) the rise with the increasing concentration of the metal ion. At relatively high concentrations of metal ion concentration increases are no longer accompanied by a significant increase in metal adsorption on the adsorbent (SG and HAS) where the curve tends to a constant or experienced a decrease.

Adsorption isotherm describes the relationship between substances adsorbed in a certain amount of weight of adsorbent (SG and HAS) in units of the balance. Langmuir adsorption isotherm can be expressed by the equation:
where \( C \) is the equilibrium concentration, \( m \) is the amount of substance adsorbed per gram of adsorbent, \( b \) is the adsorption capacity and \( K \) is the equilibrium constant. By plotting the data obtained from the results of research to chart \( \frac{C}{m} \) vs \( C \) produces a straight line with slope \( \frac{1}{b} \) and intercept \( \frac{1}{bK} \). From the graph of \( \frac{C}{m} \) vs \( C \) can be determined the parameters of Langmuir adsorption isotherm. The total energy of adsorption per mole can be calculated from the equation:

\[
E_{\text{ads}} = -\Delta G_{\text{ads}}^o = RT \ln K
\]

K is the adsorption equilibrium constant obtained from Langmuir equation and the total adsorption energy equal to the Gibbs free energy (Oscik, 1982). Table 1 shows the values calculated adsorption capacity (\( b \)) and the adsorption energy (\( E \)) in the SG and the HAS adsorbent.

### Table 1 Parameter thermodynamics of metal adsorption

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Metal Ions</th>
<th>Parameter isotherm adsorption Langmuir</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( b ) (( \mu )mol/g)</td>
<td>( K ) (L/mol)</td>
<td>( E ) (kJ/mol)</td>
</tr>
<tr>
<td>SG</td>
<td>Cr(III)</td>
<td>10.05</td>
<td>16164,32555</td>
<td>24,1702</td>
</tr>
<tr>
<td>HAS</td>
<td>Cr(III)</td>
<td>43.67</td>
<td>14129,90997</td>
<td>23,8347</td>
</tr>
</tbody>
</table>

**Adsorption capacity.** From Table 1 it can be created relationship diagram between the metal adsorption capacity of the solution is adsorbed metal Cr(III) on the adsorbent as shown in Figure 3.

![Figure 3 The relationship between the adsorbed metal adsorption capacity the SG and HAS metals in solution](image)

Figure 3 shows the adsorption capacity of the metal in the SG and HAS highly variable. After modification SG with (3-aminopropyl)-trimetoksisilan (APS) through the sol-gel process became HAS overall adsorption capacity for Cr(III) increased.

**Adsorption energy.** From Table 1 it can also be created relationship diagram between adsorption energies of solution of metals adsorbed metal Cr(III) on the adsorbent as shown in Figure 4.
Figure 4 The relationship between the energy of adsorption by adsorbed metal the SG and HAS metals in solution

From Figure 4 shows that the adsorption energy of metal in solution at SG and HAS which is respectively SG.Cr(III) > HAS.Cr(III). Based on these data the metal adsorption energies on SG and HAS Cr(III) which are respectively 33.40 and 22.86 kJ / mol, can be categorized as chemical adsorption occurs. As described by Adamson (1997) that the chemical adsorption if the adsorption energy of more than 20.92 kJ / mol.

CONCLUSION

1. Rice hull ash can be used as a source of silica to create a hybrid amino-silica through sol-gel process.
2. Metal adsorption studies on amino-silica hybrid (HAS) obtained very high that is comparison with SG.
3. Energy data of metal ion Cr(III) on HAS adsorption energy is generally relatively low which are respectively 23,8347 kJ/mol.

REFERENCES