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by
Potential of Coal Fly Ash as Pellet Adsorbent to Reduce Level Hg$^{2+}$ in Liquid Waste

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ABSTRACT
Fly ash can be used as adsorbent, because it is cheap and effective to absorb the waste in the aquatic environment. In addition, fly ash has a main component in the form of silica (SiO$_2$), alumina (Al$_2$O$_3$), iron oxide (Fe$_2$O$_3$) and a number of unburned carbon, this component has an important role in the adsorption process. Fly ash is inexpensive adsorbent, efficient, simple preparation, easy to operate and can be used to absorb heavy metal ions. Pure fly ash was used to adsorb Hg and Pb in aqueous solution, but the adsorption capacity for Hg quite low at 17%. Fly ash dust cannot be applied in the adsorption column because after a while it will form an impermeable solids. In a stirred tank will also result in problems with the fly ash material separation of the solution, so that the use of fly ash pellets in the adsorption column will not cause problems and waste water can easily seep into the column containing the pellets without the risk of clogged. In addition, the use of fly ash dust can change the pH of the waste water and become strong alkaline with a pH of more than 11 after the wastewater treated. The use of fly ash pellets only change slightly the pH of wastewater after treatment is not more than pH 8 and is still within the permissible limits. In this study, fly ash was applied as adsorbent of Hg$^{2+}$ in the form of fly ash composite pellet-chitosan cross linked with glutaraldehyde.

Key words: chitosan, fly ash, FTIR, Hg

INTRODUCTION
Coal combustion generated much kind of byproducts including fly ash (Yao, et al. 2014). The process of coal combustion generated by Steam Power (power plant), currently including in Indonesia, the amount of fly ash produced is very large. Major industries which have the power plant itself also produce fly ash from the use of coal as fuel. But the utilization of coal combustion are not offset by the processing of fly ash which is still quite low at 15% of the amount produced (Bilin et al. 2001), thus forming a pile of fly ash.
Fly ash can be used and utilized as an adsorbent, because it is cheap and effective way to absorb the waste in the aquatic environment (Ramadan, et al., 2010). In addition to the fly ash has a major component in the form of silica (SiO$_2$), alumina (Al$_2$O$_3$), iron oxide (Fe$_2$O$_3$), and the amount of unburned carbon, these components have an important role in the adsorption process (Wang and Wu, 2006).
According to Papandreou et al. (2007), which resembles a fly ash dust cannot be applied to adsorption column because after a while will be formed solids impermeable. In a stirred tank will also result in problems with the fly ash material separation of the solution, so that the use of fly ash pellets in the adsorption column will not cause problems and waste water can easily seep into the column containing the pellets without the risk of blockage. In addition, the use of fly ash dust can alter the pH of the wastewater and become strong alkaline with a pH of more than 11 after the wastewater treated. The use of fly ash pellets only change slightly the pH of wastewater after treatment is not more than pH 8 and is still within the permissible limits.
Chitosan is a biopolymer of D-glucosamine produced from the chitin deacetylation using strong alkalis. The uses of chitosan often utilize crosslinking to modify the chemical structure and texture by binding to the amine or hydroxyl (Poona, et al. 2014). Chitosan is a membrane that can be bonded with glutaraldehyde cross the amino group (–NH$_2$). Crosslinking occurs can form...
pores that can enhance the adsorption properties. Pores formed in the membrane of chitosan will be the immobilization of fly ash (fly ash) (Gu et al. 2001). Chitosan is often used as a co-polymer for the adsorption process.

Hg is a heavy metal which is carcinogenic and potentially threatens human health at very low concentrations. Some data have shown that mercury can cause brain damage, disorders of the liver, kidneys, gastrointestinal tract and central nervous system and is toxic to cells by binding to the intracellular sulphydryl groups (Inbaraj, et al., 2009). The maximum limits of ionic Hg levels in drinking water of 2.0 mg L⁻¹ and the total ion Hg permitted waste of 10.0 mg L⁻¹ (Kumar et al. 2013).

This research aims to make the adsorbent in the form of pellets in the form of granules from fly ash by means composited chitosan cross linked with glutaraldehyde and try to lower the concentration of Hg in solution with an adsorbent.

MATERIALS AND METHODS

Materials

The materials used in this study is fly ash coal, chitosan (Industrial Grade) from shrimp shells obtained from Biotech Surindo, Glutaraldehyde 25% of Merck, Oxalic Acid (H₂C₂O₄), sulfuric acid (H₂SO₄), Hydrochloric Acid (HCl), sodium hydroxide (NaOH), Mercury Sulfate (HgSO₄) and distilled water.

2. Procedures

2.1. Fly Ash modification with Chitosan

Put 2 g of fly ash into 20 mL chitosan gel while stirring using a magnetic stirrer at room temperature then the composite formed is taken using a pipette dropwise into a solution of NaOH 2N, it performed until the solution runs out in order to obtain granules. Then the granules were separated from NaOH solution and soaked 24 hours in a solution of 2% glutaraldehyde. After 24 hours, the granules filtered and washed with distilled water until the pH of the solution became neutral. Then the granules are dried in an oven for 24 hours at a temperature of 60-70 °C.

2.2. Treating wastewater contain Hg²⁺ with fly ash-chitosan granules

Prepare 100 mL HgSO₄ solution, add fly ash-chitosan granules. Then put each of these erlenmeyer in a shaker, set the corresponding variable speed shaker and adsorption time of 60 minutes. After the adsorption process is completed followed by a process of filtration and the filtrate was analyzed using Atomic Absorption Spectroscopy (AAS).

2.3. Calculation cation absorbed by the fly ash granules and adsorption capacity

The amount of metal ions that are absorbed by the fly ash granules during batch adsorption processes is determined by the following equation:

\[
\%\text{ion Hg adsorbed} = \left(\frac{C_o - C_f}{C_o}\right) \times 100
\]

Where: \(C_o\) and \(C_f\) are the initial concentration and concentration after adsorption time (60 minutes) in ppm Hg metal ions in solution.

Adsorption capacity of adsorbent fly ash-chitosan granules is determined by the following equation:

\[
q_e = \frac{(C_o - C_f)V}{m}
\]

Where: \(V\) is the volume of solution and \(m\) is the mass of adsorbent added.
RESULTS

Characterization of fly ash before modification

Figure 1. FT-IR spectra of fly ash chemical activation (not modified)

Characterization of modified fly ash

Figure 2. FT-IR spectra crosslinked composite pellets (modified fly ash)

Table 1. Hg adsorbed ion concentration in a solution by the composite pellets fly ash-chitosan

<table>
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<tr>
<th>Co</th>
<th>Ca</th>
<th>Ce</th>
<th>qe</th>
<th>Ce/qe</th>
<th>log qe</th>
<th>log Ce</th>
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<tr>
<td>0.0296</td>
<td>0.0223</td>
<td>0.0073</td>
<td>1.1150</td>
<td>0.006547</td>
<td>0.0473</td>
<td>2.1367</td>
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<td>0.0228</td>
<td>0.0068</td>
<td>1.1400</td>
<td>0.005965</td>
<td>0.0569</td>
<td>2.1675</td>
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<td>0.0240</td>
<td>0.0056</td>
<td>1.2000</td>
<td>0.004667</td>
<td>0.0792</td>
<td>2.2518</td>
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<td>0.0216</td>
<td>0.0070</td>
<td>1.1300</td>
<td>0.006195</td>
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<tr>
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<td>0.0021</td>
<td>1.3250</td>
<td>0.00234</td>
<td>0.1222</td>
<td>2.5086</td>
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Description: Ce = Concentration of metal ions at time t (mg L\(^{-1}\))
Co = Concentration of metal ions initially (mg L\(^{-1}\))
Ca = Concentration of metal ions adsorbed (mg L\(^{-1}\))
qe = The amount of metal ions adsorbed at time t (mg g\(^{-1}\))
DISCUSSION

Figure 1, an FT-IR spectrum of fly ash has not been modified to show some dominant group among others carbonyl and hydroxyl. Infra-red spectrum showed a fly ash-OH group which is at 3448.72 cm⁻¹ wave, absorption at 2999.52 cm⁻¹ indicates -CH stretching vibration, while the group -C = O is at 1635.64 cm⁻¹ wave number.

Figure 1 and Figure 2, a spectrum which shows the difference between the functional groups of fly ash that has not been modified and fly ash which has been modified. In the picture clearly visible difference between the peak produced fly ash that has not been modified and has been modified especially at wave number 3433.29 cm⁻¹ (NH) and 1635.64 cm⁻¹ (C = O). At the peak of the second wave number widened indicating fly ash has been modified. Spectra of fly ash at 1087 wave numbers, 555 and 462 cm⁻¹ indicates the asymmetric stretching bond of Si-O-Si bond respectively, are symmetric stretching of Si-O-Si bond and the vibration of the alkoxy groups. The functional group to absorb heavy metals such as Si-OH, NH₃⁺ and Al⁻ also seen on-chitosan composite fly ash at wave numbers 3433 and 2932 cm⁻¹.

Cross-binding process aimed at stabilizing the adsorbent under acidic conditions, due to the acidic conditions of amine groups on the adsorbent will be protonated ions that cause the structure be destroyed, so the adsorbent is not able to adsorb metals to the maximum. Adsorption capacity of pellets composite Hg in solution can be determined by calculating the capacity of adsorption, which in this study the adsorption capacity is calculated at pH 6, the mass of fly ash 4 g, mass pellet composite 2 g and a stir speed of 180 rpm which is the optimum condition obtained from previous calculations. The adsorption capacity expressed in mg of metal ions per g of adsorbent (mg/g). The concentration of a solution containing Hg²⁺ ions initially amounted to 0.0296 mg/L.

CONCLUSION

Characterization of raw materials and finished with an instrument ftr of manufacture pellets composite fly ash-chitosan cross linked glutaraldehyde indicate that there has been a change in the structure of the functional groups of the raw material to the finished material in the form of a shift of the peaks in the ftr spectrum, and this indicates that the product has undergone a pore opening so that the product to be more effective in the process adsorption of heavy metals. Characterization of raw materials and finished with an instrument FTIR of manufacture pellets composite fly ash-chitosan crosslinked glutaraldehyde indicate that there has been a change in the structure of the functional groups of the raw material to the finished material in the form of a shift of the peaks in the FTIR spectrum, and this indicates that the product has undergone a pore opening so that the product to be more effective in the process adsorption of heavy metals.

REFERENCES


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<th>Rank</th>
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<td>Submitted to King Fahd University for Petroleum and Minerals</td>
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<td>1</td>
</tr>
<tr>
<td>5</td>
<td>&quot;Disposal and Utilization of Coal Combustion, Gasification, and Coking Residues&quot;, Coal Production and Processing Technology, 2015.</td>
<td>Publication</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>etd.lib.metu.edu.tr</td>
<td>Internet Source</td>
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<td>------------------------------------------------------------------------------------------------</td>
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<tr>
<td>7</td>
<td>&quot;Adsorption of lithium ions on novel nanocrystal MnO&quot;2&quot;</td>
<td>Zhang, Q.H.</td>
<td>Chemical Engineering Science, 200709</td>
</tr>
<tr>
<td>8</td>
<td>&quot;Application of charcoal for desalinating Ni(II) and Zn(II) from aqueous solutions through batch mode&quot;</td>
<td>Joginder Singh, Renu Sharma, Amjad Ali</td>
<td>Journal of Water Reuse and Desalination, 2013</td>
</tr>
<tr>
<td>9</td>
<td>Submitted to Asian Institute of Technology</td>
<td></td>
<td>Student Paper</td>
</tr>
<tr>
<td>10</td>
<td>ft.unlam.ac.id</td>
<td></td>
<td>Internet Source</td>
</tr>
<tr>
<td>11</td>
<td>Submitted to University of Birmingham</td>
<td></td>
<td>Student Paper</td>
</tr>
<tr>
<td>12</td>
<td>&quot;A review on the applications of coal combustion products in China&quot;</td>
<td>Jing Li, Xinguo Zhuang, Xavier Querol, Oriol Font, Natalia Moreno</td>
<td>International Geology Review, 2017</td>
</tr>
<tr>
<td>14</td>
<td>&quot;Removal of</td>
<td>Yang, Xunan, Mengting Guo, Yinghai Wu, Qunhe Wu, and Renduo Zhang.</td>
<td></td>
</tr>
</tbody>
</table>
Emulsified Oil from Water by Fruitting Bodies of Macro-Fungus (Auricularia polytricha), PLoS ONE, 2014.

15. Submitted to Plano Independent School District
   Student Paper

16. scholar.ufs.ac.za:8080
   Internet Source

17. Submitted to Universiti Sains Malaysia
   Student Paper

   Publication

19. answers.yahoo.com
   Internet Source

   Publication

   Publication