The Effectiveness of Zeolite/Claystone/Activated Charcoal Composite in Reducing Levels of Mercury (Hg) in the Waste Resulting from the Activities of Unlicensed Gold Mining (PETI) in Sintang

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Abstract. Research on zeolite/clay/activated charcoal composites as Hg heavy metal adsorbents has been carried out. Zeolite and clay were previously activated using NaOH while activated charcoal was activated using HCl. The adsorbent characterization was carried out by Fourier Transform Infrared Analyzer (FTIR), X-Ray Diffraction (XRD), and mercury levels using Atomic Absorption Spectroscopy (AAS). Hg metal adsorption experiments were carried out by varying the composition of zeolite / claystone / activated charcoal. The location of the study was in Gold Mining without Permit (PETI) in the Kapuas Sub-watershed, Ulak Jaya Village, Sintang. The results showed that zeolite / claystone / activated charcoal succeeded in reducing mercury levels in mining waste.

1. Introduction
The gold mining industry is one of the sectors that the Indonesian government has relied on to bring in foreign exchange. In addition to bringing in foreign exchange, the mining industry also opens up employment opportunities and for districts and cities is a source of local own-source revenue (PAD) [1]. Gold mining in Indonesia in general still uses mercury (Hg) in the panning process as a binder of the gold element. This mining technique harms the environment in the form of the release of heavy metal mercury (Hg) into the atmosphere that can endanger the ecosystem and cause serious harm to health [2]. Mercury is known to be a heavy metal which has very high toxicity. The use of mercury in an industry often results in environmental pollution, primarily through wastewater [3]. Most areas in West Kalimantan have high gold content. The gold contained in the land attracts the interest of small scale miners / traditional miners. One of the locations of illegal gold mining (PETI) is in the Village of Ulak Jaya Sintang, Sintang District, Sintang District, West Kalimantan. This gold mining is done traditionally, where the processing process does not use high technology and only uses elementary equipment.

Unlicensed Gold Mining Habits (PETI) in Ulak Jaya Sintang Village, Sintang District, Sintang District, West Kalimantan, which dispose of waste directly into the Kapuas River Basin (DAS) to become black and smelly. Tugaswati in her writing explained that the metal concentration of Hg in several fish species in the Kapuas River and the Landak River reached 50 µg/g; 100 times higher than the frequency permitted by the World Health Organization (WHO) for seafood products, 0.5 mg/kg [4]. Seeing how this pollution will be very dangerous if left unchecked, it is necessary to take
anticipatory steps by utilizing zeolite, claystone and activated charcoal to reduce mercury content in gold mining wastewater. This step is considered effective also can reduce costs in practice prevention. In principle, the process is the absorption or adsorption of natural zeolite and metal ions in the gold mining liquid waste. According to Sutopo it is known that zeolites can reduce iron (Fe) levels from 1.466 mg/L to 0.120 mg/L, manganese (Mn) from 2.220 mg/L to 0.060 mg/L, copper (Cu) from 0.430 mg/L to 0.030 mg/L, and zinc (Zn) from 0.180 mg/L to 0.110 mg/L [5].

1.1. Zeolite as an absorbent (absorbent) of mercury (Hg)

Experiments using zeolites as absorbent (absorbent) of mercury (Hg) contained in the water this is possible because zeolites have the nature of absorbing and have hollow structures. According to Government Regulation No. 82 of 2001 glasses of water containing mercury as raw material for drinking water (class I) a maximum of 0.0010 mg/L, if the number exceeds this number will interfere with the health of its consumption.

The zeolite structure can be seen in Figure 1. Based on the structure of porous solids that have cavities and great thermal stability, zeolite-like material can be used as a carrier of catalyst metals or adsorbents.

![Figure 1. Composition and Structure of Zeolites](image)

1.2. Claystone

Clay or claystone is a pozzolanic material by-product from the rest of the coal. Claystone is formed because of the non-combustible minerals contained in coal, such as Silica (Si), Alumina (Al) and Iron (Fe). The mineral content in claystone varies depending on the type of coal used. Because of the high content of silica and alumina in it, claystone can be used as a source of silica and alumina in the synthesis of zeolite material. Clay minerals or claystone can be used as a catalyst, adsorbent and as a resin for ion exchange, for the purpose of exchanging ions, clay must first be activated with the aim of increasing the absorption of clay [6]. Claystone or claystone has great potential as an adsorbent because of its abundant, large surface area with active groups such as silanol and aluminol in its skeletal structure and easily dispersed in water [7].

Rahmawati research states that the adsorption data of fourteen organic molecules on Cox claystone through experiments for polar compounds, namely acetate, adipate, benzoate, phthalates and citrate in decarbonated and clay fractions (<2 mm) [8]. Adsorption from a single carboxylic function is low, as evidenced by acetate and adipate. Adsorption of small polycarboxylic acids is significant as evidenced by phthalate, succinate, oxalate, gluconate, EDTA and citrate. Nusa's research proved that claystone can reduce the pH content of 6.83, BOD 16 mg/L, TSS 0.761 mg/L and Oil Fat 4.21 mg/L. Although in the ANOVA test, there was no significant effect between stirring time and different concentrations on pH and BOD. But discharged household wastewater is still above the standard quality of the Decree of the Minister of Environment No.112 of 2003 for pH 6-9, BOD of 100 mg/L, TSS of 100 mg/L and Fat oil of 10 mg/L [9].
1.3. Activated Charcoal

Mercury (Hg) absorbent using activated H3PO4 activated charcoal that activated charcoal is very good in the absorption process. This is proven by the absorption of Ni (II) metal which is absorbed by 95.08% while the Pb (II) metal is absorbed by 52.77%. Activated charcoal has a composition composed of elements of carbon, calcium, sulfur, phosphorus, lignite and cellulose. High carbon and cellulose content (36.00%) and lignite (20.90%) contained active charcoal so that it can be used in the adsorption process. The content contained in rice husk charcoal is not much different from the element content contained in activated carbon. The ability of activated charcoal as absorbent material is not the same from one another, because absorption is not necessarily good for the other absorption process. Differences in pore particle size and activation levels can affect the optimization of the use of activated charcoal [10].

This research uses experimental methods in the laboratory to obtain results data. This research broadly includes four stages, namely the preparation and characterization of adsorbents, adsorbent activation, adsorbent performance testing, and determination of adsorption isotherms. Furthermore, the results of the data are tested in the field with the aim to get a match between the laboratory results and the conditions in the field.

The data in this study consisted of two types, namely, quantitative data and qualitative data. Quantitative data are in the form of laboratory results on the effectiveness of zeolite, claystone and activated charcoal composites in the processing of mercury (Hg) waste in unlicensed Gold Mining (PETI) activities. While the qualitative data is questionnaire data about the social impact of the use of zeolite, claystone and active charcoal composites in the processing of mercury (Hg) waste in the Unlicensed Gold Mining activities (PETI) in the Kapuas Sub-Watershed, Sak Jaya Village, Sintang.

2. Results

2.1. Zeolite Analysis and Activation of gold mining waste

FTIR analysis was performed to determine zeolite functional groups and the effect of the zeolite activation process was carried out with 1M HCl. The use of this concentration was in accordance with the results reported by Sastiono [11], which activated mordenite and clinoptilolite zeolite types and obtained CEC results from the zeolites increased, but the use of HCl of more than 1 N has decreased the CEC value. According to Tri zeolites will experience dealumination that will continue to occur if the greater the concentration of acid used [12].

The results of IR zeolite spectra, before and after activation are shown in Figure 2, and summarized in Table 1:
Figure 2. FTIR Spectra of Natural and Activated Zeolite Samples

From Figure 2 the absorption of natural zeolite FTIR identified at wave number 3440.19 cm$^{-1}$ is the peak of the hydrated -OH group, this ftir spectrum is in accordance with Research Heraldy also shows that OH absorption occurs at successive wave numbers 3442.7; 3435.0 and 3424 cm$^{-1}$ [13]. The vibration of buckling OH from H$_2$O adsorbed according to Suroto occurred at wave number 1637.5 also occurred in natural zeolites at wave number 1642.6 cm$^{-1}$. In the study of Heraldy Al-O or Si-O stretching vibrations appeared at wavenumbers 1052.3 and 1043.3 cm$^{-1}$ whereas in studies from Suroto Al-O or Si-O stretching vibrations occurred at wave number 1055.0 cm$^{-1}$. In this study, Al-O or Si-O stretching vibrations from natural zeolites appeared at wave number 1046.61 cm$^{-1}$. The vibration of Si-O buckling natural zeolite according to research by Heraldy appeared at wavenumber 794.6 cm$^{-1}$ while research from Suroto vibration buckling Si-O appeared at wavenumbers 777.4 cm$^{-1}$ and 796.5 cm$^{-1}$. In this study, natural zeolites have the vibrations of buckling Si-O at wave number 797.6 cm$^{-1}$, which is not much different than that of the reference. Figure 2 shows that active zeolite spectra are almost the same as natural zeolite spectra. This shows that the role of activation does not change the structure of natural zeolites.

Table 1. Functional Group of Natural and Activated Zeolite Samples

| Functional Group         | Wave number (cm$^{-1}$) | Literature | Natural Zeolite | Active Zeolite |
|-------------------------|-------------------------|------------|----------------|---------------|
| -OH hydrated            |                         | 3442.7$^{(1)}$ | 3440.19         | 3421.87       |
|                         |                         | 3435$^{(2)}$  |                |               |
|                         |                         | 3442.7$^{(2)}$ |                |               |
|                         |                         | 3424$^{(4)}$  |                |               |
| vibration buckling OH   |                         | 1637.5$^{(2)}$ | 1642.46         | 1629.92       |
| from H$_2$O             |                         |            |                |               |
| stretching vibrations   |                         | 1055.0$^{(2)}$ | 1046.61         | 1052.21       |
| Al-O or Si-O            |                         | 1043.3$^{(1)}$ | 1052.3$^{(1)}$  |               |
| vibration buckling Si-O |                         | 796.5$^{(2)}$  | 797.6           | 797.6         |
| vibration buckling T-O  |                         | 794.6$^{(1)}$  |                |               |
|                         |                         | 471.6$^{(1)}$  | 441            | 465.83        |
2.2 Analysis and Activation of claystone on gold mining waste

Activation of claystone is made from clay samples washed with distilled water several times and filtered until the clay is completely clean from impurities, then dried in an oven at 120 °C for 2 hours, after which it is crushed and sieved with 80 mesh size. Clay samples that have been prepared are then taken ±100 g and immersed in an Erlenmeyer containing NaOH solution with a concentration variation of 1.5 M, then heated for 8 hours. After it was washed two times with distilled water, one time with a composite of methanol and distilled water (1: 1) and two times with methanol, then dried at room temperature.

The following graph shows before and after activation of claystone on gold mining waste.
From the two graphs above shows a very significant change after gold mining waste is activated by claystone. The concentration of mercury (Hg) drops, which means the levels are reduced, and it shows that claystone is effective for trapping harmful substances in waste.

2.3. Activation and activation of activated charcoal from gold mining waste

The chemical activation of activated charcoal is carried out by the addition of a 4 M HCl solution which aims to dissolve impurities on the surface of the charcoal so that the pores of the charcoal will open and its surface area increases. The effect of activation on activated charcoal can be observed in the FTIR spectra shown in Figure 6. The results of the FTIR spectra in Figure 6 show the appearance of new peaks in activated charcoal after activation. A new peak appears at wave number 1037 cm\(^{-1}\) which is the absorption of C-O. The emergence of new peaks is caused by the dissolution of impurities during the activation process. Based on the data in Table 2 shows that there are some differences between activated charcoal before and after activation, such as the shifting of wavenumbers from 3427 cm\(^{-1}\) to 3421 cm\(^{-1}\) which shows the absorption of the -OH group experiencing peak widening.

The absorption peaks of C=O, C=C, and C-O after activation look sharper, indicating an increase in absorption intensity. Increased intensity is possible because of impurity on the activated charcoal after it dissolves by the activation.

![Figure 5. FTIR spectra of activated charcoal before activation (a) and after activation (b)](image)

### Table 2. Functional Group

| No | Functional Group | Wave number (cm\(^{-1}\)) |
|----|------------------|----------------------------|
|    |                  | Literature | Before activated | After activated |
| 1. | O-H              | 3425\(^{(1)}\) | 3427       | 3421       |
| 2. | C=O              | 1705\(^{(1)}\) | 1701       | 1705       |
| 3. | C=C              | 1589\(^{(1)}\) | 1582       | 1576       |
| 4. | C-O              | 1300-800\(^{(2)}\) | 873       | 914; 1037  |

Note \(^{(1)}\) Kurniati et al (2011),\(^{(2)}\) Silverstain et al (2000)
The results of FTIR analysis showed that there were O-H, C=O, C=C and C-O uptake in the activated char spectra, which showed the presence of active groups. Analysis of the mineral content of activated charcoal was done by XRD. The results of XRD analysis of activated charcoal before and after activation are shown in Figure 6. The activated charcoal diffractogram was identified in the minerals cristobalite, fayalite and standard manganoan contained in the ICSD (Inorganic Crystal Structure Database) shown in Appendix 4. Peak diffraction of activated charcoal before activation is shown in 2θ = 24.22º which is the mineral cristobalite while the peak of diffraction of activated charcoal after activation is shown at 2θ = 21.91º (cristobalite), 26.723 (fayalite), 27.86 (manganoan) and 35.84 (manganoan + fayalite). The diffractogram comparison after activation shows the appearance of a new peak. The appearance of a new peak indicates that the impurity has dissolved due to the activation process. Soluble impurity will open the pores on the surface of activated charcoal and cause an increase in mineral content.

![Diffractogram of activated charcoal before activation (a) and after activation (b)](image)

**Figure 6.** Diffractogram of activated charcoal before activation (a) and after activation (b)

### 2.4. Effectiveness of Zeolite, Claystone and Activated Charcoal Composites in suppressing Mercury

Per the results of the Baristan laboratory tests, when using the leading composites from Zeolite, Claystone and Activated Charcoal can reduce levels of Mercury (Hg) in wastewater from gold mining (Table 3).
Table 3. Composite test results for waste

| Number of analysis | Code of Sample | Result / Mercury / Hg Total (mg/L) |
|--------------------|----------------|-----------------------------------|
| P. 3223 -19        | First waste    | 64,0                              |
| P. 3224 -19        | HgNO\(_2\) (prepar) | 10,7                             |
| P. 3225 -19        | Final waste    | < 0,0002                          |
| P. 3226 -19        | Zeolit (pure) / P | 0,570                            |
| P. 3227 -19        | Claystone(pure) / P | 61,7                            |
| P. 3228 -19        | Charcoal(pure) / P | 40,0                             |
| P. 3229 -19        | Zeolit50:25:25 / P | 3,349                           |
| P. 3230 -19        | Clay 50:25:25 / P | 3,409                            |
| P. 3231 -19        | Charcoal50:25:25 / P | < 0,0002                       |
| P. 3232 -19        | Zeolit (pure) / L | < 0,0002                        |
| P. 3233 -19        | Clay (pure) / L | 29,6                             |
| P. 3234 -19        | Charcoal (pure) / L | 35,7                             |
| P. 3235 -19        | Zeolit50:25:25 / L | 0,914                           |
| P. 3236 -19        | Clay 50:25:25 / L | < 0,0002                        |
| P. 3237 -19        | Charcoal50:25:25 / L | < 0,0002                       |

Based on the data in the above test results found the value of Mercury contained in the initial waste of 64.0 then through laboratory tests combined with Zeolite, Claystone and Activated Charcoal that has not been composite or pure each of them can only reduce the mercury content in the waste by Zeolite Pure 0.570, Claystone 61.7, and Activated Charcoal 40.0. These results indicate that the reduction of mercury levels in the waste does not comply with the mercury standard that is equal to 0.005 Hg by the Decree of the Minister of Environment No.202 of 2004 concerning Wastewater Quality Standards for Businesses and Mining Activities of Gold Ore and or Copper (Table 4).

Table 4. Wastewater Quality Standards for Gold and Copper Ore Mining Activities

| Parameter | Measure | Maximum level | Analysis Method |
|-----------|---------|---------------|-----------------|
| pH        | -       | 6 – 9         | SNI 06-6989-11-2004 |
| TSS       | mg/L    | 200           | SNI 06-6989-3-2004 |
| Cu        | mg/L    | 2             | SNI 06-6989-6-2004 |
| Cd        | mg/L    | 0,1           | SNI 06-6989-18-2004 |
| Zn        | mg/L    | 5             | SNI 06-6989-7-2004 |
| Pb        | mg/L    | 1             | SNI 06-6989-8-2004 |
| As        | mg/L    | 0,5           | SNI 06-2913-1992 |
| Ni        | mg/L    | 0,5           | SNI 06-6989-22-2004 |
| Cr        | mg/L    | 1             | SNI 06-6989-22-2004 |
| Hg        | mg/L    | 0,005         | SNI 06-2462-1991 |
But after being tested using Zeolite, Claystone and Activated Charcoal which has been composite, the results are quite significant where the mercury levels are reduced and are below the quality standard. Based on the results of laboratory tests, the levels of Mercury (Hg) in gold mining waste decreases to 0.914 with a Zeolite composite with a ratio of 50:25:25. While using Claystone composites with the same comparison value, the mercury content decreases to 0.0002 and using Activated Charcoal with the same ratio can also reduce mercury levels up to 0.0002. This finding is by the provisions of the standard quality standard for mercury content, meaning that the use of Zeolite, Claystone and Activated Charcoal composites to reduce mercury levels in the gold mining waste at Sintang is very useful.

3. Conclusion
Based on the discussion above, it is confirmed that zeolite, claystone and activated charcoal are capable and effective in reducing mercury (Hg) levels in waste products from unlicensed gold mining (PETI) in the Kapuas Sub-watershed, Ulak Jaya Sintang Village. With these findings so that it can be utilized as well as possible to anticipate the increasingly severe natural damage due to gold mining waste. The goal is that the preservation of nature can be utilized more optimally by residents around the mine.

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