Adsorption Effectivity Test of Andisols Clay-Zeolite (ACZ) Composite as Chromium Hexavalent (Cr(VI)) Ion Adsorbent

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Abstract. Adsorption of chromium hexavalent (Cr(VI)) ion in aqueous solution was investigated. This research was purposed to study the influence of the composition of ACZ, temperature activation, and contact time against adsorption capacity of Cr(VI) ion in aqueous solution. Determination of adsorption effectivity using several parameter such as composition variation of ACZ, contact time, pH, activation temperature, and concentration. In this research, andisol clay and zeolite has been activated with NaOH 3 M and 1 M, respectively. Temperature variation used 100, 200, and 400 °C. While composition variation ACZ used 0:100, 25:75, 50:50, 75:25, 100:0. The pH variation was used 2 – 6 and concentration variation using 2, 4, 6, 8, 10, and 12 ppm. Characterization in this research used such as UV-Vis, Surface Area Analyzer (SAA) and Acidity Analysis. Result of this research is known that optimum composition of ACZ was 50:50 with calcination temperature 100 °C. Optimum adsorption of Cr(VI) at pH 4 with removal percentage 76.10 % with initial concentration 2 ppm and adsorption capacity is 0.16 mg/g. Adsorption isotherm following freundlich isotherm with value $K_f = 0.17$ mg/g and value $n$ is 0.963. Based on results, ACZ composite can be used as Cr(VI) ion adsorbents in aqueous solutions.

1. Introduction
Chromium hexavalent (Cr(VI)), is toxic and suspected to carcinogenic for all life form [1,2], Cr(VI) usually found in electroplating, leather tanning, paint, steel fabrication, and textile dyeing [3]. Cr(III) and Cr(VI) state usually exist on environment. Cr(VI) have more high mobility then Cr(III) and is known to capable of permeating cell membrane and is a powerful mutagen for human and animal [4]. According to the Regulation of the Minister of Environment of Indonesia on the Standard of Wastewater Quality that the maximum limit of Cr(VI) ions in waste is 0.1 mg/L.

Conventional methods for the removal of Cr(VI) ion from wastewater include adsorption [5], coagulation-flocculation [6], ion exchange [7], filtration [8], and reverse osmosis [9]. The adsorption process is well known to be one of the most effective techniques and low cost for the removal of Cr(VI) ion in wastewater. The adsorption capacity of the sorbent is related to the radius, the specific surface area and the number of pores [4]. A few materials that can be used as adsorbent for Cr(VI) removal and easy to be found such as zeolite and andisol clay [10,11]. According to Sugiyarto (2013), andisol clay could be good adsorbent for heavy metals removal including Cr(VI) ion and could be

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found in few mountain in java island such as Mt Papandayan, Mt Wilis, and Mt Arjuna. In andisol clay usually found allophane minerals that have high specific surface area, porosity and ion exchange capacity and could be apply to wastewater treatment [10]. Zeolite are the crystalline microporous aluminosilicates that have molecular sieve and adsorbing ability for small molecules such as water. Zeolite are good adsorbent for removal heavy metals ion and contamination/pollution control [12]. Zeolite have SiO$_4$ and AlO$_4$ tetrahedral framework that forming stable arrangement through oxygen atom [13].

Andisol clay is still considered to have a lower adsorption capacity against Cr(VI) ions than zeolites. So, the modification of andisol clay by forming andisol-clay-zeolite composite is used to improve andisol clay adsorption capacity [14]. This is due to the excess of zeolites that have better adsorption capability than soil andisol may help to increase the adsorption capacity of the andisol soil [15].

In this research, zeolite will be added to the andisol clay to form the ACZ composite as Cr(VI) ion adsorbent and to study the effect of composition, activation, and contact time on Cr(VI) ion adsorption process in aqueous solution. ACZ composite are expected to have a better adsorption capacity that could be applied in industrial wastewater treatment.

2. Experimental

2.1. Adsorbent Preparation

Natural andisol clay from Mt. Lawu and zeolite from Wonosari are dried in the free air. After drying the soil andisol and zeolite mashed and sifted with 150 mesh then washed with aquades then dried with temperature 105 °C for 4 hours. Dry andisol clay was activated by soaked in 3 M NaOH solution and stirred with heating 70 °C for 5 hours then washed with aquades until the pH of andisol clay was neutral then dried at 105 °C. The dried natural zeolite was activated by soaking in 1 M NaOH solution and stirred with 90 °C for 1 hour then washed with aquades until the pH of the zeolite was neutral then dried at 105 °C.

2.2. ACZ Composite Preparation

Activated andisol soils and zeolite were mixed into 100 ml aquadest with weight variation (g/g) 0:100 (ZAA), 25:75 (ZAB), 50:50 (ZAC), 75:25 (ZAD), 100: 0 (ZAE). The mixture is then stirred for 1 hour. Each mixture was activated with temperature variations of 100, 200, and 400 °C for 3 hours. The composite is used as the Cr(VI) ion adsorbent in the aqueous solution.

2.3. Testing Adsorption effectivity of ACZ to Cr(VI) ion

0.1 g of ACZ composite was introduced into 10 ml Cr(VI) solution 2 mg/L with pH 2, 3, 4, 5 and 6 variations. The best pH variations were tested using variation of contact time 20, 40, 60, 80, 100, and 120 minutes. The obtained mixture was filtered and the filtrate was added 1.5-Diphenylcarbazide and was performed by determining Cr(VI) values using UV-VIS Spectroscopy following SNI 6989.71: 2009.

2.4. Isotherm Adsorption analysis of ACZ composite

0.1 g of ACZ composite was introduced into 10 ml Cr(VI) solution with variation of concentration 2, 4, 6, 8, 10, 12 mg/L. The obtained mixture was filtered and the filtrate was added with 1.5-Diphenylcarbazide and determination of Cr(VI) values using UV-VIS spectroscopy.

3. Result and Discussion

3.1. Characterization of ACZ

3.1.1. Surface area, Acidity and Pore Size Characterization. Surface area, acidity and pore size characterization is used to determine effectivity of andisol-clay composite adsorption against Cr(VI) ion. Acidity of Adsorbent is used to determine active site of adsorbent that used to adsorb Cr(VI) ion. Surface area, acidity, pore size characterization of Andisol clay and zeolite will be showed in table 1.
Table 1. Surface area, acidity and pore size characterization of Andisol Clay and Zeolite

| Adsorbent         | Surface Area (m²/g) | Acidity (mmol/g) | Pore Size (Å) |
|-------------------|---------------------|------------------|---------------|
| Natural Andisol   | 91.30               | 0.47             | 25.06         |
| Clay              |                     |                  |               |
| Activated Andisol | 54.36               | 1.24             | 51.94         |
| Clay              |                     |                  |               |
| Natural Zeolite   | 45.95               | 3.88             | 76.56         |
| Activated Zeolite | 55.68               | 4.82             | 86.91         |
| ACZ Composite     | 48.61               | 4.94             | 95.90         |

Table 1 showed that andisol clay and zeolite activated with NaOH could increase surface area and acidity of andisol clay and zeolite. Increasing surface area and pore size of andisol clay and zeolite showed that impurities on andisol clay and zeolite dissolved during the activation process. Increasing of acidity showed that active site from andisol clay and zeolite increase during activated process and could increase adsorption capacity.

3.2. Adsorption Effectivity of ACZ Composite on Cr(VI). The adsorbent effectivity test on Cr(VI) ion was performed to determine the optimum capability of the ACZ composite adsorbent. This adsorption effectivity test includes several tests such as the effect of contact time, pH, and the activation temperature of the ACZ composite. Adsorption effectivity of ACZ against Cr(VI) ion with variation composition and variation temperature will showed in figure 1 and 2.

![Figure 1. Adsorption effectivity of ACZ Composite against Cr(VI) ion with variation composition](image-url)
Figure 2. Adsorption effectivity of ACZ Composite against Cr(VI) ion with variation temperature

In figure 1 show that ZAC is optimum composition of ACZ composite with the optimum contact time of adsorption is 60 munites. At this composition, Cr(VI) ion removal is 76.10 % with initial concentration is 2 mg/L. ZAC that activated with different temperature showed in figure 2 that optimum temperature is 100 °C. It is caused by more higher temperature could broke the structure of ACZ composite. Rouzière et al. (2016) state the andisol clay would be broken in temperature above 500 °C caused –OH group release during calcination process [16,17]. Therefore, the adsorption capacity of ACZ composite would be decrease when temperature increase. The adsorption capacity of ZAC with temperature variation and pH variation will showed in figure 3 and 4.

Figure 3. Adsorption capacity of ZAC with temperature variation
In figure 3 show that adsorption capacity of ZAC at 100 °C is 0.16 mg/g. Decrease of adsorption capacity caused by increasing activated temperature of ZAC that could breake the composite structure. In figure 4 show that the optimum condition of Cr(VI) ion adsorption at pH 4. In aqueous solution, Cr(VI) occur in few ion such as \( \text{Cr}_2\text{O}_7^{2-} \), \( \text{HCrO}_4^- \) and \( \text{CrO}_4^{2-} \) [18]. In pH 4, the dominant species of Cr(VI) is \( \text{HCrO}_4^- \) that will interact with active site on ZAC. Reaction mechanism between ZAC with Cr(VI) ion will showed in scheme 1.

\[
\begin{align*}
\text{Al-OH} & \xrightarrow{\text{H}^+} \text{Al-OH}_2^+ + \text{HCrO}_4^- \\
\text{Al-OH}_2^+ + \text{HCrO}_4^- & \rightarrow \text{Al-OH} + \text{HCrO}_4
\end{align*}
\]

Scheme 1. Reaction mechanism between ZAC surface with Cr(VI) ion

In scheme 1 showed that interaction between ZAC surface with Cr(VI) ion that aluminol group will protonized and form \( \text{–OH}_2^+ \) which facilitate to form metal binding with \( \text{HCrO}_4^- \). In ZAC surface, aluminol group will have different characteristic in different pH. Aluminol group could protonized at pH below 5, while at pH above 5 could relase \( \text{H}^+ \) ion and make aluminol group have negative charge [19].

3.3. Isotherm Adsorption Analysis of ACZ Composite. Isotherm adsorption analysis is used to determine adsorption perform on ZAC. Type of isotherm adsorption of ZAC against Cr(VI) ion will showed in figure 5 and figure 6.
In figure 5 showed that freundlich isotherm adsorption of ZAC against Cr(VI) ion. Freundlich isotherm analysis based on physically adsorption which assumed formed multilayer of adsorbed molecules on adsorbent surface. Freundlich isotherm of ZAC showed that r value is 0.994 with $K_f$ value is 0.17 mg/g and n values is 0.963 which mean the adsorption process is favorable [1].

In figure 6 showed that Langmuir isotherm adsorption of ZAC against Cr(VI) ion. Langmuir isotherm analysis based on chemically adsorption which assumed formed monolayer of adsorbed molecules on adsorbent surface. Langmuir isotherm of ZAC showed that r value is 0.327 with $Q_{\text{max}}$ 1.25 mg/g and b value is 0.169 L/g. The isotherm adsorption for ZAC will showed in table 2.

| Isotherm | $Q_{\text{max}}$ (mg/g) | $K_f$ (mg/g) | $n$ | $r$ |
|----------|------------------------|--------------|-----|-----|
| Langmuir | 1.25                   | 0.17         | 0.963 | 0.327 |
| Freundlich |                          |              |       | 0.994 |
In table 2 show that adsorption of ZAC against Cr(VI) ion following freundlich isotherm which means the adsorption process occurs in physically adsorption where the interaction between ZAC surface with Cr(VI) ion is van der waals bonding [20].

4. Conclusion
Result of this research is optimum composition of ACZ composite is 50:50 (ZAC) with activation temperature 100 °C and optimum contact time is 60 minute. Adsorption capacity of ZAC is 0.16 mg/g with removal of Cr(VI) ion is 76.10 %. Isotherm adsorption result is showed that adsorption process of Cr(VI) ion followed freundlich isotherm or adsorption on physically with freundlich coefficient \( (K_f) \) is 0.17 mg/g and \( r \) value of freundlich isotherm is 0.994. Physically adsorption based on weak van der waals interaction between ZAC adsorbent with Cr(VI) ion in aqueous solution. From this result we known that ZAC can be used as water treatment in wastewater.

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