

The Adsorption of Cr^{3+} onto Na^+ -Saturated Kaolinite

Jaslin Ikhsan
Chemistry Education Department
Universitas Negeri Yogyakarta
Yogyakarta, Indonesia
jikhsan@uny.ac.id

Endang Widjajanti LFX
Chemistry Education Department
Universitas Negeri Yogyakarta
Yogyakarta, Indonesia

Erfan Priyambodo
Chemistry Education Department
Universitas Negeri Yogyakarta
Yogyakarta, Indonesia

Abstract—Chromium is one of the parameters of the heavy metal pollutant in the environment. An adsorption of chromium can be used to reduce the content of chromium cation. The study aimed to reduce the concentration of Cr cations in the water waste by using adsorbents kaolinite and Na-kaolinite with the pH variation of the solution. The adsorbents used were kaolinite and Na-saturated kaolinite. There were four steps to conduct this study, including the preparation of kaolinite, making waste simulation, testing the adsorbent, and the data analysis of cation adsorbed. Before the adsorbents were used, it was characterized using the FTIR and XRD methods. The results of the characterization by FTIR showed that the kaolinite and Na-kaolinite adsorbents didn't give significant difference; both adsorbents had the uptake of the clusters that were almost the same. While the XRD characterization on the adsorbent kaolinite appeared with spectra of $2\theta = 21.23$ and 41.93 which indicated the presence of quartz with contrast on Na-kaolinite that was not visible. On the other hand, Na-kaolinite appeared with spectra of $2\theta = 12.6$, which indicated the presence of halloysite. The percentage of the cation Cr^{3+} that adsorbed was increased concurrently along with the increasing of pH. It indicated that the pH gave significant effect toward the adsorption process. The adsorbent of Na-kaolinite was stronger in adsorbing Cr^{3+} as compared with kaolinite at low pH, because the addition of Na^+ on the kaolinite could result in the distance between the layers became larger and the reduced cluster of quartz in the sample.

Keywords: adsorption, chromium, FTIR, XRD, kaolinite

I. INTRODUCTION

Water pollution due to the contamination of heavy metals is a serious environmental problem. Water pollution by heavy metals will escalate along with the increasing of existing industry [1]. Heavy metal that accumulates in the water can be toxic to animal lives, plants and humans in low concentrations and even in a little amount. The heavy metals that usually found in water are Hg(I), Cd(II), Pb(II), Cr(III), Fe(III), and Cu(II) [2].

Chromium (Cr) is one of the heavy metals that are potentially pollutants in environment. Chromium is a

metal that is widely used by many people in the field of industries such as leather tanning, metal plating, and paint. Some of the industries are not responsible by disposing metal waste chrome directly into waters without any prior processing. The water containing chromium in a concentration of low and high can cause environmental problems. Toxic effects in chrome can cause serious problems for plants, animals and humans (Wu et al., 2018).

There are several methods that can be used to reduce the concentration of heavy metals such as; precipitation, adsorption, and ion exchange. Adsorption method has advantages compared to other methods. Adsorption has a simple process, fast, cheap on cost, and has a high efficiency rate to reduce the levels of heavy metal ions contained in the water (Mohadi et al., 2014).

Adsorption method is a method that representative in reducing the concentration of heavy metals found in water in the environment. Adsorption method is generally based on the interaction between metal and functional groups contained in the adsorbent, which is through formation of the complex and cations exchange. The material that is usually used as the adsorbent in the adsorption process of heavy metals are materials that contain tannins (activated carbon, sawdust, bark), zeolite, chitosan, seaweed, lignin, and kaolinite (clay) [5].

Kaolinite is a mineral found in sedimentary rocks which is known as clay stone. Kaolinite is a white-coloured mineral that has many functions. Kaolinite is powdery white and has a hexagonal crystal [5]. Kaolinite has chemical composition of hydrous aluminium silicate ($2\text{H}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). The composition of pure kaolinite is 46.54% SiO_2 ; 39.5% Al_2O_3 ; and 13.96% H_2O (Tribe et al., 2012). In Indonesia, the hill that contains kaolinite can also be found in the regions of Sumatra, Sulawesi and Kalimantan [5].

This study was conducted to reduce the concentration of cations of Cr using kaolinite adsorbent on the variation of the pH of the solution. The pH affects the adsorption process of cations because the high or low values of pH affect the

percentage of the cations adsorbed by the adsorbent. The adsorbent used in this study is adsorbent with the basic ingredients of clay mineral which is kaolinite. The kaolinite that was used is technical kaolinite. This study used two kinds of adsorbents that would compare the ability of the adsorbent to its ability to adsorb cations Cr^{3+} . The adsorbents used were kaolinite and Na-saturated kaolinite adsorbent. The saturation of kaolinite was to replace various cations that are bound to natural kaolinite by Na^+ .

II. RESEARCH METHOD

A. Materials

This study used kaolinite from Akashi-shi, Hyogo, Japan and Na-saturated kaolinite as adsorbents. Cations of Cr^{3+} is from $Cr(NO_2)_3 \cdot 6H_2O$. The spectrophotometers used included SEM-EDX from Hitachi SU3500, AAS is from Shimadzu AA 7000, and FTIR.

B. Procedure of the Research

1) Preparation of Adsorbents Kaolinite and Na-kaolinite

Kaolinite in amount of 60 grams was added into in 500 mL of water and a solution of 1M 1000 mL $NaNO_3$. The solution then stirred for an hour. The solution that had been stirred further then resided for a week. The solution was filtered and washed until it reached the neutral pH using water. Kaolinite, which had become neutral, subsequently dried for an hour with a temperature of $100^{\circ}C$ for further sieved using a sieve of 150 mesh. The adsorbent was characterized using FTIR and XRD.

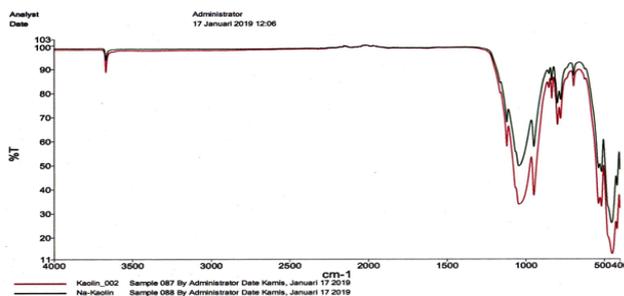


Fig. 1. FTIR Analysis of Adsorbent Kaolinite and Na+-saturated Kaolinite

2) Testing the Adsorbent

An amount of 0.5 g adsorbent kaolinite was contacted to a 25 mL of a solution of Cr^{3+} by stirring for 30 minutes. The same thing was also done on the adsorbent Na-kaolinite. The adsorbent which had been contacted to a solution of Cr^{3+} then filtered. The filtrate produced was then centrifuged then tested use SSA to determine the concentration of the cations Cr^{3+} adsorbed.

3) Making Process of Cr^{3+} Solutions

Stock solution of Cr^{3+} for sample of adsorption was prepared from solid $Cr(NO_2)_3 \cdot 6H_2O$, and with the concentration of 50 ppm.

III. RESULTS AND DISCUSSION

A. Characterization of Adsorbents Kaolinite and Na-Kaolinite

The kaolinite and Na-kaolinite which had been prepared and then characterized using FTIR which intended to determine whether or not the cluster was OH, the bond of Al-O and Si-O on the kaolinite which played an important role in the adsorption process. The data obtained from the analysis of the FTIR were quantitative and qualitative data. Quantitative data included the value of the absorbance compound at a specific wavelength. While the qualitative data obtained included the analysis of the cluster function (the peak). The results of characterization of adsorbents kaolinite and Na-kaolinite using FTIR can be seen in Figure 1 and Table I.

TABLE I. ABSORPTION PEAK OF KAOLINITE AND NA+ SATURATED KAOLINITE [1-4]

Kaolinite (cm ⁻¹)	Na-kaolinite (cm ⁻¹)	Theoretically (cm ⁻¹)	Description
417.52	417.61	430	Vibration Si-O stretch
447.01	451.45	468	Vibration Si-O stretch
515.88	516.34	520	Vibration Si-O-Al ^{IV}
534.87	535.14	537	Vibration Si-O-Al ^{IV}
694.94	694.92	694	Stretch vibration O-Si-O
778.22	778.07	778	Si-O quartz
797.74	797.81	797	Si-O quartz
834.74	834.72	844	(AlMgOH)
853.54	853.37	844	(AlMgOH)
947.16	947.85	936	Vibration Al-O-H stretch
1043.66	1043.76	1026	Vibration Al-O
1119.72	1119.90	1114	Stretch vibration Si-O
2107.89	2111.30	3500-2000	Vibration of O-H surface
3673.95	3673.84	3670	Vibration OH- (Al-O-H stretch surface)

Adsorption band that appeared at the wave number 3673 cm^{-1} was a vibration OH stretching which bonded with Al on the surface [8]. The absorption band at wave numbers 2107 cm^{-1} and 2111 cm^{-1} were from vibration of OH surface groups of H-bending to H_2O [5]. Adsorption band that appeared at the wave number 1119 cm^{-1} , 1043 cm^{-1} , 694 cm^{-1} , 535 cm^{-1} showed vibration of strings Si-O-, vibration Al-O vibration helping O-Si-O, vibration of Si-O-Al(IV), which was a typical absorption of the mineral

kaolinite [6], [7]. The peak of absorption on the region 400 cm^{-1} was the absorption results of the vibration gain of the Si-O while the absorption peaks in the region 515.88 cm^{-1} ; 516.34 cm^{-1} ; 534.87 cm^{-1} and 535.14 cm^{-1} was the absorption results of the vibration gain of the Si-O-Al (octahedral) by Madejova [4] observed in the region of 520 cm^{-1} . In addition, the peak absorption of 800 cm^{-1} is AlMgOH which was the partial substitution of Al octahedral Mg had been observed Madejova [4] in the catchment area 844 cm^{-1} . On the kaolinite and Na-kaolinite there were also observed uptake on the area $778\text{-}797\text{ cm}^{-1}$ which was a typical adsorption of the Si-O quartz [8].

Overall, the results of the spectra analysis of the characterization using FTIR to the adsorbent kaolinite and Na-kaolinite produced the results of the spectra with changes that were not significant, so that there was a semblance of the results of the uptake that were identified in the results of the FTIR characterization of adsorbents kaolinite and Na-kaolinite. This was possible due to the addition of Na^+ that is quite small.

Beside FTIR characterization, adsorbent kaolinite and Na-kaolinite were also characterized using XRD. XRD is an instrument that is used to identify the material of the crystal and non-crystal. XRD is used to determine the field and the characteristics of the crystal structure from a wide variety of samples using the scattering x-rays. Analysis of characterization using XRD was intended to know the material of crystals and non-crystals contained in the adsorbent kaolinite and Na^+ -saturated kaolinite. The results were shown in Figure 2.

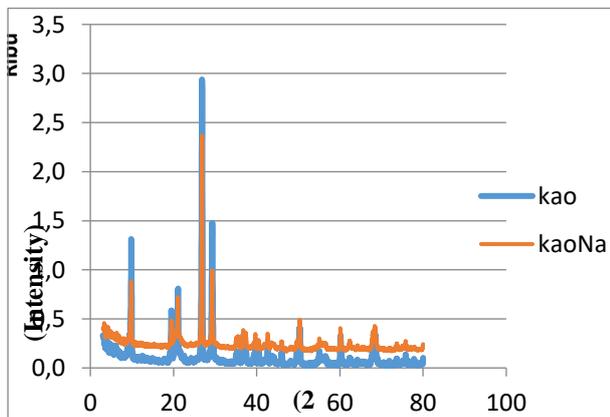


Fig. 2. XRD Diffractogram of Kaolinite and Na^+ saturated Kaolinite

From Figure 2, the spectra of XRD for kaolinite, it showed the main fraction of kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) which was shown at $2\theta = 36.766$; 42.66 ; 45.978 and 54.99 . In addition, there was the fraction of impurities such as muscovit ($\text{KAl}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$) which was shown at $2\theta = 37.355$, calcite (CaCO_3), which was shown at $2\theta = 29.292$, dolomite ($\text{CaMg}(\text{CO}_3)_2$) was indicated at $2\theta = 35.46$; and quartz (SiO_2) which was shown at $2\theta =$

21.054 ; 21.23 ; 26.850 and 39.657 (Nugraha & Kulsum, 2017; Sdiri et al., 2011).

On Na-kaolinite appeared a peak at $2\theta = 12.6^\circ$ which was equivalent to the distance between the layers (d_{001}) of kaolinite of 7.0 \AA . This was the value of d for halloysite (Estiaty & Fatimah, 2014; Supeno, 2009). Halloysite is a mineral which belongs to the members of the kaoliniteite, which can make the distance between layers (d -spacing) enlarged (Istinia et al., 2003). This peak was not detected in the kaolinite before saturated. Cluster of quartz in kaolinite after saturation was also reduced on the value d of 4.18 \AA and 2.153 \AA . This peak corresponded with the peaks of quartz that were detected on the study by Bakri et al. (2008) on the d of 4.20 \AA and 2.34 \AA . This indicates that the saturation of Na^+ resulted in the distance between the layers become larger and the reduced cluster of quartz in the samples shows that the saturation process started successfully reduced the impurities in the kaolinite, mainly the mineral quartz, although not too significant.

Na-kaolinite clay has a reflection intensity that is relatively slenderer at its peak when compared with natural clay. It can be more clearly seen in Figure 2. This shows the crystallinity of the clay Na-kaolinite is in one kind (homocation Na^+) compared to the natural clay that is still relatively heterocation. The reflection intensity of the X-ray diffraction indicates the concentration, the perfection of crystal and the density of the arrangement of the atoms in the crystal. The sleeker the reflection intensity of a material, the better the properties of the crystallites and the more approximate the arrangement of the atoms [15].

B. The Influence of pH and Adsorbent toward the Cation Adsorbed

The results of the adsorption of Cr^{3+} using adsorbents kaolinite and Na-kaolinite showed the additional value of the pH followed by the percentage of the cation adsorbed.

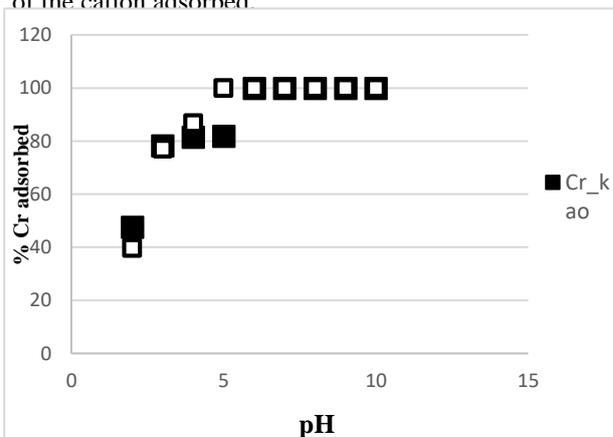
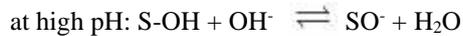
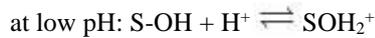


Fig. 3. The Connection % Cr that Adsorbed with the Variation of pH Solution on the Adsorbent Kaolinite and Na^+ -saturated Kaolinite

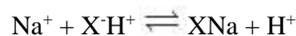
Functional groups on the active sites of clay kaolinite (SiOH) were protonated at low pH, so that forming SiOH_2^+ and experienced deprotonation at high pH so that forming SiO^- . As for the reaction that occurs:



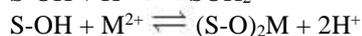
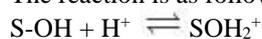
The level of pH could determine protonation-deprotonation of the active cluster that contained in the kaolinite. So at the high pH, the cation had a high affinity to the active cluster. As a result, at high pH could increase the adsorption on the cation [8,9].

In the Figure 3, it can be seen the relationship of the adsorption of Cr^{3+} by the kaolinite and Na-kaolinite adsorbents. On the picture it can be seen that the percentage of Cr^{3+} adsorbed on both adsorbents did not experience a significant difference. Overall, the percentage of Cr^{3+} adsorbed on the adsorbent Na-kaolinite was high compared with adsorbent kaolinite. From both data, it was possible because the saturation of Na^+ cations on the Na-kaolinite adsorbent during the process of sample preparation kaolinite bring about the enlargement of cation exchange capacity by Cr^{3+} cations. The cation radii of Cr^{3+} that is smaller than that of Na^+ can take part significantly on the adsorption on which Cr^{3+} by exchanging the Na^+ as it was reported by Ikhsan et al. [8] that adsorption of cation can occur via cation exchange reaction.

According to Ikhsan et al. [8] the adsorption of cations on kaolinite which had a side of XH and S-OH included two adsorption process which separated and different, they were adsorption at high pH which was the adsorption on the side edges of the S-OH and the other adsorption process was at low pH. Because the ions have two charged-then its ability to replace a cations-charged that is bound by the face of the clay is very large. Therefore, characterization of the adsorption can be explained by ion exchange reactions. This reaction is very likely to occur because the side of the face of the clay are negatively charged due to the substitution of isomorphous. Because in general, in a solution the negative charge it binds to the cation Na^+ derived from the electrolyte used then the side of the face of the clay can be symbolized XH so that ion exchange reactions can be written as follows:



On the addition of Na^+ , on the adsorbent kaolinite causes a change in the side of the face near the beginning XH turned into XNa, even just a little. Side of the face plays a role in the exchange of the charge. The reaction is as follow : [9]



IV. CONCLUSION

The conclusion obtained from the study was the characterization of adsorbents kaolinite and Na-kaolinite using FTIR and XRD did not show significant differences. The percentage of the cation adsorbed in Cr^{3+} by the kaolinite and Na-kaolinite is increasing concurrently with the increase in pH. The adsorption of Cr^{3+} by the adsorbent Na-kaolinite gives the percentage of the cation adsorbed is higher compared with adsorbent kaolinite. This is due to the addition of Na^+ on the adsorbent which is able to eliminate the cluster of quartz and enlarge the distance between the layers in kaolinite.

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