

Effect of Magnetite/Zeolite Synthesis Method on The Adsorption Ability of Co (II) ions

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Abstract: This research aims to obtain an adsorbent in the form of a magnetite/zeolite composite made directly (MZ DM) or indirectly (MZ NDM) and apply it to the adsorption of Co^{2+} ions. The research procedure involved natural zeolite activation, magnetite synthesis, indirect and direct magnetite/zeolite synthesis, and adsorption ability tests on Co^{2+} ions at varying contact times and adsorbate concentrations. The research results show that the XRD data of the magnetite/zeolite composite adsorbent, whether synthesized directly (MZ DM) or indirectly (MZ NDM), has peaks respectively at $2\theta = 35.52^\circ, 53.46^\circ, 62.5^\circ$ and $2\theta = 30.04^\circ, 35.52^\circ, 53.46^\circ, 63.8$. Even though the magnetite peak is relatively low, it dominates the composite adsorbent material so the peaks in the zeolite diffractogram do not appear. From the data, the adsorption efficiency of Co^{2+} ions in the 1-60 minutes and a concentration of 100 - 500 ppm, MZ DM adsorbent is slightly higher but not significantly different from MZ NDM. These data show that the differences in synthesis methods do not affect the character of magnetite/zeolite, and both are very efficient ($> 94\%$) as Co^{2+} ion adsorbents.

Keywords—composite; magnetite/zeolite; cobalt (II); method, adsorption

1. INTRODUCTION

Industrial development in Indonesia is increasing, and regulations regarding industrial waste are becoming increasingly stringent to realize environmentally sound development, so effective and efficient waste processing is very important. The rapid growth of industry not only has positive impacts but also negative impacts. One of them is producing dangerous waste, such as cobalt metal waste, because this metal waste tends to accumulate in organisms, causing various diseases and disorders [1]. Even though cobalt is an essential element needed for growth and reproduction in living things, it can accumulate in the body of organisms if the concentration in water is high. The high concentration of cobalt is dangerous for humans who consume contaminated fish or plants considering that heavy metals are teratogenic and can cause damage to various body organs [2].

Several methods for reducing heavy metal ions include neutralization, precipitation [3], [4], ion exchange [5], biosorption, and adsorption [6], [7], [8]. Adsorption is a popular method for removing heavy metals from wastewater, especially when natural materials are available in large quantities or certain industrial waste products may have the potential to be cheap adsorbents, such as natural zeolites. Zeolite is a unique adsorbent consisting of empty cavities, a specific shape, and pore size. It also has a large surface area, so it is very effective in absorption. This causes zeolite to have

a high adsorption capacity as an adsorbent. Based on chemical, physical, and structural characteristics, zeolites are suitable for applications in various fields, such as adsorption, separation, ion exchange, and catalysts [9]. Therefore, if modified, Indonesian natural zeolite can be used as a material of higher quality and high efficiency.

Along with technological developments, research on zeolite adsorbents is also increasingly developing with modifications to natural zeolites. Natural zeolites can be modified to improve their physical and chemical properties. One modification that can be done is to provide magnetic properties such as Fe_3O_4 . Modifying magnetite on zeolite as an adsorbent can improve its surface and pore properties [10].

Magnetite is a fascinating material to study among other transition metal oxidations. These materials are found in the form of iron oxide minerals in the form of magnetite (Fe_3O_4), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), and hematite ($\alpha\text{-Fe}_2\text{O}_3$). Magnetic iron oxides are magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_4$) [11]. The synthesis of magnetite and maghemite has been carried out using various methods, including sol-gel reaction methods, chemical solutions, sonochemically, and coprecipitation [12].

This research produces magnetite using the coprecipitation method. In previous research, the magnetite/zeolite composite was used as a catalyst in the synthesis of methyl esters [13], chosen because it can produce a new substance that can absorb pollutants and is also magnetic, so it is excellent as a metal ion adsorbent. In previous research magnetite/zeolite has been used as a

methylene blue dye degrader [14], herbicide remover [15], heavy metal remover [16], [17]. Removal of Cu^{2+} , Cd^{2+} , and Pb^{2+} metal ions using magnetite/zeolite made from red mud and coal gangue has been carried out Yan [18], adsorbent in wastewater treatment [19].

Taking advantage of this opportunity, a natural magnetite/zeolite composite synthesis was carried out, where magnetite was synthesized by coprecipitation. This composite was applied as a Co^{2+} ion adsorbent.

2. METHODOLOGY

2.1 Materials and equipment

The materials used are $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ Merck, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ Merck, distilled water, PEG 6000 Sigma Aldrich, natural zeolite, HF 40% Merck, NH_4OH 25% Merck, and $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ Merck.

Meanwhile, the equipment and instruments used were glassware, magnetic stirrers, sieves, analytical balances (Ohaus), BINDER oven, MERCK pH indicator, VULCAN 3-130 Furnace, MAXQ 2000 shaker, Shimadzu 6000 X-RD Diffractometer and Atomic Absorption Spectroscopy (AAS) Perkin Elmer Analyst 200.

2.2 Synthesis of Fe_3O_4

The method for synthesizing magnetite is coprecipitation. Precursors of 20.85 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 40.545 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were put into 80 ml of distilled water, then 300 ml of 10% NH_4OH was added. The mixture was heated at 60°C for 90 minutes with a stirrer speed of 450 rpm. After that, wash it 5-7 times until the 10% NH_4OH smell disappears, then dry it in the oven at 80°C for around 3 hours.

2.3 Indirect Synthesis of magnetite/zeolite Composite (MZ NDM)

The zeolite was activated first by soaking in 1% HF solution for 30 minutes. After washing until the pH is neutral the activated zeolite is dried until it has a constant weight. On the other hand, 15 g of Fe_3O_4 (the result of synthesis in the previous stage) and 15 g of activated zeolite (1:1 w/w) were dissolved in 50 mL of distilled water and added with 15 g of PEG 6000 and then shaken using a magnetic stirrer at room temperature at a speed of 450 rpm for 30 minutes. Then it is filtered and washed until the pH is neutral. Next, it is dried until constant weight. The resulting magnetite/zeolite is coded MZ NDM.

2.4 Direct Synthesis of magnetite/zeolite (MZ DM)

Synthesis magnetite/zeolite composites using the coprecipitation method. A total of 20.85 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 40.545 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 15 g of zeolite, and 15 g of PEG 6000 were put into 100 ml of distilled water, then 300 ml of 10% NH_4OH was added. The mixture was heated at 60°C for 90 minutes with a stirrer speed of 450 rpm. After that, it is washed 5-7 times until the smell disappears. Finally, it is

heated in the oven at 80°C for around 3 hours. The magnetite/zeolite obtained is coded MZ DM.

2.5 Adsorption Ability Test on Co^{2+} ions

The Co^{2+} solution is obtained by dissolving $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ in distilled water. The effect of contact time was tested by adding 1.0 g of MZ DM magnetite/zeolite in 10 ml of 500 ppm Co^{2+} solution and shaking for 1, 10, 15, 30, 45, and 60 minutes. Meanwhile, the effect of adsorbate concentration was tested by adding 1.0 g of MZ DM magnetite/zeolite in 10 ml of Co^{2+} solutions of 100, 200, 300, 400, and 500 ppm. Then, the filtrate liquid was characterized using Atomic Absorption Spectroscopy (AAS) to determine the concentration of Co^{2+} that had been adsorbed. Adsorption of Co^{2+} ions was also carried out using MZ NDM magnetite/zeolite adsorbent.

3. RESULTS AND DISCUSSIONS

The activation of natural zeolite aims to clean pores and remove impurities by modifying its properties, such as increasing surface area and acidity. Activation of zeolite using 1% HF acid produces a zeolite framework that is easy to substitute with metal ions and does not damage the structure. Characterization using XRD will provide information regarding the crystallinity of a particular mineral because each mineral has a characteristic diffractogram pattern. XRD characterization of activated natural zeolite is shown in Figure 1.

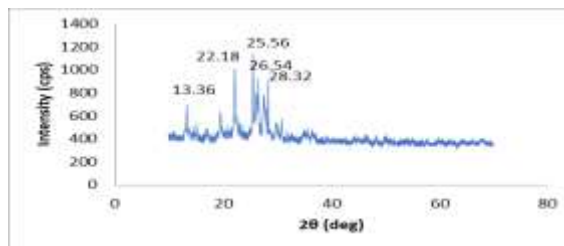


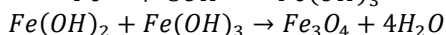
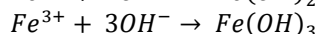
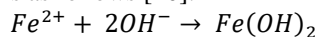
Fig.1 XRD diffraction pattern of activated zeolite

Figure 1 shows the XRD diffractogram of activated zeolite, which is then matched with JCPDS data. The diffraction angle (2θ) of activated natural zeolite is $2\theta = 13.36^\circ$; 22.18° ; 25.56° ; 26.54° ; and 28.32° where at $2\theta = 13.36^\circ$; 22.18° ; and 25.56° indicates the presence of mordenite minerals according to JCPDS no 29-1257, at $2\theta = 26.54^\circ$ shows quartz minerals according to JCPDS no 5-0490 and at $2\theta = 28.32^\circ$ shows clinoptilolite minerals according to JCPDS no 17-0143.

3.1 SYNTHESIZED MAGNETITE

Magnetite iron oxide was used in this study using the coprecipitation method. The formation of magnetite involves bases such as NH_4OH to precipitate [9]. This excess precipitating material can be removed by washing with

distilled water. The reaction for forming Fe_3O_4 by coprecipitation is as follows [20].



The amount of Fe^{2+} and Fe^{3+} consumed is based on a mole ratio of 1:2. The results of 3.24 g black magnetite were obtained, which is in accordance with the calculations. The XRD characterization of the synthetic product can be seen in Figure 2.

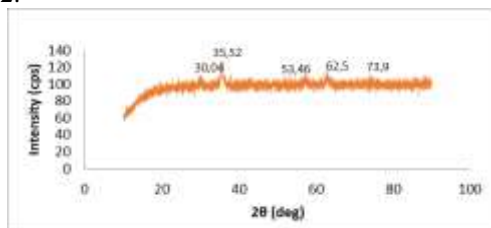


Fig. 2. Diffractogram pattern of synthesized magnetite

The XRD diffractogram in Figure 2 shows a peak at $2\theta = 30.04^\circ, 35.52^\circ, 53.46^\circ, 62.5^\circ,$ and 73.9° . When compared with the Joint Committee of Powder Diffraction Standard (JCPDS) number 89-2355, there is the same peak at $2\theta = 30.08^\circ, 35.43^\circ, 53.41^\circ, 62.52^\circ,$ and 73.97° . Figure 2 shows the types of minerals that contain magnetite.

3.2 MAGNETITE/ZEOLITE SYNTHESIZED INDIRECTLY (MZ NDM)

Magnetite/zeolite modification is carried out so that zeolite recovery in the adsorption process can be carried out more easily and quickly. Magnetite/zeolite is formed from iron oxide which enters the zeolite space through an ion exchange process or is absorbed on the negatively charged surface of the zeolite.

Figure 3 shows changes in the XRD diffractogram of activated natural zeolite (Figure 1) and magnetite/zeolite. This change is quite significant because many peaks disappear and the number of peaks that appear is less than in zeolite before being modified with magnetite. This is due to the presence of magnetite covering the zeolite.

The peak diffractogram can be observed in magnetite/zeolite (MZ NDM) having several peaks at $2\theta = 26.84^\circ, 30.02^\circ, 35.9^\circ, 53.32^\circ,$ and 63.38° . The magnetite/zeolite shows the presence of magnetite and activated zeolite because it is in accordance with the diffractogram of magnetite and activated zeolite, namely in magnetite with a peak of $2\theta = 30.04^\circ, 35.52^\circ,$ and 53.46° while in zeolite with a peak of $2\theta = 26.54^\circ$.

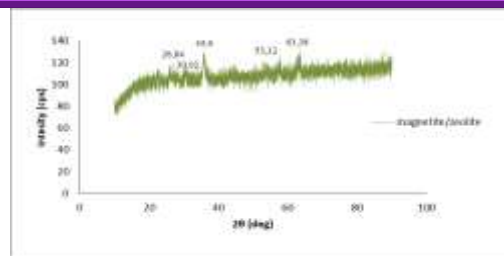


Fig. 3. Diffractogram pattern of indirectly synthesized magnetite/zeolite (MZ NDM)

3.3 MAGNETITE/ZEOLITE SYNTHESIZED DIRECTLY (MZ DM)

Activated natural zeolite was added with PEG 6000 and mixed with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and NH_4OH 10%. This process will produce magnetite/zeolite. Based on the XRD characterization, the peak intensity in magnetite/zeolite synthesized directly is the same as in magnetite/zeolite indirectly. The similarities are indicated by the presence of magnetite and activated zeolite because it is in accordance with Figure 4 that the diffractogram of magnetite and activated zeolite is for magnetite with a peak of $2\theta = 35.52^\circ, 53.46^\circ;$ and 62.5° while in zeolite the peak is $2\theta = 28.32^\circ$.

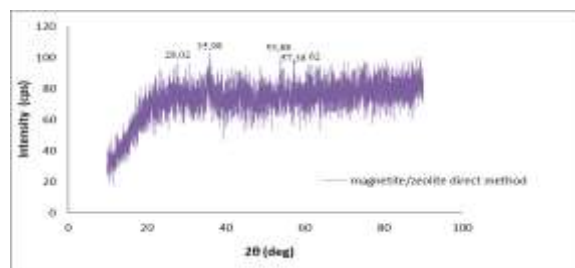


Fig. 4 Diffractogram pattern of directly synthesized magnetite/zeolite (MZ DM)

3.4 IDENTIFICATION COMPOUNDS ADSORPTION ABILITY OF MZ DM AND MZ NDM ON CO^{2+} IONS

To determine the adsorption ability of magnetite/zeolite MZ DM and NDM, the absorption of Co^{2+} ions was tested. The magnetic properties of transition group metals can be seen. The electron configuration of $_{27}\text{Co}^{2+}$ is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$, which shows that Co has several of unpaired electrons, making it easier to be attracted by a magnetic field.

Effect of Contact Time

Contact time greatly influences the diffusion and attachment processes of adsorbate molecules to the adsorbent. Contact time aims to determine whether the adsorbent has reached a saturation point. It has exceeded the equilibrium absorption time so that it can no longer absorb Co^{2+} ions. The relationship between contact time and adsorption efficiency by magnetite/zeolite adsorbents made directly (MZ DM) or indirectly (MZ NDM) can be seen in Figure 5.

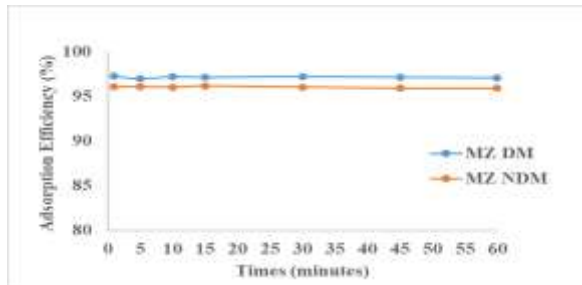


Fig. 5. Adsorption efficiency of magnetite/zeolite MZ DM and MZ NDM towards Co^{2+} ions based on time variations

Figure 5 shows that the adsorption efficiency of Co^{2+} ions by MZ DM and MZ NDM magnetite/zeolite adsorbents is very high. This can be understood because Co^{2+} ions are paramagnetic, thus encouraging more significant adsorption on magnetite/zeolite, which has magnetic properties. The tendency of the two adsorbents was almost the same from the lowest contact time of 1 minute to 60 minutes, indicating a stagnant adsorption percentage, meaning that in a relatively fast and short time, they could adsorb Co^{2+} ions to the maximum. In Figure 5 it can also be seen that the adsorption efficiency of the MZ NDM adsorbent is slightly lower than that of MZ DN. The reason for this data is the possibility that the magnetite particles that have been synthesized, when composited with zeolite, experience agglomeration or are trapped in the zeolite pores, thereby slightly reducing the ability to attract Co^{2+} ions.

Effect of Concentration

Adsorption is an event where a solid substance, usually called an adsorbent, has a tendency to absorb molecules of gas or liquid adsorbate. Apart from contact time, the adsorbate concentration is another factor influencing adsorption. The higher the adsorbate concentration, the more adsorbed it will be. The relationship between the adsorption efficiency of magnetite/zeolite MZ DM and MZ NDM on the concentration of Co^{2+} ions can be seen in Figure 6.

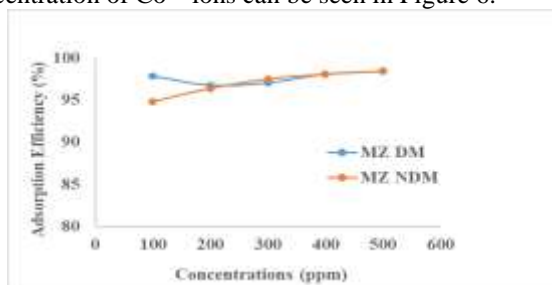


Fig. 6. Adsorption efficiency of magnetite/zeolite MZ DM and MZ NDM towards Co^{2+} ions at various Co^{2+} ion concentrations

Figure 6 shows the relationship between the concentration of Co^{2+} ions as an adsorbate and Co^{2+} ions. In the picture, it can be seen that the difference in adsorption efficiency only occurs at a concentration of 100 ppm. This

difference is relatively small, only around 3%, while it tends to be the same in the concentration range of 200-500 ppm. When the adsorbate concentration is high, the Co^{2+} metal ion, apart from being attracted to the surface by the influence of the magnetic properties of the adsorbent, will also move from the outer surface into the pores of the adsorbent. Thus, the amount adsorbed is greater.

Based on data on the influence of contact time and Co^{2+} ion concentration, it can be said that magnetite/zeolite, whether synthesized directly (MZ DM) or indirectly (MZ NDM), has an excellent ability to adsorb Co^{2+} ions. The two components that make up the adsorbent work together as an adsorbent. Zeolite has a large surface area and a specific pore size to absorb Co^{2+} ions well. Magnetite added/composited to zeolite can provide magnetic properties to encourage interactions between Co^{2+} ions and the adsorbent.

4. CONCLUSIONS

Based on the results and discussion, it can be concluded that magnetite has been successfully composited with zeolite in both MZ DM and MZ NDM. Apart from that, the adsorption capabilities of MZ DM and MZ NDM for Co^{2+} ions in the contact time range of 1-60 minutes and Co^{2+} ion concentrations of 100-500 ppm are also excellent. The formation of the magnetite/zeolite composite adsorbent and its adsorption capacity are not influenced by the manufacturing method, so based on this research, we recommend using the direct method because it is more efficient.

5. ACKNOWLEDGMENT

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