Synthesis and characterization of composite magnetite-bentonite from Indonesian local minerals

M Moersilah*, A Rahman, E Alanas, Y Yuliani and R Rosmalia
Department of Chemistry, Universitas Negeri Jakarta, Jl. Rawamangun Muka, Jakarta, Indonesia

* m.kinasih705@gmail.com

Abstract. The use of modified natural materials as adsorbents has been widely reported. In this study, synthesize, and characterization of magnetite-bentonite composite compositions from local Indonesian minerals was reported. Composites are synthesized by inserting iron ion into the bentonite layers with a mole ratio of 1:1 Fe$^{2+}$/Fe$^{3+}$ ion; 1:1.5; and 1:2, hereinafter referred to as composite A, composite B, and composite C respectively. All composites were then calcined at a temperature of 400°C for 1 hour. The iron oxide formed in the area between bentonite layers has a magnetite structure and has high thermal stability. This can be seen from the diffraction pattern obtained from XRD analysis. The specific surface area of the composite also increased compared to pure bentonite. Before being modified, pure bentonite had a surface area of 47.824 m$^2$/g, and after the insertion of iron oxide, there was an increase. Composite A is 87.482 m$^2$/g composite B is 83.774 m$^2$/g, and composite C is 98.336 m$^2$/g.

1. Introduction

The rapid development of the industrial sector, in addition to providing various facilities for humans, for example, efficiency of time, energy, and cost, it also has a negative impact on human life itself, for example, water pollution by coloured organic compounds or heavy metal ions. The problem of waste management is a significant problem that must be resolved by various groups, both industry, government, and society. Lack of systematic and practical handling of this problem can cause huge losses [1]. An innovative technology that gets special attention to solve environmental problems is to use magnetic materials. Magnetic particles can be used to adsorb contaminants in water or gas. After the adsorption is carried out, the adsorbent can be separated from the medium through a simple magnetic process. Some examples of this technology are the use of magnetic particles to accelerate the coagulation of impurities [2], the use of magnetic coatings and polymers such as resins to remove radionuclides, and the use of polymers coated with magnetic particles for handling oil spills [3].

However, all these materials have a small surface area and low adsorption capacity, thereby limiting their use. New developments to obtain magnetic composites with high surface area and adsorption capacity are carried out by combining activated carbon of iron oxide or iron oxide clay as a composite to remove contaminants in water. The potential for clay reserves in Indonesia is enormous and is spread in almost all regions, especially on the islands of Java, Sumatra, and Kalimantan, but their utilization is not yet optimal. Clay can be defined as a mixture of sand, dust particles, and parts of clay that have different characteristic properties in roughly the same size. One of the characteristics of clay particles is
having a positive ionic charge that can be exchanged. This material has absorbency with changing humidity levels. Clay has a considerable surface area [4].

Pure clay has a low price and provides materials that function as cation exchangers, which are often used to adsorb metal, organic, and inorganic contaminants. This is closely related to the value of clay adsorption capacity, which can also be referred to as the Cation Exchange Capacity (CEC). CEC value of clay depends on high surface area and negative charge on the structure, which can attract and hold bulky metal cations or organic compounds [5]. Bentonite clay is a type of rock that contains many montmorillonite minerals. Bentonite is a nanometer-sized absorbent material, so with its size the bentonite will have a larger surface area and high absorption. However, with the tiny size of the bentonite, the bentonite tends to form a stable suspension in water. So, the use of bentonite as an absorbent will have difficulty at the end of the process, namely when taking back bentonite, which has absorbed contaminants. One solution to solve this problem is the incorporation of bentonite with iron oxide [6].

The structure of bentonite will intercalate when combined with metal oxides, where the oxide will be between the bentonite plane sheets. Combining iron oxide with bentonite will produce a new material that has two main properties. Namely, adsorption properties derived from bentonite, used to absorb various contaminants in water, and are magnetically originating from magnetic particles that are composite in the bentonite structure network. This magnetic property is used to reassemble composite particles dissolved in a waste liquid by using the principle of simple magnetization. As a result of this process, the surface area will increase [7]. In previous studies, Fe was chosen as an insertion ion and natural clay as a carrier. This research was conducted by Alekseeva, et. al., who successfully synthesized iron oxide clay composites from FeCl$_3$ and FeSO$_4$ solutions by varying the weight of iron oxide clays and using H$_2$ reductors. From this study, information was obtained that the most optimum iron oxide clay removes contaminants in water is iron oxide clay with a weight ratio of 2:1. In this research, the synthesis of bentonite iron oxide composites is reported. This composite synthesis was carried out by the precipitation (precipitation) method of a mixture of Fe$^{3+}$ and Fe$^{2+}$ solution [8].

2. Methods
Magnetite synthesized by dissolving iron (II) sulfate into aqua DM with a temperature of 70°C to form a yellow solution. Then added concentrated ammonia. If a greenish-blue solution formed, the result of the destruction of Fe$_2$O$_3$ solution added. The resulting black solution is then allowed to stand for some time before filtering. After filtering, the precipitate obtained was washed with aqua DM to remove sulfate ions (SO$_4^{2-}$). If it is sulphate free, the precipitate dried in an oven at 120°C. The black solid that has been dried and then crushed and sieved using a 100-mesh sieve.

3. Results and discussion
Montmorillonite-iron oxide composites are made through several stages, the stage of iron oxide insertion in the space between layers of montmorillonite (pilarization), the cation exchange stage on the surface of montmorillonite sheets with an iron metal polycation, and the stage of iron oxide precipitation with the addition of concentrated ammonia in previous studies [8]. This base replacement is intended to control the size of the iron oxide that will form.

This intercalated polycation of ferrous metal will replace cations that are interchangeable between montmorillonite layers and are easily exchanged with calcination of iron metal polycation will turn into oxides (iron oxides) which can support the montmorillonite layers. This formation process is carried out at a temperature of 70°C because an increase in temperature will provide a supply of thermal energy to carry out these various stages. Iron ions that have large kinetic energy will be more easily diffused between layers of montmorillonite, which have undergone swelling due to the dissolution process in water. Likewise, the cation exchange process on the surface of montmorillonite will increase so that the more number of Fe ions bound to the surface of montmorillonite, these ions will then undergo precipitation with the addition of NH$_3$ bases where nucleation of magnetic particles tends to occur more rapidly at higher temperatures high.
Characterization using XRD method gives information on the size of iron oxide formed in the montmorillonite interlayer. The results obtained can be used to determine the magnitude of the shift in distance between silicate clay layers. If there is intercalation, a shift in the distance between layers will be indicated by changes in the basal spacing $d_{001}$. If the distance between the layers increases, the surface area will also increase [9]. The peaks that indicate the presence of montmorillonite mineral are peaks 5.91°; 19.997°; 35.066°; 54.472°; and 62.061°. While the typical peak of magnetite is shown at 20 = 35.770° and 20 = 35.671° is the typical peak for maghemites [10]. By using the XRD method, the composite gives a typical diffractogram pattern.

**Figure 1.** XRD powder diffractogram of composite iron oxide montmorillonite pattern of natural iron ore, non-calcined bentonite-iron oxide composites, calcined bentonite-iron oxide composites, calcined iron oxide synthesis. The stars referred to Fe$_3$O$_4$ peaks diffraction.

The diffractogram shows that the composite did not show any peaks at 2θ = 5.91° and 2θ = 19.92°, which is a characteristic of montmorillonite minerals. This indicates the possibility of forming a house of cards that can be observed at a small angle of 2θ with low intensity. The structure of the card house is shown in Figure 1. With the formation of the card house structure, this intercalation product has a mesoporous structure (Karna Wijaya, 2005). The XRD results will be strengthened by BET data.

**Table 1.** Specific Surface Area and Pore Diameter Data for Iron Oxides, Bentonites, Composites A, B, and C.

| Sample         | Surface area (m$^2$/g) | Pore diameter (Å)  |
|---------------|------------------------|--------------------|
| Iron oxide    | 21.533                 | 1.46766×10$^{-2}$  |
| Bentonit      | 47.824                 | 6.06321×10$^{-1}$  |
| Composite A   | 87.482                 | 1.44049×10$^{-2}$  |
| Composite B   | 83.774                 | 1.28408×10$^{-2}$  |
| Composite C   | 98.361                 | 1.14796×10$^{-2}$  |

Composites showed a significant peak in the 2θ region of 35.657°. This informs that the iron oxide formed is maghemite. This change can occur due to the calcination process. The X-ray diffraction pattern of montmorillonite-iron oxide composite in Figure 1, shows an amorphous diffraction pattern with no crystallinity. Amorphous diffraction patterns are shown by vast peaks. The results of the characterization of montmorillonite-iron oxide composites have indicated that the material has a size on the nanometer scale. This is consistent with the theory that X-ray diffraction patterns are extensive in material, so there are crystals that are very small in size. This statement is reinforced by the results of...
calculations using the Scherrer equation. The size of the iron oxide crystals formed in the composite can be known to be 364.5361 nm.

**Figure 2.** The isothermal adsorption curve of nitrogen-BET gas by iron oxide (red), bentonite (green), composite A (blue), composite B (purple), and composite C (brown).

The condition of iron oxide insertion in the space between the montmorillonite silicate layers was also observed in the results of the specific surface area analysis presented in Table 1. This specific surface area was obtained based on the determination of the monolayer capacity which showed how many molecules could be adsorbed on the surface of the solid material. In pillared montmorillonite, an increase in surface area by the N\textsubscript{2} gas adsorption method is usually used as a criterion for the success of the pilarization process [11].

**Figure 3.** BJH pore size distribution curves for bentonite (series 1), iron oxide (series 2), composite A (series 3), composite B (series 4), and composite C (series 5).
The montmorillonite-iron oxide composite has a larger specific surface area compared to montmorillonite before modification (Table 1). This happened because, in addition to the pilarization process, a card house structure was also formed as is known from the XRD data. The pilarization process results in the emergence of new pores with micropore size, while the structure of the card house causes a meso-sized pore that contributes to an increase in specific surface area.

4. Conclusion

The process of iron oxide intercalation has been successfully synthesized, proven by BET, and XRD data. The iron oxide, the form of maghemite in the interlayer gallery and surface of montmorillonite, has an average crystal size of about 364.5361 nm. The surface area of pure montmorillonite increased from 47,824 m$^2$/g to 67,850 m$^2$/g after being intercalated by iron oxide.

Acknowledgement

We thank the LPPM for supporting fund BLU POK Fakultas Matematika dan Ilmu Pengetahuan Alam Universitas Negeri Jakarta, grant number: 50/SPK PENELITIAN/5.FMIPA/2019.

References

[1] Pandey S 2017 A comprehensive review on recent developments in bentonite-based materials used as adsorbents for wastewater treatment J. Mol. Liq. 241 1091–113
[2] Mohammed A A and Isra’a S S 2018 Bentonite coated with magnetite Fe3O4 nanoparticles as a novel adsorbent for copper (II) ions removal from water/wastewater Environ. Technol. Innov. 10 162–74
[3] Bajpai A, Sharma M and Gond L 2019 Nanocomposites for Environmental Pollution Remediation Sustainable Polymer Composites and Nanocomposites (Springer) pp 1407–40
[4] Yan L, Li S, Yu H, Shan R, Du B and Liu T 2016 Facile solvothermal synthesis of Fe3O4/bentonite for efficient removal of heavy metals from aqueous solution Powder Technol. 301 632–40
[5] Van Lam P, Duong N B, Trang Q T T and Tuan V A 2018 Removal of Pb2+ and Cd2+ ions from aqueous solutions using Fe3O4/Bentonite nanocomposite Vietnam J. Chem. 56 617–22
[6] Chang J, Ma J, Ma Q, Zhang D, Qiao N, Hu M and Ma H 2016 Adsorption of methylene blue onto Fe3O4/activated montmorillonite nanocomposite Appl. Clay Sci. 119 132–40
[7] Caglar B, Guner E K, Keles K, Özdokur K V, Cubuk O, Coldur F, Caglar S, Topcu C and Tabak A 2018 Fe3O4 nanoparticles decorated smectite nanocomposite: Characterization, photocatalytic and electrocatalytic activities Solid State Sci. 83 122–36
[8] Alekseeva O V, Rodionova A N, Bagrovskaya N A and Agafonov A V 2016 Synthesis, structure, and properties of a bentonite–magnetite composite Prot. Met. Phys. Chem. Surfaces 52 819–24
[9] Alonso-Dominguez D, Pico M P, Álvarez-Serrano I and López M L 2018 New Fe2O3-Clay@ C nanocomposite anodes for Li-ion batteries obtained by facile hydrothermal processes Nanomaterials 8 808
[10] Ayazi Z, Khoshhesab Z M and Norouzi S 2016 Modeling and optimizing of adsorption removal of Reactive Blue 19 on the magnetite/graphene oxide nanocomposite via response surface methodology Desalin. Water Treat. 57 25301–16
[11] Lu H, Wang J, Li F, Huang X, Tian B and Hao H 2018 Highly efficient and reusable montmorillonite/Fe3O4/humic acid nanocomposites for simultaneous removal of Cr (VI) and aniline Nanomaterials 8 537