Structure modification of natural zeolite for waste removal application

W B Widayatno
Research Center for Physics, Indonesian Institute of Sciences, Tangerang Selatan, Indonesia

E-mail: wahy012@lipi.go.id

Abstract. Tremendous industrialization in the last century has led to the generation of huge amount of waste. One of the recent hot research topics is utilizing any advance materials and methods for waste removal. Natural zeolite as an inexpensive porous material with a high abundance holds a key for efficient waste removal owing to its high surface area. However, the microporous structure of natural zeolite hinders the adsorption of waste with a bigger molecular size. In addition, the recovery of natural zeolite after waste adsorption into its pores should also be considered for continuous utilization of this material. In this study, the porosity of natural zeolite from Tasikmalaya, Indonesia, was hydrothermally-modified in a Teflon-lined autoclave filled with certain pore directing agent such as distilled water, KOH, and NH4OH to obtain hierarchical pore structure. After proper drying process, the as-treated natural zeolite is impregnated with iron cation and heat-treated at specified temperature to get Fe-embedded zeolite structure. XRD observation is carried out to ensure the formation of magnetic phase within the zeolite pores. The analysis results show the formation of maghemite phase ($\gamma$-Fe$_2$O$_3$) within the zeolite pore structure.

1. Introduction
Vast industrialization in the last decades has brought various emerging environmental problems around the globe. One of the big issue to be concerned is the water quality which is getting worse due to the contamination of heavy metals, oil spills, solid and liquid wastes, as well as bacteria. The socio-economic impacts caused by the degradation of water quality, such as the losses of agricultural production, the damage of tourism potential, the decline of public health quality, the ecosystem injury, and the potential of biological extinction, have been studied by many researchers [1 - 4]. To date, many studies and technological approaches have been also carried out to diminish the problem sources, as well as to suppress the occurred effects [3, 5 - 8].

Utilizing porous materials as an adsorbent to capture the pollutant from the water is one popular approach for improving the water quality [6, 8 - 11]. The pollutant is expected to be trapped within the pores of the materials herein. Some studies demonstrate the powerful performance of this trapping mechanism by developing new kind of porous materials [12 - 16]. Nevertheless, some issues such as the separation difficulty of the adsorbent from the solution, the complex synthesis process, and the indispensable production cost, need to be addressed in order to meet the economic value [9].

This study was conducted to address the above problems. Natural zeolite from Tasikmalaya area in Indonesia, was utilized and structurally-modified to obtain the maghemite phase ($\gamma$-Fe$_2$O$_3$). Previous
studies elaborated the utilization of natural zeolite for removal of heavy metals from water [17-19]. However, their works do not include the insertion of magnetic phase. It is expected from this study that the magnetic properties of this phase can facilitate easier separation of the adsorbent from the solution.

2. Materials and methods
Natural zeolite from Tasikmalaya region in West Java, Indonesia, was used as a parent material. In order to study the effect of calcination environment on the formation of maghemite phase, the parent (non-treated) material was subjected into 5 wt.% iron nitrate solution prior to calcination in air and inert (N₂) gas stream, both at 500 °C for 2h. The parent and as-calcined samples were then marked as parent, non-treatment (NT), and non-treatment with gas (NTG), respectively.

The pore structure modification of the zeolite was carried out in a Teflon-lined autoclave filled with different pore directing agents (PDA), i.e. distilled water, 1M KOH, and 1M NH₄OH, at 200 °C for 24 h. Herein, the zeolite was hanged above the PDAs solution instead of immersed into it, to ease the collection process while avoiding the uncontrolled structural change of the zeolite. Figure 1 illustrates the arrangement during the modification process. In the case of base-treated samples, the collected samples were washed using distilled water until neutral. The neutralized samples were then dried overnight in a drying oven at 110 °C. The dried samples were then also subjected into 5 wt.% iron nitrate solution and calcined at 500 °C for 2 h to obtain the magnetic phase. For ease, the parent and treated zeolites were marked as parent, Z-H₂O, Z-KOH, and Z-NH₄OH, respectively.

![Figure 1. Setup arrangement for modification process.](image)

The structure of parent, NT, NTG, and treated zeolites were compared by X-ray Diffraction (Smartlab, Rigaku, Japan). The morphology and pore distribution of the samples were qualitatively examined by observing Field Effect Scanning Electron Microscope (FE-SEM JIB-4610F, JEOL, Japan) images.

3. Results and discussion

3.1. Effect of calcination environment
While unexpected due to its low magnetic properties, hematite (α-Fe₂O₃) is the stable form of iron oxide up to around 600 °C in air. Thus, the strict control of oxygen amount is necessary to obtain iron oxide phase with a better magnetic properties (FeO, Fe₃O₄, γ-Fe₂O₃, etc.). Some previous studies utilized careful impregnation with lower post-treatment temperature to avoid the formation of hematite [7, 20]. Herein, the elevated post-treatment temperature with different environment was used in order to observe its effect on the formation of iron oxide phase.
Figure 2 shows the XRD profile of parent zeolite as well as calcined Fe-impregnated zeolite (without prior treatment) in air and N$_2$ gas stream, denoted as NT and NTG, respectively. The strong maghemite peak at (220) was obtained by utilizing N$_2$ gas stream. Meanwhile, the weak maghemite peak at (440) was obtained without gas stream. In addition, some unreacted iron phase was observed. This phenomenon was not observed when using N$_2$ stream, which is likely due to the limited reaction of N$_2$ and residual nitrate from the precursor (equation 1). This reaction reduces the reaction of nitrate and oxygen, as well as lets some oxygen finish the oxidation of iron phase.

$$2\text{Fe(NO}_3\text{)}_3 + 1.25\text{N}_2 \xrightarrow{\text{heat}} \gamma\text{-Fe}_2\text{O}_3 + 6.5\text{NO}_2 + 2\text{NO}$$  \hspace{1cm} (1)

Figure 2. X-Ray diffraction profile of parent (a), NT (b), and NTG (c) zeolites in different observation angle range.

3.2. Effect of zeolite treatment

Figure 3 depicts the XRD profile of parent and Fe-impregnated zeolite (NT, Z-H$_2$O, Z-KOH, and Z-NH$_4$OH) after calcination at 500 °C for 2 h in air. It can be seen that prior treatment of zeolite in a water, KOH, as well as NH$_4$OH steam provides the similar result with that of NTG zeolite. The expected maghemite phase can be obtained easily. Moreover, there is no trace of unreacted iron phase within those samples, providing cheaper alternative for getting pure maghemite phase without expensive continuous gas stream.

Z-H$_2$O sample possess maghemite phase with many crystal orientation. The multi-crystal orientation was also observed for Z-KOH, with less amount of crystal orientation compared with that of Z-H$_2$O. Interestingly, by treating zeolite with NH$_4$OH steam, one can obtain single-orientation maghemite phase. This is likely due to the nature of NH$_4$OH as a “mild” pore structure-directing agent which can provide homogeneous pore structure as a host for the growth of maghemite crystal.

Figure 4 shows the electron micrograph comparison of Z-H$_2$O, Z-KOH, and Z-NH$_4$OH, respectively. It is clear that the grain morphology of Z-H$_2$O as well as Z-KOH is qualitatively rough compared with that of Z-NH$_4$OH. In addition, the morphology is quite heterogeneous with some spotted agglomerated particles. On the contrary, the Z-NH$_4$OH shows more homogeneous distribution with a much longer rod-like particles shape. This is in line with the XRD result which demonstrates
the strong correlation between the smooth and more homogeneous morphology with that of the formation of single-orientation maghemite phase.

Figure 3. X-Ray diffraction profile of parent (a), NT (b), Z-H2O (c), Z-KOH (d), and Z-NH4OH (e) zeolites in different observation angle range.
Figure 4. Electron micrograph of (a) Z-H$_2$O, (b) Z-KOH, and (c) Z-NH$_4$OH.

4. Conclusions
The structure modification of natural zeolite from Tasikmalaya, Indonesia, to obtain the Fe-embedded zeolite structure has been carried out successfully. XRD observation shows the important role of calcination environment to obtain pure maghemite phase. Meanwhile, the utilization of different pore structure-directing agent demonstrates its effect on the formation of single-orientation maghemite phase with more homogeneous morphology and size distribution. Considering the lower environmental impact and commercial price of NH$_4$OH than that of KOH, utilizing NH$_4$OH could be the best option for further studies to get single-orientation magnetic zeolite.

Acknowledgments
The author would like to thank Ms. Galih Padmasari from State Islamic University of Yogyakarta (UII – Yogyakarta) for helpful assistance during the experiment.

References
[1] Peters N E and Meybeck M 2000 Water Int. 25 185
[2] Reddy V R and Behera B 2006 Ecol. Econom. 58 520
[3] Chang S E, Stone J, Demes K and Piscitelli M 2014 Ecol. Soc. 19 26
[4] Beyer J, Trannum H C, Bakke T, Hodson P V and Collier T K 2016 Marine Poll. Bull. 110 28
[5] Muyibi S A, Ambali A R and Eissa G S 2008 Water Resour. Manag. 22 485
[6] Adebajo M O, Frost R L, Kloprogge J T, Carmody O and Kokot S 2003 J. Porous Mater. 10 159
[7] Oliveira L C A, Petkowicz D I, Smaniotto A and Pergher S B C 2004 Water Res. 38 3699
[8] Zhang W, Liu N, Cao Y, Lin X, Liu Y and Feng L 2017 Adv. Mater. Interfaces 4 1600029
[9] Mehta D, Mazumdar S and Singh S K 2015 Journal of Water Process Engineering 7 244
[10] Misaelides P 2011 Microporous Mesoporous Mater. 144 15
[11] Shi W, Shao H, Li H, Shao M and Du S 2009 J. Hazard. Mater. 170 1
[12] Dabwan A H A, Imai D, Kaneco S, Senmatsu I, Nakahama K, Katsumata H, Suzuki T and Ohta K 2008 J. Environ. Sci. 20 172
[13] Amin M N, Kaneco S, Kato T, Katsumata H, Suzuki T and Ohta K 2008 Chemosphere 70 511
[14] Alsbaiee A, Smith B J, Xiao L, Ling Y, Helbling D E and Dichtel W R 2016 Nature 529 190
[15] Yang R X, Wang T T and Deng W Q 2015 Scientific Reports 5 10155
[16] Wang J, Zhang P, Liang B, Liu Y, Xu T, Wang L, Cao B and Pan K 2016 ACS Appl. Mater. Interfaces 8 6211
[17] Erdem E, Karapinar N and Donat R M 2004 J. Colloid Interface Sci. 280 309
[18] Wingenfelder U, Hansen C, Furrer G and Schulin R 2005 Environ. Sci. Technol. 39 4606
[19] Taamneh Y and Sharadqah S 2017 Appl. Water Sci. 7 2021
[20] Gutiérrez M, Escudey M, Escrig J, Denardin J C, Altbir D, Fabris J D, Cavalcante L C D and García-González M T 2010 Clays Clay Miner. 58 589