Research Article

Witri Wahyu Lestari*, Irwinsyah, Teguh Endah Saraswati, Yuni Krisyuningsih Krisnandi, Ubed Sonai Fahrudin Arrozi, Eddy Heraldy, Grandprix T. M. Kadja

Composite Material Consisting of HKUST-1 and Indonesian Activated Natural Zeolite and its Application in CO\(_2\) Capture

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Abstract: In this study, composite materials consisting in HKUST-1 [Cu\(_3\)(BTC)\(_2\)] (BTC: benzene 1, 3, 5-tricarboxylate) and an Indonesian activated natural zeolite (ANZ) from Klaten, Central Java, were successfully prepared and characterized. The purpose of this research was to determine the effect of the combination of these two materials on the characteristics of the composite as well as to determine its CO\(_2\) gas adsorption ability. The composite HKUST-1-ANZ (ANZ@HKUST-1) was synthesized in two different techniques, i.e., solvothermal and sonication method. The obtained materials exhibited X-ray diffractogram characteristics of both HKUST-1 and ANZ. Fourier-transform infrared (FTIR) analysis showed a combination of peaks from HKUST-1 and ANZ, i.e., peaks assigned to carboxylate groups and bonds between Cu-O from HKUST-1, as well as N-H bending and SiO from ANZ. The addition of ANZ to HKUST-1 decreased its surface area and nitrogen sorption capacity. Application of the composites as CO\(_2\) capture materials shows their CO\(_2\) adsorption capacity is increased (ca. 12%) comparing to the initial materials.

Keywords: HKUST-1, ANZ, composite, adsorption, CO\(_2\) capture

1 Introduction

Global warming is a major environmental issue faced by our planet. According to the Intergovernmental Panel on Climate Change (IPCC) data, in the 21st century, the earth’s temperature will increase between 1.4 and 6.4°C [1]. One of the reasons for the earth’s temperature increase is overabundance of CO\(_2\) gas. Currently, around 80% of the world’s gas emissions are originated from CO\(_2\), and this will continue to increase in line with developments in the transportation and industrial sectors [2,3]. Several methods have been developed to reduce CO\(_2\) emissions, one of which is adsorption with porous materials such as metal-organic frameworks (MOFs), zeolites, activated carbon, and mesoporous silica [4-6].

As a class of hybrid porous materials constructed from metal ions or clusters and organic linkers, MOFs have been applied to gas storage and capture, including CO\(_2\) [2]. Some MOFs, such as MOF-177 [Zn\(_x\)(BTC)\(_y\)] (BTC: benzene 1,3,5 tribenzoate) [7], MIL-101 [Cr(O)-(BDC),\(\text{H}_2\text{O}\)] (BDC: benzene 1,3,5-tricarboxylate) [8], HKUST-1 [Cu\(_3\)(BTC)\(_2\)] (BTC: benzene 1,3,5-tricarboxylate) [9], and MgMOF-74 [Mg(dobdc)]...
(dobdc: 2,5 dioxide 1,4-benzenedicarboxylate), have been reported as CO$_2$ gas adsorbents [10]. However, MOFs possess some disadvantages such as having weak interactions with CO$_2$, high sensitivity to water and moisture in some cases, leading to the active sites of MOFs to be able to connect easily to water [11,12]. This phenomenon reduces the adsorption capacity of CO$_2$. Therefore, it is necessary to combine MOFs with other materials (including porous materials) to increase their stability and create additional binding sites. Zhu et al. synthesized HKUST-1/MCF (mesocellular foam) to be employed as CO$_2$ adsorbents. This composite can increase the adsorption capacity of CO$_2$ gas up to 3.89 mmol/g at a pressure of 1 bar [13]. HKUST-1 was also combined with graphene oxide (GO) by Liu et al. and applied as an adsorbent of CO$_2$ and CH$_4$ gases where the CO$_2$ gas adsorption capacity reached 8.26 mmol/g at 273 K and 1 atm [14]. Another MOF composite, Cu-BDC with MCM-41, has a Si-O group similar to zeolite; the CO$_2$ adsorption of Cu-BDC with MCM-41 composite reached 5.5 mmol/g at a pressure of 20 bar [15].

Natural zeolite, with resource capacity of 447,490,160 tons, is, possibly, the largest mineral commodity in Indonesia. The abundance of this material is due to volcanic slabs located from Sumatra to Sulawesi. On the island of Java, the distribution of zeolites has reached 285,595,000 tons in 2008 [16]. According to Kusdarto et al., natural zeolites can be used as CO$_2$ gas adsorbents, therefore the utilization of local materials will enhance the efficacy of natural zeolites in Indonesia [16,17]. The incorporation of zeolites into MOFs results in a new material feature that is expected to enhance gas adsorption capability due to suitable pore size arrangement, surface area, and the incorporation of the additional active sites of zeolites and MOFs. The presence of an open metal site on HKUST-1 is attractive for gas-binding. Moreover, active zeolites also contain active groups of ammonium (NH$_4^+$) and hydroxyl (-OH) groups that potentially bind to gases. To the best of our knowledge, there have been no reports on composite materials fabricated from activated natural zeolite from Indonesia and MOFs to date. Therefore, in this study, we have investigated the influence of various percent additions (compositions) of active natural zeolite (ANZ) to HKUST-1, synthesized by both solvothermal and sonication methods to form the composite material ANZ@HKUST-1, on the material’s physical and chemical properties and on its application in CO$_2$ gas capture.

2 Materials and Methods

2.1 Materials

All chemicals and reagents used were of analytical grade and were used as purchased without any further purification. Natural zeolite was obtained from Klaten, Central Java, Indonesia (particle size 170/240 mesh). Benzene-1,3,5-tricarboxylic acid (95%) and Cu(NO$_3$)$_2$·3H$_2$O 99% were commercially obtained from Sigma Aldrich, Germany. Ethanol (p.a.) 96%, NaOH and NH$_4$Cl (p.a.) (98%) were purchased from Emsure. HCl 37% (Mallinckrodt) was used as received.

2.2 Procedures

2.2.1 Synthesis of HKUST-1 [Cu$_3$(BTC)$_2$(H$_2$O)$_3$], C$_{18}$H$_6$Cu$_3$O$_{12}$, (BTC: benzene 1, 3, 5-tricarboxylate)

The solvothermal method was used to synthesize HKUST-1 according to a previously reported procedure [18]; HKUST-1 was activated at 473 K for 2 h before the CO$_2$ adsorption test.

2.2.2 Preparation of Activated Natural Zeolite (ANZ)

The activation of natural zeolite was performed according to a modified literature procedure [19]. Natural zeolite (10 g) was heated under reflux with HCl (250 mL, 6 M) for 30 minutes at 323 K. The mixture was subsequently filtered and neutralized. The treated zeolite was then dried at room temperature for 12 h and was allowed to dry in an oven at 403 K for 3 h. Thereafter, the dried zeolite was further heated under reflux with NH$_4$Cl (250 mL, 1 M) for one week at 363 K. After completion, the mixture was filtered and neutralized with purified water, resulting in the active natural zeolite (ANZ), which was further activated at 403 K for three hours.

2.2.3 Preparation of the Composite ANZ@HKUST-1

The ANZ@HKUST-1 composite was synthesized in situ based on a modified procedure [20]. During HKUST-1 synthesis, Cu(NO$_3$)$_2$·3H$_2$O and H$_3$BTC ligand were added to zeolite in percentages of 2, 5, 20, and 50 wt% (in this case, ANZ acts as a filler). Meanwhile, ex-situ synthesis of ANZ@HKUST-1 was conducted based on a modified procedure
The ANZ@HKUST-1 composite was synthesized using the sonication method in which ANZ was added to pre-synthesized HKUST-1 in the proportion of 80, 95, and 98 wt% (in this case HKUST-1 served as filler), and then ethanol (20 mL) was added, and the mixture was sonicated for 1 hour at room temperature.

2.3 Materials Characterization

The HKUST-1, natural zeolite (NZ), activated natural zeolite (ANZ), and ANZ@HKUST-1 composites were analyzed by X-ray diffraction (XRD; Rigaku Miniflex 600 Benchtop) to observe the crystallinity and phase purity of the materials. Differential thermal/thermogravimetric analysis (DT/TGA; STA Linseis PT-1600) with a heating rate of 20°C/min to a temperature of 900°C under nitrogen flow was used to analyze the thermal stability of the materials. The morphologies and particle sizes of the materials were measured using scanning electron microscopy (SEM; FEI Inspect-S50) equipped with an energy dispersive X-ray (EDX) analyzer. The surface area, porosity, and pore distribution were estimated from nitrogen sorption isotherm measured by Quadrasorb Evo, Quantachrome Instruments at 77K. The sample was activated for 12 h prior to measurement. The functional groups of the materials were analyzed using Fourier-transform infrared (FTIR) spectroscopy (Shimadzu IR Prestige-21) with a KBr background at wavenumber 400–4000 cm\(^{-1}\) in the air.

2.4 \(\text{CO}_2\) Adsorption Tests on HKUST-1, ANZ, and ANZ@HKUST-1

\(\text{CO}_2\) adsorption was measured using the volumetric method according to a literature procedure [22, 23] based on the acidimetric titration principle using NaOH. \(\text{CO}_2\) gas was flowed to the sample through a flow meter at 50 mL/min within 10 minutes at gas pressure of 2 bars. \(\text{CO}_2\) gas is an acid oxide that is not adsorbed by the sample and will react with the base solution to form salt and water, as shown in equation 1.

\[
\text{CO}_2(g) + 2 \text{NaOH (aq)} \rightarrow \text{Na}_2\text{CO}_3 (aq) + \text{H}_2\text{O (l)} \tag{1}
\]

The resulting carbonate salt was then titrated with HCl solution. In our previous work [23], phenolphtalein indicator was added into the carbonate solution followed by titration using HCl solution; then continued by addition of methyl orange indicator and again titrated with HCl solution. The required HCl titration volumes in the first and second stages were recorded. The amount of residual \(\text{CO}_2\) was determined from the conversion of the difference in the amount of HCl required for the titration of Na\(\text{CO}_3\) in the first and second stages. The remaining \(\text{CO}_2\) of the sample was then compared with the remaining \(\text{CO}_2\) of the blank to determine the amount of \(\text{CO}_2\) adsorbed. The adsorption test for the \(\text{CO}_2\) blank was determined without the sample (adsorbent).

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and Discussion

3.1 Materials Characterization

The X-ray diffractograms of the HKUST-1 and ANZ@HKUST-1 composites were compared with standard XRD patterns of HKUST-1 (CCDC No. 112954) [24] and ANZ. The XRD pattern of ANZ was simultaneously compared with mordenite (ICSD No. 9632) and Clinoptilolite (JCPDS No. 39-1383) as shown in ESI Figure S1. The natural zeolite from Klaten is typically composed of mordenite and clinoptilolite [25], however, after the activation process, the mordenite phase becomes dominant [26]. The diffraction pattern of the solvothermal synthesized ANZ@HKUST-1 shows the characteristic peaks of HKUST-1 CCDC No. 112954 (Figure 1) at 2 theta 9.45° (hkl 2 2 0); 11.64° (hkl 2 2 2); and 13.45° (hkl 4 0 0). The resulting characteristic peaks of HKUST-1 have a high intensity which indicates that the solvothermally synthesized HKUST-1 has good crystallinity. The ANZ@HKUST-1 diffraction pattern also shows diffraction peaks corresponding to the characteristic peaks of ANZ, which has a characteristic diffraction pattern at 2 theta of 19.5° (hkl 3 3 0); 22.2° (hkl 1 5 0); 25.6° (hkl 2 0 2); 26.5° (hkl 3 5 0); and 27.6° (hkl 5 1 1), in which the two highest peaks were being observed at 2 theta 25.6° and 26.5°.

A small peak was observed at 2 theta 18.07° in the in situ synthesized ANZ@HKUST-1 composite. Based on the refinement results, this peak indicates the residual remains of the benzene-1,3,5-tricarboxylate ligand (BTC) (JCPDS 451880) derived from the solvothermally synthesized ANZ@HKUST-1. As a comparison, there was no peak in the ex-situ synthesized ANZ@HKUST-1 composite synthesized under ultrasonic irradiation indicating no remaining BTC ligands. It can be seen that the in situ method of synthesized ANZ@HKUST-1 composites slightly inhibited the formation of HKUST-1, therefore a few remaining ligands uncoordinated to Cu(II) metal ions can still be observed.
The FTIR spectrum of the ANZ@HKUST-1 composite was then compared with the spectra of HKUST-1 and ANZ. In Figure 2, ANZ@HKUST-1 shows compatibility with the FTIR spectrum of HKUST-1 in which the peaks at wavenumbers of 1621 and 1367 cm$^{-1}$ indicate a stretching vibration of C=O and C-O from the carboxylate group of HKUST-1. The composite material also shows compatibility with the ANZ FTIR spectrum due to the absorption peak at 1058 cm$^{-1}$ and 447 cm$^{-1}$ which are attributed to the T-O (T = Si or Al) stretching and bending vibration mode, respectively. In the FTIR spectra of the in situ synthesized ANZ@HKUST-1 composites, there is still a C=O peak at 1700 cm$^{-1}$ with a somewhat higher intensity, indicating the residual H3BTC ligand from the HKUST-1 as a consequence of the presence of zeolite which slightly blocked the formation of HKUST-1.

The SEM image of HKUST-1 (Figure 3) shows that HKUST-1 has an octahedral shape with an average particle diameter of ca. 15.64 ± 4.2 μm, as reported in a previous paper [27]. The SEM image of ANZ@HKUST-1 (Figure 3 (c-d)) clearly shows that zeolite flakes were deposited onto the surface of HKUST-1, which is in agreement with the work reported in a related paper [13]. Furthermore, Figure 3 (c-d) depicts that the decrement of HKUST-1 particle diameter and the distortion of its octahedral morphology as the amount of ANZ is increased. This is supported by the fact that the addition of ANZ (crystallite size 5.77 ± 1.09 μm) leads to the crystalline damage in HKUST-1 as shown in XRD patterns (Figure 1) and SEM images (Figure 3, and ESI Figure S2).

According to the content of Si and Al elements analyzed by EDX, ANZ@HKUST-1 composites in various composition (20, 50, and 80%) were successfully prepared. The element Si, which is one of the main constituents of the zeolite composite of HKUST-1, was found in the region of ± 1.8 keV. The Al element found in ANZ@HKUST-1 (Table 1) had lower wt% content than Si. This is because, some Al was leached from the structure in the form of Al(OH)$_3$ during zeolite activation, which has also been reported previously [28]. The wt% of the Si and Al content in the composite material did not match the theoretical estimation, possibly because of ANZ penetration into the structure of HKUST-1, or due to the non-homogeneous distribution of ANZ in the HKUST-1 composite. Anyhow, the composition of HKUST-1 was insignificantly altered.

Nitrogen sorption isotherm analysis (Figure 4) shows that both starting materials HKUST-1 and ANZ exhibited isotherm type I and pseudo-Langmuir isotherm and, therefore, could be classified as a microporous material [29]. After composites formed, with ANZ as a filler, the type of adsorption-desorption curves of ANZ-HKUST-1 20% and ANZ-HKUST-1 50% were changed to type IV with hysteresis loop, indicating the introduction of mesoporous character [29]. However, when ANZ is 80%, the adsorption-desorption profile of ANZ-HKUST-1 80% is similar to that of parent ANZ. It is seen that HKUST-1 has...
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![FTIR spectra of HKUST-1, ANZ, and ANZ@HKUST-1 composites with various ANZ additions.](image)

**Figure 2:** FTIR spectra of HKUST-1, ANZ, and ANZ@HKUST-1 composites with various ANZ additions.

![SEM images of (a) HKUST-1; (b) ANZ; ANZ@HKUST-1: (c) ANZ 20%, (d) ANZ 50%, and (e) ANZ 80% (provided in 20,000 magnification).](image)

**Figure 3:** SEM images of (a) HKUST-1; (b) ANZ; ANZ@HKUST-1: (c) ANZ 20%, (d) ANZ 50%, and (e) ANZ 80% (provided in 20,000 magnification).

**Table 1:** Percentage of elements on the composite ANZ@HKUST-1.

| Elemental composition (%) | C    | O    | Cu   | Si    | Al   |
|---------------------------|------|------|------|-------|------|
| ANZ 20%                   | 29.08| 20.41| 48.83| 1.24  | 0.45 |
| ANZ 50%                   | 38.07| 29.38| 31.04| 1.15  | 0.36 |
| ANZ 80%                   | 26.35| 25.8 | 35.34| 7.16  | 1.67 |
| ANZ                       | -    | 44.69| -    | 46.56 | 8.19 |
| HKUST-1                   | 29.19| 20.03| 50.78| -     | -    |
the highest N$_2$ adsorption-desorption capacity whereas the ANZ@HKUST-1 composite had a smaller nitrogen sorption isotherm than HKUST-1 because ANZ had the smallest N$_2$ adsorption value. In the observation of the pore size distribution analyzed using Barrett, Joyner, and Halenda (BJH) method, the average pore size of HKUST-1 was 1.87 nm and its pore distribution was in the microporous region (less than 2 nm). The pore distribution of the ANZ@HKUST-1 composite increased with increasing ANZ composition. This is because ANZ has a pore distribution in the micro- and meso regions of 1.9 nm, and 4.9 nm, respectively. The pore distribution analysis also shows that the mesopore size in zeolite did not appear when combined with HKUST-1. This indicates that ANZ covers HKUST-1, thus increasing the degree of microporosity of the ANZ@HKUST-1 composite. This fact is in accordance with literature reference [13] which discussed the HKUST-1 pore distribution increasing after combining with MCF to form a composite material.

The surface area of the composite material ANZ@HKUST-1 gradually decreased with the increase of weight % of ANZ since ANZ possessed a much lower surface area than HKUST-1 (Table 2). However, another reason could be that ANZ covered the surface of HKUST-1, and consequently, the surface area decreased as the addition of ANZ increased.

Three mass change steps were observed in the HKUST-1 thermogram (Figure 5). In the first step, a mass drop occurred for HKUST-1 (20.41%) at the temperature range of 98 – 132°C, indicating the possible loss of 8 water molecules from the surface and pores of HKUST-1. Then, at the temperature range of 132–283°C, a second mass loss of 5.72% was observed, indicating the possible loss of 2 water molecules that bind to Cu$^{2+}$ metal ions. Furthermore, a third mass loss corresponded to the fracture of the HKUST-1 structure above 293°C, resulting in a mass decrease of 42.8%. The mass changes began to stabilize above 331°C, which indicated the formation of CuO oxide with a residue of 31.09%. This result is consistent with a study conducted by Lin et al.[27] who synthesized HKUST-1 in solvothermal method with a final residue of 33 wt%.

In the ANZ thermogram, a decrease in mass of 16.56% was observed at the temperature range of 34 - 107°C, estimated to be the loss of water molecules attached to ANZ. The second decrease in mass of 13.44% occurred at 107 - 600°C, was estimated to be the loss of hydroxyl and NH$_3$ in the ANZ structure. ANZ had a mass decrease of 30% at the temperature range of 34 – 600°C. According to Mansouri et al., TGA on zeolite shows dehydration or a loss of water molecules at temperatures of 38 – 120°C [30]. According to Botto et al., there is a decrease of ANZ mass at 380°C, indicating the loss of NH$_3$ from the NH$_4^+$ ions present in ANZ, thus leaving the H$^+$ cations on ANZ [31].
Furthermore, composite materials with ANZ compositions of 20 and 50 wt% have similar thermograms with HKUST-1, which indicate the mass changes in the three regions. The first change likely results from the loss of water molecules from HKUST-1 and ANZ. The second mass loss is attributed to the loss of water molecules binding to Cu$^{2+}$ metal ions on HKUST-1, and a third loss in mass might be due to structural damage of HKUST-1. According to the thermogram of ANZ@HKUST-1 composites, it is suggested that the addition of ANZ to HKUST-1 improved the thermal stability of HKUST-1 at temperatures from 283°C to 305°C. This result is in agreement with the results of a previous study [15] concluding that the thermal stability of MOF composite is higher than that of the initial MOF material. The thermal profile of ANZ-HKUST-1 80 wt% seems to follow a similar trend, in which the mass loss due to water molecule release is the lowest (ca. 5%), and the third mass loss corresponded to the fracture of the HKUST-1 structure took place in the wider temperature range (298 - 350°C). It was expected to be confirmed that the smaller quantity of HKUST-1 possibly led to release few water molecules. Therefore, ANZ-HKUST-1 80 wt% has higher thermal stability than ANZ-HKUST-1 20 and 50 wt% due to more ANZ content, and the materials remain stable at 600°C.

### 3.2 CO$_2$ Adsorption Test

The CO$_2$ adsorption test (Figure 6) shows that there was an increase in CO$_2$ adsorption capacity when ANZ was added to HKUST-1 at 2, 5, 95, and 98 wt%. In the 2% and 5% ANZ composites, there was an increase in adsorption capacity of 12.1% and 12%, respectively, in comparison with the adsorption capacity of HKUST-1. This is because the ANZ that was added to HKUST-1 did not block the pores of HKUST-1 itself, thus increasing the amount of porosity in the ANZ@HKUST-1 composite. Moreover, ANZ has additional active sides, O-H$^+$ and NH$_4^+$, which can bind CO$_2$ through hydrogen bonds, leading to the increasing of the adsorption capacity of CO$_2$ (see Figure 7). The ANZ 95 and 98% composites also have higher adsorption capacity of 12.2% and 5.6%, respectively, than the initial adsorption capacity of HKUST-1 and ANZ. Similarly, the reason for this could be that HKUST-1 did not block the micropores of ANZ, consequently increasing the number of micropores on the composite ANZ@HKUST-1.

However in other variations, a more balanced composition of ANZ and HKUST-1 tend to decrease the CO$_2$ adsorption capacity of the material, as evidenced by ANZ composites 20, 50 and 80 wt%. In these three composites, it was estimated that a higher weight percentage ratio, meaning more ANZ would cover the pores of HKUST-1 therefore the ANZ@HKUST-1 composite could not maximally adsorb CO$_2$. This CO$_2$ gas adsorption result correlated to the nitrogen sorption isotherm analysis shows that the combination of HKUST-1 and ANZ has narrowed the pore size distribution from 5.0 nm to < 2.0 nm. Because CO$_2$ gas has a molecule size of 0.33 nm, it
was likely to be adsorbed on the micropores (1.87–1.9 nm) of the ANZ@HKUST-1 composite. Therefore, one of the reasons for the increase of CO$_2$ gas adsorption capacity is caused by the pore size of material that corresponds well to the size of the CO$_2$ gas molecule, as shown by the composite of ANZ 2, 5, 95, and 98 wt%. An increase in CO$_2$ adsorption capacity shown by the composites in this study is in accordance with a previous report [13], in which a synthesized composite of HKUST-1#MCF-NH$_2$ therein, showed an increase in the adsorption capacity from 3.35 mmol/g to 3.89 mmol/g at 1 bar and 25°C.

## 4 Conclusions

In this study, we successfully prepared a composite material, ANZ@HKUST-1. The incorporation of HKUST-1 with ANZ improves thermal stability although it decreases the surface area and porosity of HKUST-1. The CO$_2$ gas adsorption results show that the addition of ANZ 2, 5, 95, and 98 wt% increase the CO$_2$ gas adsorption capacity up to 12% over the initial materials. The method of the composites synthesis (whether in situ or ex-situ) does not significantly affect the adsorption result; the main factors affecting CO$_2$ adsorption are the surface area, the pores, and the active sides of both materials. To conclude, the potential use of the ANZ@HKUST-1 composites in CO$_2$ capture and separation for example as filler in mixed matrix membrane (MMMs) area should be explored further.

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## References

[1] Quadrelli R., Peterson S., The energy–climate challenge: Recent trends in CO$_2$ emissions from fuel combustion, Energy Policy, 2007, 35, 5938-5952.

[2] Cheng Y., Huang Q., Eic M., Balcom B.J., CO$_2$ dynamic adsorption/desorption on Zeolite 5A Studied by $^{13}$C Magnetic Resonance Imaging, Langmuir, 2005, 21, 4376-4381.

[3] Rao A.B., Rubin E.S., A Technical, Economic, and Environmental Assessment of Amine-Based CO$_2$ Capture Technology for Power Plant Greenhouse Gas Control, Environ. Sci. Technol., 2002, 36, 4467-4475.

[4] Salmasi M., Fatemi S., Rad M.D., Jadiﬁ F., Study of carbon dioxide and methane equilibria adsorption on silicoaluminoophosphate-34 zeotype and T-type zeolite as adsorbent, Int. J. Environ. Sci. Technol., 2013, 10, 1067-1074.

[5] Millward A.R., Yaghi O.M., Metal–Organic Frameworks with Exceptionally High Capacity for Storage of Carbon Dioxide at Room Temperature, J. Am. Chem. Soc., 2005, 127, 17998-17999.

[6] Llewellyn P.L., Bourrelly S., Serre C., Vimont A., Daturi M., Hamon L., De Weireld G., Chang J.S., Hong D.Y., Kyu Hwang Y., Hwa Jhung S., High Uptakes of CO$_2$ and CH$_4$ in Mesoporous Metal-Organic Frameworks MIL-100 and MIL-101, Langmuir, 2008, 24, 7245-7250.

[7] Adhikari A.K., Lin K.S., Improving CO$_2$ adsorption capacities and CO$_2$/N$_2$ separation efficiencies of MOF-74(Ni,Co) by doping palladium-containing activated carbon, Chem. Eng. J., 2014, 284, 1348-1360.

[8] Petit C., Burrell J., Bandosz T.J., The synthesis and characterization of copper-based metal-organic framework/graphite oxide composites, Carbon, 2011, 49, 563-572.

[9] Liu X.W., Sun T.J., Hu J.L., Wang S.D., Composites of metal–organic frameworks and carbon-based materials: preparations, functionalities and applications, J. Mater. Chem. A, 2016, 4, 3584-3616.

[10] Liu S., Sun N., Wei W., Sun Y., Synthesis of HKUST-1#MCF compositing materials for CO$_2$ adsorption, Micro. Meso. Mater., 2016, 226, 476-481.

[11] Liu S., Sun L., Xu F., Zhang J., Jiao C., Li F., Li S., Wang Z., Wang X., Jiang X., Zhou H., Yang L., Schick C., Nanosized Cu-MOFs induced by graphene oxide and enhanced gas storage capacity, Energy Environ. Sci., 2013, 6, 818-823.

[12] Kusdarto, The Potential of Zeolites in Indonesia (Potensi Zeolit di Indonesia), J. Zeolit Indonesia, 2008, 7, 672-678.
[20] Li W., Zhang Y., Li Q., Zhang G., Metal-Organic Framework Composite Membranes: Synthesis And Separation Applications, Chem. Eng. Sci., 2015, 135, 232-257.

[21] Lee J.Y., She Q., Huo F., Tang C.Y., Metal-Organic Framework-Based Porous Matrix Membranes For Improving Mass Transfer In Forward Osmosis Membranes, J. Membr. Sci., 2015, 492, 392-399.

[22] Kizzie A.C., Wong-Foy A.G., Matzger A.J., Effect Of Humidity On The Performance of Microporous Coordination Polymers As Adsorbents For CO₂ Capture, Langmuir, 2011, 27, 6368-6373.

[23] Lestari W.W., Ribowo A.H., Astuti S., Irwinsyah, Pamungkas A.Z., Krisnandi Y.K., Fabrication of hybrid coating material of polypropylene itaconate containing MOF-5 for CO₂ capture, Prog.Org. Coat., 2018, 115, 49-55.

[24] Chui S.S.Y., Lo S.M.F., Charmant J.P., Orpen A.G., Williams I.D., A Chemically Functionalizable Nanoporous Metal [Cu₃(TMA)₂(H₂O)₃]ₙ, Science, 1999, 283, 1148-1150.

[25] Hasanah D.N., Transformasi Zeolit Alam Wonosari menjadi Fasa Mordenit Murni dengan Metode Dealuminasi dan Seed Assisted Synthesis secara Hidrotermal. Bachelor project, Sebelas Maret University, Surakarta, 2017, (in Indonesian).

[26] Saputra O.A., Frameswari M.D., Kinanti V.T.D., Mayasari O.D., Sutarni Y.D., Apriany K., Lestari W.W., IOP Conf. Ser.: Mater. Sci., 2017, 172, 012039, 1-10.

[27] Lin K.S., Adhikari A.K., Ku C.N., Chiang C.L., Xuo H., Synthesis And Characterization of Porous HKUST-1 Metal Organic Frameworks For Hydrogen Storage, Int. J. Hydrogen Energy, 2012, 37, 13865-13871.

[28] Apriananto L., Konversi Polietilena dari Sampah Plastik Mejadi Hidrokarbon Cair dengan Bantuan Katalis Zeolit Alam, Bachelor project, Dipenogoro University, Semarang, Indonesia, 2003, (in Indonesian).

[29] Sing K.S.W., Everett D.H., Haul R.A.W., Moscou L., Pierotti R.A., Rouquerol J., Siemieniewska T., Reporting Physisorption Data For Gas/Solid Systems with special Reference to the Deterermination of Surface Area and Porosity, Pure Appl. Chem., 1985, 57, 603-619.

[30] Mansouri N., Rikhtegar N., Panahi H.A., Atabi F., Shahraki B.K., Porosity, Characterization And Structural Properties of Natural Zeolite-Clinoptilolite-As A Sorbent, Environ. Prot. Eng., 2013, 39, 139-152.

[31] Botto I.L., Canafoglia M.E., Lick I.D., Cabello C.I., Schalamuk I.B., Minelli G., Ferraris G., Environmental Application of Natural Microporous Aluminosilicates: NOx Reduction by Propane Over Modified Clinoptilolite Zeolite., In Anales de la Asociación Química Argentina, 2004, 92, 139-153.