

Synthesize and Investigate the Applicability of Carbon Dioxide Capture of Zeolite-based Geopolymer Materials

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In today's world, people are facing the challenges of extreme weather events, global warming, and the rapid degradation of nature and the environment. One of the major contributors to these issues is the increased concentration of carbon dioxide (CO₂), a greenhouse gas, in the atmosphere following the industrial revolution. In response to this crucial situation, this study focuses on the zeolite-based geopolymer material synthesis with various zeolite compositions. X-ray diffraction (XRD) analysis confirmed the retained structure of the powdery zeolite. These materials are designed to exhibit stability under various conditions and to investigate their capability to capture CO₂ through gas flow. The study assesses the performance of these materials in capturing CO₂, aiming to provide a foundation for the development of effective CO₂ capture materials and the reduction of greenhouse gas emissions. The sample with zeolite X content of 45.6 wt% has a CO₂ adsorption capacity of 21±1 mg/g with an inlet gas of 3 %v CO₂ and remained almost same adsorption capacity after two times of heat regeneration.

1. Introduction

The climate change challenge has become a significant concern due to the more carbon emission and related activity affecting environmental qualification (Abdullahi et al., 2018). The primary cause of the greenhouse effect is the excessive elevation in carbon dioxide (CO₂) concentration within the Earth's atmosphere attributed to the combustion of fossil fuels for approximately 85 % of the current global energy demand (Abdullahi et al., 2018). The CO₂-captured method development is necessary to reduce its over-increasing emission.

Over the past decade, there has been extensive research and development on various CO₂ capture technologies (Lee and Park, 2014). These include membrane-based systems, chemical absorption using different solvents, cryogenic separation techniques, electrochemical processes, among others (Pardakhti et al., 2019). Notably, adsorption utilizing solid adsorbents has emerged as a prominent approach due to its advantageous characteristics, including high efficiency, low energy requirements, and the ability to undergo regeneration (Khraisheh et al., 2020).

Zeolites represent a class of microporous, crystalline aluminium silicate solids exhibiting a three-dimensional structure. Their inherent properties, including a well-developed capillary system, substantial surface area, thermal stability, and shape-selective adsorption, position them as highly promising adsorbent (Nguyen et al., 2021). Notably, zeolites exhibit the capacity to selectively adsorb CO₂, thus making them suitable for carbon capture, storage, and utilization (Boer et al., 2023). Numerous research endeavours have focused on transforming zeolite powders into pellets or beads, primarily driven by the recognition that powder form poses higher gas flow resistance than bead or pellet catalyst shaping in fixed-bed adsorption columns (Luzzi et al., 2021). A simple strategy for zeolite shaping is embedding powders in a composite structure with the role of a binding agent (Luzzi et al., 2021). Geopolymer has been one of the most studied binding agents with inorganic polymers of SiO₂-base for linking small particles (Cong and Cheng, 2021).

Geopolymer is a general term for materials synthesized from alkalization of aluminosilicate sources. They have a disordered spatial network structure formed from polysialate chains. The general chemical formula of geopolymer is as shown in the following Eq(1):



in which M is the alkali metal; z is the ratio of SiO₂ in the geopolymer structure can be 1,2,3; n is the degree of polymerization. Depending on the Si/Al ratio, the geopolymer has different types of monomers:

Si/Al = 1: The monomer is a polysialate (-Si-O-Al-O-).

Si/Al = 2: The monomer is polysialate-siloxo (-Si-O-Al-O-Si-O-).

Si/Al = 3: The monomer is a polysialate-disiloxo (-Si-O-Al-O-Si-O-Si-O-).

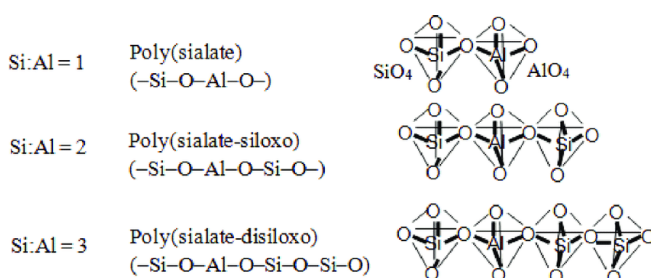


Figure 1: Geopolymers consist of monomers with various ratios of Si:Al (Younas et al., 2020)

Geopolymerization is a type of reaction for exothermic water splitting, water is used as the solvent and is eliminated after polymerization. The geopolymerization process can be divided into the following 4 steps according to Jia et al. (2020): (1) Process of dissolving aluminosilicates in alkaline solutions: Sources of soluble aluminosilicates to form aluminum and silicon containing units; (2) Dispersion: Si and Al tetrahedra with O will diffuse from the solid particle surface to the liquid phase; (3) Polymerization process: The silicate contained in the agent supports the alkaline silicate solution to interact to the Si and Al tetrahedra. The Al tetrahedra in this process will change from the initial coordination bonds of 4, 5, 6 to the coordination bonds of 4 AlO₄ to combine with SiO₄ and polymerize into a three-dimensional network structure; and (4) Water separation curing: Solution dispersion happens between the gel phase and the rest. Along with the formation of a pore system in the gel phase, some of the water will evaporate while another adsorbs in the structure and the system will cure to form a geopolymer.

This research focuses on preparing a zeolite-based geopolymer and possibly using the material in CO₂ capture. In particular, pellet adsorbent for CO₂ capture was designed by a combination of zeolite X and geopolymer. Geopolymer is a strong and durable substrate for zeolite as well as zeolite having a well-developed capillary system, substantial surface area, thermal stability, and potential adsorption. This combination of these properties promises to create zeolite-based geopolymers with applications in environmental remediation, especially columnar CO₂ adsorption. In fact, the raw materials to synthesize geopolymer can come from natural ingredients or waste sources of other processes (Kaolin in this study), and the role of geopolymer is also the inorganic binding agent. The synthesis process happens at room temperature without the presence of toxic chemicals. That shows this procedure becomes eco-friendly, energy-saving, and suitable for the green synthesis trend. Besides, the CO₂ adsorption with this material in more specific conditions (temperatures, regeneration capacity) was also investigated for additional understanding of how the samples behave when adsorption is in progress.

2. Methodology

2.1 Zeolite-based geopolymer synthesis

After calcining kaolin into metakaolin (The calcination is done with reference procedure (Bessa et al., 2017), the zeolite-based geopolymer was synthesized according to the reference procedure (Papa et al., 2018) and modified to match zeolite X. Zeolite X in this study was synthesized by the published procedure (Long et al., 2016) while the metakaolin was obtained by calcining kaolin (from Lam Dong Minerals and Building Materials JSC) at 650 °C for 2 h. Other chemicals (NaOH, H₂SO₄) were purchased from Xilong Chemical Co. and directly used. The details of the preparation procedure are shown in Figure 2. Zeolite X was dispersed in distilled water to get mixture A. Metakaolin and liquid glass were stirred in the 6 M NaOH solution to form mixture B. A and B were then mixed well before the molding process. The tablets were manually removed from the mold and dried

at 80 °C for 24 h. The washing process with H₂SO₄ 0.01 M was conducted to adjust pH < 7 before the re-drying (80 °C, 24 h) for the final product obtained. Three zeolite-based geopolymer samples (M1, M2, M3) were prepared in this study. The mass percents of zeolite X and metakaolin of these sample are shown in Table 1.

2.2 Investigation of adsorption capacity

The measurement of CO₂ adsorption was conducted in dynamic mode using a continuous flow system. The input CO₂ gas stream was mixed with the N₂ gas stream to achieve a CO₂ concentration of 3.0% v, then the gas flowed through the dehumidifier column, as moisture greatly affects the CO₂ adsorption capacity (Gang Li et al., 2008). The gas flow continued to pass through the U-tube containing the sample (1.0 g). The tube was placed in the furnace, and the output gas flow went to the CO₂ sensor (NDIR CO₂ sensor) when adsorption or discharge was performed. In this study, the CO₂ adsorption capacity was investigated at room temperature (30-31 °C) and low temperature (0-1 °C). The CO₂ adsorption process was carried out after the samples were pretreated at 300 °C under N₂ gas flow of 0.1 L/min for 2 h. The CO₂ adsorption capacity (mg/g) was calculated by: $q = (44. F/RT) * (\sum(C_{CO_2_{in}} - C_{CO_2_{out}}) \Delta t)/m$, in which F is the gas flow rate; T is the temperature; C_{CO₂ in/out} are the CO₂ concentration; m is the mass of the adsorbent. Two methods for regenerating the CO₂ adsorbed materials were also tested for comparison and understanding the recyclability of the zeolite-based geopolymer CO₂ adsorbent. The saturated CO₂ adsorbent was subjected to a vacuum with a pressure lower than 0.05 atm for 0.5 hours in the first method, or it was heated to 300°C for 3 hours in an N₂ flow in the second method.

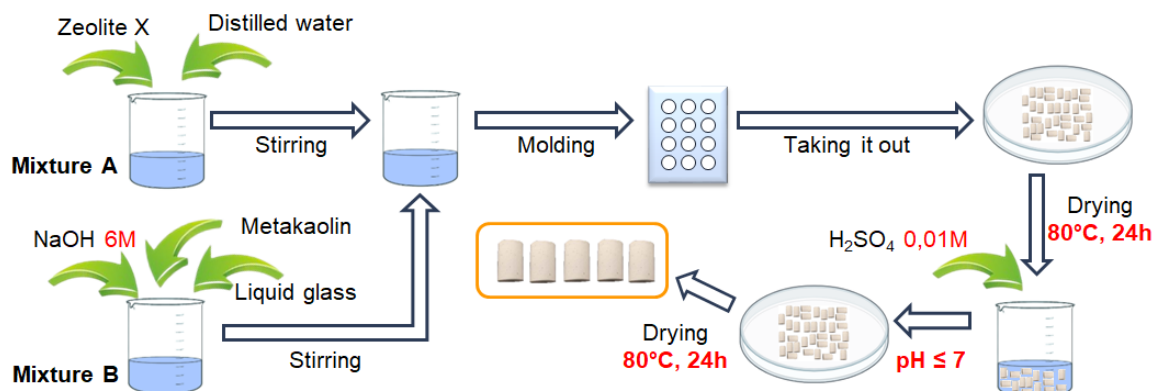


Figure 2: Process for synthesizing zeolite-based geopolymers from powdered zeolite X and metakaolin.

3. Results and discussions

3.1 Physicochemical properties of zeolite-based geopolymer beads

The results of preparing 3 samples of materials are stable under the conditions of synthesis and investigation, namely, they are stable in the sample washing solution for about 15 min and the material layer height does not decrease significantly during the adsorption investigation. Samples with different zeolite mass percent, BET surface area are named as shown in the Table 1. The morphology of the beads was shown in Figure 3. All the beads have a cylinder shape with the size of $\varnothing \sim 5$ mm, $h \sim 5$ mm (\varnothing is the cycle base diameter and h is the height of the cylinder).

Table 1: Some structural parameters of Zeolite-based geopolymer beads

Parameter	M1	M2	M3
Zeolite NaX content (wt%)	22.8	45.6	49.0
Metakaolin content (wt%)	77.2	54.4	51.0
External surface area (m ² /g)	20	22	25
Micropore surface area (m ² /g)	47	182	198
BET surface area (m ² /g)	67	204	223

The XRD results of M1, M2, M3 are shown in Figure 4. It indicates that the geopolymerization process with alkali has impacted the structure while preserving the distinctive traits of zeolite X and metakaolin within the material. Since geopolymer is formed by alkalization reaction of active aluminosilicate sources such as metakaolin (Jia et al., 2020). Therefore, the sample with high metakaolin may contain more amorphous phase. The reduction in

XRD peak intensity in the material patterns may be because of the augmentation of the amorphous phase within the material's structure, a result of metakaolin's transformation during geopolymerization.

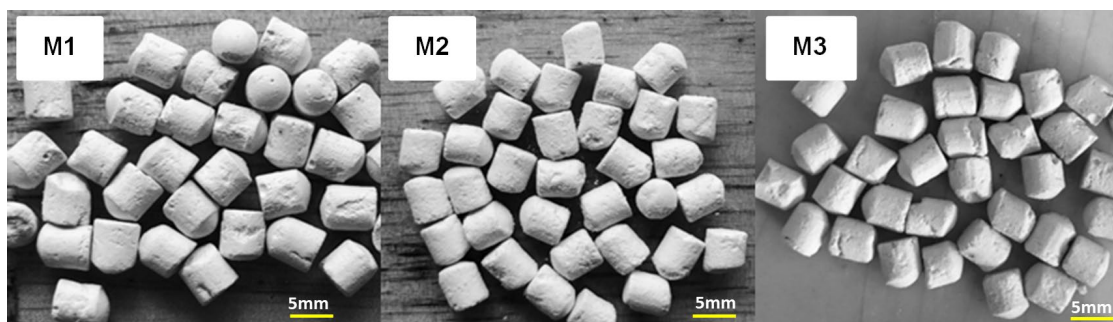


Figure 3: Photograph of the three zeolite-base polymer materials

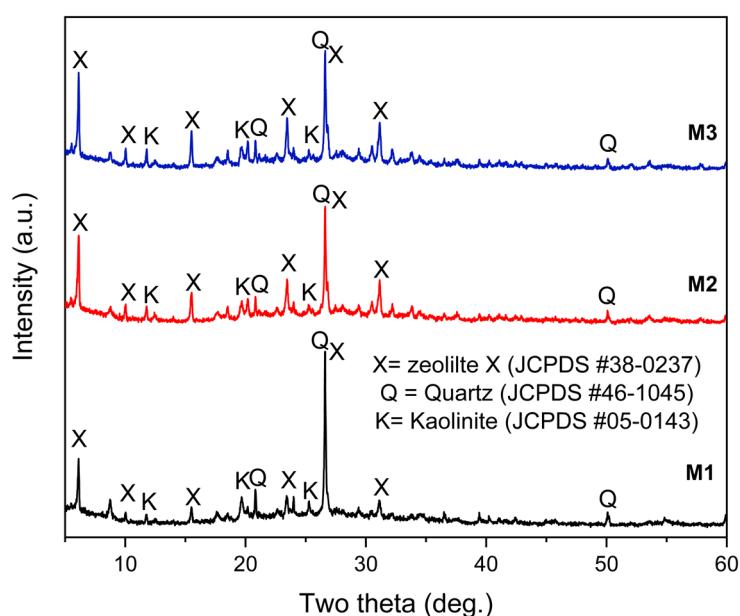


Figure 4: XRD patterns of the zeolite-based geopolymer samples (M1, M2, M3)

3.2 CO₂ capture capacity of zeolite-based geopolymer beads

Comparison of the CO₂ adsorption at room temperature conditions and at low-temperature conditions was shown in Figure 5. It is evident that lowering the temperature leads to an increase in the adsorption capacity for all three samples compared to room conditions. For example, CO₂ adsorption capacity of the sample M1 rise from about 4 mg/g at 30 °C to about 9 mg/g at 0 °C. In the case of sample M2, they were 21 mg/g at 30 °C and 31 mg/g at 0 °C. This phenomenon can be explained by the fact that adsorption process is an exothermic process which is favorable at low temperatures (Khraisheh et al., 2020 and Lee and Park, 2014). During both the adsorption processes under room temperature and chilled conditions, samples M2 and M3 exhibit significantly higher adsorption capacities compared to sample M1. This can be attributed to the higher zeolite X content in M2 (45.62 %) and M3 (49.04 %). There is no notable difference between samples M2 and M3 which may be due to the relatively similar zeolite content in these two samples. In comparison, at almost similar condition it was reported that for powder zeolite X adsorption capacity was about 88 mg/g at 30 °C (Aquino et al., 2020). The decrease in mass transfer rate when the material is in pellet form together with the partial zeolite content of the material could be the cause of the difference in CO₂ adsorption capacity. Heating or lowering the pressure are two common methods for regeneration CO₂ adsorbents (Lee and Park, 2014). The CO₂ adsorption capacity of sample M2 after two methods of regeneration (vacuum and heating) are also presented in the column chart (Figure 5c). The adsorption capacity at room temperature was nearly zero in the vacuum generation cases.

Which proves that the vacuum method is insufficient for complete regeneration of the zeolite-based geopolymer material. By heating method at 300 °C of sample M2, the adsorption capacities approach that of the initial measurement evidence that the effective thermal desorption.

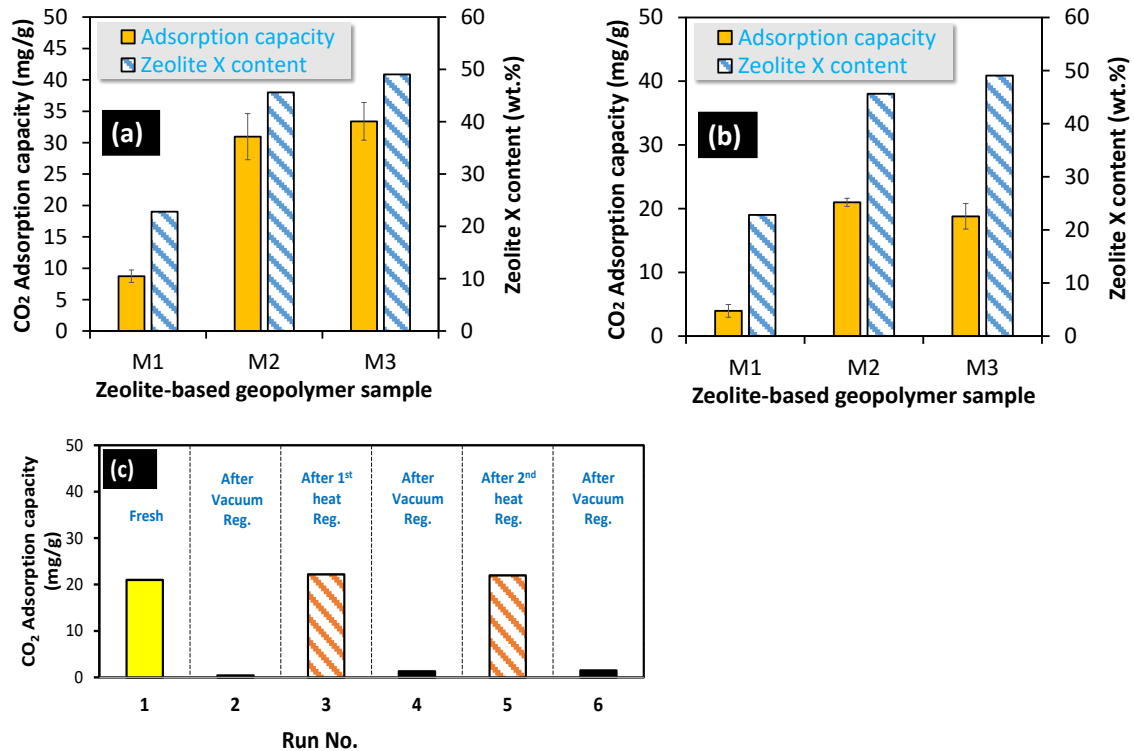


Figure 5: CO₂ adsorption capacity of the zeolite-based geopolymer materials (a) at low temperature condition (0-1°C); (b) at room temperature condition (30-31°C); (c) at room temperature after two methods of regeneration (3%v CO₂ concentration, 1.0g of materials)

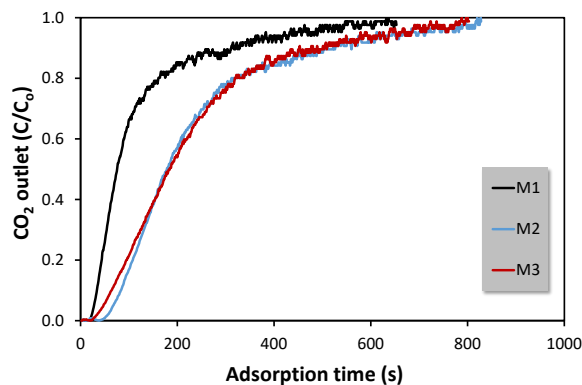


Figure 6: Comparison of CO₂ dynamic adsorption by the zeolite-based geopolymer (Temperature 0-1 °C; adsorbent: 1.0g; CO₂ in N₂: 3.0 v%)

In addition to evaluating the adsorption capacity, it is also valuable to assess the slope of the graph representing the ratio of CO₂ output concentration (C) to the maximum CO₂ concentration (C₀) over time. The slope of the S-shaped adsorption curve is influenced by various factors, including the rate and mechanism of the adsorption process, the equilibrium nature of the adsorption, fluid velocity, inlet gas concentration, and the height of the adsorbent layer (Boer et al., 2023). It is notable that the less steep the adsorption curve, the more efficient the adsorption process (Mfoumou et al., 2022). Samples with higher zeolite X content show less steep of the adsorption curve. Which proves that higher zeolite content geopolymer material performed better adsorption efficiency.

4. Conclusions

This study reported a new approach for forming a ready-to-use pellet CO₂ adsorbent. The zeolite-based CO₂ adsorbent was successfully obtained through the geopolymerization of a low-cost material (metakaolin) as a chelating agent in combination with zeolite X. The material demonstrated promising application as a CO₂ capture material. It was observed that samples with higher zeolite X content exhibited better adsorption capabilities. It was also determined that the materials could not be regenerated effectively using vacuum methods. Regeneration through heat was found to be more successful. These findings highlight the potential of zeolite-based geopolymer materials as an effective and economical solution for CO₂ capture, with the added advantage of heat-regenerability for prolonged use.

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References

- Abdullahi H., Sinniah G.K.S.O., Siong H.C., 2018, Contributions of Housing Sector towards Low Carbon Society Development Literature Synthesis, 4th International Conference on Low Carbon Asia and Beyond, 24th-26th October, Johor Bahru, Malaysia.
- Aquino T.F., Estevam S.T., Viola V.O., Marques C.R., Zancan F.L., Vasconcelos L.B., Riella H.G., Pires M.J., Morales-Ospino R., Torres A.E.B., Bastos-Neto M., 2020, CO₂ adsorption capacity of zeolites synthesized from coal fly ashes, *Fuel*, 276, 118143.
- Bessa R.d.A.R., Costa L.d.S., Oliveira C.P., Bohn F., Nascimento R.F.d., Sasaki J.M., Loiola A.R., 2017, Kaolin-based magnetic zeolites A and P as water softeners, *Microporous and Mesoporous materials*, 245, 64-72.
- Boer D.G., Langerak J., Pescamona P., 2023, Zeolites as Selective Adsorbents for CO₂ Separation, *ACS Applied Energy Materials*, 6(5), 2634-2656.
- Cong P., Cheng Y., 2021, Advances in geopolymer materials: A comprehensive review, *Journal of Traffic and Transportation Engineering*, 8(3), 283-314.
- Li G., Xiao P., Webley P., Zhang J., Singh R., Marshall M., 2008, Capture of CO₂ from high humidity flue gas by vacuum swing adsorption with zeolite 13X, *Adsorption*, 14, 415-422.
- Jia D., He P., Wang M., Yan S., 2020, *Geopolymer and Geopolymer Matrix Composites*, Springer, Gateway East, Singapore.
- Khraisheh M., Almomani F., Walker G., 2020, Solid Sorbents as a Retrofit technology for CO₂ Removal from natural Gas Under High pressure and temperature conditions, *Scientific Reports*, 10(1), 269.
- Lee S.-Y., Park S.-J., 2014, A review on solid adsorbents for carbon dioxide capture, *Journal of Industrial and Engineering Chemistry*, 23, 1-11.
- Long N.Q., Vuong H.T., Ha H.K.P., Kuniawan W., Hinode H., Baba T., 2016, Preparation, characterization and H₂S adsorptive removal of ion-exchanged zeolite X, *ASEAN Engineering Journal Part B*, 51, 4-12.
- Luzzi E., Aprea P., Luna M.S., Caputo D., Filippone G., 2021, Mechanically Coherent Zeolite 13X/Chitosan Aerogel Beads for Effective CO₂ Capture, *ACS Applied Materials and Interfaces*, 13(17), 20728-20734.
- Mfoumou C.M., Ngoye F., Belin T., Mignard S., 2022, Dynamic Adsorption and Desorption of CO₂ from Mixtures CH₄ and C₃H₈ on X Type Zeolites, *American Journal of Environmental Protection*, 10(2), 83-90.
- Nguyen Q.L., Tran H.G.H., Nguyen T.T.P, Bui T.L., Dang C.V., Le N.Q.T., Nguyen T.G.H., Nguyen V.D., Ngo T.A., 2021, Mesostructured Zeolites Prepared by One-Pot Top-Down Synthesis Route for Carbon Dioxide Adsorption, *Chemical Engineering Transactions*, 83, 67-72.
- Papa E., Medria V., Amaria S., Manauda J., Benitoa P., Vaccaria A., Landi E., 2018, Zeolite-geopolymer composite materials: Production and characterization, *Journal of cleaner production*, 171,76-84.
- Pardakhti M., Jafari T., Tobin Z., Dutta B., Moharrer E., Shemshaki N.S., Suib S., Srivastava R., 2019, Trends in solid adsorbent materials development for CO₂ capture, *ACS Applied materials & interfaces*, 11(38), 34533-34559.
- Younas M., Rezakazemi M., Daud M., Wazir M.B., Ahmad S., Ullah N., Inamuddin, Ramakrishna S., 2020, Recent progress and remaining challenges in post-combustion CO₂ capture using metal-organic frameworks (MOFs), *Progress in Energy and Combustion Science*, 80, 100849.