

PRELIMINARY STUDY ON PERFORMANCE OF Zn-DOPED ZEOLITE IN LOW-TEMPERATURE CO₂ ADSORPTION

Ang Gaun Yu^{1a}, Zhi Hua Lee^{2ab*}, Chee Yung Pang^{3a} and Gulnaziya Issabayeva^{4ab}

Abstract: Zeolite has been identified as a potential low-temperature CO₂ adsorbent with the highest adsorption capacity among adsorbents in its category. However, its adsorption capacity remains relatively low, limiting its industrial application for CO₂ adsorption. Additionally, there is a need to increase the optimal adsorption temperature of this porous material to effectively adsorb CO₂ emitted from flue gas, which has an average temperature of 100 - 125°C. To address these challenges, a preliminary study on Zn-doped zeolite has been conducted. This study aims to investigate the ability of Zn-doped zeolite to enhance CO₂ adsorption capacity and its effect on the optimal temperature for CO₂ adsorption. Zinc-doped zeolite was synthesized by doping zinc oxide into natural zeolite using a zinc ion exchange method at different doping concentrations (0.2 M & 1.0 M). Undoped natural zeolite was studied as a benchmark. Their CO₂ adsorption performance was tested using TGA at 30°C, 50°C, and 100°C. The effects of temperature and doping concentration on adsorption capacity were investigated. The adsorbent samples were characterized using X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray (EDX) analysis. It was found that increasing the temperature from 30°C to 50°C increased the CO₂ adsorption capacity, but the capacity decreased when the temperature was further increased to 100°C. Furthermore, increasing the doping concentration tended to enhance the CO₂ adsorption capacity. The highest adsorption capacity of 0.0281 g CO₂/g sorbent was observed in zinc-doped zeolite with a 1.0 M doping concentration at 50°C. The improvement was mainly attributed to the zinc oxide doped on the zeolite, which provided a functional group that formed chemical bonds with CO₂. This study also found that the adsorption rate of CO₂ was predominantly influenced by temperature, while the effect of doping concentration was less significant. All testing and characterization results suggested that the zinc-ion exchange method improved the CO₂ adsorption capacity of zeolite.

Keywords: Zeolite, CO₂ adsorption, adsorption capacity, low temperature.

1. Introduction

Global warming has become a serious global threat, primarily caused by the greenhouse effect, where greenhouse gases accumulate in the atmosphere, increasing the Earth's average surface temperature (Klugmann-Radziemska, 2022). Approximately 400 million tons of carbon dioxide (CO₂) are emitted annually from human activities, making it the primary greenhouse gas (Sharma et al., 2022). To address global warming, CO₂ capture has emerged as a direct approach to mitigate its adverse effects on ecosystems and human societies.

Zeolite has been identified as a potential CO₂ adsorbent due to its low cost, mild regeneration conditions, and stability during the adsorption process (Rajakrishnamoorthy et al., 2023). It possesses excellent properties, including a very high BET surface area, thermal stability (Pham et al., 2016), and a tunable

structure (Jha & Singh, 2016) suitable for various applications. Notably, zeolite has the highest adsorption capacity among low-temperature range CO₂ adsorbents, such as activated carbon. Research has shown that zeolite achieves its highest adsorption capacity at 25°C, suggesting its suitability for low-temperature CO₂ capture (Chen et al., 2023).

However, its adsorption capacity remains relatively low compared to high-temperature range adsorbents like calcium oxide, limiting its industrial application for CO₂ adsorption. This porous material needs to increase the optimal adsorption temperature for adsorbing CO₂ emitted from flue gas, which averages 100 - 125°C. Given the tunable properties of zeolite, this study investigates zeolite doped with zinc oxide. Zinc was selected as the metal-based dopant due to its low cost, non-toxicity, high stability, and wide availability (Munawar et al., 2020). Additionally, zinc-doped zeolitic imidazolate framework-67 (ZIF-67) has shown enhanced water stability (Qian et al., 2018), an important characteristic for CO₂ adsorbents used in flue gas containing water vapor. Zn-doped CHA-type zeolite has demonstrated better kinetics and absorbability for low-concentration (400 ppm) CO₂ adsorption compared to 13X-zeolites (Fu et al., 2022).

In this paper, a preliminary study was conducted on Zn-doped zeolite for pure CO₂ adsorption. Undoped zeolite was

Authors information:

^aDepartment of Chemical Engineering, Lee Kong Chian Faculty of Engineering and Science, Universiti Tunku Abdul Rahman (Sungai Long Campus), Bandar Sungai Long, Cheras, 43000 Kajang, Selangor Darul Ehsan, MALAYSIA. E-mail: yuanggaun@utar.my¹; pcy1997@utar.my³

^bCentre for Advanced and Sustainable Materials Research (CASMR), Universiti Tunku Abdul Rahman (Sungai Long Campus), Bandar Sungai Long, Cheras, 43000 Kajang, Selangor Darul Ehsan, MALAYSIA. E-mail: gulnaziya@utar.edu.my⁴

*Corresponding Author: leezh@utar.edu.my²

Received: February 7, 2024

Accepted: May 7, 2024

Published: July 31, 2024

used as a benchmark. The study aims to investigate the ability of Zn-doped zeolite to enhance CO₂ adsorption capacity and its effect on the optimal temperature for CO₂ adsorption. Natural zeolite was used, and the scope includes examining the effects of temperature and Zn-doping concentration on the CO₂ adsorption capacity of the adsorbents.

2. Materials and methods

Natural zeolite in granular form and zinc hydroxide were supplied by R & M Chemicals and Bendosen, respectively. These chemicals were used without further purification or treatment. Zinc hydroxide solutions at different concentrations (0.2 M and 1.0 M) were prepared by dissolving zinc hydroxide in distilled water.

2.1 Sample Preparation

In total, 5 g of zeolite was mixed with 100 ml of 0.2 M zinc hydroxide solution. The mixture was stirred and heated at 70°C for 2 hours to increase the diffusion rate of the zinc ion into the zeolite structure for ion exchange. The mixture was then filtered to separate the treated zeolite in solid form from the solution, followed by continuous rinsing with distilled water. The wet treated zeolite was dried in an oven at 80°C overnight. After drying, the zeolite was calcined in a furnace at 270°C for 4 hours. The synthesis procedure was repeated using a 1.0 M zinc hydroxide solution. This study treated natural zeolite with zinc hydroxide at two different concentrations: 0.2 M and 1.0 M.

2.2 CO₂ Adsorption Performance

To examine the adsorption performance of the natural and zinc-doped zeolite, CO₂ adsorption experiments were conducted using a thermogravimetric analyzer (TGA, Perkin Elmer Simultaneous Thermal Analyzer 8000). TGA combines a microbalance and a furnace chamber, allowing the weight change of a sample placed in the furnace chamber to be recorded with changes in temperature and time under a specific gas flow. In this study, the adsorbent sample was held at a preset adsorption temperature under the flow of pure CO₂. The weight change of the adsorbent samples was recorded until stabilization. The experimental testing flow diagram is illustrated in Figure 1.

Approximately 20 mg ± 0.5 mg of the sample was loaded into the TGA. The sample was heated from ambient temperature to 500°C at 10°C/min under a 30 mL/min flow of pure NO₂ and held for 10 minutes as a pre-treatment to remove any water vapor and impurities. The sample was then cooled to the adsorption temperature at a rate of 20°C/min, and CO₂ flow was initiated upon reaching the desired adsorption temperature. The temperature was held at 100°C for 2 hours. The weight changes in the adsorbent during the adsorption process were recorded. Since zeolite-based adsorbents adsorb CO₂ without losing weight by forming by-products, the CO₂ adsorption capacity was determined by calculating the sample's weight percentage increase. The unit of adsorption capacity was converted to g/g by dividing the initial weight percentage, as shown in Eq (1).

$$\text{Adsorption Capacity } \left(\frac{g}{g}\right) = \frac{\text{Final Weight \%} - \text{Initial Weight \%}}{\text{Initial Weight \%}} \quad (1)$$

To determine the optimum CO₂ adsorption temperature, the sample was analysed over different temperatures at which CO₂ started to flow in at 30°C, 50°C and 100°C.

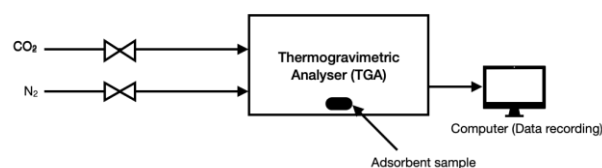


Figure 1 Schematic diagram of thermogravimetric analyzer setup in CO₂ adsorption performance testing.

2.3 Characterisation

The sample's surface morphology and element composition were derived using Hitachi S-3400N SEM with an accelerating voltage of 15 kV. The XRD pattern of the sample was recorded at room temperature using Shimadzu 6000. The analysis was conducted in the 2θ range of 20° to 80° using Cu-Kα radiation. The XRD pattern was interpreted to determine the presence of zinc oxide and its intensity.

3. Results and discussion

3.1 Effect of Adsorption Temperature

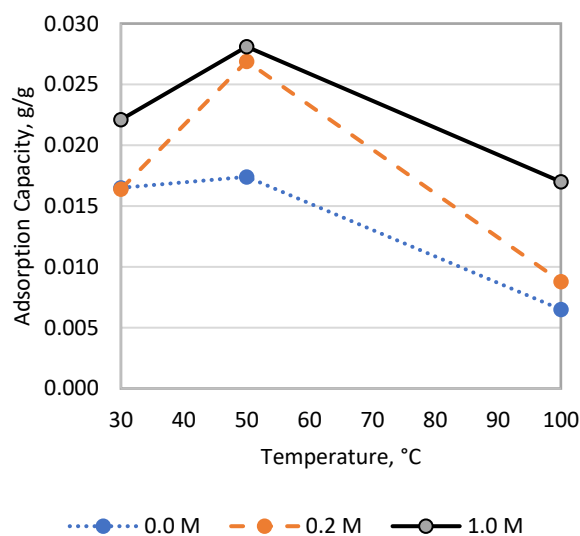


Figure 2. CO₂ adsorption capacities of undoped natural zeolite (0.0 M), doped natural zeolite treated with 0.2 M and 1.0 M of zinc hydroxide solution.

The adsorption capacities of the undoped natural zeolite and zinc-doped natural zeolite treated with 0.2 M and 1.0 M zinc hydroxide solutions are depicted in Figure 2. All adsorbent samples exhibited a similar trend: adsorption capacities increased with the initial rise in adsorption temperature, then decreased when the temperature was further increased to

100°C. Additionally, the increment in the adsorption capacity of untreated natural zeolite from 30°C to 50°C was not significant.

Theoretically, zeolite is a physical adsorbent that adsorbs CO₂ through van der Waals forces. Physical adsorbents have higher adsorption capacities at lower temperatures because higher temperatures weaken van der Waals forces (Zhang et al., 2023). This can be observed in the adsorption curve of natural zeolite in Figure 2. It has the highest adsorption capacity at low temperatures, with a slight increase at 50°C, but its adsorption capacity decreased to around 0.0065 g/g when the temperature was raised to 100°C.

However, doping natural zeolite with zinc oxide introduces chemical adsorption (chemisorption) as a contributing factor to CO₂ adsorption (Kusumastuti et al., 2019). Chemisorption requires slightly higher temperatures to gain enough activation energy for zinc oxide to form chemical bonds with CO₂ (Hagen, 2015). This explains why the increments in adsorption capacity from 30°C to 50°C for zinc-doped zeolite, as observed in Figure 2, are more significant and higher than those of natural zeolite. When the temperature further increased to 100°C, the van der Waals forces and the chemical interaction between zeolite and CO₂ weakened, decreasing adsorption capacity (Kusumastuti et al., 2019).

Since the activation energy for physisorption is low, the increase in the adsorption capacity of undoped natural zeolite from 30°C to 50°C is not significant. This minor increment can be attributed to the temperature difference not being large enough to substantially weaken the van der Waals forces.

3.2 Effect of Doping Concentration

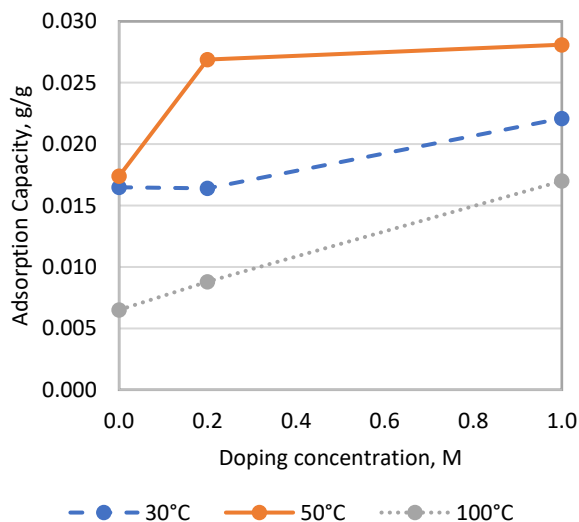


Figure 3. Comparison graph of adsorption capacity and doping concentration of the zeolite-based adsorbent samples.

Besides the effect of temperature, the CO₂ adsorption capacity is also influenced by the doping concentration. Figure 3 illustrates the relationship between adsorption capacity and doping concentration for the zeolite-based adsorbent samples.

According to Figure 3, the CO₂ adsorption capacity increases with doping concentration. This is because a higher doping concentration results in more zinc ions binding to the zeolite as extra-framework cations, which increases the amount of zinc oxide formed during calcination (Huong & Lee, 2017). Zinc oxide then forms chemical bonds with CO₂ (Gankanda et al., 2016), leading to an increased adsorption capacity as more CO₂ is adsorbed.

Additionally, Figure 3 shows that the increase in adsorption capacity for zinc-doped zeolite at 50°C was relatively low compared to 30°C and 100°C after the doping concentration of 0.2 M. As previously mentioned, CO₂ adsorption on zinc-doped zeolite is a combination of physisorption and chemisorption. At 50°C, both physisorption and chemisorption contribute significantly to CO₂ adsorption. When the doping concentration increases, the amount of zinc oxide doped onto the zeolite also increases, which can be confirmed by XRD and SEM results. However, when the amount of zinc oxide reaches a certain level, excess zinc oxide can lead to pore blockage, creating diffusion resistance and preventing CO₂ from being adsorbed (Bezerra et al., 2014). This results in a plateau in CO₂ adsorption capacity, as the contribution from physisorption ceases. Therefore, further increases in doping concentration at 50°C only yield minor improvements in CO₂ adsorption capacity.

This phenomenon was observed only at 50°C because it is the optimum temperature for CO₂ adsorption on zinc-doped zeolite. At this temperature, zinc-doped zeolite exhibited a higher CO₂ adsorption capacity compared to other temperatures, so the increase in adsorption capacity from 0.2 M to 1.0 M was not as significant as at other temperatures.

3.3 Characterisation

3.3.1 X-ray Diffraction (XRD)

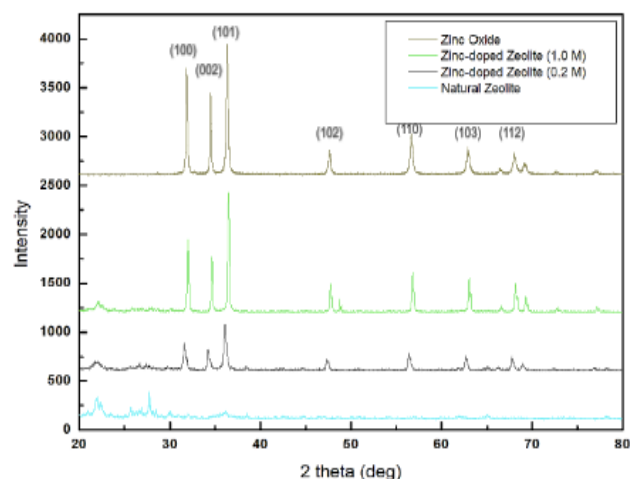


Figure 4. XRD diffractogram of zeolite-based adsorbent samples studied and pure ZnO.

The results of XRD are represented by the XRD diffraction patterns shown in Figure 4. The peaks observed in the zinc-doped zeolite (0.2 M and 1.0 M) XRD patterns are almost identical to the peaks found in the raw zinc oxide XRD pattern

(RRUFF Project, 2018). The major characteristic peaks attributed to zinc oxide appear at 2θ values of 31.8° , 34.5° , 36.3° , 47.6° , 56.6° , 62.9° , 66.4° , 68.0° , and 69.1° . This indicates that zinc oxide was successfully doped onto the zeolite structure through zinc ion exchange.

Additionally, comparing the patterns of 0.2 M and 1.0 M zinc-doped zeolite reveals that the peak intensity of 1.0 M zinc-doped zeolite is higher than that of 0.2 M zinc-doped zeolite. This is because a higher doping concentration leads to more zinc oxide formation, resulting in higher peak intensity. Consequently, the higher peak intensity in 1.0 M zinc-doped zeolite indicates a greater amount of zinc oxide, which provides more functional groups for CO_2 adsorption, thereby resulting in higher CO_2 adsorption capacity (Gankanda et al., 2016).

3.3.2 Scanning Electron Microscopy (SEM)

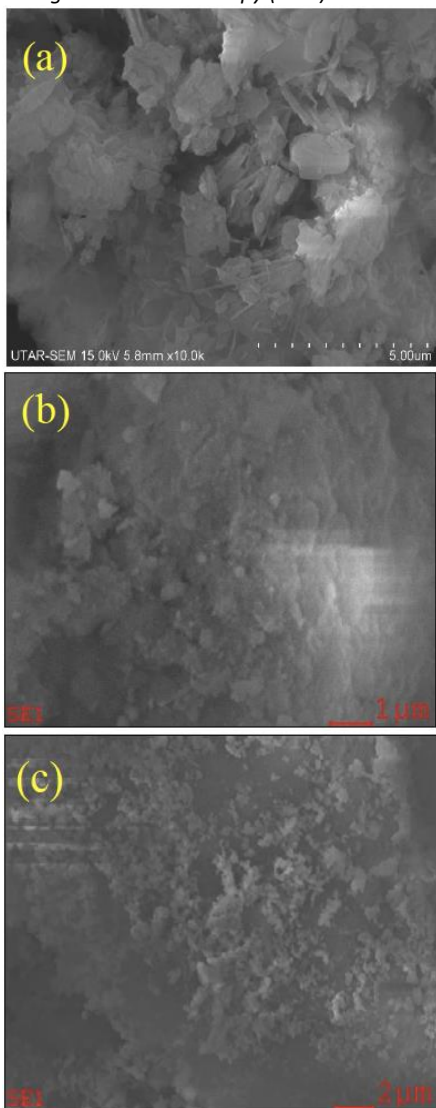


Figure 5. SEM Image of (a) Natural Zeolite, (b) 0.2 M Zinc-doped Zeolite and (c) 1.0 M Zinc-doped Zeolite

Figure 5 exhibits the SEM images of natural zeolite and zinc-doped zeolite. Natural zeolite displays a needle-like morphology with agglomerates, explaining its low adsorption capacity due to the limited number of pores and low pore size. In contrast, zinc-

doped zeolite shows a granular morphology with numerous clusters. Additionally, many small granules are visibly distributed over the surface of the structure, suggesting that zinc oxide particles have been successfully doped onto the zeolite.

3.3.4 Energy Dispersive X-ray (EDX)

The EDX results, detailing the elemental composition of O, Al, Si, K, and Zn for all samples, are shown in Table 1. These results confirm the successful doping of zinc oxide into the raw zeolite through zinc ion exchange, evidenced by the atomic percentage of zinc (Zn). While natural zeolite contains no zinc, zinc-doped zeolite with 0.2 M and 1.0 M doping concentrations contain 3.74 at% and 8.46 at%, respectively.

Additionally, the atomic percentage of silicon (Si) decreased following zinc doping, indicating that the doping process primarily involved the exchange of silicon ions with zinc ions. Silicon ions at the center of the zeolite structure are not exposed to CO_2 molecules and thus do not contribute to CO_2 adsorption (Huong & Lee, 2017). By exchanging Si ions with Zn ions, the zinc ions present within the zeolite facilitate zinc oxide formation on the surface during calcination, providing functional groups for chemical bonding with CO_2 (Gankanda et al., 2016). Consequently, the CO_2 adsorption capacity of zinc-doped zeolite is higher compared to natural zeolite.

Table 1. EDX analysis of the adsorbent samples

Adsorbent Samples	Element, at%					
	O	Al	Si	K	Zn	Si/Al ratio
Natural zeolite	61.18	4.43	32.94	0.95	0	7.4
0.2 M Zinc-doped zeolite	57.45	6.68	30.71	1.42	3.74	4.6
1.0 M Zinc-doped zeolite	55.99	4.97	29.71	0.86	8.46	6.0

By comparing their Si/Al ratio, natural zeolite has the highest ratio of 7.4. A high Si/Al ratio is preferable, since the higher the ratio, the higher thermal stability and hydrophobicity (Jha & Singh, 2016). Natural zeolite is more resistant to thermal degradation and moisture than zinc-doped zeolite.

4. Conclusion

Zinc-doped zeolite was successfully synthesized, tested, and characterized as a CO_2 adsorbent. The CO_2 adsorption capacity of zinc-doped zeolite increased as the temperature rose from 30°C to 50°C but decreased when the temperature further increased to 100°C . Compared to natural zeolite, there was a significant improvement in CO_2 adsorption capacity for zinc-doped zeolite. The highest adsorption capacity of $0.0281 \text{ g CO}_2/\text{g sorbent}$ was observed in zinc-doped zeolite with 1 M doping concentration at 50°C . This capacity was approximately 1.6 times higher than natural zeolite and 1.04 times higher than 0.2 M zinc-doped zeolite, indicating that higher doping concentrations lead to increased adsorption capacity. The improvement in CO_2

adsorption capacity was primarily due to the additional chemical interactions after doping zeolite with zinc oxide. The optimum temperature and doping concentration for the highest adsorption capacity were 50°C and 1.0 M, respectively.

Additionally, the adsorption kinetics of zeolite were studied. It was found that the adsorption rate of natural zeolite decreased as the temperature increased due to its physisorption nature. Conversely, the adsorption rate of zinc-doped zeolite increased as the temperature rose from 30°C to 50°C but decreased when the temperature reached 100°C. This behavior is attributed to the combination of physisorption and chemisorption in CO₂ adsorption. The difference in adsorption rate between 0.2 M and 1.0 M doping concentrations was insignificant, indicating that the adsorption rate was influenced by temperature but not significantly affected by doping concentration. In conclusion, although the improvement in CO₂ adsorption capacity through zinc ion exchange is still insufficient for industrial application, this novel approach shows promise and can be utilized for further research.

5. Acknowledgement

The authors would like to acknowledge for the financial support given by Universiti Tunku Abdul Rahman Research Fund (UTARRF) (Project No.: IPSR/RMC/UTARRF/2022-C2/L02).

6. References

- Bezerra, D. P., Silva, F. W. M. da, Moura, P. A. S. de, Sousa, A. G. S., Vieira, R. S., Rodriguez-Castellon, E., & Azevedo, D. C. S. (2014). CO₂ adsorption in amine-grafted zeolite 13X. *Applied Surface Science* 314: 314–321.
- Chen, C., Yu, J., Song, G., & Che, K. (2023). Desorption performance of commercial zeolites for temperature-swing CO₂ capture. *Journal of Environmental Chemical Engineering* 11(3): 110253.
- Fu, D., Park, Y., & Davis, M. E. (2022). Zinc Containing Small-Pore Zeolites for Capture of Low Concentration Carbon Dioxide. *Angewandte Chemie International Edition* 61(5): e202112916.
- Gankanda, A., Cwiertny, D. M., & Grassian, V. H. (2016). Role of Atmospheric CO₂ and H₂O Adsorption on ZnO and CuO Nanoparticle Aging: Formation of New Surface Phases and the Impact on Nanoparticle Dissolution. *The Journal of Physical Chemistry C* 120(34): 19195–19203.
- Hagen, J. (2015). *Industrial Catalysis: A Practical Approach*. 3rd ed. New Jersey: John Wiley & Sons.
- Hauchhum, L., & Mahanta, P. (2014). Carbon dioxide adsorption on zeolites and activated carbon by pressure swing adsorption in a fixed bed. *International Journal of Energy and Environmental Engineering* 5(4): 349-356.
- Huong, P.-T. & Lee, B.-K. (2017). Improvement of selective separation of CO₂ over N₂ by transition metal-exchanged. *Microporous and Mesoporous Materials* 241: 155-164.
- Jha, B. & Singh, D. N. (2016). *Advanced Structured Materials*. 1st ed. Singapore: Springer.
- Klugmann-Radziemska, E. (2022). 9.10 - The Environmental Benefits of Photovoltaic Systems: The Impact on the Environment in the Production of Photovoltaic Systems: With a Focus on Metal Recovery. In T. M. Letcher (Ed.), *Comprehensive Renewable Energy (Second Edition)*, pp. 140–151. Oxford: Elsevier.
- Kusumastuti, R., Sriyono, Pancoko, M., Butar-Butar, S-L., Putra, G.E., and Tjahjono, H. (2019). Study on the mechanism of CO₂ adsorption process on zeolite 5A as a molecular sieve in RDE system: An infrared investigation. *Journal of Physics: Conference Series* 1198: 032009.
- Munawar, K., Mansoor, M.A., Olmstead, M.M., Zaharinie, T., Zubir, M.N.M., Haniffa, M., Basirun, W.J., & Mazhar, M. (2020). Fabrication of Ag-ZnO composite thin films for plasmonic enhanced water splitting. *Materials Chemistry and Physics* 255: 123220.
- Pham, T.-H., Lee, B.-K., & Kim, J. (2016). Novel improvement of CO₂ adsorption capacity and selectivity by ethylenediamine-modified nano zeolite. *Journal of the Taiwan Institute of Chemical Engineers* 66: 239-248.
- Qian, X., Ren, Q., Wu, X., Sun, J., Wu, H., & Lei, J. (2018). Enhanced water stability in Zn-doped zeolitic imidazolate framework-67 (ZIF-67) for CO₂ capture applications. *Chemistry Select* 3: 657.
- Rajakrishnamoorthy, P., Saravanan, C.G., Natarajan, R., Karthikeyan, D., Sasikala, J., Josephin, J.S.F., Vikneswaran, M., Sonthalia, A., & Varuvel, E.G. (2023). Exhaust emission control of SI engines using ZSM-5 zeolite supported bimetals as a catalyst synthesized from coal fly ash. *Fuel* 340: 127380.
- Sharma, K., Park, Y.-K., Nadda, A.K., Banerjee, P., Singh, P., Raizada, P., Banat, F., Bharath, G., Jeong, S.M., & Lam, S.S. (2022). Emerging chemo-biocatalytic routes for valorization of major greenhouse gases (GHG) into industrial products: A comprehensive review. *Journal of Industrial and Engineering Chemistry* 109: 1-20.
- Zhang, J., Huang, D., Shao, J., Zhang, X., Zhang, S., Yang, H., & Chen, H. (2023). A new nitrogen-enriched biochar modified by ZIF-8 grafting and annealing for enhancing CO₂ adsorption. *Fuel Processing Technology* 231: 107250.