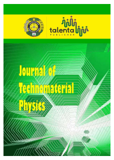
Journal of Technomaterial Physics
Journal homepage: https://talenta.usu.ac.id/JoTP



Preparation and Characterization of Hierarchical Zeolite from Natural Zeolite Using Tandem Acid–Base Treatments

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ARTICLE INFO

Article history:
Received 04 March 2026
Revised 27 March 2026
Accepted 31 March 2026
Available online 02 April 2026

E-ISSN: 2656-0755
P-ISSN: 2656-0747

How to cite:
I. R. Saragi and D. Y. Christine, "Preparation and Characterization of Hierarchical Zeolite from Natural Zeolite Using Tandem Acid–Base Treatments," Journal of Technomaterial Physics, vol. 08, no. 01, pp. 42-49, Feb. 2026, doi: 10.32734/jotp.v8i1.24887.

ABSTRACT

Hierarchical zeolite was successfully synthesized from Lampung natural zeolite via sequential tandem acid–base treatments. The combined dealumination–desilication approach generated additional mesoporosity while preserving the zeolite's crystalline framework, as confirmed by X-ray diffraction (XRD). Nitrogen adsorption–desorption isotherms revealed a transformation from Type I to Type IV behavior, indicating successful mesoporous formation. The BET surface area increased from 4.795 to 16.855 m²/g, accompanied by a significant increase in mesopore volume. Elemental analysis showed that the Si/Al ratio decreased from 8.42 to 2.44 due to the dominant extraction of silicon during alkaline treatment. The modified zeolite (Zeolite-PTAB) exhibited enhanced Cu^{2+} adsorption capacity (19.3 mg/g) compared to raw zeolite (16.1 mg/g), with removal efficiency improving from 53.7% to 64.3%. These findings demonstrate that tandem acid–base treatment provides a simple and effective strategy for upgrading Indonesian natural zeolite into a hierarchical adsorbent for heavy-metal removal applications.

Keywords: Adsorption, Dealumination, Hierarchical, Natural Zeolite, Tandem Acid-Base Treatments

ABSTRAK

Zeolit hierarki berhasil disintesis dari zeolit alam Lampung melalui perlakuan sekuensial tandem asam–basa. Pendekatan kombinasi dealuminasi–desilikasi menghasilkan struktur pori hierarki dengan tetap mempertahankan kristalinitas material, sebagaimana dikonfirmasi oleh analisis XRD. Isoterm adsorpsi–desorpsi nitrogen menunjukkan transformasi dari tipe I menjadi tipe IV, yang mengindikasikan keberhasilan pembentukan mesopori. Luas permukaan BET meningkat dari 4,795 menjadi 16,855 m²/g, disertai peningkatan signifikan pada volume mesopori. Analisis unsur menunjukkan bahwa rasio Si/Al menurun dari 8,42 menjadi 2,44 akibat dominannya ekstraksi silikon selama perlakuan alkali. Zeolit termodifikasi (Zeolit-PTAB) menunjukkan kapasitas adsorpsi Cu^{2+} yang lebih tinggi (19,3 mg/g) dibandingkan zeolit tanpa modifikasi (16,1 mg/g), dengan efisiensi penyisihan meningkat dari 53,7% menjadi 64,3%. Hasil ini menunjukkan bahwa perlakuan tandem asam–basa merupakan strategi yang sederhana dan efektif untuk meningkatkan kinerja zeolit alam Indonesia sebagai adsorben hierarki untuk aplikasi penghilangan logam berat.

Kata kunci: Adsorpsi, Dealuminasi, Hierarki, Zeolite Alam, Perlakuan Asam-Basa

1. Introduction

Zeolites are crystalline hydrated aluminosilicate minerals classified as tectosilicates, consisting of a three-dimensional framework of SiO_4 and AlO_4 tetrahedra connected through shared oxygen atoms[1]. This framework generates well-defined microporous channels that provide zeolites with high surface area, ion-exchange capability, and strong adsorption properties. Due to their unique ion-exchange and adsorption properties, zeolites are widely utilized in environmental remediation [2], agriculture[3], wastewater treatment[4] and catalyst[5].

Indonesia possesses abundant natural zeolite deposits, particularly in the Lampung region where clinoptilolite is commonly found. Clinoptilolite is a silica-rich zeolite with the general formula $(Na,K,Ca)_4Al_6Si_{30}O_{72}\cdot 24H_2O$ and is known for its good thermal stability, adsorption capacity, and ion-exchange properties. These advantages make Lampung natural zeolite an attractive low-cost material for environmental applications.

Despite their high surface area, natural zeolites are predominantly microporous (pore diameter < 2 nm), which imposes significant diffusion limits on relatively large molecules. To overcome these limitations, the development of hierarchical zeolites containing both micropores and mesopores (2–50 nm) has attracted significant attention. The introduction of mesoporosity improves diffusion pathways, increases external surface area, and enhances accessibility to active sites without completely sacrificing intrinsic microporous characteristics. Several strategies have been proposed to generate hierarchical structures, including templating methods, desilication, dealumination, and post-synthetic modifications [6]–[11].

Several strategies have been developed to generate hierarchical structures in zeolites, including templating methods, dealumination, desilication, and post-synthetic modification. Acid treatment (dealumination)[12] selectively removes framework aluminum, potentially improving structural stability, whereas alkaline treatment (desilication)[13] removes silicon atoms and generates additional mesoporosity. While both dealumination and desilication treatments have been extensively investigated individually in previous studies, sequential tandem acid–base modification offers a more controlled approach to simultaneously tailor framework composition and pore architecture [14].

Copper contamination commonly originates from electroplating industries, printed circuit board manufacturing, mining activities, and metal finishing processes. Wastewater generated from these industries often contains significant concentrations of Cu^{2+} ions, which may contaminate natural water bodies if discharged without adequate treatment. Heavy metal contamination, particularly copper (Cu^{2+}), represents a serious environmental concern due to its toxicity and persistence in aquatic environments [15]–[20]. Although Cu^{2+} is an essential trace element for biological systems, excessive exposure may cause severe health disorders, including liver and kidney damage. Moreover, copper ions are non-biodegradable and tend to accumulate in aquatic ecosystems. According to the Indonesian drinking water quality standard (Minister of Health Regulation No. 492/MENKES/PER/IV/2010), the maximum allowable concentration of copper in drinking water is 2 mg/L. Therefore, efficient removal of Cu^{2+} from wastewater is essential.

Among available treatment methods such as chemical precipitation, membrane filtration, and reverse osmosis, adsorption remains one of the most practical and cost-effective approaches [21]. Natural zeolite is particularly attractive due to its low cost, availability, and environmental compatibility. However, structural modification is often required to improve its adsorption performance.

Therefore, this study aims to modify Lampung natural zeolite via sequential tandem acid–base treatments to generate hierarchical mesoporosity while maintaining structural integrity. The structural transformation was systematically characterized using XRD, BET surface area analysis, SEM, and elemental analysis. Furthermore, the adsorption performance toward Cu^{2+} ions was evaluated to establish the relationship between framework modification and functional performance. This work provides insight into a simple and scalable strategy to upgrade Indonesian natural zeolite for environmental remediation applications.

2. Methods

2.1 Materials

The primary raw material used was natural zeolite obtained from Kalianda, Lampung, which appears as a fine white powder. The chemical reagents used for modification and analysis included hydrochloric acid (HCl 0.6 M), sodium hydroxide (NaOH 0.2 M), sodium chloride (NaCl 0.5 M), hydrogen peroxide (H_2O_2 30%), and copper(II) nitrate trihydrate ($Cu(NO_3)_2\cdot 3H_2O$). Buffering agents for pre-treatment included sodium acetate, sodium citrate, sodium bicarbonate, and sodium dithionite.

2.2 Preparation and Pre-treatment Material

The natural zeolite underwent a series of preparation steps to remove impurities and standardize the cation content as follows:

a. Physical activation: the natural zeolite was ground and sieved to obtain a particle size of 100 mesh prior to activation. The raw zeolite was stirred in deionized water (1:3 w/v) for three hours, then heated at 300 ◦C to remove polar impurities and open the pore structure.
b. Chemical Pre-treatment: the activated zeolite was stirred in a sodium acetate buffer (pH 5) at 80 ◦C for one hour to dissolve carbonate minerals. Organic matter was subsequently removed by oxidation with H_2O_2 (30%) at 80◦C for one hour. Finally, iron oxides were extracted using a citrate-bicarbonate-dithionite buffer at 80◦C for 30 minutes.
c. Cation Exchange Treatment: the pre-treated zeolite was dispersed in 0.5 M NaCl solution at a solid-to-liquid ratio of 1:10 (w/v) and stirred in a water bath at 80 °C for 2 × 8 h to homogenize the exchangeable cations within the zeolite framework. The resulting solid was then filtered and washed repeatedly with warm deionized water until chloride ions were no longer detected in the filtrate.

2.3 Tandem Acid-Base Post-Modification

The hierarchical structure was created using sequential dealumination and desilication as follows:

a. Dealumination (Acid Treatment): 10 g of treated zeolite was refluxed in 0.6 M HCl at 100°C for 2 h. This process was repeated twice to increase the Si: Al ratio by leaching aluminum from the framework.
b. Desilication (Base Treatment): the dealuminated sample was stirred in 0.2 M NaOH (3.3:100 w/v) at 65∘C for 30 minutes to direct mesopore formation. The final modified product was labeled Zeolite-PTAB.

2.4 Adsorption Experiment

Raw zeolite and Zeolite-PTAB (0.1 g each) were added to 10 mL of a 300 ppm Cu^{2+} solution prepared from copper(II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$). The suspension was stirred at 25 °C for different contact times of 30, 60, 120, and 180 minutes. After adsorption, the mixture was centrifuged at 6000 rpm for 3 minutes to separate the solid adsorbent from the filtrate. The concentration of Cu^{2+} remaining in the solution was subsequently determined using UV–Visible spectroscopy.

2.5 Characterization

The structural and chemical properties of the zeolites were analyzed using the following instrumentation. The X-Ray Diffraction (XRD) was conducted with $CuK\alpha$ radiation over a range of $2\theta=5-90^\circ$ to monitor changes in crystallinity. The BET Analysis was used to determine specific surface area, pore volume, and pore diameter via nitrogen adsorption-desorption isotherms after degassing at 300◦C. SEM-EDS was employed to observe surface morphology and elemental composition (Si, Al, Na) after coating samples with a thin layer of platinum, Atomic Absorption Spectroscopy (AAS) was used for bulk elemental analysis of Si, Al, and Na after dissolving samples in an HCl: HF (3:1) mixture. Adsorption Performance for Cu^{2+}. The adsorption capacity of the modified zeolite was tested using a 300 ppm Cu^{2+} solution. 0.1 g of adsorbent was added to 10 mL of the copper solution and stirred at 25◦C for intervals of 30, 60, 120, and 180 minutes. After centrifugation, the remaining copper concentration in the filtrate was determined via UV-Visible spectroscopy at a maximum wavelength of 610 nm following the addition of 0.5 mL concentrated NH_4OH.

3. Result and Discussion

3.1 X-Ray Diffraction Analysis

The XRD analysis results presented in Figure 1 illustrate the diffraction patterns of Lampung natural zeolite across various stages of modification. The diffraction peaks observed at approximately $2\theta \approx 22.4°$, 26.6°, 30.0°, and 32.0° (JCPDS/PDF No. 39-1383) correspond to the characteristic reflections of clinoptilolite-type zeolite, which are consistent with the standard reference pattern reported in the literature. In the higher 2θ region (35–80°), several low-intensity diffraction peaks were observed. These peaks are attributed to minor crystallographic reflections of the clinoptilolite structure and may also include contributions from naturally associated mineral impurities, such as quartz, commonly found in natural zeolite deposits. However, no new diffraction peaks corresponding to secondary crystalline phases were detected after modification, indicating that the tandem acid–base treatment did not introduce additional impurities or alter the primary zeolite framework. These peaks can be indexed to the typical crystallographic planes of clinoptilolite, such as (004), (200), (402), and related reflections. The preservation of the main diffraction peaks confirms that the zeolite framework remained structurally stable during the tandem acid–base modification.

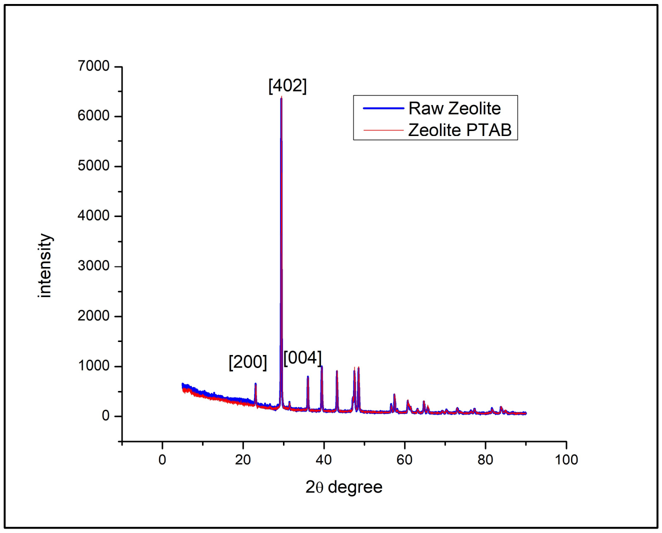

Figure 1. X-ray diffraction patterns of raw zeolite and Zeolite-PTAB showing the preservation of the clinoptilolite framework after tandem acid–base treatment.

However, a slight reduction in peak intensity is observed for the modified sample, suggesting partial framework rearrangement due to silicon extraction during alkaline desilication. Importantly, no additional diffraction peaks corresponding to impurity phases were detected, indicating that the modification process did not introduce new crystalline phases.

While acid treatment is typically associated with framework dealumination, the subsequent alkaline treatment plays a more dominant role in determining the final framework composition. During desilication, hydroxide ions selectively attack Si–O–Si bonds, leading to silicon extraction and partial framework rearrangement [22]. In contrast, AlO_4^- tetrahedral units exhibit greater resistance toward alkaline hydrolysis due to electrostatic repulsion between negatively charged framework sites and OH^- species. Consequently, silicon removal becomes more significant than aluminum extraction, resulting in a lower Si/Al ratio [9].

3.2 *Atomic Absorption Spectroscopy Analysis*

The bulk elemental composition of the zeolite samples was determined using Atomic Absorption Spectroscopy (AAS) after complete dissolution of the samples in an HCl: HF (3:1) mixture. The results of this analysis are summarized in Table 1. The Si/Al ratio decreased markedly from 8.42 in raw zeolite to 2.44 after tandem acid–base treatments, indicating significant framework modification.

In addition, the Na content decreased significantly after the modification process, indicating that part of the exchangeable cations in the zeolite framework was removed during acid treatment and subsequent washing steps. During desilication, hydroxide ions selectively attack Si–O–Si bonds, leading to silicon extraction, and the elemental composition presented in Table 1 was obtained from bulk elemental analysis and expressed as weight percentage (wt%).

Table 1. Bulk elemental composition and Si/Al ratio of raw zeolite and Zeolite-PTAB determined by AAS

Sample	%Na	% Si	% Al	Si/Al
Raw Zeolite	0.1194	2.4558	0.2917	8.4189
Zeolite- PTAB	0.0094	1.2871	0.5220	2.4449

3.3 *Surface Area Analyzer*

Nitrogen adsorption–desorption analysis was conducted to evaluate the development of porosity after tandem acid–base treatments. Figure 2 shows that the raw zeolite exhibits a Type I adsorption isotherm, which is characteristic of microporous materials where adsorption mainly occurs through pore filling at low relative pressure. According to the IUPAC classification, Type I isotherms are typically observed for materials with predominantly microporous structures.

In contrast, Zeolite-PTAB displayed a Type IV isotherm with a hysteresis loop, indicating mesopore formation. Type IV behavior indicates the occurrence of capillary condensation within mesopores, suggesting that the tandem acid–base treatment successfully generated additional mesoporous structures in the modified zeolite. The transformation from Type I to Type IV adsorption behavior, therefore, confirms the development of hierarchical pore structure in Zeolite-PTAB [23]. The textural parameters are summarized in Table 2.

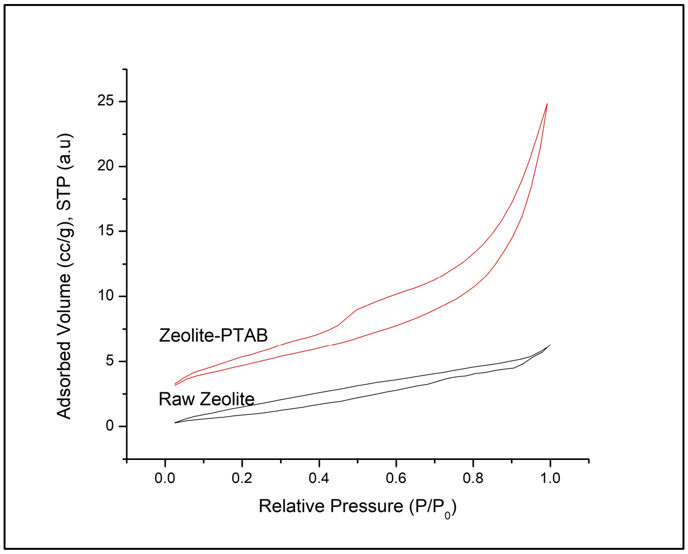

Figure 2. BET Analysis of Raw Zeolite and Zeolite PTAB

As shown in Table 2, the BET surface area increased significantly from 4.795 m²/g to 16.855 m²/g after modification, representing approximately 3.5-fold enhancement. This increase indicates that the tandem acid–base treatment successfully generated additional porosity in the zeolite structure. Similar increases in surface area after alkaline desilication treatments have been reported for modified natural zeolites [10], although the absolute values depend strongly on the zeolite type and treatment conditions. The external surface area of Zeolite-PTAB (15.375 m²/g) was considerably higher than its micropore surface area (1.48 m²/g), indicating that mesoporosity became dominant after treatment. The negligible micropore surface area observed in raw zeolite may be attributed to the limited accessibility of nitrogen molecules to narrow micropores during BET measurement.

Table 2. BET surface area and pore characteristics of raw zeolite and Zeolite-PTAB

Sample	SBET (m²/g)	Smicro (m²/g)	Sexternal (m²/g)	Vtotal (cc/g)	Vmicro (cc/g)	Vmeso (cc/g)	Pore diameter (nm)
Raw Zeolite	4.795	4.795	0.000	0.0097	0.000	0.0097	5.116
Zeolite-PTAB	16.855	1.480	15.375	0.0348	0.001	0.0338	3.988

3.4 Scanning Electron Microscopy Analysis

The morphology of the natural zeolite was examined using scanning electron microscopy (SEM), as shown in Figure 3. The natural zeolite appears as a greenish powder before treatment. After the activation process, no significant macroscopic changes in the material's appearance were observed. The SEM image reveals that the zeolite particles exhibit irregularly aggregated structures, forming clusters. The aggregated morphology observed in the SEM image is typical for natural clinoptilolite and may contribute to the formation of interparticle mesoporosity. The particles appear tightly packed, forming irregular agglomerates with rough surfaces. This morphology is commonly observed in natural clinoptilolite and is associated with the stacking of aluminosilicate crystals.

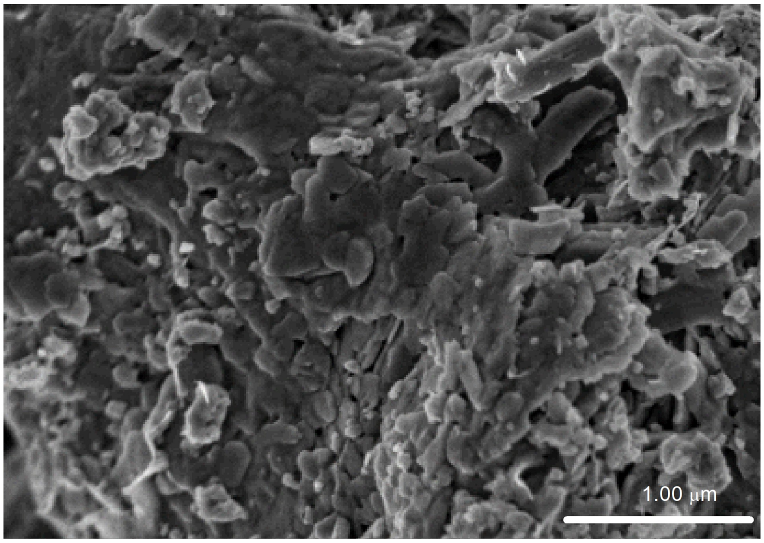

Figure 3. SEM micrograph of natural zeolite at 30,000× magnification

3.5 Cu^{2+} Adsorption Performance

Figure 4 presents the adsorption capacity of Cu^{2+} ions on raw zeolite and Zeolite-PTAB as a function of contact time. The adsorption capacity of raw zeolite increased from 0.2 mg/g at 30 minutes to 16.1 mg/g at 180 minutes. The adsorption capacity obtained in this study (19.3 mg/g) is comparable with previously reported values for modified natural zeolites used for Cu^{2+} removal, which typically range from 15 to 30 mg/g [10].

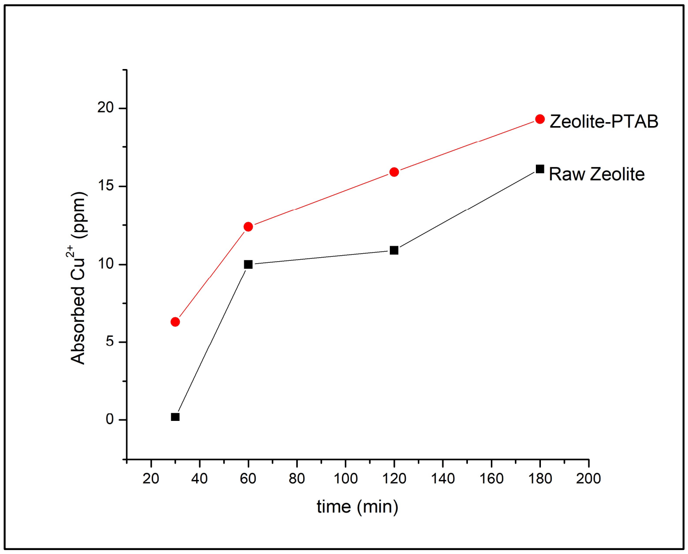

Figure 4. Adsorption capacity of Cu^{2+} ($[Cu(NH_3)_4]^{2+}$) on Raw Zeolite and Zeolite-PTAB

Figure 4 shows that removal efficiency improved from 53.7% (raw zeolite) to 64.3% (Zeolite-PTAB). The enhanced performance is attributed to increased surface area and improved pore accessibility resulting from the hierarchical structure. The adsorption of Cu^{2+} on zeolite is primarily governed by ion exchange mechanisms between Cu^{2+} ions in solution and exchangeable cations such as Na^+ present in the zeolite framework. In addition, the increased external surface area and improved pore accessibility resulting from the hierarchical structure facilitate the diffusion of Cu^{2+} ions into the pore system, thereby enhancing adsorption efficiency. The faster initial uptake observed in Zeolite-PTAB indicates improved diffusion pathways and greater availability of active sites[10].

4. Conclusion

Hierarchical zeolite was successfully synthesized via tandem acid–base treatment of Lampung natural zeolite. Structural analysis confirmed the preservation of crystallinity, while compositional analysis revealed the dominant extraction of silicon during alkaline treatment. Surface area increased more than threefold, and mesoporosity was confirmed by Type IV isotherm behavior. Zeolite-PTAB demonstrated improved Cu^{2+} adsorption capacity and removal efficiency compared to raw zeolite. The tandem modification strategy offers a practical, low-cost approach to upgrading Indonesian natural zeolite for environmental remediation applications. Future studies should investigate adsorption isotherm modeling and regeneration performance to evaluate industrial feasibility.

Acknowledgments

This work was supported by TALENTA- PERINTIS Research Grant No. 1/UN5.4.10.S/PPM/KP-TALENTA/PD/2024 from Universitas Sumatera Utara. We also acknowledge the Dean of the Faculty of Mathematics and Natural Science, Universitas Sumatera Utara, for the generous support in the making process of this paper.

References

[1] Istadi, W. Alqurni, and T. Riyanto, ‘Enhancing hierarchical factor (HF) and catalytic performance of Bayah’s natural zeolite catalyst for hydrocracking of palm oil to biofuels’, *Int. J. Renew. Energy Dev.*, vol. 15, no. 2, pp. 216–229, 2026, doi: 10.61435/ijred.2026.61669.

[2] S. Gao, J. Li, X. Wang, Y. Chen, and H. Zhang, ‘Synthesis of zeolites from low-cost feeds and its sustainable environmental applications’, *J. Environ. Chem. Eng.*, vol. 11, no. 1, p. 108995, 2023, doi: 10.1016/j.jece.2022.108995.

[3] E. Cataldo, A. Salviulo, M. P. Colombani, and G. Giordano, ‘Application of zeolites in agriculture and other potential uses: A review’, *Agronomy*, vol. 11, no. 8, 2021, doi: 10.3390/agronomy11081547.

[4] Y. Li, L. Li, and J. Yu, ‘Applications of zeolites in sustainable chemistry’, *Chem*, vol. 3, no. 6, pp. 928–949, 2017, doi: 10.1016/j.chempr.2017.10.009.

[5] Y. K. Krisnandi, R. R. Mukti, D. E. S. Purnama, and H. Nur, ‘Synthesis and characterization of crystalline NaY-zeolite from Belitung kaolin as catalyst for n-hexadecane cracking’, *Crystals*, vol. 9, no. 8, 2019, doi: 10.3390/cryst9080404.

[6] S. Tanirbergenova, A. T. Zhumakanova, A. M. Zharmagambetova, and N. Z. Tashmukhambetova, ‘Effect of acid treatment on the structure of natural zeolite from the Shankhanai deposit’, *Processes*, vol. 13, no. 9, 2025, doi: 10.3390/pr13092896.

[7] Y. N. Abdulai, M. A. A. Aziz, S. Al-Fatesh, A. Fakeeha, and A. E. Abasaeed, ‘Tailoring acid–base properties in Ni/ZSM-5 catalysts via sequential ion exchange and surface modification for stable dry reforming of methane’, *Mol. Catal.*, vol. 594, p. 115819, 2026, doi: 10.1016/j.mcat.2026.115819.

[8] G. Ancora, F. Morari, J. C. Julio, L. Marchese, C. Bisio, and E. Gianotti, ‘Insights into the role of hierarchical porosity in zeolite architectures for selective uptake of metal ions in solution’, *RSC Adv.*, vol. 15, no. 25, pp. 20092–20110, 2025, doi: 10.1039/d5ra03012a.

[9] Y. Han, K. Larmier, M. Rivallan, and G. D. Pirngruber, ‘Generation of mesoporosity in H–Y zeolites by basic or acid/basic treatments: Towards a guideline of optimal Si/Al ratio and basic reagent’, *Microporous Mesoporous Mater.*, vol. 365, p. 112906, 2024, doi: 10.1016/j.micromeso.2023.112906.

[10] D. S. Oliveira, R. B. Lima, S. B. C. Pergher, and V. P. S. Caldeira, ‘Hierarchical zeolite synthesis by alkaline treatment: Advantages and applications’, *Catalysts*, vol. 13, no. 2, 2023, doi: 10.3390/catal13020316.

[11] W. J. Roth, B. Gil, K. A. Tarach, and K. Góra-Marek, ‘Top-down engineering of zeolite porosity’, *Chem. Soc. Rev.*, vol. 54, no. 16, pp. 7484–7560, 2025, doi: 10.1039/d5cs00319a.

[12] M. C. Silaghi, C. Chizallet, J. Sauer, and P. Raybaud, ‘Dealumination mechanisms of zeolites and extra-framework aluminum confinement’, *J. Catal.*, vol. 339, pp. 242–255, 2016, doi: 10.1016/j.jcat.2016.04.021.

[13] D. Verboekend and J. Pérez-Ramírez, ‘Design of hierarchical zeolite catalysts by desilication’, *Catal. Sci. Technol.*, vol. 1, no. 6, pp. 879–890, 2011, doi: 10.1039/c1cy00150g.

[14] Y. Han, K. Larmier, M. Rivallan, and G. D. Pirngruber, ‘Generation of mesoporosity in H–Y zeolites by basic or acid/basic treatments: Towards a guideline of optimal Si/Al ratio and basic reagent’, *Microporous Mesoporous Mater.*, vol. 365, p. 112906, 2024, doi: 10.1016/j.micromeso.2023.112906.

[15] N. Elboughdiri, ‘The use of natural zeolite to remove heavy metals Cu (II), Pb (II) and Cd (II) from industrial wastewater’, *Cogent Eng.*, vol. 7, no. 1, 2020, doi: 10.1080/23311916.2020.1782623.

[16] S. R. Zekavat, F. Raouf, and S. S. A. Talesh, ‘Simultaneous adsorption of Cu2+ and Cr (VI) using HDTMA-modified zeolite: isotherm, kinetic, mechanism, and thermodynamic studies’, *Water Sci. Technol.*, vol. 82, no. 9, pp. 1808–1824, 2020, doi: 10.2166/wst.2020.448.

[17] E. Restiawaty, V. A. Gozali, T. A. S. E. Wibisono, and Y. W. Budhi, ‘Utilizing modified clinoptilolite for the adsorption of heavy metal ions in acid mine drainage’, *Case Stud. Chem. Environ. Eng.*, vol. 9, p. 100706, 2024, doi: 10.1016/j.cscee.2024.100706.

[18] J. N. Enemmoh, D. Harbottle, M. Yusuf, and T. N. Hunter, ‘Combined clinoptilolite and Fe(O)OH for efficient removal of Cu(II) and Pb(II) with enhanced solid–liquid separation’, *Discov. Chem. Eng.*, vol. 5, no. 1, 2025, doi: 10.1007/s43938-025-00075-y.

[19] M. Ugrina, I. Nuić, and J. Milojković, ‘Study on the performance of copper(II) sorption using natural and Fe(III)-modified natural zeolite–sorption parameters optimization and mechanism elucidation’, *Processes*, vol. 13, no. 9, 2025, doi: 10.3390/pr13092672.

[20] C. M. van Genuchten, K. Wang, C. Kjøller, and K. Dideriksen, ‘Molecular-scale investigation of Cu(II) interactions with synthetic and natural zeolites during removal and recovery’, *Environ. Sci. Water Res. Technol.*, vol. 12, no. 1, pp. 314–327, 2026, doi: 10.1039/d5ew00972c.

[21] F. Fu and Q. Wang, ‘Removal of heavy metal ions from wastewaters: A review’, *J. Environ. Manage.*, vol. 92, no. 3, pp. 407–418, 2011, doi: 10.1016/j.jenvman.2010.11.011.

[22] S. Rasamimanana, S. Mignard, and I. Batonneau-Gener, ‘Hierarchical zeolites as adsorbents for mesosulfuron-methyl removal in aqueous phase’, *Microporous Mesoporous Mater.*, vol. 226, pp. 153–161, 2016, doi: 10.1016/j.micromeso.2015.12.014.

[23] M. Thommes, K. Kaneko, A. V. Neimark, J. P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, and K. S. W. Sing, ‘Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC technical report)’, *Pure Appl. Chem.*, vol. 87, no. 9–10, pp. 1051–1069, 2015, doi: 10.1515/pac-2014-1117.