

Article

Waste Aluminum Dust-Derived Functional Zeolites for Heavy Metal Removal and Water Softening: Synthesis, Purification, and Ion-Exchange Modification

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Abstract

Waste aluminum dust generated from aluminum refining and machining processes contains high fractions of Al_2O_3 and SiO_2 , making it a potential secondary aluminosilicate resource for zeolite synthesis. In this study, waste aluminum dust was converted into functional zeolite materials through dry fusion purification, NaOH-assisted hydrothermal synthesis, acid purification, Si/Al ratio control, and cation-exchange modification. The raw dust was subjected to dry fusion at 1600 °C under an Ar atmosphere to remove metallic impurities and obtain an aluminosilicate precursor. Na-type zeolite was then synthesized using 50 wt.% NaOH solution at 90 °C for 24 h. The as-synthesized Na-type zeolite exhibited an estimated chemical purity of 97.501 wt.% based on measured residual impurities, with Mg, Ca, K, and Ti remaining as major impurities. HCl leaching at 0.25 M for 24 h increased the estimated chemical purity based on measured residual impurities to 98.469 wt.% while retaining the major zeolitic diffraction features. The Si/Al ratio was further controlled using water glass, and the maximum Si/Al ratio of 1.77 was obtained at a Na-type zeolite-to-water-glass mass ratio of 1:2 after reaction at 90 °C for 6 h. The purified and composition-controlled zeolite was subsequently modified with Mg^{2+} and K^+ ions to prepare Mg-modified and K-modified zeolites. Under fixed batch conditions using a relatively high zeolite dosage and a single initial concentration, Mg-modified zeolite reduced Pb, Hg, Cr(VI), and Cd concentrations from 100 ppm to 0.004, 0.00059, 0.018, and 0.004 ppm, respectively, while K-modified zeolite reduced the total hardness of synthetic hard water from 308.3 to 40.13 ppm as CaCO_3 . These results should be interpreted as preliminary batch-performance results under the tested conditions rather than as maximum adsorption capacities or a complete adsorption-mechanism evaluation. Overall, this study demonstrates the feasibility of valorizing waste aluminum dust into purified and cation-modified zeolite materials for potential water-treatment applications. Further adsorption isotherm, kinetic, dosage-dependent, BET surface area, pore-volume, pore-size distribution, and quantitative phase analyses are required to evaluate adsorption capacity, adsorption mechanism, true zeolite phase purity, and framework–performance relationships.

Keywords: waste aluminum dust; zeolite synthesis; dry fusion; Na-type zeolite; acid leaching; Si/Al ratio; ion exchange; heavy metal removal; water softening; aluminum dross recycling

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1. Introduction

The aluminum refining, recycling, and machining industries generate large quantities of aluminum-containing residues, including aluminum dross, salt slag, and fine waste aluminum dust. These residues commonly contain Al_2O_3 , metallic Al, AlN , SiO_2 , chloride salts, and various metal oxides, depending on the raw material source and processing conditions [1,2]. Because of their salt content, hydrolyzable phases, and impurity-bearing nature, aluminum residues can cause environmental and handling problems if they are directly landfilled or insufficiently treated [1–4]. At the same time, their high contents of aluminum- and silicon-bearing phases indicate that they can be considered secondary resources for the production of value-added aluminosilicate materials rather than merely industrial wastes.

Conventional treatment routes for aluminum dross and related residues have mainly focused on metallic aluminum recovery, salt removal, stabilization, cryolite synthesis, alkaline extraction of aluminum species, or conversion into adsorbent-type materials [5–7]. Although these approaches can partially recover valuable components or reduce environmental risks, the non-metallic alumina-rich fraction is still often underutilized. In particular, the fine dust fraction generated during aluminum refining and machining processes contains both useful Al–Si components and undesirable impurities such as Mg, Ca, Fe, Zn, Ti, alkali salts, and chlorides. Therefore, an effective valorization process should simultaneously address impurity removal, conversion of the Al–Si fraction into a reactive precursor, and synthesis of a functional material with practical applications.

Zeolites are crystalline microporous aluminosilicates composed of corner-sharing SiO_4 and AlO_4 tetrahedra. Their negatively charged frameworks are balanced by exchangeable cations such as Na^+ , K^+ , Ca^{2+} , or Mg^{2+} , which gives zeolites a high ion-exchange capacity, adsorption ability, and tunable surface chemistry [6,7]. Owing to these structural characteristics, zeolites have been widely used in water treatment, adsorption, catalysis, and environmental remediation [6–9]. In particular, low-silica zeolites such as LTA, NaP, X-type, and related Na-type zeolites are effective for the removal of heavy metal ions and hardness-causing Ca^{2+} and Mg^{2+} ions from aqueous solutions through ion exchange and adsorption processes [9–12].

The synthesis of zeolites from industrial and agricultural solid wastes has attracted increasing attention as a sustainable alternative to conventional reagent-based synthesis. Coal fly ash, boiler ash, waste glass, photovoltaic glass, rice husk ash, sugarcane bagasse ash, and lithium-processing residues have been investigated as alternative Si and/or Al sources for zeolite synthesis [13–24]. For example, coal fly ash-derived zeolites have been prepared through alkaline fusion and hydrothermal treatment and applied for the removal of heavy metal ions from aqueous solutions [13,14]. Other studies have demonstrated the feasibility of converting waste glass- or ash-derived Si sources into zeolitic materials for wastewater treatment and environmental remediation [15–19]. These studies clearly show that waste-derived zeolites can serve as low-cost adsorbents and ion exchangers while simultaneously contributing to solid-waste valorization.

Recent studies have also attempted to use aluminum-industry residues as aluminum sources for zeolite synthesis. Ritter et al. synthesized highly crystalline LTA and SOD zeolites by co-recycling aluminum salt slag and rice husk ash, demonstrating that aluminum salt slag can act as an alumina source when combined with a silica-rich waste [20]. Kang et al. reported the synthesis of zeolite from aluminum dross and waste LCD glass powder through a waste-to-waste integration approach, using aluminum dross as the Al source and waste glass as the Si source [21]. These studies confirm the potential of aluminum dross or salt slag as zeolite precursors [20,21,23,24]. However, most previous studies have focused on mixed-waste streams or specific aluminum dross fractions, and relatively limited attention has been given to fine waste aluminum dust generated from aluminum

refining and machining processes. Moreover, the integration of dry purification, zeolite synthesis, acid purification, Si/Al ratio control, and targeted cation-exchange functionalization has not been sufficiently explored in a single process route.

In this study, waste aluminum dust was used as a secondary aluminosilicate resource for the synthesis of functional zeolites. The process consisted of dry fusion purification to remove metallic and soluble impurities, including reducible Fe- and Zn-bearing oxides and water-soluble chloride and alkali salt species such as NaCl, KCl, Na₂O, K₂O, and Cl-containing compounds; NaOH-assisted hydrothermal synthesis of Na-type zeolite; HCl leaching for purity improvement; Si/Al ratio control using water glass; and subsequent cation-exchange modification using Mg²⁺ and K⁺ ions. Mg-modified zeolite was evaluated as an adsorbent for Pb, Hg, Cr, and Cd removal, while K-modified zeolite was applied as an ion exchanger for water softening by removing Ca²⁺ and Mg²⁺. The novelty of this work lies in the integrated conversion of waste aluminum dust into high-purity and application-specific zeolite materials through sequential purification, composition control, and ion-exchange functionalization. This approach provides a potential route for the valorization of aluminum-industry waste into functional water-treatment materials.

2. Materials and Methods

2.1. Experimental Materials

Waste aluminum dust generated from aluminum refining and machining processes was used as the starting material for zeolite synthesis. The raw dust mainly consisted of Al₂O₃ and SiO₂, together with minor impurity-containing phases such as Fe-, Zn-, Ti-, Ca-, Mg-, Na-, K-, and chloride-bearing compounds. According to the XRF analysis, the raw waste aluminum dust contained 78.8388 wt.% Al₂O₃ and 8.8266 wt.% SiO₂ as the major components, while minor components included Cl, Na₂O, K₂O, ZnO, Fe₂O₃, CaO, MgO, TiO₂, V₂O₅, and SO₃. Because these impurities can affect zeolite crystallization, product purity, and subsequent ion-exchange performance, the raw waste aluminum dust was first purified by a dry fusion process before Na-type zeolite synthesis. The raw materials and chemical reagents used in this study are summarized in Table 1. Silica powder was added as an auxiliary Si source during dry fusion, and carbon powder was used as a reductant for the carbothermic reduction of reducible metal oxides. Sodium hydroxide solution was used as the alkaline reagent for Na-type zeolite synthesis. Hydrochloric acid was used for acid purification of the synthesized Na-type zeolite. Water glass, i.e., sodium silicate solution, was used as an additional Si source to control the Si/Al ratio of the purified zeolite, and the Si/Al ratio was adjusted in the range of approximately 1.455–1.769 depending on the water glass addition amount and reaction time. Magnesium chloride and potassium chloride were used as cation-exchange reagents to prepare Mg-modified and K-modified zeolites, respectively. Standard solutions of Pb, Hg, Cr, Cd, Ca, and Mg were used to evaluate heavy metal removal and water-softening performance. The Cr standard solution used in this study was a Cr(VI) standard solution prepared from potassium dichromate. Therefore, chromium in the adsorption experiment was considered to be present as Cr(VI) oxyanion species, such as CrO₄²⁻, HCrO₄⁻, and/or Cr₂O₇²⁻, depending on the solution pH and concentration. Accordingly, Cr(VI) removal was distinguished from the removal of cationic heavy metals such as Pb, Hg, and Cd in the mechanistic discussion.

Table 1. Raw materials and chemical reagents used in this study.

Material/Reagent	Manufacturer/Source	Assay/Purity/ Concentration/Grade	Role in This Study
Waste aluminum dust	Aluminum refining and machining process	Industrial waste residue; used as received	Starting aluminosilicate-containing industrial waste
SiO ₂ powder	Daejung Chemicals (Siheung, Republic of Korea)	Extra pure grade	Auxiliary Si source for dry fusion
Carbon powder	Daejung Chemicals	CP reagent grade	Reductant for dry fusion purification
NaOH	Daejung Chemicals	Assay ≥98.0%	Alkaline reagent for Na-type zeolite synthesis
HCl solution	Daejung Chemicals	35.0–37.0% HCl	Acid leaching reagent for zeolite purification
Water glass	Daejung Chemicals	CP reagent grade; SiO ₂ 28.0–30.0%, Na ₂ O 9.0–10.0%	Additional Si source for Si/Al ratio control
MgCl ₂	Sigma-Aldrich (St. Louis, MO, USA)	Assay ≥98.0%; anhydrous grade	Mg ²⁺ source for Mg-modified zeolite preparation
KCl	Junsei Chemical Co., Ltd. (Tokyo, Japan)	Purity ≥99.0%	K ⁺ source for K-modified zeolite preparation
Pb standard solution	KANTO CHEMICAL CO., INC. (Tokyo, Japan)	1000 mg L ⁻¹ Pb	Heavy metal removal test
Hg standard solution	KANTO CHEMICAL CO., INC.	1000 mg L ⁻¹ Hg	Heavy metal removal test
Cr standard solution	KANTO CHEMICAL CO., INC.	1000 mg L ⁻¹ Cr(VI); potassium dichromate-based standard solution	Cr(VI) oxyanion removal test
Cd standard solution	KANTO CHEMICAL CO., INC.	1000 mg L ⁻¹ Cd	Heavy metal removal test
Ca standard solution	KANTO CHEMICAL CO., INC.	1000 mg L ⁻¹ Ca	Synthetic hard water preparation
Mg standard solution	KANTO CHEMICAL CO., INC.	1000 mg L ⁻¹ Mg	Synthetic hard water preparation

To clarify the overall experimental design and the role of each processing step, the experimental stages, processing conditions, products, and analytical methods used in this study are summarized in Table 2.

Table 2. Summary of the experimental stages, processing conditions, and analytical methods used in this study.

Stage	Purpose	Material/Input	Main Condition	Output/Product	Main Analysis
Raw material characterization	To evaluate the feasibility of waste aluminum dust as an aluminosilicate source	Waste aluminum dust	As-received powder	Raw material composition and crystalline phases	XRD, XRF
Dry fusion purification	To remove or reduce chloride salts and reducible metal oxide impurities and	Waste aluminum dust, SiO ₂ , and carbon powder	1600 °C, Ar atmosphere, 1 h	Purified aluminosilicate precursor	XRD, XRF

	obtain an aluminosilicate-rich precursor				
Na-type zeolite synthesis	To convert the purified Al–Si precursor into Na-type zeolite	Purified aluminosilicate precursor and 50 wt.% NaOH solution	90 °C, 24 h	Na-type zeolite	XRD, ICP-OES
Acid purification	To reduce residual impurities while maintaining the zeolite framework	Na-type zeolite and acid solution	H ₂ SO ₄ , HNO ₃ , or HCl; optimized at 0.25 M HCl for 24 h	Purified Na-type zeolite	XRD, ICP-OES
Si/Al ratio control	To adjust the zeolite composition for subsequent functionalization	Purified Na-type zeolite and water glass	90 °C, 6–24 h; optimized at Na-zeolite: water glass = 1:2 for 6 h	Si/Al-controlled Na-type zeolite	XRD, compositional analysis
Cation-exchange modification	To prepare functional zeolites for water treatment	Si/Al-controlled Na-type zeolite and MgCl ₂ or KCl solution	1 M MgCl ₂ or 1 M KCl, 25 °C, 24 h	Mg-modified zeolite and K-modified zeolite	XRD, SEM-EDX
Heavy metal removal test	To evaluate batch removal performance of Mg-modified zeolite	100 ppm Pb, Hg, Cr, or Cd solution and Mg-modified zeolite	200 g Mg-modified zeolite in 5000 mL solution, 400 rpm, 30 min, 25 °C	Treated solution	ICP-OES
Water-softening test	To evaluate hardness removal performance of K-modified zeolite	Synthetic hard water and K-modified zeolite	500 g K-modified zeolite in 5000 mL solution, 400 rpm, 30 min, 25 °C	Softened water	ICP-OES

2.2. Overall Experimental Procedure

The overall experimental procedure is shown in Figure 1. The process consisted of six sequential steps: raw material characterization, dry fusion purification, Na-type zeolite synthesis, acid purification, Si/Al ratio control, and cation-exchange functionalization for water-treatment applications. First, the chemical composition and crystalline phases of the raw waste aluminum dust were analyzed to evaluate its suitability as an aluminosilicate source. Second, dry fusion purification was performed at high temperature to remove reducible metallic impurities and water-soluble salts and to obtain an aluminosilicate-rich precursor. Third, the purified precursor was reacted with concentrated NaOH solution under alkaline hydrothermal conditions to synthesize Na-type zeolite. Fourth, the synthesized Na-type zeolite was purified by HCl leaching to remove residual impurities while maintaining the zeolitic framework. Fifth, the Si/Al ratio of the purified zeolite was adjusted using water glass as an additional Si source. Finally, the Si/Al-ratio-controlled Na-type zeolite was modified by cation exchange using Mg²⁺ and K⁺ ions. The Mg-modified zeolite was used for heavy metal removal, whereas the K-modified zeolite was used for water softening.

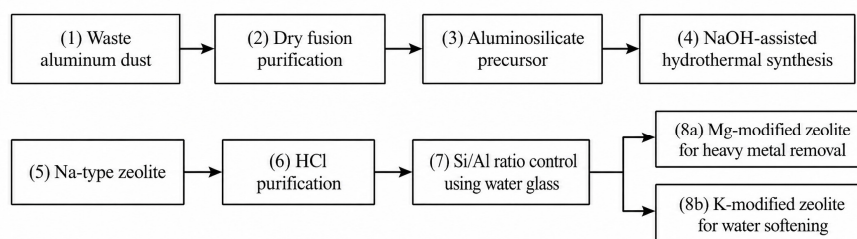


Figure 1. Overall experimental flow for the synthesis, purification, Si/Al ratio control, and cation-exchange functionalization of zeolites derived from waste aluminum dust.

2.3. Dry Fusion Purification of Waste Aluminum Dust

Dry fusion purification was performed to remove metallic impurities from the waste aluminum dust and to prepare an aluminosilicate precursor for subsequent Na-type zeolite synthesis. Waste aluminum dust was mixed with SiO_2 and carbon powder, placed in a graphite crucible, and heated in a Kanthal furnace under an Ar atmosphere. The Ar flow rate was maintained at $300 \text{ cm}^3 \text{ min}^{-1}$. The furnace was heated to 1600°C and held for 1 h. This dry fusion condition was selected to obtain an aluminosilicate-rich precursor while reducing impurity components present in the waste aluminum dust. High-temperature treatment under an Ar atmosphere was used to promote the separation of reducible metal oxide impurities and to suppress excessive oxidation during fusion. The treatment temperature of 1600°C was selected based on the need to sufficiently melt and homogenize the aluminosilicate-containing matrix and to enable slag/metal separation of reducible impurities. Preliminary experimental observations also showed that this condition produced a stable aluminosilicate-rich precursor suitable for subsequent NaOH-assisted zeolite synthesis. After the reaction, the product was cooled, and the aluminosilicate-rich slag fraction was separated from the metallic phase. The metallic phase was expected to consist mainly of reduced Fe-bearing metallic species and other reducible metal impurities, such as Zn-bearing species, originally present in the waste aluminum dust. The recovered slag was washed with distilled water to remove soluble salts and residual impurities, followed by vacuum filtration and drying. The dried product was used as the aluminosilicate precursor for Na-type zeolite synthesis. A schematic illustration of the dry fusion purification and slag/metal separation process is shown in Figure 2. During dry fusion, reducible metal oxides, such as Fe_2O_3 and ZnO , can be converted into metallic phases by carbothermic reduction, whereas Al_2O_3 - and SiO_2 -rich components remain predominantly in the slag phase. The thermodynamic feasibility of this selective reduction behavior was evaluated using Gibbs free energy calculations, as described in Section 2.5.

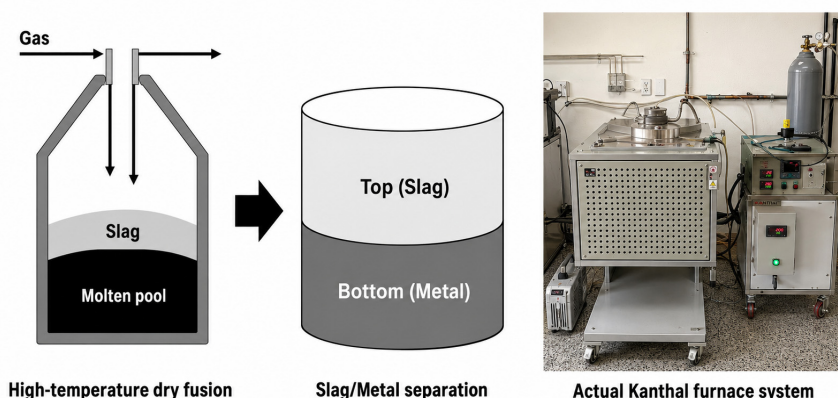


Figure 2. Schematic illustration of the dry fusion purification process and slag/metal separation.

2.4. Synthesis of Na-Type Zeolite

The aluminosilicate precursor obtained after dry fusion purification was used for Na-type zeolite synthesis. In a typical experiment, 10 g of the purified aluminosilicate precursor was mixed with 100 mL of 50 wt.% NaOH solution in a sealed reactor. The suspension was stirred at 300 rpm and reacted at 90 °C for 24 h. During alkaline treatment, Al_2O_3 - and SiO_2 -containing phases reacted with NaOH to form sodium aluminate, sodium silicate, and sodium aluminosilicate intermediates. These dissolved or partially dissolved species subsequently underwent rearrangement, condensation, and crystallization to form Na-type zeolite. The representative reactions considered for NaOH-assisted precursor formation are summarized in Section 2.5, together with the corresponding Gibbs free energy calculations. After the reaction, the solid product was washed with 1 L of distilled water under stirring at 300 rpm for 1 h to remove residual NaOH and soluble by-products. The washed solid was recovered by vacuum filtration and dried at 95 °C for 24 h to obtain Na-type zeolite.

2.5. Thermodynamic Evaluation of Dry Fusion and NaOH-Assisted Precursor Formation

To support the process design from a thermodynamic perspective, Gibbs free energy changes were calculated for representative reactions involved in dry fusion purification and NaOH-assisted precursor formation. The calculations were performed using HSC Chemistry (version 6.12) over the relevant temperature ranges for each process. For comparison with the experimental conditions, the ΔG° values for dry fusion reactions were evaluated at 1600 °C, whereas those for NaOH-assisted precursor formation were evaluated at 90 °C. For dry fusion purification, the carbothermic reduction reactions of Fe_2O_3 , CuO , SiO_2 , and Al_2O_3 were considered. These reactions were selected to compare the reducibility of impurity oxides with the thermodynamic stability of Al_2O_3 - and SiO_2 -containing phases under the high-temperature dry fusion condition. As summarized in Table 3, the reduction reactions of Fe_2O_3 and CuO showed negative ΔG° values at 1600 °C, indicating that these impurity oxides can be thermodynamically reduced to metallic phases. In contrast, the reduction reactions of SiO_2 and Al_2O_3 showed positive ΔG° values at the same temperature, suggesting that these oxide components remain relatively stable and can be retained in the aluminosilicate-rich slag phase. This thermodynamic tendency supports the selective removal of reducible metallic impurities during dry fusion purification.

For Na-type zeolite synthesis, the reactions of NaOH with Al_2O_3 - and SiO_2 -containing phases were considered as representative reactions for the formation of sodium aluminate, sodium silicate, and sodium aluminosilicate intermediates. The calculated ΔG° values at 90 °C were negative for all three reactions, indicating that the formation of these precursor species is thermodynamically favorable under the alkaline hydrothermal conditions used in this study. However, because zeolite crystallization in aqueous alkaline media involves dissolution, ionic speciation, nucleation, and crystallization, the calculated ΔG° values were used only as thermodynamic indicators for precursor formation and not as direct proof of the complete zeolite crystallization mechanism. The representative reactions and calculated ΔG° values are summarized in Table 2. The ΔG° values for dry fusion reactions were converted from kcal to kJ, and all values are presented per reaction as written.

Table 3. Representative reactions and calculated Gibbs free energy changes for dry fusion purification and NaOH-assisted precursor formation.

Process	Representative Reaction	Selected Temperature	ΔG° Per Reaction, kJ	Thermodynamic Implication
Dry fusion	$\text{Fe}_2\text{O}_3 + 3\text{C} \rightarrow 2\text{Fe} + 3\text{CO(g)}$	1600 °C	−483.5	Fe oxide reduction is thermodynamically favorable.
Dry fusion	$\text{CuO} + \text{C} \rightarrow \text{Cu} + \text{CO(g)}$	1600 °C	−272.4	Cu oxide reduction is thermodynamically favorable.
Dry fusion	$\text{SiO}_2 + 2\text{C} \rightarrow \text{Si} + 2\text{CO(g)}$	1600 °C	25.2	SiO_2 reduction is not strongly favored; SiO_2 can remain in the slag phase.
Dry fusion	$\text{Al}_2\text{O}_3 + 3\text{C} \rightarrow 2\text{Al} + 3\text{CO(g)}$	1600 °C	247.9	Al_2O_3 remains thermodynamically stable in the aluminosilicate-rich slag phase.
Dry fusion	$\text{TiO}_2 + 2\text{C} \rightarrow \text{Ti} + 2\text{CO(g)}$	1600 °C	40.8	TiO_2 reduction is thermodynamically less favorable than the reduction of Fe_2O_3 and CuO ; therefore, Ti-bearing phases are expected to remain in the slag or residual solid rather than being readily separated into the metallic phase.
Zeolite synthesis	$\text{Al}_2\text{O}_3 + 2\text{NaOH(l)} \rightarrow 2\text{NaAlO}_2 + \text{H}_2\text{O(l)}$	90 °C	−45.3	Sodium aluminate formation is thermodynamically favorable.
Zeolite synthesis	$\text{SiO}_2 + 2\text{NaOH(l)} \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O(l)}$	90 °C	−98.8	Sodium silicate formation is thermodynamically favorable.
Zeolite synthesis	$\text{Al}_2\text{O}_3 + 2\text{SiO}_2 + 2\text{NaOH(l)} \rightarrow 2\text{NaAlSiO}_4 + \text{H}_2\text{O(l)}$	90 °C	−155.5	Sodium aluminosilicate precursor formation is thermodynamically favorable.

Note: The ΔG° values are given per reaction as written. The dry fusion values were converted from kcal to kJ.

2.6. Acid Purification and Si/Al Ratio Control

The synthesized Na-type zeolite was purified by acid leaching to remove residual impurities while maintaining the zeolite framework. Preliminary acid selection tests were performed using H_2SO_4 , HNO_3 , and HCl . In each test, 2 g of Na-type zeolite was mixed with 5 mL of acid solution and 50 mL of distilled water. The suspension was stirred at room temperature for 24 h. After leaching, the solid residue was washed thoroughly with distilled water, recovered by vacuum filtration, dried, and analyzed by X-ray diffraction to evaluate structural stability after acid treatment. Based on the acid selection results, HCl was selected for further purification experiments. For HCl purification, Na-type zeolite was mixed with diluted HCl solution at a solid-to-liquid ratio of 1:10. The reaction was carried out at 25 °C with stirring at 300 rpm for 24 h. After acid leaching, the solid residue was washed with distilled water until the filtrate became nearly neutral, recovered by vacuum filtration, and dried at 95 °C for 24 h. The Si/Al ratio of the purified Na-type zeolite was controlled using water glass as an additional Si source. In each experiment, 200 g of purified Na-type zeolite was dispersed in 5000 mL of distilled water. Water glass was added at Na-zeolite-to-water-glass mass ratios of 1:0.5, 1:1, and 1:2, corresponding to 100, 200, and 400 g of water glass, respectively. The reaction was carried out at 90 °C under stirring at 300 rpm for 6, 12, or 24 h. After reaction, the solid product was recovered by vacuum filtration, washed with distilled water, and dried at 95 °C for 24 h.

2.7. Cation-Exchange Modification and Water-Treatment Tests

The purified and Si/Al-controlled Na-type zeolite was further modified by cation exchange using MgCl_2 and KCl solutions to prepare functional zeolites for water-treatment applications. Because Na^+ ions in the Na-type zeolite act as exchangeable charge-balancing cations in the aluminosilicate framework, they can be partially replaced by other cations, such as Mg^{2+} or K^+ , through ion-exchange treatment. The overall procedures for cation-exchange modification and subsequent performance tests are illustrated in Figure 3. For Mg-modified zeolite preparation, 100 g of Na-type zeolite was added to 10 L of 1 M MgCl_2 solution, as shown in Figure 3a. The suspension was stirred at 300 rpm for 24 h at 25 °C to allow ion exchange between the exchangeable Na^+ ions in the zeolite framework and Mg^{2+} ions in the solution. After the ion-exchange reaction, the solid product was recovered by vacuum filtration, thoroughly washed with distilled water to remove residual salts, and dried at 95 °C for 24 h. The resulting product was denoted as Mg-modified zeolite. For K-modified zeolite preparation, 100 g of Na-type zeolite was added to 1 L of 1 M KCl solution, as shown in Figure 3c. The suspension was stirred at 300 rpm for 24 h at 25 °C under the same ion-exchange conditions. After reaction, the solid product was recovered by vacuum filtration, washed with distilled water, and dried at 95 °C for 24 h. The resulting product was denoted as K-modified zeolite.

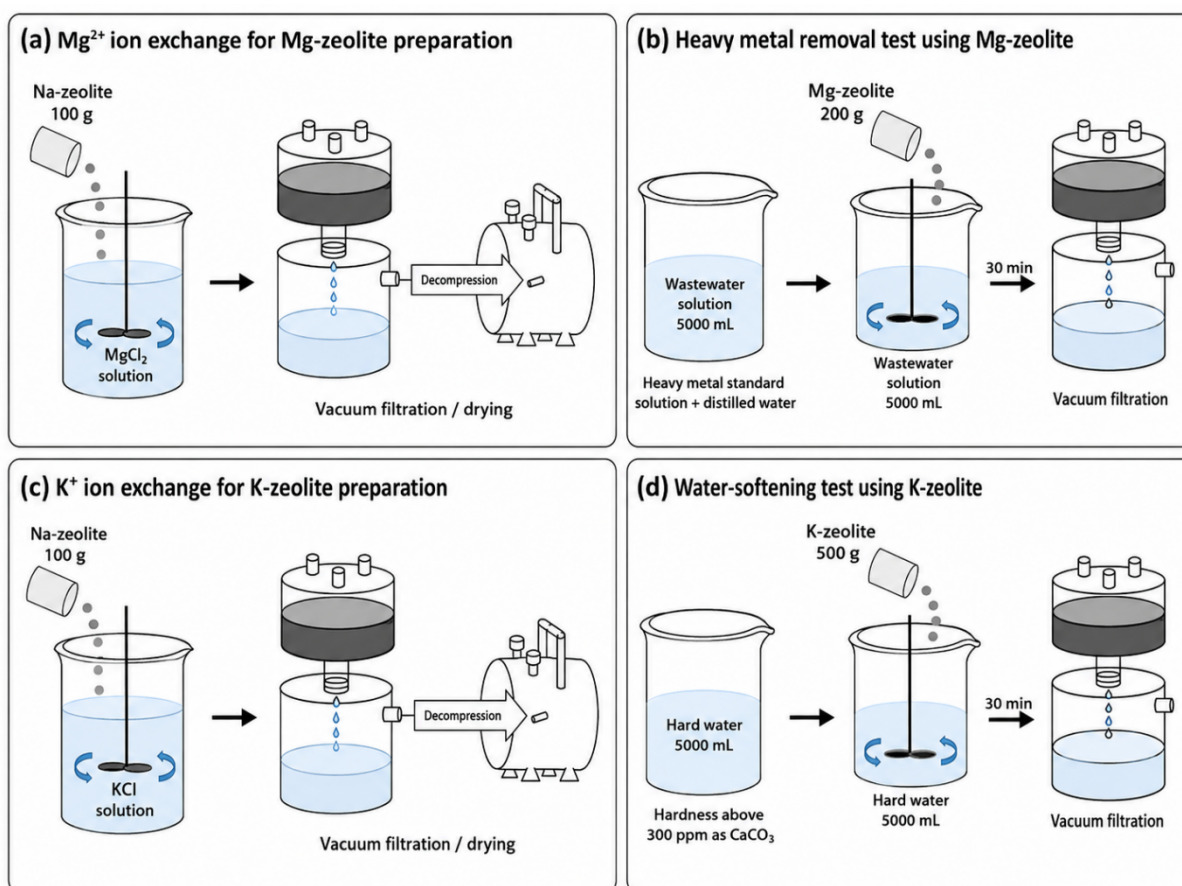


Figure 3. Schematic illustration of the experimental procedures for cation-exchange modification and subsequent water-treatment tests. (a) Preparation of Mg-modified zeolite by Mg^{2+} ion exchange, (b) heavy metal removal test using Mg-modified zeolite, (c) preparation of K-modified zeolite by K^+ ion exchange, and (d) water-softening test using K-modified zeolite.

The heavy metal removal performance of Mg-modified zeolite was evaluated using single-metal aqueous solutions containing Pb, Hg, Cr, and Cd. As shown in Figure 3b,

each test solution was prepared by diluting a 1000 ppm standard solution with distilled water to an initial concentration of 100 ppm, and the total solution volume was adjusted to 5000 mL. For the Cr removal test, the Cr test solution was prepared by diluting Chromium Standard Solution 1 (Cr 1000 mg/L, Product No. 08037-2B, KANTO CHEMICAL CO., INC.) with distilled water to 100 ppm. According to the SDS, this standard solution contains potassium dichromate ($K_2Cr_2O_7$) as the chromium source and 0.06% nitric acid; therefore, chromium was introduced as Cr(VI). No additional pH adjustment was performed before the removal experiment. The initial pH of the diluted 100 ppm Cr(VI) solution was not measured in the original experiment. Then, 200 g of Mg-modified zeolite was added to the test solution, and the suspension was stirred at 400 rpm for 30 min at 25 °C. After treatment, the solid and liquid phases were separated by vacuum filtration, and the residual metal concentration in the filtrate was determined by ICP-OES. The water-softening performance of K-modified zeolite was evaluated using synthetic hard water containing Ca^{2+} and Mg^{2+} , as illustrated in Figure 3d. The initial concentrations of Ca^{2+} and Mg^{2+} were 45 and 47 ppm, respectively, corresponding to 112.5 and 195.8 ppm as $CaCO_3$. Thus, the initial total hardness of the synthetic hard water was 308.3 ppm as $CaCO_3$. For each test, 500 g of K-modified zeolite was added to 5000 mL of the synthetic hard water, and the suspension was stirred at 400 rpm for 30 min at 25 °C. After filtration, the residual Ca^{2+} and Mg^{2+} concentrations were measured by ICP-OES, and the remaining total hardness was calculated as $CaCO_3$. The crystalline phases of the Mg-modified zeolite and K-modified zeolite products were subsequently analyzed by X-ray diffraction to confirm whether the zeolite framework was maintained after cation exchange.

2.8. Characterization and Calculations

The crystalline phases of the raw waste aluminum dust, purified aluminosilicate precursor, synthesized Na-type zeolite, acid-treated zeolite, and cation-exchanged zeolites were characterized by X-ray diffraction (XRD). XRD analysis was used to identify the crystalline phases formed during dry fusion purification, Na-type zeolite synthesis, acid purification, and cation-exchange modification. The obtained diffraction patterns were compared with standard reference data to confirm the formation and structural stability of the zeolite phases. XRD analysis was performed using an Ultima IV diffractometer (Rigaku Corporation, Tokyo, Japan) with Cu $K\alpha$ radiation to identify crystalline phases. The chemical compositions of the raw waste aluminum dust and purified solid products were determined by X-ray fluorescence (XRF) analysis. XRF analysis was performed using an XRF-1800 spectrometer (Shimadzu Corporation, Kyoto, Japan) to determine the bulk chemical compositions of the raw and purified solid products. XRF was used to evaluate the compositional change before and after dry fusion purification, particularly the removal of impurity components and the enrichment of Al_2O_3 - SiO_2 -based aluminosilicate components. Residual impurity contents in the synthesized and purified zeolites were further quantified by inductively coupled plasma optical emission spectroscopy (ICP-OES). The concentrations of Pb, Hg, Cr, Cd, Ca, and Mg in aqueous solutions before and after treatment were also measured by ICP-OES. ICP-OES analysis was conducted using an Optima 8300 spectrometer (PerkinElmer, Waltham, MA, USA) to quantify residual impurities in the zeolite products and residual metal ion concentrations in aqueous solutions. The morphologies and elemental distributions of the synthesized and ion-exchanged zeolite products were further examined by scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX). SEM-EDX analysis was performed using an EM-30N scanning electron microscope (COXEM Co., Ltd., Daejeon, Republic of Korea) to observe the particle morphology and elemental distribution of Na-zeolite, Mg-modified zeolite, and K-modified zeolite. SEM was used to observe the particle morphologies of Na-zeolite, Mg-modified zeolite, and K-modified zeolite, whereas

EDX elemental mapping was used to qualitatively confirm the distribution of framework-related elements, such as Al and Si, and exchange-related cations, such as Na, Mg, and K. Because EDX is surface-sensitive and semi-quantitative, it was used as supplementary compositional evidence and was not used as the sole quantitative method for determining zeolite purity or ion-exchange capacity. The quantitative evaluation of zeolite purity and impurity removal was mainly based on ICP-OES and XRF analyses. For the heavy metal removal tests, the residual concentrations of Pb, Hg, Cr, and Cd were used to calculate the removal efficiency and adsorption capacity of Mg-modified zeolite. The removal efficiency of each metal ion was calculated using Equation (1):

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where C_0 and C_e are the initial and final concentrations of the metal or Cr(VI) oxyanion in solution, respectively.

The adsorption capacity of Mg-modified zeolite was calculated using Equation (2):

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where q_e is the adsorption capacity of the zeolite, V is the solution volume, and m is the mass of zeolite used in the removal test.

For the water-softening tests, the residual concentrations of Ca^{2+} and Mg^{2+} were used to calculate the total hardness of the treated water. The total hardness was expressed as CaCO_3 and calculated using Equation (3):

$$\text{Total hardness as } \text{CaCO}_3 = 2.5[\text{Ca}^{2+}] + 4.1[\text{Mg}^{2+}] \quad (3)$$

where $[\text{Ca}^{2+}]$ and $[\text{Mg}^{2+}]$ are the calcium and magnesium ion concentrations in solution, respectively. The coefficients 2.5 and 4.1 were used to convert Ca^{2+} and Mg^{2+} concentrations into CaCO_3 -equivalent hardness [21].

The hardness reduction efficiency was calculated using Equation (4):

$$\text{Hardness reduction efficiency (\%)} = \frac{H_0 - H_e}{H_0} \times 100 \quad (4)$$

where H_0 and H_e are the initial and final total hardness values of the water, respectively, expressed as CaCO_3 equivalent.

All analytical results were used to evaluate the effects of dry fusion purification, acid treatment, Si/Al ratio control, and cation-exchange modification on the structural and functional properties of the waste aluminum dust-derived zeolites.

3. Results and Discussion

3.1. Characterization and Purification of Waste Aluminum Dust

The raw waste aluminum dust was first characterized by XRD and XRF to evaluate its suitability as an aluminosilicate source for zeolite synthesis. As shown in Figure 4, the XRD pattern of the raw material revealed Al_2O_3 as the major crystalline phase, together with AlN, NaCl, KCl, and ZnO as impurity-containing phases. The presence of chloride salts indicates that water-soluble components were present in the raw dust, whereas ZnO and other metal oxide phases suggest that further purification was necessary before zeolite synthesis. The XRF result in Figure 4 further confirmed that the raw waste aluminum dust contained a high fraction of aluminosilicate-forming components. The Al_2O_3 and SiO_2 contents were 78.84 wt.% and 8.83 wt.%, respectively, indicating that the raw material could serve as a secondary Al–Si source for zeolite synthesis. However, impurity components such as Cl, Na_2O , K_2O , ZnO, Fe_2O_3 , CaO, MgO, TiO_2 , V_2O_5 , and SO_3 were also detected. These impurities may interfere with zeolite crystallization, reduce product purity, and affect subsequent ion-exchange performance. Therefore, dry fusion purification was required to convert the raw dust into a more suitable aluminosilicate precursor. After dry

fusion purification and subsequent washing, several impurity components, including Cl, ZnO, Fe₂O₃, V₂O₅, and SO₃, were removed or decreased below the detectable range, while Na₂O and K₂O were substantially decreased. These results indicate that water-soluble chloride and alkali salt species were removed mainly by washing after dry fusion, whereas reducible metal oxide impurities, such as Fe- and Zn-bearing phases, were separated through carbothermic reduction and slag/metal separation.

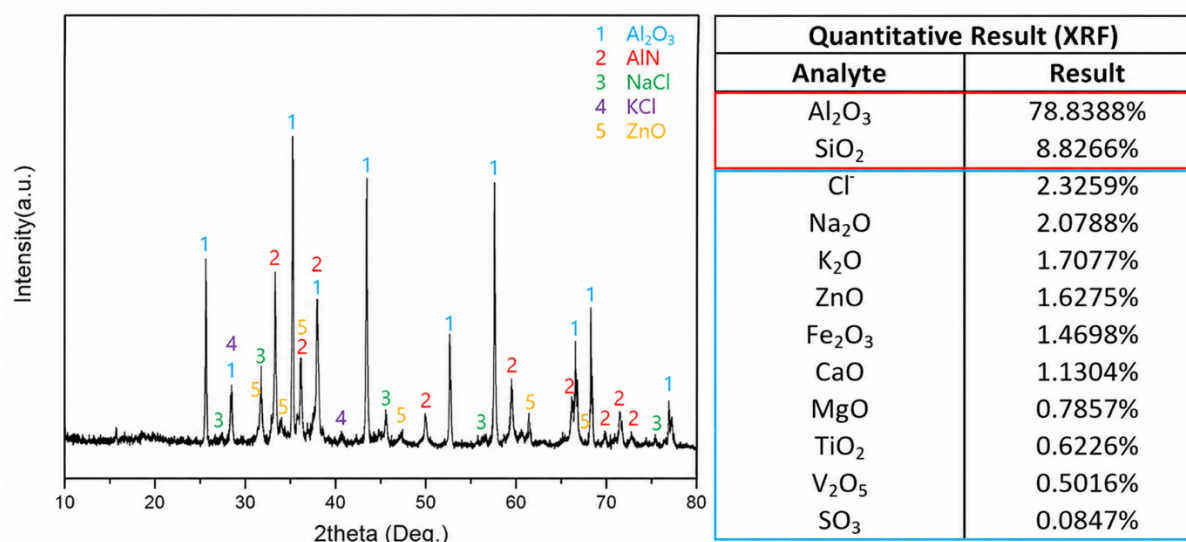


Figure 4. XRD pattern and XRF quantitative analysis of raw waste aluminum dust. The numbered diffraction peaks were assigned by comparison with standard JCPDS/PDF reference patterns: (1) Al₂O₃, PDF No. 46-1212; (2) AlN, PDF No. 25-1133; (3) NaCl, PDF No. 05-0628; (4) KCl, PDF No. 41-1476; and (5) ZnO, PDF No. 36-1451.

The effect of dry fusion purification on the chemical composition of the waste aluminum dust is shown in Table 4. After dry fusion, the relative SiO₂ content increased from 8.83 wt.% to 38.77 wt.%, while the relative Al₂O₃ content decreased from 78.84 wt.% to 57.59 wt.%. However, this increase in SiO₂ content should not be interpreted solely as enrichment caused by purification because SiO₂ powder was intentionally added during the dry fusion step as an auxiliary Si source. Therefore, the observed compositional change reflects the combined effects of externally added SiO₂, removal or reduction of impurity components, washing of soluble salts, and slag/metal separation during dry fusion purification. Several impurity components, including Cl, Na₂O, K₂O, ZnO, and Fe₂O₃, decreased or were removed below the detectable range. This compositional change indicates that water-soluble salts and reducible metallic impurities were effectively reduced or separated during dry fusion and subsequent washing. Therefore, the purified product should be described as an aluminosilicate-rich precursor prepared through SiO₂-assisted dry fusion purification, rather than as a product enriched in SiO₂ solely by purification. The formation of this Al₂O₃–SiO₂-based precursor is suitable for subsequent Na-type zeolite synthesis.

Table 4. Chemical composition of raw and purified aluminum dust determined by XRF, showing impurity removal and relative compositional changes after SiO₂-assisted dry fusion purification.

Analyte	Raw Aluminum Dust (wt.%)	Purified Aluminum Dust (wt.%)	Change (wt.–Point)	Interpretation
Al ₂ O ₃	78.838	57.586	−21.2520	Relative decrease due to added SiO ₂ and compositional redistribution; not direct evidence of Al mass loss
SiO ₂	8.826	38.765	29.939	Increased due to external SiO ₂ addition and relative compositional change after impurity removal

Cl	2.3259	N.D.		Removed or below detection after purification
Na ₂ O	2.0788	0.36	−1.7188	Substantially decreased
K ₂ O	1.7077	0.2305	−1.4772	Substantially decreased
ZnO	1.6275	N.D.		Removed or below detection after purification
Fe ₂ O ₃	1.4698	N.D.		Removed or below detection after purification
CaO	1.1304	1.0485	−0.0819	Slightly decreased
MgO	0.7857	0.7569	−0.0288	Slightly decreased
TiO ₂	0.6226	1.472	0.8494	Relatively increased due to acid-/fusion-resistant Ti-bearing residues and relative compositional change
V ₂ O ₅	0.5016	N.D.		Removed or below detection after purification
SO ₃	0.0847	N.D.		Removed or below detection after purification

Note: N.D. indicates not detected or not reported in the purified XRF result shown in the original figure. Change values are calculated only for analytes with numerical data in both samples.

However, the decrease in Al₂O₃ content after dry fusion and purification should be interpreted carefully. The XRF values represent relative oxide weight percentages in the analyzed solid products and do not directly provide a complete mass balance of aluminum recovery. During dry fusion, SiO₂ and carbon were added to adjust the aluminosilicate composition and promote impurity separation. In addition, slag/metal separation, washing, and subsequent purification can change the relative oxide composition of the remaining solid product. Therefore, the decrease in Al₂O₃ content from the raw dust to the purified precursor does not directly indicate that the same fraction of aluminum was lost from the entire process. Nevertheless, this compositional change suggests that aluminum loss or redistribution may occur during purification, and a complete mass balance based on input/output solid masses and Al contents will be required to determine the actual Al recovery and product yield. Similarly, because SiO₂ was externally added during dry fusion, the increase in SiO₂ wt.% cannot be quantitatively separated into the contribution from added SiO₂ and the compositional change originating from the waste aluminum dust itself without a complete mass balance. A rigorous input–output mass balance including the initial waste aluminum dust, added SiO₂, added carbon, recovered slag, separated metallic phase, washing residues, and final solid product would be required to quantitatively determine the contribution of each process stream to the final Al₂O₃ and SiO₂ contents. This issue is recognized as a limitation of the present study and should be addressed in future process optimization and scale-up studies.

The behavior of Ti-containing impurities should also be interpreted in relation to the thermodynamic stability of TiO₂ during dry fusion purification. As shown in Table 3, the calculated ΔG° value for the carbothermic reduction reaction $\text{TiO}_2 + 2\text{C} \rightarrow \text{Ti} + 2\text{CO(g)}$ was +40.8 kJ at 1600 °C. This positive ΔG° value indicates that TiO₂ reduction was not thermodynamically favorable under the present dry fusion condition. Therefore, unlike Fe₂O₃ and CuO, which showed negative ΔG° values and could be reduced to metallic phases, Ti-bearing phases were not expected to be readily reduced and separated into the metallic phase. This thermodynamic stability explains why Ti-bearing residues remained in the aluminosilicate-rich precursor after dry fusion purification. Accordingly, the apparent increase in TiO₂ content from 0.62 wt.% to 1.47 wt.% after purification should be interpreted as a relative compositional increase caused by the removal of other impurity components, external SiO₂ addition, and the persistence of reduction-resistant Ti-bearing residues, rather than as actual Ti enrichment. This persistence of Ti-bearing phases also explains why Ti remained one of the major residual impurities during subsequent HCl purification.

It should also be noted that the dry fusion step was conducted at 1600 °C under an Ar atmosphere, which is an energy-intensive condition. The dry fusion temperature of 1600 °C was adopted as a proof-of-concept processing condition to obtain an aluminosilicate-rich precursor and promote impurity separation in this study, rather than as an

optimized industrial processing parameter. Therefore, the present process should be regarded as a laboratory-scale proof-of-concept route for converting waste aluminum dust into an aluminosilicate precursor rather than as a fully optimized industrial process. For industrial application, the energy demand of the dry fusion step should be reduced or compensated by process integration, heat recovery, continuous furnace operation, utilization of waste heat from aluminum-related processes, or optimization of the fusion temperature and atmosphere. A detailed techno-economic and life-cycle assessment comparing the proposed route with commercial zeolite synthesis and other zeolite synthesis routes from aluminum residues would be necessary to evaluate the industrial viability and sustainability of the process.

3.2. Synthesis of Na-Type Zeolite from the Purified Aluminosilicate Precursor

The purified aluminosilicate precursor was reacted with 50 wt.% NaOH solution at 90 °C for 24 h to synthesize Na-type zeolite. The XRD pattern of the synthesized product is shown in Figure 5. The major diffraction peaks were assigned to a Na-type zeolite phase, confirming that the purified Al–Si precursor was successfully converted into a zeolitic aluminosilicate structure under the alkaline hydrothermal condition. The product was referred to as Na-type zeolite because it was synthesized under highly alkaline NaOH conditions, in which Na⁺ ions act as the main charge-balancing exchangeable cations in the aluminosilicate zeolite framework. In addition, the subsequent Mg²⁺ and K⁺ ion-exchange experiments further indicate that exchangeable Na⁺ ions were present in the synthesized zeolite product. Therefore, the term “Na-type zeolite” was used to describe the as-synthesized zeolite before Mg²⁺ or K⁺ ion-exchange modification. Minor residual peaks associated with alumina or aluminosilicate phases were also observed, indicating that a small fraction of the precursor remained incompletely converted or coexisted with the zeolite phase.

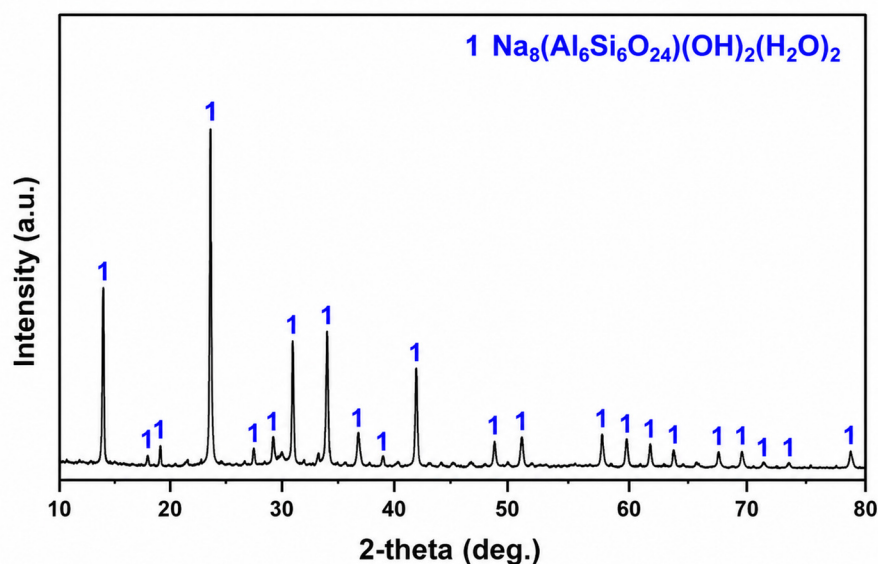


Figure 5. XRD pattern of Na-type zeolite synthesized from purified waste aluminum dust using NaOH at 90 °C for 24 h. The diffraction peaks were assigned to Na-type zeolite/sodalite, Na₈(Al₆Si₆O₂₄)(OH)₂(H₂O)₂, by comparison with the standard JCPDS/PDF reference pattern, PDF No. 00-037-0196.

The residual impurity contents of the synthesized Na-type zeolite were analyzed by ICP-OES and are summarized in Table 5. The as-synthesized product contained Mg, Ca, K, and Ti as the main residual impurities, with a total impurity content of approximately

2.499 wt.%, corresponding to an estimated chemical purity of 97.501 wt.% based on measured residual impurities. Although the zeolite phase was successfully formed, the residual impurity level indicated that additional purification was necessary to obtain a high-purity zeolite product. In particular, Ti and Mg were the dominant residual impurities and could affect crystallinity, ion-exchange behavior, and subsequent functionalization. It should be noted that this estimated chemical purity value was calculated by subtracting the measured residual impurity contents from 100% and should not be interpreted as true zeolite phase purity. Because quantitative phase analysis, such as Rietveld refinement, was not performed, the possible presence of unreacted alumina/silica, amorphous aluminosilicate, or secondary aluminosilicate phases cannot be completely excluded.

Table 5. Impurity contents and estimated chemical purity based on measured residual impurities of synthesized Na-type zeolite determined by ICP-OES.

Impurity Element	Mg	Ca	K	Ti	Total Measured Impurities	Estimated Chemical Purity Based on Measured Residual Impurities
Concentration (wt.%)	0.57	0.038	0.081	1.81	2.499	97.501

3.3. Acid Purification of Na-Type Zeolite Using HCl

Acid leaching was performed to improve the purity of the synthesized Na-type zeolite while maintaining the zeolitic framework. First, H_2SO_4 , HNO_3 , and HCl were compared as acid leaching reagents. As shown in Figure 6, the XRD patterns after acid treatment revealed clear differences in structural stability depending on the acid type. Among the tested acids, HCl treatment provided a more favorable balance between removal of residual impurities, particularly Mg, Ca, K, and partially Ti, and retention of the zeolite diffraction pattern. Acid leaching, particularly using HCl , has also been reported as an effective approach for reducing impurity-bearing phases and controlling the composition of waste-derived aluminosilicate precursors or zeolitic materials [22,24]. Therefore, HCl was selected for subsequent purification experiments.

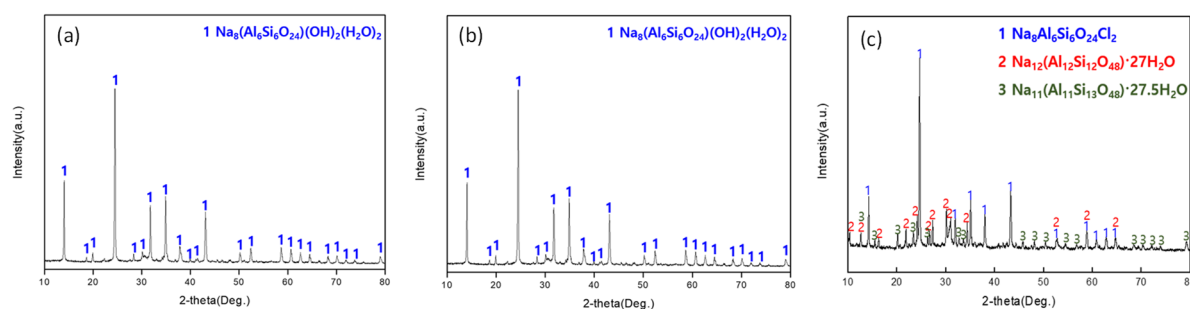


Figure 6. XRD patterns of Na-type zeolite after acid leaching using (a) H_2SO_4 (95%), (b) HNO_3 (70%), and (c) HCl (35–37%) for acid solution selection. The diffraction peaks were assigned by comparison with standard JCPDS/PDF reference patterns: hydroxycancrinite/cancrinite-type sodium aluminosilicate, $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$, PDF No. 46-1457; chloride sodalite, $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$, PDF No. 37-0476; and zeolite A/LTA-type sodium aluminosilicate hydrate, $\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48} \cdot 27\text{H}_2\text{O}$, PDF No. 47-0162.

The effect of HCl concentration on zeolite structure and impurity removal was then investigated. The HCl concentrations used in this study were not stoichiometric values but were selected as experimental screening conditions to determine an appropriate balance between impurity removal and zeolite structural stability. Therefore, a concentration range of 0.05–0.80 M was investigated, and the intermediate range of 0.23–0.30 M was further examined to identify the optimum condition. The XRD patterns of Na-type zeolite

treated with different HCl concentrations are shown in Figure 7. At low HCl concentrations of 0.05–0.20 M, the characteristic zeolite diffraction peaks were largely retained, suggesting that the framework was not significantly damaged. However, the impurity removal efficiency was insufficient, as summarized in Table 6. The total impurity content remained above 2.33 wt.% even after treatment with 0.20 M HCl, mainly because Ti removal was limited.

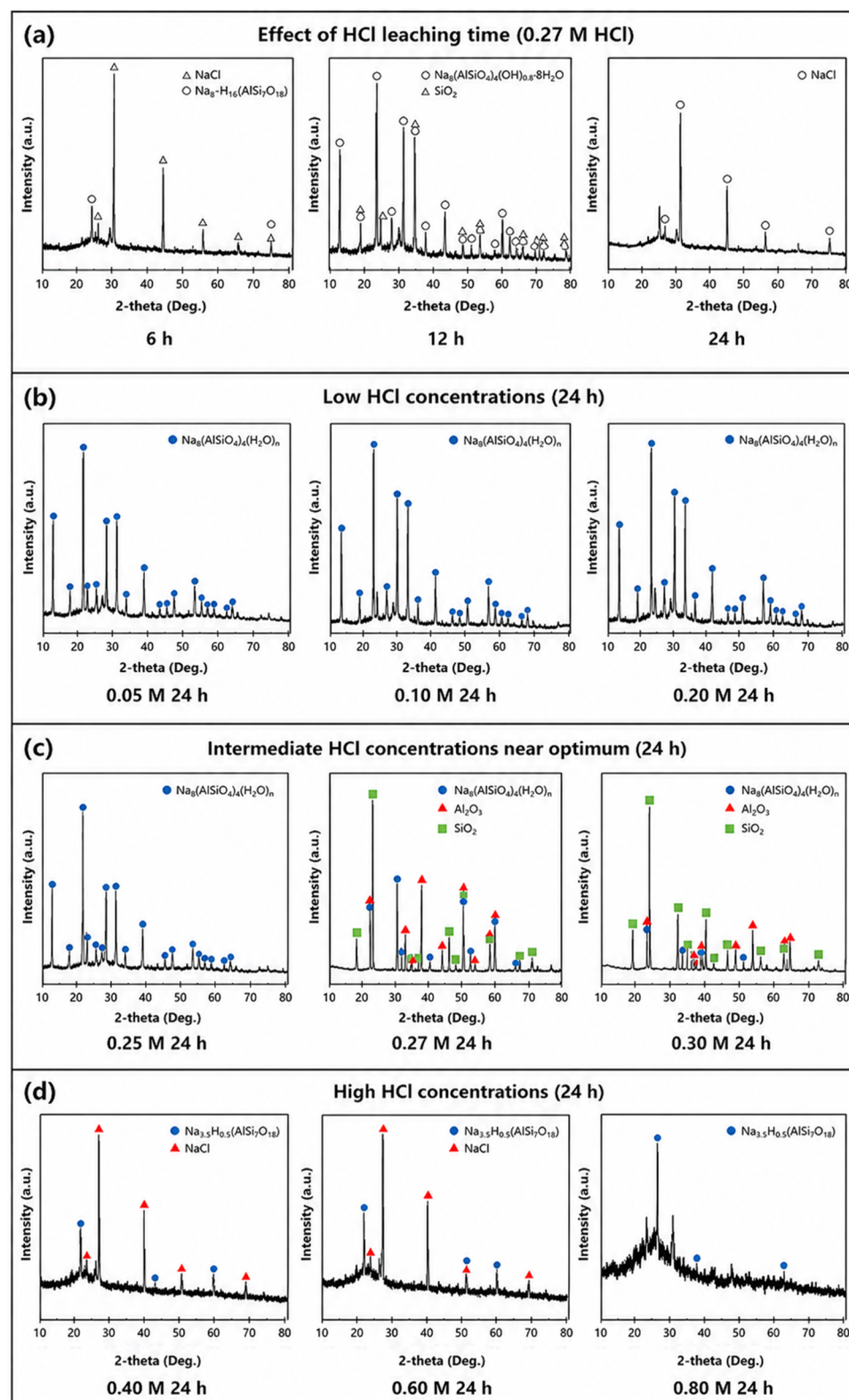


Figure 7. HCl concentration-dependent XRD patterns of Na-type zeolite after acid leaching: (a) effect of HCl leaching time for 6, 12, and 24 h; (b) low HCl concentrations of 0.05, 0.10, and 0.20 M for 24 h; (c) intermediate HCl concentrations of 0.25, 0.27, and 0.30 M for 24 h; and (d) high HCl concentrations of 0.40, 0.60, and 0.80 M for 24 h. The main phases were identified using standard JCPDS/PDF reference patterns: sodium hydrogen aluminum silicate (01-080-1394), NaCl (00-005-0628, 01-077-2064), sodium aluminum silicate hydrate (01-088-1190, 00-040-0102), SiO₂ (00-046-1045, 01-070-2535), and Al₂O₃ (01-089-7715, 01-080-0786).

Table 6. Effect of HCl concentration on impurity contents and estimated chemical purity based on measured residual impurities of Na-type zeolite.

HCl Concentration	Mg (wt.%)	Ca (wt.%)	K (wt.%)	Ti (wt.%)	Total Measured Impurities (wt.%)	Estimated Chemical Purity Based on Measured Residual Impurities (wt.%).	Interpretation
As-synthesized	0.57	0.038	0.081	1.81	2.499	97.501	Synthesized Na-zeolite before acid purification
0.05 M	0.56	0.056	0.074	1.93	2.507	97.493	Insufficient impurity removal
0.10 M	0.49	0.04	0.051	1.8	2.381	97.619	Limited purification
0.20 M	0.48	0.029	0.054	1.77	2.333	97.667	Partial impurity removal; purity still below 98 wt.%
0.23 M	0.35	0.036	0.019	1.81	2.215	97.785	Improved purification; Ti removal still limited
0.25 M	0.098	0.008	0.015	1.41	1.531	98.469	Optimum purification condition
0.27 M	0.34	0.0016	0.057	1.92	2.319	97.681	Excessive leaching tendency and relative Ti enrichment
0.30 M	0.28	0.024	0.079	1.98	2.363	97.637	Over-leaching condition

Note: The estimated chemical purity values were calculated from the measured residual impurity contents and do not represent true zeolite phase purity. Quantitative phase analysis, such as Rietveld refinement, would be required to determine true zeolite phase purity.

When the HCl concentration was increased to 0.40 M and above, the XRD patterns showed a decrease in zeolite peak intensity and the appearance or relative enhancement of secondary phases, indicating a degradation tendency of the crystalline zeolitic phase under excessive acid leaching conditions. Therefore, the optimal concentration was further investigated in the intermediate range of 0.23–0.30 M. As shown in Table 6, 0.25 M HCl treatment resulted in the lowest total impurity content of 1.531 wt.%, corresponding to an estimated chemical purity of 98.469 wt.% based on measured residual impurities. Under this condition, Mg, Ca, and K were effectively removed, and Ti was also reduced from 1.81 wt.% in the as-synthesized zeolite to 1.41 wt.%. The corresponding XRD pattern in Figure 7 shows that the characteristic zeolite peaks were retained, indicating that purification was achieved while retaining the major crystalline zeolitic features. The importance of the HCl leaching step is demonstrated by the decrease in total impurity

content and the improvement in estimated chemical purity based on measured residual impurities. The as-synthesized Na-type zeolite contained residual Mg, Ca, K, and Ti impurities, with a total impurity content of 2.499 wt.% and an estimated chemical purity of 97.501 wt.% based on measured residual impurities. After treatment with 0.25 M HCl for 24 h, the total impurity content decreased to 1.531 wt.%, corresponding to an estimated chemical purity of 98.469 wt.% based on measured residual impurities. In particular, Mg, Ca, and K were effectively removed under this condition. Therefore, HCl leaching was necessary as a post-synthesis purification step to improve the purity of Na-type zeolite before Si/Al ratio control and cation-exchange modification. The estimated chemical purity values reported in this study were calculated from the measured residual impurity contents determined by ICP-OES and should not be interpreted as true zeolite phase purity. Because quantitative phase analysis, such as Rietveld refinement, was not performed, unreacted alumina/silica, amorphous aluminosilicate, or secondary aluminosilicate phases may still be present. Therefore, the reported purity values should be regarded as estimated chemical purity based on measured residual impurities rather than quantitative zeolite phase purity.

In contrast, treatment with 0.27 and 0.30 M HCl resulted in higher apparent impurity contents and lower zeolite crystallinity. This apparent increase in Ti content at higher HCl concentrations should not be interpreted as Ti being newly introduced or actively enriched from an external source during HCl leaching. A more reasonable explanation is that Ti-bearing residues were relatively resistant to HCl dissolution, whereas more soluble impurity components, such as Mg, Ca, and K, and partially dissolved aluminosilicate species were removed during acid treatment. As a result, the relative weight percentage of Ti in the remaining solid increased mathematically as the more soluble components were leached away. Therefore, the increase in Ti content at 0.27 and 0.30 M HCl reflects relative enrichment of acid-resistant Ti-bearing residues in the residual solid rather than actual addition of Ti. Thus, 0.25 M HCl was selected as the optimal condition because it provided the best balance between impurity removal and retention of the major zeolitic diffraction features.

It should be noted that the structural integrity of the acid-treated zeolites was evaluated mainly based on the retention or weakening of characteristic zeolitic XRD peaks. Therefore, the XRD results indicate crystalline-phase retention or degradation tendency rather than a complete quantitative assessment of framework integrity or structural collapse. Quantitative microstructural characterization, such as BET surface area, pore volume, pore-size distribution, and SEM observation of acid-treated samples, would be required to more rigorously determine framework preservation, porosity variation, or structural collapse after acid leaching.

3.4. Si/Al Ratio Control Using Water Glass

After acid purification, water glass was added as an additional Si source to control the Si/Al ratio of the purified Na-type zeolite. The purpose of this step was to adjust the composition of the zeolite for subsequent ion-exchange-based water-treatment applications. The effects of water glass addition amount and reaction time on the crystalline structure and Si/Al ratio were evaluated by XRD and compositional analysis. The XRD patterns obtained under different water glass addition amounts and reaction times are shown in Figure 8. The zeolite diffraction peaks were maintained under all tested conditions, indicating that the water glass treatment did not cause severe collapse of the zeolite framework. However, changes in peak intensity and background features were observed depending on the water glass amount and reaction time, suggesting changes in the degree of silicate incorporation, surface deposition, or rearrangement of aluminosilicate species. For the water-glass-treated samples shown in Figure 8, the diffraction peaks were

assigned to Na-type aluminosilicate zeolite-related phases based on peak matching with the original XRD peak list. However, because specific JCPDS/PDF reference numbers could not be unambiguously assigned for all water-glass-treated compositions, the phase assignment was described conservatively as Na-type aluminosilicate zeolite-related phases rather than as a single definite crystalline phase. Therefore, Figure 8 was used mainly to confirm that the zeolitic diffraction features were retained after water glass treatment, while the Si/Al ratio control was quantitatively evaluated by compositional analysis.

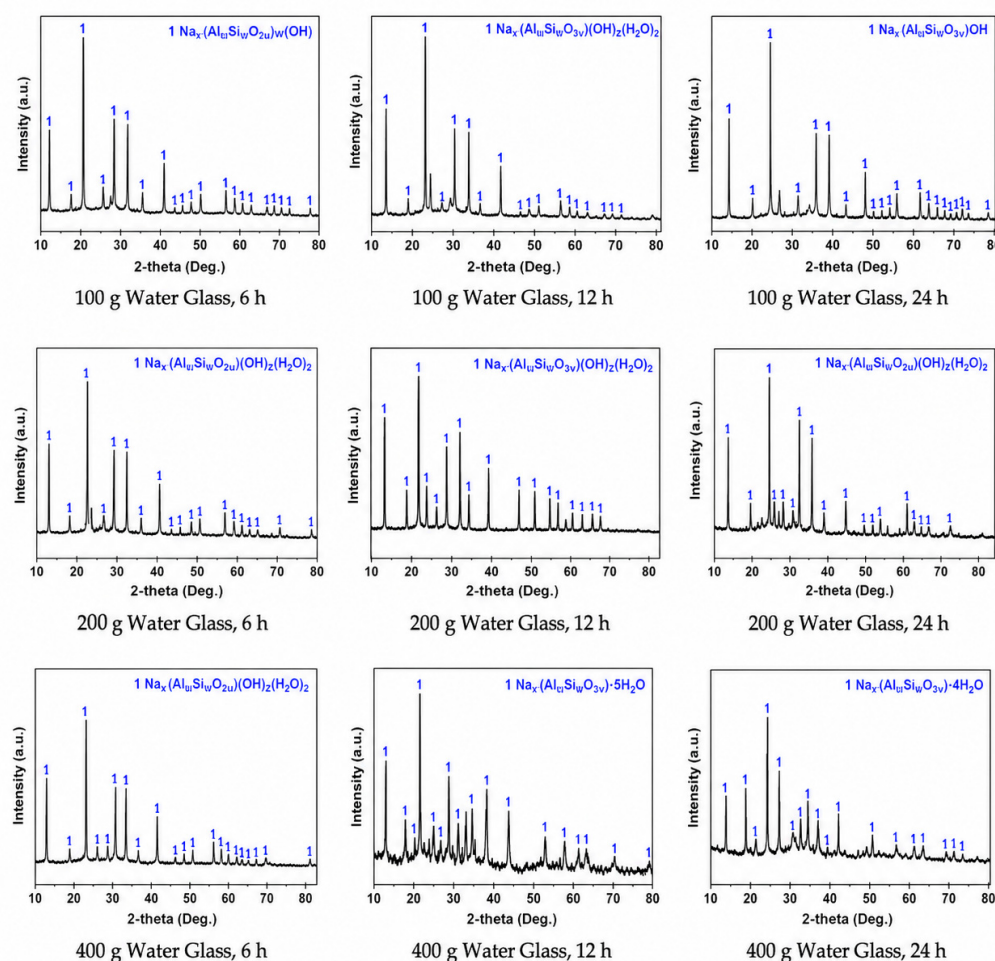


Figure 8. XRD patterns of Na-type zeolites treated with different water glass addition amounts and reaction times for Si/Al ratio control.

It should be noted that the framework integrity of the water-glass-treated samples was evaluated mainly based on the retention of characteristic zeolitic XRD features. Therefore, XRD peak intensity alone cannot quantitatively determine framework integrity, porosity variation, or microstructural collapse. Accordingly, the present discussion was revised to describe the results as retention of major zeolitic diffraction features and compositional adjustment rather than as complete proof of structural stability. Further microstructural characterization, such as BET surface area, pore volume, pore-size distribution, and SEM observation of water-glass-treated samples, would be required to more rigorously evaluate the effect of water glass treatment on zeolite framework integrity and porous structure.

The Si/Al ratios obtained under each condition are summarized in Table 7. The values in the 6 h, 12 h, and 24 h columns represent the Si/Al atomic ratios of the zeolite products after water glass treatment for each reaction time. The Si/Al ratio varied depending on

both the water glass addition amount and reaction time, indicating that the final composition was affected by multiple competing processes rather than by water glass addition alone. The highest Si/Al ratio of 1.769 was obtained at a Na-zeolite-to-water-glass mass ratio of 1:2 after 6 h of reaction at 90 °C. This result indicates that sufficient Si supply was achieved under this condition while the major zeolitic diffraction features were retained. However, the Si/Al ratio did not show a simple monotonic increase with increasing reaction time. Under the same 1:2 water glass condition, the Si/Al ratio decreased from 1.769 after 6 h to 1.273 after 12 h and then increased again to 1.576 after 24 h. This non-monotonic behavior indicates that a longer reaction time did not necessarily increase the Si/Al ratio. A more appropriate interpretation is that the final Si/Al ratio reflects a balance among silicate incorporation into the aluminosilicate structure, dissolution–reprecipitation of aluminosilicate species under alkaline conditions, surface deposition of silicate species, and removal of loosely bound or unreacted silicate species during washing. Therefore, the 1:2 water glass ratio with a 6 h reaction time was selected as the optimal condition for Si/Al ratio control because it produced the highest Si/Al ratio among the tested conditions while retaining the major zeolitic diffraction features, not because the Si/Al ratio increased monotonically with reaction time.

Table 7. Si/Al ratios of Na-type zeolites prepared under different water glass addition amounts and reaction times.

Purified Na-Zeolite: Water Glass Mass Ratio	Water Glass Addition (g)	Si/Al Ratio After 6 h	Si/Al Ratio After 12 h	Si/Al Ratio After 24 h
1:0.5	100	1.500	1.536	1.654
1:1	200	1.607	1.455	1.524
1:2	400	1.769	1.273	1.576

3.5. Cation-Exchange Functionalization of Zeolites

The Si/Al-controlled Na-type zeolite was modified by Mg^{2+} and K^+ ion exchange to prepare application-specific zeolites for water treatment. In this study, the products obtained after Mg^{2+} and K^+ treatment are referred to as Mg-modified zeolite and K-modified zeolite, respectively, rather than completely exchanged stoichiometric Mg- or K-modified zeolites. The XRD patterns of the Mg- and K-modified zeolites are shown in Figure 9. The major diffraction peaks of the Mg- and K-modified zeolites were assigned by comparison with the corresponding PDF reference cards, as indicated in the figure caption. In the Mg-modified zeolite, Mg-containing aluminosilicate-related crystalline phases were observed, together with secondary Mg–Al–Si–O-related peaks. In the K-modified zeolite, the major peaks were assigned to a sodalite-structured K-containing aluminosilicate phase. These results indicate that Mg- and K-containing aluminosilicate-related crystalline phases were formed after cation-exchange modification. However, the Mg-modified zeolite contained secondary phase peaks, indicating that it should not be interpreted as a completely single-phase product. In addition, XRD alone cannot quantitatively prove the extent of Na^+ replacement by Mg^{2+} or K^+ because ion exchange is fundamentally a compositional modification process and may occur without the formation of a distinct new crystalline phase or clear peak shift. Therefore, the XRD results should be interpreted mainly as evidence for identification of the major crystalline phases, secondary phase formation, and retention of the major aluminosilicate-related diffraction features after ion-exchange treatment, rather than as quantitative proof of stoichiometric cation exchange.

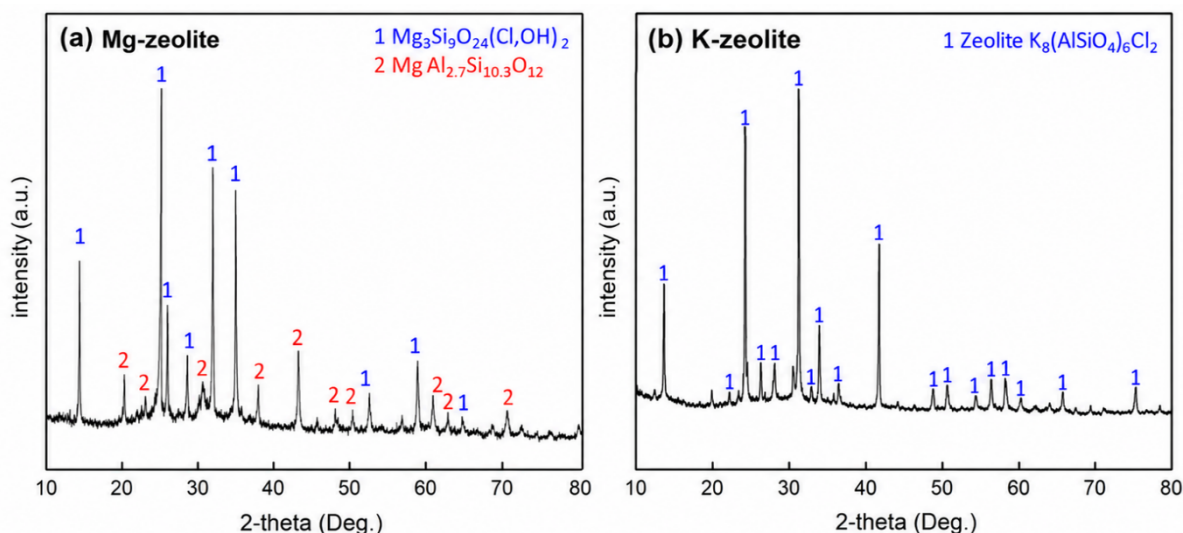


Figure 9. XRD patterns of (a) Mg-modified zeolite and (b) K-modified zeolite prepared by cation-exchange modification. In the Mg-modified zeolite, the major diffraction peaks were assigned to $\text{Mg}_3\text{Si}_9\text{O}_{24}(\text{Cl},\text{OH})_2$ based on PDF# 01-073-6147, while secondary peaks were assigned to $\text{MgAl}_{2.7}\text{Si}_{10.3}\text{O}_{12}$ based on PDF# 00-048-0326. In the K-modified zeolite, the major diffraction peaks were assigned to sodalite-structured K-containing aluminosilicate, $\text{K}_8(\text{AlSiO}_4)_6\text{Cl}_2$, based on PDF# 41-1191.

To provide additional evidence for cation-exchange modification, SEM-EDX analysis was performed for the Na-, Mg-, and K-modified zeolite products, as shown in Figure 10. The SEM images of Na-zeolite, Mg-modified zeolite, and K-modified zeolite showed aggregated fine particles with similar irregular granular morphologies, indicating that the cation-exchange treatment did not cause severe morphological collapse of the zeolite products. The EDX elemental maps showed that Al and Si were distributed throughout all zeolite products, supporting the retention of the aluminosilicate framework after ion-exchange treatment. In the Na-zeolite, Na was detected together with Al and Si. After Mg^{2+} ion-exchange treatment, Mg was clearly detected in the Mg-modified zeolite, while after K^+ ion-exchange treatment, K was detected in the K-modified zeolite. These results provide supplementary elemental evidence that Mg^{2+} and K^+ were introduced into the zeolite products during the cation-exchange modification step. However, residual Na was also observed in the ion-exchanged products, indicating that Na^+ was not completely replaced by Mg^{2+} or K^+ under the present experimental conditions. Therefore, the ion-exchanged products should be interpreted as Mg- and K-modified zeolites rather than completely exchanged stoichiometric Mg- or K-modified zeolites.

SEM-EDX analysis was used only as supplementary evidence for particle morphology, elemental distribution, and Mg/K introduction. Because SEM-EDX is surface-sensitive and semi-quantitative, it was not used as quantitative proof of product purity, cation-exchange efficiency, or complete ion exchange. Quantitative determination of cation-exchange efficiency would require additional bulk elemental analysis, such as ICP-OES or XRF after complete dissolution, or cation-exchange-capacity measurements. Therefore, the present study verifies the introduction of Mg and K as functionalizing cations, but does not claim complete stoichiometric exchange of Na^+ by Mg^{2+} or K^+ . In addition, the present structural and compositional analyses should not be interpreted as sufficient evidence to establish a quantitative framework–performance relationship. Because BET surface area, pore volume, pore-size distribution, adsorption isotherm, kinetic, and dosage-dependent adsorption analyses were not performed, the role of zeolite porosity and surface structure in the subsequent removal performance could not be quantitatively

determined. Therefore, the cation-exchange modification results presented in this section should be regarded as evidence of Mg and K introduction and retention of major aluminosilicate-related features, while the detailed adsorption mechanism, cation-exchange efficiency, and framework–performance relationship remain subjects for future investigation.

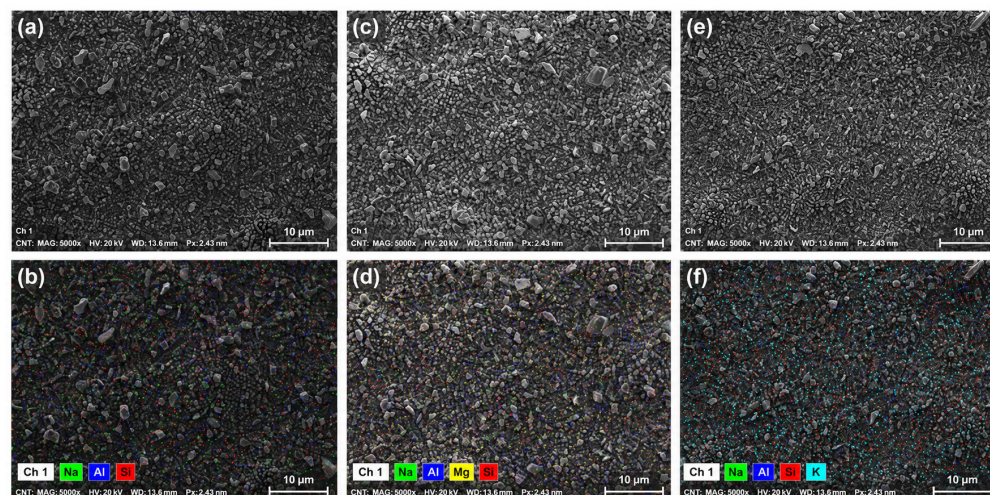


Figure 10. Figure 10. SEM images and EDX elemental maps of the synthesized and ion-exchanged zeolite products obtained at 5000× magnification: (a,b) Na-type zeolite, (c,d) Mg-modified zeolite, and (e,f) K-modified zeolite. The EDX maps show the presence of Mg in the Mg-modified zeolite and K in the K-modified zeolite, supporting the introduction of Mg and K as functionalizing cations during the ion-exchange treatment. Residual Na observed in the ion-exchanged products indicates incomplete replacement of Na⁺ under the present conditions.

3.6. Heavy Metal Removal Performance of Mg-Modified Zeolite

The heavy metal removal performance of Mg-modified zeolite was evaluated using single-metal aqueous solutions containing Pb, Hg, Cr, and Cd. The residual metal concentrations after treatment and the calculated removal efficiencies are summarized in Table 8. The initial concentration of each metal was 100 ppm, and the residual concentrations after treatment were 0.004 ppm for Pb, 0.00059 ppm for Hg, 0.018 ppm for Cr, and 0.004 ppm for Cd. These values correspond to removal efficiencies higher than 99.9% for all tested metals. Because 200 g of Mg-modified zeolite was used for 5000 mL of solution, the adsorbent dosage was 40 g L^{−1}, which is much higher than the typical dosages used for adsorption-isotherm evaluation. Therefore, the high removal efficiencies above 99.9% should be interpreted primarily as a consequence of the high adsorbent dosage under the present batch test condition, not as evidence of exceptionally high intrinsic affinity or superior structural adsorption capacity. The calculated adsorption capacities were approximately 2.5 mg g^{−1} for each metal under the present experimental conditions. This indicates that the present experiment was designed to evaluate batch removal performance under a high-dosage condition rather than to determine the maximum adsorption capacity, $q_{\max}$. Therefore, direct benchmarking with reported $q_{\max}$ values for other zeolite-based adsorbents should be conducted cautiously because adsorption isotherm experiments were not performed in this study. Additional experiments using lower adsorbent dosages, such as 1–5 g L^{−1}, and different initial metal concentrations would be required to determine the actual maximum adsorption capacity and adsorption isotherm parameters.

It should also be noted that adsorption isotherm, kinetic, and porosity analyses were not performed in the present study. Therefore, Langmuir/Freundlich isotherm parameters, pseudo-first-order/pseudo-second-order kinetic parameters, thermodynamic

adsorption quantities, and BET-based porosity parameters were not determined. Accordingly, the present results should be regarded as fixed-condition batch removal performance rather than as a complete adsorption-mechanism, maximum-capacity, thermodynamic, or kinetic-rate evaluation. To clarify the adsorption behavior of Mg-modified zeolite in more detail, further studies using different initial metal concentrations, lower adsorbent dosages, and different contact times would be required to determine $q_{\max}$, adsorption isotherm parameters, and adsorption kinetic parameters. In addition, porosity characterization, such as BET surface area, pore volume, and pore-size distribution analyses, would be necessary to correlate the zeolite framework structure with heavy metal adsorption performance.

The removal behavior may be attributed to ion exchange between exchangeable cations in the zeolite and dissolved metal ions, as well as surface adsorption on the aluminosilicate framework. In the case of Cr, chromium was introduced as Cr(VI) using a potassium dichromate-based standard solution. Because Cr(VI) generally exists as oxyanion species depending on solution pH, its removal cannot be explained solely by simple cation exchange with the negatively charged zeolite framework. In this study, no additional pH adjustment was performed; however, the initial pH of the diluted 100 ppm Cr(VI) solution was not measured in the original experiment. Therefore, the Cr removal mechanism was interpreted cautiously. The observed Cr removal by Mg-modified zeolite may involve surface adsorption or complexation, interaction with Mg-bearing sites, and/or precipitation-related processes rather than only framework-based ion exchange. Further detailed pH-dependent Cr speciation analysis would be required to fully clarify the Cr removal mechanism.

Table 8. Residual concentrations, removal efficiencies, and calculated adsorption capacities for Pb, Hg, Cr(VI), and Cd after treatment with Mg-modified zeolite under the tested batch conditions.

Metal	Initial Concentration (ppm)	Residual Concentration (ppm)	Removal Efficiency (%)	Adsorption Capacity, q_e (mg g ⁻¹)
Pb	100	0.004	99.996	2.5
Hg	100	0.00059	99.999	2.5
Cr	100	0.018	99.982	2.5
Cd	100	0.004	99.996	2.5

3.7. Water-Softening Performance of K-Modified Zeolite

The water-softening performance of K-modified zeolite was evaluated using synthetic hard water containing Ca²⁺ and Mg²⁺. The initial Ca²⁺ and Mg²⁺ concentrations were 45 and 47 ppm, respectively, corresponding to an initial total hardness of 308.3 ppm as CaCO₃. After treatment with K-modified zeolite, the residual Ca²⁺ and Mg²⁺ concentrations decreased to 7.65 and 5.04 ppm, respectively. The hardness removal performance is summarized in Table 9. The final total hardness was calculated to be 40.13 ppm as CaCO₃, corresponding to a hardness removal efficiency of approximately 87.0%. This value is below 60 ppm as CaCO₃, indicating that the treated water reached the soft-water range under the tested condition. The decrease in hardness can be attributed to ion exchange between K⁺ in the K-modified zeolite and divalent hardness ions such as Ca²⁺ and Mg²⁺ in solution. However, as with Mg-modified zeolite, XRD alone does not provide quantitative evidence of cation exchange because replacement of exchangeable Na⁺ ions by Mg²⁺ or K⁺ can occur without forming a new crystalline phase or causing distinct peak shifts. Therefore, XRD was used mainly to confirm framework retention after ion exchange, whereas chemical analysis, such as ICP-OES, XRF, EDS, or cation-exchange-capacity measurements, would be required to quantify the degree of Mg²⁺ or K⁺ exchange.

Table 9. Water-softening performance of K-modified zeolite.

Parameter	Initial Value	Final Value	Unit	Removal Efficiency (%)
Ca ²⁺ concentration	45	7.65	ppm	83.0
Mg ²⁺ concentration	47	5.04	ppm	89.3
Total hardness	308.3	40.13	ppm as CaCO ₃	87.0

4. Conclusions

In this study, waste aluminum dust was systematically converted into functional zeolite materials through dry fusion purification, NaOH-assisted hydrothermal synthesis, acid purification, Si/Al ratio control, and cation-exchange modification. The raw material characterization confirmed that waste aluminum dust contained a high fraction of Al₂O₃ and SiO₂, indicating its potential as a secondary aluminosilicate source for zeolite synthesis. However, XRD and XRF analyses also revealed the presence of impurity phases and components such as AlN, NaCl, KCl, ZnO, Fe₂O₃, CaO, MgO, TiO₂, and chloride-containing species. These results demonstrated that purification of the raw dust was necessary before zeolite synthesis. Dry fusion purification reduced or removed several impurity components and produced an aluminosilicate-rich precursor suitable for subsequent Na-type zeolite formation. However, this dry fusion step should be regarded as a laboratory-scale purification route because it was conducted at 1600 °C under an Ar atmosphere.

Na-type zeolite was synthesized from the purified aluminosilicate precursor using 50 wt.% NaOH solution at 90 °C for 24 h. XRD analysis confirmed the formation of a Na-type zeolitic phase, while ICP-OES analysis showed that the as-synthesized product still contained residual Mg, Ca, K, and Ti impurities, corresponding to a purity of approximately 97.501 wt.%. Therefore, an additional acid purification step was required to improve the purity while retaining the major zeolitic diffraction features. Among the acid purification conditions investigated, HCl treatment provided the most suitable balance between impurity removal and retention of the zeolitic diffraction pattern. Low HCl concentrations were insufficient to remove residual impurities, whereas excessive acid concentrations caused weakening of the zeolitic diffraction peaks and apparent enrichment of acid-resistant Ti-bearing residues. The optimum condition was determined to be 0.25 M HCl for 24 h, under which the total impurity content decreased to 1.531 wt.%, corresponding to a zeolite purity of approximately 98.469 wt.%. This result indicates that controlled HCl leaching can reduce residual impurities while retaining the major crystalline zeolitic features.

The Si/Al ratio of the purified Na-type zeolite was further controlled using water glass as an additional Si source. The Si/Al ratio varied depending on the water glass addition amount and reaction time, indicating that the zeolite composition could be adjusted through post-synthesis silicate treatment. The highest Si/Al ratio of 1.77 was obtained at a purified Na-type zeolite-to-water glass mass ratio of 1:2 after reaction at 90 °C for 6 h. Longer reaction times did not necessarily increase the Si/Al ratio, suggesting that silicate incorporation, dissolution–reprecipitation behavior, and removal of loosely bound silicate species during washing may collectively influence the final composition. Therefore, the Si/Al ratio control should be interpreted as condition-dependent compositional adjustment rather than a simple monotonic increase with water glass amount or reaction time.

The Si/Al-ratio-controlled Na-type zeolite was then modified by Mg²⁺ and K⁺ ion exchange to prepare application-specific zeolite materials. Under the preparation route established in this study, Na-type zeolite was synthesized from the dry-fusion-purified precursor using 50 wt.% NaOH at 90 °C for 24 h, purified using 0.25 M HCl for 24 h, and further treated with water glass at a purified Na-type zeolite-to-water-glass mass ratio of

1:2 at 90 °C for 6 h to obtain a maximum Si/Al ratio of 1.77. The Si/Al-ratio-controlled zeolite was then modified by Mg^{2+} ion exchange using 1 M MgCl_2 solution at 25 °C for 24 h. Under the fixed batch condition used in this study, Mg-modified zeolite was tested for the removal of Pb, Hg, Cr(VI), and Cd from 100 ppm single-metal solutions using 200 g of zeolite in 5000 mL of solution for 30 min at 25 °C. The residual concentrations of Pb, Hg, Cr(VI), and Cd decreased to 0.004, 0.00059, 0.018, and 0.004 ppm, respectively, corresponding to removal efficiencies higher than 99.9%. However, these results were obtained at a relatively high adsorbent dosage of 40 g L^{-1} and a single initial concentration. Therefore, they should be interpreted as preliminary fixed-condition batch removal performance rather than as evidence of maximum adsorption capacity, intrinsic adsorption superiority, or q_{max} . The calculated adsorption capacity under the present experimental condition was approximately 2.5 mg g^{-1} .

For water softening, K-modified zeolite prepared using 1 M KCl solution at 25 °C for 24 h reduced the total hardness of synthetic hard water from 308.3 to 40.13 ppm as CaCO_3 under the tested condition of 500 g K-modified zeolite in 5000 mL of synthetic hard water for 30 min, corresponding to a hardness removal efficiency of approximately 87.0%. SEM-EDX analysis further supported the morphological retention and elemental distribution of the Na-type, Mg-modified, and K-modified zeolite products. The SEM images showed that the zeolite products maintained aggregated fine-particle morphologies after ion-exchange modification, while EDX elemental mapping confirmed the presence of Mg in Mg-modified zeolite and K in K-modified zeolite as supplementary evidence for cation-exchange modification. Residual Na was also observed in the ion-exchanged products, indicating that the ion exchange was not complete under the present experimental conditions. Because SEM-EDX is surface-sensitive and semi-quantitative, the present results confirm Mg and K introduction only as supporting compositional evidence and do not quantify the degree of cation exchange.

Overall, this study demonstrates the feasibility of valorizing waste aluminum dust as a waste-derived secondary resource for producing purified and cation-modified zeolite materials. The proposed process integrates raw-material purification, zeolite synthesis, acid purification, composition control, and cation-exchange modification into a single valorization route. The resulting Mg- and K-modified zeolites showed preliminary batch water-treatment performance under the tested fixed conditions for heavy metal/Cr(VI) removal and water softening, respectively. These results should not be interpreted as a complete adsorption-mechanism study or as a quantitative framework–performance correlation. Therefore, the proposed approach provides a potential strategy for converting aluminum-industry waste into value-added functional materials for environmental and industrial water-treatment applications.

However, the dry fusion step at 1600 °C under an Ar atmosphere is energy-intensive, and the present study did not include a complete mass-balance, techno-economic, or life-cycle assessment. Therefore, the industrial viability and sustainability of the proposed route should be further evaluated by considering energy demand, heat-recovery or continuous-process options, Al recovery, product yield, and comparison with conventional zeolite synthesis routes from aluminum residues. In addition, BET surface area, pore volume, pore-size distribution, adsorption isotherm, kinetic, and dosage-dependent adsorption analyses were not performed in the present study. Therefore, the heavy metal and Cr(VI) removal results should be regarded as preliminary batch-performance results obtained under the tested high-dosage condition. Further studies involving Langmuir/Freundlich isotherm modeling, pseudo-first-order/pseudo-second-order kinetic analysis, contact-time-dependent adsorption tests, dosage-dependent adsorption experiments, and BET surface area, pore-volume, and pore-size distribution analyses will be necessary to quantitatively determine the maximum adsorption capacity, adsorption rate,

adsorption mechanism, and relationship between zeolite framework properties and water-treatment performance. Furthermore, because framework retention after acid leaching and Si/Al ratio control was mainly evaluated using XRD, further microstructural characterization of the post-treated samples, including SEM observation and BET-based porosity analysis, will be necessary to quantitatively confirm framework integrity and porosity preservation.

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