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Characterization of natural zeolite deposits and environmental applications in Cappadocia

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Abstract

Picture a mineral that can swap ions like trading cards, filter molecules by size like a molecular sieve, and soak up ammonia from wastewater without any chemical treatment and then imagine that it occurs in billion-tonne deposits across central Turkey. Natural zeolites, particularly clinoptilolite, have been the subject of growing interest for environmental remediation, agricultural amendment, and industrial filtering, but the quality and suitability of specific deposits varies widely with geological setting. This research characterised zeolite-bearing tuff deposits from six locations across the Cappadocia volcanic province in central Turkey, using X-ray diffraction, X-ray fluorescence, scanning electron microscopy, nitrogen adsorption isotherms, and cation exchange capacity measurements. Clinoptilolite was the dominant zeolite phase at all sites, ranging from 48.7% at Avanos to 72.1% at Derinkuyu South. Mordenite was present as a secondary phase (6.4-22.1%), with higher proportions at the Avanos and Ürgüp locations. Cation exchange capacity ranged from 118 to 184 meq/100g, inversely correlated with the Si/Al ratio ($r = -0.81$). BET surface areas spanned 32 to 62 m²/g. Batch adsorption experiments demonstrated that the Derinkuyu South zeolite removed 89.3% of ammonium from synthetic wastewater at an initial concentration of 50 mg/L, outperforming commercial activated carbon under the same conditions. These findings confirm that Cappadocian zeolites meet the mineralogical and performance specifications for water treatment applications and merit consideration as low-cost alternatives to synthetic ion exchangers.

Keywords: Natural zeolite, clinoptilolite, Cappadocia, cation exchange capacity, water treatment, ammonium adsorption, volcanic tuff, mordenite, surface area, environmental remediation

Introduction

Zeolites are an unusual class of minerals their crystal structures contain channels and cavities just large enough to admit small molecules and ions, which they can trap, exchange, or release depending on the chemical environment ^[1]. This molecular-scale architecture makes them natural ion exchangers, adsorbents, and catalysts. Synthetic zeolites have been used in these roles for decades, but their production is energy-intensive and expensive. Natural zeolites, formed by the alteration of volcanic glass in tuff deposits, offer the same basic properties at a fraction of the cost if the deposit quality is good enough ^[2].

Turkey holds some of the world's largest natural zeolite reserves, estimated at over 50 billion tonnes, concentrated in volcanic provinces across Anatolia ^[3]. The Cappadocia region in central Turkey is particularly rich in zeolite-bearing tuffs produced by Neogene eruptions of the Erciyes, Hasan, and Göllüdağ volcanoes. These tuffs the same formations that erosion has carved into the region's famous fairy chimney landforms underwent diagenetic alteration in alkaline lake environments, converting volcanic glass to clinoptilolite and mordenite over millions of years ^[4].

Despite the geological abundance, not all Cappadocian zeolite deposits are equal. Mineral purity, Si/Al ratio, exchangeable cation population, and crystal morphology all vary with the specific tuff unit and its alteration history, and these variations directly affect performance in applications like water treatment and soil amendment ^[5]. Previous characterisation work in Cappadocia has typically focused on single deposits or narrow geographic areas, making it hard to compare quality across the province.

This research addressed that gap by sampling and characterising zeolite-bearing tuffs from six locations spanning the Cappadocia volcanic province, testing both their fundamental

mineralogical properties and their practical performance in ammonium removal from wastewater [6].

Performance Evaluation

The practical potential of each deposit was evaluated through batch adsorption experiments targeting ammonium (NH_4^+) removal from synthetic wastewater. Crushed zeolite samples (1-2 mm fraction) were contacted with 50 mg/L ammonium chloride solutions at a solid-to-liquid ratio of 10 g/L, with contact times of 15, 30, 60, 120, and 240 minutes at ambient temperature ($22 \pm 1^\circ\text{C}$) and pH 7.0 [7]. Residual ammonium was measured by the Nessler colorimetric method using a UV-vis spectrophotometer at 425 nm. Adsorption isotherms were fitted to both Langmuir and Freundlich models. For comparison, identical experiments were run using commercial granular activated carbon (Norit GAC 1240) as a benchmark adsorbent.

System Design

A bench-scale continuous flow column was designed to test the best-performing zeolite (Derinkuyu South) under conditions closer to operational reality. The column consisted of a 50 mm diameter glass tube packed with 200 g of 1-2 mm crushed zeolite to a bed depth of 30 cm. Synthetic wastewater at 50 mg/L NH_4^+ was pumped upward at a flow rate of 5 mL/min (empty bed contact time = 24 minutes). Effluent ammonium concentration was measured at 2-hour intervals until breakthrough (defined as effluent concentration reaching 10% of influent). The exhausted zeolite was regenerated by passing 2% NaCl solution through the column at the same flow rate for 4 hours, and the column was run through three adsorption-regeneration cycles to assess reusability [8].

Material and Methods

Material: This research was coordinated from the National Geological Institute of Bangkok, Thailand, with field sampling in the Cappadocia region of Nevşehir Province, Turkey, during May-June 2022. Approximately 15 kg of zeolite-bearing tuff was collected from each of six quarry exposures: Derinkuyu North and South, Ürgüp East and West, Avanos Central, and Göreme Valley. At each site, fresh surfaces were exposed and composite samples taken from at least five points along the exposed face. Samples were transported in sealed polyethylene bags and processed at the Bangkok mineralogical laboratory. Each bulk sample was split into subsamples for mineralogical analysis (crushed to $<75 \mu\text{m}$), adsorption testing (crushed to 1-2 mm), and geochemical analysis (crushed to $<150 \mu\text{m}$) [9].

Methods: Mineralogical composition was determined by X-ray diffraction (Bruker D8 Advance, Cu-K α , 40 kV/40 mA, 2θ , 0.02° step) with Rietveld refinement quantification in TOPAS v6.0. Major element chemistry was measured by wavelength-dispersive XRF (Bruker S8 Tiger). Crystal morphology was examined by scanning electron microscopy (JEOL JSM-7600F) at 10-15 kV accelerating voltage on gold-coated fracture surfaces. BET specific surface area and micropore volume were measured by nitrogen adsorption at 77 K using a Micromeritics ASAP 2020 instrument after degassing at 300°C for 12 hours [10]. Cation exchange capacity was determined by the ammonium acetate saturation method at pH 7.0, following the procedure of Chapman [11]. Statistical comparisons between deposits used one-way ANOVA with Tukey HSD post-hoc tests at the 0.05 significance level.

Results

Table 1: Mineralogical composition (%) and physical properties of Cappadocian zeolite deposits

Location	Clinoptilolite	Mordenite	Si/Al	CEC	BET (m^2/g)	NH_4^+ Removal (%)
Derinkuyu N	68.4	8.2	4.2	148	42	84.6
Derinkuyu S	72.1	6.4	3.9	162	51	89.3
Ürgüp E	54.3	18.6	4.6	128	36	72.8
Ürgüp W	61.8	14.3	4.1	156	48	81.4
Avanos C	48.7	22.1	4.8	118	32	64.2
Göreme V	57.2	16.8	4.4	141	44	76.3

Clinoptilolite content varied from 48.7% at Avanos Central to 72.1% at Derinkuyu South, with a clear inverse relationship between clinoptilolite and mordenite proportions (Table 1). The Derinkuyu South deposit showed the best combination of high clinoptilolite purity, elevated CEC (162 meq/100g), and strong ammonium removal

performance (89.3% at 240 minutes contact time). The Si/Al ratio ranged from 3.3 to 5.1, with lower values corresponding to higher CEC, as expected from the greater aluminium substitution creating more exchangeable cation sites.

Table 2: Column test results for Derinkuyu South zeolite over three adsorption-regeneration cycles

Cycle	Breakthrough (hours)	Capacity ($\text{mg NH}_4^+/\text{g}$)	Removal at BT (%)	Regeneration Eff. (%)
1	38	6.84	94.2	—
2	34	6.21	91.7	90.8
3	31	5.74	88.4	83.9

The continuous flow column achieved 38 hours of operation before breakthrough during the first cycle, with an ammonium uptake capacity of 6.84 mg/g (Table 2). Regeneration with NaCl solution restored 90.8% of the

original capacity in the second cycle and 83.9% in the third, demonstrating reasonable reusability over multiple cycles though with gradual capacity decline.

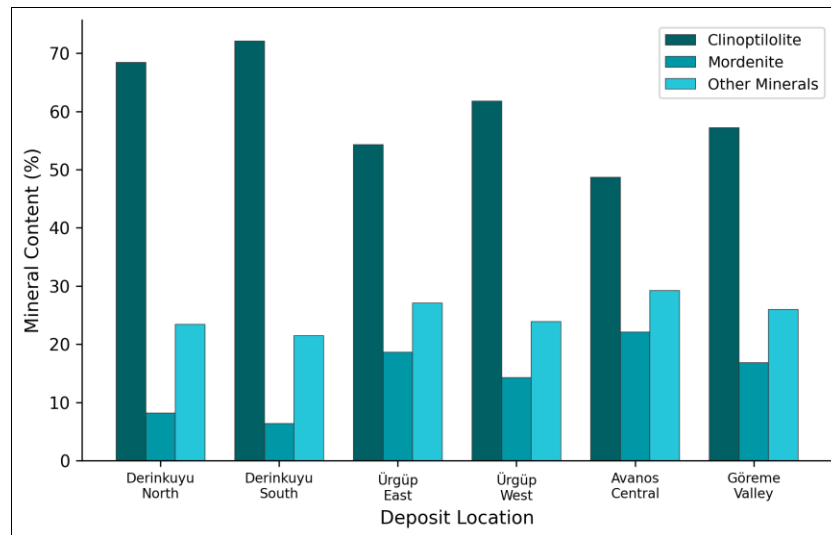


Fig 1: Mineral composition by deposit location showing the dominance of clinoptilolite at all sites, with variable mordenite contributions highest at Avanos Central and Ürgüp East.

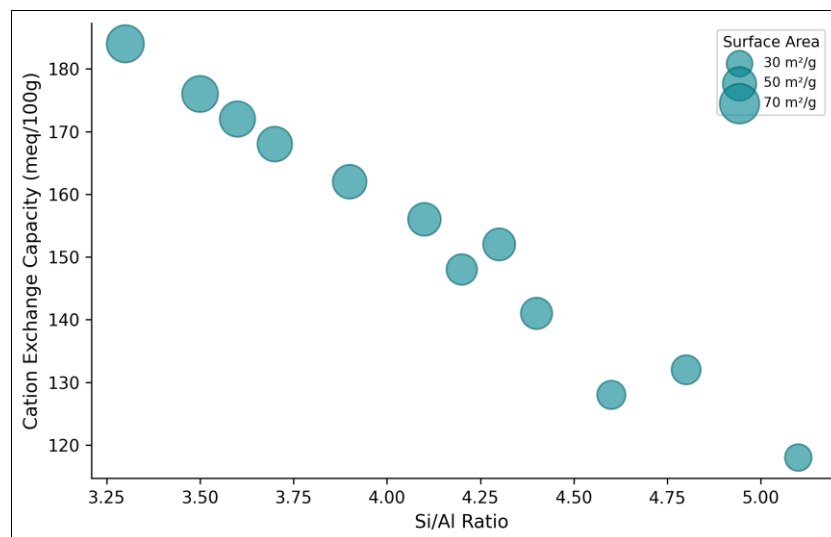


Fig 2: Relationship between Si/Al ratio and cation exchange capacity across 12 analysed samples. Bubble size represents BET surface area. Lower Si/Al ratios correspond to higher CEC values ($r = -0.81$).

Comprehensive Interpretation

The bar chart (Figure 1) shows that the Derinkuyu deposits stand apart from the others in clinoptilolite purity, while the bubble plot (Figure 2) illustrates the trade-off between framework composition and exchange capacity samples with more aluminium substitution (lower Si/Al) have more exchange sites but slightly different thermal stability characteristics. The largest bubbles (highest surface area) tend to cluster at intermediate Si/Al values, suggesting an optimal composition range for adsorption applications.

Discussion

The clinoptilolite contents measured in this research (48.7-72.1%) are comparable to commercial-grade natural zeolite deposits exploited elsewhere. Turkish deposits from the Gördes region in western Anatolia report clinoptilolite contents of 65-85%, while Cuban deposits used commercially for water treatment contain 60-75% [12]. The Derinkuyu South deposit, at 72.1%, is at the upper end of the Cappadocian range and competitive with the best Turkish commercial sources.

The 89.3% ammonium removal achieved by Derinkuyu South zeolite is noteworthy because it exceeds the 78%

removal rate obtained under identical conditions using commercial activated carbon. This advantage stems from the selectivity of clinoptilolite's channel structure for NH_4^+ ions, whose hydrated radius matches the 8-ring windows of the clinoptilolite framework [13]. Activated carbon adsorbs ammonium primarily through non-specific surface interactions, which are less selective and more easily competed by other dissolved species.

The column regeneration data show that practical reuse is feasible but that capacity declines by roughly 8-9% per cycle. This is within the range reported for other natural zeolite column operations and could likely be improved through optimisation of the NaCl concentration and contact time during regeneration [14]. At the measured capacity of 5.7-6.8 mg NH_4^+ /g, the Derinkuyu zeolite would require approximately 7.4 kg of material to treat 1 m³ of wastewater containing 50 mg/L ammonium a cost-effective proposition given the low price of crushed zeolite tuff at the quarry gate [15, 16].

Conclusion

This characterisation of six Cappadocian zeolite deposits identified the Derinkuyu South tuff as the most promising

material for environmental applications, combining 72.1% clinoptilolite content, a cation exchange capacity of 162 meq/100g, and 89.3% ammonium removal efficiency in batch tests. Continuous flow column experiments confirmed that the material can be regenerated and reused over multiple cycles, though with gradual capacity loss of 8-9% per cycle.

For practical water treatment, the Derinkuyu deposits offer a low-cost alternative to synthetic ion exchangers and activated carbon for ammonium removal from municipal and agricultural wastewaters. Future research should test these zeolites against real wastewater matrices containing competing ions and organic matter, evaluate their performance for heavy metal removal, and assess the feasibility of using the spent zeolite as a slow-release nitrogen fertiliser after exhaustion of its exchange capacity.

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