

# Evaluating the Potential of Ammonium-Natural Clinoptilolite Zeolite as a Slow-Release Fertilizer: A Study on Preparation, Characterization, and Ammonium Release Kinetics

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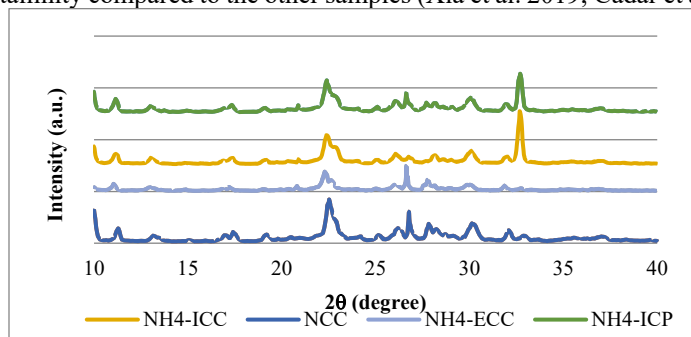
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The escalating use of chemical fertilizers and improper wastewater management have led to a dangerous rise in nitrate levels in groundwater, threatening its quality and raising concerns about its long-term sustainability (Tokazhanov et al. 2020). Natural zeolites are abundant, low-cost resources with valuable cation exchange properties. Microwave synthesis has been found to significantly reduce the synthesis time and increase the rate of formation of zeolites (Zeng et al. 2021). In this study, ammonium-clinoptilolite zeolites were prepared by microwave-assisted modification and impregnation to compare their ammonium ion exchange performance for evaluating their potential as slow-release fertilizers.

The natural clinoptilolite granulated chip (NCC) was obtained from San Luis Potosí, Mexico. The microwave-assisted modification of NCC (Masterwave BTR, Anton Paar, Austria) was modified using an ion exchange process with ammonium chloride (NH<sub>4</sub>Cl, CTR Scientific, Mexico), at high temperature and for a short duration (150 °C for 7.5 min). This treatment yielded a material designated as NH<sub>4</sub>-ECC. The NH<sub>4</sub>-impregnated clinoptilolite chips (NH<sub>4</sub>-ICC) and powder (NH<sub>4</sub>-ICP) forms were prepared with the same percentage of NH<sub>4</sub> content as NH<sub>4</sub>-ECC under wet conditions for 1 h. The final ion exchange reaction is expressed as follows:  $\text{Zeo-Na} + \text{NH}_4\text{Cl} \leftrightarrow \text{Zeo-NH}_4 + \text{NaCl}$ .

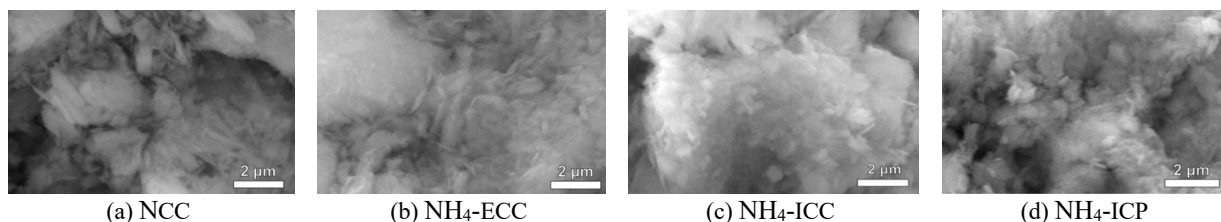
The effect of different ionic strengths (deionized water, low (0.03 M), medium (0.1 M), and high (0.3 M) NaCl solutions) on the release of ammonium from the zeolite was evaluated. This study used two replicates, centrifuging the samples at 200 rpm for various time intervals (10-400 min). After filtration, the ammonium concentration in the solutions was measured using a Thermo Scientific™ 9512HPBNWP model ion electrode. Non-linear regression methods were compared to determine the best-fitting kinetic model. The ammonium release kinetics were then adjusted by a non-linear method using statistical software R version 4.2 (R v4.2).

X-ray diffraction (XRD) analysis using a Bruker D550 model was used to characterize the mineralogy of the samples (Figure 1). The XRD patterns indicate that the structure of natural clinoptilolite zeolite and the modified zeolites is mostly maintained after high temperature and chemical treatments (Ateş et al., 2012). The crystallinity of NH<sub>4</sub>-NCC, NH<sub>4</sub>-ECC, NH<sub>4</sub>-ICC, and NH<sub>4</sub>-ICP was determined to be 47.88%, 57.8%, 49.56%, and 48.17%, respectively. No major changes in crystallinity were detected by X-ray diffraction. However, XRD patterns of NH<sub>4</sub>-ECC exhibits higher crystallinity compared to the other samples (Xia et al. 2019; Cadar et al. 2020; Babić et al. 2021).



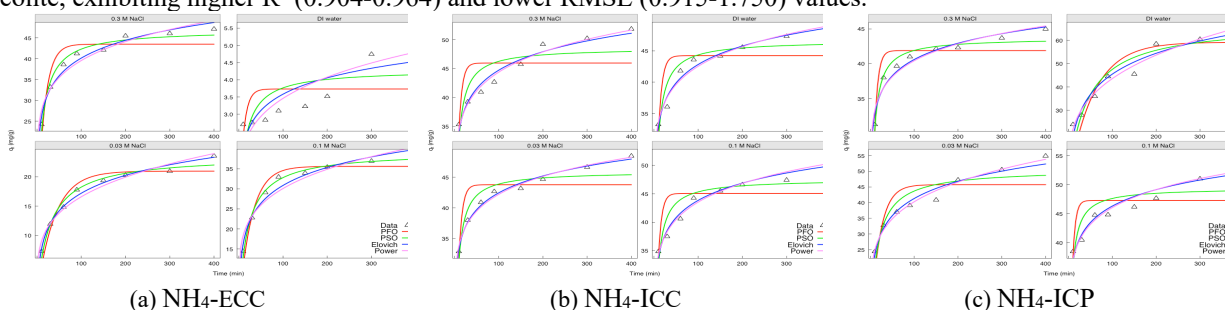
**Figure 1.** X-ray diffraction patterns of NCC, NH<sub>4</sub>-ECC, NH<sub>4</sub>-ICC, and NH<sub>4</sub>-ICP.

Scanning electron microscopy (SEM, model JSM-8440; JEOL) was used to analyze microstructures of samples (Figure 2). As shown in Figure 2 (a, c, d, e), the SEM images reveal an irregular morphology with channels and pores present within the zeolite structure of both the natural zeolite particles and the  $NH_4^+$ -modified zeolites (Mihok et al. 2020). These images indicate that  $NH_4^+$ -modification zeolites using microwave-assisted synthesis and the impregnation method does not affect the morphology of the zeolite.



**Figure 2.** SEM images of (a) NCC, (b)  $NH_4$ -ECC, (c)  $NH_4$ -ICC, and (d)  $NH_4$ -ICP.

The adsorption kinetics of  $NH_4^+$  release from the modified  $NH_4^+$ -zeolites (Figure 3) were measured at different ionic strengths. The amount of desorbed  $NH_4^+$  at time  $t$  ( $q_t$ ) ranged from 23.63 to 50.63  $mg L^{-1}$ . The amount of  $NH_4^+$  released increased with increasing ionic strength, except for ICP, which differed from the others. This difference can be attributed to the faster desorption of  $NH_4^+$  ions from the powdered form of the modified zeolite at lower ionic strength.  $NH_4$ -ECC exhibited a lower  $q_t$  range (23.63–46.91  $mg L^{-1}$ ) compared to the other samples. The kinetic studies confirmed that the Elovich model effectively describes the release of ammonium from the microwave-irradiated zeolite, exhibiting higher  $R^2$  (0.904–0.964) and lower RMSE (0.915–1.750) values.



**Figure 3.** Kinetic study of  $NH_4^+$  release from modified zeolite with different ionic strengths of NaCl solution.

Microwave-assisted modification not only enhances the  $NH_4^+$ -retaining capacity of the zeolite but also offers a shortened synthesis time and slower ammonium release across all ionic strength conditions. Therefore, this modified zeolite can be utilized as slow-release ammonium-based fertilizers, leading to a more prolonged fertilizer effect and reduced leaching waste, ultimately optimizing agricultural crop processes.

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