

# Zeolite-Ammonium interactions: the physical-chemistry of the desorption process



FOREST SCIENCES



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# INTRODUCTION

Zeolites are naturally occurring volcanogenic minerals formed as a result of complex chemical and physical processes in rocks undergoing various changes in nature [1]. The structural characteristic and mineralogy of the zeolite influence their cation exchange capacity and consequently their ability to remove ammonium  $(NH_4^+)$  from an aqueous solution [2]. Natural zeolites have been explored as an effective adsorbent for nutrient removal from wastewater. Nutrient enriched zeolites may be then reused as slow releasing fertilizer or undergone to a regeneration process to recover nutrient such as NH<sub>4</sub><sup>+</sup> in a circular economy perspective [3]. The regeneration of zeolites can be carried out by different methods. The most popular regeneration technique is commonly achieved using ionic brines, e.g., sodium chloride (NaCl), where the Na<sup>+</sup> ion replaces the adsorbed  $NH_{4^+}$  by releasing it into the liquid phase [4].

#### RESULTS

Regardless of the mineralogical composition, zeolites functionalised with NaCl desorbed more than not functionalised zeolites in static adsorption experiment (ZSS 27.6 and ZSC 27.9 vs. ZSN 22.9 and ZSC 24.2 mg  $NH_{4^+}$  g<sup>-1</sup>) (Fig. 1). Such differences were explained by higher amount of  $NH_{4^+}$  adsorbed by functionalised zeolites, than the not-functionalised ones.

Fig. 1. Amount of  $NH_4^+$  desorbed by Slovak and Cuban zeolites during 24 h. Treatments are: Slovak untreated clinoptilolite Cuban (ZNS), untreated clinoptilolite (ZNC), Slovak treated clinoptilolite with NaCl (ZSS) and Cuban treated clinoptilolite with NaCl (ZSC). Values are mean ± standard deviations of three replicates.



# AIM OF THE WORK

In this study, the ability of two zeolites with different mineralogy in desorbing ammonium (NH<sub>4</sub><sup>+</sup>) following a treatment with 1 M NaCl solution was assessed. The physicalchemistry of NH4<sup>+</sup> desorption process was studied by static desorption tests and desorption kinetics.



## MINERALOGICAL COMPOSITION

From a mineralogical point of view, the two zeolites differed in the content of Mordenite: the Cuban zeolite was richer (47%) than the Slovak one (20%) (Table 1).

The desorption kinetics were best approximated by the monomodal pseudo first-order model (Fig.2), thus suggesting only one mechanism of NH<sub>4</sub><sup>+</sup> desorption from zeolites (Fig. 3). Furthermore, desorption kinetics revealed that NaCl functionalised zeolites (ZSS and ZSC) desorbed more but slower than the not-functionalised zeolites (ZNS and ZNC) (Fig. 2).



**Fig.2** Monomodal pseudo-first order NH4+ desorption kinetics. Values are **Fig. 3.** Monomodality of  $NH_{4^+}$ mean ± standard deviations of three replicates. substitution on the surface of zeolites by Na<sup>+</sup>

ZEOLITE	HEULANDITE	MORDENITE	CLINOPTILOLITE	STELLERITE
SAMPLE				
ZNS	47%	20%	17%	16%
ZNC	53%	47%	: <b>.</b> ⊤:	

Table 1. Mineralogical composition (%) of tested zeolites.

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#### CONCLUSIONS

- The mineralogical composition of zeolites is of key importance in affecting the amount of NH<sub>4</sub><sup>+</sup> desorbed
- NaCl functionalization affect the rate of desorption.

# REFERENCES

Ghazavi, R. (2015) The application effects of natural zeolite on soil runoff, soil drainage and some chemical soil properties in [1] arid land area. International Journal of Innovation and Applied Studies. 13 (1), 172–177.

Widiastuti, N., Wu, H., Ang, H.M., and Zhang, D. (2011) Removal of ammonium from greywater using natural zeolite. [2] Desalination. 277 (1-3), 15-23.

Mannina, G., Badalucco, L., Barbara, L., Cosenza, A., Di Trapani, D., Gallo, G., et al. (2021) Enhancing a transition to a circular [3] economy in the water sector: The eu project wider uptake. Water (Switzerland). 13 (7), 1–18.

Canellas, J. (2018) Tertiary Ammonium Removal With Zeolites. School of Water, Environment and Energy Research Degree, [4] Cranfield University.