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Zeolite–Ammonium interactions: the physical-chemistry of the adsorption process

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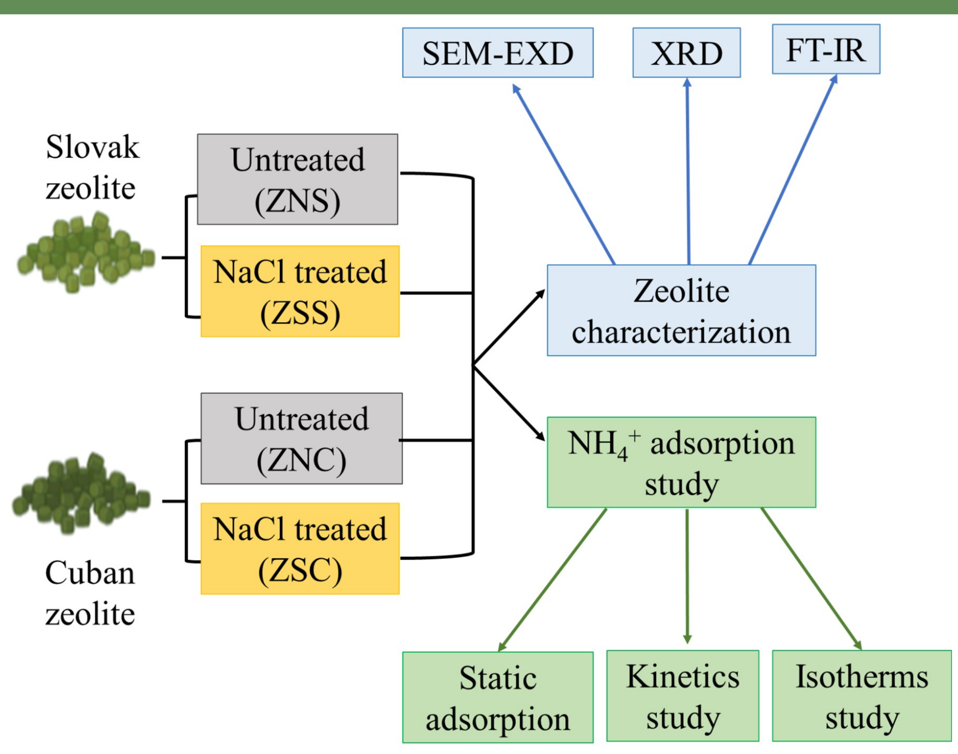
INTRODUCTION

Wastewaters have plenty of organic and inorganic compounds. Most of them are nitrogen-, and phosphorus-enclosing materials that can be considered plant nutrients [1]. Porous materials, such as zeolites, are considered very suitable for wastewater treatment and nutrient adsorption [2]. One potential application is the use of natural zeolites to remove nutrients, such as NH_4^+ from wastewater, thus reducing the risk of eutrophication of the aquatic environment and reusing enriched NH_4^+ zeolite as slow release fertiliser [3]. Due to the formation process, natural zeolites [2] have different operational capacity mainly related to the mineralogical composition.

AIM OF THE WORK

In this study, the ability of Slovak and Cuban zeolites with different mineralogy in adsorbing ammonium (NH_4^+) from a mono-component solution was assessed. Zeolites were treated or not treated with NaCl. The physical-chemistry of NH_4^+ adsorption process was studied by static adsorption tests, adsorption kinetics and adsorption isotherms.

METHODS



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).

Table 1. Mineralogical composition of zeolites (%)

ZEOLITE	HEULANDITE	MORDENITE	CLINOPTILOLITE	STELLERITE
SAMPLE				
ZNS	47%	20%	17%	16%
ZNC	53%	47%	-	-

RESULTS

Regardless of the mineralogical composition, zeolites treated with NaCl adsorbed more and faster NH_4^+ than the not treated one (Fig. 1). Such differences were explained by the low/high density water model (Fig. 2). The Cuban zeolite adsorbed more NH_4^+ than the Slovak one (32.9 vs. 29.3 mg NH_4^+ g^{-1}) in static adsorption experiment (Fig. 1).

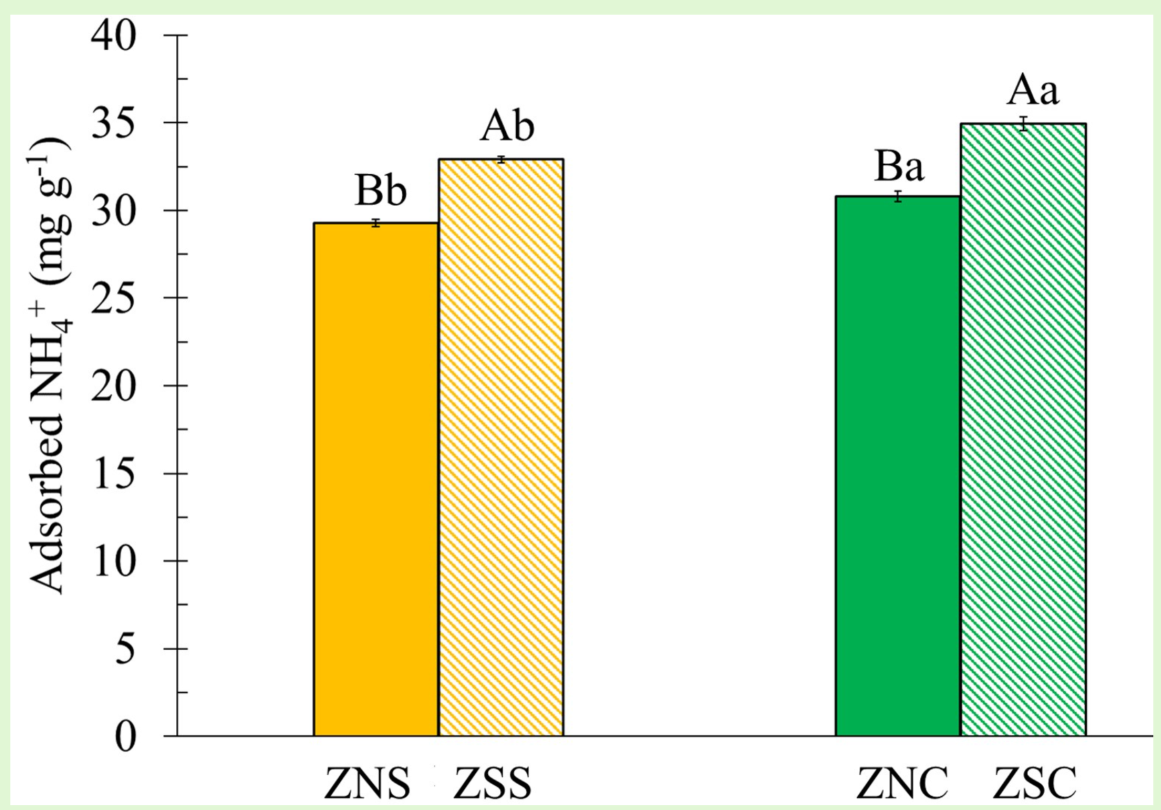


Fig.1. Amount of NH_4^+ adsorbed by the Slovak and Cuban zeolites during 24 h from a mono-component solution with an initial concentration of 20,000 mg NH_4^+ L^{-1}. Treatments are: Slovak untreated zeolite (ZNS), Cuban untreated zeolite (ZNC), Slovak treated zeolite with NaCl (ZSS) and Cuban treated zeolite with NaCl (ZSC). Values are mean ± standard deviation of three replicates.

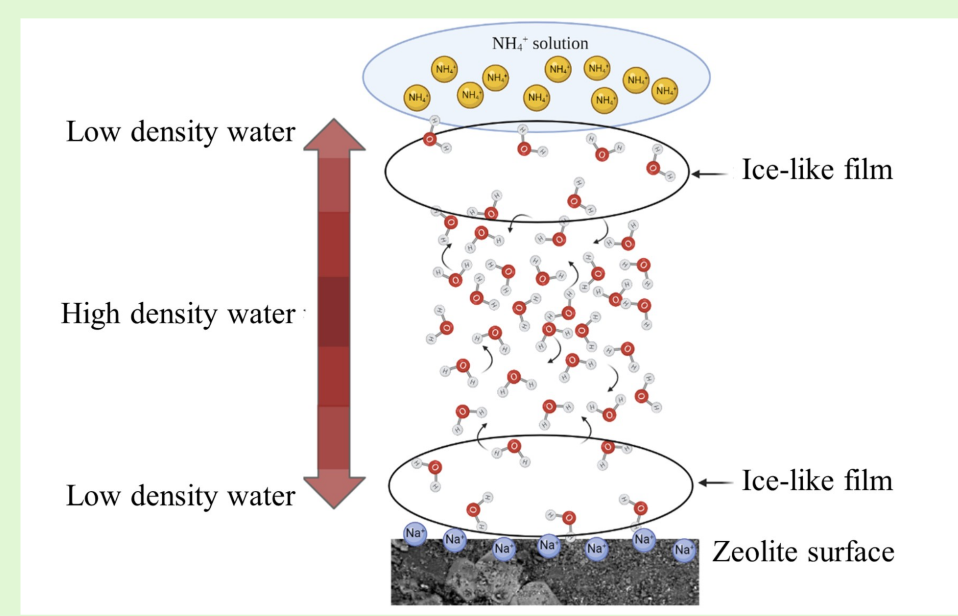


Fig.2. A model of the exchange between NH_4^+ solution and cations on zeolite surface. The exchange is driven by the water density gradient occurring between the two different surface (Modified by Conte & Schmidt, 2017).

The adsorption kinetics were best approximated by the bimodal pseudo-first order model, thus suggesting two different mechanisms of NH_4^+ adsorption onto zeolites. Furthermore, adsorption kinetics revealed that following the treatment with NaCl, the Slovak zeolite improved the adsorption rate of NH_4^+ (Fig. 3).

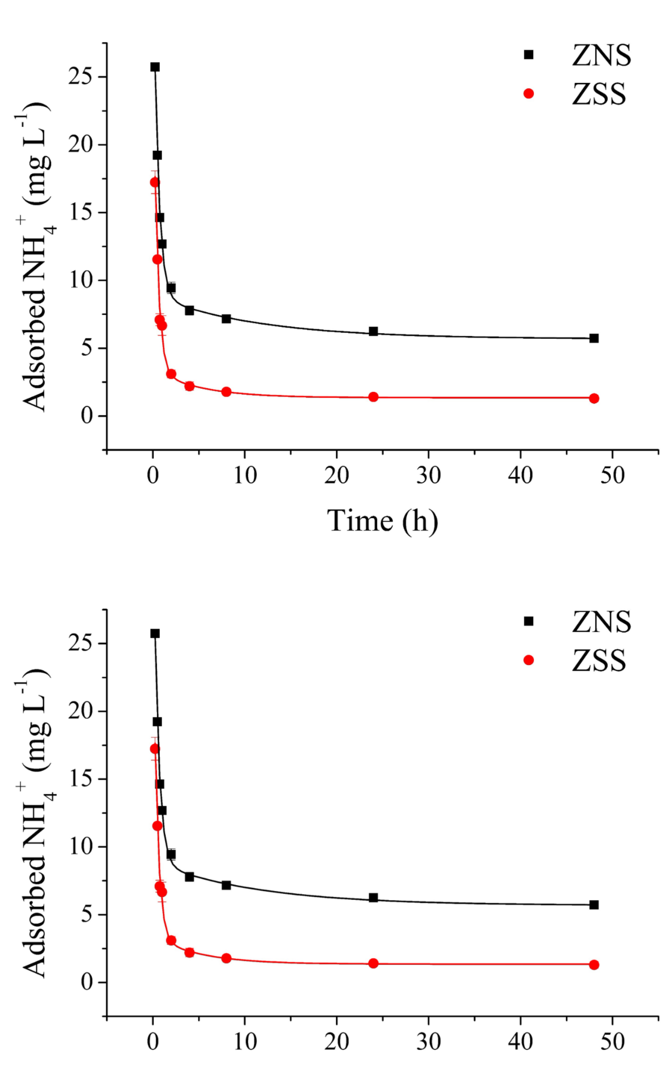


Fig.3. Bimodal pseudo-first order model to study the NH_4^+ adsorption kinetics of zeolites during 48 hours from a mono-component solution with an initial concentration of 50 mg NH_4^+ L^{-1}. Values are mean ± standard deviation of three replicates.

Langmuir-Sips model, compared to Langmuir and Freundlich models, provided the better fit of the equilibrium data. Parameters calculated by applying the Langmuir-Sips model suggested that the NaCl treatment increased the number of active sites only for the Slovak zeolite (Fig. 4).

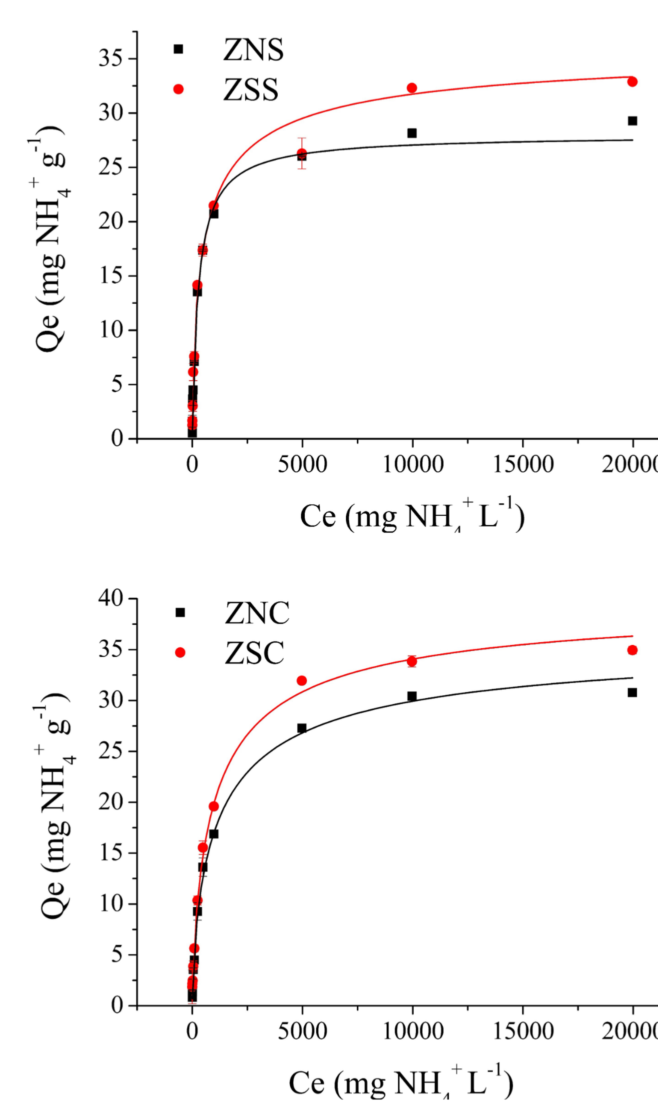


Fig.4. The Langmuir Sips isotherms. Values are mean ± standard deviation of three replicates.

CONCLUSIONS

- The mineralogical composition of zeolites greatly affected NH_4^+ adsorption as well as the number of active sites on zeolite following the NaCl treatment.
- The higher the presence of Mordenite, the greater the amount of NH_4^+ adsorbed.

ACKNOWLEDGEMENT

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