Testing adsorption properties of natural zeolites for nutrients in wastewater

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Abstract Low-cost and efficient removal of nutrients in decentralized wastewater treatment plants is still challenging. The installation of supplementary adsorption systems may, in some cases, be appropriate. This work focused on two types of untreated natural zeolites, clinoptilolite and chabasite, with the objective of their characterization and testing of the adsorption properties. Characterization tests were first made on the samples. Inductively coupled plasma analyses showed a Si/Al ratio of 4.09 and 2.40 for clinoptilolite and chabasite respectively. X-ray diffraction tests showed different material purity (93% for clinoptilolite, and 73% for chabasite). The Brunauer–Emmett–Teller (BET) test showed that the specific area of the chabasite was 10-fold than clinoptilolite. Batch adsorption tests were conducted by introducing a known mass of sample in a mixing rotative reactor and measuring the contaminant equilibrium concentration. Column adsorption tests were done by introducing the water-ammonium solution into a PMMA column. Experimental measurements were compared to a general adsorption model. In all tests, the adsorption capacity of clinoptilolite was higher, despite the lower Si/Al ratio and higher specific area of chabasite. Such a result is attributed to the purity of the material. Natural zeolites confirm to be good candidates for ammonium adsorption in decentralized wastewater treatment plants, although their detailed preliminary characterization is fundamental.

Keywords: Wastewater treatment, adsorption, ammonium, zeolites.

1. Introduction

Biological and chemical treatments are often the most effective method for nutrient removal in wastewater, but their complexity can make them difficult to implement in certain contexts. Adsorption can, in some case, be considered a viable alternative for wastewater purification. The crucial challenge in the adsorption process is to select an appropriate adsorbent with the optimal characteristics, including high adsorption capacity, selectivity, rapid adsorption kinetics and reusability. Natural zeolites are abundant materials on the planet, potentially suitable for this purpose. Zeolites have been widely studied in the last decades for contaminant adsorption from wastewater. Nevertheless, the adsorption behaviour of zeolites still needs to be fully understood. In the present study, two types of natural unmodified zeolites (clinoptilolite and chabasite) were characterised and tested by means of a series of experimental measurements. The objective was to characterise the adsorption capacity of these materials against water dissolved ammonium ion (NH_4^+), to assess their possible application in water treatment plants. In addition to material characterisation, the experimental measurements included a series of tests under both static and dynamic conditions.

2. Methods

X-ray diffraction (XRD) tests, and inductively coupled plasma (ICP) analyses were conducted to ascertain the nature of the samples and facilitate interpretation of the results. To quantify the adsorption capacity, batch and column tests were conducted. Batch tests consisted of the introduction of a known mass of sample in a mixed reactor and, after the equilibrium time, measuring the contaminant concentration. For each sample, a mass of 10 g was dosed in 20 mm tubes. Tubes were filled with 50 ml of synthetic water with known initial contaminant concentration (liquid-solid weight ratio 5:1). Tubes were then inserted in a rotative mixer and stirred for 14 h at a temperature of 21 °C. Subsequently, the contaminant concentration in the liquid phase was measured.

Column adsorption tests were also conducted. A polymethyl methacrylate column of height and diameter of 115 cm and 4.97 cm respectively was used. The column was filled with 500 g of adsorber. Zeolite samples were first washed with ultrapure water, then dried for 1 h at 110°C. Two gravel layers of 30 cm height, one at the top and one at the bottom of the column, were inserted to allow a uniform distribution of the flow. Water and ammonium solution was pumped into the column at a flow of 0.28 ml s^{-1}. The initial ammonium concentration was 10 mg L^{-1}. Samples were taken every 2 h. Ammonium concentration was measured using a spectrophotometer (Onda UV31-scan).

To evaluate the dynamics mechanism between the adsorbate and the adsorbent, pseudo-first order and pseudo-second order models were applied to the measured data.

3. Results

XRD analyses were performed on zeolite samples to ascertain the degree of purity. For clinoptilolite, the spectrum analysis indicated that 93% of the composition was pure clinoptilolite, while for the remaining 7% tridymite (6%) and cristobalite (<1%) were detected. For chabasite, 73% of the spectrum corresponded to pure chabasite, while sanidine (17%) and biotite (10%) were also detected. The average specific BET area measured with the porosimeter was 31 m^2 g^{-1} and 294 m^2 g^{-1} for clinoptilolite and chabasite respectively. The measured Si/Al ratio of clinoptilolite and chabasite was 4.09 and 2.40 respectively.

The results of batch adsorption tests for ammonium are reported in Figure 1. Figure 1 shows that clinoptilolite has higher adsorption capacity than chabasite. The adsorption capacity at equilibrium concentration C_{eq} = 10 mg L^{-1} are 1.66 mg g^{-1} and 1.47 mg g^{-1} for clinoptilolite and chabasite respectively. The adsorption behaviour of these materials is better represented by the Freundlich isotherm.

The adsorption column test lasted approximately 500 h for clinoptilolite and 600 h for chabasite respectively. Retardation factor was in the range 742 – 1334 for clinoptilolite, and 515 – 534 for chabasite. The experimental data were in higher agreement with the pseudo-first order model. The calculated adsorption capacity at equilibrium is reported in Table 1.

Table 1. Calculated adsorption capacity q_e.

Sample	**Pseudo-1st order model q_e (mg g^{-1})**	**R^2**	**Pseudo-2nd order model q_e (mg g^{-1})**	**R^2**
Clinoptilolite	2.55	0.987	3.12	0.978
Chabasite	2.30	0.987	2.94	0.978

4. Discussion

Overall, the results found in this study report an adsorption capacity comparable to existing solid sorbents. In an extensive review conducted by Shoumkova (2012), adsorption capacities between 1.3 mg g^{-1} and 21.7 mg g^{-1} for both untreated and treated zeolites were reported. Regarding adsorption kinetics, the results reported in bibliography are contrasting if compared to the present study. The reason of the discrepancy between clinoptilolite and chabasite may be attributed to particle size and material purity.

In conclusion, the use of these materials seems appliable, especially in the context of sustainable low-cost purification technologies for developing countries. However, a detailed chemical characterization of materials seems appropriate before its application.

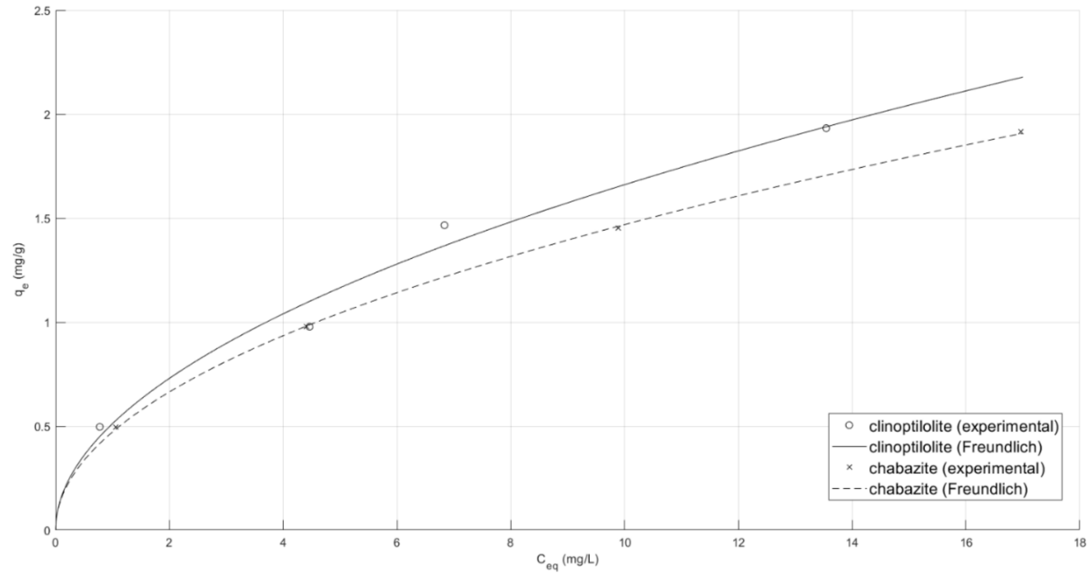

Figure 1. Adsorption isotherms for clinoptilolite and chabasite at 21°C.

References

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