ZEOLITE AS A BINDING AGENT FOR AMMONIA IONS AND AS A SOIL ADDITIVE. PART 1 AMONNIA ADSORPTION BY THE ZEOLITE

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ABSTRACT

The Serbian natural zeolite (CLI) can be used effectively in the removal of ammonia ions from aqueous solutions and as a binding agent to mitigate ammonia loss from cattle manure. Experiments showed that the concentration of NH_4^+ ions in the zeolite increases with the contact time and the initial concentration of ions in solution, but decrease with temperature. Addition of 10 wt.% zeolite to fresh cattle manure increases retention of the released ammonia by 90% in comparison to the system without zeolite. Results indicated that the ammonia-containing zeolite (NH_4-CLI) could be used as a soil additive.

Key words: zeolite, removal of ammonia ions, retention of ammonia, manure, soil additive.

INTRODUCTION

Nitrogen (N) is one of the most critical elements affecting plant growth. During the growth of plants it is necessary that these compounds are added to the soil to ensure the best growth and yield of crops. The loss of nitrogen (N_2) from the applied N-fertilizer due to leaching, volatilization and denitrification leads to not only a decrease in the N-fertilizer efficiency, but also causes the air and groundwater contamination [1]. Therefore, there is a need for efficient binding agent which could prevent nitrogen leaching and, in the same time, prolong its availability during plant growth. In this work, Serbian natural zeolite was used in order to: (1) study the kinetics of binding of ammonia ions from aqueous solution by Serbian natural zeolite, in order to determine the capacity of the zeolite, and to get an insight into the mechanism of ammonia binding by the zeolite; (2) investigate the efficiency of the zeolite as a binding agent in mitigating the ammonia loss from fresh cattle manure.

EXPERIMENTAL

The investigations related to ammonia adsorption from aqueous solution were carried out using the natural zeolite tuff containing 73% clinoptilolite (Zlatokop deposit, Vranjska Banja) with a grain size in the range 0.063-0.1 mm. The zeolite was preliminarily washed with deionized water and ethanol to remove soluble amorphous impurities, and then it was dried in an oven at 105°C to a constant mass. The NH_4^+ sorption was studied in a batch mode experiments: 1 g of zeolite was mixed with 100 dm^3 of the model solution of chosen concentration; model solutions of NH_4Cl in deionized water were used as the liquid phase [2]. Three parameters were varied: initial concentration of ammonium ions, temperature and the contact time. The initial concentration was 5, 10, 25, 50 and 100 mg NH_4^+ dm^{-3}. The NH_4^+ sorption isotherms were determined at 298, 308 and 318 K using the batch method. The suspension was shaken in a thermostated water bath for a time period from 30 min to 24 h. The solid, NH_4-enriched zeolite (NH_4-CLI) was separated by filtration. The ammonia concentration in solutions was determined photometrically using the Nessler method.

Ammonia desorption experiments were conducted in a similar way, by placing NH$_4$-CLI into the desorbing solution (KCl and NaCl) in batch reactors and varying its concentration from 0.1 to 0.001 mol dm^{-3}.

The capture of ammonia released during fermentation of the fresh cattle manure was studied using a modification of the methodology described by Sharadqah and Al-Dwairi [3]. Five glass jars (volume 0.5 dm^3) were filled with manure (obtained from a cattle farm near Šabac) up to 2/3 volume and tightly closed. Into four of the jars, well homogenized mixture of the manure and zeolite was added in the ratio varying from 5 to 20 wt. %. The fifth jar served as a control (zeolite was not added). In each jar, a porcelain crucible containing 10.0 cm^3 of 0.1M H$_2$SO$_4$ was placed on a tripod. The jars were kept tightly closed by parafilm and a plastic lid for 24 hours. After 24 h, the crucibles were replaced by new ones containing fresh H$_2$SO$_4$, and the solutions from the old ones were transferred into 100.0 cm^3 volumetric flasks. The same procedure was repeated every day during 10 days, taking care that the jars were kept open for the shortest possible time. The concentration of ammonium ions in the H$_2$SO$_4$ solutions was determined photometrically.

RESULTS AND DISCUSSION

Adsorption results presented in Fig. 1a reveal that the sorption capacities of zeolite tuff increase with the initial NH$_4^+$ solution concentration and slightly decrease with temperature. The sorption capacity at 298 K varied from 0.37 mg NH$_4^+$ g^{-1} (for C_0 = 5 mg NH$_4^+$ dm^{-3}) to 6.45 mg NH$_4^+$ g^{-1} (for C_0 = 100 mg NH$_4^+$ dm^{-3}). A slight decrease in the sorption capacity was found at 318 K: from 0.36 mg NH$_4^+$ g^{-1} (for C_0 = 5 mg NH$_4^+$ dm^{-3}) to 6.10 mg NH$_4^+$ g^{-1} (for C_0 = 100 mg NH$_4^+$ dm^{-3}). This result shows that the sorption process is an ion-exchange in which NH$_4^+$(aq) from water solution replaces Na$^+$, K$^+$ and Ca^{2+} from the zeolite lattice. A similar reaction occurs when NH$_4$-CLI was in a contact with NaCl or KCl solutions (Fig. 2b).
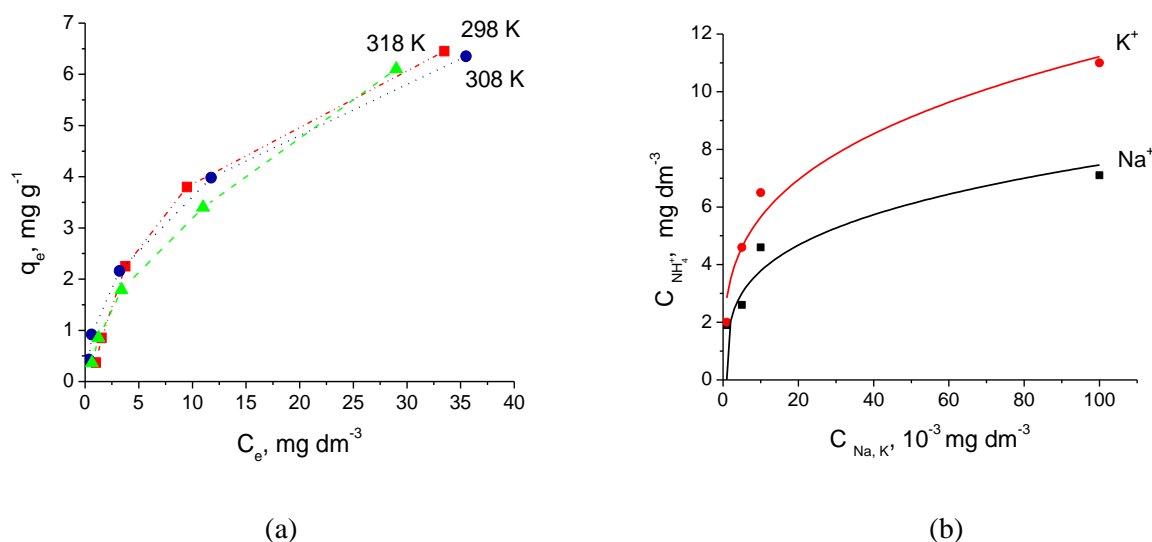

(a) (b)

Figure 1. (a) The sorption isotherms for NH$_4^+$(aq) on CLI; q_e is the amount of the sorbed ion and C_e is the solution concentration at equilibrium; (b) Desorption of NH$_4^+$ from NH$_4$-CLI in NaCl and KCl solutions.

The results presented in Figure 1a also show that the reaction is exothermic in nature.

Langmuir and Freundlich models were used to describe the equilibrium isotherm data [4]. For Langmuir isotherm the value of the separation factor (R_L) is of special importance and for Freundlich it is the value of the power (1/n). In all the experiments, the obtained data for R_L and 1/n in the removal of NH$_4^+$ from aqueous medium by the zeolite, according to the

literature [2, 5, 6], prove that the sorption is a favorable process. Therefore, it can be concluded that the natural zeolite is suitable as a sorbent for the NH_4^+ ions present in aqueous solution.

The NH_4^+ sorption dependence on time was studied at 298, 308 and 318 K for solutions with C_0 = 5-100 mg NH_4^+ dm^{-3}. The obtained results show that the binding of hydrated NH_4^+-ions by zeolite increases with the contact time. The uptake values of NH_4^+ from solution showed that in the early stages of sorption (in the first 30-60 min) the NH_4^+ uptake increased sharply and thereafter proceeded more gradually (Figure 2).

The experimental data were analyzed using the pseudo-second-order model equation (Lagergren's equation) [7]. A linear dependence was obtained, indicating that the ion exchange reaction is the second order. The correlation coefficient (R^2) was close to 1, proving that this model describes well the kinetics for all the studied concentrations. On the basis of the data presented, it can be concluded that the rate constant (k_2) decreases with concentration, while the adsorption capacity at equilibrium (q_e) increases (Table 1).
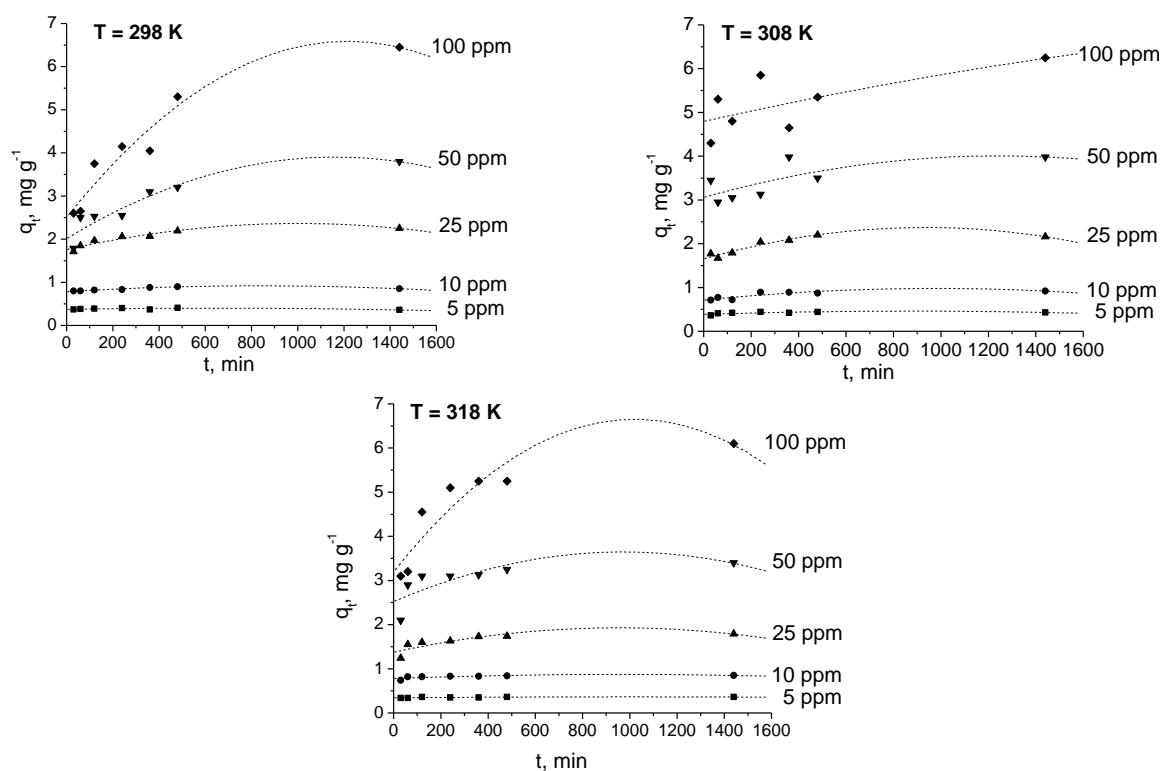

Figure 2. Sorption kinetics for NH_4^+ on the CLI for different initial NH_4^+ concentrations and temperature; q_t is the amount of the sorbed NH_4^+ after time t.

Table 1. Kinetic parameters obtained by the Lagergren's equation for the sorption of NH4+ on the CLI.

C_0 [mg dm^{-3}]	25 °C				35 °C			
	k_2 [g mg^{-1} h^{-1}]	R^2	q_e [mg g^{-1}]	Removed NH_4^+ [%]	k_2 [g mg^{-1} h^{-1}]	R^2	q_e [mg g^{-1}]	Removed NH_4^+ [%]
5	43.0506	1.0000	0.4015	78.72	45.3405	0.9994	0.4296	90.75
10	9.4806	0.9986	0.8843	88.00	0.3191	0.9937	3.2916	91.07
25	3.4487	1.0000	2.1186	78.86	1.8441	0.9977	2.1510	83.84
50	0.7076	0.9806	3.1626	65.26	31.1856	0.9990	3.1172	77.18
100	0.5163	0.9947	4.4209	41.33	0.6198	0.9861	6.0901	47.45

Table 1 (in continue)

C_0 [mg dm^{-3}]	45 °C			
	k_2 [g mg^{-1} h^{-1}]	R^2	q_e [mg g^{-1}]	Removed NH$_4^+$ [%]
5	355.88	0.9999	0.3550	83.29
10	25.59	0.9999	0.8406	85.98
25	2.77	0.9987	1.7612	81.18
50	1.92	0.9990	3.2237	69.44
100	0.30	0.9963	5.7837	58.33

Table 2 lists the amount of ammonia released by fresh manure during its fermentation, and the amount of ammonia bound by the zeolite. The data show that the addition of the zeolite contributes to the retention of the liberated ammonia. It is evident that the addition of 10 wt. % zeolite, compared to the control which is without zeolite, increases the retention of ammonia by 90%. The percentage of the preserved ammonia ranges between 67 and 98%.

Table 2. The amount of ammonia released by fresh manure and bound by the zeolite

Sample	Conc. of zeolite in manure [%]	Conc. of NH$_3$ released by manure [mg]	mg released NH$_3$ / kg manure	Preserved ammonia [%]
1	0	1.200	7.000	/
2	5	0.400	2.300	67
3	10	0.110	0.640	91
4	15	0.036	0.290	97
5	20	0.018	0.100	98

CONCLUSION

Experimental conditions such as the initial concentration of ammonium ions in water solutions, the temperature and the contact time have influence on the ammonia sorption capacity of the zeolite. The results of the present study indicate that the addition of the zeolite to the fresh cattle manure increases the retention of ammonia up to 98% in comparison to the control. Based on the results, the natural zeolite can be recommended not only for the treatment of water contaminated by ammonia but also for possible agricultural purposes as a soil additive since it released in contact with K$^+$(aq) and Na$^+$(aq) preserved ammonia.

AKNOWLEGMENT

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