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The effect of particle sizes on ammonium adsorption kinetics and desorption by natural zeolites

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Abstract

Reducing the particle size of the adsorbents is an efficient way of manipulating the adsorption/desorption characteristics of the adsorbate. Therefore, we tested the effect of micronisation of two natural clinoptilolite specimens on the ammonium (NH4+) adsorption/desorption. One g of adsorbent equilibrated with 20 mL solution containing 0-600 mg NH4+ L-1 at constant ionic strength. The adsorbate was extracted by molar KCl solution. Sorption kinetic was studied at 50, 300 and 600 mg L-1 concentrations for 5, 10, 20, 30 min; 1, 2, 4, 8, 16, and 24 h. The sorption data well confirmed both Freundlich and Langmuir sorption models. The Langmuir adsorption capacities (16667 mg kg-1) of both zeolites were similar but the sorption maximum of Gordes zeolite with 250-500 µm was smaller (14286 mg kg-1). The particle size dependency was apparent for Gordes zeolite. The desorption ratio was dependent on initial NH4+ concentration, particle size, and zeolite type. In general, there was an increase in desorption ratio up to 300-400 mg L-1 initial ammonium concentrations. Results of the kinetic study indicated that the adsorption data better fitted the pseudo second-order kinetic model than the Elovich model. Zeolite having well-structured porous nature can be used in larger particle size to scavenge NH4+ from the polluted water sources, but initial sorption rate can be improved by particle size reduction. The sorption data indicated that the zeolites may be used for NH4+ removal from the polluted water sources or improving the sorption capacity of coarse soils to alleviate ammonium leaching problem.

Keywords: Natural clinoptilolite-zeolite, ammonium, adsorption, desorption, particle size, sorption kinetics

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Introduction

Nitrogen (N) is the essential element for all life forms on the Earth. However, its deficiency on agricultural lands and excessiveness in the surface/ground waters are problematic. These two environmental problems are highly interrelated to each other. High mobility of mineral forms of N in agricultural ecosystems leads leaching problem which cause pollution in surface and/or, to a lesser extent, in ground waters and lower nitrogen use efficiency of the crop plants. These deleterious environmental problems may be relieved by reducing the mobility of mineral N forms without complicating the plant uptake and removing the excessive N in water bodies through the adsorption processes.

Various methods of NH$_4^+$ removal from water bodies, especially those of municipal sewage, domestic and industrial wastewater or decomposed from organic N compounds in those wastewater and wastes can be accomplished by biological, physical and chemical means or combination of these methods (Crini and Lichtfouse, 2019). The ion exchange method usually utilizes organic resins, which are very selective. However, they are very expensive (Crini, 2005); therefore, zeolites are preferred (Misaelides, 2011; Wang and Peng, 2010). In this aspect natural clinoptilolite-zeolite is cheap, environmentally friendly, natural and specific adsorbent for NH$_4$-N. The most important property of zeolites is the very high ion exchange capacity expressing the ability of the material to scavenge cations from the solutions (Hedstrom, 2001). Zeolites have been particularly useful in removing cationic species such as ammonium, potassium and some heavy metals from water (Sprynskyy et al., 2006; Ji et al., 2017). Unlike many other organic resins and inorganic aluminosilicates, crystalline zeolites exert very high selectivity for low-field-strength cations such as those of monovalent over divalent or polyvalent cations having high-field-strength (Ming and Mumpton, 2003). This nature of zeolites make it excellent adsorbent for removing NH$_4^+$ from polluted water bodies or fixing NH$_4^+$ in the agricultural lands and preventing it from the nitrification processes thus leaching away through water sources (Li, 2003; Tarkalson and Ippolito, 2011).

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The magnitude of the adsorption surface is one of the most significant adsorbent properties determining the amount of adsorbed ions (Dobrowski, 2001). Therefore, the aim of this study was to test NH_4^+ sorption, kinetics and desorption of two micronized natural clinoptilolite – zeolite specimens as a function of initial NH_4^+ concentration.

Material and Methods

Zeolite preparation and properties

Two natural clinoptilolite - zeolites with different sizes were kindly supplied by Rota Madencilik Sti. (RZ) and Gordes Zeolite Ltd Sti (GZ). The zeolite samples were sequentially ground to pass through 500, 250, 106 and 53 µm stainless steel screens to obtain 250-500, 106-250, 53-106 and < 53 µm micronized particle sizes, respectively. Some chemical properties of the zeolite specimens were illustrated in Table 1. The zeolite specimens in general are the hydrated Ca, K, Na, Mg alumina-silicates, however, RZ with higher porosity mineralogically purer than GZ. The GZ consist of as much as 5% cristobalite and tridimite which are tectosilicates.

Table 1. Some properties of the experimental zeolites (Rota Mining Ltd. Şti,. 2017; Gördes Mining Ltd. Şti., 2017)

Properties	**Rota zeolite**	**Gordes zeolite**
Mineral composition	Clinoptilolite 90-95%	Clinoptilolite 70-85%
Surface area (m^2 g^{-1})	39.0	40.7
Porosity (%)	47.5	39.0
CEC (cmol kg^{-1})	150-210	160-200
P concentration (mg kg^{-1})*	188-270	121-200
K concentration (mg kg^{-1})*	8044-12192	6300-11902

* measured in the HNO_3/HCl (3:1, V: V) digest for different particle sizes (53-500 µm) used in this study. CEC: cation exchange capacity

Adsorption

The ammonium adsorption data were obtained by batch sorption technique. One gram of subsamples of zeolites, in triplicates, were equilibrated with a concentration range of NH_4^+ (0, 50, 100, 200, 400, and 600 mg NH_4^+ L^{-1} as NH_4Cl prepared in 0.01 M $CaCl_2$ solution) at 20±1°C by continuous mixing on a reciprocal shaker for 24 h. The $CaCl_2$ solution was used to maintain constant ionic strength resembling typical arid region's soil solution. After 24 h the supernatants were obtained by centrifugation and filtration procedures. The supernatants were then analysed for NH_4^+ by steam-distillation with the presence of light MgO (Mulvaney, 1996). The distilled NH_3 were kept in 2% (W/V) boric acid indicator mixture (methyl red and brome cresol green) solution and titrated with 0.05 M HCl. The magnitude of adsorbed NH_4^+ was computed from the equation given below:

$$Si = \frac{(Co - Ce) \times V}{W}$$

Where *Si* is the amount of NH_4 adsorbed by unit mass of zeolite (µg g^{-1}), C_0 the initial concentration of NH_4^+ (µg mL^{-1}), *Ce* the equilibrium concentration of NH_4^+ (µg mL^{-1}), *V* solution volume (25 mL), *W* the amount of zeolite used (g).

Then the following linear adsorption equations were fitted to sorption data by regression analysis.

Langmuir: $Ce/Si = Ce/b + 1/ab$

Freundlich model which can have non-linear form of $Si = K_f\ C^n$ can be written linear by taking log of the equation as: $\log Si = \log K_f + n \log C_e$

Where *b* maximum NH_4^+ adsorption capacity (mg kg^{-1}), *a* constant related to bounding energy (mL g^{-1}), *n* a measure of adsorption intensity and *Kf* corresponding to the amount of NH_4^+ adsorbed (mg kg^{-1}) when the *Ce* is equal to 1 mg NH_4^+ L^{-1}. To evaluate the success of the model describing the sorption data, determination coefficient of the fit was used.

Adsorption kinetics

The NH_4^+ sorption kinetics were studied at 50, 300 and 600 mg NH_4^+ L^{-1} initial concentrations for 5, 10, 20, 30 min; 1, 2, 4, 8, 16 and 24 h. The experimental conditions were identical to those of adsorption study. The sorption kinetics data were fitted to linear Elovich, and second order models which can be written below (Ho and McKay, 2002):

Elovich equation: $qt = \beta \ln (\alpha \beta) + \beta \ln t$

Where *qt* is the amount of NH_4^+ sorbed at a time *t* (mg kg^{-1}), *α* initial sorption rate (mg L^{-1} min^{-1}) and *β* desorption constant (kg mg^{-1}). The model constants were obtained from the linear q_t versus *ln t* plot.

Pseudo-second order model: $\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} t$

where q_e and q_t are the sorption capacity of NH_4^+ at equilibrium and at a time *t2*, respectively, *k* is the rate constant (1 min^{-1}) for pseudo-second order sorption. The linear plot of t/q_t versus *t* gives a slope of $1/q_e$ and an intercept of $1/kq_e^2$ (l h^{-1}).

The appropriateness of the sorption kinetics models was tested with the regression analysis as described for Freundlich and Langmuir models.

Desorption

In order to determine the desorption ratio of the adsorbed NH_4^+, 1 M neutral KCl solution was used to extract plant available NH_4^+. The desorption ratio (DR) at different initial concentrations was calculated from the equation below:

$$\mathrm{DR}(\%) = \frac{Si - Sides}{Si} x100$$

where *Sides* is the amount of NH_4^+ extracted by molar KCl solution. By this way it was possible to extract some information about the sorption mechanism of NH_4^+ as a function of particle size and initial NH_4^+ concentration.

Results and Discussion

Sorption Parameters

The effect of particle size on the Langmuir model parameters were given in Table 2. Rota zeolite did not respond to particle size differences whereas coarse Gördes zeolite had a sorption maxima significantly lower. Fine grains of Gördes zeolite showed the same sorption maxima as Rota zeolite. Particle-size dependency of the sorption process can be explained by the porous structure and continuity of the sorbent. In this respect Gördes zeolite having lower porosity responded to reduced particle size. The obtained maximum sorption values were highly similar to those (11000- 17300 mg NH_4^+ kg^{-1}) reported by Lin et al. (2014). Liu and Lao (2001), Hedstrom and Amofah (2008), Higarashi et al. (2008) found that the maximum adsorption values was inversely related with the particle size as in Gördes zeolite. The maximum adsorption values reported are between 14350-17810 mg N kg^{-1} and are very similar to those found in this study. Ashrafizadeh et al. (2008) using the 50 mg N L^{-1} solution in the column study have determined the maximum adsorption capacity of 17800 mg NH_4^+ kg^{-1} in Iranian clinoptilolite. Continuous flow-through column tests have resulted in much higher than these values (48300 mg NH_4^+ kg^{-1}) and relatively similar (15700-25000 mg NH_4^+ kg^{-1}) at maximum adsorption (Langwaldt, 2008). Indeed, Wang et al. (2006) noted that (11.2-115.6 mg NH_4^+ L^{-1} concentration limits have determined the maximum adsorption 1740 mg NH_4^+ kg^{-1}. In another study, Jha and Hayashi (2009) found ammonium retention capacity 0.89, 1.15 and 1.39 mmol g^{-1} (x18x1000 mg kg^{-1}), respectively for Japanese clinoptilolite-zeolite, natural, alkali-applied and milled zeolites which are close to the maximum adsorption of Gördes and Rota zeolites.

Table 2. The effect of particle size on the Langmuir isotherm parameters

Diameter (µm)	Gördes zeolite a	b	Max ads (mg kg^{-1})	R^2	Rota zeolite a	b	Max ads (mg kg^{-1})	R^2
< 53	0.0119	0.00006	16667	0.952	0.0056	0.00006	16667	0.950
53-106	0.0146	0.00006	16667	0.926	0.0061	0.00006	16667	0.959
106-250	0.0173	0.00006	16667	0.879	0.0067	0.00006	16667	0.987
250-500	0.0144	0.00007	14286	0.994	0.0077	0.00006	16667	0.948

Bonding energy cofficients, *a*, of the zeolite specimens were significantly different. It was nearly two times greater in Gördes zeolite. Despite there were some fluctuation in bonding energy coefficient for Gördes zeolite, Rota zeolite showed a consistent decrease upon particle size reduction. Such behaviour of Gördes zeolite may be related to condensed structure-induced and mineralogical heterogeneity (Table 1).

Freundlich isotherm parameters were given in Table 3. The Freundlich isotherms described better the sorption data regarding the determination coefficient (0.970-0.992) of the isotherms. Freundlich *n* values of GZ varied between 0.811-0.651 L kg^{-1} and generally increased NH_4^+ affinity of surfaces due to decrease in particle size but 53-106 µm. The *n* parameter of Freundlich isotherm in RZ varied between 0.789-0.738 L kg^{-1} and a steady increase was observed with decreasing particle size. This indicates that the added NH_4^+ ion is retained at larger ratio on the surfaces by a relatively reduced particle size. In other words, reducing the particle size increased the sorption sites on zeolite to the NH_4 ion. When the NH_4^+ affinity of the two zeolite sources is compared, that of the Gördes zeolite is generally higher.

Table 3. The effect of particle size on the Freundlich isotherm parameters

Diameter (µm)	Gördes zeolite Log Kf	n	R^2	Rota zeolite Log Kf	n	R^2
< 53	2.109	0.811	0.990	2.378	0.790	0.970
53-106	2.019	0.789	0.991	2.386	0.753	0.983
106-250	2.367	0.651	0.983	2.386	0.767	0.977
250-500	2.107	0.765	0.991	2.368	0.738	0.992

Log Kf values were between 2.019-2.367 L kg^{-1} in GZ whereas it ranged between 2.368-2.386 L kg^{-1} in RZ. The *Kf* values were significantly higher in Rota zeolite. Ivanova et al. (2010) studied the NH_4^+ adsorption of clinoptilolite-zeolite at 60-800 mg L^{-1} concentration limits and *1/n* (*n* in this study) value was determined to be 0.290. In the same study, they determined the *Log Kf* value to be 1.319. Both values are smaller than the coefficients determined in this study. Cyrus and Reddy (2011) in their study *Kf* value 222.7 and 302.2; *1 / n* or *n* value were found in the range of 0.844-0.725. The *n* values we found in this study are very close to the 0.81-0.65 range. When logarithms of *Kf* values in the study are taken, 2.348-2.480 values are obtained which are almost the same as the values obtained in our study. Erdoğan and Ülkü (2011), also used GZ in their adsorption study with lower concentration range, reported a *Kf* value of 1.79 and *1/n* (*n* in this study) value of 0.360. The particle size (0.6-2.8 mm) of the zeolites used by these researchers is much larger than the zeolites used in this study. Therefore, the differences between the coefficients obtained were considered to be due to the large particle size and lower initial loadings of NH_4^+.

Ammonium desorption

The amount of NH_4 ions adsorbed by zeolites extracted with molar KCl solution is given in Table 4. The desorbed amounts at "0" initial NH_4^+ concentration were the adsorbed amounts from the environment during the formation of the zeolite mineral. Therefore, these values were negative due to no additional sorption were took place.

Desorption rate showed significant differences as a function of initial concentration, particle size and zeolite types. In general, the amount of ammonium desorbed, regardless of particle size, increased continuously to an initial concentration up to 300-400 mg NH_4^+ L^{-1}. At higher concentrations, there were fluctuations generally above 49.8%. The amount of NH_4^+ that was desorbed to an initial concentration below 100 mg L^{-1} was generally smaller than 20%, indicating that the zeolite retained NH_4^+ at a high energy level. The increase in desorption rate with rising concentrations indicated that the NH_4^+ in this region was largely held in the form of exchangeable ions by electrostatic bonds. Since the sorption energy of an ion to a homogenous sorption site is inversely exponential to surface saturation (Bache and Williams, 1971), the occurrence of two distinct fluctuations implies that there may be two different type sorption sites or mechanisms.

Table 4. NH_4^+ desorption ratio as a function of initial ammonium concentration and particle size of the zeolites

Initial NH_4^+ conc (mg L^{-1})	Gördes zeolite				Rota zeolite			
	Particle size (µm)							
	< 53	53-106	106-250	250-500	< 53	53-106	106-250	250-500
0	-362	-150	-320	-345	-378	-308	-195	-201
50	9.2	9.0	21.5	8.4	7.9	11.1	13.0	11.6
100	9.5	12.6	20.3	19.3	18.3	18.1	14.2	12.7
200	54.7	53.4	53.5	61.3	54.9	55.0	57.3	57.2
300	62.9	62.6	59.7	61.1	63.5	57.1	59.3	54.3
400	49.8	60.5	53.7	53.6	55.3	62.2	55.8	58.9
500	69.8	63.1	63.7	66.2	62.8	59.7	61.2	63.0
600	63.1	59.4	68.9	65.4	64.6	61.0	67.7	64.2

Sorption Kinetics

The result showed that the pseudo-second order model was better described the sorption kinetics of NH_4^+ on zeolite by considering the R^2 of the models (Table 5). Plot of measured sorption data at 300 mg L^{-1} initial concentration as representative vs. reaction time (Figure 1) indicated that there are a large mounts readily adsorption of NH_4^+ on surface and following a diffusion controlled slow adsorption. In fact, this nature of the adsorption process can be well described by the second-order model that showed determination coefficient above 0.998. It is similarly found that the pseudo-second order model well confirmed the experimental data (Wen et al., 2006; Zhao et al., 2013; Temel and Kuleyin, 2016).

Table 5. The parameters of pseudo-second order and Elovich models for ammonium adsorption on zeolite samples

		Pseudo-second order model				Elovich model		
	Initial NH_4^+ concentration	Particle size	qe (mg kg^{-1})	k (kg mg^{-1} dak^{-1})	R^2	q (mg kg^{-1})	β (L dak^{-1})	R^2
Gördes Zeolite	50 mg L^{-1}	Ø<53 µm	782.3	0.187	1.000	561	32.7	0.965
		53<Ø<106 µm	854.8	0.072	0.998	540	42.7	0.973
		106<Ø<250 µm	764.0	0.117	0.999	543	31.0	0.956
		250<Ø<500 µm	778.9	0.081	0.998	545	30.7	0.972
	300 mg L^{-1}	Ø<53 µm	4565	0.236	1.000	3680	126.6	0.965
		53<Ø<106 µm	4460	0.269	1.000	3664	116.8	0.949
		106<Ø<250 µm	4260	0.180	0.999	3427	166.6	0.973
		250<Ø<500 µm	4274	0.258	1.000	3479	116.4	0.948
	600 mg L^{-1}	Ø<53 µm	8375	0.198	0.999	6637	250.7	0.961
		53<Ø<106 µm	7901	0.335	1.000	6709	177.7	0.906
		106<Ø<250 µm	7401	0.412	1.000	6539	127.7	0.913
		250<Ø<500 µm	7319	0.417	1.000	6476	122.9	0.976
Rota zeolite	50 mg L^{-1}	Ø<53 µm	860.0	0.218	0.999	697	23.63	0.936
		53<Ø<106 µm	875.0	0.172	0.999	656	32.01	0.951
		106<Ø<250 µm	882.0	0.153	0.999	671	30.14	0.906
		250<Ø<500 µm	871.0	0.219	0.999	715	22.37	0.974
	300 mg L^{-1}	Ø<53 µm	5210	0.194	0.999	4261	131	0.986
		53<Ø<106 µm	5216	0.229	0.999	4405	114.6	0.972
		106<Ø<250 µm	5158	0.169	0.999	4291	113.0	0.985
		250<Ø<500 µm	4974	0.242	0.999	4203	108.8	0.983
	600 mg L^{-1}	Ø<53 µm	9597	0.247	0.999	7919	242	0.951
		53<Ø<106 µm	9423	0.366	1.000	7884	230	0.938
		106<Ø<250 µm	9083	0.383	1.000	7913	171	0.957
		250<Ø<500 µm	8951	0.223	0.999	7597	189	0.978

The results calculated by pseudo-second order model revealed that *qe* parameter is highly related to initial NH_4^+ concentration and to a lesser extent, particle size for an initial NH_4^+ concentration in question. The respective *qe* parameter ranges of GZ and RZ were 764-854.8 and 860-882 mg kg^{-1} for 50 mg NH_4^+ L^{-1}, 4260-4565 and 4974-5216 mg kg^{-1} for 300 mg NH_4^+ L^{-1} and 7319-8375 and 8951 and 9597 mg kg^{-1} for 600 mg NH_4^+ L^{-1} initial concentrations. The capacity sequence was always in favour of RZ regardless to particle size. The highest capacity were found in 53<Ø<106 µm particle size for GZ and Ø<53 µm for RZ at initial concentration of 50 mg NH_4^+ L^{-1}. In general the highest capacity were always observed for the smallest particle sizes. The separation was even more evident at 600 mg NH_4^+ L^{-1} initial concentration. However, the difference between the coarse and the fine particles was always larger in GZ. This behaviour may be attributed to the smaller porosity of GZ. In contrast, the gap between different particle sizes of RZ was rather negligible at low initial concentration and became apparent as the initial concentration increased.

Elovich model was able to describe the experimental data reasonably well with R^2 values ranging from 0.906-0.985 (Table 5). Since this model is marginal at very low and very high surface saturations, there may be some limitation to use it despite its ability to describe a number of different processes. The estimated model parameters for NH_4^+ sorption by the natural zeolites were found to be dependent on the zeolite type, initial concentration and, to a lesser extent, particle size. In general, the higher *q* was observed for the smaller particle sizes that can indicate enhancement in the reaction rate (Chien and Clayton, 1980; Kithome et al., 1998). However, the *β* parameter did not show any particle size-dependent trend. Rota zeolite had higher *q* and lower *β* values, therefore, it can be said that RZ could be superior over GZ in terms of reaction rate.

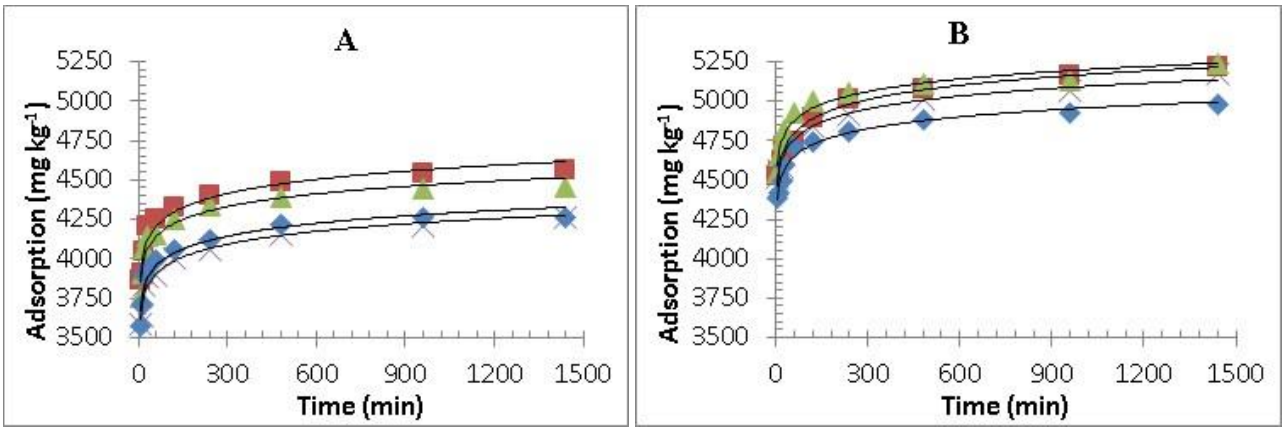

Figure 1. Adsorption kinetics of ammonium at 300 mg L^{-1} initial concentration. A: Gördes and B: Rota zeolite. ■ Ø<53, ▲ 53<Ø<106, ♦ 106<Ø<250, and x 250<Ø<500 µm.

Conclusions

Appropriateness of adsorption models, desorption and adsorption kinetics of NH_4^+ on two natural Turkish clinoptilolite-zeolites with different particle sizes were compared in this study. Adsorption of NH_4^+ on zeolites can be well described by both Langmuir and Freundlich models. The sorption maxima of the zeolite can be particle size dependent as its porosity low. Zeolite having well-structured porous nature can be used in larger particle size to scavenge NH_4^+ from the polluted water sources, but initial sorption rate can be improved by particle size reduction. Alternatively, the nature of NH_4^+ sorption and desorption may enable to use zeolite as NH_4^+ carrier fertilizer for maintaining fertility and protecting environment from nitrogen pollution in especially acid soils.

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Author contributions

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Conflict of interest

The authors declare that there are no conflict of interest regarding the project and manuscript.

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