

AMMONIUM ADSORPTION ON NATURAL ZEOLITE (CLINOPTILOLITE): ADSORPTION ISOTHERMS AND KINETICS MODELING

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A batch sorption process for removal of ammonium ions from aqueous solution using natural zeolite was studied. Three different particle sizes of zeolite (1-2 mm, 2-4 mm and 4-10 mm) were used in the experiments. Sorption of ammonium ions on natural zeolite were carried out at 298 K with the initial concentrations of ammonium in the range of 1000 – 7000 mg $\text{NH}_4^+\text{-N}/\text{dm}^3$. Equilibrium data were fitted by Freundlich and Langmuir isotherm and sorption kinetic data by pseudo-first and second order. The parameters were estimated by linear and non-linear method. Results show that non-linear method may be superior way to compute the parameters. The Langmuir isotherm model fitted better the experimental data with a maximum monolayer adsorption capacity of 58.36 mg $\text{NH}_4^+\text{-N}/\text{g}$ (1-2 mm), 49.02 mg $\text{NH}_4^+\text{-N}/\text{g}$ (2-4 mm) and 46.46 mg $\text{NH}_4^+\text{-N}/\text{g}$ (4-10 mm), respectively. Also, the pseudo-second-order kinetic model was the best applicable model to describe the sorption kinetics. The obtained results suggest that the natural zeolite is a good adsorbent for removal of ammonium ions from aqueous solution and that ion exchange increased with decreasing of particle sizes of natural zeolite.

Key words: ammonium ions, natural zeolite, sorption isotherms, linear and non-linear regression.

Adsorpcija amonijevih iona na prirodni zeolit (clinoptilolite): Adsorpcijske izoterme i kinetičko modeliranje.

U ovom radu ispitivano je uklanjanje amonijevih iona iz vodene otopine adsorpcijom na prirodni zeolit. Korištene su tri različite veličine čestica zeolita (1-2 mm, 2-4 mm i 4-10 mm). Sorpcija amonijevih iona na zeolit provedena je pri 298 K s početnim koncentracijama amonijevih iona od 1000 - 7000 mg $\text{NH}_4^+\text{-N}/\text{dm}^3$. Eksperimentalni rezultati su prikazani adsorpcijskim modelima, Langmuir-ovom i Freundlich-ovom izotermom i kinetičkim modelima, pseudo-prvi i pseudo-drugi red. Parametri su procijenjeni linearnom i nelinearnom regresijom. Nelinearna regresija bolje procjenjuje parametre. Langmuir-ova adsorpcijska izoterma daje bolje slaganje s eksperimentalnim rezultatima te kapacitet zeolita iznosi 58.36 mg $\text{NH}_4^+\text{-N}/\text{g}$ (1-2 mm), 49.02 mg $\text{NH}_4^+\text{-N}/\text{g}$ (2-4 mm), odnosno, 46.46 mg $\text{NH}_4^+\text{-N}/\text{g}$ (4-10 mm). Također, pseudo-drugi red bolje opisuje kinetiku sorpcije. Iz dobivenih rezultata, vidljivo je da je zeolit dobar adsorbens za uklanjanje amonijevih iona iz vodene otopine i da ionska izmjena raste sa smanjenjem veličine čestica zeolita.

Ključne riječi: amonijevi ioni, prirodni zeolit, sorpcijske izoterme, linearna i nelinearna regresija.

INTRODUCTION

Nowadays, the presence of nitrogen excess in the environment has caused eutrophication of lakes and rivers all over the world [1]. Nutrient compounds such as ammoniacal nitrogen ($\text{NH}_4\text{-N}$) which is a

colorless, toxic, odorous and corrosive gas [2], are often present in communal and some industrial wastewaters [1], leachates and condensates that may evolve during composting process [3,4]. Higher

concentration of ammonium may cause a sharp decrease of dissolved oxygen in natural waters and toxicity to aquatic organisms [5]. Hence, removing ammonium from wastewater is of great importance in nitrogen pollution control.

The traditional methods for ammonium removal from waste streams are based on physicochemical and biological treatments. Nowadays, ion exchange and adsorption are more interesting as possible treatment methods [6]. The removal of the ammonium ions from aqueous solutions through adsorption on natural zeolites (clinoptilolite) is found to be very promising [7]. Natural zeolites are aluminum silicate minerals with high cation exchange capacities (CECs) and high selective properties [6].

Inside the framework structure of zeolite, alkali or alkaline-earth cations are reversibly fixed in the cavities and can easily be exchanged by surrounding positive ions

like Na^+ , K^+ , Ca^{2+} , Mg^{2+} [5,8]. In contrast to the aluminium and silicone structure atoms, which are mutually bound by chemical (covalent) bonds over common oxygen atoms, cations are bound with the aluminosilicate structure mainly by weaker electrostatic bonds, which cause their mobility and capability of being exchanged with solution cations [9].

Ion exchange capacity, selectivity, particle size of zeolite, pH value and temperature of aqueous solution are important factors for adsorption of ammonium ions on zeolite [6].

The aim of this study was to investigate the adsorption potential of different particle sizes of zeolite for the removal of ammonium ions from aqueous solution. Adsorption isotherms and kinetics were investigated and different adsorption isotherm models were used to evaluate the experimental data by linear and non-linear method.

MATERIALS AND METHODS

Materials

The standard solution used in this study was ammonium sulfate p.a. (Kemika, Croatia). The zeolite (clinoptilolite) used in the experiments was from the Krapina region, Croatia. It was crushed in laboratory jaws crusher (Matest, A092 TE, Italy) and sieved to particle size fractions between 1

and 10 mm (SIEVE-SHAKER, Model RA-86-1, WS Tyler, SAD). Zeolite was washed with demineralized water to remove the particles adhered to surface, and dried at 378 K for 2 hours. Adsorption experiments were carried out using different sizes of the zeolite, 1-2 mm, 2-4 mm and 4-10 mm.

Adsorption studies

Adsorption experiments were carried out by adding 0.5 g of zeolite of different particle sizes into 100 cm³ Erlenmeyer flasks containing 50 cm³ of different initial concentrations (1000-7000 mg NH_4^+ -N/dm³) of ammonium solution. All flasks were shaken at 200 rpm for 24 hours at 298 K. After filtration (membrane pore size 0.45

µm, Sartorius, Germany) the concentrations of ammonium ions in aqueous solution were determined spectrophotometrically (Spectrophotometer DR/2400, Hach at USA) at $\lambda = 680$ nm [10]. Measured concentrations are expressed as mg NH_4^+ -N/dm³. The adsorption capacity at equilibrium q_e (mg

$\text{NH}_4^+\text{-N/g}$ was determined by using following equation:

$$q_e = \frac{(\gamma_o - \gamma_e) \cdot V}{m} \quad (1)$$

where γ_o and γ_e represent the initial and equilibrium concentration of ammonium ion in aqueous solution ($\text{mg NH}_4^+\text{-N/dm}^3$); V is

Batch kinetics studies

Kinetic experiments were identical to those of equilibrium tests. The aqueous samples were withdrawn at preset time intervals and the concentrations of ammonium ions were determined spectrophotometrically [10]. The amount of sorption at time t , q_t ($\text{mg NH}_4^+\text{-N/g}$), was calculated by expression:

the volume of the ammonium solution (dm^3) and m is the amount of adsorbent (g).

The removal efficiency (%) of zeolite can be calculated as follows [11]:

$$\text{Removal percentage} = \frac{\gamma_o - \gamma_e}{\gamma_o} \cdot 100 \quad (2)$$

$$q_t = \frac{(\gamma_o - \gamma_t) \cdot V}{m} \quad (3)$$

where γ_t ($\text{mg NH}_4^+\text{-N/dm}^3$) is the liquid phase concentration of ammonium ions at different time.

RESULTS AND DISCUSSION

Adsorption isotherm

Adsorption isotherms are basic requirements for the design of sorption system [12]. These data provide information about the capacity of the adsorbent or the amount required for removing a unit mass of pollutant under the system conditions.

Different sizes of zeolite were used as adsorbent to determine the adsorption capacity of ammonium ions, Fig.1. From Figs.1 and 2 it can be seen that adsorption capacity and removal efficiency rises with decrease in particle size of zeolite.

This is because the smaller the particle size the greater the specific surface area, which promotes external surface

adsorption, and implies that the cations in zeolite of smaller particle size are exchanged much more easily with those in aqueous solution [5,11].

Also, Fig.1 shows that the ammonium adsorption capacity of zeolite increased with the increase of initial ammonium concentration in aqueous solutions, indicating that plenty of readily accessible sites are available at the start of adsorption.

After equilibration, when the adsorbent becomes saturated, a plateau is reached indicating that no more sites are available for further adsorption.

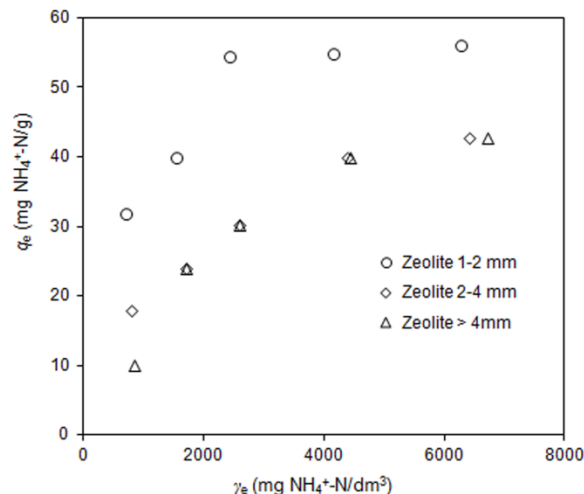


Figure 1. Adsorption isotherms of ammonium adsorption on different particle sizes of zeolite (1-2 mm, 2-4 mm and 4-10 mm)

Slika 1. Adsorpcijske izoterme adsorpcije amonijevih iona na različite veličine čestica zeolita (1-2 mm, 2-4 mm and 4-10 mm)

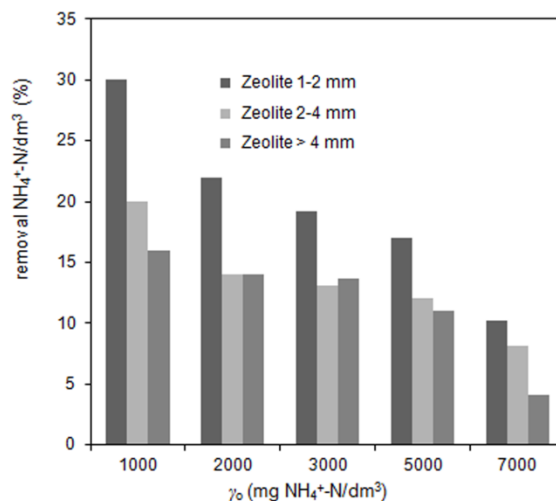


Figure 2. Effect of particle sizes on the removal of NH₄⁺ ion at different initial concentrations

Slika 2. Utjecaj veličine čestica zeolita na uklanjanje NH₄⁺ iona pri različitim početnim koncentracijama

The ion-exchange isotherms characterize the equilibrium relationships between the amounts of exchanged ion by zeolite and its equilibrium concentration in solution [11,13]. To characterize the exchange equilibrium of NH₄⁺ ions by zeolite, the Freundlich and Langmuir models

in the concentration range of 1000 to 7000 mg NH₄⁺-N/dm³ were used.

The Freundlich isotherm is an empirical equation used to describe multilayer adsorption with interaction between adsorbed ions [14]. The Freundlich equation is expressed as [13, 15]:

$$q_e = K_F \cdot \gamma_e^{\frac{1}{n}} \quad (4)$$

where K_F (an indicator of adsorption capacity) and $1/n$ (is the adsorption intensity) are Freundlich constants. The dimension $1/n$ gives an indication of the favorability of adsorption and values $n > 1$ represent favorable adsorption conditions [11]. Equation (4) may also be written in the logarithmic form as

$$\ln q_e = \ln K_F + \frac{1}{n} \cdot \ln \gamma_e \quad (5)$$

where values of K_F and n are calculated from the intercept and slope of the plot.

The Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogenous adsorbent surface. A basic assumption is that all adsorption sites are equivalent and adsorption on active sites is independent of whether the adjacent is occupied [12]. The Langmuir adsorption model can be expressed as [13,16]:

$$q_e = \frac{q_o \cdot b \cdot \gamma_e}{(1 + b \cdot \gamma_e)} \quad (6)$$

and linearized equation:

$$\frac{\gamma_e}{q_e} = \frac{1}{bK_L} + \frac{1}{b} \cdot \gamma_e \quad (7)$$

where q_e is the amount of pollutant adsorbed on the sorbent at equilibrium (mg NH_4^+ -N/g), K_L is the Langmuir adsorption constant related to the energy of adsorption (dm^3/mg) and b is the mono-layer adsorption capacity of adsorbent (mg NH_4^+ -N/g).

Therefore, a plot of γ_e/q_e versus γ_e gives a straight line of slope $1/b$ and intercept $1/(b \cdot K_L)$.

Adsorption of NH_4^+ by zeolite can also be evaluated to see whether it is favorable by using a dimensionless parameter or separation factor R_L that is given by [13,14]:

$$R_L = \frac{1}{(1 + K_L \cdot \gamma_o)} \quad (8)$$

where γ_o (mg NH_4^+ -N/ dm^3), is the highest initial concentration of adsorbate and K_L is Langmuir constant. The R_L parameter is considered as more reliable indicator of exchange. There are four probabilities for the R_L value: (i) for favorable exchange, $0 < R_L < 1$, (ii) for unfavorable exchange, $R_L > 1$, (iii) for linear exchange, $R_L = 1$, and (iv) for irreversible exchange, $R_L = 0$ [13]. The values of R_L in this study have been found to be 0.093, 0.169 and 0.3225, respectively, indicating that adsorption of ammonium ions on different sizes of zeolite is favorable.

The values of K_F , K_L , n , b and R^2 for different particle sizes of zeolite, are given in Table 1. Fig. 3 (a)–(c), shows the experimental equilibrium data for ammonia concentrations from 1000 to 7000 mg NH_4^+ -N/ dm^3 and the predicted theoretical Freundlich and Langmuir isotherm. The isotherm parameters were estimated by linear and non-linear regression analysis using Least Square method implemented in Scientist software (Fig. 4 and Table 1). It can be seen that parameters were better estimated by non-linear regression method.

Also, very high regression correlation coefficient, R^2 , was obtained by Langmuir model. The obtained results suggest that Langmuir model was suitable for describing the sorption equilibrium of ammonia ions by zeolite. The Langmuir parameter b shows that maximum NH_4^+ exchange increases with decreasing particle size.

Table 1. Langmuir and Freundlich isotherm constants and correlation coefficients for ammonium adsorption on different particle sizes of zeolite**Tablica 1.** Parametri Langmuirove i Freundlichove izoterme dobiveni adsorpcijom amonijevih iona na različite veličine čestica zeolita

Adsorbent	Particle size, mm	Isotherm	Parameters	Linear regression	Non-linear regression
				Value	Value
Zeolite	1-2	Langmuir	K_L (dm ³ /mg)	0.0014	0.0016
			b (mg NH ₄ -N/g)	63.69	58.36
			R^2	0.956	1.000
		Freundlich	K_F (mg NH ₄ -N/g)	0.0122	0.0416
			n	3.170	3.860
			R^2	0.949	1.000
	2-4	Langmuir	K_L (dm ³ /mg)	0.0007	0.0005
			b (mg NH ₄ -N/g)	56.95	49.02
			R^2	0.960	1.000
		Freundlich	K_F (mg NH ₄ -N/g)	0.9370	0.0123
			n	2.271	2.180
			R^2	0.987	1.000
4-10	Langmuir	K_L (dm ³ /mg)	0.0003	0.0003	
		b (mg NH ₄ -N/g)	52.12	46.46	
		R^2	0.968	1.000	
	Freundlich	K_F (mg NH ₄ -N/g)	0.1120	0.0136	
		n	1.435	1.710	
		R^2	0.968	1.000	

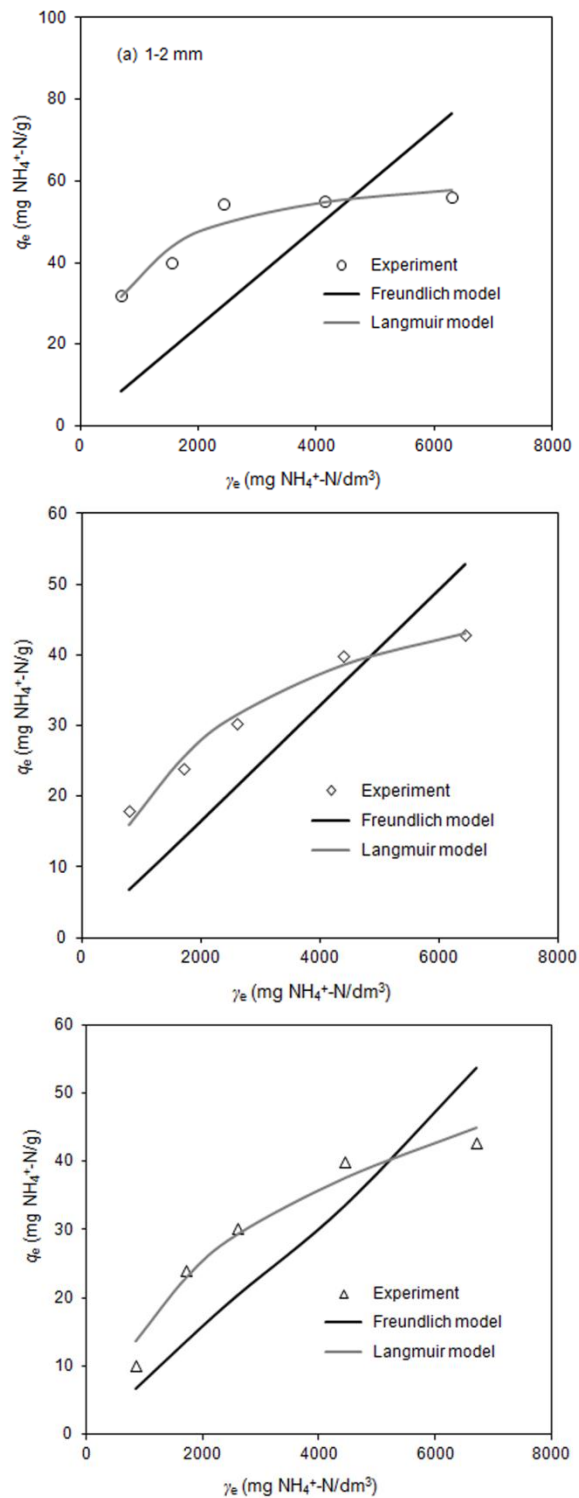


Figure 3. Isotherm plots for ammonia adsorption on different particle sizes of zeolite: (a) 1-2 mm, (b) 2-4 mm and (c) 4-10 mm

Slika 3. Langmuir-ova i Freundlich-ova adsorpcijska izoterma dobivena adsorpcijom amonijevih iona na različite veličine čestica zeolita: (a) 1-2 mm, (b) 2-4 mm and (c) 4-10 mm

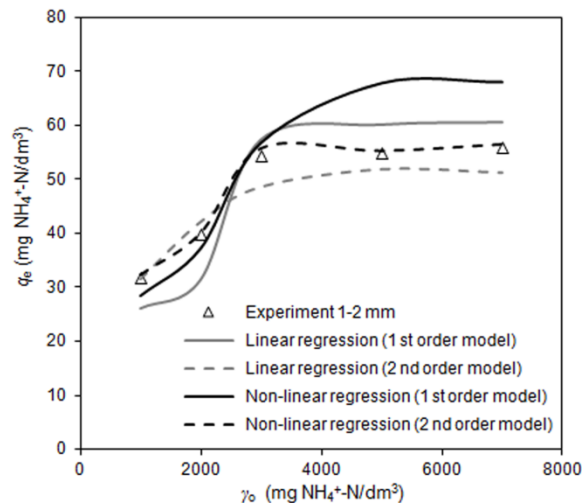


Figure 4. Estimated q_e values by linear and non-linear method

Slika 4. Linearna i nelinearna procjena q_e parametra

Sorption kinetics data

The adsorption kinetics was investigated for better understanding of the dynamics of adsorption of ammonium ions onto zeolite. Fig.5 shows the effect of the contact time on the removal of ammonium ions with different particle sizes of zeolite at the lowest and the highest concentration, 1000 and 7000 mg $\text{NH}_4^+\text{-N/dm}^3$.

The adsorption uptake was found to be fast and it increased with an increase of contact time. The faster initial adsorption rate may be due to the availability of the uncovered sorption sites of the adsorbent at the start of experiment. After 5 hours the adsorption process reached equilibrium (Fig.5) and the remaining vacant surface sites were difficult to be occupied due to the formation of repulsion among ammonia ions on the surface and in the bulk phase [16].

These phenomenon lead to a decrease of adsorption rate, what was well exhibited by plateau line after 7 h of sorption occurred (Fig.5) and it confirms that the process has reached the steady-state condition [16].

In order to predict the mechanism involved during the present sorption process

and the potential rate controlling such as chemical reaction processes, two kinetic models were used to fit the experimental data, pseudo-first order and pseudo-second order. The parameters were evaluated according linear and non-linear method. The kinetic parameters are helpful for the prediction of adsorption rate, which gives important information for designing and modeling the processes [17].

Results of present study suggest that non-linear method is better than linear method in determining kinetic parameters of a particular kinetic model (Fig.4, Table 2 and 4). This is mainly because transforming a non-linear kinetic model to a linearized form tends to alter the error distribution, and thus distort the parameters. Non-linear analysis conducted on the same abscissa and ordinate results in the same error distribution and is therefore a better way to obtain the kinetic parameters than linear method [18]. Also, it has been reported that it is not suitable to use the correlation coefficient of a linear regression analysis for comparing the best appropriate model [17,18].

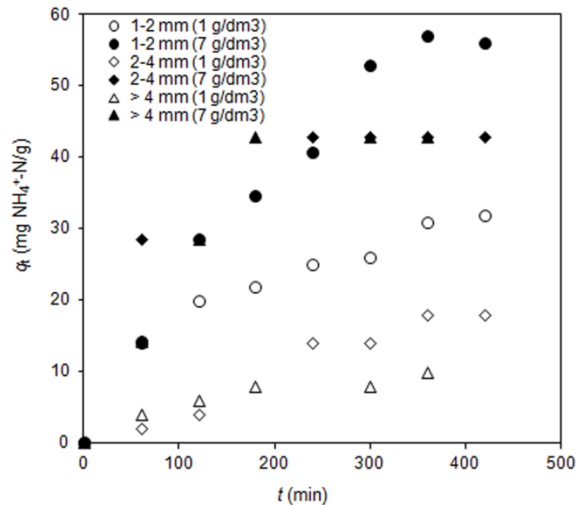


Figure 5. Effect of contact time on adsorption of ammonium on different particle sizes of zeolite
Slika 5. Utjecaj kontaktnog vremena na adsorpciju amonijevih iona na različite veličine čestica zeolita

The pseudo-first-order kinetic model known as the Lagergren equation, has been widely used to predict adsorption kinetics. A kinetic model of pseudo-first order is given in the form [17,18]:

$$\frac{dq_t}{dt} = k_f (q_e - q_t) \quad (9)$$

Integrating Eq. (9) for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, Eq. (9) may be rearranged for linearized data plotting as shown by Eq. (10):

$$\log(q_e - q_t) = \log_e - \frac{k_f}{2.303} \cdot t \quad (10)$$

where q_e and q_t (mg $\text{NH}_4^+\text{-N/g}$) are the amount of ammonium adsorbed at equilibrium and at time t and k_f is the pseudo-first-order rate constant (1/min). The slope and intercept of plots of $\log(q_e - q_t)$ versus t were used to determine the first-order constant k_f and equilibrium adsorption capacity q_e by linear regression (Table 2 and 3).

Table 2. Characteristic parameters of the different kinetic models (pseudo-first and second order) estimated by linear regression for ammonia sorption on different particle sizes of zeolite

Tablica 2. Procjena parametra linearnom regresijom za različite kinetičke modele (pseudo-prvi i drugi red) pri sorpciji amonijevih iona na različite veličine čestica zeolita

Zeolite		Pseudo-first order			Pseudo-second order			
γ_0 , mg NH ₄ ⁺ - N/dm ³	d_p , m	$q_{e, exp}$ mg NH ₄ ⁺ - N/g	k_1 , 1/min	$q_{e, calc}$ mg NH ₄ ⁺ - N/g	R^2	k_2 , g/mg min	$q_{e, calc}$ mg NH ₄ ⁺ - N/g	R^2
1000	1-2	31.89	0.00530	26.07	0.928	0.00060	31.65	0.948
2000		39.86	0.00645	31.46	0.909	0.00051	42.19	0.959
3000		54.42	0.00806	57.48	0.966	0.00030	48.63	0.927
5000		54.92	0.00737	60.24	0.893	0.00010	51.87	0.913
7000		56.02	0.00507	60.69	0.937	0.00015	51.25	0.952
1000	2-4	17.95	0.00599	21.26	0.917	0.00063	20.79	0.921
2000		23.96	0.00484	18.88	0.847	0.00073	25.06	0.920
3000		30.24	0.00507	22.44	0.864	0.00069	31.45	0.948
5000		39.95	0.00415	42.19	0.884	0.00015	49.75	0.902
7000		42.78	0.02648	85.90	0.939	0.00074	45.87	0.981
1000	4-10	9.98	0.02303	8.28	0.859	0.00136	11.00	0.934
2000		23.94	0.02441	52.47	0.931	0.00091	26.46	0.972
3000		30.25	0.02695	85.54	0.810	0.00041	35.21	0.941
5000		39.96	0.03201	98.15	0.759	0.00016	51.55	0.938
7000		42.80	0.02625	106.92	0.919	0.00029	50.51	0.917

Table 3. Characteristic parameters of the different kinetic models (pseudo-first and second order) estimated by non-linear regression for ammonia sorption on different particle sizes of zeolite

Tablica 3. Procjena parametra nelinearnom regresijom za različite kinetičke modele (pseudo-prvi i drugi red) pri sorpciji amonijevih iona na različite veličine čestica zeolita

Zeolite		Pseudo-first order			Pseudo-second order			
γ_o , mg NH ₄ ⁺ - N/dm ³	d_p , mm	$q_{e, exp}$ mg NH ₄ ⁺ - N/g	k_1 , 1/min	$q_{e, calc}$ mg NH ₄ ⁺ - N/g	R^2	k_2 , g/mg min	$q_{e, calc}$ mg NH ₄ ⁺ - N/g	R^2
1000	1-2	31.89	0.00986	28.56	0.964	0.00030	32.36	0.975
2000		39.86	0.01191	37.35	0.938	0.00034	40.15	0.960
3000		54.42	0.00757	56.87	0.984	0.00009	55.80	0.989
5000		54.92	0.00202	67.90	1.000	0.00005	55.34	1.000
7000		56.02	0.00310	68.10	0.999	0.00003	56.56	1.000
1000	2-4	17.95	0.00619	19.68	0.989	0.00051	18.94	0.995
2000		23.96	0.00098	22.46	0.962	0.00039	25.59	0.975
3000		30.24	0.00116	28.06	0.943	0.00042	33.26	0.961
5000		39.95	0.00390	53.19	0.999	0.00003	40.56	0.999
7000		42.78	0.01360	42.89	0.940	0.00001	43.70	0.941
1000	4-10	9.98	0.00787	10.06	0.982	0.00057	13.01	0.988
2000		23.94	0.01059	24.74	0.960	0.00038	26.12	0.971
3000		30.25	0.00743	32.52	0.985	0.00016	31.36	0.990
5000		39.96	0.00529	46.99	0.995	0.00006	41.42	0.997
7000		42.80	0.00849	59.48	0.980	0.00001	43.45	0.985

The pseudo-second-order model is based on the assumption that the rate-limiting step may be a chemical sorption involving forces through the sharing or exchange of electrons between adsorbent and adsorbate [14]. The pseudo-second-order kinetic model is given as [17]:

$$\frac{dq_t}{dt} = k_s(q_e - q_t)^2 \quad (11)$$

For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of equation (11) becomes:

$$q_t = \frac{t}{\frac{1}{k_s \cdot q_e^2} + \frac{t}{q_e}} \quad (12)$$

which has a linear form:

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e} \cdot t \quad (13)$$

where q_e and q_t (mg NH₄⁺-N/g) are the amount of ammonium adsorbed at equilibrium and at time t and k_s is the pseudo-second-order rate constant (g/mg min). Fig.6 shows the plots of q_t against t for the pseudo-second order model for sorption of ammonium onto natural zeolite.

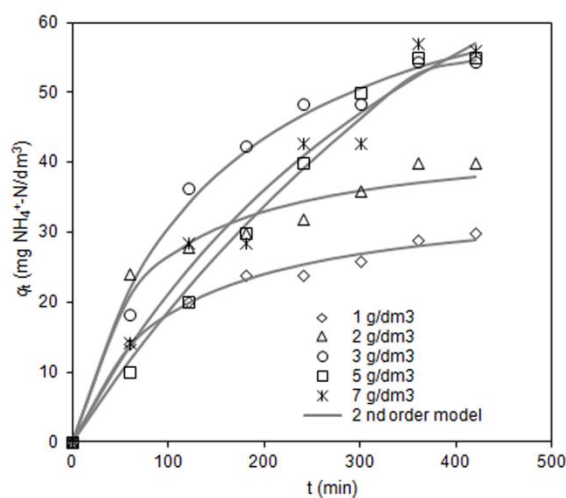


Figure 6. Pseudo-second-order kinetic model plots of ammonium adsorption on zeolite (1-2 mm)
Slika 6. Kinetički model pseudo-drugog reda adsorpcije amonijevih iona na zeolit (1-2 mm)

The best-fit model was selected based on both regression correlation coefficient (R^2) and the calculated q_e values. Low R^2 values and notable variances between the experimental and theoretical uptakes shown in Table 2 and 3 reveal clearly the poor fitting of pseudo-first-order model. Thus, the adsorption of ammonium ions on natural zeolite is not a first-order

reaction. Fitting kinetics parameters of adsorption of ammonium ions onto zeolite according to pseudo-second-order model (Eq.13) are tabulated in Tables 2 and 3. The results show that pseudo-second-order model fits the experimental data quite well, the R^2 values reach the unity and the experimental and theoretical uptakes are in good agreement (Fig.4).

This indicates that this model can be applied for the entire concentration range of adsorption process, suggesting that chemisorption might be the rate-limiting step that controlled the adsorption process of

ammonium on the zeolite [5]. Also, from Table 2 and 3 it can be seen that the pseudo-second-order rate constant (k_s) decreased with increased initial concentration.

CONCLUSION

The present work showed that natural zeolite, clinoptilolite, from Croatia can be used as an adsorbent for removal of ammonia ions from aqueous solutions. The ammonium ions adsorption was found to decrease with increasing particle size in range of 1-10 mm. The Langmuir model fitted well the experimental data with a maximum adsorption capacity of 58.36 mg

$\text{NH}_4^+\text{-N/g}$, 49.02 mg $\text{NH}_4^+\text{-N/g}$ and 46.46 mg $\text{NH}_4^+\text{-N/g}$ for particle sizes between 1-2 mm, 2-4 mm and 4-10 mm, respectively.

Kinetic studies suggest that ammonium adsorption on zeolite could be described more favorably by the pseudo-second order kinetic model than by pseudo-first order and the parameters are better estimated by non-linear method.

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