Scientific paper

Sorption Kinetic Studies of Ammonium from Aqueous Solution on Different Inorganic and Organic Media

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Abstract

In this study, the sorption of ammonium from aqueous solution onto activated carbon, natural zeolite, peat and potting soil was studied by performing batch kinetic sorption experiments. The activated carbon wasn't efficiently removing ammonium at concentrations higher than 50 mg L^{-1}. Sorption isotherms of ammonium on zeolite, peat and potting soil were determined at 25 °C and 200 rpm with the initial concentration of 50–7000 mg L^{-1}. Equilibrium data were fitted by Freundlich, Langmuir and Temkin isotherm and parameters were evaluated according these models. Langmuir model gives better fit to experimental data than Freundlich and Temkin models. Maximum adsorption capacities were for activated carbon 0.631 mg g^{-1}, zeolite 58 mg g^{-1}, peat 595 mg g^{-1} and for potting soil 575 mg g^{-1}. The equilibrium kinetic data were analyzed using adsorption kinetic models: the pseudo-first and second–order equations and were found to follow the pseudo-second-order kinetic model. A comparison between linear and non-linear regression method for estimating the adsorption and kinetics parameters was examined. The obtained results showed that non-linear method may be a better way to determine the kinetic parameters. Thermodynamic studies showed exothermic and endothermic nature of the adsorption of NH_4^+ on inorganic and organic adsorbents, respectively. From present results it can be seen that zeolite, peat and potting soil are good adsorbents for removal ammonium from aqueous solution.

Keywords: Adsorption of ammonium ions; Inorganic and organic adsorbents; Kinetics; Linear method; Non-linear method, Thermodynamic studies.

1. Introduction

Ammonia is a colorless, toxic, odorous and corrosive gas produced from several sources, wastewater treatment plants, in outlet gases from composting plants and fertilizer plants, chemical and manufacturing industries.[1] Ammonia is also found as ammonium ion (NH_4^+) in wastewaters,[2] leachate[3] and condensate evolved during composting process.[4] Excess ammonia-nitrogen can cause a health problem involving many living species including humans and animals. It also contributes to the eutrophication of lakes and rivers, depletion of dissolved oxygen and toxicity to aquatic organisms. Therefore, it is important to control emission of this compound for the protection of public health and environment.[5]

The traditional methods for ammonium removal from waste streams are based on physicochemical and biological treatments. Nowadays, ion exchange and adsorption become more interesting as possible treatment methods.[6] Adsorption is often referred to as passive uptake and physical-chemical binding of chemical species or ions to a solid surface.[7] Inorganic materials, natural zeolites (clinoptilolite) are the most important cation exchangers that exhibit high ion exchange capacity, selectivity and compatibility with the natural environment. It is found that zeolites are very promising for adsorption of ammonium ions from aqueous solutions. The advantages of zeolites are: wide spreading in nature, low cost, high selectivity towards the ammonium ions in the presence of other concurrent cations in the wastewaters.[8] Also, inorganic materials are inert to biological degradation. The use of organic materials for sorption of ammonium is adequate because of their high availability, low cost and the presence of complex microbial communities capable of degrading ammonium ions as pollutant.[9,10] Ammonium which is adsorbed on different organic materials can be used for agricultural purpose.

The aim of the study was to investigate the adsorption potential of selected inorganic and organic materials for the removal of ammonium 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. Also, the influence of pH value and temperature was investigated.

2. Materials and Methods

2. 1. Materials

The standard solution used in this study was ammonium sulfate p.a. (Kemika, Croatia). The inorganic materials used in the experiments were zeolite (clinoptilolite) from the Krapina region, Croatia and activated carbon – silcarbon K835, Germany. Farkaš et al. (2007) used the same natural zeolite for their experiments. Their results showed that the chemical composition of clinoptilolite is: SiO_2 (64.93%), Al_2O_3 (13.39%), Fe_2O_3 (2.07%), Na_2O (2.40%), K_2O (1.30%), CaO (2.00%), MgO (1.08%) and loss on ignition at 1000 °C was 9.63%. These adsorbents were washed with demineralized water to remove the particles adhered to surface, and dried at 105 °C for 2 hours. The organic materials which were used were peat and potting soil from Olaines Kudra, Latvia and Zrinjevac, Zagreb. They were only dried to calculate the moisture of samples. The dried zeolite was crushed with laboratory jaw crusher (Matest, A092 TE, Italy) and granulometric analysis was conducted on rotary sieve shaker (Sieve-Shaker Model RA-86-1, WS Tyler, SAD). Physical characteristics of selected adsorbents are presented in Table 1.

Table 1. Physical characteristics of sorbents.

	Zeolite	Activated carbon	Peat	Potting soil
pH value	6.7	9.3	4.7	6.5
Moisture, %	2.89	2.25	26.99	37.68
Particle size, mm	1.0 – 2.0	0.6 – 2.4	0.15–0.78	0.08–0.47

2. 2. Characterization of the Adsorbents

Fourier Transform InfraRed Spectroscopy – FTIR (Perkin Elmer, USA) analysis was performed in order to establish the structural changes during the modification of activated carbon, zeolite, potting soil and peat with ammonium ions. Pressed pellets were prepared by grinding the powder specimens with spectroscopic grade KBr for FTIR spectra test. The spectra were recorded from 4000–450 cm^{-1}.

2. 3. Adsorption Studies

Adsorption experiments were carried out by adding 0.5 g of different sorbents, zeolite, activated carbon, peat and potting soil into 100 mL Erlenmeyer flasks containing 50 mL of different initial concentrations (50–7000 mg L^{-1}) of ammonium solution. The sorption experiments were conducted 24 hours and the samples were taken every one hour. All flasks were shaken at 200 rpm. After filtration (membrane pore size 0.45 μm, Sartorius, Germany) the concentrations of ammonium ions in aqueous solution were determined spectrophotometricaly (Spectrophotometer DR/2400, Hach at USA) at λ = 680 nm, using sodium citrate, sodium nitroprussiate dihydrate and sodium-salicylate.[11] The linearity range was from 0 to 0.5 mg N L^{-1} and the detection range was to 0.5 mg N L^{-1}. The solutions were acidified with 1:3 H_2SO_4 to preserve them for further experiments. Concentrations of NH_4^+ were expressed as mg N L^{-1}.

The amount of ammonium ion adsorbed q_e (mg g^{-1}) was determined by using following equation:

$$q_e = \frac{(C_o - C_e)\cdot V}{m} \tag{1}$$

where C_o and C_e represent the initial and equilibrium concentration of ammonium ion (mg L^{-1}); V is the volume of the ammonium ion in solution (L) and m is the mass of dry adsorbent (g).

The ammonium removal percentage can be calculated as follows:

$$\text{removal percentage} = \frac{C_o - C_e}{C_o}\cdot 100 \tag{2}$$

2. 4. Batch Kinetics Studies

Kinetic experiments were identical to those of equilibrium tests. The aqueous samples were taken at preset time intervals and the concentrations of ammonium ions were determined spectrophotometricaly.[11] The amount of sorption at time t, q_t (mg g^{-1}), was calculated by expression:

$$q_t = \frac{(C_o - C_t)\cdot V}{m} \tag{3}$$

where C_t (mg L^{-1}) is the liquid phase concentrations of ammonium ions at different time.

2. 5. Effect of pH

The effect of pH solution (pH = 2–9) on sorption of ammonium ions on activated carbon, zeolite, potting soil and peat was determined by agitating 0.5 g of different adsorbents and 50 mL of ammonium sulphate solution (C_o = 100 mg L^{-1}). Agitation was provided for 4 h contact time which was sufficient to reach equilibrium with a constant agitation speed of 200 rpm. The pH value was adjusted by adding a few drops of diluted NaOH or HCl.

3. Results and Discussion

3. 1. Characterization of the Adsorbents

The particle size of inorganic and organic materials which were used in this study were in the range with other proposed in literature.[5,8,12,13]

To establish if the structure of activated carbon, zeolite, peat and potting soil is modified during adsorption of ammonium ions, FTIR analysis was performed (Figure 1a-d). The number of adsorption peaks in the spectra indicated the complex nature of the analyzed samples. Figure 1a shows that the FTIR spectra of activated carbon were not significantly changed after adsorption of ammonium ions. The peak localized at 1047.13 cm^{-1} in FTIR spectra of zeolite corresponds to the vibration of the bands connected with the internal Si-O(Si) and Si-O(Al) vibrations in tetrahedral or alumino- and silico-oxygen bridges.[14] The changes in the FTIR spectra of zeolite indicated a little shift of these band positions and changes in their intensity. The broad and strong band ranging from 3700 to 3000 cm^{-1} might attribute to –OH stretching vibrations which are presented in FTIR spectra of all investigated adsorbents (Figure 1a-d). The peaks at 2919.94 and 1384.41 (Figure1c-d) are attributed to the symmetric and asymmetric C–H stretching vibration, and the band around 1615 cm^{-1} (potting soil, peat) is due to asymmetric and symmetric stretching vibrations of C=O.[15,16] The peaks ranging from 1200 to 950 cm^{-1} are due to C–O stretching. The wave numbers of potting soil (similar for peat) shifted from 3409.02, 1641.08, 1384.41 and 1035.55 cm^{-1} to 3382.34, 1634.80, 0 (peak disappeared) and 1046.79, respectively, after ammonium adsorption suggesting that hydroxyl, phenol and carboxyl groups might be the main active groups for ammonium adsorption on potting soil and peat.[15,16]

3. 2. Effect of Solution pH on Aammonium Adsorption

The removal of NH_4^+ from aqueous solution using different sorbents was studied at pH values 2–9 and the data obtained were given in Figure 2. The adsorption effi-

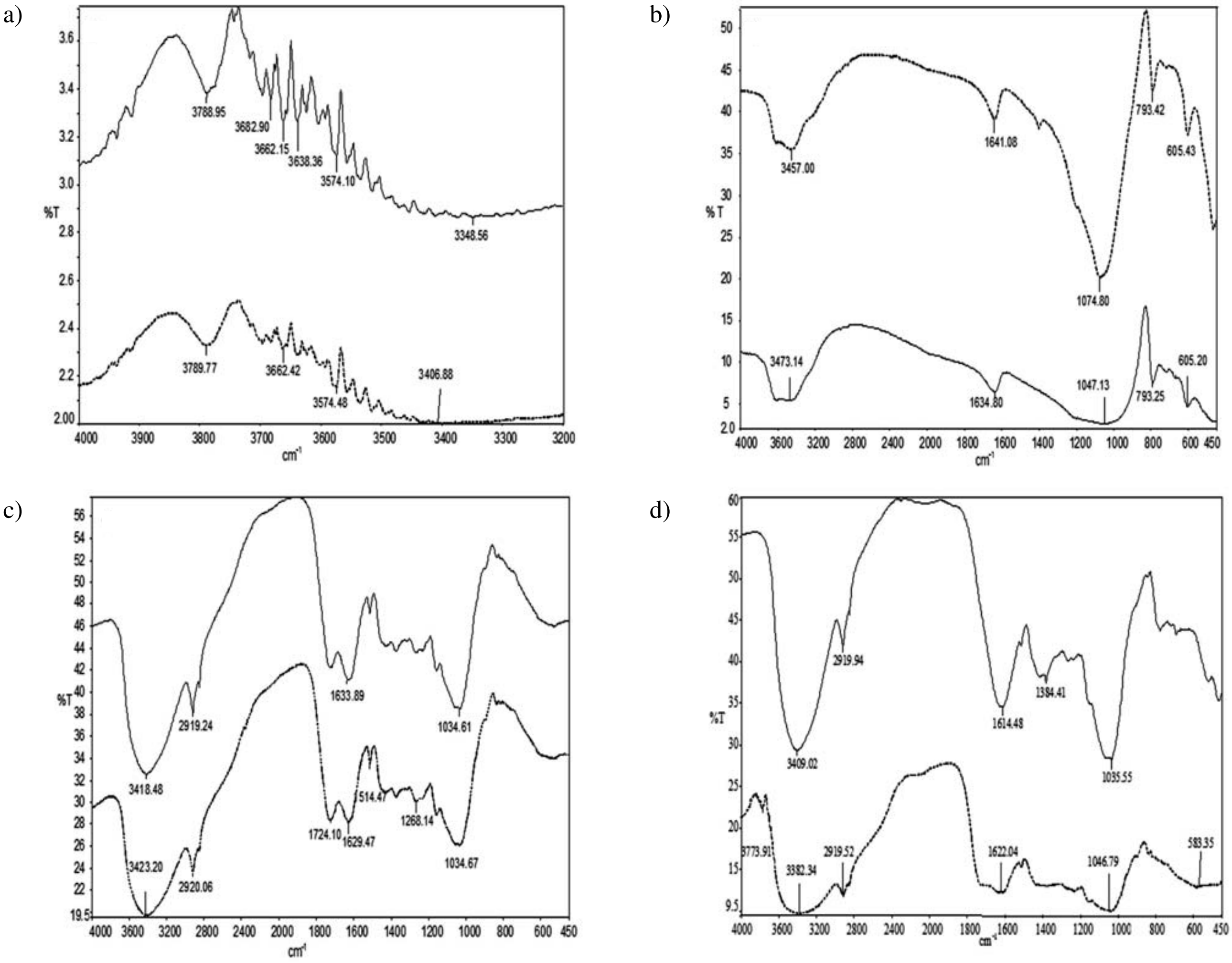

Figure 1: FTIR spectra of a) activated carbon, b) zeolite, c) peat and d) potting soil before (–) and after ammonium adsorption (---).

ciency of zeolite, potting soil and peat, increased by raising the pH from 4 to 8, and reached a maximum value at pH 7, and then it decreased at pH 9. The decrease in the NH_4^+ removal efficiency after pH 8 may be due to the conversion of ammonium ions (NH_4^+) to ammonia gas (NH_3).[6,17,18] Also, at low pH (below 4) the adsorption efficiency decreased due to the competition of H^+ and NH_4^+ ions for the active sites on the adsorbent surface.[6,19]

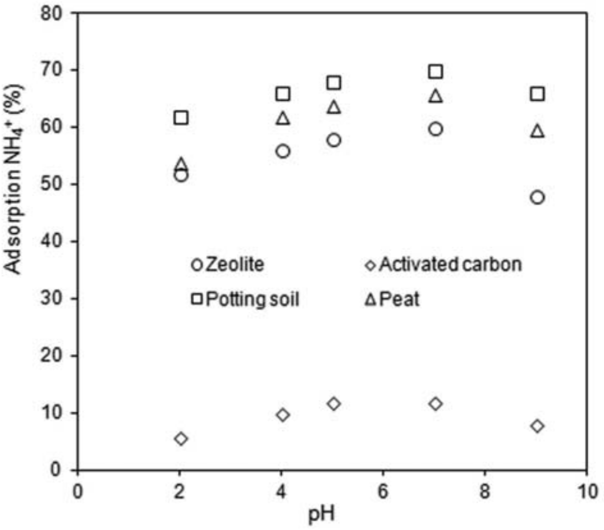

Figure 2: The effect of pH on adsorption of NH_4^+ using inorganic and organic adsorbents (activated carbon, zeolite, peat and potting soil) ($C_o(NH_4^+)$ = 100 mg L^{-1}; $m_{adsorbent}$ = 0.5 g; V = 50 mL; t = 240 min; T = 25 °C).

3. 3. Adsorption Isotherm

Adsorption isotherms describe how pollutants interact with adsorbent materials and so they are critical to optimize the use of adsorbents. In order to optimize the design of an adsorption system for removal of ammonium ions from aqueous solutions, it is important to establish the most appropriate correlation for the equilibrium curve (Figure 3). From Figure 3 it can be seen that the ammonium adsorption capacity of zeolite, peat and potting soil 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. The obtained results show that zeolite has lower adsorption capacity than potting soil and peat. Also, it can be seen from Figure 3 that the adsorption isotherm for activated carbon in concentration range from 50 to 7000 mg L^{-1} lies almost on the axis C_e. The adsorption capacity of activated carbon was calculated for concentration range from 5 to 100 mg L^{-1} (results are not shown). Adsorption capacities of adsorbents from present study were compared with other adsorbents reported in previous researches for ammonium removal and is compiled in Table 2. From Figure 4 it can be seen that removal percentage of ammonia is the highest for peat and potting soil. Zeolite has a high removal percentage at lower concentrations < 500 mg L^{-1} but as concentration of ammonium increases the removal percentage decreases. Activated carbon was not efficiently removing ammonium ions from aqueous solution.[5]

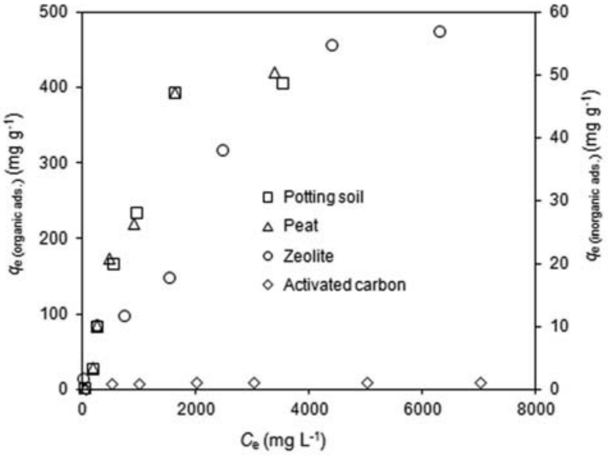

Figure 3: Adsorption isotherms of ammonium adsorption on inorganic (activated carbon and zeolite) and organic (potting soil and peat) materials (V = 50 mL, $m_{adsorbent}$ = 0.5 g, T = 25 °C and pH = 2.1).

Table 2. Comparison of adsorption capacity of different adsorbents for ammonium ions removal from water.

Adsorbent	Contact time (h)	Concentration range (mg L^{-1})	Particle size of adsorbent, mm	Adsorption capacity (mg g^{-1})	Reference
Activated carbon (AC)	2	35–280	0.70 – 1.25	10.25	[5]
Natural zeolite	5	60–800	1.25	9.22	[8]
Natural zeolite	4	1000–7000	1.0–2.0	58.00	Present study
Strawberry leaf powder	14	25–1000	0.30	6.05	[15]
Peat	10	0–0.8	–	1.59	[9]
Peat	5	1000–7000	0.15–0.78	595.00	Present study
Potting soil	5	1000–7000	0.08–0.47	575.00	Present study

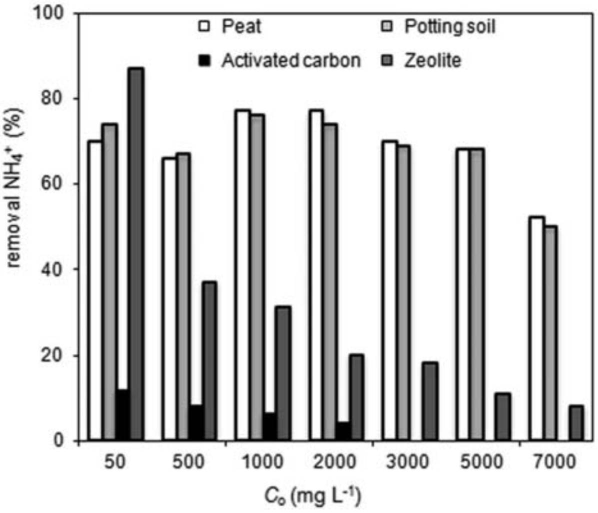

Figure 4: Percentage of removed NH_4^+ from aqueous solutions by sorption on different adsorbents.

The adsorption equilibrium data were analyzed using Freundlich, Langmuir and Temkin isotherm models in the concentration range of 1000 to 7000 mg L^{-1}. This concentration range was selected because the wider concentration range between 50 and 7000 mg L^{-1} did not give a good estimation of adsorption parameters.

The concentrations of ammonium ions between 50 to 1000 mg L^{-1} in solutions were less diluted than concentrations between 1000–7000 mg L^{-1} for spectrophotometrical measurements of ammonium ions and it resulted in analytical error. The error increases as the concentration is higher.

The Freundlich isotherm is an empirical equation used to describe multilayer adsorption with interaction between adsorbed ions.[20] The Freundlich equation is expressed as:[21]

$$q_e = K_F \cdot C_e^{\frac{1}{n}} \tag{4}$$

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.[16] Equation (4) may also be written in the logarithmic form as

$$\ln q_e = \ln K_F + \frac{1}{n} \cdot \ln C_e \tag{5}$$

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.[16,22] The Langmuir adsorption model can be expressed as:[23]

$$q_e = \frac{q_{\max} \cdot b \cdot}{(1 + b \cdot C_e)} \tag{6}$$

and linearized equation:

$$\frac{C_e}{q_e} = \frac{1}{b \cdot q_{\max}} + \frac{1}{q_{\max}} \cdot C_e \tag{7}$$

where q_e is the amount of pollutant adsorbed on the sorbent at equilibrium (mg g^{-1}), b is the Langmuir adsorption constant related to the energy of adsorption (L/mg) and $q_{\max}$ is the mono-layer adsorption capacity of adsorbent (mg g^{-1}). Therefore, a plot of C_e/q versus C_e gives a straight line of slope $1/q_{\max}$ and intercept $1/(b \cdot q_{\max})$. Adsorption of NH_4^+ by zeolite, peat and potting soil can also be evaluated to see whether it is favorable by using a separation factor R_L that is given by:[15]

$$R_L = \frac{1}{(1 + b \cdot C_o)} \tag{8}$$

where C_o (mg L^{-1}), is the highest initial concentration of adsorbate and b is Langmuir constant. If the value of R_L is higher than 1, adsorption is considered to be unfavorable but if it is between 0 and 1 it is favorable.[19] The values of R_L for zeolite, peat and potting soil in this study have been found to be 0.0820, 0.1369 and 0.1369, respectively, indicating that adsorption of ammonium ions on zeolite, peat and potting soil are favorable.

Temkin and Pyzhec[24] considered the effect of the adsorbate interaction on adsorption. They suggested that these interactions would influence the heat of adsorption of all the molecules in the layer and it would decrease linearly with coverage. The Temkin isotherm has been used in the following form, Eq. (9):

$$q_e = \frac{RT}{b}(\ln K_T + \ln C_e) = A + B \cdot \ln C_e \tag{9}$$

and linearized equation:

$$q_e = \frac{RT}{b}\ln A + \frac{RT}{b}\ln C_e \tag{10}$$

where

$$B = \frac{RT}{b} \tag{11}$$

The adsorption data can be analyzed according to Eq. (10). A plot of q_e versus ln *Ce* enables the determination of the constants *A* (K_t) and *B*. The constant *B* is related to the heat of adsorption and *A* (K_t) is Temkin equilibrium constant (L mg^{-1}).

The values of K_F, b, n, $q_{\max}$, A, B and R^2 for zeolite, peat and potting soil are given in Table 3. Figure 5 a–c, shows the experimental equilibrium data for ammonium concentrations from 1000 to 7000 mg L^{-1} and the predicted theoretical Freundlich, Langmuir and Temkin isotherm. The isotherm parameters were estimated by linear and non-linear regression analysis. The non-linear regression analysis was estimated using Least Square method

Table 3. Langmuir, Freundlich and Temkin isotherm constants and correlation coefficients for adsorption of ammonium on zeolite, peat and potting soil.

Method	**Isotherm**	**Parameters**		**Adsorbent**	
			Zeolite	**Peat**	**Potting soil**
Linear regression	Langmuir	b (L mg^{-1})	0.0014	0.0006	0.0006
		$q_{\max}$ (mg g^{-1})	63.69	714.29	714.29
		R^2	0.956	0.983	0.994
Non-linear regression		b (L mg^{-1})	0.0016	0.0009	0.0009
		$q_{\max}$ (mg g^{-1})	58.36	595.02	575.21
		R^2	1.000	1.000	1.000
Linear regression	Freundlich	K_F (mg g^{-1})	0.0122	0.2402	0.2719
		n	3.17	1.66	1.63
		R^2	0.949	0.931	0.924
Non-linear regression		K_F (mg g^{-1})	0.0416	0.2311	0.2424
		n	3.86	1.47	1.63
		R^2	1.000	1.000	1.000
Linear regression	Temkin	A (L mg^{-1})	0.0020	0.0095	0.0077
		B	23.41	133.88	132.65
		R^2	0.943	0.941	0.931
Non-linear regression		A (L mg^{-1})	0.0011	0.0062	0.0051
		B	10.10	97.86	95.61
		R^2	0.999	0.998	0.998

implemented in Scientist software. The correlation coefficients obtained from non-linear method for Langmuir, Freundlich and Temkin were identical. Thus, to estimate which model describes better the experimental data the regression coefficients of linear method were used. Based on correlation coefficients the highest R^2 was obtained by Langmuir model. Finally, it can be concluded that Langmuir model was suitable for describing the sorption equilibrium of ammonium ions by zeolite, potting soil and peat. The Langmuir parameter $q_{\max}$ shows that peat and potting soil have a much higher adsorption capacity than zeolite.

3. 4. Sorption Kinetics Data

The study of adsorption kinetics is very useful for understanding the mechanisms that are involved, dynamics of adsorption of ammonium ions onto zeolite, peat and potting soil and also for design of future facilities for adsorption on a large scale. Kinetics data for peat and potting soil were similar and because of that only results of peat were presented. Figure 6 shows the sorption kinetics of ammonium ions on the zeolite and peat at the lowest and the highest concentrations, 500 and 7000 mg L^{-1}. As can be seen, the sorption rate was quite fast at the initial stage and with time it gradually slowed down. The faster initial rate may be due to the availability of the uncovered sorption sites of the adsorbent at the start of experiment. More than 90% of the amount of ammonium adsorbed at equilibrium was reached in 4 hours.[18]

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. Results of present study suggest that non-linear method is better than linear method in determining kinetic parameters of a particular kinetic model (Table 4a and b). 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.[7,25] 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.[26] The pseudo-first-order kinetics model known as the Lagergern equation is one of the most widely used rate equation to describe the adsorption of an adsorbate from given liquid phase. A kinetic model, pseudo-first order is given in the form:[27]

$$\frac{dq_t}{dt} = k_f(q_e - q_t) \tag{12}$$

Integrating this for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, Eq. (12) may be rearranged for linearized data plotting as shown by Eq. (13):

$$\log(q_e - q_t) = \log_e - \frac{k_f}{2.303} \cdot t \tag{13}$$

where q_e and q_t (mg g^{-1}) are the amount of ammonium adsorbed at equilibrium and at time t and k_f is the pseudo-first-order rate constant (min^{-1}). The slope and intercept of plots of $\log(q_e–q_t)$ versus t were used to determine the

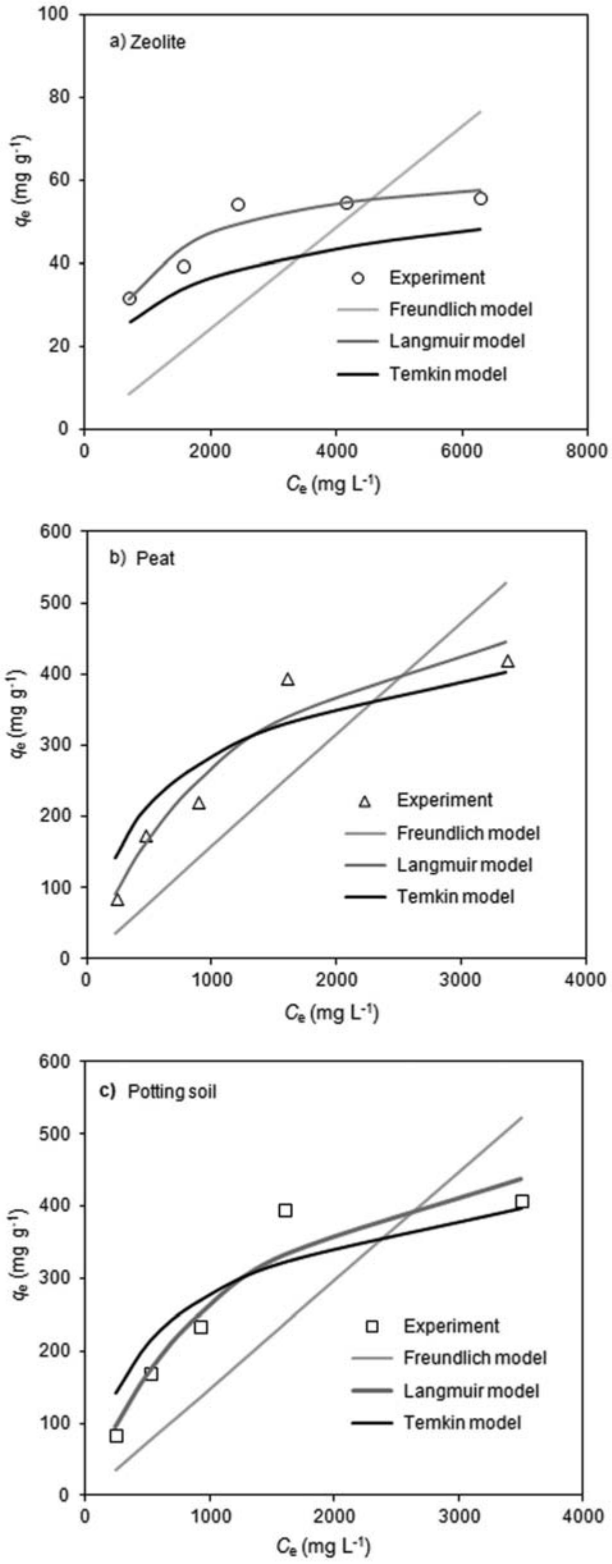

Figure 5: Isotherm plots for ammonia adsorption on a) zeolite, b) peat and c) potting soil.

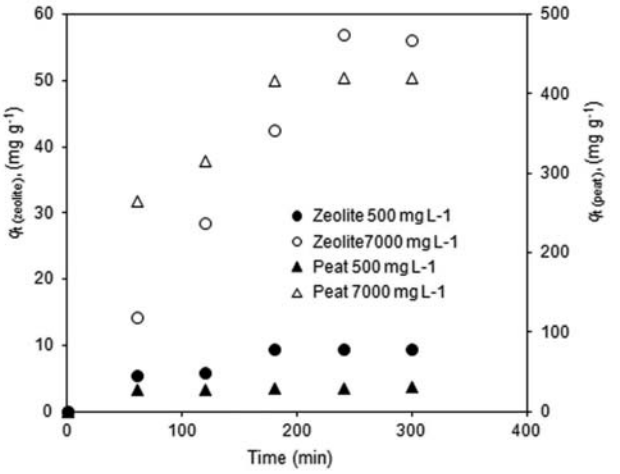

Figure 6: Effect of contact time on adsorption of ammonium on zeolite and peat (V = 50 mL, m $_{\text{adsorbents}}$ = 0.5 g, T = 25 °C and pH = 2.1).

first-order constant k_f and equilibrium adsorption capacity q_e by linear regression (Table 4a and b). From Figure 7 it can be seen that pseudo-first order does not fit well for the whole range of contact time and is generally applicable over the initial 20 to 30 minutes of the sorption process.[28]

The pseudo-second-order model is based on the assumption that the rate-limiting step may be a chemical sorption involving forces trough the sharing or exchange of electrons between adsorbent and adsorbate.[20] The pseudo-second-order kinetic model is given as:[28, 29, 30]

$$\frac{dq_t}{d_t} = k_s(q_e - q_t)^2 \tag{14}$$

For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of equation (15) becomes:

$$q_t = \frac{t}{\dfrac{1}{k_S \cdot q_e^{\,2}} + \dfrac{t}{q_e}} \tag{15}$$

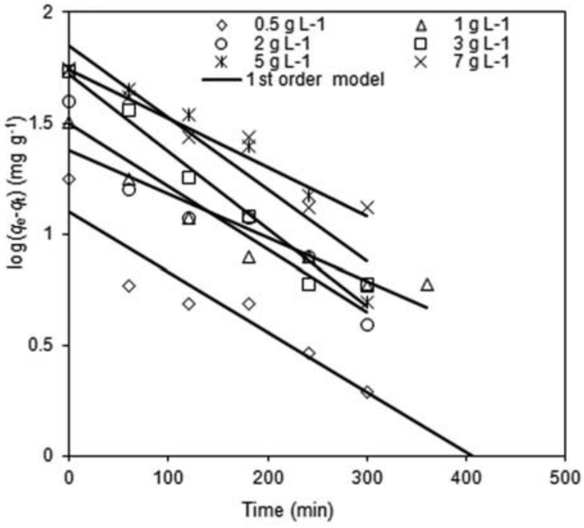

Figure 7: Pseudo-first-order kinetic model plots of ammonium adsorption on natural zeolite.

Table 4. Characteristic parameters of the different kinetic models (pseudo-first and second order) estimated by linear and non-linear regression for ammonia sorption on a) zeolite and b) peat.

a) Zeolite			***Pseudo-first order***			***Pseudo-second order***		
	C_o (mg L^{-1})	$q_{e,exp}$ (mg g^{-1})	k$_f$ (min^{-1})	$q_{e,\ calc}$ (mg g^{-1})	R^2	k$_s$ (g mg^{-1} min^{-1})	$q_{e,\ calc}$ (mg g^{-1})	R^2
Linear regression	500	17.87	0.0062	12.64	0.878	0.0014	18.59	0.969
	1000	31.89	0.0053	26.07	0.928	0.0006	31.65	0.948
	2000	39.86	0.0064	31.46	0.909	0.0005	42.19	0.959
	3000	54.42	0.0081	52.48	0.966	0.0003	52.63	0.927
	5000	54.92	0.0074	71.24	0.893	0.0001	55.87	0.913
	7000	56.02	0.0051	55.69	0.937	0.0001	55.25	0.952
Non-linear regression	500	17.87	0.0149	16.60	0.913	0.0010	19.16	0.969
	1000	31.89	0.0099	28.56	0.964	0.0005	35.36	0.975
	2000	39.86	0.0119	37.35	0.938	0.0003	44.15	0.960
	3000	54.42	0.0076	56.87	0.984	0.0001	55.80	0.989
	5000	54.92	0.0020	67.90	1.000	0.0001	57.34	1.000
	7000	56.02	0.0031	78.10	0.999	0.0001	58.56	1.000
b) Peat			***Pseudo-first order***			***Pseudo-second order***		
	C_o (mg L^{-1})	$q_{e,exp}$ (mg g^{-1})	k$_f$ (min^{-1})	$q_{e,\ calc}$ (mg g^{-1})	R^2	k$_s$ (g mg^{-1} min^{-1})	$q_{e,\ calc}$ (mg g^{-1})	R^2
Linear regression	500	38.54	0.0191	21.39	0.741	0.0012	29.67	0.980
	1000	85.54	0.0233	51.61	0.850	0.0045	86.21	0.970
	2000	174.84	0.0281	130.32	0.961	0.0001	175.44	0.950
	3000	220.85	0.0318	220.85	0.992	0.0006	227.27	0.999
	5000	394.79	0.0329	395.46	0.986	0.0006	400.00	0.999
	7000	421.12	0.0175	533.70	0.876	0.0001	434.78	0.974
Non-linear regression	500	38.54	0.0633	29.67	0.841	0.0106	29.90	0.968
	1000	85.54	0.0454	85.37	0.894	0.0018	88.05	0.982
	2000	174.84	0.0409	175.26	0.975	0.0007	182.24	0.997
	3000	225.45	0.0304	222.22	0.968	0.0003	225.56	0.977
	5000	404.79	0.0305	380.26	0.989	0.0002	405.89	0.995
	7000	421.12	0.0141	440.76	0.979	0.0001	425.78	0.981

which has a linear form:

$$\frac{t}{q_t} = \frac{1}{k_s q_e^{2}} + \frac{1}{q_e} \cdot t \tag{16}$$

where q_e and q_t (mg g^{-1}) are the amount of ammonium adsorbed at equilibrium and at time t and k_s is the pseudo-second-order rate constant (g mg^{-1} min^{-1}). Figure 8a and b shows the plots of q_t against t for the pseudo-second order model for sorption of ammonium onto natural zeolite and peat.

The best-fit model was selected based on both regression correlation coefficient (R^2) and the calculated q_e values. It is seen from Table 4a and b and Figure 9 that the theoretical $q_{e(calc)}$ values for zeolite and peat calculated from the pseudo-first order did not give reasonable values with regard to the experimental uptake ones, $q_{e(exp).}$ This suggests that this sorption system is not a first-order. The $q_{e(calc)}$ values agree very well with the experimental values for the case of the pseudo-second-order kinetics, and a regression coefficient of above 0.95 shows that the 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 and peat.[25] Also, from Table 4a and b it can be seen that the pseudo-second-order rate constant (k_s) decreased with increased initial concentration.

3. 5. Thermodynamic Studies

Thermodynamic parameters were calculated to confirm the adsorption nature of the present study. The thermodynamic constants, free energy change ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) were calculated to evaluate the thermodynamic feasibility of the process and to confirm the nature of the adsorption process.[29,31] The Gibb's free energy change of the process is related to the K_c by the following equation, Eq. (17):

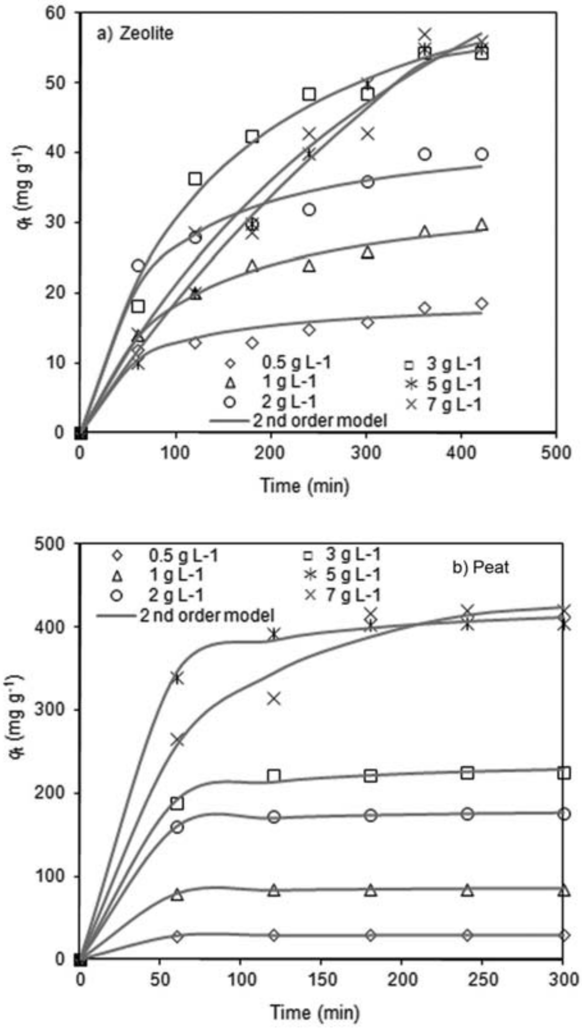

Figure 8: Pseudo-second-order kinetic model plots of ammonium adsorption on a) zeolite and b) peat.

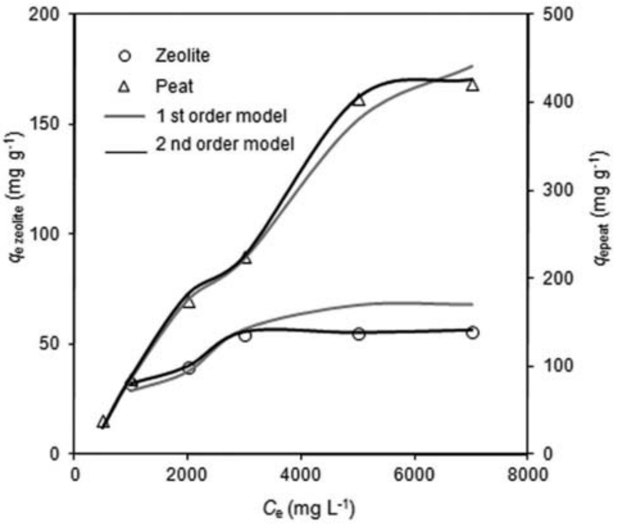

Figure 9: Estimated q_e values for pseudo-first and second order model.

$$\Delta G^o = -RT\ln Kc \tag{17}$$

where T is temperature in K, R the ideal gas constant (8.314 J mol^{-1}K^{-1}) and K_c is the thermodynamic equilibrium constant, which is defined as, Eq. (18):

$$K_c = \frac{C_o - C_e}{C_e} \tag{18}$$

where C_o is initial concentration of ammonium solution, mg L^{-1}, and C_e is the equilibrium concentration of solution, mg L^{-1}. According to thermodynamics, the Gibb's free energy is also related to the enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) at constant temperature by the van't Hoff equation, Eq. (19):

$$\ln K_c = -\frac{\Delta G^o}{RT} = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \tag{19}$$

In order to determine the thermodynamic parameters, experiments were carried out at different temperature in the range of 25–55 °C (Figure 10). The values of entalphy ($\Delta H°$) and entropy ($\Delta S°$) were calculated from the slope and intercept of the plot ln K_c versus T^{-1}. The calculated values are listed in Table 5.

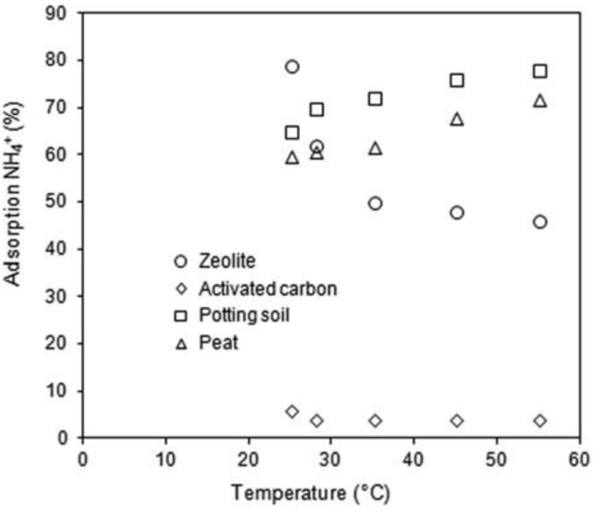

Figure 10: The effect of temperature on NH$_4^+$ adsorption on inorganic and organic adsorbents (activated carbon, zeolite, peat and potting soil) (C_o(NH$_4^+$) = 100 mg L^{-1}; m$_{adsorbent}$ = 0.5 g; V = 50 mL; t = 240 min; T = 25 °C).

Figure 10 indicates the effect of the temperature (25, 28, 35, 45 and 55 °C) on the adsorption of NH$_4^+$ ions by activated carbon, zeolite, potting soil and peat. The amount of NH$_4^+$ removed from aqueous solution by adsorption on activated carbon and zeolite decreased by rising temperature from 25 to 55 °C. On the contrary, the amount of NH$_4^+$ removed from aqueous solution by adsorption on peat and potting soil increased by rising tem-

Table 5. Thermodynamic parameters for the adsorption of NH_4^+ by different adsorbents

Adsorbent	T, K	K_c	$\Delta G°$, kJ mol^{-1}	$\Delta H°$, kJ mol^{-1}	$\Delta S°$, J mol^{-1} K^{-1}
Zeolite	298	4.76	–3.87	–20.39	–58.25
	301	2.63	–2.42		
	308	2.00	–1.77		
	318	1.92	–1.73		
	328	1.85	–1.68		
Activated carbon	298	1.06	–0.15	–1.06	–3.08
	301	1.05	–0.13		
	308	1.04	–0.10		
	318	1.03	–0.08		
	328	1.02	–0.05		
Potting soil	298	2.86	–2.60	11.68	48.40
	301	3.33	–3.01		
	308	3.57	–3.26		
	318	4.17	–3.77		
	328	4.55	–4.13		
Peat	298	2.50	–2.27	9.83	40.41
	301	2.56	–2.36		
	308	2.63	–2.48		
	318	3.13	–3.01		
	328	3.57	–3.47		

perature from 25 to 55 °C. For both, activated carbon and zeolite, the values of $\Delta H°$ were negative, indicating the exothermic nature of the process, which further explain the fact that the adsorption efficiency decreased with the increase of temperature. Negative values of ΔS° indicate a decrease in randomness at the solid/solution interface during the adsorption process while low value of ΔS° indicates that no remarkable change on entropy occurs.[29] The positive values of $\Delta H°$ for peat and potting soil indicated the endothermic nature of the process. Change in the entropy, ΔS° was found to be for peat and potting soil 40.41 and 48.40 J mol^{-1} K^{-1}, respectively, for NH_4^+ removal from aqueous solution. This result implies that NH_4^+ ions on solid phase (surface of adsorbent) were in a much more chaotic distribution compared to the relatively ordered state of bulk phase (aqueous solution).[17] The negative values of $\Delta G°$ for investigated adsorbents confirmed the feasibility and spontaneous nature of the adsorption process.

It is clear that the adsorption process using organic materials can occur in a wide temperature range as compared to inorganic (mineral) materials. For the most mineral materials investigated, the adsorption capacity increases with increasing the temperature up to 25–35 °C and above this range of temperature, the adsorption capacity of adsorbents decreases.[32]

4. Conclusions

From obtained experimental results and their evaluation it can be concluded that zeolite, peat and potting soil are good adsorbents for removal of ammonium ions from aqueous solution. Activated carbon showed low potential for removal of ammonium at concentration higher than 50 mg L^{-1}. The removal percentage was about 75% for peat and potting soil at concentration < 5000 mg L^{-1}, 90% for zeolite at concentration < 500 mg L^{-1}. The equilibrium data have been analyzed using Freundich, Langmuir and Temkin isotherms. The Langmuir isotherm was demonstrated to provide the best fit for the sorption of ammonium to zeolite, peat and potting soil. The adsorption capacity for inorganic materials, activated carbon and zeolite, were 0.631 mg g^{-1} and 58 mg g^{-1}, respectively, for organic materials, peat and potting soil were 595 mg g^{-1} and 575 mg g^{-1} at 25 °C, respectively. Kinetic studies suggest that ammonium adsorption on zeolite, peat and potting soil as adsorbents could be described more favorably by the pseudo-second order kinetic model and the parameters are better estimated by non-linear method.

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6. References

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Povzetek

Raziskovali smo adsorpcijo amoniaka iz vodnih raztopin na aktivnem oglju naravnem zeolitu, šoti in glini pri 25 °C pri začetni koncentraciji med 50–7000 mg NH_4^+–N L^{-1}. Eksperimentalne podatke smo analizirali z Freundlichovo and Langmuirjevo izotermo, kjer se Langmuirjev model izkazal bolje. Ugotovili smo, da adsorpcija na aktivno oglje pri koncentracijah nad 50 mg NH_4^+–N L^{-1} ni več učinkovita, medtem ko so največje sorpcisjke kapacitete na zeolitu 58 mg NH_4^+–N g^{-1}, na šoti 595 mg NH_4^+–N g^{-1} in za glino 575 mg NH_4^+–N g^{-1} suhe snovi.

Z uporabo dveh kinetičnih modelov, psevdo-prvega in drugega reda, smo proučevali tudi kinetiko adsorpcije, pri čemer drugi model bolje opiše hitrost procesa. Zeolit, šota in glina so torej dobri adsorbenti za odstranjevanje amoniaka iz vodnih raztopin.