

Article

Kinetic and Equilibrium Studies of Sorption of Ammonium in the Soil-Water Environment in Agricultural Areas of Central Poland

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Academic Editor: Samuel B. Adelaju

Received: 14 July 2016; Accepted: 13 September 2016; Published: 22 September 2016

Abstract: Sorption characteristics of nitrogen compounds is necessary in ascertaining their fate in the soil-water environment. This paper presents a laboratory “batch” experiment for determining the sorption parameters of ammonium in the soil-water environment. Three agricultural soils (silt loam, loam, and sand) with different contents of the clay fraction, significantly affecting the range of the adsorption of contaminants on the surface of solid particles, were chosen as research material. Considering the composition of ammonium nitrate (a commonly used fertilizer in Poland), ammonium solutions with a concentration of 0–52 mg NH₄⁺/L were used as markers. Pseudo-first order, pseudo-second order, and intra-particle diffusion kinetic models were used to describe the mechanisms of ammonium adsorption. Experimental data obtained from the equilibrium tests have been analysed using two-parameter (Freundlich, Langmuir, Temkin) and three-parameter (Redlich-Peterson, Hill, Sips) models. In order to adjust the parameters of the considered isotherms to the experimental data, the method of minimization of the sum of squared errors was used. Additionally, the maximum sorption capacities and reduction ratios of ammonium versus time were assessed. It was observed that the presence of silt loam and loam in the soil profile can increase the possibility of ammonium adsorption up to almost 20%. Taking into consideration the results of the batch tests, it was concluded that ammonium adsorption attains equilibrium within 48 h. Experimental data was best followed by the pseudo-second order equation and the adsorption isotherm conformed to the Redlich-Peterson model for loam and sand.

Keywords: migration; ammonium nitrate; soil; sorption; isotherm; batch tests

1. Introduction

Agriculture is commonly regarded as the major source of contamination in the soil-water environment worldwide. Excessive use of manure and fertilizers has a negative impact on the groundwater quality and drinking water supplies, which can be detrimental to human health [1–4]. One of the most problematic issues connected with the nitrogen cycle in agricultural areas (Figure 1) is nitrogen leaching to groundwater and surface water as a result of the abusive use of fertilizers [5–7]. The composition of nitrogen fertilizers is dominated by ammonium nitrate, which provides half of the nitrogen in the ammonium form and half in the nitrate form. These forms are easily available for crops but, in high concentrations, may cause hazardous effects to the aquatic system. Excessive concentrations of ammonium may cause a decrease of dissolved oxygen in natural waters and toxicity to aquatic organisms [8]. Ammonium ions can be adsorbed by clay particles, contrary to nitrates, which are easily transported in the soil-water environment and, subsequently, may lead to eutrophication [9–11].

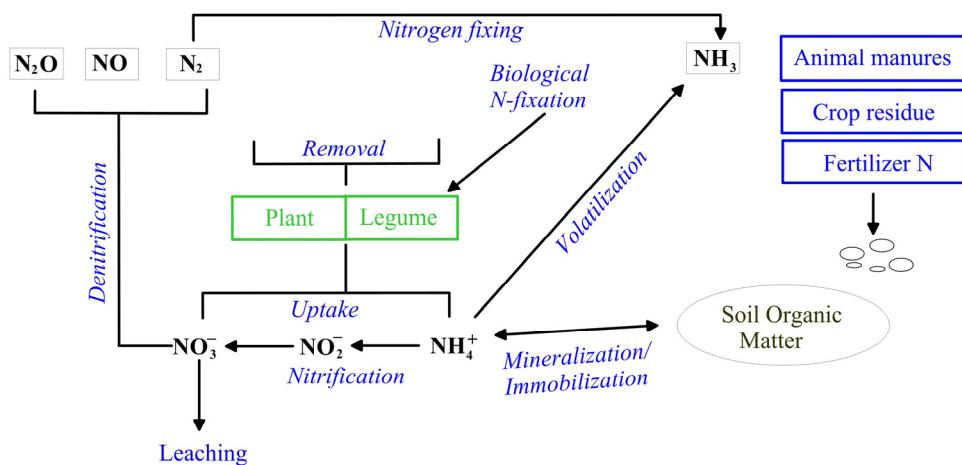


Figure 1. Simplified scheme of the nitrogen cycle in agricultural areas.

Leaching of nitrogen compounds depends on several factors, i.e. fertilization level, type of fertilizer, time and method of application, properties of soils (pH, texture, organic matter content), types of plants, agronomic practices, level of animal production, weather conditions, and watershed land use [12–16]. Due to the leaching of nitrates from the soil profile and the resulting possibility of spreading contaminants in the soil-water environment, it is reasonable to undertake extensive research aiming to recognize the basic processes, especially sorption, responsible for the migration of these contaminants [3,7,9,17–19].

Among the processes responsible for the migration of contaminants in the soil-water environment, the most significant are advection, diffusion, dispersion, biodegradation, and sorption. The role of particular processes associated with the migration of contaminants depends mainly on the type, the physical and chemical properties of pollution, and the properties of the medium in which the migration takes place [17,20,21]. Extremely important in solving problems related to risk assessment and groundwater protection in agricultural areas is recognition of the sorption processes occurring in natural soils [10,12]. For ammonium ions, the key reactive processes controlling subsurface migration include sorption as a result of cation exchange and biological degradation [22]. Adsorption of positively-charged ammonium ions occurs on the surface of negatively-charged clay particles. Mackin and Aller [23], Çelik et al. [24], Balci and Dince [25], Mikołajkow [26], Abdulgawad et al. [27], Tosun [28], Buragohain [29], and Ismadji et al. [30] reported that montmorillonite has a higher adsorption capacity compared to kaolinite, fine and coarse sand, and for this reason natural clays are one of the most essential sorbents due to their availability and easy application in removal of nitrogen forms from the environment.

Whereas many studies have been conducted in order to characterize the phenomena of sorption processes of various contaminants onto different sorbents [31–41], only very few reports have been presented on the evaluation of the adsorption of contaminants originating from agricultural sources. This gap in knowledge can result in reduced possibilities in the assessment of risks posed by ammonium contamination arising from many sources [22].

In reference to the issues mentioned above, the main aims of this study were: (1) to assess the sorption capacities of agricultural soils from Central Poland; (2) to determine the kinetics of sorption of ammonium into soils with various contents of the clay fraction (0%–21%); and (3) to estimate the ammonium sorption characteristics using two- and three-parameter models.

2. Materials and Methods

2.1. Study Area

The study area of approximately 40 ha covers two adjacent fields of crop production, located in Imielin (Figure 2), Central Poland ($52^{\circ}4'28.99''$ N, $21^{\circ}11'3.65''$ E) in the Masovian Voivodeship, Konstancin Jeziorna commune.

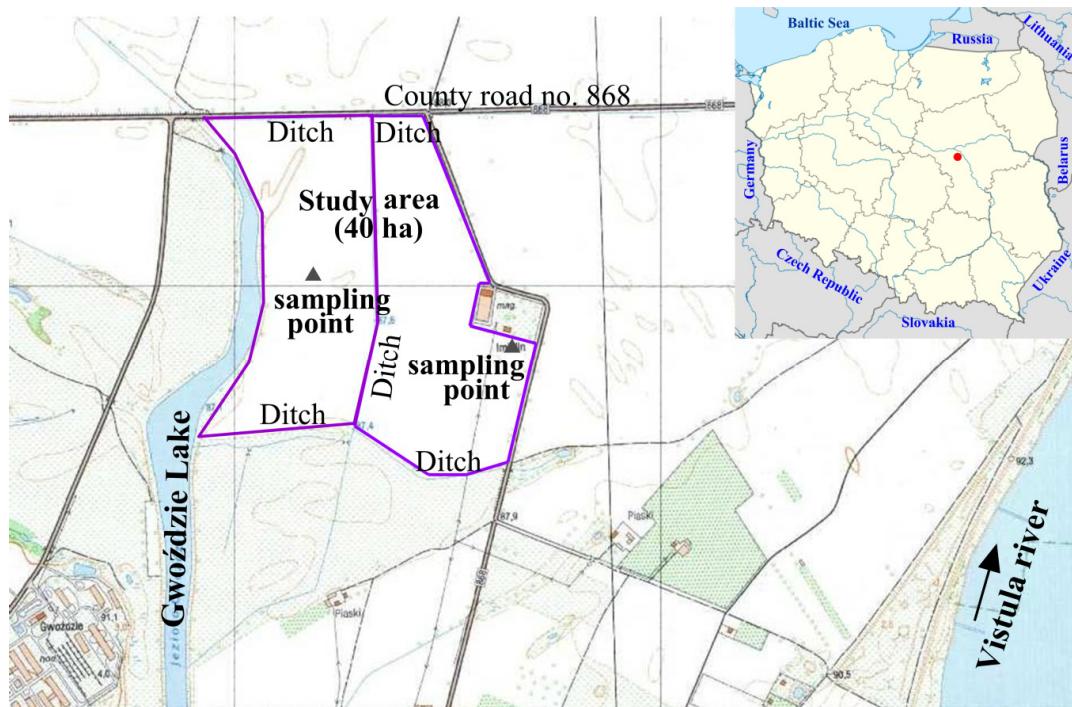


Figure 2. Location of the study fields.

According to the geomorphological classification of Poland, the study area is located within the Central Masovian Lowland macroregion, the Warsaw Plain and the Middle Vistula Valley mesoregions. The area lies approximately at 88 m above sea level (a.s.l.). Shallow drillings indicate the presence of silt loams with a thickness of 1 m below the subsoil. Silty sands and medium sands have been identified below the silty clays. The study area lies approximately 1.5 km from the Vistula River and at a distance of c. 300 m from the Gwoździe Lake. To the south, west, and north, the field is surrounded by drainage ditches. There is no housing development in the vicinity of the study area.

2.2. Materials

In this study three soil samples were used as adsorbents. The samples were collected from the field of winter wheat cultivation located in the Imielin experimental site in the central part of Poland (Figure 2). According to the U.S. Department of Agriculture soil survey staff [42], the tested soils were classified as silt loam, loam, and sand, respectively (Figure 3). The physical and chemical properties of the applied soils are presented in Table 1.

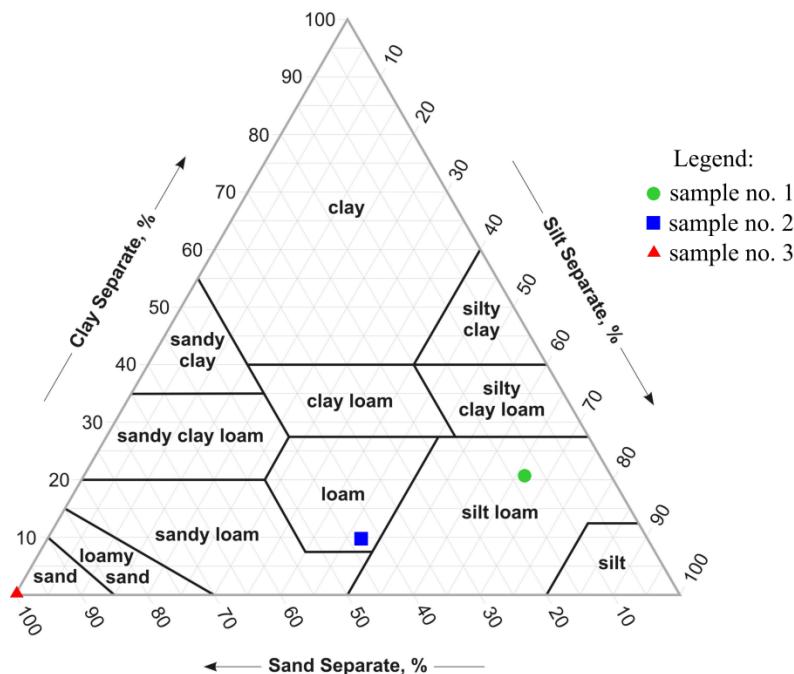


Figure 3. Classification of soil texture of the studied soils.

Table 1. Physical and chemical properties of the tested soils.

Adsorbent	Bulk Density	Porosity	pH	Electrical Conductivity	Organic Matter	Hydraulic Conductivity
	[Mg/m ³]	[-]	[-]	[μS/cm]	[%]	[m/s]
Silt loam	1.63	0.40	7.4	363	3.1	1.9×10^{-8}
Loam	1.60	0.40	7.5	160	2.3	3.6×10^{-6}
Sand	1.70	0.34	7.2	155	0.1	3.0×10^{-5}

2.3. Kinetic Tests

The kinetics of adsorption is one of the important characteristics defining the efficiency of adsorption [43]. The study of sorption kinetics provides valuable insights into the reaction pathways and into the mechanism of sorption reactions [44–46]. Before determining the adsorption isotherms, the kinetics of adsorption of ammonium onto natural soils had been studied using three kinetic models (Table 2). Constants of sorption were determined using the pseudo-first order equation of Lagergren [47] based on solid capacity, the pseudo-second order equation based on solid phase sorption, and the intra-particle diffusion model, respectively.

Table 2. Kinetic models of ammonium sorption into agricultural soils.

Kinetic Model	Equation	Plot	Reference
Pseudo-first order	$\log (q_e - q_t) = \log (q_e) - \frac{k_1 t}{2.203}$	$\log (q_e - q_t)$ vs. t	[47]
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_0}$ $q_0 = k_2 \cdot q_e^2$	$\frac{t}{q_t}$ vs. t	[47,48]
Intraparticle diffusion	$q_t = k_i \cdot t^{1/2} + C_i$	q_t vs. $t^{0.5}$	[49]

where: q_e —amount of ions adsorbed per unit mass of the adsorbent at equilibrium time, [mg/g]; q_t —amount of ions adsorbed per unit mass of the adsorbent at time t [mg/g]; t —contact time, [min]; k_1 —the pseudo-first order rate constant, [1/min]; k_2 —the pseudo-second order rate constant, [g/mg min]; k_i —intraparticle diffusion rate constant, [mg/g min^{1/2}]; C_i —intercept, directly proportional to the thickness of the boundary layer, [mg/g].

Prior to the laboratory analyses, the soil samples were prepared by drying at room temperature and sieved through a $\Phi 1$ mm sieve. For kinetic studies, 5 g of each soil sample were mixed with 50 mL of the ammonium nitrate solution (52 mg NH_4^+ /L, pH = 6.62, electrical conductivity (EC) = 1.706 mS/cm), maintaining a constant solid-to-liquid ratio of 1:10. Similarly, blank and control samples were prepared using the treatment solution without the soil sample and a soil sample with distilled water, respectively. The time periods of shaking were chosen according to US EPA [50] and were carried out for 1, 4, 8, 16, 24 and 48 h on a rotary shaker GFL 3040 with the speed of 14 min^{-1} . After the time of a desired period of shaking, the solutions were filtered through paper filters and prepared for chemical analysis. Samples were analysed for their ammonium and nitrate contents by Nessler [51] and cadmium reduction method [52], respectively, using a spectrophotometer UV-VIS DR 6000 (Hach Lange type, Düsseldorf, Germany). Electrical conductivity and pH were measured using a 18.52.01 multimeter (Eijkelkamp type, Giesbeek, the Netherlands). All samples were analysed in duplicate.

The percent contributions of ammonium adsorbed ($\%R$) and ammonium adsorption capacity (q) were calculated using the following expressions:

$$\%R = \frac{C_0 - C_e}{C_0} \cdot 100\% \quad (1)$$

and:

$$q = \frac{(C_0 - C_e) \cdot V}{m} \quad (2)$$

where: C_0 —initial concentration of ammonium in the solution, [mg/L]; C_e —final ammonium concentration in the solution, [mg/L]; V —volume of the solution, [mL]; m —amount of sorbent on the dry basis, [g].

2.4. Equilibrium Studies

Substantial parameters simulating nitrogen compound leaching include adsorption isotherm coefficients. In this study, the relationship between the amount of the contaminant adsorbed into the soil surface and the equilibrium concentration of the adsorbate in the solvent at an equilibrium in a constant temperature were estimated by various adsorption isotherm models. The isotherms relate the ammonium uptake per unit mass of the adsorbent to the equilibrium adsorbate concentration in the bulk fluid phase [53]. The equilibrium behaviour of natural soils during ammonium adsorption was investigated using the Freundlich, Langmuir, Temkin, Redlich-Peterson, Sips, and Hill models at room temperature (22°C) (Table 3). Batch equilibrium studies were run in duplicate with a solid-to-liquid ratio of 1:10, using 5 g of air-dried soil samples and 50 mL of ammonium nitrate solution with following concentrations of ammonium: 10, 20, 30, 45, 50, and 52 mg NH_4^+ /L. The bottles containing the soil-ammonium nitrate solution were sealed tightly and placed on a rotary shaker GFL 3040. The shaking process at a speed of 14 min^{-1} was carried out according to the U.S. Environmental Protection Agency (EPA) [50] for 48 h. After the desired time of shaking, the working solutions were filtered through paper filters and then pH, electrical conductivity, and ammonium and nitrate concentrations were determined (methods described in the section “Kinetic Tests”). All of the reagents used in the tests were of analytical reagent grade.

Table 3. Two- and three-parameter isotherm models used in the studies.

Isotherm	Equation	Model Parameters	Reference
Two-parameter models			
Freundlich	$q_e = K_F \cdot C_e^{1/n}$	K_F, n	[54]
Langmuir	$q_e = \frac{q_{max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e}$	q_{max}, K_L	[55]
Temkin	$q_e = B \cdot \ln(A \cdot C_e)$	B, A	[56]
Three-parameter models			
Redlich-Peterson	$q_e = \frac{K_R \cdot C_e}{1 + b_r \cdot C_e^g}$	K_R, b_r, g	[57]
Sips	$q_e = \frac{q_{max} \cdot b \cdot C_e^{1/m}}{1 + b \cdot C_e^{1/m}}$	q_{max}, m, b	[58]
Hill	$q_e = \frac{q_H \cdot C_e^{n_H}}{K_D + C_e^{n_H}}$	q_H, K_D, n_H	[59]

where: K_F —Freundlich constant related to the adsorption capacity, [(mg/g)(L/mg)ⁿ]; C_e —concentration of the adsorbate in the solution at equilibrium, [mg/L]; n —Freundlich constant related to the adsorption intensity, [-]; q_{max} —maximum adsorption capacity, [mg/g]; K_L —Langmuir constant related to the adsorption energy, [L/mg]; B —Temkin constant related to the heat of adsorption, [L/g]; A —Temkin isotherm constant, [-]; K_R —Redlich-Peterson isotherm constant, [L/g]; b_r —Redlich-Peterson isotherm constant, [L/mg]; g —Redlich-Peterson isotherm exponent, [-]; m —Sips isotherm model exponent, [-]; b —Sips equilibrium constant, [(L/mg)m]; q_H —Hill isotherm maximum uptake, [mg/g]; K_D —Hill constant related to energy of adsorption, [-]; n_H —exponent of Hill isotherm, [-].

3. Results and Discussion

3.1. Effect of Contact Time on the Reduction of Ammonium and Sorption Capacity of Soils

Contact time is one of the most effective factors in batch adsorption process [23,53]. The results showed that ammonium sorption attained an equilibrium within 48 h (Figure 4), which means that no significant sorption and/or desorption of this compound were recorded after this time [8]. It was observed that with increasing contact time, reduction of the ammonium ions increased, reaching the maximum value of 19.4%, 18.5%, and 14.4% for silt loam, loam, and sand, respectively (Table 4).

The sorption capacity of the tested soils determined at equilibrium time (48 h) were found to be as follows (Figure 4): $q_t = 0.1011$ mg/g, $q_t = 0.0958$ mg/g, and $q_t = 0.0752$ mg/g for silt loam, loam, and sand, respectively, which indicates the great impact of the clay and organic matter contents on the sorption capacity of the soils. Similar variations in the sorption capacities, dependent on the soil type, were presented by Abdulgawad et al. [27].

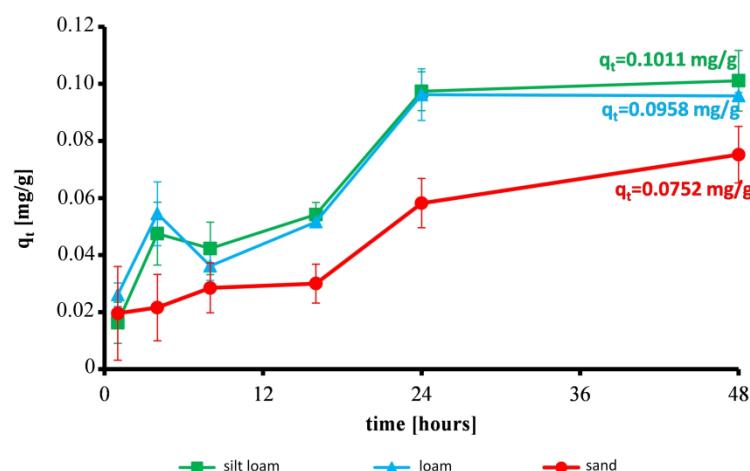


Figure 4. Ammonium sorption capacity versus time and standard deviation error bars for the experimental data.

Table 4. Effect of contact time on the reduction of ammonium on agricultural soils.

Soil	Contact Time [h]					
	1	4	8	16	24	48
Reduction of ammonium [%]						
Silt loam	3.1	8.1	9.1	10.4	18.7	19.4
Loam	5.0	6.9	10.5	11.3	18.4	18.5
Sand	3.8	4.2	5.5	5.8	11.2	14.4

3.2. Kinetic Tests

Table 5 shows the parameters of three kinetic models chosen for this study. Comparison of the values of correlation coefficients (R^2) values of the pseudo-first order, pseudo-second order, and intra-particle diffusion models shows that the ammonium sorption data were best described by the pseudo-second order kinetic model.

Table 5. Kinetic parameters for ammonium adsorption onto natural soils.

Parameter	Soil			
	Silt Loam	Loam	Sand	
Pseudo-first order kinetic model				
q_e	mg/g	0.1011	0.0960	0.0752
k_1	1/min	0.0016	0.0024	0.0016
R^2	-	0.89	0.80	0.89
Pseudo-second order kinetic model				
q_e	mg/g	0.1189	0.1110	0.0880
k_2	mg/g min	0.0140	0.0167	0.0306
v_0	mg/g min	0.0002	0.0002	0.0002
R^2	-	0.91	0.87	0.94
Intra-particle diffusion				
k_{int}	mg/g min ^{1/2}	0.0018	0.0016	0.0013
C_i	mg/g	0.0080	0.0161	0.0029
R^2	-	0.86	0.77	0.89

The results of the studies by Sharifnia et al. [60] have shown that the kinetics of ammonium sorption follows the pseudo-second order kinetic model (Figures 5–7). Weber and Morris [49] suggested that the mechanism of sorption is via intra-particle diffusion when the plot of q_t versus $t^{1/2}$ is linear, and if the sorption process is controlled by more than one mechanism, the plot of q_t versus $t^{1/2}$ is multi-linear [61]. Our study shows that certainly more than one process is responsible for the sorption of ammonium onto agricultural soils. Based on the coefficients of determination, $R^2 = 0.91$, $R^2 = 0.87$, $R^2 = 0.94$ for silt loam, loam, and sand, respectively, it can be concluded that this model best describes the sorption of ammonium onto agricultural soils. Taking into consideration the high values of R^2 for the pseudo-first and intra-particle diffusion models, we can assume that the sorption of ammonium can be additionally controlled by physical processes and surface and pore-volume diffusion, respectively [47,49].

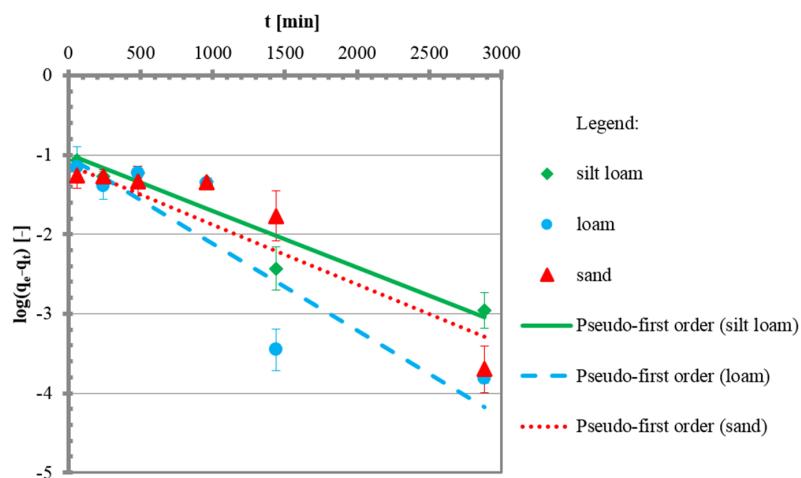


Figure 5. Kinetics of ammonium removal by soils according to the pseudo-first order equation and standard deviation error bars for the experimental data.

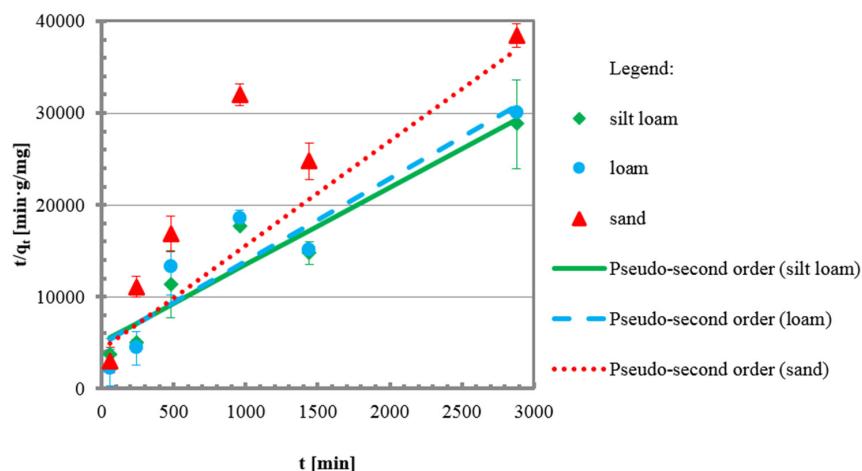


Figure 6. Kinetics of ammonium removal by soils according to the pseudo-second order equation and standard deviation error bars for the experimental data.

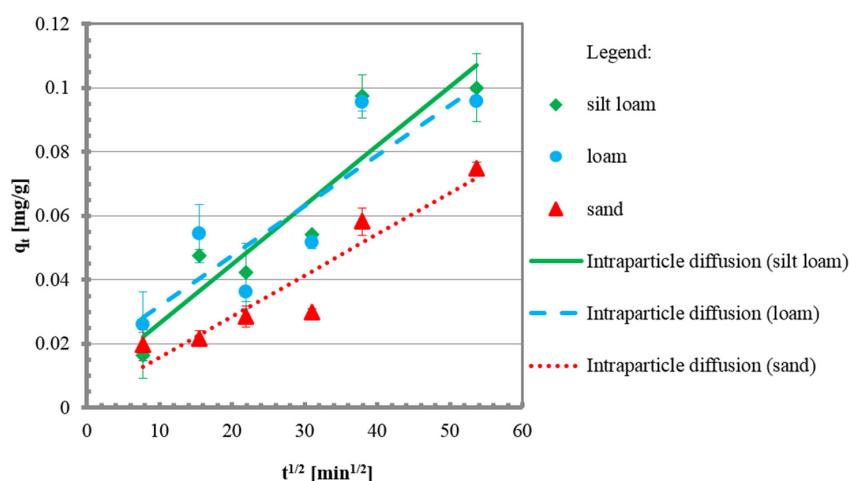


Figure 7. Kinetics of ammonium removal by soils according to the intra-particle diffusion model and standard deviation error bars for the experimental data.

3.3. Equilibrium Studies

Data obtained from the equilibrium studies have been analysed using two-parameter (Freundlich, Langmuir, Temkin) and three-parameter (Redlich-Peterson, Hill, Sips) models.

As pointed out in our research, the classification of all the tested models for the description of adsorption equilibrium isotherms of ammonium onto agricultural soils can be described as follows:

- for silt loam: Sips ($R^2 = 0.89$) = Hill ($R^2 = 0.89$) > Redlich-Peterson ($R^2 = 0.88$) > Langmuir ($R^2 = 0.81$) > Temkin ($R^2 = 0.72$) > Freundlich ($R^2 = 0.66$),
- for loam: Redlich-Peterson ($R^2 = 0.94$) > Hill ($R^2 = 0.83$) > Langmuir ($R^2 = 0.79$) > Sips ($R^2 = 0.72$) > Temkin ($R^2 = 0.63$) > Freundlich ($R^2 = 0.59$),
- for sand: Redlich-Peterson ($R^2 = 0.88$) > Langmuir ($R^2 = 0.65$) > Freundlich ($R^2 = 0.63$) > Hill ($R^2 = 0.56$) > Temkin ($R^2 = 0.43$) > Sips ($R^2 = 0.39$).

The n value of the Freundlich isotherm indicates the degree of nonlinearity between the solution concentration and adsorption [62]. Briefly, if $n = 1$, then adsorption is linear; if $n < 1$, then adsorption is a chemical process; and if $n > 1$, then adsorption is a physical process. Adsorption is considered as satisfactory when the Freundlich constant n attains values within the range 1–10. In this study, the n value was found to be 4.17, 6.41, and 6.59 for silt loam, loam, and sand, respectively (Table 6), which indicates the physical character of ammonium adsorption onto agricultural soil.

Table 6. Parameters of ammonium adsorption onto agricultural soils according to Freundlich, Langmuir, and Temkin models.

Soil	Freundlich			Langmuir			Temkin		
	K_F	n	R^2	q_{max}	K_L	R^2	A	B	R^2
Silt loam	0.071	4.17	0.66	0.18	0.36	0.81	9.50	0.029	0.72
Loam	0.048	6.41	0.59	0.09	0.40	0.79	2.31	0.019	0.63
Sand	0.034	6.59	0.63	0.06	0.79	0.65	0.18	0.030	0.43

Based on the Langmuir isotherm, the efficiency of the adsorption process can be predicted by the dimensionless equilibrium parameter R_L , called the separation factor, which is expressed by the following equation [63]:

$$R_L = \frac{1}{1 + K_L \cdot C_0} \quad (3)$$

where: K_L —Langmuir constant, [L/mg], C_0 —initial concentration of ammonium in the solution, [mg/L].

Adsorption is considered as irreversible when $R_L = 0$, favourable when $0 < R_L < 1$, linear when $R_L = 1$, and unfavourable when $R_L > 1$. In this study, R_L values were found to be 0.05–0.21 for silt loam, 0.05–0.20 for loam, and 0.02–0.10 for sand, indicating that the adsorption of ammonium onto agricultural soils is favourable.

The results of the studies of Sharifnia et al. [60] and Karadag et al. [64] have shown that the equilibrium data of ammonium sorption were fitted well by the Langmuir and Freundlich isotherm models. Abdulgawad et al. [27] claimed that ammonium adsorption on montmorillonite, kaolinite, coarse and fine sand obeys the Freundlich adsorption isotherm. A nearly similar tendency is presented in the research conducted by Moradzadech et al. [41].

Results of this study indicate that among the six commonly used adsorption models (Figure 8), the Redlich-Peterson model has the best fitting with the experimental data for loam and sand ($R^2 = 0.94$ and $R^2 = 0.88$, respectively). For silt loam, the best fitting between experimental and modelled data was obtained using the Sips and Hill models ($R^2 = 0.89$). Our research has revealed that among the two-parameter models, the Langmuir isotherm best reflects the mechanism of ammonium sorption ($R^2 = 0.81$, $R^2 = 0.79$ and $R^2 = 0.65$ for silt loam, loam, and sand, respectively).

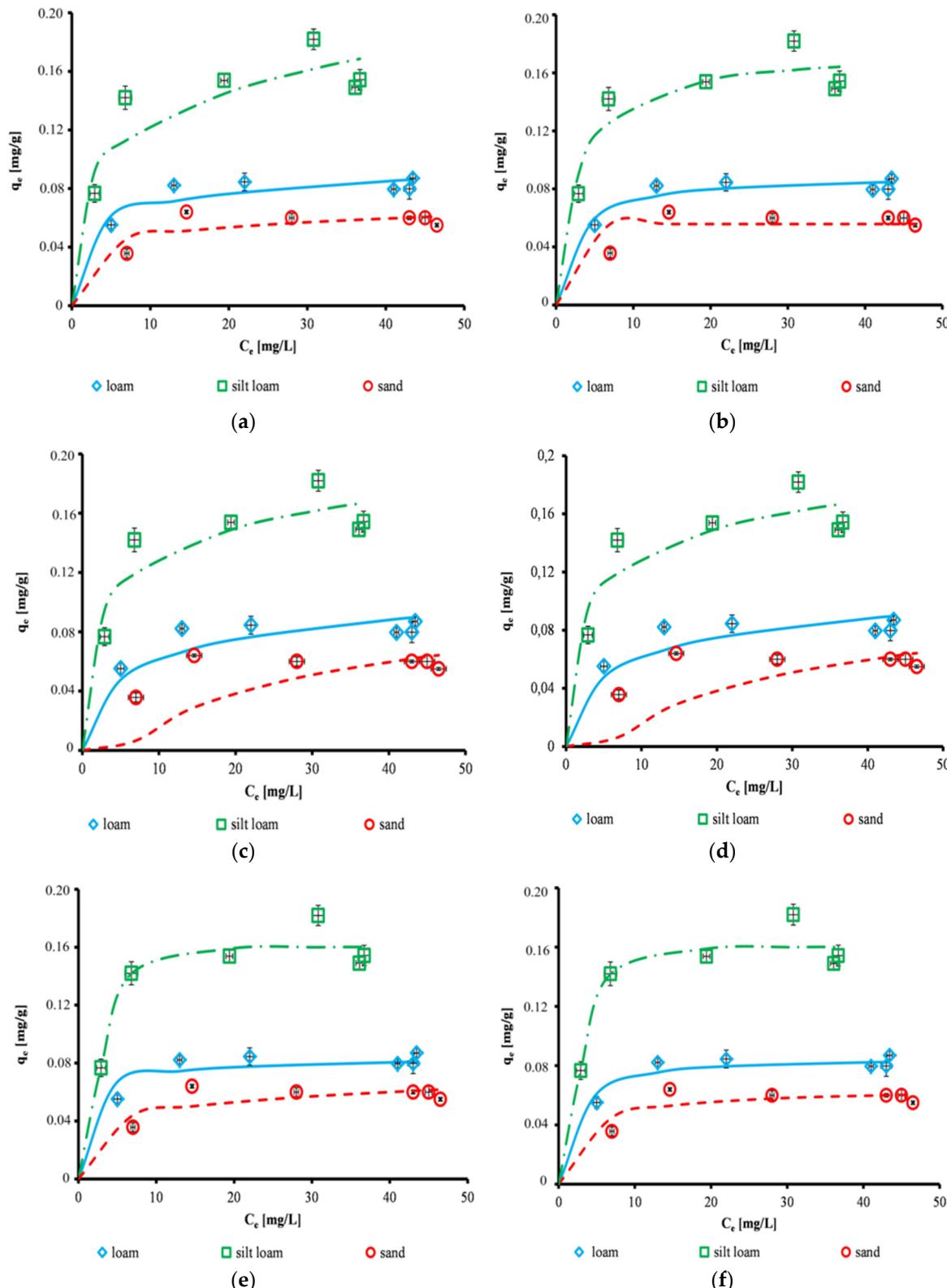


Figure 8. Freundlich (**a**), Langmuir (**b**), Temkin (**c**), Redlich-Peterson (**d**), Sips (**e**), and Hill (**f**) isotherm models and standard deviation error bars for ammonium adsorption onto loam, silt loam, and sand, respectively.

Furthermore, the studies of many other researchers [28,39,65–67] demonstrated that models with two parameters always less accurately describe the sorption processes than those with more than two parameters. This was also confirmed by the results obtained in our studies (Table 7).

Table 7. Parameters of ammonium adsorption onto agricultural soils according to Redlich-Peterson, Sips and Hill models.

Soil	Redlich-Peterson				Sips				Hill			
	K_R	b_R	g	R^2	q_{max}	n	b	R^2	q_{max}	K_d	m	R^2
Silt loam	0.035	0.062	1.32	0.88	0.16	0.40	0.07	0.89	0.16	15.25	2.48	0.89
Loam	0.017	0.064	1.27	0.94	0.09	1.88	1.27	0.72	0.09	2.59	1.17	0.83
Sand	0.006	0.006	1.71	0.88	0.50	5.57	0.02	0.39	0.07	2.58	0.89	0.56

4. Conclusions

Understanding the adsorption behaviour of ammonium in the soil-water environment is priceless for the knowledge of nitrogen chemistry in soils. An essential issue in agricultural areas is to identify the transport and fate of ammonium in soils in order to improve the efficiency of the application of nitrogen fertilizers. The present investigation has shown that ammonium is adsorbed more in silt loam and loam compared to sand. Therefore, it can be considered that in the environment ammonium will reach the aquifer faster in sandy soils and soils with a low organic matter content than in cohesive soils with higher clay and organic matter contents. On the basis of the values of the regression coefficients, it is concluded that ammonium sorption into agricultural soils can be approximated more appropriately by the pseudo-second order kinetic model rather than by the pseudo-first order and the intra-particle diffusion kinetic model. Sorption parameters obtained from the batch tests reflect the results described in literature for similar materials.

In summary, batch tests can be considered as an efficient method to provide input data for numerical modelling of ammonium transport (with particular focus on sorption processes) in the soil-water system in order to assess contaminant migration in agricultural areas for the purpose of surface and groundwater protection.

Acknowledgments: This research was partially financed by the European Regional Development Fund under the Innovative Economy Operational Programme: BIOPRODUCTS, innovative production technologies of pro-healthy bakery products and pasta with reduced caloric value (POIG.01.03.01-14-041/12).

Author Contributions: Anna Sieczka and Eugeniusz Koda conceived the subject of the paper, prepared and wrote the article. Anna Sieczka was responsible for laboratory tests and data analysis. Eugeniusz Koda provided the expertise on the research.

Conflicts of Interest: The authors declare no conflict of interest.

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