

NH_4^+ adsorption and adsorption kinetics by sediments in a drinking water reservoir

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Abstract: The sorption isotherm and sorption kinetics of NH_4^+ by the Fen River reservoir sediment were investigated for a better understanding of the NH_4^+ sorption characteristics and parameters. The results showed that Q (adsorption content) increased with the increase of C_{eq} (equilibrium concentration), sorption isotherms could be described by Freundlich equation (R^2 from 0.97 to 0.99). Cation exchange capacity (CEC) had a significant correlation with the parameters K and n (R^2 was 0.85 and 0.95, respectively). The ENC_0 (C_{eq} as Q was zero) of S1, S2, S3 and S4 was 1.25, 0.57, 1.15 and 1.14 mg L^{-1} , respectively, and they were less than the NH_4^+ concentrations in reservoir water. The sediments released NH_4^+ to the Fen River reservoir water and acted as a pollution source, in the form of complex and heterogeneous adsorbents. The NH_4^+ adsorption kinetic process was composed of 'fast' and 'slow' reaction patterns and could be fitted using both Elovich equation and Pseudo second-equation. More than one-step may be involved in the NH_4^+ sorption processes, and interior diffusion was not dominant ion action.

Introduction

Nitrogen is one of the most important nutrients for plant growth. In recent years, the fertilizer has been excessively applied for plant growth and economic benefit. However, these behaviors usually lead to much fertilizer losses and soil erosion, and then give rise to serious environmental problems (Brankov et al. 2012; Darvishi et al. 2016). NH_4^+ is usually found in aqueous environments, which is the major component among the nitrogen-contaminating compounds in lakes or rivers and is produced in sediments during the decomposition of organic matter by various heterotrophic organisms (Machin and Aller 1984). After NH_4^+ release to solution by the processes of air stripping, chemical treatment, selective ion exchange and biological nitrification-denitrification (Metcalf 2003, Kelly 1996, de-Bashan et al. 2004), it also can be reoxidized, reincorporated into organisms, adsorbed onto particles, migrate to other parts of the sediments, can be diffused along concentration gradients to other regions of the sediment or to the overlying water.

Sediments usually act as a sink for ammonium. However, under certain conditions, the sediments may act as a source and support the trophic status of the lake ecosystem (Zhou et al. 2001, Kaiserli et al. 2002). When present in extremely high concentrations, NH_4^+ may also be a constituent of authigenic minerals (Martens et al. 1978). Physical chemistry of adsorption and desorption are fundamental and important processes for element transference, and have obviously

effect on the content of a nutrient. Reservoir plays a special role in society and people's life, the water and sediment of reservoir directly affect the water quality and ecological environment, as well as human's physical health. Therefore, studies on adsorption and desorption characteristics are significant for the understanding of the role of sediments in the biogeochemical cycling of ammonium in shallow lakes and reservoirs. The objective of this study was to investigate NH_4^+ adsorption isotherm of the sediments from the Fen River reservoir, to calculate collected parameters and analyze the adsorption characteristics, and understand the kinetics process of NH_4^+ adsorption.

Materials and methods

Study area

The Fen River reservoir is a subtropical reservoir located at $38^\circ 02' 59'' \text{N}$ and $111^\circ 54' 58'' \text{E}$ in Shanxi Province, China. It was formed by damming of the Fen River in 1958. The reservoir has a maximum storage capacity of $7.0 \times 10^8 \text{ m}^3$, controlling 5268 km^2 upstream areas, and it could irrigate $90 \times 10^3 \text{ ha}$ fields. The upstream area of the Fen River reservoir consists of loess hilly gully region, soils in this area are impoverished and easily eroded. The area experiences a typical continental monsoon climate, the mean annual precipitation is 456 mm and the mean annual temperature is 9.5°C . The concentration of NH_4^+ in the reservoir was higher than in the river, which was 0.15–0.18 mg L^{-1} and 0.12–0.16 mg L^{-1} respectively.

Methods

In this study, four sediment samples S1, S2, S3 and S4 were taken from the Fen River reservoir using a special messenger-activated core-sampler (ETC-200) in August, 2014 (Fig 1). Water depth of the sample stations was 5 m for S1 and S3, and 7 m for S2 and S4, respectively. The collected samples were stored in an icebox and transported immediately to the laboratory, and then centrifuged for 10 min at 5,000 rpm to remove most of the water. Subsequently the samples were air dried, passed through a 100 mesh sieve and stored at 4°C.

Sediment pH was measured in distilled water (w/v ratio of 1:2.5). NH₄⁺ was extracted with 2 mol L⁻¹ KCl and measured by indigotin spectrophotometry. Total nitrogen (TN) was measured by Kjeldahl apparatus (Kjelflex k-360) after digestion with sulphuric acid (H₂SO₄). Total phosphorus (TP) content was determined using the molybdenum-blue complex method after extraction with HClO₄/H₂SO₄ at 370°C (Krom et al. 1981). The organic matter (OM) was measured by the dichromate volumetric method. Cation exchange capacity (CEC) was measured by ammonium acetate exchanging method. Particle size distribution of the sediment was determined using the hydrometer method (Bouyoucos 1951). The sediments characteristics are depicted in Table 1.

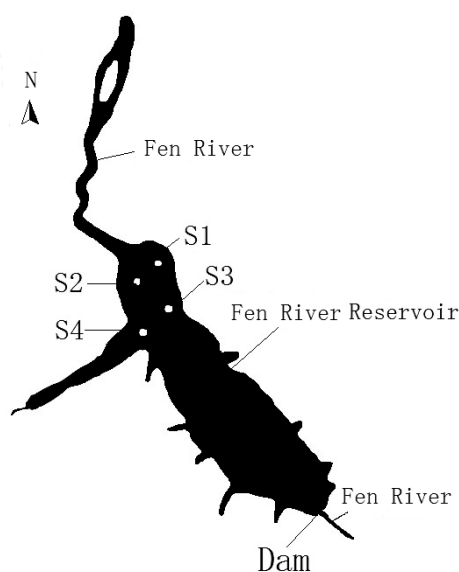


Fig. 1. Map of sampling sites at the Fen River reservoir

For NH₄⁺ adsorption experiment, 0.5 g sediment samples were loaded into a series of 50 mL tubes, then 25 mL NH₄Cl solution in concentrations of 0, 0.5, 1, 2, 5, 10, 15, 20, 30 and 50 mg L⁻¹, respectively, was injected, two drops of toluene (0.1% chloroform) were added to restrict microbial activity. After shaking at 250 rpm on an orbital shaker at 25°C for 24 h, suspensions were centrifuged at 3,500 rpm for 10 min. Then the supernatants were filtered through a 0.45 µm filter membrane. The NH₄⁺ concentration (C_{eq}) in the supernatant solution was determined by the salicylate-hypochlorous acid spectrophotometric method using UV-750. The adsorbed amount of NH₄⁺ by the sediment was calculated by the difference between C_o and C_{eq} . The formula (1) was:

$$Q = (C_o - C_{eq}) \times \frac{v}{w} \quad (1)$$

Where, Q is the sorbed amount (mg kg⁻¹), C_o is the initial NH₄⁺ concentration (mg L⁻¹), C_{eq} is the equilibrium concentration (mg L⁻¹), w is the sample weight (g), and v is the solution volume (mL) of NH₄Cl.

For adsorption kinetics, 0.5 g samples were loaded into a series of 50 ml polyethylene centrifuge tube, then mixed with 25 mL NH₄Cl solution of 2 mg L⁻¹ that was selected as near the grade five of water in China (2 mg L⁻¹ for lake and reservoir). Two drops of toluene (0.1% chloroform) were also added to restrict microbial activity. The centrifuge tubes were capped and shaken at 250 rpm on an orbital shaker at 25°C for different times range from 0 to 720 min (5, 15, 30, 60, 120, 240, 720 min). After shaking, the suspensions were centrifuged and the supernatants were filtered in accordance with the above method. The NH₄⁺ concentration (C_{eq}) in the supernatant and the adsorbed amount by the sediment was determined and calculated as described by the method of NH₄⁺ adsorption experiment.

All data were the mean values of three replicates. The Office Excel and SPSS 13.0 software were used for calculation and statistical analysis, and Origin 8.0 was used to fit curves and calculate parameters.

Results and discussion

NH₄⁺ adsorption isotherm and related parameters

The adsorption isotherms were one of the most important data to understand the mechanism of the adsorption systems.

Table 1. Sediment characteristics

	S1	S2	S3	S4
pH	7.45±0.23	7.28±0.18	7.36±0.22	7.4±0.16
NH ₄ ⁺ (mg kg)	28.07±2.41	15.01±3.21	26.72±1.96	24.36±2.36
TN (mg kg)	415.42±20.32	436.72±18.46	370.04±25.30	398.45±27.18
TP (mg kg)	842.84±28.14	648.25±19.76	581.61±24.32	742.35±22.34
OM (mg kg)	415.55±17.62	350.02±20.15	427.93±16.87	406.72±20.13
CEC (cmol kg)	54.54±8.64	67.01±6.71	59.56±5.48.62	52.39±7.23
Sand (%)	26.39±4.32	25.72±5.32	29.58±5.46	27.46±3.25
Silt (%)	35.23±3.25	34.53±4.53	36.02±5.32	33.56±4.32
Clay (%)	38.38±2.56	39.75±3.28	34.4±3.25	38.98±2.33

Langmuir and Freundlich adsorption isotherms were two important isotherms which were usually used in the sediment-water system (Hou et al. 2003).

The present study showed that the NH_4^+ adsorption by sediments from the Fen River reservoir fitted to the Freundlich adsorption isotherm and did not fit to the Langmuir isotherm within the controlled range of NH_4^+ concentration in the overlying water during the simulation experiment. Freundlich isotherm:

$$Q = K \cdot C_{eq}^{1/n} \quad (2)$$

Where Q (mg kg^{-1}) was the adsorption amount; C_{eq} was the equilibrium concentration in the overlying water (mg L^{-1}); K (L kg^{-1}) and n was constants, being indicative of the extent of the adsorption and the degree of nonlinearity between solution concentration and adsorption, respectively, and when n was almost equivalent to 1, the ion adsorption by sediments was linear (Machin and Aller 1984).

The fitting curves and parameters of the Freundlich isotherm are presented in Fig. 2 and Table 2, which was not consistent with the linear relationship of previous reports (Machin and Aller 1984, Hou et al. 2003, Rosenfeld 1979, Rysgaard et al. 1999). However, similar to other reports (Balci and Dincel 2002, Dixit et al. 2002, Ugurlu and Karaoglu 2011, Ma et al. 2011), Q increased with the increase of C_{eq} . Table 2 showed that Freundlich equations could better describe the NH_4^+ adsorbed process, and R^2 ranged from 0.97 to 0.99. K values were relatively lower for S4 and S3 (26.49–38.11 L kg^{-1}), and higher for S1 and S2 (41.85–87.12 L kg^{-1}), while n values were lower for S4 and S1 (1.60–1.95), and higher for S2 and S3 (2.36–2.95).

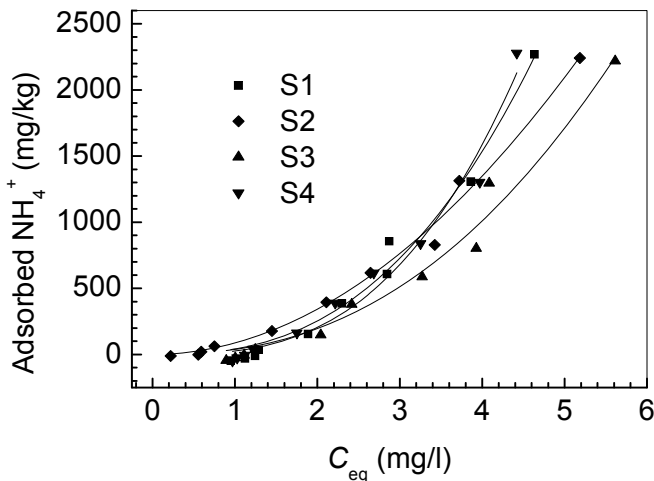


Fig. 2. NH_4^+ adsorption isotherm

Table 2. The parameters of Freundlich isotherm

	S1	S2	S3	S4
K	41.85	87.12	38.11	26.49
n	2.60	1.98	2.36	2.95
R^2	0.98	0.99	0.98	0.97

The adsorbed NH_4^+ was negative while C_{eq} was less than a specific value (Fig. 2). It demonstrated that sediments released NH_4^+ . Therefore, when the adsorbed NH_4^+ was zero, it was considered important and it has a special meaning. Similar to the report by Zhou et al. (2005), we called the C_{eq} adsorption/desorption equilibrium concentration (ENC_0) while the adsorbed NH_4^+ was zero, in other words when C_{eq} is lower than ENC_0 sediments will release NH_4^+ , otherwise they will adsorb NH_4^+ . The ENC_0 values in Fig. 2 were 1.25, 0.57, 1.15 and 1.14 mg L^{-1} respectively for S1, S2, S3 and S4. This indicates that S2 was easier adsorbing NH_4^+ than S1, S3 and S4. The NH_4^+ concentrations were ranged from 0.12–0.15 mg L^{-1} in the Fen River reservoir, more than the concentration in rivers, and less than ENC_0 . Therefore, the sediments in the Fen River reservoir released NH_4^+ to reservoir water and acted as a pollution source, according to the comparison of values of NH_4^+ concentration in reservoirs and rivers.

It was reported that EPC_0 has a positive relationship with NAP (native adsorbed phosphorus) (Aminot and Andrieux 1996) in sediment (Zhou et al. 2005, Aminot and Andrieux 1996). There was a similar relationship ($R^2=0.97$) between ENC_0 and NH_4^+ in sediments. As a result, we could estimate the ENC_0 value from the NH_4^+ content, furthermore we could judge roles sediment played in water by comparing the values of ENC_0 and NH_4^+ concentration.

The relationship between CEC and parameter K or n , and the correlation between OM and K are showed in Fig. 3, CEC being positively related to the K ($R^2=0.85$) and negatively related to n (0.95). CEC was a very important parameter that influenced the NH_4^+ adsorption extent and the degree of nonlinearity of adsorption process. The diversity of K and n suggested differences in the extent of the adsorption and the degree of nonlinearity. K had a negative relationship with OM of the sediments ($R^2=0.68$). It indicated that organic material may have a diluting effect on the exchange capacity in fine-grained sediments, and that organic coatings may block ion exchange sites on clay surfaces (Holmboe and Kristensen 2002).

Adsorption kinetics

NH_4^+ adsorption process was a complex kinetic process. The contents of adsorbed NH_4^+ increased rapidly over the first 120 min and then exhibited slow increases over the remainder of the experiment (Fig. 4 left). This 'fast' and 'slow' adsorption patterns indicated that significant adsorption occurs after the first 2 h, which was similar with the previous report (Morin and Morse 1999). The mechanism of adsorption depended on the physical and/or chemical characteristics of the adsorbent as well as on the mass transport process. In order to investigate the mechanism of adsorption, the pseudo-first-order kinetics model, the pseudo-second-order kinetics model, Elovich model and the intra-particle diffusion model were usually used to analyze and model these dynamical adsorption data. However, in the present study, the sediment NH_4^+ adsorption kinetics in the Fen River reservoir was found to conform to Elovich equation. The equations were as follows:

$$\text{Elovich equation: } Q = \alpha + \beta \ln t \quad (3)$$

$$\text{Pseudo first-equation: } \ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

Pseudo second-equation: $t/q_t = 1/(k_2 q_e^2) + t/q_e$ (5)

Intra-particle diffusion equation: $q_t = k_i t^{1/2}$ (6)

Where Q and t was the amount adsorbed at time t (mg kg⁻¹), respectively, q_t and q_e were the amount adsorbed at time t and equilibrium (mg kg⁻¹), respectively, t was the sorption time (min), and k_1 and k_2 were sorption contents, α and β were sorption rate content (mg (kg·h)⁻¹) and desorption rate content (mg (kg·h)⁻¹). In the data fitting process, the q_e was designed as the adsorbed amount at the time 720 min. Fitting curves are shown in Fig. 3.

The pseudo first-equation, second-equation and Elovich equation were useful in describing adsorption on highly heterogeneous adsorbents (Demirbas et al. 2008). Therefore,

using these models could effectively describe the NH₄⁺ adsorption kinetics process by the Fen River reservoir sediment. The NH₄⁺ adsorption kinetics process was modeled using Elovich (Fig. 4 left) equation and pseudo-second-order (Fig. 4 right) model. The figure on the left indicates that the amount of adsorbed NH₄⁺ increased rapidly with the increasing time within the initial dozens minute. After this time, the adsorption process slowly reached equilibrium with a slow adsorption rate.

The correlation coefficients and other parameters calculated from the pseudo-first-order, pseudo-second-order and Elovich models are given in Table 3. It was observed that the first-order kinetics model did not adequately fit the experimental values ($R^2 \geq 0.52$) (Table 3). In contrast, the Elovich equation and pseudo-second order for sorption of NH₄⁺ on sediment agreed well with the data. It indicated that the sediment in the Fen

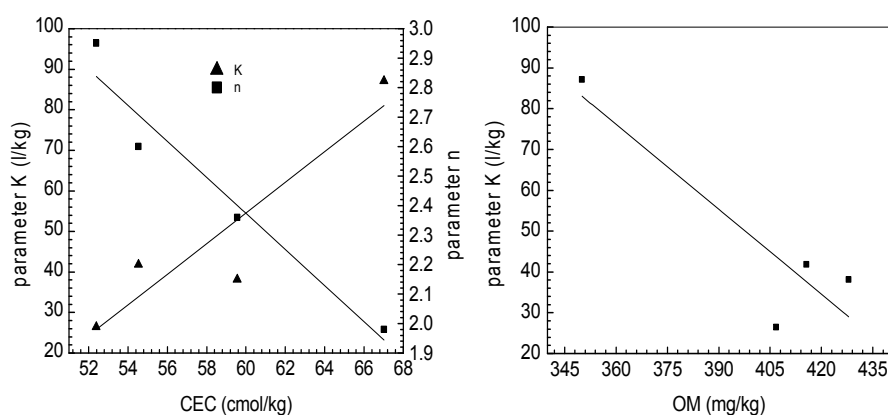


Fig. 3. Relationship between Freundlich isotherm parameters with CEC and OM

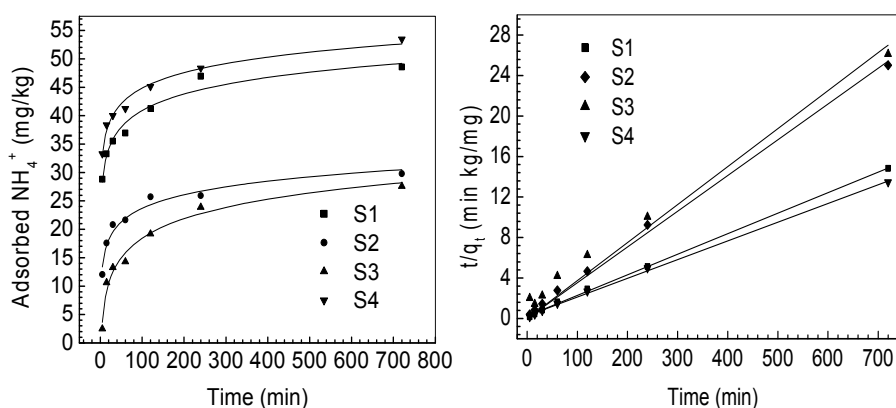


Fig. 4. NH₄⁺ Adsorption kinetic process

Table 3. The parameters of Elovich equation

Sample	Elovich equation			Pseudo first-equation		Pseudo second-equation		
	α	β	R^2	K_1	R^2	K_2	q_e	R^2
S1	21.55	4.20	0.96	-0.013	0.62	0.0016	49.29	0.99
S2	7.85	3.44	0.96	-0.028	0.92	-3.76	28.33	0.99
S3	-4.33	4.94	0.98	-0.030	0.97	-2.05	26.67	0.96
S4	26.71	3.94	0.98	-0.011	0.52	0.0013	54.04	0.99

Rvier reservoir had a complex and heterogeneous adsorbents and more than one-step involved in the sorption processes, which agreed with other studies (Ji et al. 2007, Gurses et al. 2004, Qzcan et al. 2006). However, the Intra-particle diffusion equation could not fit the data, it indicated that the interior diffusion was not dominant ion action during the ion sorption process.

Conclusion

The present study showed that the NH_4^+ adsorption by sediments from the Fen River reservoir fitted to the Freundlich adsorption isotherm. Q increased with the increase of C_{eq} . CEC was an important factor influenced by the ammonium adsorption, and had a significant positive and negative correlation with the parameters K and n , while K had a negative relationship with OM. The sediments in the Fen River reservoir released NH_4^+ to reservoir water and acted as a pollution source. ENC_0 had a positive relationship with the NH_4^+ contained in sediments. We were able to estimate that the ENC_0 value from the NH_4^+ content and judged sediments acted as “ NH_4^+ pollution source” or “ NH_4^+ source sink” by comparing the values of ENC_0 and NH_4^+ concentration in water. The sediment in the Fen River reservoir was a complex and heterogeneous adsorbent, and more than one-step may be involved in the NH_4^+ sorption processes. The NH_4^+ adsorption kinetics process was composed of ‘fast’ and ‘slow’ reaction patterns and could be fitted by Elovich equation and Pseudo second-equation. Further studies are needed to analyze the sediment which could adsorb NH_4^+ , and evaluate the effects of this sediment behavior on the reservoir ecosystem and surrounding environment.

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