Adsorption and desorption characteristics of ammonium in eight loams irrigated with reclaimed wastewater from intensive hogpen

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Abstract There are many reports of NO_3^- violating safety standards in the neighboring areas of concentrated animal feeding operations (CAFOs), which have become the bottleneck of the CAFOs development. The high concentration of ammonium nitrogen ($\text{NH}_4^+\text{-N}$), which transforms into nitrate nitrogen ($\text{NO}_3^-\text{-N}$) through nitrification, and then leaches into the groundwater, is a potential threat to the environment. Adsorption and desorption characteristics of ammonium can reduce the amount of $\text{NH}_4^+\text{-N}$ in soils, which effectively prevents or slows down the nitrate leaching. Researches on the adsorption and desorption of ammonium mainly focus on the simple NH_4^+ solution. Researches on the adsorption and desorption from hogpen wastewater are few, which is a complex system coexisting with many ions. In this paper, ammonium was selected as the object of pollutant, a batch of equilibration experiments was conducted to evaluate the adsorption–desorption and its kinetics in eight loams, typically found in Northern China, irrigated with original wastewater (OW) and reclaimed

wastewater (RW) from intensive hogpen and a simple one consisting of clean water (CW). This study showed that the Freundlich and Langmuir model described the ammonium adsorption properties very well in multi-ion coexistent system of hogpen wastewater; the ammonium adsorbed amount in the corresponding matrices followed by $\text{OW} < \text{RW} < \text{CW}$ tendency, although the adsorption model parameters had great diversity. The adsorbed amount increased as the adsorption time went on and then approached to a stable state. CW had the shortest reaction time to reach equilibrium, whereas OW had the longest. The normal adsorption kinetics equation could not depict the adsorption behavior of loams but characterized by the ExpAssoc equation well. The study could provide references for the wastewater treatment and recycling, and rural water pollution controlling.

Keywords Hogpen wastewater · Loams · Adsorption and desorption · $\text{NH}_4^+\text{-N}$ · Kinetics

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Introduction

The rapid development of concentrated animal feeding operations (CAFOs) had made great contributions to economic construction and living standards of the residents in urban and rural areas, and had become the pillar industry for the rural economy and even for the whole national economic development. But CAFOs brought great amount of dejection and wastewater as it provided people with rich products. According to estimates, the output of wastewater was more than 2.7 billion tons in 2006; if washing water were to be estimated, the actual amount would exceed 10 billion tons (Zhu and Huang 2010). For various reasons, much of the wastewater was discharged without proper

treatments, and contained excess amount of nutrients, salts, BOD₅, chemical oxygen demand (COD), heavy metals, microbial pathogens, antibiotics, and natural and synthetic hormones. This posed a great threat to surrounding soils, surface and ground water, even to human health. Meanwhile, the dejection and wastewater contains relatively high concentrations of N, P, K, trace elements and other nutrient substances necessary for plant growth. The wastewater has long been the most important water and fertilizer resource in agricultural production (Jokela 1992; Kapkiyai et al. 1999). Comprehensive consideration of the three characteristics (water source, fertilizer source, and pollution source), the reuse of it for irrigation through proper treatments is a simple and effective way (Scott et al. 2008); there are many reports about the reuse of wastewater for field crops and vegetables (Wu et al. 2007; Singh and Agrawal 1985).

In general, the treatment of wastewater is to reduce the high concentrations of COD, BOD₅ TSS and to conserve fertilizer. Wastewater often contains relatively high concentrations of N, P, inorganic cations and anions, organic matter, and other compounds. Ammonium is one of the dominant inorganic chemical constituents in CAFOs wastewater with concentrations varying from 600 to 2,000 mg/L, accounting for almost 99 % of the soluble N (Ham and DeSutter 1999). Consequently, the high concentration of NH₄⁺-N is a potential threat to the environment and human health. NO₃⁻-N migrates much faster than ammonium under the same condition. A number of researches have been reported on nitrate level exceeding the safety limit in the neighboring areas of CAFOs (Ciravolo et al. 1979; Eli et al. 2004; Pierre et al. 2005; Karr et al. 2001; Evans et al. 1984; Sloan et al. 1999; David et al. 2005; Donald et al. 2001). Adsorption and desorption characteristics of ammonium played an important role in the regulation of the NH₄⁺-N amount in soils. They prevented or slowed down the transformation and transportation of N. This could be achieved by enhancing the soil sorption of waste-derived ammonium which in turn decreased the substrate, i.e. ammonium, concentration for the nitrification process. Thus, adsorption and desorption phenomenon becomes a regulatory factor for possible NO₃⁻-N leaching. Knowledge of ammonium adsorption and desorption behaviors in soils may help in understanding as well as regulating the rate of NH₄⁺-N in relation to NO₃⁻-N leaching to groundwater. However, the research about adsorption and desorption in soils mainly focuses on the simple ammonium solution. No studies have been conducted to study the adsorption of ammonium from a more complex system such as CAFO wastewater. Comparing solutions of NH₄⁺ salts with those of CAFO wastewater, one could expect to observe different behaviors in soil adsorption and desorption of NH₄⁺. This is

because CAFO wastewater has a higher ionic strength, high concentrations of certain cations and salts, a higher pH value compared to a solution of an NH₄⁺ salt. One or more of these features may play an important role in the differential adsorption–desorption behaviors between the simple and complex matrix systems. Researches on adsorption and desorption from wastewater are scarce. What is more, the soils that have been studied for ammonium adsorption in the past were only focused on vermiculitic type clay loam (Evangel et al. 1986; Lumbanraja and Evangelou 1990; Lumbanraja and Evangelou 1994) and kaolinitic, sandy soils (Wang and Alva 2000), and some tropical soils (Dalal 1975; Paricha and Singh 1977).

At present, the processing techniques of wastewater fall into two main types: natural and industrialized treatment, of which anaerobic treatment is the most widely used because of its low investment and operating cost, good purifying effect, high-efficiency of utilization of energy and environment. Based on the original wastewater (OW) and reclaimed wastewater (RW) with anaerobic treatment from intensive hogpen, batch equilibration experiments were conducted to evaluate the adsorption and desorption of ammonium in eight loams of North China, exposed to a complex matrix (OW and RW) and a simple matrix [aqueous solution of 0.01 M CaCl₂ containing (NH₄Cl)]. The primary objective of this study was to understand the adsorption and desorption characteristics of ammonium in loams and to provide theoretical bases for wastewater reuse and risk assessment of groundwater nitrate contamination. It is believed that of great importance to the fertilization management and environmental protection.

Materials and methods

Materials

Wastewater sample includes the OW and RW of hogpen. The simple matrix NH₄Cl solution with 99.5 % purity provided by Beijing Chemical Plant was the contrast solution. Wastewater was collected from the Yililai pig farm in Yangliuqing Town of Tianjin City. The pig farm has 19 brick-concrete piggeries with approximate area of structure 7,000 m² and produces around 8,600 pigs annually. The main sources of hogpen wastewater were urine, washing water (mainly includes washing feces water, flushing water of flume, cleaning water of ground and equipment), and a little factory sewage. In the production process, adopting dry cleaning manure technique to reduce the wastewater discharged and pollutant concentration. The amount of wastewater disposal was 20–30 m³/day. The wastewater sample was the effluent from the wastewater treatment processes at different locations in the flow

Fig. 1 Hogpen wastewater process flow diagram. 1 feed port, 2 grating, 3 sludge collector, 4 automatic control system, 5 lift pump, 6 warming flume, 7 skylight window, 8 airway tube, 9 overflow pipe, 10 feeding pipe, 11 caliduct and heat sink, 12 stuffing, 13 sludge interceptor wall, 14 OW outlet, 15 RW outlet

system, the process of flow diagram was shown in Fig. 1. The first effluent sample was the OW, which was collected into the pretreatment tank through the sewage drains, then filtered and homogenized. The OW was raised to a high-rate anaerobic treatment pond to remove most of the COD. The effluent sample after anaerobic treatment was the RW. The water-quality indices of OW and RW were shown in Table 1.

The experimental loam soils were collected in Northern China, categorized by texture into loam, silty loam, and sandy loam. The soils were sampled from the surface (0–30 cm) of the selected locations, air dried, and ground, finally sieved through a 1-mm sieve to eliminate plant debris and soil clods. The soil particle composition and some important characteristics were listed in Tables 2 and 3.

Batch adsorption–desorption experiments

Adsorption studies were conducted according to OECD guidelines 106 (OECD 2000). 2.5 g of soil was mixed with 25 mL RW (in 0, 1, 3, 4, 6, 10 and 20 diluted concentrations) in a 50 mL polyethylene centrifuge tube, shaken at 180 strokes/min for 24 h in the dark under the temperature of 25 °C, then centrifuged at 4,000 r/min for 10 min. The

Table 1 The chemical composition of irrigation wastewater

	NH ₄ ⁺ -N (mg/L)	NO ₃ ⁻ -N (mg/L)	TN (mg/L)	TP (mg/L)	COD (mg/L)	SS (mg/L)
OW	900	2.84	1,985	247	6,578	2,684
RW	450	2.45	300	12	305	268

supernatants were filtered (0.45 μm) and analyzed for NH₄⁺-N. The amount of ammonium adsorbed by soil was calculated based on the initial and final NH₄⁺-N concentrations in the solution. The concentrations of CW and OW remained same as RW.

The residual soil samples from the above-mentioned adsorption experiment were mixed with 25 mL of 0.04 mol/L CaCl₂ solution in a 50 mL polyethylene centrifuge tube and shaken for 24 h by using the same conditions as described for the adsorption experiments. Supernatants were obtained by centrifugation, filtering, and then analyzed for NH₄⁺-N. The amount of NH₄⁺-N desorbed was calculated based on the NH₄⁺-N concentration in the supernatants after adjusted for the NH₄⁺ in the entrained soil solution from the adsorption experiments.

Each experiment was repeated three times and the NH₄⁺-N concentration was measured by ISC1500 Ion

Table 2 The soil particle composition of eight soils

No.	Soils	Particle size distribution (%)			Soil texture	Soil classification system of China	Sampling point
		Sand	Silt	Clay			
1	TY	34	55	11	Loam	Moisture soil	Yangliuqing, Xiqing, Tianjin
2	BY	54	36	10	Loam	Moist soil	Yongledian, Tongzhou, Beijing
3	BH	36	47	17	Silty loam	Cinnamon soil	Sijiqing, Haidian, Beijing
4	BD	30	50	20	Silty loam	Moisture soil	Beiyechang, Daxing, Beijing
5	BG	48	41	11	Silty loam	Brown alluvial soil	Yingezhuang, Tongzhou, Beijing
6	BX	38	29	9	Silty loam	Brown alluvial soil	Xingezhuang, Tongzhou, Beijing
7	TD	58	29	13	Silty loam	Coastal saline soil	Beiweidi, Dagang, Tianjin
8	HQ	66	20	14	Silty loam	Sandy soil	Qiqiha'er, Heilongjiang

Table 3 Some physicochemical properties of eight soils

Soils	NH ₄ ⁺ -N (mg/kg)	NO ₃ ⁻ -N (mg/kg)	TN (g/kg)	Organic matter (g/kg)	CEC (mmol/kg)	pH	EC (μs/cm)
TY	65.53	211.53	0.55	8.84	105	7.93	8,360
BY	20.20	10.03	0.42	6.55	100	8.40	1,710
BH	34.43	9.47	0.88	15.10	169	8.25	1,680
BD	54.92	11.88	0.53	8.60	150	8.29	2,140
BG	16.40	8.64	1.65	26.30	177	7.75	1,770
BX	20.36	18.77	0.53	8.48	114	8.09	1,310
TD	37.77	247.03	0.93	16.10	112	8.21	11,960
HQ	31.43	17.92	1.32	22.90	185	8.38	2,040

Table 4 Four adsorption models of soils

	Number	Model	Equation	Adjustable model parameters
	1	Henry	$S = KC$	K = adsorption equilibrium constant;
	2	Langmuir	$C/S = 1/(S_{\max}K) + C/S_{\max}$	S_m = maximum amount adsorbed per gram of soil(mg/kg); $MBC = S_{\max} \times K$ = maximum buffer capacity of soil
	3	Freundlich	$S = KC^{1/n}$	K = distribution coefficient; $1/n$ = the isotherm nonlinearity factor
	4	Temkin	$S = a + \ln C$	a = undetermined coefficients

S = amount adsorbed per gram of soil (mg/kg);
 C = equilibrium solution concentration (mg/L)

Chromatograph. The data of ammonium adsorbed amount and concentration in soils were fitted by Henry, Langmuir, Freundlich and Temkin models, which were shown in Table 4.

Adsorption kinetics experiments

2.5 g of soil was mixed with 25 mL RW in 6 diluted concentrations in a 50 mL polyethylene centrifuge tube, shaken at 180 strokes/min for 1, 3, 5, 8, 12, 14, 24, 36, 48 h in the dark under the temperature of 25 °C, centrifuged by

using the conditions described as the above adsorption–desorption experiments, and analyzed NH₄⁺-N concentrations. The amount of NH₄⁺-N was calculated based on the differences between the initial and final NH₄⁺-N concentrations in the supernatants. The concentrations of CW and OW remained same as RW.

Each experiment was repeated three times and the concentrations of NH₄⁺-N were measured by ISC1500 Ion Chromatograph. The data relations of ammonium absorbed amount and adsorption time were fitted by five kinetics models, which were shown in Table 5.

Table 5 Five kinetics models of soils

Number	Model	Equation
1	First-order kinetic equation	$\ln S = a + bt$
2	Second-order kinetic equation	$1/s = a + bt$
3	Parabolic diffusion equation	$S = a + bt^{1/2}$
4	Elovich equation	$S = a + b \ln t$
5	ExpAssoc equation	$S = A_1(1 - e^{-t/a}) + A_2(1 - e^{-t/b})$

S = amount adsorbed per gram of soil at time t (mg/kg);
 t = adsorption time (h); a , b , A_1 , A_2 = fitting parameters

Results and analysis

Adsorption–desorption of ammonium in soils

Figure 2 shows the adsorption–desorption isotherms in eight soils exposed to OW, RW and CW. As could be seen, the ammonium adsorbed amount in eight soils showed the $OW < RW < CW$ tendency. For RW, the equilibrium concentration range was 0–300 mg/L and the amount of ammonium adsorbed was in the range 0–3,000 mg/L. For OW it was 0–500 and 0–1,000 mg/L. Whereas for CW it was 0–100 and 0–4,000 mg/L. Among the eight loams, ammonium adsorbed amount exposed to CW differed little, which could be ignored. For OW and RW, at low concentrations the ammonium adsorbed amounts were very similar, while at high concentrations the difference gradually became evident and showed a $TY > TD > BH > BY > BG > BX > HQ > BD$ variation trend. Overall, the ammonium adsorbed amount of eight loams increased with the concentration exposed to the three solutions. The whole tendency of adsorption and desorption isotherm was accordant. The two aspects of the experiments, however, were not invertible. They exhibited a certain hysteresis effect; that is, the ammonium desorbed amount had a little bit decrease than adsorbed amount.

Adsorption model fitting and characteristic parameters

Table 6 displays the ammonium adsorption data of eight loams exposed to OW, RW and CW, which were fitted by Henry, Freundlich, Langmuir and Temkin models. As can be seen, the Freundlich and Langmuir models were the best models, for the correlation coefficients were all above 0.85. For different water quality, CW was obviously better than OW and RW, while OW and RW were not effective enough. The Freundlich and Langmuir models could reflect some adsorption properties on soils; it is relatively reasonable to describe the NH_4^+ -N adsorption properties by Freundlich and Langmuir models.

Fig. 2 Adsorption–desorption isotherms of eight soils exposed to OW, RW and CW. The absorption N amount is shown with solid lines, whereas dashed lines show desorption N amount

Among eight tested soils, it is shown in Table 6 that the Langmuir parameters K and S_{max} demonstrated no regularity in variation. For example, S_{max} was 811.03–1,544.16 mg/L in OW and the order was $BY < TD < BD < BG < BH < BX < TY < HQ$; for RW S_{max} was 1,330.48–3,358.36 mg/L and the order was $TY < BD < BY < BX < TD < BG < HQ < BH$; for CW S_{max} was 6,218.39–9,744.51 mg/L and ordered in $BD < BY < BX < TD < BG < TY < HQ < BH$. Similarly, the Freundlich parameter $1/n$ had no obvious regularity.

With regard to different water samples, the S_{max} parameter was the highest for CW, followed by RW and OW.

Adsorption kinetics of ammonium in loams

One loam (TY), two clay loams (BH and BD), and two sandy loams (TD and HQ) were selected for the N

Table 6 The fitting results of four adsorption models for CW, RW and OW

Water sample	Soil type	Henry			Langmuir			Freundlich			Temkin		
		a	K_d	R^2	$S_{\max}$	K	R^2	$1/n$	K_f	R^2	a	K	R^2
OW	TY	230.7	1.32	0.87	1,336.42	0.0048	0.95	0.85	35.44	0.93	−401.5	182.4	0.92
	BY	174.2	1.16	0.96	811.03	0.0058	0.92	0.73	32.65	0.98	−351.6	153.3	0.89
	BH	293.9	0.84	0.79	1231.90	0.0072	0.96	0.84	102.23	0.93	−110.0	110.3	0.93
	BD	150.7	1.42	0.74	958.67	0.0065	0.93	0.6	35.19	0.85	−552.7	199.0	0.64
	BG	68.89	1.26	0.98	1,045.67	0.0033	0.98	0.75	15.4	0.99	−482.2	146.9	0.81
	BX	68.89	1.16	0.98	1,240.79	0.0038	0.97	0.5	20.81	0.99	−1,111	352.0	0.75
	TD	217.5	1.10	0.72	819.44	0.0088	0.90	0.95	48.6	0.85	−465.0	184.6	0.94
	HQ	112.7	1.81	0.96	1,544.16	0.0027	0.94	0.78	17.99	0.93	−555.3	205.7	0.84
RW	TY	64.7	5.40	0.98	1,330.48	0.0079	0.97	0.49	55.88	0.96	−978	384.8	0.71
	BY	121.7	3.64	0.98	1,914.71	0.0037	0.96	0.63	28.04	0.99	−783.8	310.5	0.79
	BH	173.8	4.60	0.96	3,358.36	0.0027	0.97	0.71	26	0.97	−832.5	359.2	0.79
	BD	139.5	1.65	0.86	1,402.76	0.0070	0.89	0.53	45.71	0.85	−358.0	188.4	0.71
	BG	103.8	2.61	0.98	2,841.37	0.0015	0.91	0.74	12.55	0.94	−512.8	213.0	0.77
	BX	256.9	1.40	0.74	1,983.68	0.0068	0.97	0.54	56.03	0.98	−219.0	152.3	0.98
	TD	55.9	5.53	0.98	2,399.07	0.0040	0.91	0.66	29.24	0.95	−1,434	487.2	0.85
	HQ	168.0	2.40	0.88	3,283.40	0.0018	0.98	0.74	17.04	0.94	−358.0	188.4	0.74
CW	TY	178.9	65.06	0.99	9,218.91	0.0089	0.98	0.54	106.99	0.98	−816.3	822.0	0.82
	BY	330.4	49.79	0.98	7,643.31	0.0108	0.99	0.49	146.86	0.99	−612.1	726.6	0.86
	BH	174.3	64.44	0.99	9,744.51	0.0076	0.99	0.3	111.19	0.99	−915.2	955.1	0.83
	BD	461.2	46.17	0.98	6,218.39	0.0169	0.97	0.5	238.18	0.99	−206.7	739.0	0.83
	BG	289.0	43.67	0.99	8,622.01	0.0067	0.95	0.61	110.92	0.97	−589.8	675.5	0.83
	BX	491.5	44.78	0.98	7,761.61	0.0126	0.97	0.6	326.54	0.96	−212.4	751.2	0.82
	TD	102.5	48.15	0.94	8,238.62	0.0084	0.99	0.43	55.97	0.93	−1,092	883.7	0.81
	HQ	282.3	60.65	0.99	9,271.92	0.0830	0.97	0.63	106.99	0.98	−179.5	722.6	0.80

adsorption kinetics experiments, using five kinetic models to fit the adsorption kinetics, shown in Table 7. It could be found that the ExpAssoc equation was the best fitting model. With regard to water samples, the relative coefficients of the five soils reached absolute significance levels ($R^2 > 0.90$).

The ammonium adsorption kinetics and ExpAssoc fitting curves can be seen from Fig. 3. It could be found that the adsorption rate was high at the initial time, and decreased gradually as time went on. Simultaneously the adsorbed amount showed greater volatility in the previous 12 h, and then tended to be stable. The adsorption equilibrium time was inconsistent, that CW was the shortest and OW the longest. Meanwhile, the ammonium adsorbed amount and the relative coefficients presented the tendency of $CW > RW > OW$, which was consistent with the adsorption experiment results.

Discussions

Nitrates taken by soil seepage water enter underground seepage zone and groundwater after leaving the crop root

area. This part of nitrogen is often not used by anti-nitro-bacteria in plants and topsoil and will eventually enter the groundwater. The strength of nitrification in the transfer from NH_4^+ -N to NO_3^- -N is the key to measuring the loss value of nitrate leaching. It has been reported that NO_3^- -N formed from NH_4^+ -N in animal waste makes a significant contribution to the elevated NO_3^- -N levels in groundwater in many locations. As early as 1960s to 1970s, the NO_3^- -N pollution problem in soil and groundwater caused by livestock manures appeared in many countries and regions with well-developed animal husbandry. Ciravolo et al. (1979) reported that Cl^- and NO_3^- -N concentrations in the groundwater around a swine waste lagoon constructed on a sandy subsurface soil in the coastal plain region of Virginia exceeded the USEPA drinking water standard of 10 mg/L NO_3 -N. In south Netherlands, the livestock manures produced by animal husbandry exceeded the amount of normal agricultural use, resulting in the soil NO_3^- -N pollution. Animal manures in Belgium are approximately 41.0 million tons every year, and 8.0 million tons in excess of the standard (Eli et al. 2004). Brittany province, which occupied 40 % of France's intensive livestock production, had one region whose NO_3^- -N concentrations in public water

Table 7 The fitting results of five adsorption kinetic models for CW, RW and OW

Water sample	Soil type	$\ln S = a + bt$			$1/S = a + bt$			$S = a + bt^{1/2}$			$S = a + b \ln t$			$S = A_1(1 - e^{-t/a}) + A_2(1 - e^{-t/b})$				
		a	b	R^2	a	b	R^2	a	b	R^2	a	b	R^2	A_1	a	A_2	b	R^2
OW	TY	5.052	0.019	0.29	0.000	7E-03	0.36	109.46	39.76	0.31	88.06	73.68	0.43	177.37	5.77	177.37	5.77	0.67
	BH	5.300	0.008	0.21	0.000	5E-03	0.23	181.33	16.16	0.23	175.05	28.91	0.30	116.9	2.81	116.9	2.81	0.69
	BD	5.481	0.000	0.00	0.000	4E-03	0.01	246.82	1.15	0.00	232.83	7.90	0.02	95.69	0.18	95.69	0.18	0.86
	TD	4.765	0.022	0.60	0.000	9E-03	0.54	59.92	35.06	0.67	62.86	55.57	0.68	123.61	11.10	123.61	11.10	0.80
	HQ	5.452	0.003	0.04	0.000	5E-03	0.08	225.49	9.90	0.05	213.84	21.08	0.09	135.77	0.73	135.77	0.73	0.54
RW	TY	5.71	0.018	0.38	0.003	5E-05	0.37	216.97	64.10	0.49	198.4	111.8	0.59	221.48	2.98	221.58	2.91	0.69
	BH	6.42	0.005	0.23	0.220	-9E-06	0.22	557.21	36.36	0.30	550.8	61.68	0.35	358.70	0.81	358.70	0.81	0.82
	BD	6.07	0.003	0.19	0.002	-9E-06	0.20	414.22	14.05	0.19	423.4	18.80	0.14	233.49	0.0006	233.49	0.0006	0.86
	TD	5.82	0.004	0.07	0.003	-1E-05	0.08	324.64	15.26	0.08	202.6	66.45	0.34	170.37	0.65	170.37	0.65	0.77
	HQ	5.97	0.017	0.44	0.002	-4E-05	0.37	286.16	77.56	0.57	318.3	27.47	0.10	316.7	6.53	316.7	6.53	0.78
CW	TY	7.903	0.004	0.50	0.000	2E-06	0.49	2,639.22	135.38	0.32	84.47	56.06	0.56	1,476.43	0.001	1,476.43	0.001	0.92
	BH	8.041	0.001	0.16	0.000	3E-07	0.15	3,105.50	27.76	0.07	50.35	111.4	0.50	1,584.90	0.001	1,584.90	0.001	0.98
	BD	7.969	0.003	0.49	0.000	1E-06	0.47	2,798.50	113.37	0.44	148.2	36.41	0.22	1,530.57	0.012	1,530.57	0.012	0.96
	TD	5.569	0.074	0.20	0.000	-3E-06	0.39	1,951.34	356.34	0.77	63.26	40.02	0.77	1,455.22	1.73	1,455.22	1.73	0.94
	HQ	7.956	0.004	0.57	0.000	1E-06	0.54	2,706.00	182.18	0.56	47.27	136.10	0.31	1,562.53	0.34	1,562.53	0.34	0.93

exceeded drinking water standard in the early 1980s. In 2004, there were 6 regions exceeding the standard and 21 regions being close to the standard (Pierre et al. 2005). Karr et al. (2001) found high concentrations of NO_3^- -N in groundwater from commercial swine farms in the mid-Atlantic coastal plain. Average annual NO_3^- -N concentrations from 5 to 30 mg/L have been reported in subsurface drainage beneath spray fields in North Carolina (Evans et al. 1984; Sloan et al. 1999). In Oklahoma, the NO_3^- -N discharged from pig farm by coastline resulted in drinking water pollution. US EPA issued an emergency statement in June 2001, which demanded that these livestock farms take measures to make the drinking water safe again (David et al. 2005). In Indiana, the research results of Disease Control Center showed that spontaneous abortions were closely related to the high NO_3^- -N content in the drinking water near the livestock farms (Donald et al. 2001). Because of the latent threat of NO_3^- -N to human health, World Health Organization (WHO) advised that NO_3^- -N in drinking water should not exceed 50 mg/L, believed that NO_3^- -N consumed by an adult weighing 60 kg should be less than 220 g, so the pollution of NO_3^- -N to groundwater, caused by CAFOs such as pig farms, had aroused wide attentions of many scientists.

It was understood that much of the NO_3^- -N that could lead to contamination of groundwater was derived from NH_4^+ -N in hogpen lagoon effluent. As the levels of NH_4^+ -N in soil solution increased, fixation and adsorption of ammonium on exchanging sites of clay minerals and organic matters also increased. It often took 2 weeks for NH_4^+ -N to transfer into NO_3^- -N, the soil could only keep high concentrations in a short time after fertilization (Liu et al. 2003; Zhu and Zhang 2010). At other times the concentrations were low (generally lower than 3 mg/kg). This fact made experiments on the NH_4^+ -N adsorption and desorption in soils hard. Ammonium adsorption in soil has been limited to the batch equilibrium experiments with various solutions such as NH_4Cl (Thompson and Blackmer 1992; Lumbanraja and Evangelou 1994; Wang and Alva 2000), NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, and $\text{NH}_4\text{H}_2\text{PO}_4$ (Dalal 1975). No researches have been found to study the interactions of ammonium with soils exposed to CAFOs wastewater (especially hogpen wastewater), which has a much more complex matrix than the above listed ammonium salt solutions. Wastewater from intensive hogpen is rich in organic substances and has a relatively higher ionic strength, higher concentrations of major cations and anions, and a higher pH value compared with a normal soil solution (Yasuhara et al. 1984; Ham and DeSutter 1999). This may be quite different from the previous studies where NH_4^+ ions were derived from simple NH_4^+ salt solutions.

Of NH_4^+ -N in the soil, there is always a dynamic balance in the adsorption and desorption process. When there

Fig. 3 Adsorption kinetics and ExpAssoc fitting curves of $\text{NH}_4^+\text{-N}$ in five soils

are other ions or substance around, it will destroy this balance, to produce competitive adsorption and therefore a new balance is advanced. In this paper, eight representative loams in North China were selected to carry out adsorption and adsorption kinetic batch balance experiments of three water qualities (OW, RW, and CW). It was found that the adsorbed amount and $S_{\max}$ of equilibrium liquid, with the same concentrations for all eight loams, showed the rule of $\text{OW} < \text{RW} < \text{CW}$. The adsorbed amount exposed to OW and RW were significantly lower than that of CW. The main reason was that the large number of competitive positive ions in competing with NH_4^+ , which influenced the adsorption extent of $\text{NH}_4^+\text{-N}$ and effectiveness in loams. As TY exposed to RW for example, the changing curves of NH_4^+ , K^+ , Ca^{2+} , Na^+ and Mg^{2+} adsorbed

Fig. 4 The changing curves of NH_4^+ , K^+ , Ca^{2+} , Na^+ and Mg^{2+} adsorbed amount with time in TY exposed to RW

amount with respect to time were shown in Fig. 4. As the adsorption progressed, K^+ and NH_4^+ appeared as adsorption whereas Ca^{2+} , Na^+ , and Mg^{2+} were separated out. This phenomenon was mainly due to multi-ion coexistence, so soils would show preferences in ions and cations exchange reactions come in combination with adsorption. For example, NH_4^+ and K^+ have a similar ionic radius and physical properties, and thus would compete for outer adsorption sites as well as interlayer fixation sites in soil, obeying the ideal cations exchange theory (Rich and Black. 1964; Kittrick 1966). Thus, the amount of ammonium adsorbed plus fixed should be less when K^+ and NH_4^+ are simultaneously added to the soil than in the absence of K^+ (Lumbanraja and Evangelou 1990). This observation was also applicable for other soils (Levy et al. 1986). Meanwhile, because of ion-exchange adsorption, Ca^{2+} , Na^+ and Mg^{2+} precipitated gradually, which made the adsorption equilibrium time of RW and OW greater than that of CW. The experimental results of adsorption kinetics confirmed this.

Conclusions

Through the study of this thesis, we can draw the following three conclusions:

1. Exposed to the three tested water, the ammonium adsorbed amounts of eight loams increased with the equilibrium concentrations. The ammonium adsorbed amount and $S_{\max}$ both showed $\text{OW} < \text{RW} < \text{CW}$ tendency. It is mainly because OW and RW were multi-ion coexistent systems and the loams had apparent competitive adsorption on $\text{NH}_4^+\text{-N}$.
2. The Freundlich and Langmuir model could describe the $\text{NH}_4^+\text{-N}$ adsorption properties of eight tested loams exposed to CW, RW and OW very well. The adsorption model parameters K , $S_{\max}$ and $1/n$ had great diversity, demonstrating no regularity in variation.

3. The adsorption rates of the eight tested soils were high at the initial time, and then decreased gradually. During the initial 12 h, the ammonium adsorbed amount showed greater volatility and then approached a stable state. The adsorption equilibrium time for CW was the shortest and that for OW was the longest. The ExpAssoc equation could depict the Kinetic behavior of NH_4^+ -N very well.

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