Journal of Environmental Sciences Vol.9, No.4, pp.411—416, 1997 ISSN 1001—0742

Migration process of ammonium ion in saturated silty sand and sandy loam

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Abstract—The adsorption characteristics of ammonium ion in saturated silty and sandy loam were studied by means of dynamic soil column experiments. The migration of ammonium ion in soil was modelled with a combined equilibrium and kinetic adsorption model(Cameron's model). The results indicated that the longitudinal dispersion coefficients(D) in silty sand and sandy loam were 0.175 cm^2/min and 0.093 cm^2/min, respectively. The dynamic adsorption capacity of silty sand was 0.156 mg/g and 0.400 mg/g when ammonium ion in water were 13.7 mg/L and 41.0 mg/L respectively; the dynamic adsorption capacity of sandy loam was 1.33 mg/g when concentration of ammonium ion in influent was 51.0 mg/L.

Keywords: ammonium ion; saturated silty sand; saturated sandy loam; migration; dynamic soil column experiment.

1 Introduction

In recent years, the most serious pollutants to soil and groundwater are heavy metals, pesticides and fertilizers in China. Of these, nitrogen is an essential nutrient for plants, and often a limiting one, widely use of nitrogen-containing fertilizers has become commonplace. Nitrogenous compounds exist also in domestic wastewater. Excessive nitrogen compounds may be leached from the root zone and through the soil into groundwater by land treatment of municipal wastewater or use of nitrogenous fertilizers. It do great harm to environment and human being. In order to prevent nitrogen compounds from polluting groundwater, it is necessary to fully understand their attenuation in soil-groundwater system and all related processes, and it will present a scientific basis for developing soil pollution control criteria and adopting corresponding control measures.

Nitrogenous fertilizers include organic nitrogen, ammonia, nitrites and nitrates. The nitrogenous compounds in wastewater exist mainly in the forms of organic nitrogen(about 35%—40%) and ammonia (about 60%—65%; Jiang, 1990). The nitrogenous compounds in nitrogen-containing fertilizers are mostly in form of ammonia nitrogen. Urea which is largely used in agriculture hydrolyzes easily to become ammonia. Therefore, only ammonia will be discussed in this paper and a mathematical model developed to stimulate the adsorption processes of ammonium ion in soil, to calculate the concentration of ammonia to be leaked in groundwater through soil profile, and then to determine whether wastewater will pollute groundwater when it is used to irrigate agricultural land.

2 Fundamental theories

The transportation and transformation of pollutants through a saturated soil are determined by transference of water, and various kinds of physical, chemical and biological reactions between pollutants and soil (Cameron, 1977; Kinzelbach, 1987).

If we only consider the adsorption-desorption processes for specific chemicals in a soil, the assumption that the adsoprtion model may be represented by a first-order kinetic model is commonly made. A first-order reversible kinetic model may be written as:

$$\frac{\partial s}{\partial t} = k_1 \frac{n}{\rho} C_s - k_2 s, \tag{1}$$

where k_1 and k_2 are adsorption and desorption constants respectively, c_s is the concentration of mobile solute in units of mass per volume of solution phase, s is the adsorbed phase concentration in units of mass of adsorbed chemical per mass of soil, ρ is the bulk density of the soil, and n is the volumetric water content. When a solute moves downwards at steady hydraulic flow in saturated uniform porous media with constant water content, the chemical transport model with combined kinetic and equilibrium components may be written as:

$$\frac{\rho}{n} \frac{\partial s_1}{\partial t} + (1 + k_3) \frac{\partial c_s}{\partial t} = D \frac{\partial^2 c_s}{\partial^2 t} - u \frac{\partial c_s}{\partial z}, \tag{2}$$

where s_1 is the adsorbed concentration in kinetic fraction of soil, k_3 is the adsorption equilibrium constant, D is the hydraulic dispersion coefficient, u is the seepage velocity.

The analytical solution of Equation (1) and (2) may be obtained by the use of Laplace transform. From breakthrough curve derived from the dynamic soil column experiment, computer programs can be written to evaluate these parameters in above equation, and the distribution curve of the special chemical in soil profile will also be obtained.

3 Experimental determination of parameters in the chemical transport model

3.1 Experiment materials

Two soils, silty sand and sandy loam from the agricultural land in North China, were used in the experiments. Their dry density ρ is 1.1—1.8 g/cm^3. Soil samples were air-dried at room temperature and passed through a 2 mm sieve, and then packed in bags. Their water content were determined before use.

Dynamic soil column experiments were performed in three glass column 40 mm internal diameter and 400 mm long.

3.2 Experiment methods

Each column was packed in the following order: supporting gravel layer, experiment soil sample layer, protective layer. There was a nylon mesh between two layers. Experimental soil sample layer was packed and consolidated layer by layer to an average bulk dry density 1.1—1.8 g/cm^3. The column was rinsed with clean water for a week to reduce the background value and to stabilize the pore structure and the seepage velocity. During the experiment, experimental water sample flows continuously through the soil column and effuse from its bottom at a steady hydraulic flow controlled by constant head equipment. The seepage velocities in silty sand and sandy loam are

6×10^{-3}—1×10^{-4} cm/s and 1×10^{-4}—6×10^{-4} cm/s respectively.

At the beginning of each experiment, dispersion experiment was conducted. Tracer solution (a conservative material NaCl solution, concentration is 270 mg/L, was used in this experiment) flows continuously through the soil column. The effluent was collected at regular intervals and analyzed for chloride concentration, and then the *c-t* curve (breakthrough curve) was obtained. The dispersion coefficients (D) could be calculated by:

$$D = \frac{L^2(t_{0.5} - t_{0.16})^2}{2t_{0.5}^2 t_{0.16}}, \tag{3}$$

where L is the length of column, $t_{0.5}$ and $t_{0.16}$ are the abscissas at $c/c_0=0.5$ and $c/c_0=0.16$ in the *c-t* curve respectively.

After dispersion coefficients was determined, the column was rinsed with deionized water, and then the ammonia nitrogen breakthrough curves were determined.

4 Results and discussion

4.1 Dispersion experiment

Fig.1 is the breakthrough curve for tracer in the silty sand's dispersion experiment. From Fig.1, we got $t_{0.5}=17.1$ min and $t_{0.16}=15.3$ min. The length L of soil layer in the experiment was 21.8 cm. When these values are given to Equation(3), then the dispersion coefficients D_1 (0.175 cm^2/min) for silty sand and D_2(0.0093 cm^2/min) for sandy loam are resulted.

The experimental results indicated that the dispersion coefficients for various soil layers had great difference, the dispersion coefficient of silty sand was far greater than that of sandy loam.

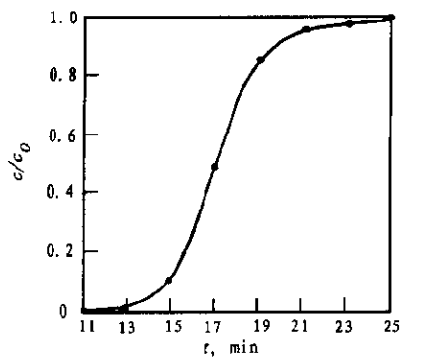

Fig.1 The breakthrough curve for tracer in silty sand

4.2 Ammonia nitrogen breakthrough experiments

Because the concentration of ammonia nitrogen in the general domestic and municipal wastewater is in the range of 10—50 mg/L(Jiang, 1990), the concentrations of ammonia nitrogen solutions in three different breakthrough experiments are 13.7, 41.0 and 51.0 mg/L respectively.

Fig.2 and 3 show the experimental results of different soil samples. In solving transport equation and adsorption model it was convenient to express the parameters and independent variables as dimensionless quantities. The following dimensionless transformations were used in this study:

$$T = vt/L;\quad B = ul/4D;\quad \xi = z/L;\quad C = c_s/c_0;$$

$$N = \rho s/nc_0;\quad N_1 = \rho s_0/nc_0;\quad K_1 = Lk_1/u;\quad K_2 = Lk_2/u;\quad K_3 = k_3.$$

The standardized curve was obtained by applying above dimensionless transformations. Computer programs were written to evaluate these parameters in above equations. At the beginning, we input initial values of model parameter, K_1, K_2 and K_3, then adjust these model

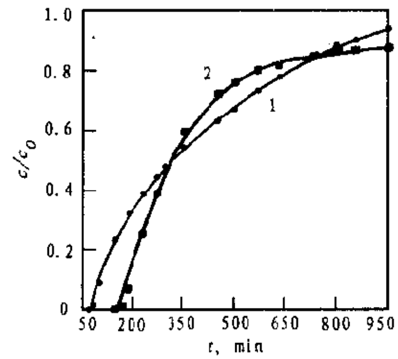

Fig.2 The breakthrough curve for ammonia nitrogen in silty sand

1. $c_1 = 13.7$ mg/L; 2. $c_0 = 41.0$ mg/L

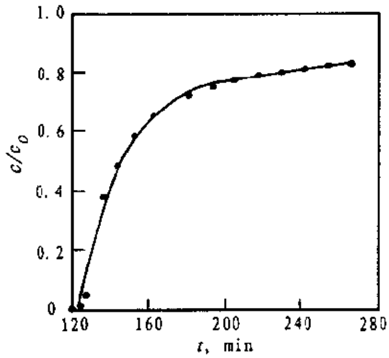

Fig.3 The breakthrough curve for ammonia nitrogen in sandy loam

parameters to make calculated model curve fit with the experimental breakthrough curve. The values of model parameters, k_1, k_2 and k_3 were obtained and shown in Table 1.

Table 1 Values of model parameters

Parameters	Silty sand(No.1)	Silty sand(No.2)	Sandy loam
c_0, mg/L	13.7	41.0	51.0
K_1	1.6	0.35	0.25
K_2	0.1	0.03	0.012
K_3	14	14	50
k_1, min^{-1}	0.1	0.021	0.001
k_2, min^{-1}	0.06	0.002	0.00006
k_3	14	14	50

Fig.4 is breakthrough curve for ammonia nitrogen in a silty sand. The solid line through the points represented the optimized fit of the model. It showed excellent agreement with the experimental data. The other two experiments could draw out similar results (the figures were omitted).

4.3 Adsorptive capacity of soils

When the soil layer in the column was completely saturated by ammonia, the saturated adsorptive capacity could be calculated according to the following equation:

$$S_{eq} = \frac{n}{\rho}\left(\frac{k_1}{k_2} + k_3\right)c_s, \qquad (4)$$

where s_{eq} was the adsorptive capacity, mg/g. The values of n, ρ, k_1, k_2, k_3, c_s were substituted in Equation(4), the adsorptive capacities of soils were obtained and shown in Table 2.

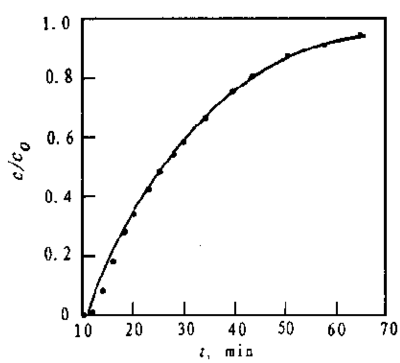

Fig.4 The breakthrough curve for ammonia nitrogen in sandy loam

The solid line is the best fit of the combination model to the data

The experimental results indicated that all soil samples strongly adsorb ammonium ions. Factors which affected adsorptive capacity of soil include soil types and their composition and concentration of ammonia in influent.

Soil types have greatly influence on the adsorptive capacity. Particle size plays an important role. It also influences soil porosity, which in turn influences seepage velocity. The seepage velocity through sandy loam layer is smaller than that through silty sand layer by about 10 times, slow flow presents more chance for ammonium ion to be adsorbed on particle surface. Therefore, the adsorptive capacity of sandy loam is far greater than that of silty sand.

The sandy loam samples taken from North China are a kind of clay whose main component is illites. The illite is characterized by a layered structure consisting of sheets of silicon oxide which is called the tetraledral sheet. There are hexagonal pores in the tetraledral sheet. The pore size is similar to the size of ammonium ion, so ammonium ion is easily entered and plugged into the pores and attracted by negative charge on the pore surface, then fixed firmly in this specific structure. Therefore, ammonium ions are strongly adsorbed on soil particles.

Table 2 Adsorptive capacity of soils

Type of soil	c_0, mg/L	s_{eq}, mg/g
Silty sand	13.7	0.156
Silty sand	41.0	0.400
Sandy loam	51.0	1.33

The adsorptive capacity is also influence by the concentration of ammonia nitrogen in influent. Table 2 illustrates that the greater the concentration of ammonium ion, the greater the adsorptive capacity of soil.

4.4 Distribution curves of ammonium ion in soil profile

After the model parameters K_1, K_2, K_3 were obtained, values of concentration $C(T, \xi)$ (dimensionless) at different depth ξ ($\xi = z/L$, where z is the vertical depth and L is the length of soil layer) for a fixed time were calculated, and the standardized concentration distribution curves in the soil profile were plotted. A concentration distribution curve could be obtained at each point of time. In Fig.5 and 6, we only plotted the concentration curves at T_0(at breakpoint), $T_{0.5}$(at half saturated) and $T_{0.8}$(at 80 per cent saturated) in the column No.1 and column No.2.

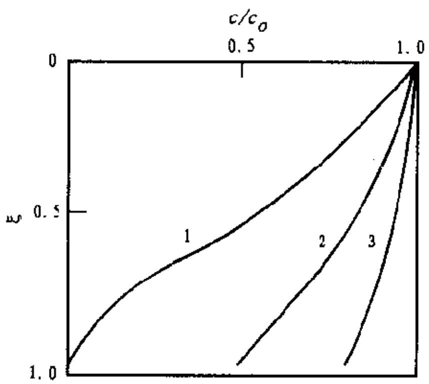

Fig.5 The concentration distribution curves for ammonia nitrogen in soil column No.1
1. $T_0 = 11$ min; 2. $T_{0.5} = 26$ min;
3. $T_{0.8} = 44$ min

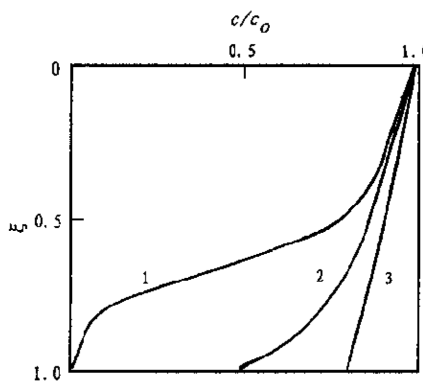

Fig.6 The concentration distribution curves for ammonia nitrogen in soil column No.2
1. $T_0 - 10$ min; 2. $T_{0.5} - 16$ min;
3. $T_{0.8} = 32$ min

Fig.5 and 6 illustrate the breakthrough processes of nitrogen ammonia with respect to depth and time in soil column. These concentration distribution curves were very useful to determine the suitable thickness of protective soil in land treatment system for municipal wastewater.

5 Conclusions

Silty sand and sandy loam adsorb ammonium ions intensively. Factors which influence on adsorptive processes between soil and ammonium ion include soil types and their composition, cóncentration of ammonia nitrogen in influent and seepage velocity of water. The adsorptive capacity of sandy loam is far larger than that of silty sand. The higher the concentration of ammonia nitrogen in influent, the greater the adsorptive capacity is.

When concentrations of ammonia nitrogen in influents are 13.7 mg/L and 41.0 mg/L, the dynamic adsorptive capacities of silty sand are 0.175 cm^2/min and 0.0093 cm^2/min respectively. The dynamic adsoprtion capacity of sandy loam is 1.33 mg/g when concentration of ammonium ion in influent is 51.0 mg/L.

The permeation processes in the soil can be simulated by the Cameron equilibrium and kinetic adsorption model well. The breakthrough curve by curve fitting shows excellent agreement with the experiment data.

The parameters k_1, k_2 and k_3 in Cameron equilibrium and kinetic adsorption model can be obtained by curve fitting, and are used to plot the concentration distribution curves of ammonium ion in soil profile. The experimental results can be used to determine the suitable thickness of protective soil in land treatment system of wastewater.

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(Received December 9, 1996)