

氨氮在饱水粉砂土和亚砂土层中 吸附过程及其模拟*

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摘要 为在土地处理系统中选择合适保护土层厚度, 防止 NH_4^+ 对地下水污染, 通过动态土柱试验, 研究了 NH_4^+ 在饱和粉砂土层和亚砂土层中的吸附性能。用 Cameron 平衡-动态吸附模型模拟了 NH_4^+ 在土层中的迁移过程, 求得了不同土层和不同浓度条件下模型的各参数值, 并求解出不同时刻, 不同氨氮浓度条件下的沿程 NH_4^+ 浓度分布曲线。研究表明, 在实验条件下, 粉砂土和亚砂土的纵向弥散系数分别为 0.175 和 0.0093 cm^2/min ; 当水中氨氮浓度为 13.7 和 41.0 mg/L 时, 粉砂土动态饱和吸附容量分别为 0.156 和 0.400 mg/g ; 当氨氮浓度为 51.0 mg/L 时, 亚砂土的动态饱和吸附容量为 1.33 mg/g 。

关键词 氨氮, 饱水亚砂土层, 饱水粉砂土层, 迁移, 土柱试验, 氨氮。

目前, 对土壤和地下水污染最严重的是重金属、农药和氮素化合物。氮素化合物会通过城市污水土地处理和氮肥的使用, 大量进入土壤, 并经过土层下渗, 污染地下水, 对环境和人类健康造成严重危害。为了防止这种现象的发生, 有必要研究污染物质在土壤及地下水中的迁移转化规律, 为制订相应的污染控制标准和采取控制措施提供科学依据。氮素化合物包括有机氮、氨氮、亚硝酸盐和硝酸盐氮。本文以氨氮为研究对象, 寻求一种数学模式, 在给定的污水中氨氮浓度的情况下, 计算出经过一段土层的运移后, 进入地下水时的浓度, 从而判断在给定浓度下的污水用于农田灌溉, 是否会对地下水造成污染。

1 基本理论^[2,3]

污染物在饱水条件下土层中的迁移转化, 主要是土壤水运移及物质与土壤间各种物理、化学、生物等作用所致。溶质在饱和均匀多孔介质中随恒定水流作恒定垂直向下流动, 在动态条件下, 吸附模式可表达成一级动态模式:

$$\frac{\partial s}{\partial t} = k_1 \frac{n}{\rho} c_s - k_2 s \quad (1)$$

式中, k_1 和 k_2 是吸附和解吸常数。

具有动态和平衡 2 个吸附过程的迁移模式可写成:

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

式(1)和(2)可以通过 Laplace 变换求解。根据土柱试验所得穿透曲线, 用计算机求解, 即可得到各项参数, 从而求得污染物垂直下渗时沿程浓度分布随时间的变化曲线。

2 运移方程参数的实验测定

2.1 实验材料和方法

(1) 实验材料 土样: 华北地区常见的砂土和亚砂土, 其干容重 $\rho = 1.1 - 1.8 \text{ g/cm}^3$ 。土样取回后, 经凉干、碾碎、过 2 mm 筛, 装入袋中备用, 用前测其含水率。氨氮: $(\text{NH}_4)_2\text{SO}_4$ 。实验设备: 动态土柱试验在 3 根玻璃柱中进行, 柱有效长 40 cm, 内径 4.0 cm。

(2) 实验方法 土样中依次装填卵石承托层, 实验土样层, 保护层, 各层间用尼龙网分隔。实验土样分层装填, 逐层压实, 控制柱内

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土样干容重接近自然状态,使装填土实测干容重 ρ 在 $1.1\text{--}1.8\text{ g/cm}^3$ 范围内。用清水洗柱 1 周,以降低柱内待测溶质本底浓度,并稳定孔隙结构和渗透流速。实验时,实验水样用恒水头装置自柱顶注入,由下端出水口流出,用阀门控制流速,使流速在粉砂土及亚砂土中达西流速分别在 $6\times 10^{-3}\text{--}1\times 10^{-4}\text{ cm/s}$ 和 $1\times 10^{-4}\text{--}6\times 10^{-4}\text{ cm/s}$ 范围内。

先进行弥散实验:将浓度为 c 的示踪剂(保守物质,本实验用 NaCl , 270 mg/L)溶液连续注入土柱,定时测定出水浓度,作出 $c\text{--}t$ 曲线即穿透曲线,用下式求得弥散系数:

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

式中, L 为柱长(cm); $t_{0.5}$ 和 $t_{0.16}$ 分别为从穿透曲线上 $c/c_0=0.5$ 和 0.16 处查得的横坐标(min)。

测定弥散系数后的土柱,经去离子水洗柱

后,进行氨氮溶液穿透曲线测定。

2.2 实验结果与分析

(1) 弥散实验 图 1 为粉砂土弥散试验示踪剂的穿透曲线。从图 1 中可查得 $t_{0.5}=17.1\text{ min}$, $t_{0.16}=15.3\text{ min}$, 试验所用土柱土层长 $L=21.8\text{ cm}$, 代入式(3)可算得粉砂土的弥散系数 D_1 为 $0.175\text{ cm}^2/\text{min}$, 亚砂土的弥散系数 $D_2=0.0093\text{ cm}^2/\text{min}$ 。

由于不同土层中,渗透流速 v 不同,因而,不同土壤的弥散系数相差很大。在这里,粉砂土的弥散系数远大于亚砂土的弥散系数。

(2) NH_4^+ 穿透实验 在一般的生活污水和城市污水中, $\text{NH}_4\text{--N}$ 含量一般为 $10\text{--}50\text{ mg/L}$ ^[1], 本试验所作的 3 组 $\text{NH}_4\text{--N}$ 穿透实验所用试液浓度分别为 13.7 , 41.0 和 51.0 mg/L 。

图 2 和图 3 为不同土质,不同试液浓度的穿透实验结果。

将试验所得 $c\text{--}t$ 曲线按模型的要求进行无

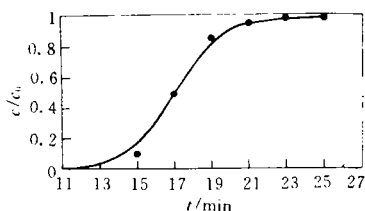


图 1 粉砂土弥散试验穿透曲线

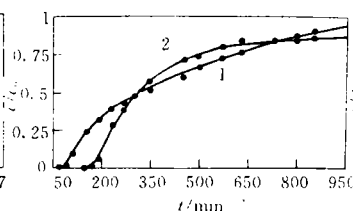


图 2 粉砂土氨氮穿透实验

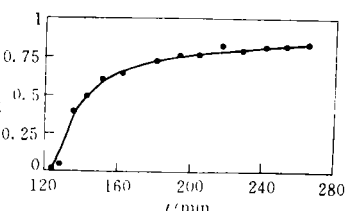


图 3 亚砂土氨氮穿透实验

1. $c_0=13.7\text{ mg/L}$ 2. $c_0=41.0\text{ mg/L}$

量纲化:横坐标用 $T=ut/L$ 代替,纵坐标用 $c=c_s/c_0$ 代替,得到求解参数所必须的标准化曲线。对模型参数 K_1 、 K_2 和 K_3 作出最初估值,用计

表 1 模型中各参数计算结果

土 质	粉砂(柱 1)	粉砂(柱 2)	亚砂(柱 3)
$c_0(\text{mg/L})$	13.7	41.0	51.0
B	40	40	42.3
K_1	1.6	0.35	0.25
K_2	0.1	0.03	0.012
K_3	14	14	50
$k_1(\text{min}^{-1})$	0.1	0.021	0.001
$k_2(\text{min}^{-1})$	0.06	0.002	6×10^{-5}
k_3	14	14	50

算机程序调整各参数的值,使模型计算曲线与试验所得曲线基本吻合为止,从而得到模型中各参数的值,如表 1 所示。

图 4 为粉砂土 $\text{NH}_4\text{--N}$ 穿透实验点计算机拟合结果,可以看出,两者十分吻合。其余 2 个实验可得出同样的结果(图略)。

(3) 土柱吸附量 当土柱完全穿透时,土柱吸附达到饱和,饱和吸附量可用下式计算^[3]:

$$s_{eq}=\frac{n}{\rho}\left(\frac{k_1}{k_2}+k_3\right)c_s\quad (4)$$

式中 s_{eq} 为土柱饱和吸附量(mg/g)。

代入各项参数,算得的土层吸附量列于表 2 中。

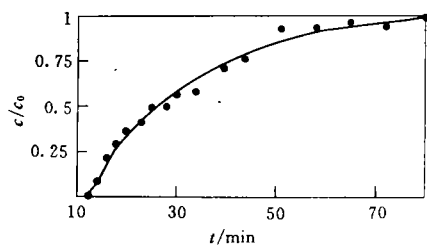


图 4 粉砂土氨氮穿透实验点曲线拟合结果

表 2 土柱饱和吸附量

序号	土质	$c_0(\text{mg/L})$	$s_{eq}(\text{mg/g})$
1	粉砂	13.7	0.156
2	粉砂	41.0	0.400
3	亚砂	51.0	1.33

可以看出，土壤对 $\text{NH}_4\text{-N}$ 具有很强的吸附作用。吸附作用受下列因素的影响：① 吸附量受土质影响很大，亚砂土的吸附量远大于粉砂土。原因一是亚砂土颗粒的粒径远小于粉砂土，因而比表面积较大，能产生更强的吸附作用；二是亚砂土层的渗透流速比粉砂土约小一个数量级，缓慢的流动提供了更多的溶质与颗粒表面的接触机会，因而吸附量更大。② 土质结构的区别也是造成吸附量差别的原因之一。华北地区亚砂土多属伊利石类，这类粘土矿物的硅氧四面体片中存在的六边形网状孔穴，其直径与 NH_4^+ 离子的直径十分近似， NH_4^+ 离子很易嵌入孔穴之中，并被孔穴中的负电荷所吸引，从而牢固地固定在此种特殊构造中，表现为强烈的吸附。③ 吸附量还受溶质浓度的影响，溶质浓度越大，吸附量越大。

2.3 模型计算下渗沿程浓度分布曲线

在求得模型参数 K_1 、 K_2 和 K_3 后即可通过模型计算出在某一时刻对应于一组沿程高度 ζ 的浓度值 $c(T, \zeta)$ (无量纲)，并绘制出标准化的沿程浓度分布曲线。对应于任一时刻都有一条沿程浓度分布曲线，本文只给出了有代表性的 T_0 (穿透点)、 $T_{0.5}$ (半饱和点) 和 $T_{0.8}$ (80%饱和点) 3 个时刻的沿程浓度分布曲线。图 5 为柱 1 和柱 2 的 NH_4^+ 沿程分布浓度曲线，柱 3 的图略。

从沿程浓度分布曲线可以看出，在达到穿透点 (T_0) 时，土柱的上半段 ($\zeta=0.5$) 吸附已近饱和，尤其是对于高浓度的溶液。这一现象从防止地下水污染的角度来看无疑是很有意义的，因为由此可以获得保护层厚度选择的依据。

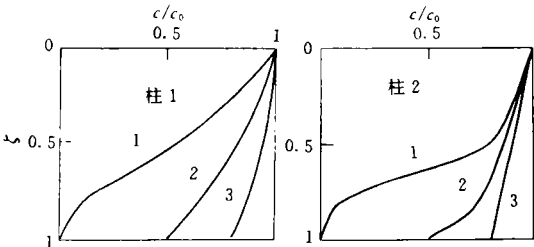


图 5 柱 1 和柱 2 氨氮沿程浓度分布曲线

1. $T_0=11\text{ min}$ 2. $T_{0.5}=26\text{ min}$ 3. $T_{0.8}=4.4\text{ min}$

3 结论

(1) 土壤对 NH_4^+ 有强烈的吸附作用。吸附作用的大小，受土质，土壤结构，溶液中 NH_4^+ 的浓度和渗透流速影响。亚砂土吸附容量大于粉砂土；溶液中 NH_4^+ 浓度越大，吸附量越大。

(2) 当水中 $\text{NH}_4\text{-N}$ 浓度为 13.7 和 41.0 mg/L 时，粉砂土的动态饱和吸附量分别为 0.156 和 0.400 mg/g；当水中 NH_4^+ 浓度为 51.0 mg/L 时，亚砂土的动态饱和吸附容量为 1.33 mg/g。

(3) 利用 Cameron 平衡-动态吸附模型能很好地模拟 $\text{NH}_4\text{-N}$ 在土层中的下渗过程，实验数值和计算机拟合曲线十分相符。

(4) 根据曲线拟合求得 Cameron 平衡-动态吸附模型参数 K_1 、 K_2 和 K_3 ，可以算出不同时间，不同深度 NH_4^+ 浓度沿程曲线。在土地处理系统中选择合适保护土层厚度，防止 NH_4^+ 对地下水污染有实际意义。

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A Research on the Ecological Effect of the Soil Animals Community by the Heavy Metal Pollution. Deng Jifu et al. (Zhuzhou Institute of Environ. Sci., Zhuzhou 412000); *Chin. J. Environ. Sci.*, 17(2), 1996, pp. 1-5

The research results show that there are 31 soil animal species in the polluted area, in which *Acarina* and *Collembola* are dominant population. The species and quantities of the soil animals are decreased with the aggravation of pollution, which can be found mainly from the growth and decline of the dominant population and decrease and disappearance of the polluted sensitive species. The big animals, such as earthworm and spider, have a strong ability to acculate heavy metal elements. The content of Cd, Pb, As in these animal's body relates proportionally to the metals in soil, but the centipede's ability in accumulating the heavy metal elements is obviously weaken.

Key words: heavy metal pollution, soil animal, ecological distribution, accumulation.

Microbial Degradation of Regenerated Cellulose Film. Zheng Lianshuang et al. (Dept. of Environ. Sci. Wuhan University, Wuhan 430072); *Chin. J. Environ. Sci.*, 17(2), 1996, pp. 6-8

The biodegradability of regenerated cellulose film was tested by soil-burial test in field, culture-dish test and CO₂ evolution test respectively. The results of test are as follows: (1) The mass loss of the film increased with the extension of soil-burial test; (2) Test strains had different abilities to degrade the film, and the order of their abilities was strain T-311 > strain A-305 > strain P-307; the biodegradation rate of the film might exceed 70% during 42 days after the film had been buried or inoculated with strain T-311; (4) In the process of biodegradation, mass loss, visible growth of test strains on the film and CO₂ evolution are both relative and different indexes for assessing biodegradation degrees of the film.

Key words: regenerated cellulose film, biodegradability, CO₂ evolution.

Adsorption Behavior of Ammonium Ion in Saturated Silty Sand and Sandy Loam. Zhu Wapeng et al. (Dept. of Environ. Eng., Tsinghua University, Beijing 100084); *Chin. J. Environ. Sci.*, 17(2), 1996, pp. 9-11

The adsorption characteristics of ammonium ion in saturated silty sand and sandy loam were studied by means of dynamic soil column experiments. The transportation of ammonium ion in soil were modelled with a combined equilibrium and kinetic adsorption model (Cameron's model). The coefficients (K_1 , K_2 and K_3) under different soil and NH₄⁺ concentration in water were obtained. The distribution curves of ammonium ion in soil were drawn. The results indicate that the longitudinal dispersion coefficients (D) in silty sand and sandy loam are 0.175 cm²/min and 0.0093 cm²/min respectively. The dynamic adsorption capacity of silty sand are 0.156 mg/g when concentration of NH₄⁺ in water is 13.7 mg/L and

0.400 mg/g when concentration of NH₄⁺ in water is 41.0 mg/L; the dynamic adsorption capacity of sandy loam is 1.33 mg/g when concentration of NH₄⁺ in water is 51.0 mg/L. Above results can be used to determine the suitable thickness of protective soil in land treatment system of wastewater.

Key words: ammonium ion, saturated silty sand, saturated sandy loam, transportation, dynamic soil column experiment.

Study on the Adsorption Mechanism of Mercury (I) with Prime Amine N₁₉₂₃ Levextrel Resin. Cheng Deping and Xia Shijun (Dept. of Chem., Hangzhou University, Hangzhou 310028); *Chin. J. Environ. Sci.*, 17(2), 1996, pp. 12-15

The adsorption mechanisms of mercury (I) with prime amine (N₁₉₂₃) levextrel resin were studied when it doesn't form salt or it is in salt forming condition. The adsorption compounds have been determined and the different mechanisms have been analysed from the results obtained by using constant mole method, slope method, saturated capacity method, IR and NMR spectra, and also discussed the different mechanism in low or high concentration of [HCl] on the theory.

Key words: mercury, mechanism, levextrel resin, primary amine N₁₉₂₃.

A Study on Effects of Simulated Acid Rain and Sulphur Dioxide on Crops. Liu Liangui et al. (Chinese Research Academy of Environmental Sciences, Beijing 100012); *Chin. J. Environ. Sci.*, 17(2), 1996, pp. 16-19

The effects of acid rain and sulphur dioxide alone and in combination on tomato, carrot and cotton was studied by simulated acid rain irrigating and SO₂ exposure. It was found that the simulated acid rain and sulfur dioxide could inhibit the growth of crops in a degree and reduce the productivity. The synthetic effect of acid rain and sulfur dioxide was more notable than alone, but their mutual effect was not marked.

Key words: simulated acid rain, sulfur dioxide, crop, inhibition, synthetic effect.

The Fluxes of Volatile Mercury over Soil Surface in Guizhou Province. Feng Xinbin et al. (State key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, 550002); *Chin. J. Environ. Sci.*, 17(2), 1996, pp. 20-22

After summing up the work of former researchers, the authors set up a instrument which can be used to measure the fluxes of volatile mercury over soil in field. From Aug. to Oct. in 1993, the authors studied the fluxes of volatile mercury over soil at five sites of three different areas (high mercury contented area, mercury polluted area and reference area). Studies showed that soil release more volatile mercury in day than at night, and that the fluxes of volatile mercury over soil has relationship with both the total mercury content of soil and air temperature.

Key words: mercury, fluxes, flux chamber, Guizhou