

Two-stage soil infiltration treatment system for treating ammonium wastewaters of low COD/TN ratios

Zhongfang Lei^{a,b}, Ting Wu^a, Yi Zhang^a, Xiang Liu^a, Chunli Wan^a, Doo-Jong Lee^{a,c,d,*}, Joo-Hwa Tay^a

^aDepartment of Environmental Science and Engineering, Fudan University, 220 Handan Road, Shanghai 200433, China; ^bGraduate School of Life and Environmental Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8572, Japan

^cDepartment of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan

^dDepartment of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan

*Corresponding author. Tel.: +886 22362 5632; Fax: +886 22362 3040; E-mail: djlee@ntu.edu.tw (D.J. Lee).

ABSTRACT

This study applied a novel two-stage soil infiltration treatment (SIT) for reaching effective nitrogen removal from high-strength and low COD/TN ratio wastewaters. The wastewater was first fed into the soil column (stage 1) at hydraulic loading rate (HLR) of $0.06 \text{ m}^3 \text{ m}^{-2} \text{ d}^{-1}$ for chemical oxygen demand (COD) removal and total phosphorus (TP) immobilization. Then the effluent from stage 1 was fed individually into four soil columns (stage 2) at $0.02 \text{ m}^3 \text{ m}^{-2} \text{ d}^{-1}$ of HLR with different proportions of raw wastewater as additional carbon source. Over the one-year field test, the stage 1 SIT removed >95% COD and >99% TP with influent COD of 861–1686 mg/L, NH_4^+ -N of 168–292 mg/L, and TP of 10.3–20.5 mg/L. Efficient denitrification was achieved in stage 2 columns. Balanced nitrification and denitrification in the two-stage SIT revealed excellent TN removal (>90%) from high-strength and low COD/TN ratio wastewaters.

Keywords: Soil infiltration treatment; nitrification; denitrification; ammonium wastewater; low COD/TN ratio

1. Introduction

High-strength ammonium nitrogen (NH_4^+ -N) wastewaters are produced by coking

plants, monosodium glutamate and chemical fertilizers industries, municipal landfills, and livestock farms, which need intensive polishing before safe disposal. Anaerobic treatment is practiced to deal with livestock wastewaters to convert organic carbonaceous matters into biogas and nitrogenous substances (such as proteins) into NH_4^+ . The digester effluent therefore has high levels of NH_4^+ -N and low chemical oxygen demand (COD). Biological nitrification-denitrification treatments can be adopted effectively when external carbon sources were present (Wong and Lee, 2011; Ge *et al.*, 2012).

Single-stage soil infiltration treatment (SIT), a cost-effective in situ treatment process, can sufficiently treat ammonium-containing wastewaters of total nitrogen (TN) < 100 mg N/L (van Cuyk *et al.*, 2001; van Cuyk and Siegrist, 2007; Kadam *et al.*, 2008; Murakami *et al.*, 2008). When dealing with wastewater of TN > 100 mg N/L, SIT failed to achieve effective nitrogen removal since quantities of nitrate nitrogen (NO_3^- -N) were left in the effluents (Ding *et al.*, 2001; Lei *et al.*, 2007; Liang and Liu, 2008). Restated, in general the denitrification activity in SIT is not sufficient to convert excess NO_3^- -N to N_2 .

This study aims at testing the feasibility of achieving separated nitrification and denitrification stage in a novel two-stage SIT process to treat high-strength and low COD/TN wastewaters. The stage 1 SIT was used for nitrification, COD degradation and TP immobilization. The stage 2 SIT was applied for denitrification with different proportions of raw wastewater supplemented as additional carbon source. The practical limitations and effects of influencing operational parameters on the two-stage SIT performance were revealed.

2. Materials and methods

2.1. Two-stage SIT testers and wastewaters

The SIT testers comprised of soil column A for stage 1 and columns B1–B4 for stage 2 (**Fig. S1 in Supplementary Materials**). The SIT soil columns were made of polyvinyl chloride with total height of 110 cm and internal diameter of 15.3 cm. The yellow brown soil sampled from the farmland in Baimi Village, Kunshan County, Jiangsu Province, China was mixed thoroughly with predetermined fly ash and rice hulls (soil:fly ash:rice hull =7:2:1 by volume), and then packed into all columns. **Table S1 in Supplementary Materials** lists the physicochemical properties of packing soils. The packing layers were 80 cm high with 5 cm of gravel layer underneath and 2 cm of sand layer above. The soils in B1–B4 were repacked to reach dense packing (lower hydraulic conductivities as in **Table S1**) so air intrusion was low that benefited occurrence of denitrification reactions.

Two high-strength NH_4^+ -N wastewaters were prepared. A synthetic wastewater was prepared that contained (per liter) about 1.4 g glucose, 0.8 g NH_4Cl , and 0.09 g KH_2PO_4 , which was characterized as pH 7.13 ± 0.12 , COD 1254.48 ± 143.92 mg/L, NH_4^+ -N 197.33 ± 12.06 mg/L, TN 197.93 ± 17.46 mg/L, TP 19.06 ± 1.14 mg/L, respectively. A real wastewater sample was prepared by 5 times dilution of the effluent from an anaerobic fermentation tank of swine wastewater (in Baimi Village, Kunshan County, Jiangsu Province, China) according to the proposed field processes and irrigation condition, in which the anaerobic effluent was irrigated after 5 times dilution with river water and overflowed to a soil infiltration trench. The diluted effluent from the fermentation tank had the following characteristics: pH 6.65–8.20, COD 861–1686 mg/L, NH_4^+ -N 168–292 mg/L, TN 182–294 mg/L, and TP 10.3–20.5 mg/L, giving a COD/TN ratio of 3.2–8.6.

2.2. Experimental conditions

Since the hydraulic conductivities of column A and columns B1–B4 were different (**Table S1 in Supplementary Materials**) and based on our preliminary trials (data not shown), the hydraulic loading rates (HLRs) of stage 1 and stage 2 were set at 0.06 and 0.02 m³ m⁻² d⁻¹, respectively. Wastewaters were fed at the top of column A and the effluent from the bottom of A was fed into B1–B4 at different mix proportions of raw wastewater. Restated, the volume ratios of effluent from A versus raw wastewater (Q_i/q_i , $i=1,2,3,4$) were fixed at 4:1, 3:2, 2:3, and 1:4 for the influents of B1, B2, B3, and B4, respectively (**Fig. S1 in Supplementary Materials**).

At the start of the test, the SIT columns were fed with synthetic wastewater for about 7 months (Experiment I). Afterwards the feed was stopped for about one month and then shifted to diluted real wastewater at different mix ratios for about 4 months (Experiment II). The influent COD/TN for column B4 was always the highest among the four stage 2 columns. The wetting/drying ratios of all five columns (A and B1–B4) were kept at 1/3. Experiments were carried out with ambient temperature ranging 4–27°C over the whole testing year. The average organic loading rates for column A and columns B1–B4 were 73.1, 7.1, 11.3, 15.6, and 20.2 g COD m⁻² d⁻¹, respectively.

2.3. Sampling and determination

Influent and effluent samples were collected and stored at 4°C and analyzed within 24 h after sampling. Determinations of COD, NH₄⁺-N, NO₂⁻-N, NO₃⁻-N, TN, and TP were conducted based on Standard Methods (APHA, 1999).

Soil samples were collected at upper (20cm), middle (50cm), and bottom (70cm) layers of the column. Each layer soil was collected by mixing one central sample with four surrounding ones. The soil samples were milled after air-dried and were analyzed within two weeks except for that of organic matter (OM). Soil OM was detected right after sampling by gravimetric method: first dried at 105±1°C and then burned off at

550±2°C. Soil pH was determined by a pH meter (HQ40d, Hach Co., USA) in the extract of soil sample:water (1:2.5, v/v) mixture after stirred for 30 min at 100 rpm. Soil TN and TP contents were measured according to Standard Methods (APHA, 1999) after sieving the samples through 0.15 mm mesh and digesting with sulphuric acid (Xu and Zheng, 1986).

2.4. Data analysis

In order to identify the dominant processes occurred in the two stages, nitrification and denitrification efficiencies in this study were estimated according to Equations (1) and (2), respectively.

$$\text{NO}_x\text{-N gain (\%)} = 100 \times \{ [\text{NO}_x\text{-N}]_e - [\text{NO}_x\text{-N}]_i \} / [\text{NH}_4\text{-N}]_i \quad (1)$$

$$\text{TIN loss (\%)} = 100 \times \{ [\text{TIN}]_i - [\text{TIN}]_e \} / [\text{TIN}]_i \quad (2)$$

where $[\text{NH}_4^+\text{-N}]$, $[\text{NO}_x^-\text{-N}]$, and $[\text{TIN}]$ are the concentrations of $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N} + \text{NO}_3^-\text{-N}$, and total inorganic nitrogen (the sum of $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$, and $\text{NO}_3^-\text{-N}$) in liquid phase, respectively. The subscripts i and e denote influent and effluent, respectively.

One-way analysis of variance (ANOVA) and F-test were performed to determine whether there was significant difference among the performances of the four soil columns at stage 2 or the two wastewater conditions. Significance was assumed if the $p < 0.05$.

3. Results and discussion

3.1. COD removal and TP immobilization

In Experiment I (synthetic wastewater as influent), the stage 1 SIT (column A) removed 95.4% COD and the stage 2 (columns B) removed 84.5–95.9% COD. In Experiment II, stage 1 and stage 2 removed 81.4% and 92.7–96.8% of influent COD,

respectively. No significant difference was found among the four stage 2 columns with respect to COD removal.

The decrease in COD removal for the stage 1 in Experiment II may be partly contributed by complicated organic substances in the digested swine wastewater as influent. All the effluent CODs from the stage 2 (B1–B4) remained low (<50 mg/L) in either Experiment I or II, implying that two-stage SIT systems could also be effective for the adsorption/absorption and biodegradation of organic compounds.

With feed TP concentrations of 10.3–20.5 mg/L, the effluent TPs from column A were averagely 0.14 mg/L and 1.43 mg/L in Experiments I and II, respectively. The effluent TPs from the stage 2 (B1–B4) were always <0.1 mg/L, showing that more than 99% of TP were removed, with most of TP removed in stage 1.

3.2. TN removal

The stage 1 column (A) removed limited quantities of TN (averagely 32.0% in Experiment I and 34.8% in Experiment II), a consequence of the applied high HLR and high organic loading rates (**Fig. 1**). Restated, the single-stage SIT could not effectively remove nitrogen from wastewaters, correlating with the reported literature. Conversely, the stage 2 of SIT removed TN during the first 5 months of Experiment I.

Correspondingly, the average TN removals were 93.0%, 93.2%, 93.1%, and 98.2% for B1, B2, B3, and B4, respectively. Afterwards, the TN removals in stage 2 decreased over time, reaching 54.8%, 52.7%, 58.3%, and 76.3%, respectively, at the end of Experiment I.

Experiment II was started up after one-month drying period, during which excessive nitrogen was thought to be removed and the soil matrix recovered its nitrogen removal capability. In Experiment II, TN concentrations in the stage 2 effluents fluctuated with time (**Fig. 1**). The average TN removals were 41.7%, 38.9%, 54.7%, and

70.5% for B1, B2, B3, and B4, respectively.

TN removal loading, the quantities of TN removed per unit column surface area per day, for B1–B4 were averagely 2.61, 2.79, 3.03, and 3.56 g N_R m⁻² d⁻¹ in Experiment I and were decreased to 1.60, 1.49, 2.29, and 3.26 g N_R m⁻² d⁻¹ in Experiment II (**Fig. 2**). B4 had the lowest reduction in TN removal loading, suggesting that high COD/TN ratio correlated with stable operation in stage 2 of the tested SITs.

3.3. Inorganic nitrogen

Figure S2 (Supplementary Materials) illustrates the average content variations of inorganic nitrogen including NH₄⁺-N, NO₂⁻-N, and NO₃⁻-N in the influents and effluents for the five SIT columns during the two experiments (I and II).

All the SIT columns exhibited excellent nitrification capabilities, and the NH₄⁺-N concentration averagely decreased by 94.7% in stage 1 and 99.2–99.9% in stage 2. Although NH₄⁺-N accounted for >98% and 70% of the influent TN in Experiment I and II, respectively, NO₃⁻-N presented 87.7–99.8% of the total inorganic nitrogen (TIN) in the effluent. Correspondingly, NH₄⁺-N concentrations were very low in the effluents (0.16–1.21% of TIN) except for column A in Experiment II (6.88% in the effluent TIN). This observation is attributed to the occurrence of ammonification reactions of organic nitrogenous substances in the digested swine wastewater due to the reduction in organic nitrogen level from 65.7 mg N/L to 30.5 mg N/L after column A.

Accumulation of NO₂⁻-N signals deterioration of nitrification and denitrification processes in soils. In this study, however, with influent NO₂⁻-N ranging between 0.013–1.285 mg/L, the effluent NO₂⁻-N concentrations were <0.05 mg/L regardless of the large temperature fluctuations encountered during the tests (**Figs. 2 and S2**).

3.4. Separated nitrification and denitrification in two-stage SIT systems

Biological nitrification/denitrification is regarded as the principal mechanism for

nitrogen removal in SIT systems (Zhang *et al.*, 2005). When both nitrification and denitrification reactions occurred in a single soil column or trench, in which nitrification took place in the upper soil layers with sufficient oxygen supply while denitrification occurred in the lower ones where oxygen was almost depleted (Ding *et al.*, 2001; van Cuyk *et al.*, 2001; Lei *et al.*, 2007; van Cuyk and Siegrist, 2007; Kadam *et al.*, 2008; Liang and Liu, 2008; Murakami *et al.*, 2008). Along the feed flow passage carbonaceous substances decrease in concentration, which may lead to insufficient carbon source needed for denitrification process at downstream regimes. In the present two-stage SIT systems nitrification and denitrification were separated in different confinements, and some additional carbon source (from raw wastewater) was supplemented to stage 2, thus sufficiently supporting the denitrification performance in stage 2.

Based on Equations (1) and (2), the average nitrification and denitrification efficiencies suggested a “balanced” nitrification and denitrification in the present two-stage SIT systems in Experiment I (**Table 1**), with nitrification process dominated the stage 1 (column A) and denitrification process did the stage 2 (column B). Specifically, the stage 1 performed stably with average nitrification efficiencies at 67.1–74.4% and denitrification efficiencies at 25.2–26.4%. Conversely, the efficiencies of the stage 2 were far less stable over time (**Table 1 and Fig. 2**).

3.5. Effects of influent COD/TN and temperature on TN removal

Carbon and nitrogen sources and temperature affect biological denitrification process when treating high-strength nitrate wastewater (Nair *et al.*, 2007; Warneke *et al.*, 2011). Insufficient carbon source may limit denitrification in SIT. **Figure 3** depicts the correlation between average influent COD/TN ratio and average TN removed load for all five columns. TN removal linearly correlated with influent COD/TN, with correlation coefficients (r) of 0.9713 for Experiment I and 0.9990 for Experiment II. At

>4 influent COD/TN, the TN removal load could be higher than $3 \text{ g N}_R \text{ m}^{-2} \text{ d}^{-1}$ (**Fig. 3**).

Therefore, the supplementary carbon source (from raw wastewater) to stage 2 is effective to enhance denitrification in stage 2.

The correlation coefficients between temperature and TN removal ranged 0.802–0.860 for B1–B4 ($p < 0.05$), implying that the temperature drop from 21 to 4 °C may deteriorate denitrification performance in stage 2 (**Figs. 1 and 2**). Low temperature was noted to have less impact on nitrification than on denitrification in SIT. Thus the decrease in denitrification efficiencies for stage 2 columns may be contributed by the drop of temperature during the tests, which probably resulted in unbalanced nitrification and denitrification in the two-stage SIT.

3.6. Changes in soil properties in the two-stage SIT systems

In stage 1, soil organic matter (OM) and TN contents increased with testing time, with difference noted among the four columns B (**Fig. S3 in Supplementary Materials**). The soil OM and TN contents decreased over time in Experiment I, likely a consequence of insufficient carbon source in the feeds (COD/TN=1.96-5.49) (**Fig. 3**). This finding correlates with that of Grischek *et al.* (1998) who treated river water using a sand and gravel aquifer.

Alkalinity, required in nitrification and produced in denitrification, could be maintained relatively stable during a balanced nitrification and denitrification process. The soil pH in stage 1 decreased from initial 7.14 to 6.94 in Experiment I and then further to 6.42 after Experiment II. This pH decrease was attributable to the effective nitrification and inhibited denitrification in column A. The average soil pH in the stage 2 increased significantly after Experiment I (pH 7.98–8.05, **Fig. S3**) due to effective denitrification.

4. Conclusions

The present two-stage SIT systems achieved sufficient and stable removal rates of COD, TP, and TN for the studied high strength wastewaters. Separated and balanced nitrification and denitrification processes were built up with intermediate supply of raw wastewater as additional carbon source. Greater than 90% of TN removal and larger than $3 \text{ g N}_R \text{ m}^{-2} \text{ d}^{-1}$ of TN removal load were obtained for the tested SITs. The two-stage SIT showed superior stability and operational performance when dealing with the high strength and low COD/TN ratio wastewaters.

Acknowledgments

The authors are grateful for supports provided by the Piggery farm of Baimi Village and the Zhangpu Town Government of Kunshan County, Jiangsu Province, China.

References

1. APHA, 1999. Standard Methods for the Examination of Water and Wastewater, 20th ed. American Public Health Association/American Water Works Association/Water Environment Federation, Washington, D.C., USA.
2. Ding, A., Zhang, Z., Fu, J., Cheng, L., 2001. Biological control of leachate from municipal landfills. *Chemosphere* 44, 1–8.
3. Ge, S.J., Peng, Y.Z., Wang, S.Y., Lu, C.C., Cao, X., Zhu, Y.P., 2012. Nitrite accumulation under constant temperature in anoxic denitrification process: The effects of carbon sources and COD/NO₃-N. *Bioresour. Technol.* 114, 137–143.
4. Grischek, T., Hiscock, K.M., Metschies, T., Dennis, P.F., Nestler, W., 1998. Factors affecting denitrification during infiltration of river water into a sand and gravel aquifer in Saxony, Germany. *Water Res.* 32, 450–460.

5. Kadam, A., Oza, G., Nemade, P., Dutta, S., Shankar, H., 2008. Municipal wastewater treatment using novel constructed soil filter system. *Chemosphere* 71, 975–981.
6. Lei, X., Fujimaki, H., Lu, Y., Zhang, Z., Maekawa, T., 2007. Ammonia removal from pretreated methane fermentation effluent through a soil trench system: A column experiment. *Chemosphere* 66, 2077–2086.
7. Liang, Z. Liu, J., 2008. Landfill leachate treatment with a novel process: Anaerobic ammonium oxidation (Anammox) combined with soil infiltration system. *J. Hazard. Mater.* 151, 202–212.
8. Murakami, M., Sato, N., Anegawa, A., Nakada, N., Harada, A., Komatsu, T., Takada, H., Tanaka, H., Ono, Y., Furumai, H., 2008. Multiple evaluations of the removal of pollutants in road runoff by soil infiltration. *Water Res.* 42, 2745–2755.
9. Nair, R.R., Dhamole, P.B., Lele, S.S., D'Souza, S. F., 2007. Biological denitrification of high strength nitrate waste using preadapted denitrifying sludge. *Chemosphere* 67, 1612–1617.
10. van Cuyk, S., Siegrist, R.L., 2007. Virus removal within a soil infiltration zone as affected by effluent composition, application rate, and soil type. *Water Res.* 41, 699–709.
11. van Cuyk, S., Siegrist, R.L., Logan, A., Masson, S., Fischer, E., Figueroa, L., 2001. Hydraulic and purification behaviors and their interactions during wastewater treatment in soil infiltration systems. *Water Res.* 35, 953–964.
12. Warneke, S., Schipper, L.A., Bruesewitz, D.A., McDonald, I., Cameron, S., 2011. Rates, controls and potential adverse effects of nitrate removal in a denitrification bed. *Ecol. Eng.* 37, 511–522.
13. Wong, B.T., Lee, D.J., 2011. Denitrifying sulfide removal and carbon methanogenesis in a mesophilic, methanogenic culture. *Bioresour. Technol.* 102,

6673–6679.

14. Xu, G., Zheng, H., 1986. Soil Microbial Analysis Manual. China Agriculture Press, Beijing, pp. 183–189 (in Chinese).
15. Zhang, J., Huang, X., Liu, C., Shi, H., Hu, H., 2005. Nitrogen removal enhanced by intermittent operation in a subsurface wastewater infiltration system. *Ecol. Eng.* 25, 419–428.

Table 1. Average nitrification and denitrification efficiencies for each SIT column during the experiments.

Column	A	B1	B2	B3	B4
Experiment I					
NO _x -N gain (%)	74.4±0.2	-242.7±2.1	-78.9±1.5	-29.9±0.7	-13.0±0.1
TIN loss (%)	25.2±0.2	87.7±1.8	85.2±1.5	86.9±2.1	94.0±2.4
Experiment II					
NO _x -N gain (%)	67.1±1.4	-4.3±0.2	43.6±1.1	29.2±0.2	24.8±0.5
TIN loss (%)	26.4±0.5	31.7±0.4	28.3±0.3	47.7±1.1	61.9±1.2

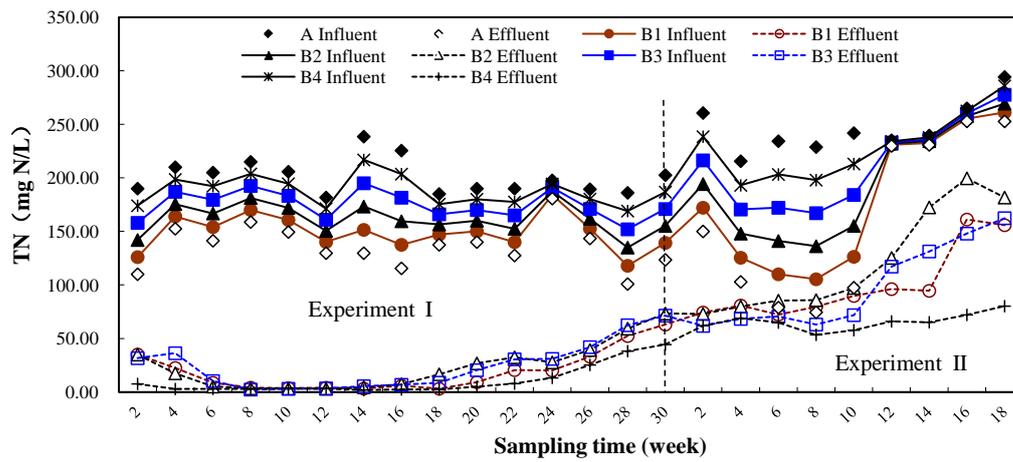


Fig. 1. Variations of influent and effluent TN concentrations for the five SIT columns during Experiments I and II.

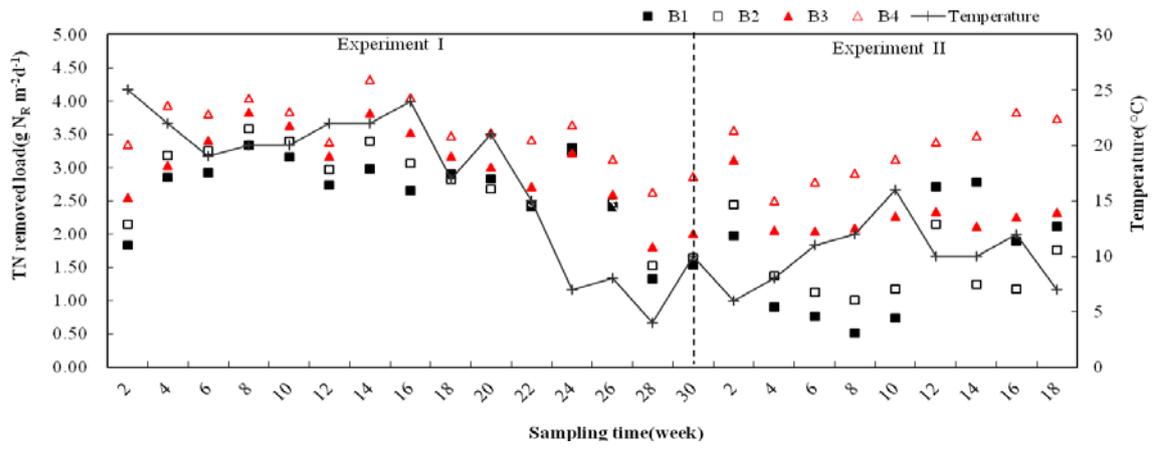


Fig. 2. Variations of average TN removed loads with temperature for the stage 2 columns (B1–B4).

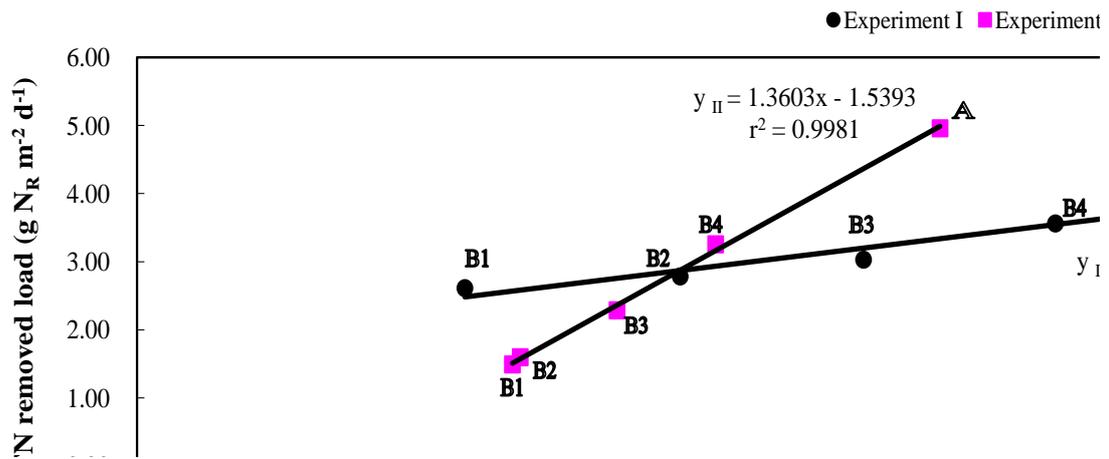


Fig. 3. Relationship between influent COD/TN ratio and average TN removed load for the five soil columns during Experiments I and II.

Supplementary Materials

Two-stage soil infiltration treatment system for treating high-strength ammonium wastewaters

Zhongfang Lei^{a,b}, Ting Wu^a, Yi Zhang^a, Xiang Liu^a, Chunli Wan^a, Doo-Jong Lee^{a,c,d}*, Joo-Hwa Tay^a

^aDepartment of Environmental Science and Engineering, Fudan University, 220 Handan Road, Shanghai 200433, China;

^bGraduate School of Life and Environmental Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8572, Japan

^cDepartment of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan

^dDepartment of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan

*Corresponding author. Tel.: +886 22362 5632; Fax: +886 22362 3040; E-mail: djlee@ntu.edu.tw (D.J. Lee).

Table S1 Main properties of original soil matrix in the five columns.

Column	Main properties				
	Organic matter (mg/g)	TN (mg/g)	TP (mg/g)	C/N ^a	Hydraulic conductivity ^b (cm/s)
A	102.6±12.1	2.11±0.09	0.319±0.058	24.3±2.72	2.91×10 ⁻¹
B1	124.0±7.9	1.92±0.12	0.288±0.102	32.3±1.54	3.19×10 ⁻²
B2	96.8±19.2	2.83±0.54	0.383±0.069	17.1±1.36	3.26×10 ⁻²
B3	103.1±4.3	2.09±0.37	0.368±0.053	24.7±1.26	4.83×10 ⁻²
B4	115.1±8.6	2.02±0.09	0.282±0.126	28.5±1.19	6.62×10 ⁻²

^aC/N ratio was calculated according to Brady and Weil (1999): soil carbon contained in soil equals to 50% of organic matter for most situations.

^bHydraulic conductivity was measured with the constant head method proposed by McWhorter and Sunada (1997).

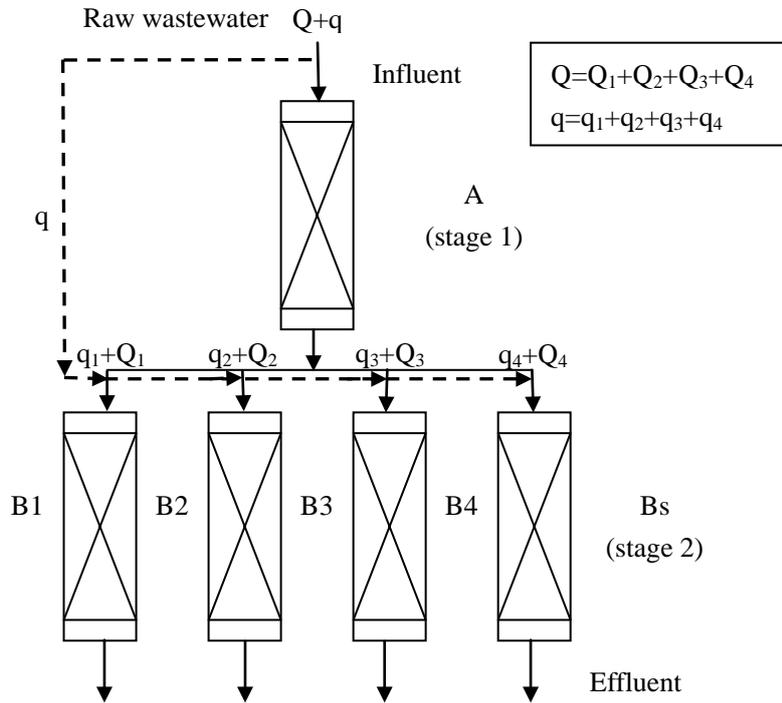


Fig. S1. Flowchart of the two-stage SIT process. The feeds into B1, B2, B3, and B4 are fixed at $Q_1:q_1=4:1$, $Q_2:q_2=3:2$, $Q_3:q_3=2:3$, and $Q_4:q_4=1:4$, respectively.
 $Q=Q_1+Q_2+Q_3+Q_4$, $q=q_1+q_2+q_3+q_4$.

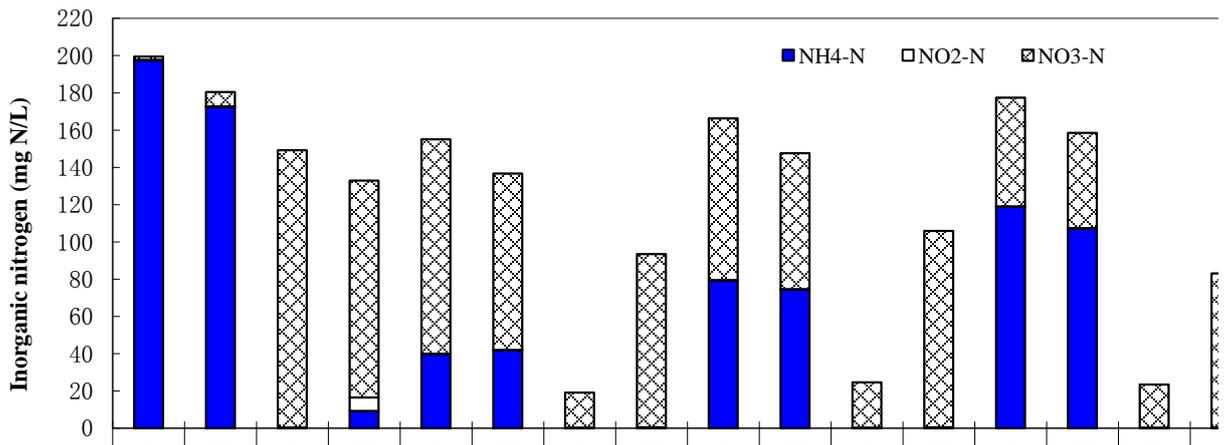


Fig. S2. Changes of inorganic nitrogen form in the influent and effluents for the five soil columns during Experiments I and II.

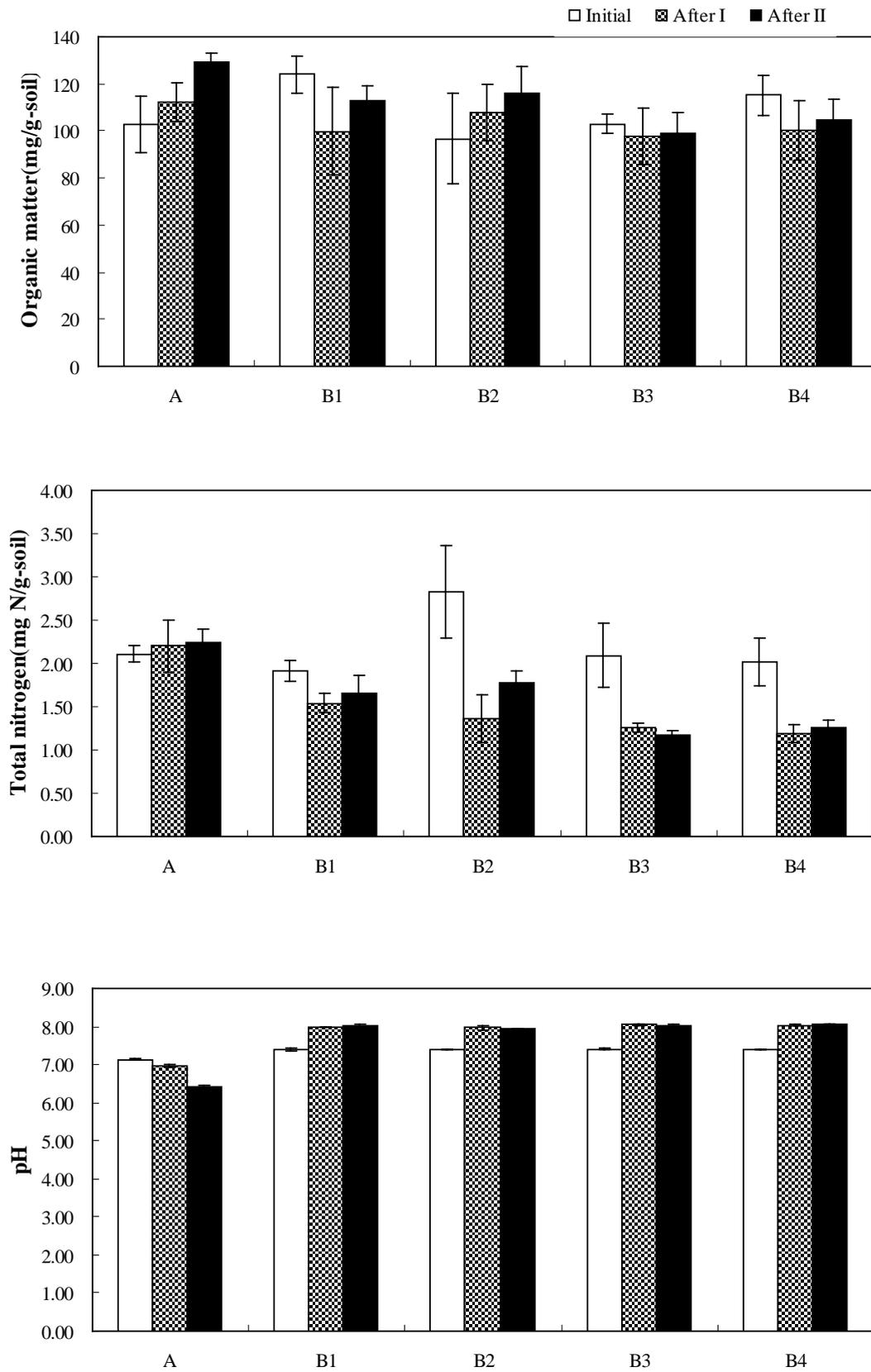


Fig. S3. Variations of soil organic matter, total nitrogen, and pH in the SIT columns after Experiments I and II.