

## Investigation of Ammonia removal from synthetic wastewater during column studies of Soil Aquifer Treatment

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### ABSTRACT

In this study, the performance of a laboratory-scale Soil Aquifer Treatment (SAT) system was investigated in order to study the ammonia, nitrite and nitrate reduction from synthetic wastewater (SWW). SAT was simulated in four 15 cm long soil columns packed with soils of sandy clay loam (SCL) texture collected from Anna University Sewage Treatment Plant (STP), Chennai, India. Soil Columns were ponded with wastewater to a depth of 2.5 cm above the soil surface and operated for a period of Ten cycles under 4 different alternating wet and dry cycles, 0.25 day wet/1.75 days dry (S1), 0.25 day wet/2.75 days dry(S2), 0.25 day wet/3.75 days dry (S3) and 0.25 day wet/7.75 days dry (S4). The effect of wetting and drying periods on SAT ammonia removal performance was assessed comparing ammonia, nitrite, nitrate nitrogen and TDS rates. The removal of ammonia was through nitrification process which is found to be a dominant removal mechanism of nitrogen. Nitrification differed according to the different drying cycles time with fixed flooding period. When the reduction performance achieved with different drying cycles were compared, it could be seen that longer drying periods with S3 column yielded with the least nitrate value of 0.46 mg/L. From this study, it was found that with the fixed wetting period, maximum drying period is required for nitrate reduction and minimum drying period is required for TDS reduction.

**Keywords**— soil aquifer treatment; synthetic wastewater; ammonia transformation; nitrite; nitrate removal

### INTRODUCTION

Soil Aquifer Treatment (SAT) is a cost effective natural wastewater treatment and reuse technology. It is an environmentally friendly technology that does not require chemical usage and is applicable to both developing and developed countries. Reuse of treated wastewater through infiltration basin serves as a medium for transport of ammonia and nitrate to groundwater through SAT (T. Kopchynski et.al. 1996; K. Gungor et.al. 2005; T.Selvakumar 2013 &2014). A great amount of ammonia is transformed to nitrate in the vadose zone, resulting in the high nitrate concentrations within groundwater aquifers. The release of excess nitrogen-containing compounds into groundwater is a major concern in aquifer recharge by SAT. SAT technology makes use of Soil to treat the reclaimed wastewater, the treatment process occurs through infiltration, Soil Percolation and transport through the groundwater aquifer (H. Bower 1996,1993 &1991). During the groundwater recharge through the Vadose zone and transport through the groundwater aquifer, water quality improvements occur that are collectively described as Soil Aquifer Treatment (M.M. Eusuff 2004). Filtration, Sorption and biodegradation processes in the soil are mechanisms that can reduce or remove microbial and other contaminants in wastewater (D.K. Powelson, 1993). SAT is a process of geo-purification designed and operated to improve the quality of the infiltrating water.

The main objective of this study is to investigate the ammonia behaviour of the synthetic wastewater during groundwater recharge by SAT under Anna University STP conditions using soil columns. Centered around this objective, this study intends to investigate ammonia transformation and removal under nitrification condition and to measure the significance of the adsorption process on fate of ammonia.

### MATERIALS AND METHODS

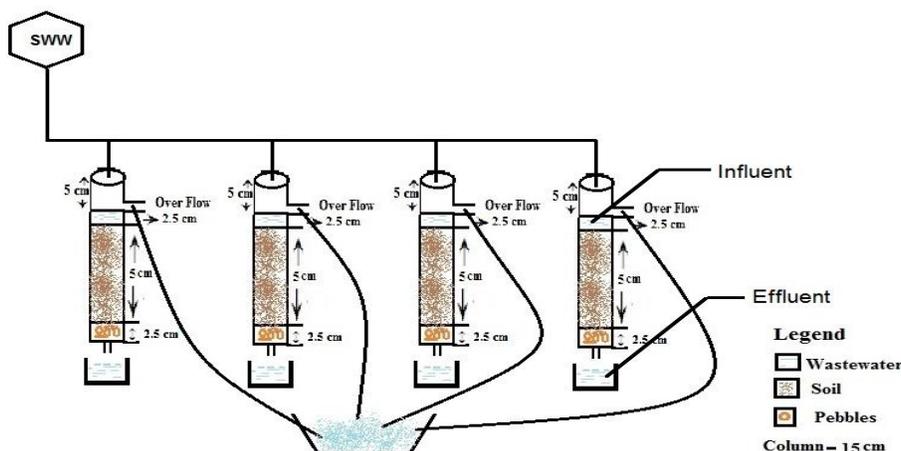
**Design and Operation of Soil columns:** A multi column SAT system was constructed in laboratory conditions. The experimental setup consisted of four identical PVC soil columns of 15 cm length and 6 cm inner diameter, one feeding tank for synthetic wastewater; feeder assembly and distributor lines. The experimental setup with columns and feeding tank are shown in Figure 1. The columns were operated under 4 different alternating wet and dry cycles, 0.25 day wet/1.75 days dry, 0.25 day wet/2.75 days dry, 0.25 day wet/3.75 days dry and 0.25day wet/7.75 days dry. SWW was applied for a period of 6 hrs (from 9 am to 3 pm). The samples taken from column were collected at the end of the first wetting day, for all 4 cycle combinations.

Soil columns were operated inside centre for water resources building, without any additional climatic temperature control inside the building during the study period. The lower part of the columns (approximately 5 cm) were filled with pebbles. The columns were provided with outlets for sample collection at bottom. All the columns were filled with 5 cm of soil. Soils were poured into the columns and no compaction of soils inside the columns was carried out.

**Table.1. Wet/Dry ratios for this short column study**

S.No	Column Id	Wetting Period (days)	Drying Period (days)	Wet/Dry ratio
1	S1	0.25	1.75	0.14
2	S2	0.25	2.75	0.09
3	S3	0.25	3.75	0.06
4	S4	0.25	7.75	0.03

**Figure1. Schematic illustration of the Soil Columns setup**



The selection of wet/dry ratio for this study ranges from 0.03 to 0.14 and is also in accordance with the EPA process design manual (Process Design manual US EPA, Sep 2006). Soil samples and properties - Anna University STP soil: Soil samples from Anna University STP were collected from depth ranging between 0 and 0.75 m (referred to as top soil). The selection of the depth range was based on the fact that previous studies indicated that most of the purification takes place at the upper most layer of the soil (A.Akber, 2003). It is the natural soil that has been collected from the STP without any treatment. In order to eliminate the interference with synthetic wastewater, it was washed several times with distilled water and left to dry. The bulk soil were homogenized, sieved and the gravel fraction > 1.7 mm excluded. Soil columns were left submerged in distilled water for 48 hrs to remove trapped air from the bottom and to remove soluble irons. This was made to minimize the interference of the soil on the behaviour of ammonia. The Soil textural classification, physical and chemical characteristics of the soil are given Table 2 and Table 3. Synthetic Wastewater (SWW): It is a solution of Ammonium chloride (NH<sub>4</sub>Cl), Calcium bicarbonate (Ca (HCO<sub>3</sub>)) and Glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>). 30.84 mg of NH<sub>4</sub>Cl was dissolved in 1 litre of distilled water to create 10 mg/L as NH<sub>3</sub> concentration. CaHCO<sub>3</sub> was added to the system as source of inorganic carbon. 66.65 mg was dissolved in 1000 ml creating 1000 mg/L as inorganic C. However, the concentration of the organic carbon in the synthetic wastewater was 1000 mg/L. It was prepared by dissolving 25 mg of C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> in 1000 ml.

**Experimental procedure and analytical methods:** During the studies, TDS, ammonia (NH<sub>3</sub>), nitrite (NO<sub>2</sub>) and nitrate (NO<sub>3</sub>) were measured in Centre for Water Resources, Anna University wet chemistry lab. These measurements were made in samples collected from the outlet of each column as well as the stock solution during all studies. Samples taken from column were collected at the end of first wetting day for all 4 cycle combinations. When the samples were taken into plastic bottles of 500 ml. their caps were right away closed to prevent air entry.

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**Table.2. STP Soil Textural Classification**

S.No	Name of the STP	% Sand	% Silt	% Clay	Textural class of soil as per USDA* Texture
1	Anna University	67	4	29	Sandy Clay Loam

\* United States Department of Agriculture

TDS measurements were made by using EQ8361 EQUINOX Pen type TDS meter. Wastewater was stored in plastic bottles and kept at 4°C in order to reduce the effects of biochemical reactions. No additives or preservatives were used to preserve wastewater quality. Wastewater was warm to the room temperature before application on soil columns. Samples were collected from the bottom of each column. The samples were filtered with 0.45µm filters and stored at 4°C, NH<sub>3</sub>, NO<sub>2</sub> and NO<sub>3</sub> were detected in each sample. Ammonia was measured using Phenate method. Ammonia was determined using the standard curve after measuring the absorbance at 640 nm of standards and samples using Visiscansystronics spectrophotometer. The calibration curve (NH<sub>3</sub>) vs absorbance was prepared using the standard stock solution of NH<sub>4</sub>Cl.

Nitrite was analysed with Visiscansystronic spectrophotometer. The method is based on the reaction of nitrite ions with sulfanylamide in acidic medium and the diazo compound obtained further reacts with diamine yielding in an azo color. The nitrite ion concentrations determined by measuring the absorbance of the azo colour at 543 nm. Nitrate was analysed using cadmium reduction method. All the analysis was conducted according to the American Public Health Association (APHA) standard methods for the examination of water and wastewater, (APHA, 1999).

**Table.3. Physical and Chemical Characteristics Of The Study Area Soil (HLS Tandon 2009)**

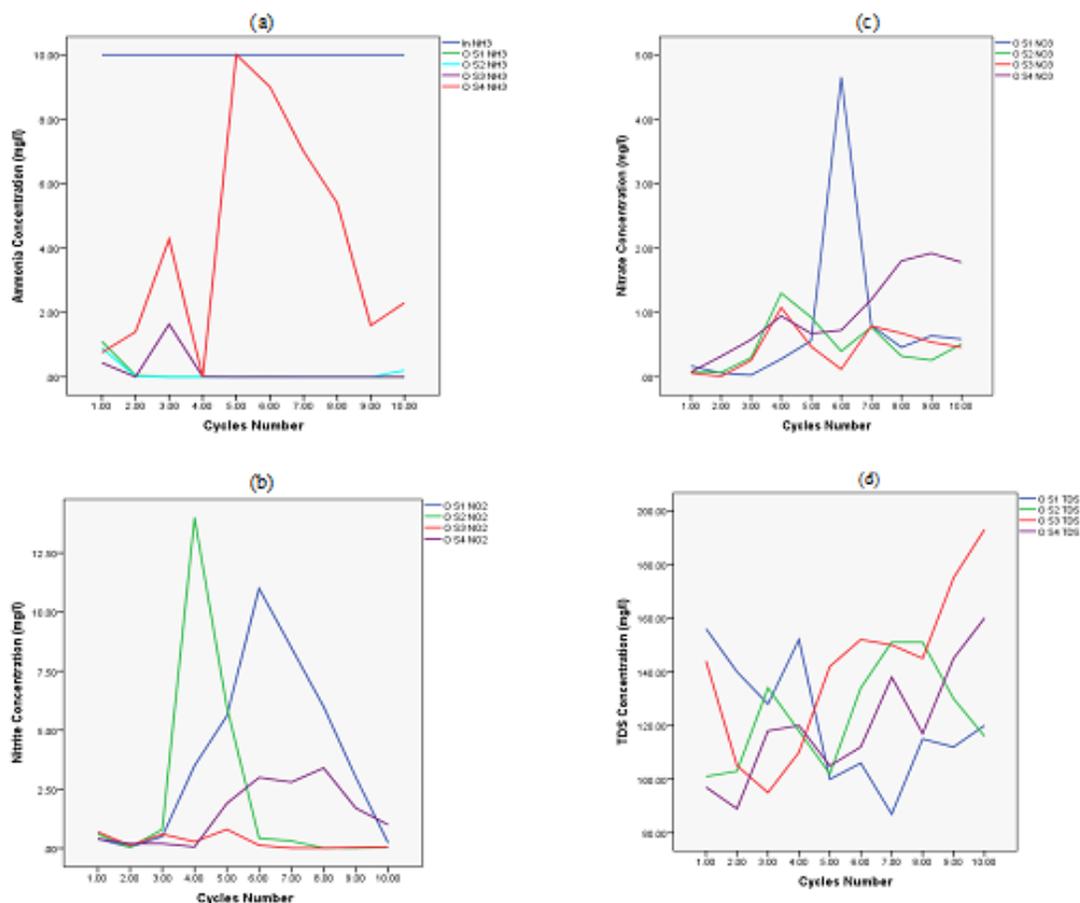
Parameter	Unit	Anna University STP
pH	-	7.25
Electrical Conductivity	mS/cm	0.198
Organic matter	%	0.32
Nitrate Nitrogen	ppm	7.0
Available Phosphorus	ppm	8.90
Potassium Exchangeable K	ppm	48
Calcium Exchangeable Ca	ppm	1550
Magnesium Exchangeable Mg	ppm	426
Sulfur Available S as SO <sub>4</sub> <sup>2-</sup>	ppm	49.1
Sodium Exchangeable Na	ppm	161
Zinc Available Zn	ppm	0.32
Manganese Available Mn	ppm	16.45
Iron available Fe	ppm	13.80
Copper Available Cu	ppm	1.48
Cation Exchange capacity	Meq/100g	19.23

## RESULTS AND DISCUSSION

**Synthetic Wastewater – NH<sub>3</sub> Distribution:** The change in ammonia concentration in synthetic wastewater as it moved down through the columns S1, S2, S3 and S4 is illustrated in Figure 2a. For S1, S2 & S3 columns for 1st two cycles only, inorganic and organic carbon source was given with 100 mg/L instead of 1000 mg/L to check the effect of carbon sources. From third cycle onwards, it was changed to 1000 mg/L. NH<sub>3</sub> values are present with minimum values ranging from 0 to 4.28 mg/L for the first 2 to 3 cycles at columns S1, S2, S3 and S4. Then ammonia is full oxidised to NO<sub>3</sub> in the subsequent cycles in all columns except S4. Due to the maximum drying period of 7 days, cracks were formed in S4 leading to the increase of ammonia value to 10 mg/L. The top surface of the columns was then scrapped as done in the infiltration basin for the field studies and the experiment was continued with subsequent reduction in ammonia values finally to zero.

**Nitrite Distribution:** Nitrite ( $\text{NO}_2$ ) develops as an intermediate product of  $\text{NH}_3$  and  $\text{NO}_3$ . Nitrite concentration in the experiment was rapidly oxidised to nitrate. The bioreaction is generally coupled and proceeds rapidly to nitrate form. Therefore, nitrite levels at any given time are usually low. Increased concentration are usually an indication of a disturbance of microbiological process, of an overloaded system or insufficient aeration capacity (Metcalf and Eddy 2004). Concentration of  $\text{NO}_2$  changes with different drying cycles as shown in Figure 2b. Columns S1 and S2 had one nitrite peak where as S3 and S4 columns had continuous nitrite peaks during each wetting.  $\text{NO}_2$  peaks attributed to continuous nitrification process near the exit of the column where aerobic conditions may exist.

**Figure.2. Synthetic wastewater (SWW) a)  $\text{NH}_3$  Distribution b)  $\text{NO}_2$  Distribution c)  $\text{NO}_3$  Distribution and d) TDS Concentration**



**Nitrate Distribution:** At the end of 10<sup>th</sup> cycle it was found that S3 column was most efficient with least nitrate content of 0.46 mg/L followed by S2, S1 and S4 column of the corresponding nitrate values with 0.51, 0.59 and 1.78 mg/L respectively. The removal of ammonia was through nitrification process which was considered to be a dominant removal mechanism of nitrogen. The transport of ammonia depends upon the availability of oxygen, nitrifier bacteria and inorganic carbon source. A common hypothesis for ammonia removal is the two-step process of autotrophic nitrification and adsorption of ammonia to the clay particle and organic fraction in the soil. The amount of adsorbance depends on the cation exchange capacity of the soil (H.Bower 1984; THR Abushbak 2004).

CEC is reported as a soil's ability to hold cations. It is an estimated value based on extracted cations from the soil analysis (Calcium  $\text{Ca}^{++}$ , Manesiam  $\text{Mg}^{++}$ , Potassium  $\text{K}^{++}$ , Sodium  $\text{Na}^{++}$  and Hydrogen  $\text{H}^{+}$ ). Since the clay and organic sites in the soil have a negative charge, the positively charged cations bond with these sites. Therefore CEC is closely related to soil texture. From Table 3, it was found that soil, the values of Ca, Mg, K, Na are 1550, 420, 48 and 161 mg/L respectively. The cation exchange capacity value was 19.23 meq/100g. Hence good adsorption of ammonia was present.

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**TDS removal:** Total dissolved solids (TDS) is another measure of salinity. It shows the amount of dissolved substances in the water, both ions and unchanged molecules. TDS is directly proportional to EC and expressed as a concentration mg/L. The TDS of the synthetic wastewater during the run for 10 cycles for S1, S2, S3 and S4 columns were presented in the Figures 2d. The TDS values ranged from 87 to 193 mg/L with the mean values of 121.60, 124.0, 141.10 and 121.10 mg/L respectively. Columns S1 and S2 have a decreasing trend with reduction in TDS values whereas columns S3 and S4 had an increasing trend in the subsequent cycles.

## CONCLUSIONS

NH<sub>3</sub> was the only form of nitrogen in the synthetic wastewater. The concentration of ammonia decreases with time and completely oxidised to nitrate at the end of the each cycles. The removal of ammonia was through nitrification process which is found to be a dominant removal mechanism of nitrogen. Nitrogen was not removed from synthetic wastewater. From this study, it was found that with the fixed wetting period, maximum drying period is required for nitrate reduction and minimum drying period is required for TDS reduction. When soil columns were flooded on short, frequent flooding cycles, almost all of the ammonium nitrogen was transformed to the nitrate form. This type of management system could be used to retain the nitrogen in the reclaimed water intended for agricultural use.

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