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# FIRST RESULTS ON NITROGEN AMMONIA REMOVAL FROM GROUND WATER BY NITRIFICATION AT CEETIA LAB

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#### Abstract

Groundwater in the aquifers of Hanoi is polluted with nitrogenous compound predominately in the form of  $\mathrm{NH_4}^+$ . Microbiological removal of nitrogen compounds by nitrification with or without further denitrification could be most appropriate technologies for Hanoi. This study focuses on development of nitrification process for nitrogen ammonia removal from ground water in Hanoi by using a novel acryl fiber (Biofill, NET Co. Ltd., Japan) fixed-bed media and indirect air introduction into filtration chamber. First results achieved show that with influent concentration of nitrogen ammonia 20 mg/l, hydraulic retention time HRT 20.2 h, an average nitrogen ammonia removal achieved was 86.2%. It shows positive results for further studies on promising alternative for groundwater quality improvement in Hanoi city.

Keywords: ammonia nitrogen, ground water, nitrification, water treatment plant.

#### Introduction

In Hanoi, especially south of the Red River, there is intensive exploitation of ground water and studies shown that river and ground water in the region are hydraulically interconnected. Pollution of ground water in the Hanoi urban area is especially evidenced by the presence of  $\mathrm{NH_4}^+$  in the Holocene and Pleistocene aquifers where the  $\mathrm{NH_4}$ -N levels may be as high as 25 to 30 mg/l. This ground water pollution is evidenced in some of the most developed areas in central Hanoi city and effects the water supply stations of Luong Yen, Tuong Mai, Bach Khoa, Ngo Si Lien. Furthermore, in the Ha Dinh and Phap Van areas, almost all wells drawing from Pleistocene aquifers are strongly polluted with high levels of  $\mathrm{NH_4}^+$ .

Analyses conducted by CEETIA in 2000 - 2001 demonstrated that NH<sub>4</sub>-N levels at the inlet to the Phap Van Water Treatment Plant were from 17.5 to 23.4 (average, 21.6) mg/l during August and September 2000, at the end of the rainy season. During April and May 2001, at the middle of the rainy season, the concentration of NH<sub>4</sub>-N was 20.8 mg/l. From field work conducted by the Kumamoto University team in November 2000 ground water NH<sub>4</sub>-N levels at Phap Van wells 1, 2 and 3 ranged from 15.4 to 28.0 (average 20.8) mg/l and at Ha Dinh wells 5, 6 and 8, from 11.6 to 13.1 (average 12.3) mg/l (According to the Vietnamese drinking water quality standard 1329/2002 QD-BYT, the limit concentrations of NH<sub>4</sub><sup>+</sup>, NO-2 and NO<sub>3</sub> are 1.5, 3 and 50 mg/l, respectively). In the south and southwest zones of Hanoi city where the Phap Van and Ha Dinh Water Treatment Plants are located hydro-geological windows linking the higher Holocene and lower Pleistocene aquifers with polluted surface waters are believed to exist. The general remarks on ground water pollution in the urban areas of Hanoi city made by CEETIA - Kumamoto University team from previous studies as follows:

- 1. Groundwater in the aquifers of Hanoi is polluted with nitrogenous compound predominately in the form of  $\mathrm{NH_4}^+$  and can be divided into the following categories:
- Very heavily polluted areas in which NH<sub>4</sub>-N levels are greater than 10 mg/l. Areas included in this category are Kim Lien, Bach Khoa, Ha Dinh, Tuong Mai and Phap Van.
- Heavily polluted areas in which NH<sub>4</sub>-N levels range from 5 to 10 mg/l. Only Quynh Mai is included in this category.
- Moderately polluted areas in which NH<sub>4</sub>-N levels range from 1 to 5 mg/l. This category includes Luong Yen, Yen Phu, Ngo Sy Lien and Don Thuy.

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- Slightly polluted areas in which NH<sub>4</sub>-N levels are only from trace to 1 mg/l. Areas include in this category are Ngoc Ha, Mai Dich, and Thuy Loi University.
- 2. NO<sub>2</sub>-N and NO<sub>3</sub>-N pollution is not significant in the ground water of Hanoi city and is consistently below regulatory limits. However there are some irregular appearances of these contaminants and attention should be given to their occurrence. The places of concern are the south side of La Thanh Dike in the Thanh Tri District, Yen So, Dong Da Hill, the Foreign Language College, Thuong Dinh, Army Hospital 103, the Quang Trung Mechanical factory, the Phosphate Factory and the Van Dien Battery Factory (with NO<sub>3</sub>-N levels ranging up to 6 or 7 mg/l).
- 3. The concentration of nitrogen compounds is higher during the dry season than the rainy season.
- 4. Pollutants levels at various locations can often be explained by hydrological conditions the structure of soil layers and the degree of groundwater extraction.

#### 5. Abatement measures considered.

Countermeasures adopted to reduce levels of nitrogenous compounds in the groundwater of Hanoi include treatment by strong oxidants such as Chlorine. While this has the drawback of high treatment costs, it includes the beneficial formation of chloramines with long lasting disinfection potential. However, the formation of harmful chlorinated organic compounds, while reduced by the formation of chloramines, is still a possibility. Associated health concerns have restricted the use of this method. Microbiological conversion methods are being considered and show the potential of converting nitrogenous compounds to non-toxic, environmentally safe forms and are thus worth further pursuing (Furukawa K. et al., JB&B, 2000).

In Vietnam there some studies on elimination of nitrogen compounds form groundwater in Hanoi areas have been carrying out, such as nitrification of nitrogen ammonia by aerated submerged fixed bed with local filtration materials (Cao The Ha, Tran Hieu Nhue et al, 2000), nitrogen ammonia removal from groundwater in Nam Du water treatment plant by enhanced aeration in pre-filtration contact chamber, feasibility studies (VIWASE Co., Soil and Water Ltd., 2002), small-scale nitrification - denitrification process for nitrogen elimination from ground water (Tran Xuan Nhi et al., 2002). Those confirm that microbiological removal of nitrogen compounds by nitrification with or without further denitrification could be most appropriate technologies for Hanoi. However, up to now, most of those are still in starting phase, requiring further studies, including in-lab and in-field, for confirmation of technico-economical effectiveness.

For effective microbiological nitrification process of nitrogen ammonia in polluted groundwater, one from critical factors is selection of aeration process and filtration material. It was analyzed that by using fixed bed by acrylic resin for attached growth of nitrifying bacteria (autotrophic micro-organisms) such as *Nitrosomonas* and *Nitrobacter* and indirect introduction of saturated dissolved oxygen into fixed bed chamber, there are some advantages could be achieved, such as: reduction of head loss in compared with direct filtration through media from minerals, increase of contact surface areas between substrate and microorganisms, reduction of risk of wash-out by air-flow of biomass into following treatment steps, and, stabilization of high treatment efficiency. This study focuses on development of nitrification process for nitrogen ammonia removal from ground water in Hanoi by using mentioned above fixed-bed media and indirect air introduction into filtration chamber, aiming at improvement of ground water quality for the Hanoi city. This is a joint research between CEETIA and Faculty of Civil Engineering, Kumamoto University, Japan.

#### **Materials and Methods**

Figure 1 shows the nitrification experimental apparatus constructed at CEETIA's Laboratory (see picture). The nitrification reactor has an effective volume V = 5.0 l. The reactor is fed by substrate which is prepared from tape water, kept in plastic box, rest for few hours for residual chlorine releasing, and then added with synthetic solutions as shown in Table 1. (Okabe S. et al., 1996, Cao T.H et al, 2001). In order to achieve  $NH_4^+$ -N concentration 20 and 40 mg/l. Seeding sludge for biomass growing has been taken from activated sludge model at CEETIA Laboratory. After it has been taken from activated sludge model, sludge has been seed in aerated plastic vase by feeding with mentioned above solution in batch regime. Twice a day, at 8.00 am and 2.00 pm. aerator is stopped for 30 min. for settling of sludge, vase is decanted and then fed again with new feeding water. Sludge height after 30-min. settling (SV<sub>30</sub>) is recorded. After 2 months of growing, from Dec. 1st 2002 to Feb. 16th 2003, 200 ml of this sludge thickened has been taken into fixed-bed media in nitrification reactor, and the new portion of nitrifying sludge had been grown again for later introducing into reactor (on March 8th 2003) in order to accelerate the treatment process.

Table 1. Solutions for substrate preparation

Solutions	Concentration (mg/l) in stage 1 (Dec. 2002 - Mar. 2003)	Concentration (mg/l) in stage 2 (Mar. 2003 – Apr. 2003)	
NH <sub>4</sub> Cl	76.4	152.8	
MgSO <sub>4</sub> .7H <sub>2</sub> O	100		
CH₃COONa. 3H₂O	28.4		
K <sub>2</sub> HPO <sub>4</sub> .3H <sub>2</sub> O	91.7		
NaHCO <sub>3</sub>	400 (from 15 May 2003)		



Figure 1. Nitrification model at CEETIA's Lab

The nitrification model started to run continuously from 16th Feb, 2003. Flow rate of feeding water through a dosing pump  $Q = 0.32 \sim 0.4$  l/h (HRT = 15.7  $\sim 12.5$  h). Oxygen flow from aerator was 0.6 ml O<sub>2</sub>/min. Parameters measured were ambient temperature, water temperature, pH, NH<sub>4</sub><sup>+</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> in influent and effluent from the reactor. Oxygen flow from aerator has also been increased from 0.6 to 0.8 ml O<sub>2</sub>/min.

#### First results and discussions

- 1. First results achieved after one month of starting experiment (i.e. from January to February 2003) show that with influent concentration of nitrogen ammonia 20 mg/l, hydraulic retention time HRT 15.7 ~ 12.5 h, an average nitrogen ammonia removal achieved was 86.2%. Furthermore, stable removal efficiency was recorded, ranging from 79.2 to 93.4%. Nitrate concentration in influent was ranging from 0.5 to 3 mg/l, while nitrate concentration in effluent was from 17.0 to 22.5 mg/l. i.e. less than permitted value for drinking water.
- 2. Increase of nitrogen ammonia concentration in influent water up to 40 mg/l lead to significant decrease of removal efficiency, as well as appearance of nitrite in effluent. Operation with longer hydraulic retention time did not change the process performance, due to high F/M ratio, and negative impact of nitrite as inhibitor for the nitrification process. Drop back of influent concentration of NH<sub>4</sub> down to 20 mg/l from beginning May 2003 gave significant improvement in process performance (62.0 ~ 96.6 % NH<sub>4</sub><sup>+</sup> removal efficiency).

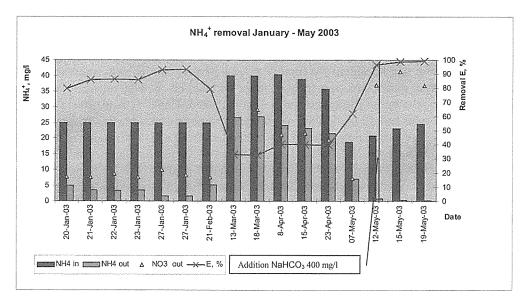


Figure 2. Nitrogen ammonia removal by nitrification

- 3. pH value decreases along the nitrification process, what fits the theoretical bio-chemical transformation of the system and relates to reduction of the alkalinity by consumption of HCO<sub>3</sub>. Low pH values (< 7) could be one from reasons of not achieving high treatment efficiency of nitrogen ammonia in the reactor. It is known that pH values > 7 have effect of limiting the conversion of nitrite into nitrous acid (which causes inhibition of ammonium oxidizers) and ensuring concentrations of free ammonia that would selectively inhibit nitrite oxidizers, thus favouring the stability of partial nitrification (Pollice A. et al., 2002). After addition of 400 mg/l NaHCO<sub>3</sub> into synthetic solution from 15 May 2003 for alkalinity and pH balancing reactor achieved very good NH<sub>4</sub><sup>+</sup> removal efficiency: up to 98.7 ~ 99.4 %. Optimum alkaline concentration will be determined in next series of experiments.
- 4. Due to low energy yield linked to the oxidation of ammonium and nitrite, respectively, the nitrifying bacteria has relatively low growth rate. In order to achieve high treatment efficiency the sludge seeding and provision of adequate growing environment are necessary. However, it is one advantage of this method linked with minimum sludge wastage during operation.

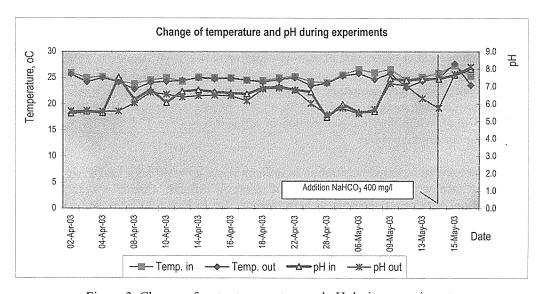


Figure 3. Change of water temperature and pH during experiments

5. Next research plans: The research team is going to continue experiments both in Laboratory and in field, with installation of experimental column at the Phap Van water treatment plant. Series of experiments on real ground water of Hanoi will be conducted. Long-term series of experiments should be carried out in order to achieve optimum operational parameters, as well as determination of influencing factors such as pH and alkalinity, presence of iron, manganese and other compounds as inhibitors in water, effect of hydraulic retention time (HRT), C: N ratio, oxygen transfer rate, biomass characteristics, etc.

## **Conclusions**

Nitrogen ammonia removal from ground water by attached-growth microbiological nitrification process with acrylic resin media and indirect aeration shows positive results and promising alternative for groundwater quality improvement in Hanoi city.

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