NITROGEN AMMONIA REMOVAL FROM GROUNDWATER BY NITRIFICATION – DENITRIFICATION PROCESS WITH A NOVEL ACRYL BIOFILM CARRIER MATERIAL

Nguyen Viet Anh[1], Pham Thuy Nga[1], Nguyen Huu Thang[1], Nguyen Van Tin[1], Tran Duc Ha[1], Tran Hieu Nhue[1], Leu Tho Bach[2], Kenji Furukawa[2]

[1] *Centre for Environmental Engineering of Towns and Industrial Areas (CEETIA), Hanoi University of Civil Engineering, Hanoi, Vietnam.*

[2] *Department of Civil Engineering and Architecture, Kumamoto University, Japan.*

(1) *Corresponding author. Address: CEETIA, DHXD, 55 Giai Phong Road, Hanoi, 10000, Vietnam.*

Tel. (+84)-4-869 8317, (+84)-91320 9689. Fax. (+84)-4-6281580.

E-mail. vietanhctn@yahoo.com, vietanhctn@gmail.com.

Abstract

Groundwater in the aquifers of Hanoi is polluted with nitrogenous compounds predominately in the form of ammonium -N (up to 30 mg/L). Microbiological removal of nitrogen compounds by nitrification followed by denitrification could be most appropriate technology for Hanoi. This study focuses on development of nitrification – denitrification process for nitrogen ammonia removal from ground water by using a novel acryl fiber (Biofill, NET Co. Ltd., Japan) for fixed-bed media. Results show that: with influent concentration of ammonium 20 mg/L, hydraulic retention time HRT = 1 h in nitrification reactor, a stable ammonia-N removal can be achieved with average efficiency 98.7% (93.2 – 99.9%). Nitrogen loading rate NLR = 0.01 – 0.62 kg $N\text{-}NH_4^+$/ (m^3.day). Alkalinity was necessary to be added in the form of $NaHCO_3$ with minimum concentration of 50 mg/L. In denitrification reactor, a required HRT to achieve stable removal of nitrate was 2 h. Average removal efficiency of nitrate was 94.2% (90.09 – 98.37%). NLR = 0.04 – 0.16 g $N\text{-}NO_3^-$/ (g VSS.day) or 0.09 – 0.39 kg $N\text{-}NO_3^-$/(m^3.day). Required ratio of sodium acetate CH_3COONa as a carbon source to be added per equivalent nitrogen removed COD/N = 6.92. Remaining concentration of COD, ammonium and nitrite were major concerns of denitrification process effluent. Post treatment by aeration and filtration are suggested to be introduced after denitrification. Research results show positive results and open a promising solution for groundwater quality improvement in Hanoi city.

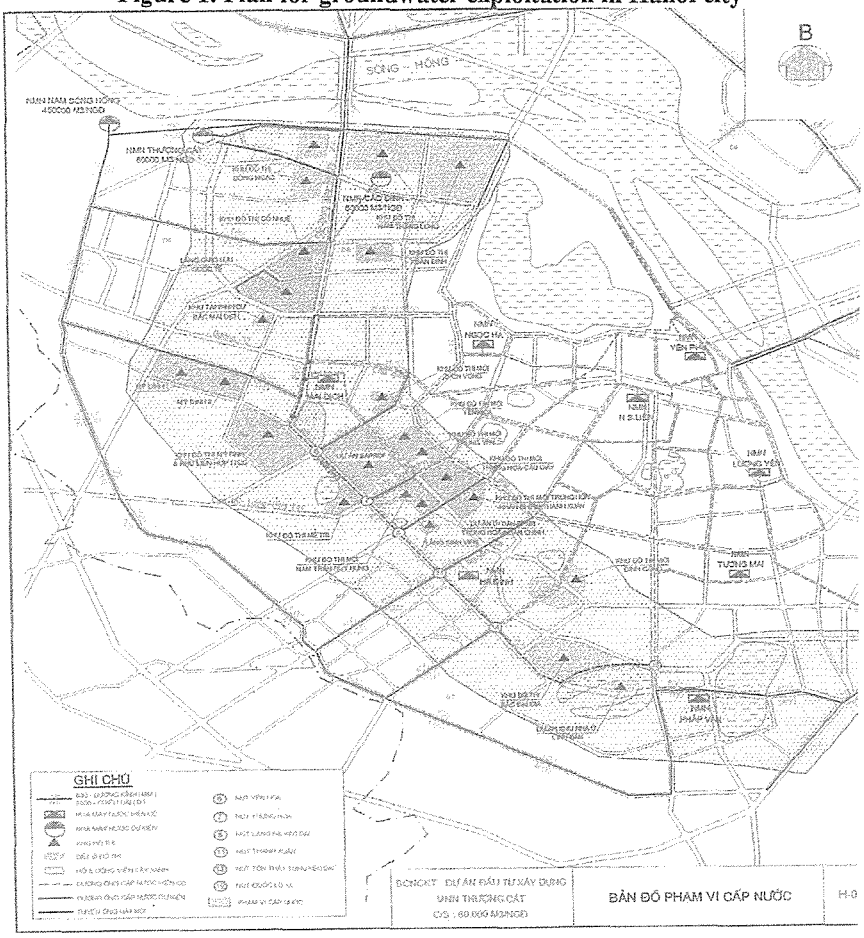
Keywords: Ammonium, COD, denitrification, ground water, Hanoi, nitrification, nitrogen, water treatment.

1. Introduction

Existing situation of groundwater pollution by ammonium in Hanoi area

Over the last ten years the population of Hanoi has increased rapidly to more than 3 millions people. In the city there is an intensive exploitation of groundwater for domestic and industrial purposes. The Hanoi water business company is exploiting main well fields with about 150 wells for the 10 water treatment plants with the total production capacities of 400,000 to 450,000 cubic meters per day (see Figure 1). Beside that, there are more than 500 industrial production wells with smaller capacity that are exploited by enterprises, research institutes, hospitals, school units … with approximately 50,000 to 60,000 cubic meters per day exploited in the city. All around city there are more than 100,000 small bore wells (so called UNICEF wells) with total capacity of about 200,000 cubic meters per day. Thus, the total volume of groundwater exploited in Hanoi area is up to 600,000 – 650,000 cubic meters per day. This volume is nearly reaching a limit of groundwater availability for the city. Under such intensive and exhausting exploitation the groundwater resource is facing the serious risk of table depletion and quality deterioration.

Figure 1. Plan for groundwater exploitation in Hanoi city

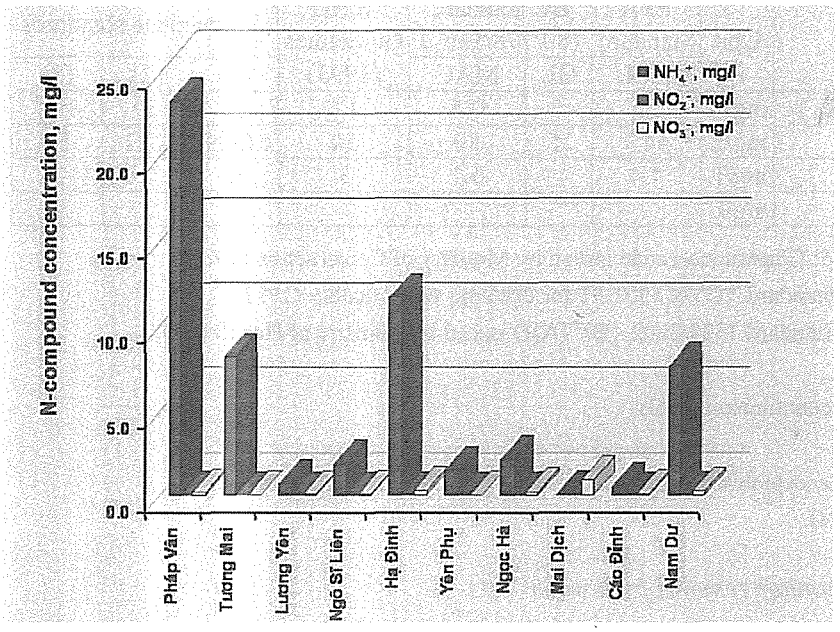


(Hanoi Water Business Company, 2004).

In recent years, ammonium concentration in the groundwater in Hanoi has become an increasing problem for water quality management in the city. The most heavily polluted areas are located mainly in the southern part of the city where nitrogen ammonia concentrations range from 20 to 30 mg/L. There is still no clear explanation of the ammonium origin in the ground water of Hanoi. Backward sewerage and drainage system, inadequate wastewater and solid waste disposal and treatment, besides development of intensive agriculture and industrial production in current period are being discussed as the pollution sources, while some other specialists explained it based on the nature of the Hanoi hydrogeology. Geological and hydrographic conditions in the Red delta are very complicated. Hydro geological ''windows" between permeable soil layers and the river bed, between upper and lower aquifers supporting some endosmosis processes, unsealed old and fallow monitoring and production water wells, etc. may transfer pollutants from surface to groundwater. All the reasons mentioned above may lead to a high pollution risk of nitrogen compounds in the unique water source of the city.

According to the results drawn from different previous studies (Ha C.T., 2004, HWBC, 1997 – 2004), ammonium content in water of the aquifers is changing from trace to 30 mg/L. Most of the areas are polluted by ammonium as Phap Van, Dinh Cong, Ha Dinh, Kim Giang, Tuong Mai, Bach Mai, Bach Khoa, Kim Lien, Quynh Mai. Among of them, some areas are lightly polluted as Luong Yen, Yen Phu, Ngo Si Lien, Don Thuy. Besides, some areas have a sign of pollution as Ngoc Ha, Mai Dich. In general, the strongly polluted areas are mainly located in the south and the center. There is the highest pollution (~ 20 mg/L) in Phap Van, after that in Ha Dinh area (~ 12 mg/L), Tuong Mai (~ 10 mg/L). It is worth to note that in the monitored areas, the nitrate and nitrite content are not high, meeting drinking water standard (See Figure 2).

Figure 2. Concentration of nitrogen compounds in main water treatment plants in Hanoi city



(Ha C.T. et al., 2004)

Presence of nitrogen compounds in water may cause some dangerous diseases for water users. Nitrate can cause lacks of vitamin and is able to combine with amine to create the nitrosamine to cause cancer for elderly. The newborn babies are highly sensitive to nitrite which is entered by the mother's milk, or by water used for making the milk formula. After entering the body, nitrate will be transformed into nitrite by intestine bacterium. Nitrite ion is more dangerous than nitrate for the people health. When reacting with amines or alkyl in the body, they can form the nitrogen compounds causing cancer. Nitrites will affect hemoglobin (Hb), which is responsible for carrying oxygen, and, turn it into methemoglobin (Mel-Hb), which can not carry oxygen. Thank to the special enzyme, Mel-Hb will change into oxygen – hemoglobin (oxygen-Hb). In small children, Mel-Hb can not change into oxygen-Hb because their enzyme systems are not completely grown. In small children, liquid in their stomach is little; the bacterium creates a lot of nitrite. On the other side, their stomach has few acids to prevent nitrate from turning into nitrite. Therefore, a big content of nitrite take hemoglobin and change it into Mel-Hb. This causes a loss of ability of oxygen transfer to the tissues and therefore causes the diseases for the babies (Viet Anh N., 2001).

Ammonium in groundwater reduces antiseptic efficiency as it reacts to chlorine to create chloramines, which antiseptic capacity is much lower than chlorine (about 1000 times). Additionally, it lowers ability of iron and manganese removal by traditional treatment technology.

Ammonium is an important nutrient. Its elevated concentration can create favorable conditions for intensive growth of aquatic organisms, including algae, which leads to deterioration of commodity water quality, especially its clarity, smell, taste and bacterium contamination.

Before 2002, in Vietnamese standard, the ammonium content in the supply water was required to be lower than 3 mg/L. Since April 2002, according to the new standard No. 1329/2002 – QD/BYT, the ammonium content must be under 1 mg/L, equal to the World Health Organization (WHO) standard. The standard of the European Union for ammonium is under 0.5 mg/L. (See the Table 1).

Table 1. The Vietnamese and international standard for nitrogen compounds in supply water

Parameter	Unit	EPA Standard	EC standard (80/778/EEC)		WHO Guidelines	Vietnamese standards		
		MCL	GL	MAC	(1993)	(1)	(2)	(3)
Ammonium (NH_4^+)	mg/L			0.5	1.5	3[a]	3[a]	1.5[a]
Nitrate (NO_3^-)	mg/L	44.3	25	50	50	6(as N)	22.1	50
Nitrite (NO_2^-)	mg/L	4.4		0.1	3	0	0	3
COD ($KMnO_4$)	mg/L					2	2	2

(1) - 20 TCN 33-85: Construction code issued by Ministry of Construction (1985).

(2) – Vietnamese Standard TCVN 5501-91 for drinking water quality (1991).

(3) – Vietnamese Standard 1329/2002 - BYT/QD issued by Ministry of Health (2002).

a – Ground water.

MCL - Maximum contaminant levels.

GL – Guidelines.

MAC - Maximum acceptable concentration.

(Ha C.T. et al, 2004).

Methods for ammonium removal from water

In groundwater, nitrogen compounds may exist in organic, nitrite, nitrate and ammonium compounds. Many technologies have been tested and applied by many countries: air striping, break-point chlorination, bio-chemical nitrification - denitrification, ion exchange, electrochemical methods, reverse osmosis, electrodialys, distillation (Viet Anh N., 2001).

However the treatment technologies for nitrogen ammonium removal from groundwater supply are still unknown not only to Vietnam but also to many other countries in the world, especially at raised ammonium concentration of 10 - 20 mg/L. This is a reason to promote this research. It is needed to find an appropriate method of high efficiency, stable operation, acceptable cost where treated water should meet the Vietnamese water quality standards. Experiences from number of researches over past years have shown that biological oxidation (nitrification) in aerated submerged bioreactor followed or not followed by denitrification (depending on initial concentration of nitrogen ammonia) is recognized as a promising method. The main advantages are: no additional treatment steps and not expensive.

Bio-chemical processes of nitrogen transformation

At first, ammonium is oxidized to nitrite by oxidizing bacteria of *Nitrosomonas* (step 1). After that Nitrite ions are oxidized to Nitrate by *Nitrobacter, Nitrospira, Nitrococcus and Nitrosocystis* (step 2) (Henze, 2002). Nitrifying species belong to group of autotrophic micro-organisms which use energy generated from nitrification reaction where nitrogen ammonia is an electron donor for building up of their cells. Carbon source of new cell production is inorganic carbon (HCO_3^-). Besides, they consume oxygen intensively.

$$NH_4^+ + \frac{3}{2}O_2 \xrightarrow{\text{Ammonium oxidyzing bacteria}} NO_2^- + 2H^+ + H_2O + 276 \div 351KJ \quad (1)$$

$$NO_2^- + \frac{1}{2}O_2 \xrightarrow{\text{Nitrite oxidyzing bacteria}} NO_3^- \quad (2)$$

By combining (1) and (2):

$$NH_4^+ + 2O_2 \longrightarrow NO_3^- + 2H^+ + H_2O \quad (3)$$

With metabolic process consideration we have (Gujer, 1974):

$$1.02\ NH_4^+ + 1.89\ O_2 + 2.02\ HCO_3^- \text{--->}$$

$$0.021\ C_5H_7O_2N + NO_3^- + 1.92\ H_2CO_3 + 1.06\ H_2O \quad (4)$$

That process is normally implemented in a biological reactor with attach-growth biomass on carrier media. Formation of biofilm on the surface of carrier material enables the increase of biochemical reactions and increases of activated sludge age.

Rate of oxidation process depends on sludge age, temperature, pH, food per microorganism (F/M) ratio, initial ammonium concentration, dissolved oxygen concentration, media characteristics, etc. Nitrifying bacteria have limited integration capability, thus selection of carrier media plays an important role in the treatment efficiency and the composition of the biochemical reaction products. Using appropriate carrier material for biofilm attach-growth may bring to retaining of biomass on the carrier media, increase of sludge age, increase and keeping of stable treatment efficiency in the same reactor volume, as well as enabling resistance of the system from possible shocks due to changes of environmental conditions.

For elimination of nitrate, heterotrophic bacteria convert nitrate into atmospheric nitrogen under anaerobic conditions. Nitrate is the oxidizing agent, which gives the process the name of anoxic. This process requires electron donors which could be organic compounds, H_2S, etc. If there is no presence of dissolved oxygen but there are biodegradable organic matters available, the heterotrophs can utilize nitrate as oxygen source for oxidation of organics (electron donor) while the nitrate (electron acceptor) is reduced into nitrogen gas as in following equation:

$$NO_3^- + \text{organics} + \text{bacteria} \rightarrow N_2 + CO_2 + H_2O + \text{biomass growth} \quad (5)$$

In fact the denitrification process is a combination of the series of the four steps:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2\,(\text{gas}) \quad (6)$$

Bacteria receive energy for their growth from denitrification process of NO_3^- into N_2 while they need a carbon source for the cell reproduction. Thus, during denitrification process, an additional carbon source may be needed. The common carbon sources are natural gas (methane containing), alcohol, sugar, sodium acetate, acid acetic, etc. where sodium acetate is one among most suitable additives. The reaction is as follows:

$$4NO_3^- + CH_3COONa \rightarrow 4NO_2^- + 2CO_2 + H_2O + NaOH \quad (7)$$

After that:

$$2NO_2^- + CH_3COONa \rightarrow N_2 + 2CO_2 + H_2O + NaOH \quad (8)$$

Combining two processes:

$$4NO_3^- + 3CH_3COONa \rightarrow 2N_2 + 6CO_2 + 3H_2O + 3NaOH \quad (9)$$

As nitrifying bacteria are slowly growing organisms and will thus be washed out of continuous flow reactors unless they are effectively immobilized. A high cell concentration is possible with immobilized biomass, which enhances volumetric efficiency. This allows for relatively small reactors and often offers protection from toxic shocks and adverse temperatures which would help to maintain stable treatment.

2. Materials and methods

Experimental model for study on nitrification and denitrification process is presented in Figure 3 and Figure 4.

Figure 3. Scheme of ammonium removal experiment

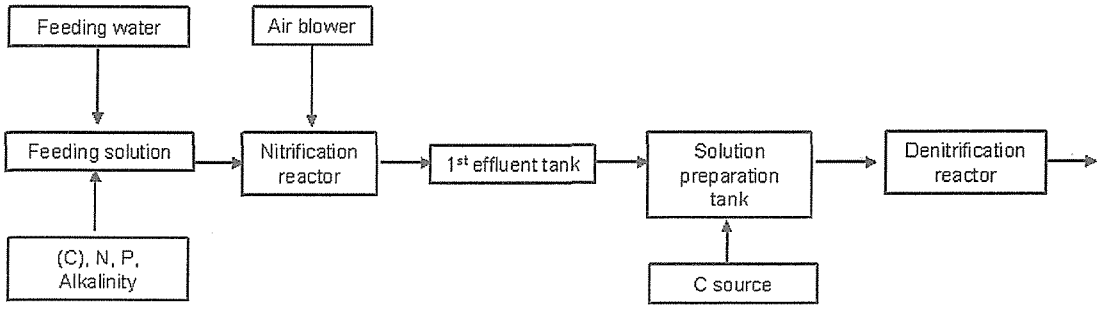
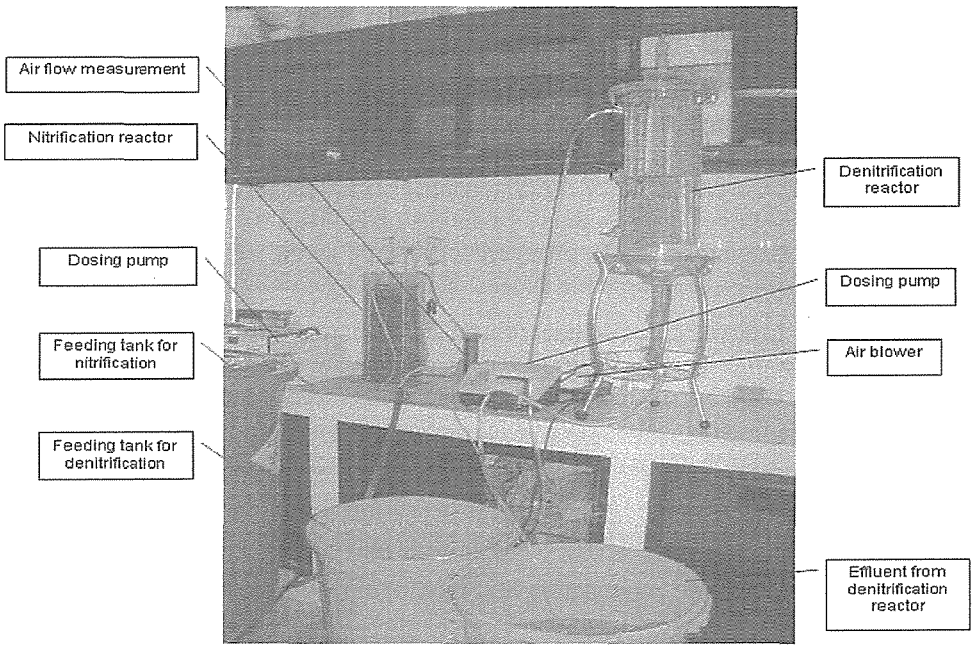


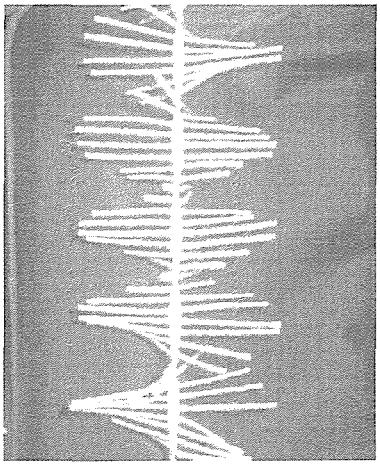
Figure 4. Experimental model at CEETIA Laboratory



The nitrification reactor

For effective microbiological nitrogen ammonia elimination from groundwater, one of the critical factors is the selection of the aeration process (in nitrification reactor) and the 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, some advantages could be achieved, such as reduction of head loss 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, stable treatment efficiency. This study focuses on the development of the nitrification process by using a novel acryl fiber (Biofill, NET Co. Ltd., Japan) (See Figure 5) and indirect air introduction into filtration chamber.

Figure 5. Acrylic carrier material Biofill Net



The nitrification reactor made by plexiglas has a rectangular shape of dimensions of B x L x H = 10 x 14.5 x 40 cm, total volume of 5.8 L. The reactor is fed by substrate which is prepared from tape water, kept in plastic tank, rest for few hours for residual chlorine releasing, and then added with synthetic solutions as shown in Table 2 (Cao T.H et al, 2001, Okabe S. et al., 2002) in order to achieve ammonia nitrogen concentration of 20 and 40 mg/L. Seeding sludge for biomass growing has been taken from activated sludge plant. The feeding solution was introduced into the reactor in a complete mixed and continuous regime 24/24h using a peristaltic pump and aquarium air blower. The air flow was measured and adjusted by a flow meter device. The reactor was covered by a black cloth to prevent from sun breathing and algae growth. Ambient temperature was kept at 20 - 25°C. Reactor was put into operation from February 2003 to July 2004.

The denitrification reactor

Denitrification reactor – cylinder made by plexiglas had a diameter of 200 mm and height of 500 mm, making total volume of 13.2 L. The same media of acrylic resin of Biofilm Net was used for the denitrification media. Nitrified water kept in a intermediate tank and mixed with additional sodium acetate as a carbon source is pumped into the denitrification reactor in up-flow regime. The model was operated continuously from February 2004 to July 2004.

Preparation of sludge

Nitrifying activated sludge was collected from running wastewater treatment plant at one hotel in Hanoi city for the sludge seeding. Acclimatization period for sludge growth and stabilizing in the reactors was approximately 2 months. Even distribution of the sludge on the whole surface area of the media in a whole reactor was one among advantages of the novel carrier material.

Preparation of feeding substrate

Synthetic substrate for the reactor feeding was prepared from tap water mixed with chemicals as described in the Table 4 in order to achieve ammonium concentration in the feeding substrate about 10, 20 and 40 mg/L. Alkali content added into the feeding was varying from 400 mg/L to 30 mg $NaHCO_3$/L, and kept at 50 mg/L as the minimum content required.

The feeding solution for the denitrification reactor was the effluent from the nitrification one added by organic matters as carbon source. In the first period, acetic acid was tried as a carbon source. In the following periods, sodium acetate was introduced instead of acetic acid at concentration varying from 260 to 400 mg/L to achieve the ratio of COD/N = 5 - 6 (Henze, 2002). That elevated COD/N ratio may help to avoid possible starvation of microorganisms and to remove soluble oxygen (if any) from the effluent liquid which negatively impacts on the following denitrification process.

Table 2. Constituents in feeding substrate for the nitrification reactor

Chemicals	Concentration (mg/L)
NH_4Cl	152.8 (from 12/2002 to 2/2003); 76.4 (from 2/2003 to 7/2004)
$MgSO_4.7H_2O$	100
$CH_3COONa.3H_2O$	28.4 (from 12/2003 to 2/2003); 0
$K_2HPO_4.3H_2O$	91.7
$NaHCO_3$	From 400 (from 12/2003) to 50 (from 16/3/2003)

Operational regimes

Operational regimes of the system are shown in Table 3 and Table.

Table 3. Operational regimes of nitrification experiments

Periods	Operational regimes
20/12/2002 – 20/1/2003	(i) Growing sludge, acclimatization step
20/1/2003 – 12/5/2003	(1) ... (3) HRT=21.2 h, N-NH_4^+ in = 20 ... 40 mg/L, $NaHCO_3$ = 0 mg/L
12/5/2003 – 23/7/2003	(4) ... (10) HRT=21.2 h, N-NH_4^+ in = 20 mg/L, $NaHCO_3$ = 400 ... 50 mg/L
23/7/2003 – 29/7/2003	(11) HRT=16 h, N-NH_4^+ in = 20 mg/L, $NaHCO_3$ = 50 mg/L
29/7/2003 – 8/8/2003	(12) HRT=8 h, N-NH_4^+ in = 20 mg/L, $NaHCO_3$ = 50 mg/L

8/8/2003 – 11/8/2003	(13) HRT=6 h, N-NH_4^+ in = 20 mg/L, $NaHCO_3$ = 50 mg/L
11/8/2003 – 14/8/2003	(14) HRT=4 h, N-NH_4^+ in = 20 mg/L, $NaHCO_3$ = 50 mg/L
14/8/2003 – 20/8/2003	(15) HRT=2 h, N-NH_4^+ in = 20 mg/L, $NaHCO_3$ = 50 mg/L
28/8/2003 – 27/8/2003	(16) HRT=1 h, N-NH_4^+ in = 20 mg/L, $NaHCO_3$ = 50 mg/L
27/8/2003 – 31/8/2003	(17) HRT=0.5 h, N-NH_4^+ in = 20 mg/L, $NaHCO_3$ = 50 mg/L
1/9/2003 – 24/9/2003	(18) HRT=2 h, N-NH4+ in = 20 mg/L, NaHCO3 = 50 mg/L
24/9/2003 – 4/10/2003	(19) HRT=2 h, N-NH4+ in = 10 mg/L, NaHCO3 = 50 mg/L
4/10/2003 – 21/10/2003	(20) HRT=1 h, N-NH4+ in = 10 mg/L, NaHCO3 = 50 mg/L
21/10/2003 – 23/4/2004	(21) HRT=2 h, N-NH4+ in = 20 mg/L, NaHCO3 = 50 mg/L
23/4/2004 – 30/7/2004	(22) HRT=1 h, N-NH4+ in = 20 mg/L, NaHCO3 = 50 mg/L

Table 4. Operational regimes of denitrification experiment

Periods	Operational regimes
5/1/2004 – 16/1/2004	(i) Return flow. 0.02 – 0.16 L CH3COOH/l, HRT =5,5 h.
16/1/2004 – 9/3/2004	(ii) ... (iii) Return flow. 130 – 340 mg CH3COONa.3H2O /l, HRT =5,5 h
9/3/4004 – 28/3/2004	(1) 260 mg CH3COONa.3H2O/l, HRT =5,5 h.
28/3/4004 – 14/4/2004	(2) 400mg CH3COONa.3H2O /l, HRT =5,5 h.
14/4/4004 – 23/4/2004	(3) 400mg CH3COONa.3H2O /l, HRT =4,07 h.
23/4/4004 – 12/5/2004	(4) 400mg CH3COONa.3H2O /l, HRT =3 h.
12/5/2004 – 16/6/2004	(5) 400mg CH3COONa.3H2O /l, HRT =2 h.
16/6/2004 – 22/7/2004	(6) 400mg CH3COONa.3H2O /l, HRT =1 h.
22/7/2004 – 26/7/2004	(7) 400mg CH3COONa.3H2O /l, HRT =0,5 h.
26/7/2004 - 30/7/2004	(8) 400mg CH3COONa.3H2O /l, HRT =1 h.

The experiments were carried out at many different operational regimes (illustrated as in Table 3 and Table *4*) in order to answer the following questions:

- Minimum allowable HRT which equals to minimum required reactor volume.

- Suitable chemicals and their minimum required dosing content, including substrate components, carbon source, alkali, etc...

- Factors which are affecting removal efficiency and stability such as temperature, alkalinity, dissolved oxygen concentration, presence of inhibiting compounds such as iron, manganese, nitrite, etc.

3. Results and discussions

The nitrification model

1. Nitrogen ammonia concentration in the influent was about 20 mg/L, which equals to the highest concentration in groundwater in some water plants in Hanoi. The removal efficiency was achieved from 93.2% to 99.9% (average 98.7%) at the minimum HRT of 1 h. Nitrogen ammonia concentration in effluent was ranged from 0 to 0.53 mg/L.

2. In the setting up period, since concentrations of nutrients such as N, P available in groundwater are often low, the nutrients need to be added into feeding solution. When the system operation has stabilized, adding of the nutrients is not necessary. Time needed to reach stability of biological reactor was about 2 months from the start of operation.

3. Acrylic carrier seems very suitable for carrier media for nitrogen removal in a biological reactors.

4. If initial ammonia concentration in groundwater is less than <11 mg/L, only nitrification process need to be carried out. Otherwise, both of the processes needed to be carried out to reach allowable quality standard of nitrate thanks to conversion of ammonium to nitrate (See Table 1).

5. The nitrogen ammonia loading rate (NLR) per unit volume of reactor was determined. That was NLR = 0.01 – 0.62 kg $N\text{-}NH_4^+/(m^3.day)$ at the high and stable ammonium removal efficiency, from 93.2% to 99.9% (in average 98.7%).

6. After nitrification process, alkalinity and pH in effluent has been reduced as HCO_3^- ion was used for nitrification reaction (such illustrated as in equation (4)). If alkalinity in the feeding substrate is not enough, alkaline should be added. Theoretically, nitrification process can happen at pH = 7 – 7.8. If pH is less than 7, the nitrification process can be inhibited. The inhibition was checked in the first period wherein alkalinity was not added into the reactor. Enough alkalinity in a stable environment can bring to high and stable treatment efficiency. Minimum alkaline content that need to be added into the model using tap water from CEETIA is 50 mg $NaHCO_3$/l. More alkalinity did not increase the treatment efficiency while it equals to more chemical expenses. Furthermore, high alkalinity dosing raises the pH value and increases concentration of ammonium gas NH_3 converted from soluble ammonium. It is well known that ammonium gas is an inhibitor for the microorganism growth.

7. Dissolved oxygen DO value always was minimum, but still higher than 4 mg/L. If DO was low, content of intermediate product nitrite was high. Nitrite was an inhibitor to removal efficiency. Temperature higher than 20°C has been appropriate for the nitrification process. Temperature less than 20°C seemed to have a disadvantage in treatment performance.

8. Exceeding sludge create negative effects on the treatment efficiency. In the last period, a lot of sludge in the form of thick biofilm accumulated, leading to unfavorable F/M ratio and possible anaerobic conditions, and, consequence reduced treatment efficiency (Fig 2/e). Sludge removal by introduction of air flow into the media followed by sludge emptying can surmount this problem.

The nitrification model

1. The model had been operated from early February 2004 to last July 2004. After 6 months in operation, the results showed that the model operated well and stably. Average denitrification efficiency was 95.1%. Minimum HRT needed to get high and stable removal efficiency (> 95%) was HRT = 2 h. If HRT reduced to 1 h or 0,5 h, treatment efficiency was low and unstable (90 – 95%). Nitrate concentration in the effluent can meet the Vietnamese standard for drinking water which should be bellow 50 mg/L. However, if the denitrification process happened completely, intermediate product of nitrite created in water was still high. Nitrite is a toxic compound, inhibiting bio-organic transforming process. That could be a reason for treatment efficiency which did not reach the maximum values .

2. pH in reactor was in a range of 6.89 – 8.19. Alkaline and pH values in the effluent were increased. The addition of alkaline into the previous step of nitrification makes the denitrification to stabilize. The theoretical optimum pH values for denitrification process are 7 – 8 (Ha C.T. et al., 2001) what has been confirmed by these experiments.

3. After treatment, nitrite in the effluent from the denitrification model was sometimes higher than that in the standard (3 mg/L). In unsuitable pH, temperature, or in presence of inhibitor(s), the denitrification reaction did not occur completely to produce an intermediate product of nitrite. It may be also due to the remaining of ammonium in inflow before the denitrification reactor. Some solutions could be proposed including increasing HRT and adjustment of F/M rate, adding sodium acetate to utilize soluble oxygen in water, and, introduction of aeration step after this treatment.

4. Concentrations of organic compounds utilized as the carbon source for reduction of nitrite and nitrate processes (not including cells production) are calculated by the following equation:

$$C_s = 0.357\ W_e (1.0\ N\text{-}NO_3^- + 0.6\ N\text{-}NO_2^- + 0.35O_2) \qquad (10)$$

wherein: W_e is an electron equivalent for organic compounds, g/m^3 (McCarty, 1969).

Converting from $N\text{-}NO_2^-$ and O_2 to $N\text{-}NO_3^-$ equivalent concentration:

$$C_s = 0.357\ W_e\ N\text{-}NO_3^-{}_{eq} \qquad (11)$$

With metabolic process consideration :

$$C_s' = 0.357\ W_e C_r N\text{-}NO_3^-{}_{eq} \qquad (12)$$

In which $C_r = C_s'/C_s$ is consumption rate (McCarthy, 1969). If we calculate organic compounds through COD (mg/L), than $W_e = 8$g COD, from where:

$$COD = 2.86\ C_r\ N\text{-}NO_3^-{}_{eq} \qquad (13)$$

Value of C_r is varying between 0.8 - 3.6 based on the chemicals used (Monteith, 1980).

In this study, while the denitrification process operated stably, the average COD_{in} was 144.1 mg/L ± 11.3 (st.dev.), COD_{out} was 32.8 mg/L ± 9.6 (st.dev.), the average of compounds of Nitrogen ($N\text{-}NO_3^-{}_{eq}$) in influent was $N\text{-}NO_3^-{}_{eq}$ (in) = 17.0 mg/L ± 1.6 (st.dev.), in effluent was $N\text{-}NO_3^-{}_{eq}$ (out) =1.0 mg/L ± 0.4 (st.dev.). C_r has been calculated as 2.42. The value was similar to that of other researches. C_r was higher than 1 means that the organics consumption for cell building was more than consumption for denitrification. That also shows the required organics ratio versus nitrogen concentration COD/N is about 6.92. From this value we can determine necessary organic loads to be fed to the reactor in order to control the effluent COD.

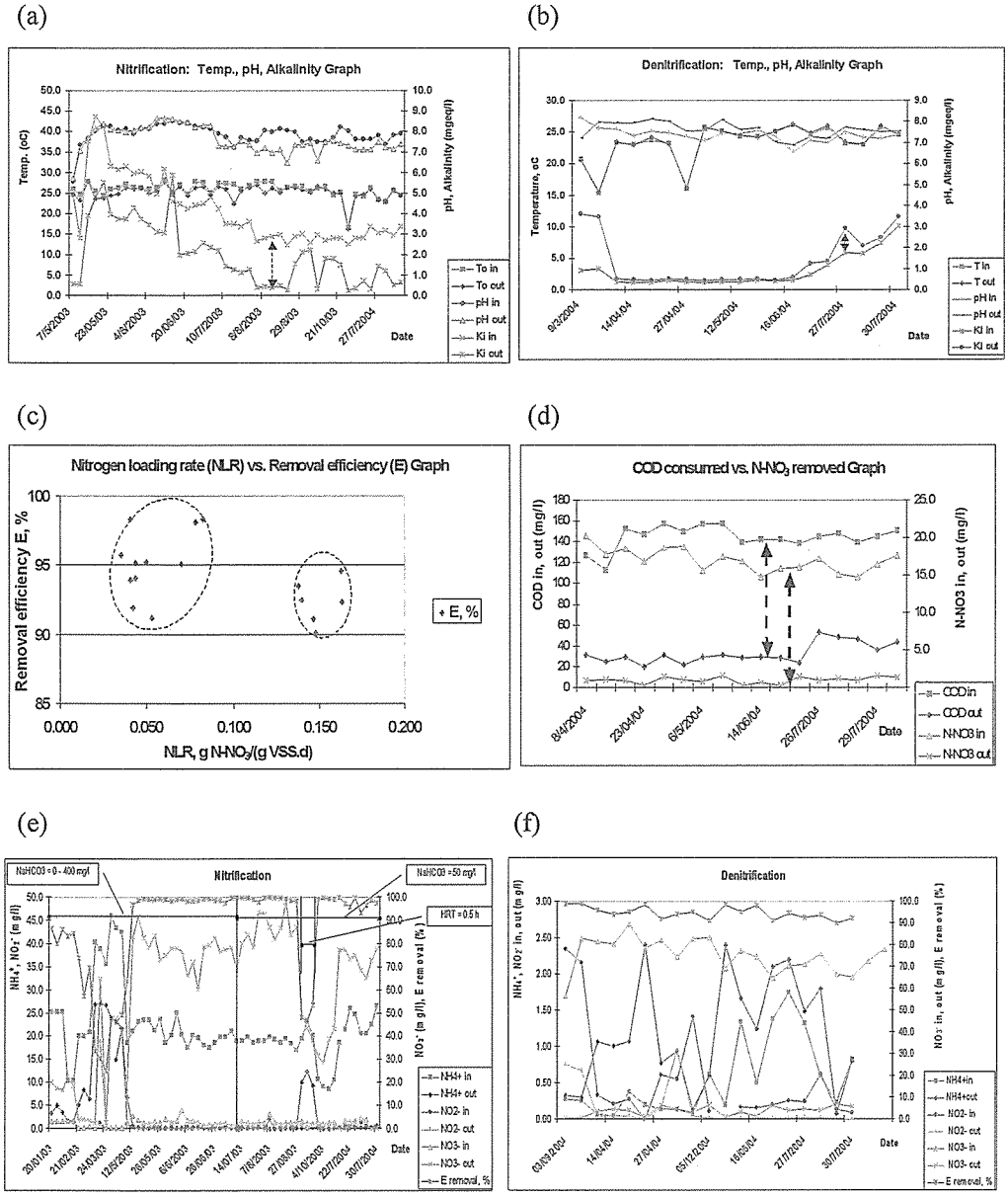
5. We also determined values of NLR in different operational regimes. NLR collected were in a range of 0.04 – 0.16 g $N\text{-}NO_3$/(g VSS.day). In this range, nitrate removal efficiency was high and stable (90.1 – 98.4%, the average of 94.2% ± 2.5 (st. dev.). Those values fit the range determined from international experiences which are from 0.03 to 0.11 g $N\text{-}NO_3^-$/(g VSS.day) (Henze, 2002, Ha C.T., 2004). When there is enough organic substrate, the novel acrylic resin allows high density of the biomass, what may lead to high treatment efficiency with higher nitrogen loading rates (NLR). However with NLR > 0.15 g $N\text{-}NO_3$/(g VSS.day) the removal efficiency was less than 95%. NLR was determined = 0.09 – 0.39 kg $N\text{-}NO_3$/(m^3.d).

6. Carbon source added into denitrification process was sodium acetate. Adding acetic acid as carbon source did not bring to good treatment efficiency as it created unfavorable conditions for microorganisms (low pH and alkalinity). Besides, adding acetic acid also creates suitable conditions for undesired fungi growth and bad odors in the waters.

7. Ammonium content in the effluent was higher than that in the influent may be because of anaerobic disintegration of dead cells of microorganisms happened in the reactor. It can be solved by supplying air after denitrification step to control ammonium, remaining organic compounds and odors control in the effluent.

8. The efficiencies in both reactors were high and stable, which means that treatment technology of ammonium in groundwater by the nitrification and denitrification with a novel carrier media of acrylic resin is feasible. However, further research is needed for getting more information of the process and for practical implementation.

Figure 6. Results of nitrogen removal experiments



(a) Nitrification reactor: changes of temperature, pH, alkalinity;
(b) Denitrification reactor: changes of temperature, pH, alkalinity;
(c) Denitrification: Relationship between N-NO_3^- (NLR, mg N-NO_3^-/ g VSS.day) and removal efficiency (E, %);
(d) Denitrification: Relationship between COD consumed and removal efficiency;
(e) Nitrification rector: Ammonium removal over operation regimes.
(f) Denitrification: Denitrification efficiency over last months.

4. Conclusion

The results from our experiments illustrated that the treatment of ammonium from polluted groundwater by biological process including nitrification and denitrification process using acrylic carrier material is a promising solution. This method has shown a high removal efficiency, reliability, stability and can be applied perfectly. The results from research also provided a lot of important information to support next study in a pilot scale and for applying of this method to the full scale in order to solve current crucial problem for water supply in Hanoi city.

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