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BIOLOGICAL AMMONIA REMOVAL BY SUBMERGED AERATED FILTER FROM HANOI GROUND WATER

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ABSTRACT

Iron, ammonia and organic matters heavily contaminate South Hanoi groundwater. Conventional treatment technology, which includes aeration - sedimentation - sand rapid filtration steps, is good in iron removal but inadequate for ammonia and organic removal. Utilization of submerged aerated filter allows oxidation of ammonia into nitrate at very high filtration velocity of 5 m.h⁻¹ to get Vietnamese standards level of 3 mg ammonia.L⁻¹. The further nitrogenous removal is expected in the following denitrification step by submerged too, but without aeration filter. The key figure in biological filtration is filtration or biomass carrier - material. It was also confirmed that application of Thanh Hoa porous bazon mineral allowed quick starting - up (within 2 weeks) to get stationary maximum NH₄⁺ conversion and the best performance.

KEYWORDS

Aerated, ammonia, biofiltration, denitrification, fixed granular bed, nitrification, submerged filter.

INTRODUCTION

Nitrogenous compounds, such as ammonia, nitrite, and nitrate, have been frequently present not only in wastewater but also in drinking water. It is well established that presence of large amount of nitrogenous compounds can cause eutrophication in receiving water bodies (Metcalf and Eddy, 1991). In drinking water the concentrations of N-compounds are limited by National Standards or Guidances. In Vietnamese practice, ammonia concentration must be lower than 3 mg.L⁻¹, while in industrialized countries this value is much more strict (Table 1).

Table 1. Standards and guidance for drinking water quality

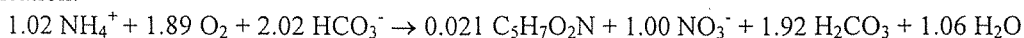
Items	Units	US EPA		EEC Standard (80/778/EEC)		WHO guidelines (1993)	VN Standard		
		MCLG	MCL	GL	MAC		1	2	3
Ammonium	mg.L ⁻¹				0.5	15	3 ^a	3 ^a	3 ^a
Nitrate (as NO ₃ ⁻)	mg.L ⁻¹	44.3	44.3	25	50	50	6	22.1	44.3
Nitrite (as NO ₂ ⁻)	mg.L ⁻¹	4.4	4.4		0.1	3	0	0	0
Nitrite + Nitrate	mg.L ⁻¹	10	10						
COD _{Mn}	mg.L ⁻¹						2	2	2

Notes: VN Standard 1 - TCN 33-35: Standards issued by Ministry of Construction; 2-TCVN 5501-1991: National Standard; 3-505 BYT/QD (April 13, 1992): Provisional Standards issued by Ministry of Health; a - for groundwater; MCLG - Maximum Contaminant Levels Goal; MCL - Maximum Contaminant Levels; MAC - Maximum Acceptable Concentration.

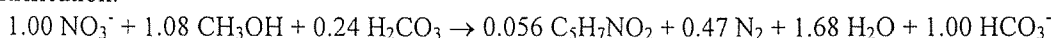
The presence of N-compounds in drinking water can cause a set of water-quality problems such as: 1- biologically instability, which means it will support growth of microorganisms during water distribution, and as a consequence, it can lead to serious secondary water quality problems, such as taste, odour, excessive bacterial counts, turbidity and accelerated corrosion; 2-it readily reacts with chlorine during post chlorination to create chloramines, which are substantially weaker disinfectants than free chlorine is. Furthermore, dissipation of chloramines during storage and distribution regenerates the $\text{NH}_4^+\text{-N}$; 3-high amount of $\text{NH}_4^+\text{-N}$ can lead to formation of $\text{NO}_2\text{-N}$, which is acutely hazardous to infants and is also implicated in the destruction of chloramines residues-secondary disinfectants. These are the reason, why we have to remove ammonia from drinking water, and that is the goal of this paper.

To achieve this goal biological oxidation of $\text{NH}_4^+\text{-N}$ into $\text{NO}_3^- \text{-N}$ by autotrophs and following by denitrification seems to be very promising. Biological oxidation of $\text{NH}_4^+\text{-N}$ into $\text{NO}_3^- \text{-N}$ and denitrification follow equations:

Nitrification:



Denitrification:



Besides removal of N - compounds, it is clear from above equations expressing denitrification process that during the process bacteria will consume organic matters, that makes the water quality better regarding to COD value (Rittman, 1995).

Because of well established low yield of autotrophs an attached growth process as a modified Degremont's Biofor and Biodrof techniques were chosen to avoid biomass loss (Degremont, 1991). The detail of the bench apparatus for lab scale nitrification is described in figure 2 below.

EXPERIMENTAL

There are three tasks for whole lab-scale work: 1- To choose a suitable carrier- material for attached growth; 2- To grow and select autotrophs, 3- To estimate nitrification- denitrification processes performance in continuous biological aerated filter-reactor (BAF).

For **selection of carrier –material**, which should be abundant in Vietnam, three different materials were trialed in three parallel batch reactors (Fig. 1). They are: 1- river quartz sand; 2- artificial keramzite form Bemex Co. (Hanoi); and 3- porous bazan from Thanh Hoa province. All they were sieved to get particles of size of 2÷4 mm except bazan, which had the size of the range of 2 ÷ 10 mm, then were washed with tape water to remove fines and used for autotrophs growing experiments.

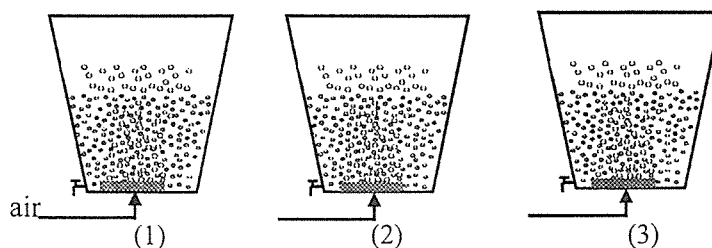


Fig. 1. Batch reactors for growing biomass and selection of carrier –material

Biomass growing and attachment

Growing procedure was taken from (Okabe *et al.*, 1996). The seed bacterial material was taken from slaughterhouse. The feeding solution contained: $\text{NH}_4\text{Cl} = 76.4 \text{ mg.L}^{-1}$; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} = 100$; $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O} = 28.4$; $\text{K}_2\text{PO}_4 \cdot 3\text{H}_2\text{O} = 91.7$, which were dissolved in free chlorine tap water. Every 2 hours of aeration a water sample was taken from each of three batch reactors for analysis of NH_4^+ ; NO_2^- ; NO_3^- ; alkalinity and COD_{Mn} . Analytical procedures were followed standard methods (Standard Methods for the Examination of Water and Wastewater, 1995).

Except the first two days, when the feeding solution with seed material was recycled, from the third day day - by - day the feeding solution was discharged and replaced by newly prepared one.

The capability of NH_4^+ -N conversion of each carrier - material was estimated via plot of conversion level (η ; %) at four-hour reaction time versus number of days of growing process. When the conversion level reached maximum steady level, the number of days spent on getting maximum conversion level is considered as the measure of performance of the carrier - material. The shorter the time, the better the performance of corresponding material.

Nitrification in continuous mode

Due to the ability of carrier - materials to entrap bacteria and provide housing for biomass, fixed biological processes possess higher biomass concentration, thus provides greater activity than conventional activated sludge processes, therefore they have the following advantages: 1- requiring less footprint, particularly due to elimination of the final clarifier; 2- no risk of biomass loss since the biomass is attached to support such that flow variations can be easily handled; 3- better adaptation on loading changes, especially in the case of dilute wastewaters; 4- shorter start - up period. These advantages are the reason why the fixed biological processes gain increasing interest within the past years and were chosen for nitrification experiments in this investigation. Apparatus for fixed bed biological nitrification was set - up described in Fig. 2.

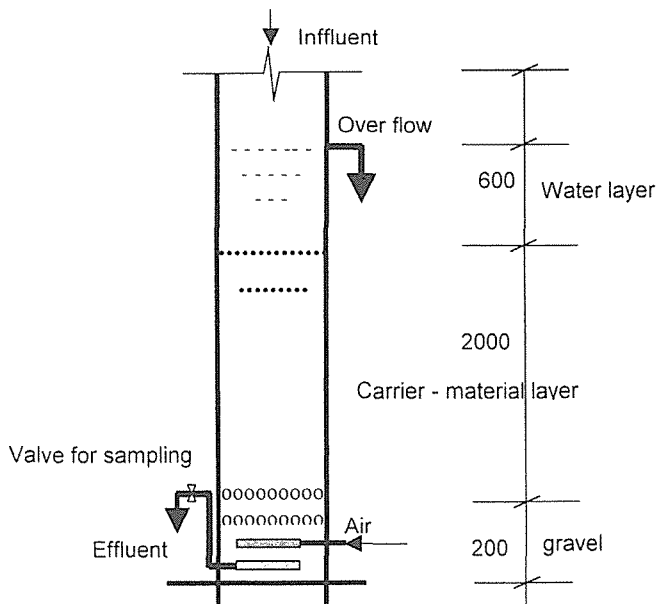


Fig. 2. Scheme of nitrification BAF - reactor

After 2 - 3 weeks of daily feeding the rates of nitrification in 3 parallel batch reactors should become approximately equal. Then the best carrier - material was moved to fill prepared column - reactor (Fig. 2).

The reactor was started - up in continuous mode with step - by - step increasing hydraulic load, corresponding to filtration velocities of $1.4 \div 6.9 \text{ m.h}^{-1}$. At each determined hydraulic load or filtration rate the substrate load was gradually increased too, that corresponded to NH_4^+ concentration of $5 \div 25 \text{ mg.L}^{-1}$. Characteristics of influent and effluent were examined each day using standard analytical methods.

During experiments the aeration rate was kept constant so that the DO content was $\geq 2 \text{ mg.L}^{-1}$ throughout all experiments.

The performance of the reactor was considered good or not satisfied when NH_4^+ concentration in effluent was $\leq 3 \text{ mg.L}^{-1}$ and $> 3 \text{ mg.L}^{-1}$ respectively.

RESULTS AND DISCUSSION

Situation in Hanoi raw ground and treated water quality

Hanoi is the only city in Vietnam, which is using exclusively only ground - water for all its consumption. At present, Hanoi Water Business Company (HN WBCo) has 8 water plants (WPs) and some smaller stations to provide nearly $450,000 \text{ m}^3/\text{d}$ to a population of 1.4 million in urban areas (JICA, 1996).

Treatment of data collected from 1996 to 2001 by Department of Quality control, HN WBCo and our lab showed among all 8 WPs of HN WBCo only 6 WPs could meet VN standards. The remained three WPs in the South (Phap Van - PV; Ha Dinh - HD; and Tuong Mai - TM WPs) have the concentration of NH_4^+ in both raw and treated waters exceeded the level of 3 mg.L^{-1} required by VN standards (figure 3). Besides, the COD values - the measure of organic matters were very high too, they ranges fromm 4 to 20 mg.L^{-1} , that is similar to observation of other authors (Nga *et al.*, 2000).

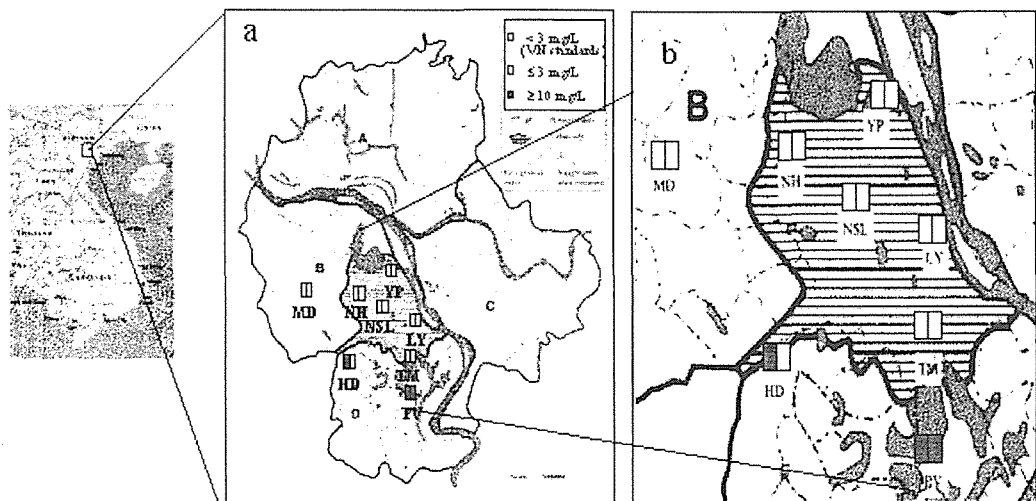


Fig. 3. Current situation in ground water contamination by ammonia at Hanoi Drinking Water Business Company's Water Plants

Herein conclusion is: in the South part of Hanoi City the quality of both raw ground and treated water is worse than that in the North Hanoi regarding to ammonia and COD concentrations. The explanation of this phenomenon could be found in above-mentioned reference and laid in the nature of organic rich soil/peat layers within the aquifer.

Biomass growing

The results of 3 parallel batch experiments on valuation of entrapping capacity of three carriers - materials were introduced in Fig. 4.

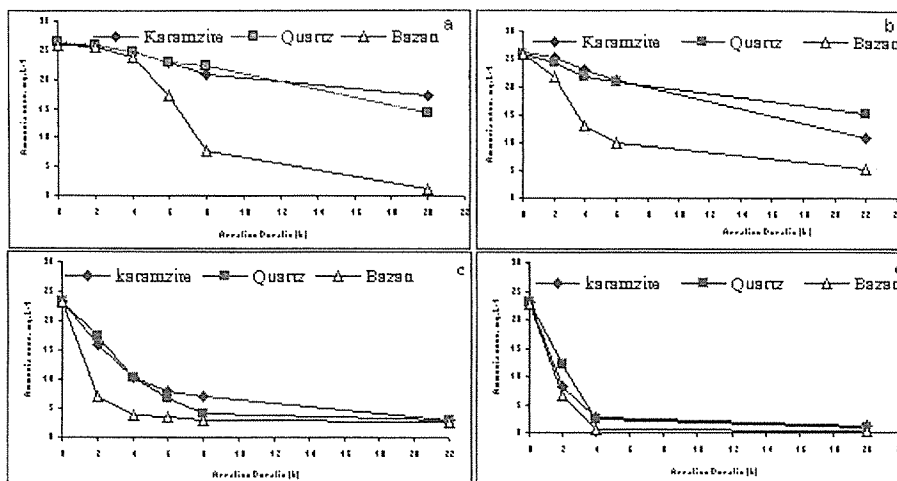


Fig. 4. NH_4^+ - content during batch growing experiment
a - 3rd day of aeration / adaptation / entrapment; *b* - 4th day; *c* - 8th day; *d* - 11th day

Through figure 4, where vertical axis of graph is expressing NH_4^+ content in treated water and horizontal axis - the duration of aeration, we can find that the behavior of keramzite and quartz sand are similar, while bazan showed highest activity toward NH_4^+ - oxidation.

During the first two days analysis was not done. Results of the 3rd day showed that little change was observed in batches with keramzite and quartz sand. But in the batch with bazan significant conversion started after 4-hour aeration (Fig. 4a). The same picture had been seen on the next - 4th day. A visible change concerned the first 2-hour for bazan and it seems that lag phase was shortened for bazan (Fig. 4b) and disappeared at all in the 8th day (Fig. 4c). At the 11th day lag phases of keramzite and quartz sand disappeared and NH_4^+ - oxidation improved significantly and approached to the level of bazan (Fig. 4d).

To make more contrast picture, every day the NH_4^+ - conversion level of all three batches after 4 hour of aeration was calculated by equation:

$$\eta_{4h} = \frac{C_{\text{NH}_4,0h} - C_{\text{NH}_4,4h}}{C_{\text{NH}_4,0h}} \times 100\%$$

Where $C_{\text{NH}_4,0}$; $C_{\text{NH}_4,4h}$ - are concentration of NH_4^+ after 0 and 4 hour aeration respectively; η_{4h} - conversion level of NH_4^+ (%) at 4 - hour aeration.

Then a plot of conversion level η_{4h} of three observed materials against duration of feeding was built (Fig. 5). From figure 5 it is clear that just after 12 days of daily continuous feeding and continuous aeration the batch with porous bazan have reached the highest NH_4^+ conversion level of 99%. After that the level was kept constant. In other hand, the two remained materials showed the similar worse performance, they could reach the highest conversion level just after 15 - 16 days. These results mean that porous structure of bazan is more favorite for bacteria entrapping, thus shorten the induction period in fixed bed systems.

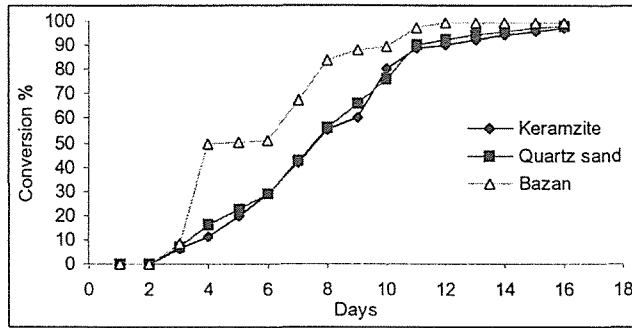


Fig. 5. Conversion level after 4 hour of aeration for three carriers - materials.

Performance of nitrification BAF

To estimate nitrification capacity the BAF column - reactor was set - up as described in Fig. 2.

To get desired concentration of NH_4^+ a calculated amount of NH_4Cl was weighted and dissolved in 1m^3 tank for stock solution filled with free chlorine tape water (water from HD WPs). Except NH_4Cl non of other chemicals was added. Stock solution was let to flow down by gravity; flow rate was controlled by control valve. Air was aerated from the bottom of the column - reactor to keep DO content in excess. Samples for analysis were taken through a control valve every day.

To check the performance of BAF reactor 5 continuous runs were conducted (Table 2)

Table 2. Experimental flow conditions for nitrification BAF

No of run	Flow, Q mL.min^{-1}	Flow Q, $\text{m}^3.\text{h}^{-1}$	Filtr. Rate m.h^{-1}	Hydraulic Load $\text{m}^3.\text{m}^{-2}.\text{d}^{-1}$	Hydraulic Load, $\text{m}^3.\text{m}^{-2}.\text{d}^{-1}$
Run No 1	200	0.012	1.4	33.3	High Rate: $9.4 \div 37.4$
Run No 2	400	0.024	2.8	66.6	Super HR: $14.0 \div 84.2$
Run No 3	600	0.036	4.2	99.8	(Meltcalf & Eddy, 1991)
Run No 4	800	0.048	5.5	133.1	
Run No 5	1000	0.060	6.9	166.4	

During each run, substrate ($\text{NH}_4^+\text{-N}$) load was gradually increased by addition of calculated amount of NH_4Cl into tape water, so that the next run had NH_4^+ -concentration in stock solution higher than NH_4^+ -concentration of the run before about $1 \div 5 \text{ mg NH}_4^+.\text{L}^{-1}$. Assuming tape water had initial concentration $[\text{NH}_4^+]_0 = 8 \text{ mg}.\text{L}^{-1}$, the volume of filtration material was 0.020 m^3 then we have (Table 3):

Table 3. Calculated substrate loading, $\text{g N}.\text{m}^{-3}.\text{d}^{-1}$

No of run	$[\text{NH}_4^+] \text{ mg}.\text{L}^{-1}$	$[\text{NH}_4^+\text{-N}], \text{ mg}.\text{L}^{-1}$	Flow - Q, $\text{m}^3.\text{h}^{-1}$				
			0.012	0.024	0.036	0.048	0.060
Run No 1	8	6.22	89.52	179.28	268.80	358.32	447.84
Run No 2	12	9.33	134.40	268.80	403.20	537.60	671.76
Run No 3	16	12.44	179.28	358.32	537.60	716.88	895.68
Run No 4	20	15.55	223.92	448.08	672.00	895.92	1119.60
Run No 5	24	18.66	268.80	537.60	806.40	1075.20	1343.52

Except two first runs with low hydraulic loads (table 2) which were conducted as adaptation measures, the last tree runs were done with planned increasing substrate load as described in table 3.

For comparison the hydraulic loading value of $9.4 \div 37.4$ and $14.0 \div 84.2 \text{ m}^3.\text{m}^{-2}.\text{d}^{-1}$ for high rate and super high rate tricking filters respectively were taken from (Meltcalf and Eddy, 1991).

It was observed that at first three hydraulic loads (less than $133.1 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{d}^{-1}$) almost all effluent samples had the concentration of NH_4^+ less than $3.0 \text{ mg} \cdot \text{L}^{-1}$ (Fig. 6).

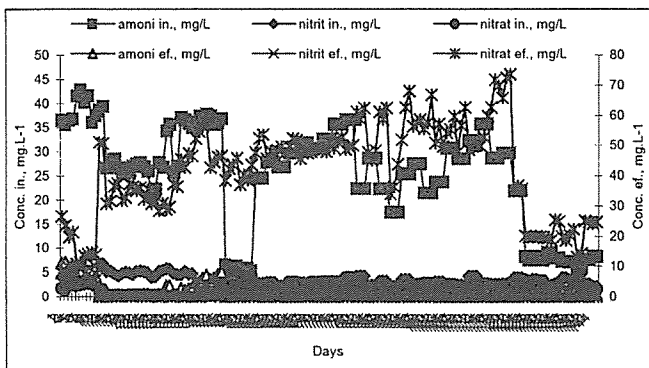


Fig. 6. Nitrification by BAF at filtration rate of $2.8 \text{ m} \cdot \text{h}^{-1}$

When filtration rate increased, the results were described in Fig. 7 and Fig. 8.

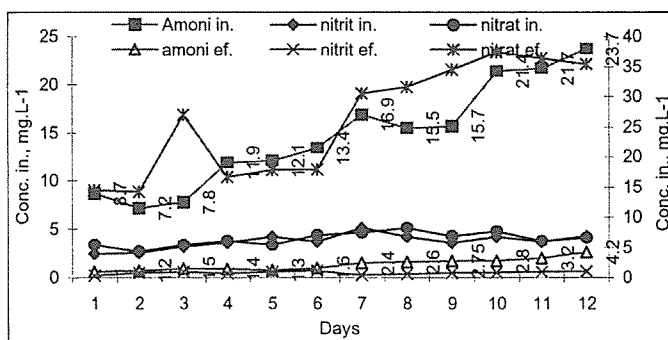


Fig. 7. Nitrification by BAF at filtration rate of $5.6 \text{ m} \cdot \text{h}^{-1}$

Results from Fig. 7 showed that in almost cases the NH_4^+ - concentration in effluent was lower than $3 \text{ mg} \cdot \text{L}^{-1}$. That means nitrification was successfully conducted using simple BAF technique at high enough filtration rate $\leq 5.6 \text{ m} \cdot \text{h}^{-1}$ or hydraulic load $\leq 133.1 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{d}^{-1}$.

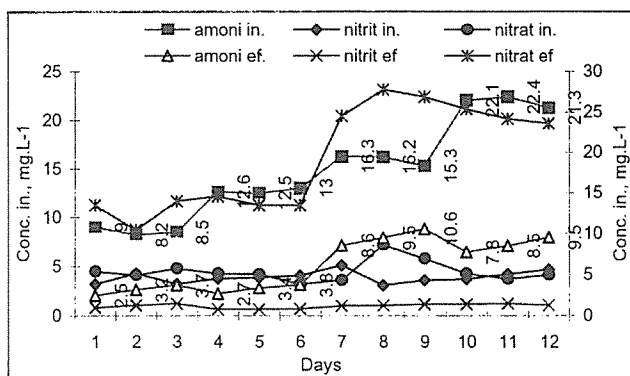


Fig. 8. Nitrification by BAF at filtration rate of $6.9 \text{ m} \cdot \text{h}^{-1}$

Only at higher filtration rate $\geq 6.9 \text{ m.h}^{-1}$ or hydraulic load $\geq 166.4 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ nitrification failed almost at all substrate loads (Fig. 8).

Hererein, we can conclude, that BAF is good enough for ammonium oxidation at the high filtration rates as rapid sand filter does for turbidity removal. By the way, within observed substrate N - loads, which coincided with existing N - concentrations in South HN ground water ($5 \div 20 \text{ mg.L}^{-1}$) nitrification successfully realized to get VN standards demands of 3 mg.L^{-1} . Other advantage of BAF nitrification - denitrification is improvement water quality in regard to organic matter's content.

A draw back of this process emerged: this was accumulation of some amount of nitrite in effluents, which is prohibited by VN standard. Hopefully, nitrite will be readily oxidized either by post chlorination or by following denitrification step.

CONCLUSION

A growing and attaching autotrophs procedure combined with selection of carrier - materials were realized. A suitable Thanh Hoa bazon mineral was found to be the best material for BAF technique for nitrification of ammonia in HN ground water.

It was proved that at existing ammonia concentrations HN ground water could be successfully treated by BAF technique at high filtration rate comparable with rapid filtration. In the case of remediation of existing WP it saves a lot of space for retrofitting units.

Application of BAF for NH_4^+ treatment promises low operation cost because it does not need in chemical, the only consumable thing is energy for aeration.

For better understanding and future designing work a pilot - scale should be done on site.

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