NH$_4$-N removal from groundwater using attached growth reactor: Case study in Chyasal, Nepal

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Abstract. The contamination of NH$_4$-N in Nepal's groundwater has become an ever-increasing drinking water quality problem. To achieve a cost-effective NH$_4$-N removal system, the attached growth reactor containing fiber carrier along the reactor was developed in the present work. Continuous dropping of the groundwater through the reactor resulted in removing NH$_4$-N from the groundwater without air supply. Further, the effects of low IC and PO$_4$-P concentrations and high Fe contamination in the groundwater on NH$_4$-N removal efficiency were also investigated. The attached growth reactors were fed with both synthetic groundwater (lab reactor done in University of Yamanashi, Japan) and raw groundwater (on-site reactor done in Chyasal, Nepal). The results show that the low IC and PO$_4$-P had no effect on NH$_4$-N removal efficiency that the efficiency can reach ~95% for the on-site reactor and ~70% for the lab reactor. However, the present of Fe in the groundwater caused for decrease in NH$_4$-N removal efficiencies to ~60% and ~30% for the on-site reactor and the lab reactor, respectively.

Keywords: NH$_4$-N removal, groundwater purification, nitrification process, attached growth reactor.

1. Introduction

At the present time, the contamination of ammonium-nitrogen (NH$_4$-N) in groundwater has become an important issue in several countries, such as Kathmandu Valley in Nepal and Hanoi in Vietnam [1, 2]. In developing and undeveloped countries, groundwater is common used as a major resource for drinking water supply. However, the NH$_4$-N cannot be removed by conventional drinking water purification process (i.e., filtration and sedimentation) [3]. Seriously, the NH$_4$-N leads to several unwanted effects, including (i) displeasure for drinking due to bad taste and smell, (ii) reduction of chlorine disinfection, (iii) corrosion of lead and copper in water supply system, and (iv) conversion of the NH$_4$-N to nitrate-nitrogen (NO$_3$-N) in which high NO$_3$-N level can cause methemoglobinemia or blue baby syndrome. Therefore, removing NH$_4$-N from groundwater resource is a critical issue in several countries, especially Chyasal area located in Kathmandu Valley, Nepal.

There are several biotechnologies which have been proposed for effective NH$_4$-N removal from groundwater such as biofix reactor, biofilter and swim-bed reactor [4-6]. However these methods require continuous aeration, which leads to increase in energy consumption and cost of purification process. Further, chemicals added (i.e., NaHCO$_3$ and Na$_2$HPO$_4$·12H$_2$O) possibly contaminate in treated water and may cause a chronic effect for health. To decrease the operation cost and avoid the use of chemicals, the attached growth reactor (using fiber carrier for bacteria attachment) which does not require aeration process and chemicals addition was developed in this research. This research focuses on two aspects on NH$_4$-N removal efficiency; (i) effect of inorganic carbon (IC) and PO$_4$-P, and (ii) effect of Fe which is commonly found in the groundwater. To achieve the precise results, the attached growth reactors were operated with synthetic groundwater (lab reactor in University of Yamanashi, Japan) and raw groundwater (on-site reactor in Chyasal, Nepal).

2. Materials and Methods

2.1. Attached growth reactor set up and operation

The attached growth reactors (lab reactor and on-site reactor) consist of two main parts; an acrylic column and a fiber carrier (NET Co. Ltd., Japan). The fiber carrier was made from polyester monofilament as a frame and absorbent acrylic fiber as a bacteria holder. It was kept along the column for bacteria attachment and water pathway. Due to the good characteristic of the fiber carrier, bacteria responsible for NH_4-N removal (i.e., nitrifiers) attached on easily, and substrates (i.e., oxygen) transferred properly. The synthetic and raw groundwater (influent) containing high NH_4-N dropped to the top of reactor with a flow rate of 4 L/day. During the influent penetrating, the nitrifiers rich on the fiber carrier converted NH_4-N to NO_2-N and NO_3-N simultaneously (nitrification process) by using oxygen from air. The schematic diagram of attached growth reactor is shown in Fig. 1, and the operation parameters following two aspects of IC and PO_4-P effect and Fe effect are summarized in Table 1.
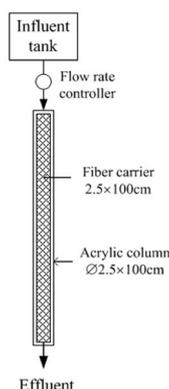

Fig. 1: A schematic diagram of attached growth reactor.

2.2. Groundwater preparation

In this research, six types of groundwater containing various concentrations of Fe, inorganic carbon (IC) and PO_4-P were prepared. These concentrations including NH_4-N are summarized in Table 1.

- *Synthetic1:* Based on the quality of Chyasal's groundwater (mg/L: NH_4-N 10.5, K^+ 21.7, Mg^{2+} 11.2, Ca^{2+} 33.9, IC 30.0 and PO_4-P 0.01), the synthetic groundwater was prepared and detailed in the previous study [7]. In addition, the NH_4-N concentration was fixed at 30 mg/L.
- *Synthetic2:* More $NaHCO_3$ and $Na_2HPO_4 \cdot 12H_2O$ added to this groundwater rather than Synthetic1 to maintain the excess IC and PO_4-P of 50 and 2 mg/L respectively. Other concentrations of K^+, Mg^{2+} and Ca^{2+} were same as Synthetic1.
- *Synthetic3:* $FeSO_4 \cdot 7H_2O$, $NaHCO_3$ and $Na_2HPO_4 \cdot 12H_2O$ added to this groundwater to maintain the concentration of Fe, IC and PO_4-P of 10, 50 and 2 mg/L, respectively. Other concentrations of K^+, Mg^{2+} and Ca^{2+} were same as Synthetic1.
- *Raw1:* Raw groundwater collecting from the dug well in Chyasal (contains Fe 10 mg/L) was added by $(NH_4)_2SO_4$, $NaHCO_3$ and $Na_2HPO_4 \cdot 12H_2O$ to maintain the NH_4-N, IC and PO_4-P concentrations of 30, 50 and 2 mg/L, respectively.
- *Raw2:* The raw groundwater mentioned in Raw1 was pre-treated by sedimentation and sand filtration to remove Fe, and then added $(NH_4)_2SO_4$. The concentration of NH_4-N, IC, PO_4-P and Fe was 30, 30, 0.01 and 0 mg/L, respectively.
- *Raw3:* The pre-treated groundwater mentioned in Raw2 was added by $(NH_4)_2SO_4$, $NaHCO_3$ and $Na_2HPO_4 \cdot 12H_2O$ to maintain the concentration of NH_4-N, IC, PO_4-P and Fe of 30, 50, 2 and 0 mg/L, respectively.

2.3. Analytical methods

The concentration of NH_4-N, NO_2-N and PO_4-P in influent and effluent were measured by Digital Pack Test (Kyoritsu Chemical-Check Lab., Corp.); and the NO_3-N concentration was measured, following the standard methods [8]. The NH_4-N removal efficiency was calculated using Eq. 1.

$$NH_4\text{-}N \text{ removal efficiency } = \left(1 - \frac{\text{Effluent } NH_4\text{-}N}{\text{Influent } NH_4\text{-}N}\right) \times 100 \qquad \text{Eq. 1}$$

Bacteria attached on the carrier were analyzed by PCR, RFLP and sequencing analysis; and the results were compared to the Genbank/EMBL/DDBJ database.

Table 1. Summary of operation parameters for all experiments.

Reactor number	Groundwater source	Concentration in influent (mg/L)			Remark
		$NH_3\text{-}N$	Fe	IC , $PO_4\text{-}P$	
Exp. 1: IC and PO_4-P effect					
1	Synthetic1	30	0	30*, 0.01*	Lab reactor
2	Synthetic2	30	0	50, 2	Lab reactor
3	Raw2	30	0	30*, 0.01*	On-site reactor
4	Raw3	30	0	50, 2	On-site reactor
Exp. 2: Fe effect					
5	Synthetic2	30	0	50, 2	Lab reactor
6	Synthetic3	30	10*	50, 2	Lab reactor
7	Raw3	30	0	50, 2	On-site reactor
8	Raw1	30	10*	50, 2	On-site reactor

* Concentration based on Chyasal's groundwater.

3. Results and discussion

The results of attached growth reactor on NH_4-N removal are discussed in following sequences; overall performance of attached growth reactors fed with synthetic and raw groundwater, effect of IC and PO_4-P contained in groundwater, and effect of Fe contaminated in groundwater.

3.1. Performance of attached growth reactors fed with synthetic and raw groundwater

In this research, the two experiments of attached growth reactor were done under two conditions, including the laboratory (fed with synthetic groundwater and operated in University of Yamanashi, Japan) and the on-site (fed with raw groundwater and operated in Chyasal, Nepal). The NH_4-N removal efficiency was ~70% and ~95% for the lab reactor and the on-site reactor, respectively (Figs. 3a and 3b). It can be seen that the attached growth reactor removed NH_4-N from the groundwater effectively at the site, while its performance was acceptable in the laboratory. Since the bacteria attached on the fiber carrier were playing the role for nitrification process (NH_4-N $\rightarrow$ NO_3-N), the type and amount of bacteria possibly caused for difference in efficiency for both reactors. As shown in Figs. 2(a) and 2(b), the lab reactor consisted of 5 phylum 3 classes of bacteria, which were dominated by *Alphaproteobacteria* (25%), *Betaproteobacteria* (24%) and *Nitrospirae* (20%). In contrast, the bacteria in the on-site reactor consisted of 8 phylum 4 classes, which *Firmicutes* (34%) and *Alphaproteobacteri*a (26%) were dominant. Therefore, the variety of bacteria at the site and the rich *Firmicutes* were significant reasons for better performance of the on-site reactor.
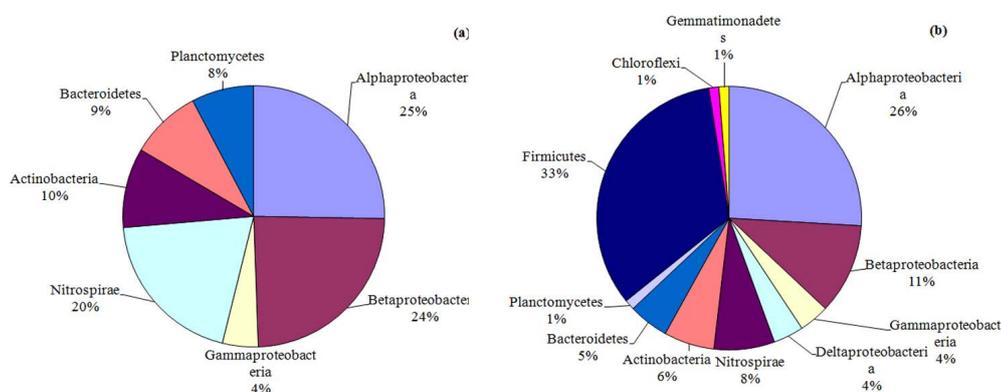

Fig. 2: Distribution of bacteria attached on the fiber carrier of (a) lab reactor fed with synthetic groundwater, and (b) on-site reactor fed with raw groundwater.

A comparison of performance of the attached growth reactor developed in this research with other reactors reported in literatures [4-6] shows that the efficiency of this attached growth reactor was good as those reactors, especially operating at the site. In addition, there are significant advantages of the reactor developed in this research; (i) no air supply, (ii) no chemicals addition, and (iii) simple design and operation. These advantages mean that the attached growth reactor is cost- and energy-efficient, and easy to operate and maintain at the site.

3.2. Effect of IC and PO$_4$-P contained in groundwater

The well-known bacteria playing a role for NH$_4$-N removal are named as nitrifiers, which require oxygen and IC for removal process. In addition, the PO$_4$-P is a key element for their growth mechanism. These lead to the operation of biological NH$_4$-N removal reactors under excess IC and PO$_4$-P in previous studies [9-10]. In this section, a low IC and PO$_4$-P (of 30 and 0.01 mg/L based on the groundwater quality in Chyasal [7]) and a high IC and PO$_4$-P (of 50 and 2 mg/L [10]) fed to the attached growth reactors. It has to be noted that there was no difference in the NH$_4$-N removal efficiency between the low and high concentrations of IC and PO$_4$-P. Both concentrations could achieve the high efficiency of approximately 70% for the lab reactors (Fig. 3a) and around 95% for the on-site reactors (Fig. 3b). The results reflect that the nitrifiers were able to be active under low IC and PO$_4$-P. This was possibly because of the synergy effect of various bacteria cultivated on the fiber carrier and/or the adequate IC and PO$_4$-P in the groundwater for removing 30 mg NH$_4$-N/L. It can be summarized that the effective NH$_4$-N removal can be achieved without adding IC and PO$_4$-P.
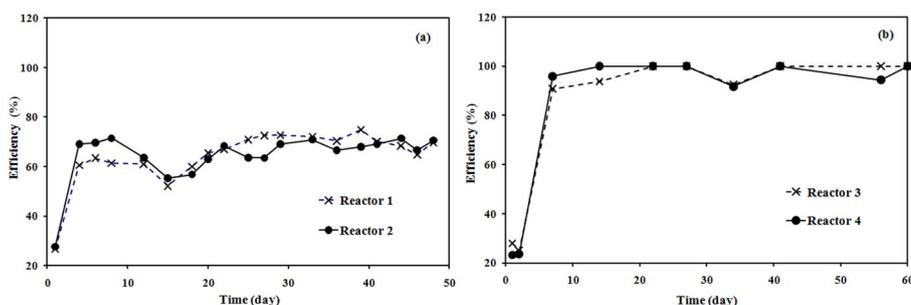

Fig. 3: Effect of inorganic carbon (IC) and PO$_4$-P on NH$_4$-N removal efficiency using (a) synthetic and (b) raw groundwater (reactors 1 and 3: without IC and PO$_4$-P addition, and reactors 2 and 4: with IC and PO$_4$-P addition).
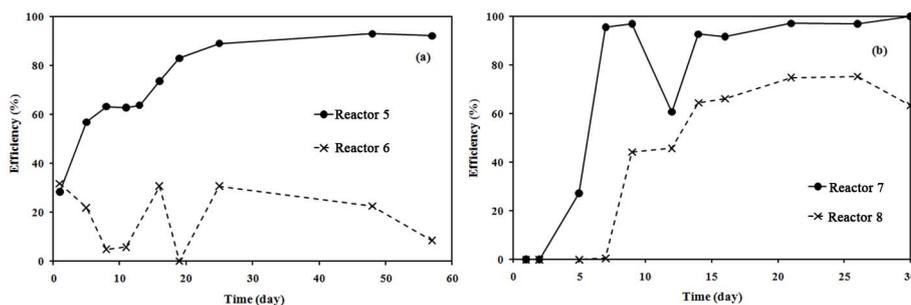

Fig. 4: Effect of Fe on NH$_4$-N removal efficiency using (a) synthetic and (b) raw groundwater (reactors 5 and 7: without Fe contaminated, and reactors 6 and 8: with Fe contaminated).

3.3. Effect of Fe contaminated in groundwater

The synthetic and raw groundwater (with and without Fe contaminated) were fed into four reactors, including reactors 5 and 6 (lab reactors) and reactors 7 and 8 (on-site reactors). The NH$_4$-N removal efficiency is presented in Figs. 4(a) and 3(b). It can be seen that the efficiency was continuously increasing and reached to the steady state in which the nitrifiers were cultivated and dense on the fibre carrier. Without Fe contaminated, the NH$_4$-N removal efficiency reached to ~93% and ~100% for reactors 5 and 7, respectively. In contrast, the highest efficiency of reactors 6 and 8 was only ~31% and ~75%, respectively. These results demonstrate that the Fe in groundwater affected on decreasing the NH$_4$-N removal efficiency.

The possible explanation was a conversion of soluble Fe (i.e., Fe^{2+}, Fe^{3+}) to solid phase of ferric oxide (i.e., $Fe(OH)_3$ and $Fe_2O_3 \cdot 4.5H_2O$ [2, 11]. The precipitation of ferric oxide on the fiber carrier reduced the space for nitrifiers attachment, and the interaction of nitrifiers and NH_4-N. This explanation is supported by difference in colour of the fiber carrier between light brown in reactors 5 and 7 and reddish-brown in reactors 6 and 8. Therefore, to achieve the effective NH_4-N removal, the groundwater should be pre-treated for removing Fe before going through the attached growth reactor.

4. Conclusion

In this research, the cost- and energy-effective attached growth reactor was developed for NH_4-N removal process using the groundwater in Chyasal (Kathmandu Valley, Nepal) as a case study. The performance of attached growth reactor based on analysis in the laboratory and the on-site shows that (i) the NH_4-N removal efficiency could reach 95-100% for the on-site reactor in Nepal, (ii) the low IC and PO_4-P in the groundwater had no effect on the NH_4-N removal, and (iii) the Fe contamination effected on decreasing the efficiency. Further, the variety of bacteria of 8 phylum 4 classes and the dominant bacteria of *Firmicutes* and *Alphaproteobacteria* resulted in high performance for the on-site reactor rather than the lab reactor (~70% NH_4-N removal). In addition, other aspects of operating the attached growth reactor (i.e., fiber carrier size and flow rate) should be studied further before applying this reactor to the pilot-scale.

5. Acknowledgements

6. References

[1] N.R. Khatiwada, S. Takizawa, T.V.N. Tran, M. Inoue. Groundwater contamination assessment for sustainable water supply in Kathmandu Valley, Nepal. *Water Science and Technology,* 2002, **46**: 147-154.

[2] D.T. Ha, R. Kusumoto, T. Koyama, T. Fuji, K. Furakawa. Evaluation of the swim-bed attached-growth process for nitrification of Hanoi groundwater containing high levels of iron. *Japanese Journal of Water Treatment Biology,* 2005, **41**: 181-192.

[3] M. Zhou, W. Fu, H. Gu, L. Lei. Nitrate removal from groundwater by a novel three-dimensional electrode biofilm reactor. *Electrochimica Acta,* 2007, **52**: 6052-6059.

[4] D.P. Khanh, D.T. Ha, K. Furukawa. Renovation of water treatment process for effective ammonia removal from Hanoi groundwater. In: *Proceedings of 1st International Symposium on Groundwater Environment,* 21-22 December 2010, Kumamoto University, Japan: 99-102.

[5] T. Stembal, M. Markic, N. Ribicic, F. Briski, L. Sipos. Removal of ammonia, iron and manganese from groundwaters of northern Croatia-pilot plants studies. *Process Biochemistry,* 40: 327-335.

[6] D.T. Ha, R. Kanda, T. Koyama, K. Furakawa. Nitrogen removal from groundwater using a swim-bed biological reactor. Japanese *Journal of Water Treatment Biology,* 2006, **42**: 65-78.

[7] W. Khanitchaidecha, T. Nakamura, T. Sumino, F. Kazama. Performance of intermittent aeration reactor on NH_4-N removal from groundwater resource. *Water Science and Technology,* 2010, **61**: 3061-3069.

[8] American Public Health Association. *Standard methods for the examination of water and wastewater.* 19th, New York, Springfield, 1995.

[9] Metcalf and Eddy. *Wastewater Engineering, Treatment and Reuse.* 4th, Singapore, McGraw-Hill, 2004.

[10] T. Sumino, K. Isaka, H. Ikuta, B. Osman. Simultaneous nitrification and denitrification using activated sludge entrapped in polyethylene glycol prepolymer. *Japanese Journal of Water Treatment Biology*, 2007, **43**: 121-128.

[11] B. Cho. Iron removal using an aerated granular filter. *Process Biochemistry,* 2005, **40**: 3314-3320.