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Journal of Environmental Sciences 2011, 23(5) 738–743

JOURNAL OF ENVIRONMENTAL SCIENCES
ISSN 1001-0742
CN 11-2629/X
www.jesc.ac.cn

Efficiency of active barriers attaching biofilm as sediment capping to eliminate the internal nitrogen in eutrophic lake and canal

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Received 01 July 2010; revised 27 September 2010; accepted 25 October 2010

Abstract

Three active barrier materials (zeolite, ceramicite and light porous media) were applied for preventing nitrogen (N) release from eutrophic lake sediments. Long term experiment of two different lake sediments were carried out and the effect of zeolite dose was evaluated. The results indicated that about 90%–100% of total N in overlying water was eliminated by using zeolite. While the N removal efficiency by ceramic was lower than that by zeolite, and light porous media present the lowest efficiency of 59%. Long term sediment incubation experiments indicated that two eutrophic sediments were both effective in preventing N release in spite of different release characteristics. Bio-zeolite capping technology was able to effectively inhibit the release of N from the sediment, and the zeolite dose was independently from N removal.

Key words: capping system; barriers; eutrophication of reservoirs; total nitrogen

DOI: 10.1016/S1001-0742(10)60469-X

Citation: Huang T L, Xu J L, Cai D J, 2011. Efficiency of active barriers attaching biofilm as sediment capping to eliminate the internal nitrogen in eutrophic lake and canal. Journal of Environmental Sciences, 23(5): 738–743

Introduction

Eutrophication is a serious problem in major reservoirs and lakes. Yet eutrophication problem has made it difficult to improve the source water quality in China. The enrichment of nitrogen and phosphorus is the fundamental causes for phytoplankton blooms. Internal release of nutrients from sediments is considered to play a critical role in eutrophication. How to reduce internal N loading has been a central question for rehabilitation of eutrophicated water source (Klapper, 1992).

Inhibition of N release from the sediment by an active barrier system (Jacobs and Fuorstner, 1999) is considered as a gentle ecotechnology. *In situ* capping of the sediment surface with a layer containing a reactive component to remove N may serve for this purpose.

The concept of subaqueous capping of contaminated sediments in lakes, rivers and coastal waters is a promising approach in developing a low-cost technology alternative to conventional methods in water protection since conventional off-site technologies, as removing pollutants from the sediment by chemical or physical means, are too complex and thus too costly where large areas of sediments are concerned. Capping sediments *in situ* involves the placement of a cover over the sediment in order to seal it off and thus to minimize contaminant release into the water column. A review of the application of sediment-capping techniques was given by Azcue et al. (1998). So far, there have been several laboratory and field scale investigations into the capping of sediments with sand or gravel layers (Wang et al., 1991; Zeman, 1994). Instead of this physical armoring, the active barrier systems were adopted, i.e., pervious geochemical barriers capable of actively demobilizing pollutants in percolating pore water by sorption or precipitation processes in this study. Since enormous amounts of material are necessary to cover large areas of sediment, it is a crucial point in the development of the capping design to identify adequate low-cost sorbents. In order to minimize the running costs, the barriers must consist of materials showing physical and chemical stabilities in a long-term view. The requirements for the potential active barrier materials can be summarized as follows: (1) availability at low cost, (2) active retention of contaminants, (3) physical and chemical stability, (4) sufficient hydraulic conductivity.

In this study, three reactive materials chosen are zeolite, ceramicite and light porous media which have already been used for biology carriers to remove ammonium in wastewater process (Leppert, 1990; Donnert and Salecker, 1999) and also tested successfully in the sediment field (Hart et al., 2003; Berg et al., 2004). Zeolite, ceramicite and light porous media are of commercial interest due to their favorable properties along with an abundant occurrence in nature. Furthermore, the availability of these materials

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as coarse grained materials facilitates their application in subaqueous environments since coarse grains settle to the ground readily and, once deposited, are relatively resistant against erosion.

Berg et al. (2004) proved the survival of macrozoobenthic organisms after the use of active barriers. But it has to be emphasized that the specific in-lake conditions, such as hydrodynamics and mainly bioturbation, considerably interfere with the barrier efficiency and significantly shorten the sustainability of sediment capping technology. Hence, this study is confined exclusively to intact barrier systems.

This work was mainly focused on the processes of N elimination by active barrier materials in lacustrine environments. N elimination capacities of different active barrier materials and the effect of zeolite dose on N elimination were studied by static experiments using natural lake waters. Long-term incubation experiments were carried out with two different lake sediments and the corresponding water using zeolite barrier.

1 Materials and methods

1.1 Study sites

The urban lake in this study, situated in the outskirt of Xi'an, China. It is a shallow (1.3 m depth), large (0.2 km^2 surface area) eutrophic gravel-pit lake. In recent years, the lake has changed from an oligo/mesotrophic to a eutrophic state due to immense nutrient inputs. The nutrient fixation capacity of the sediments is exhausted and nutrient release is considered responsible for the enhanced eutrophication process interfering with the recreational use of the lake, because the mean total nitrogen (TN) concentration in the water column has been doubled (from 1.5 to 3.8 mg/L) within this period.

Grand Canal, situated in Yangzhou, China, is one of the intercalated lakes of Beijing-Hangzhou Grand Canal. Since the early 1990s, this shallow (4.0 m depth), polymictic, and eutrophic lake has changed from a macrophyte-rich to a phytoplankton-dominated state. Despite efforts to restore the lake by reducing external nutrient loading, large cyanobacterial biomasses of low diversity have appeared in every summer, and the lake still demonstrates a year-to-year fluctuating and high internal N loading which is facilitated by hydrodynamics such as wind-induced rapid changes of stratification and mixing events.

Both studied lakes showed similar limnological characteristics (Table 1), except for the content of organic matter, which are much larger for urban lake. However, water depth and sediment composition differ significantly.

1.2 Barrier material

Three barrier materials, zeolite, ceramicite (Table 2) and light porous media, with the diameter of 1–2 mm size were obtained from Gongyi in Henan Province, China, and used as barrier materials for the laboratory experiments with natural lake sediments and waters.

1.3 Experimental setup

1.3.1 Biofilm formation of active barriers

The nitrifying bacteria (WGX15 and WGX18) and denitrifying bacteria (HF3 and HF7) used in the experiment were isolated from sediments taken from urban lake, Fenhe reservoir in Taiyuan City and Heihe reservoir in Xi'an City. The isolation and enrichment procedures were the same as reported by Huang et al. (2009).

Nitrifying bacteria medium culture contains 0.1 g/L of sodium acetate, 0.02 g/L of NH_4Cl, 0.02 g/L of K_2HPO_4, 0.01 g/L of $MgCl_2$ and 0.01 g/L of $CaCl_2$. Incubation time of bacteria is 48 hr. Denitrifying bacteria medium culture contains 0.1 g/L of sodium acetate, 0.02 g/L of $NaNO_3$, 0.02 g/L of K_2HPO_4, 0.01 g/L of $MgCl_2$ and 0.01 g/L of $CaCl_2$. Incubation time of bacteria is 48 hr.

Light weight porous media, ceramic, and zeolite of 3000 g with a 1–2 mm in diameter each were put in a plastic bucket to form biofilm. Each plastic bucket was inoculated with 650 mL of nitrifying bacteria suspension and 650 mL of denitrifying bacteria suspension under aeration condition. After 24 hr, 1300 mL of suspension was slowly taken out from each of the three plastic buckets, and then 1300 mL of sterilizated natural lake water was

Table 1 Characteristic of sediment and overlying water

Sediment source	Characteristic of sediment				Characteristic of overlying water					
	Water content (%)	Dry matter (%)	Organic matter (%)	Total nitrogen (mg/kg)	pH	Temperature (°C)	DO (mg/L)	Chl-*a* (μg/L)	TN (mg/L)	Depth (m)
Urban lake in Xi'an	64.10	22.45	13.45	1.47	6.70	27	7.28	7.85	4.74	1.30
Grand Canal in Yangzhou	60.50	36.36	3.14	1.24	6.62	22	3–5	8.53	4.20	2.50

Table 2 Chemical composition of the zeolite and ceramicite used in the experiment

	Chemical composition (wt.%)							Physical index			
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	NaO	H_2O	Volume-weight (g/cm^3)	SSA (m^2/g)	Micropores (%)
Zeolite	68–67	13–14	1–1.8	1.7–2.2	0.9–1.9	1.5–4.0	0.5–1.5	1.8	1.28	400–800	48
Ceramicite	58–74	23	1	/	/	/	/	1.2	1	398	20

/: not contained.

added to each bucket to form biofilm. After another 24 hr, above process was repeated. This process was repeated for three times in 3 days until the biofilm formation process was finished. Finally, active barriers attaching biofilm were gently washed using de-ionized water.

1.3.2 Incubation experiments

Natural lake water and sediments were collected in summer 2009 from urban lake at the deepest site (1.3 m) using an *in situ* sub-aqueous pump and sampler.

The unimpeded release of N from the nutrient-rich sediments into the overlying water with sediments covered by active barriers attaching biofilm in plexiglass columns (28 cm diameter, 39 cm high) was compared. Laboratory experiments were carried out in triplicates at room temperature in anoxic media and under light exclusion with different barrier materials.

In summer 2009, two sediment cores (30 cm in length and 6 cm in diameter) and 20 L of corresponding overlying water were sampled from urban lake and Grand Canal with a man-made sampler. One core was covered by a 3 cm thick zeolite attaching biofilm and the other was kept without any barrier as a reference. Water samples (5 mL) of both experimental series were taken once a day with a syringe and a thin plastic tube ending 5 cm above the sediment/water interface. Afterwards, the device was refilled with the original lake water from 1 m in depth to maintain a constant water volume. Long incubation experiment was lasted for 40 or 48 days.

1.4 Chemical analysis

Ammonium, organic matter and dry matter were determined according to the Standard Methods (APHA, 1998). Nitrate and nitrite were determined using UV spectrophotometry (DR5000, Hach Company, USA). The DO level was measured with a digital, portable Oxy-check (HQ30d, Hach Company, USA). Testing sediments were dried by FD-1D-50-type freeze-drying machine (Boyikang Company in Beijing, China).

2 Results

2.1 Nitrogen removal capacity of various cap materials in overlying water

The results of incubation experiments showed that an initial TN concentration of 3.75 mg/L in the overlying water from urban lake sediments was increased to 8.80 mg/L within 40 days without any barrier (Fig. 1). The ammonium releasing rate reached to 2.09 mg/day. Experiments were carried out with barrier constructions comprising three materials of zeolite, cemeratic and light porous media to reveal the optimum capping material. From Fig. 1, it can be observed that the zeolite barrier of 3 cm thick led to a decrease of TN 90%–100%. The corresponding ammonium, nitrate and nitrite removal efficiency reached 89.6%, 90.0% and 92.0%, respectively. Moreover, from day 1 to day 5, the ammonium concentration in overlying water was decreased to 1.0 mg/L and the TN removal efficiency

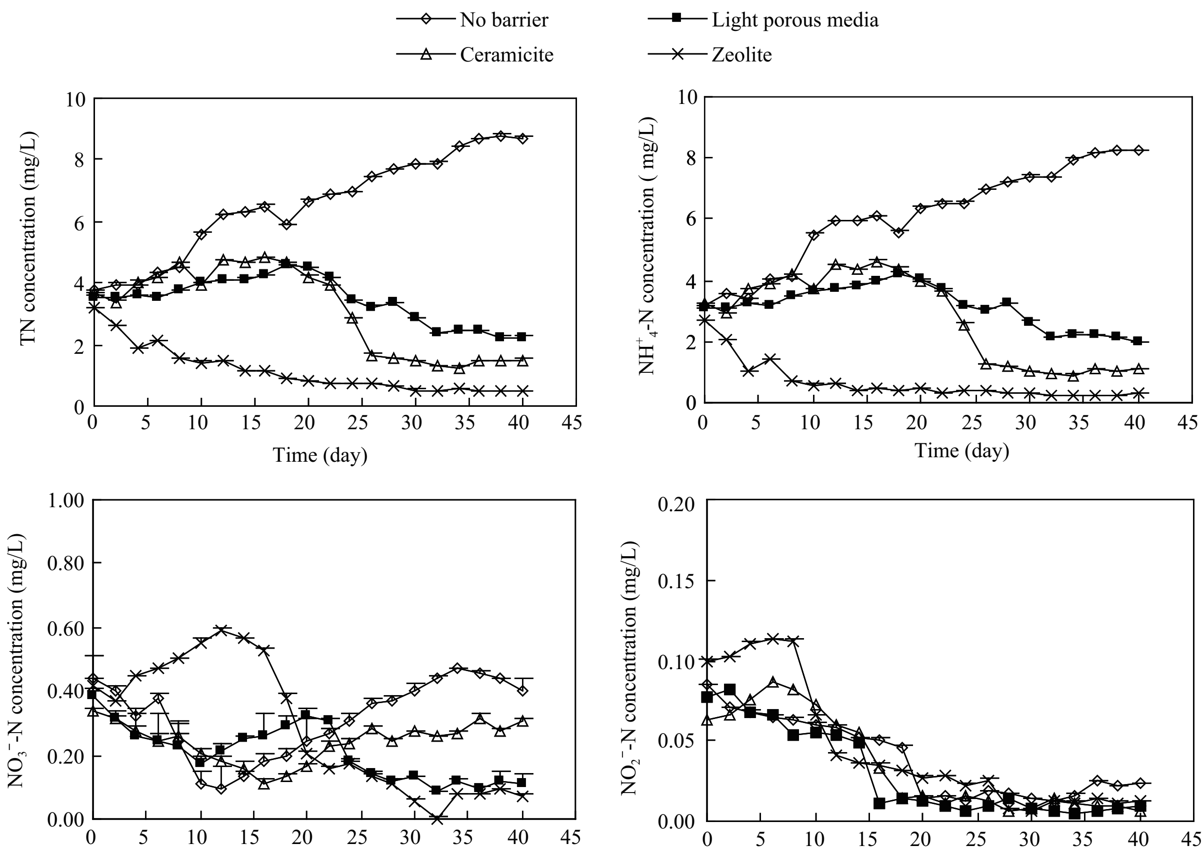

Fig. 1 Effect of cap materials on nitrogen removal in overlying water. Condition: pH 6.5–7.5; initial ammonium concentration 3.75 mg/L; initial TN concentration 3.75 mg/L; temperature 20–25°C.

was gradually increased to 50% in bio-zeolite capping system. The most effective N retention was achieved by barriers of bio-zeolite. Nitrogen release was not observed during the 40 days of incubation. However, for ceramicite system and light porous media system, the ammonium concentration in overlying water was maintained at 4.0 mg/L for long time from day 1 to day 20. During the following days, the ammonium concentration in overlying water was decreased to 1.0 and 2.0 mg/L and the nitrate concentration was increased to 0.4 mg/L and 0.1 mg/L for cemeratic and light porous media, respectively. The N elimination capacity of light porous media was only 59%. It becomes clear that the zeolite is an optimal barrier as the release of ammonium was inhibited and the maximum TN removal efficiency could be achieved.

2.2 Nitrogen removal capacity of various cap materials in sediment

During the first 15 days, the TN concentration in the sediment was decreased from 1.47 to 0.94 mg/kg, and 36% (n = 3) of nitrogen loss was observed in bio-zeolite capping barrier system compared to the reference bottle without any barrier. During the following days, a decrease of TN concentration to 0.7 mg/kg in sediment was observed in bio-zeolite system (Fig. 2). The TN removal efficiency was gradually increased to 52%. However, TN content in sediment has a slightly upward trend after 15 days, then drops down to 1.33 and 1.26 mg/kg in bio-light weight porous and bio-ceramic system, respectively. Therefore, in bio-zeolite system, 50% of TN in sediment was removed. The possible mechanism of bio-zeolite capping included ion-exchange, nitrification and denitrification.

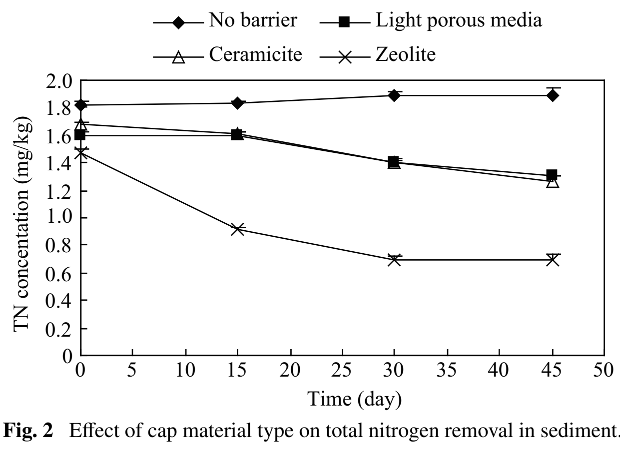

Fig. 2 Effect of cap material type on total nitrogen removal in sediment.

2.3 Comparison of N removal capacity of two sediments using bio-zeolite barriers

Bacteria isolated from aquatic sediment were inoculated in the culture containing natural zeolite to obtain bio-zeolite attaching denitrifying bacteria and nitrifying bacteria. The capping technology covering bio-zeolite on the surface layer of eutrophic sediments to remediate two eutrophic sediments was studied (Fig. 3). The results indicated that the remediation was effective for two eutrophic sediments in spite of different release characteristics. Bio-zeolite capping technology can effectively inhibit release of nitrogen from the sediment. For the sediment taken from Grand Canal, the characteristics showed initial release of sediment ammonia which was converted to nitrate nitrogen later. It was observed that residual TN concentration of in the overlying water is 0.34 mg/L (based on nitrate nitrogen), and the TN removal efficiency is 21% in the sediment after covering bio-zeolite in 48 days. For the sediments from urban lake sustained to release ammonia into overlying water, however, residual TN concentration was decreased to 0.3 mg/L (based on ammonium) and 52% of total nitrogen in sediments was removed after covering bio-zeolite layer for 40 days.

2.4 Nitrogen removal capacity of various zeolite doses

The experimental results in Fig. 4 showed that TN removal efficiency was depended on zeolite dose. During the first 6 days, ammonium removal efficiency was increased from 76.6% to 92.7% as zeolite dose was increased from 7 to 10 g/cm^2. It is known that natural zeolite with remarkably high cation exchange capacity of Al up to 6 mmol (eq)/g exceeds, by far, that of smectite clays, and thus permits a high efficient removal of ammonium cations. Here a decrease of TN concentration was observed with increasing dose during the first 6 days. However, both nitrate concentration and nitrite concentration in overlying water were increased as zeolite dose was increased from 7 to 10 g/cm^2. The result for 50 days of measurement showed that the N removal efficiency was independent of the zeolite dose. Under small zeolite dose condition N can

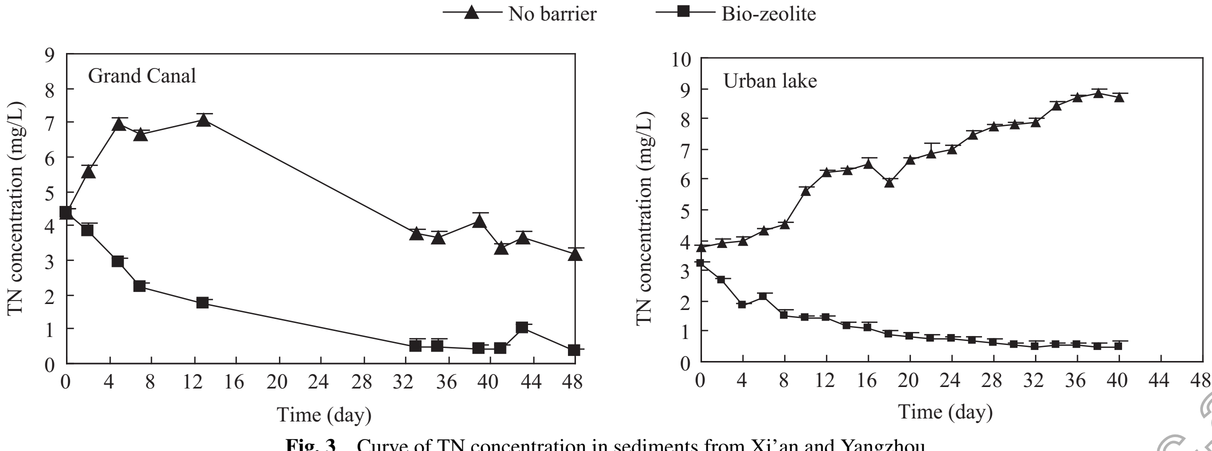

Fig. 3 Curve of TN concentration in sediments from Xi'an and Yangzhou.

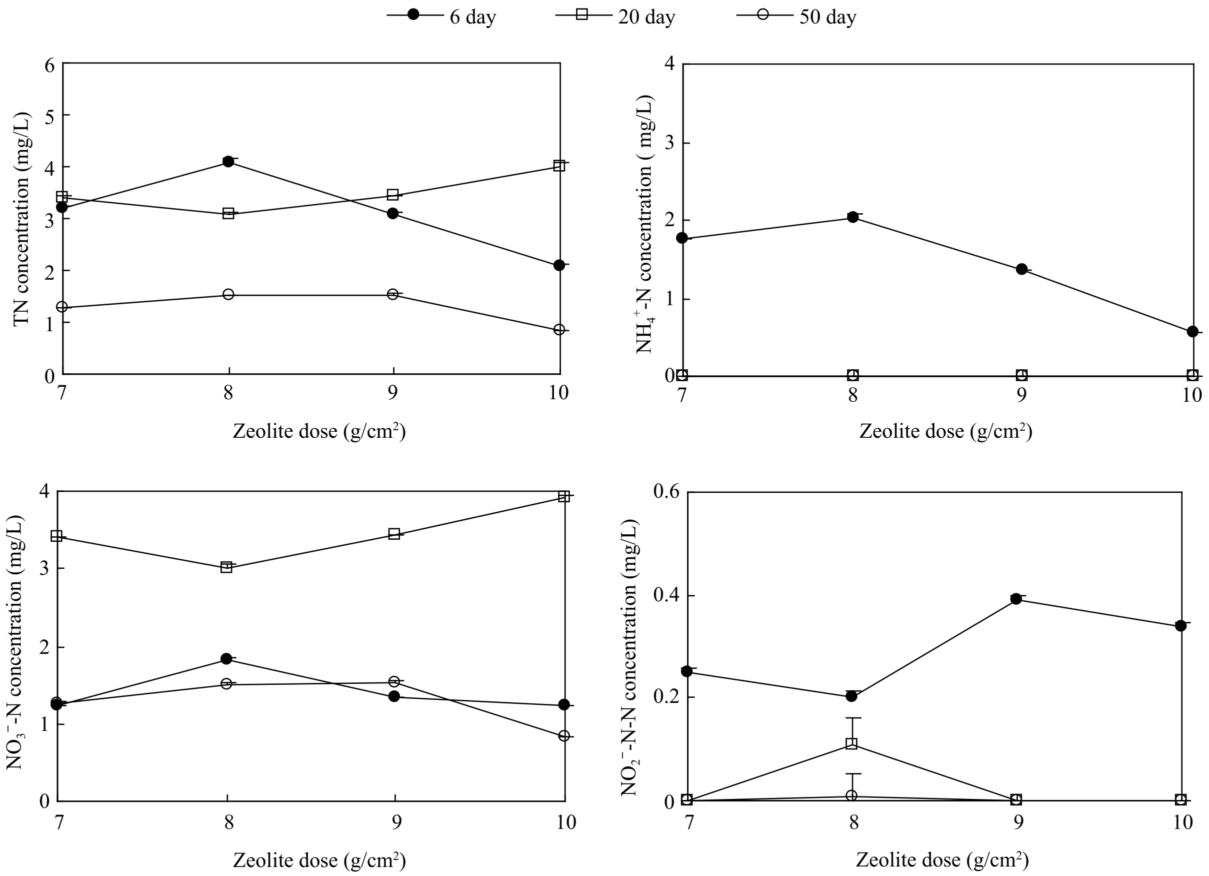

Fig. 4 Effect of bio-zeolite dose on N removal in overlying water.

still be eliminated.

3 Discussion

From the results shown above, the zeolite was found to be the best barriers for N elimination. However, zeolite can remove ammonium in the water through chemical and physical adsorption processes due to its strong adsorption force such as dispersion and electrostatic force. Zeolite contains cations which can exchange ion to ammonium with a strong absorption capacity. That is to say, ammonium of overlying water can be quickly adsorbed by zeolite. Moreover, zeolite is not effective and needs to be changed when the ammonium content absorbed is beyond its capacity. It is impossible to change zeolite in deep reservoirs or lakes. The zeolite reproduction by bacteria was proposed. If accumulated ammonium inside zeolite is utilized by bacteria, the zeolite barrier can be recovered and effective for a longer time. For this purpose, at the end of the experiment, the exhausted bio-zeolite was taken off from the testing column, and the experiment of chemical and physical desorption was then carried out to measure the capacity of biological regeneration of zeolite *in-situ*. The results are presented in Fig. 5. Here the highest ammonium removal efficiency observed is 63%–87% depending on zeolite dose while the chemical removal efficiency is

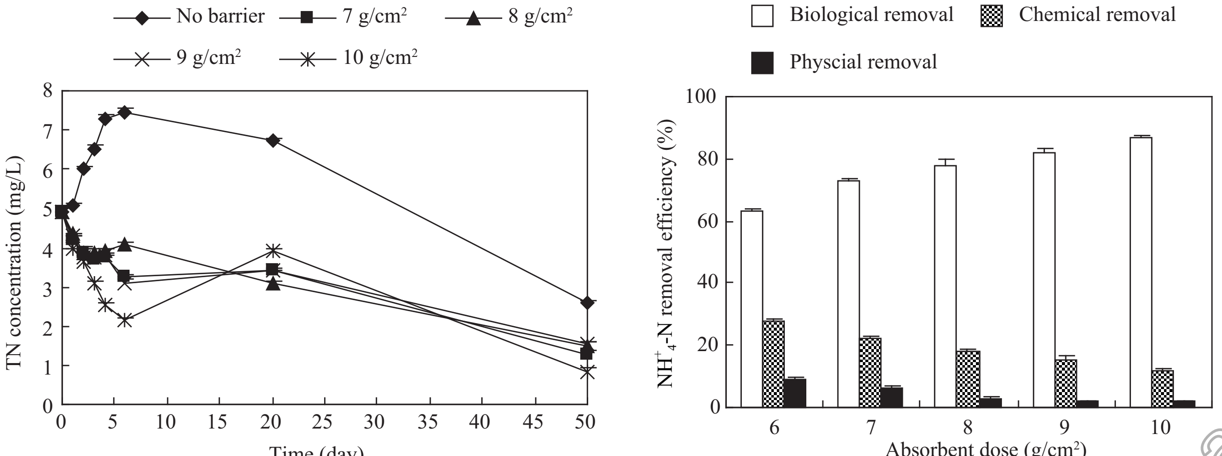

Fig. 5 Remediation for contaminated sediment.

12%–28%, and the physical removal efficiency is only 2%–9%. These results showed that bio-zeolite was permanently effective to eliminate nitrogen pollution as a large number of ammonium adsorbed by zeolite were converted to nitrogen gas and thoroughly removed. The similar results were obtained in eutrophication controlling experiment by Ye et al. (2009). This is very interesting as the biological removal is the main mechanism in bio-zeolite capping system. The possible explanation is that there are 40%–50% of uniform pores inside zeolite and pore size is mostly less than 1 nm. That is to say, zeolite has a large surface area (400–800 m^2/g zeolite). Therefore, it is easy for bacteria to attach. The adsorbing ammonium can be consumed by a large number of bacteria attaching zeolite.

4 Conclusions

In bio-zeolite capping system, removal efficiencies of ammonia nitrogen and total nitrogen are 89.6% and 84.8%, respectively, and the corresponding removal efficiencies in bio-ceramic capping system are 65.1% and 59%, whereas, the removal capacities of light weight porous media are only 35.6% and 37.8%, respectively. Therefore, the bio-zeolite capping is the most effective way for eliminating nitrogen pollution in remediation of sediments. Here we found that the biological removal is up to 87% and is the main mechanism in bio-zeolite capping system. These results showed that bio-zeolite barrier is an effective technology to eliminate nitrogen pollution because a large number of ammonium adsorbed in bio-zeolite can be converted to nitrogen gas by bacteria and thoroughly removed eventually. Therefore, under small zeolite dose condition N can still be eliminated.

Acknowledgments

This work was supported by the program of International Science & Technology Cooperation from Chinese Ministry of Science and Technology (No. 2010DFA94550, 2010KW-24-1), the National Natural Science Foundation of China (No. 50830303), the Major Science and Technology Program for Water Pollution Control and Treatment (No. 2009ZX07317-007-001) and the Program for Changjiang Scholars and Innovative Research Team in University (No. IRT0853).

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