Research on the removal of nitrogen pollutants in source water by EBO system

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Abstract. This paper describes an innovative process to solve the nitrate build-up problem using enhanced bio-contact oxidation system in situ (EBO system). The novel aspects of the process lay in the EBO system that is enhanced by a multifunctional device for water lifting and aeration (MDWLA) which has widely been applied in improving the source water quality in China. The reservoir water employed to study the nitrogen removal capacity of EBO system. The results showed that the EBO systems filled with Kaldnes suspended packing and sponge balls suspended packing respectively could efficiently remove ammonia, nitrate, nitrite, total nitrogen, COD, and turbidity from polluted surface water under conditions of dissolved oxygen 3.0~4.0 mg L\(^{-1}\) and temperature 24~28 ℃. Particularly, the maximum efficiencies of ammonia, nitrate, total nitrogen and turbidity in EBO system could reach above 71%, 76%, 77% and 90%.

1. Introduction

Until the beginning of 21st century drinking water sources were heavily contaminated by nitrates as a result of excessive fertilization or other pollution—mainly anthropogenic—sources. Elevated nitrate concentration in drinking water was a potential risk to public health since it could directly cause methaemoglobinemia (blue baby syndrome) in infants and its correlation with other diseases, including cancer, was not completely clear [1]. Because of these potential adverse effects, nitrate concentration limits in potable water had been set worldwide. Drinking water regulations were required in order to limit human risks and environmental pollution. While the United States Environmental Protection Agency (USEPA) had set maximum contaminant level goal (MCLG) of 10 mg NO\(_3\)-N and 1.0 mg NO\(_2\)-N L\(^{-1}\), the World Health Organization and European Economic Community had set standards of 11.3 mg NO\(_3\)-N and 0.03 mg NO\(_2\)-N L\(^{-1}\). This value was presently not met in a considerable amount of drinking water sources in USA, European Community, Africa, Middle East, Australia, and New Zealand and so on, so it was mandatory to remove the excess nitrate from the contaminated water in order to ensure potable use.

Many researches on the denitrification of source water had been reported, but most experiences were still been stayed on the conversion of different forms of nitrogen, which could not completely remove the nitrogen from water source.

Biological treatment was the most useful and efficient process to remove nitrogen from surface water sources. The full-scale application of this technique were mostly based on off-site bio-contact oxidation (OSBO), whereas very few tests and applications were available with the denitrification of surface water.
by the enhanced bio-contact oxidation system in situ (EBO system) [1-3]. Due to its overcoming the restriction of biological contact time, an important limiting factor for biological denitrification, the EBO system favored the improvement of nitrogen removal efficiency.

In this research, a multifunctional device for water lifting and aeration (MDWLA) was combined with the EBO system for the denitrification of surface water. The EBO system could be enhanced by MDWLA which had widely been applied in improving the source water quality in China. The main objective of this research was to investigate the feasibility and efficiency of nitrate removal using EBO system for source water denitrification in laboratory-scale. In the experiment, the EBO system with an aeration device acted as the function of MDWLA, was filled with a layer of highly efficient suspended packing materials as biological carrier, and the water samples were taken from a reservoir.

2. Materials and methods

![Figure 1. Schematic representation of EBO system](image)

2.1. Experimental system

The experimental set-up included three sets of systems (system 1, system 2 and system 3). Two sets of EBO systems (system 2 and system 3) for the effect experiment were filled with suspended packing and equipped with aeration devices acted as the function of MDWLA. One set of system (system 1) without biological carrier and aeration device was used as the blank control group. The EBO system experimental set-up consisted of a cylindrical organic class reactor, with a 20 cm of inner diameter and 750 cm of height (Fig.1). The EBO system was equipped with a water sampling pipe, an exhaust pipe and an aeration port on its top, and an air flow meter installed at the aeration port. During the entire experimental period, DO concentration and temperature in EBO system was in the range of 3.0~4.0 mg L$^{-1}$ and 24~28 $^\circ$C respectively.

Two EBO systems for efficiency experiment were filled with the Kaldnes suspended packing (system 2) and the sponge balls suspended packing (system 3) respectively as carrier for microorganism, and the filling rate for both packing materials was 2%.

Prior to operation, the carrier materials were inoculated with microorganisms for 3~4 days by pouring the high efficient bacterial liquid into the systems, then acclimatized to low-nutrient medium prepared in source water taken from a reservoir. The inoculation lasted for about 1 week for microbial growth.

2.2. Source water

In this study, the water sample was taken from a reservoir (water source characteristics: COD 6.3 mg L$^{-1}$, N-NH$_4^+$ 0.246mg L$^{-1}$, N-NO$_3^-$ 1.730mg L$^{-1}$, N-NO$_2^-$ 1.730mg L$^{-1}$, TN 1.989 mg L$^{-1}$, Turbidity 18.5NTU, pH 7.58).
2.3. Bacterial agent
The bacterial agent used in this study consisted of efficient aerobic denitrifiers isolated and cultured in the low-nutrient medium in order to remove nitrogen desirably under oligotrophic conditions.

A proper amount of the bacterial agent was inoculated in medium solution in 2000 ml bottle with a cotton plug, and cultivated under agitation (120 rpm), at 30°C and pH 7 for 48h. These pre-cultures were used to inoculate the EBO system.

2.4. Biological packing materials

2.4.1. Kaldnes suspended packing The Kaldnes suspended packing made of the modified high polymer had a diameter of 25 mm and a height of 10 mm. The suspended carrier had a specific gravity of about 1.000 after inoculated, which can rotated freely under the aeration and improve the oxygen utilization by colliding and cutting the air bubbles.

2.4.2. Sponge balls suspended packing The sponge balls suspended packing was prepared by the reticulated polyurethane materials. Due to its bigger porosity the sponge balls suspended packing had a higher specific surface area compared to other packing materials. In this research the sponge suspended packing with a 50 mm of diameter was used in the system.

2.5. Analytical methods
All samples were filtered through a 0.45 μm membrane filter before analysis and were tested within 1 h of collecting. Ammonia was determined by the Nesslerization method, nitrite by the azo dye colorimetric method, nitrate by the Szechrome NAS reagent (diphenylamine sulfonic acid chromogene) method, total nitrogen by the alkaline potassium persiflage digestion-UV spectrophotometric method according to water and exhausted water monitoring analyzed method (National Environmental Protection Committee of China, 4th Edition). NH₄-N, NO₂-N, NO₃-N, TN were analyzed with Hach DR5000 ultraviolet spectrophotometer (Hach Company, Loveland, CO, USA). Turbidity was measured by WGZ-1S turbidimeter (Shanghai Leici Instrument Inc., China).

3. Results and discussion
COD concentration in EBO systems during the experiment was presented in Fig. 2. The COD removal efficiency during the entire experiment for both systems was in the range of 8.65% to 25.81%. The consumption of COD mainly resulted from the metabolic activities of microorganism such as oxidation, reduction and synthesis, and the biological flocculation and adsorption process and nitrification also played an important role during the biodegradation of organic substances [4]. At the same time the protozoa and micro metazoa attached in suspended packing also had a certain role in degrading the organic pollutants by phagocytizing algae debris, bacteria and organic debris [5]. Bacterial colony and micro animals constituted together the multifunctional biofilm structure. However, the low utilization percentages of COD implied the scarce availability of organic carbon content in the natural organic substances in source water.
Figure 2. COD concentration variation with operation time for systems 2 and 3

As shown in Fig. 3, the nitrifying percentages of ammonia for both systems 2 and 3 were still desirable compared with system 1 under oligotrophic conditions and low initial ammonia concentration (about 0.25 mg L\(^{-1}\)). The highest ammonia removal percentages for systems 2 and 3 were observed at the 15th day, and were 71.32% and 89.59%, respectively. The decline of ammonia concentration in the early operation mainly resulted from the biosorption of the suspended carrier. However, the ammonia values increasing sharply in all system at the 5th day seemed to be caused by the conversion of organic nitrogen to ammonia when the heterotrophs consuming the organic matter. It was evident that the ammonia removal rate at the beginning of experiments was low. It was probably due to the slow growth and adaptability of autotrophic nitrifiers while the nitrification was ineffective. The experimental results showed that the ammonia concentration sharply increased in the late experiment period probably due to the detachment of the ageing biologic membrane. The changes of nitrate concentration in the systems were given in Fig. 4. It was observed that the better removal rates of nitrate were achieved in systems 2 and 3 when compared to the system 1 due to the high denitrification efficiency of bacterial agent including various oligotrophic denitrifiers which had a high tolerance for starvation. Among the three examined systems, the highest denitrification rate with 80.38% was obtained in system 2 at the 31st day. In the experiments of systems 2 and 3, nitrate levels (1.835 mg L\(^{-1}\) and 1.910 mg L\(^{-1}\), respectively) were initially higher than the level (1.730 mg L\(^{-1}\)) in system 1 as a result of the unimmobilized bacteria falling into water, as explained above. The decrease of ammonia concentration in the earlier operation was mainly caused by the biosorption of biofilm. The conversion of ammonia to nitrate resulted the slightly increase of nitrate at the 15th day as shown in Figs. 3 and 4. However, for approximately 3 weeks after the beginning of operation of the EBO systems, nitrate concentrations had fallen slowly (the concentration changes less than 0.5 mg L\(^{-1}\)), which suggested that adaptation of the bacterial population to the sub-nutrition environment occurs in a long time period. The microorganisms acclimatized themselves to the wane of nutriment by reducing their metabolizing levels, extending their specific areas, utilizing more types of substrates. During this period of time, the morphology and physiology of oligotrophic bacteria experienced a significant change, and came to a steady starvation—survival state while the cell size remained almost constant. Also the efficiency of metabolic mechanism of microorganism had been improved due to the energy deficiency [6]. After the adaptation, the nitrate removal was achieved rapidly when the natural substances were utilized as the carbon source, as shown in Figs. 1 and 4. These results indicated the necessity of utilizing higher biological contact time to enhance the denitrification efficiencies, which was the most attractive advantage for the EBO system. After 31 days of operation, the nitrate level rising slightly was probably due to the aging biofilm falling into water. At the end of the experiment, the nitrate concentrations of systems 2 and 3 remained steady and were less than 1.0 mg L\(^{-1}\), probably due to the limitation of usable organic compounds in the
substrates. This approximation was based on the assumption that denitrification can be modeled as a zero-order reaction with respect to nitrate concentrations down to very low levels [7].

Figure 3. Ammonia concentration variation with operation time for three systems

Figure 4. Nitrate concentration variation with operation time for three systems

The experimental results for nitrite variation in the three systems were illustrated in Fig. 5. It was observed that for approximately 4 weeks after the start of the experiment, the nitrite concentrations of systems 2 and 3 did not show significant changes. These findings indicated that the stable and timely conversion of ammonium to nitrate would occur when the ammonia level of source water was low. However, the nitrate concentration rapidly decreased at the 29th day while the nitrite concentration increased as a result of a reduction of nitrate to nitrite, as shown in Figs. 4 and 5. After that, nitrite concentration values started to decrease until they were not detected at the 31st day. It was observed from Figs. 5 and 3 that the nitrite accumulation occurred in systems 2 and 3 in the later period of operation due to the sharply increase of ammonia concentration while the nitrifying bacteria could not accomplish the timely conversion of nitrite to nitrate because of their slower growth rates compared with the ammonia-oxidizing bacteria.

Fig. 6 summarized the total nitrogen variation of the three systems during the entire experimental period. It was indicated that the systems 2 and 3 showed the desirable maximum total nitrogen removal efficiencies (77.62% and 78.17%, respectively) by the action of the oligotrophic denitrifiers which had
the obvious advantages of high affinity and strong adsorption capacity in the low-nutrient competition [8]. At the beginning stage ammonia, nitrate, nitrite and biodegradable organic substances were adsorbed quickly by the aerobic and facultative bacteria on the biofilm, and these pollutants were removed by the biodegradation, nitrification and denitrification. It was observed by comparing Figs 6 and 4 that the concentration variation trends for total nitrogen and nitrate were almost coincide. The concentration variation of the total nitrogen was not significant during the first 4 weeks of operation because the bacteria necessitated an adaptation time for the poor nutrient environment, as explained above. At the 31st day, the total concentrations for systems 2 and 3 reached the lowest points (0.470 mg L$^{-1}$ and 0.541 mg L$^{-1}$, respectively) during the entire experiment and did not exceed a maximum limit value of 1.0 mg L$^{-1}$. However the low denitrification efficiency of total nitrogen seemed to be caused by the lack of organic carbon compounds for use as electron donor at the end of experiments.

![Figure 5. Nitrite concentration variation with operation time for three systems](image)

![Figure 6. Total nitrogen concentration variation with operation time for three systems](image)

The change of turbidity during the entire experiment was illustrated in Fig. 7. The optimum efficiency of turbidity for systems 2 and 3 could reach above 90% because of the biological adsorption, microbiological flocculation, biodegradation and direct precipitation of the biofilm. The turbidity could be eliminated by the degradation of some organic substances which could produce the turbidity.
4. Conclusions
EBO system is potentially an interesting alternative for drinking water denitrification, as it reduces the risk of nitrogen contamination and does not require high operational costs. During the entire experiment, the optimum removal rates of COD, ammonia, nitrate, total nitrogen and turbidity reached above 25%, 71%, 76%, 77% and 90%, respectively under the conditions of dissolved oxygen 2.5~3.0 mg L\(^{-1}\) and temperature 24~28°C.

In order to achieve desirable denitrification efficiency, the enough biological contact time should be taken into account in EBO system, which was essential for the denitrifiers to adapt the oligotrophic environment.

In future research, the EBO system will be studied for the denitrification efficiency in pilot scale, which combines the bio-contact oxidation system in situ with the multifunctional device for water lifting and aeration (MDWLA).

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