The Study on the Effect of Different Filling Methods of Nitrate Removal from Groundwater

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Abstract. Under the optimum combination conditions, the degree of nitrate contamination of groundwater has been investigated by column test to research the various effects of different filling modes towards denitrification. The research shows that under the environment of pH value is 7, with the temperature of 30℃ and influent nitrate concentration 30mg/L, mixed filling of the hybrid filling has obvious advantages compared with sectional filling. In mixed filling, the nitrate removal effect is better and more stable with the removal rate being maintained at 95%. The accumulation of nitrite nitrogen mixed filling has been maintained at a low level, while nitrogen accumulation has been kept at a high level with the pH of the reaction system maintaining between 7 and 8

1. Introduction

Because of the prevalent phenomenon of surface water pollution in our country, shallow groundwater resources have been polluted to varying degrees, and the groundwater pollution coverage rate of China has reached 50% approximately, nearly half of the total cities having been affected seriously[1], especially the nitrate pollution in groundwater has been widely existed in our country. According to different transforming patterns of nitrate in groundwater, remediation technology can be divided into physical-chemical method, chemical method and bio-remediation technique[2-4]. This article aims to examine various effects resulted from different filling modes on the removal of nitrate nitrogen by column test.

2. Experimental materials

2.1. Solid carbon source and fillers

Corn straw(length 0.5-1.5cm) and sawdust (powder) were selected in the experiment as carbon sources for denitrification; quartz sand was used as inert filler; zeolite was used to ammonia absorption effect. The particle size of zeolite is 1.0-2.0mm and quartz sand particle size is 1.0-2.0mm.

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2.2. Experimental water

The water utilized in this experiment is synthetic groundwater in which nitrate concentration is 30, 50, and 70mg NO_3--N/L with certain amount of KH_2PO_4, providing phosphorus for necessary growth of microorganisms; N/P=20; pH of experimental water is controlled under the range of 7.0-8.0.

2.3. Inoculated sludge

The inoculated sludge used in this experiments from Dalian Zhiguang water sewage treatment plant aeration tank.

3. Experimengtal process and analysis methods

3.1. Experimental method

In the denitrification column test at 30 ℃, water runs into synthetic groundwater with 50 mg/L at a flow rate of 15 mL/h. Sectional filling column method and mixed filling column method are used in this experiment separately in order to compare these two kinds of filling effects on denitrification.

The reactor is two organic glass columns, of which the column diameter was 10cm and the column height was 60cm as shown in figure 1. Carbon sources are straw and sawdust; inert filler is quartz sand. Prepared for this experiment, carbon sources and inert filler are washed up with distilled water and then dried up completely. Then alcohol is used to disinfect the organic glass columns, and at the same time, carbon source and inert filler are put into the steam sterilization pot pasteurization for 30 minutes. After sterilization, the carbon source and filler are filled into these two filter: the 1 pillar is placed by quartz sand, straw and sawdust in order; the 2 pillar is filled with quartz sand, straw and sawdust mixed with quartz sand in the volume of 1:1, adding 2000mL anaerobic activated sludge and the two ends of the are filled with quartz sand in column 2 in order to prevent the outflow of quartz sand filler, creating an anaerobic condition. After standing for 24 hours, Inflow water is synthetic groundwater. This experiment adopts a method of peristaltic pump flow inlet, with peristaltic pump flow rate being controlled under 2.5mL/min. The column operates for 30 days under 30 ℃. During this period, sample water is extracted from columns to analyze the concentration of NO_3-N, NO_2-N and NH^{4+}-N.

3.2. Analysis method

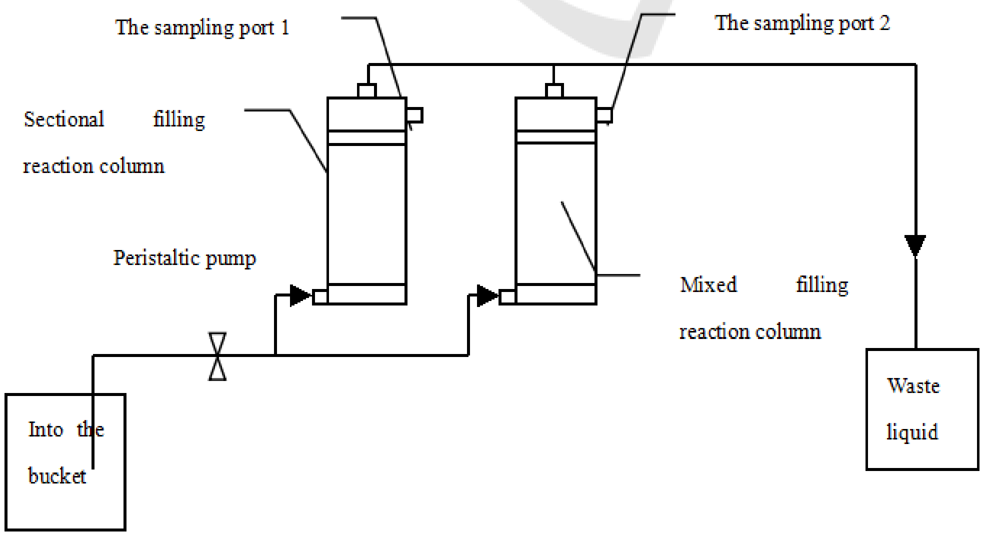

Figure 1. Reaction column packed in different ways.

After filtration of sample water, measure pH, NO_3^--N, NO_2^--N, NH_4^+-N, and determination methods are implemented based on Monitoring and Analysis Methods of Water and Wastewater (Fourth Edition). Using spectrophotometric determination to measureNO_3^--N (ultraviolet spectrophotometry), NO_2^--N(N-(1-Naphthyl)-ethylenediaminedihydrochloride spectrophotometric method) and NH_4^+-N (the indophenol blue photometric method) by UV, PH is determined by pH meter.

4. Results and discussion

With the process of denitrification and removal of nitrate nitrogen, the accumulation of nitrite nitrogen and ammonia nitrogen enables the concentration of nitrogen compounds tochange accordingly.

4.1. Effect of different filling methods on nitrate nitrogen concentration

Figure 2 shows that in the first 24 days, the concentration of nitrate nitrogen removal of thesetwo methods of filling are nearly the same, with removal rate having reached over 95%. From the twenty-fifth day, it appears to have differences, mixed filling method remains a removal rate over 95%, while sectional filling method enables the removal rate of nitrate nitrogen increases gradually, and intwenty-eighth day it has been reduced to a level under 90%. So mixed filling method on nitrate removal has embodied an obvious advantage of more lasting effect. In addition, at the early stage of reactor operation, the effluent of two filling patterns all shows yellow. In fifth day of this operation, the effluent turbidity and color disappeared.

In theexperiment of comparing the effects of these two different filling methods, the effluent of nitrate nitrogen concentration of these two kinds of filling methods is lower than that of our drinking water health standard (GB5749-2006) with limited value(10mg NO_3^--N/L). But the hybrid fillers nitrogen removal effect is better than sectional filling method nitrogen removal effect. It might attributes to that corn straw and sawdust are used bothas carbon sources andas the carrier of various microorganism to form biological membrane simultaneously. The mixture of corn straw and sawdust could make the microorganism attach on the carrier more evenly. The adhesion ability of microorganisms cool vary according to different textures of corn straw and sawdust. The biological membrane formed in sectional filling method is not heterogeneous which contributes to the adherent ability of microorganism worse than that in mixed filling method, while biological membrane formed in mixed filling method enables denitrifying bacteria and other various bacteria to distribute evenly so that it could keep a higher removal rate of nitrate.

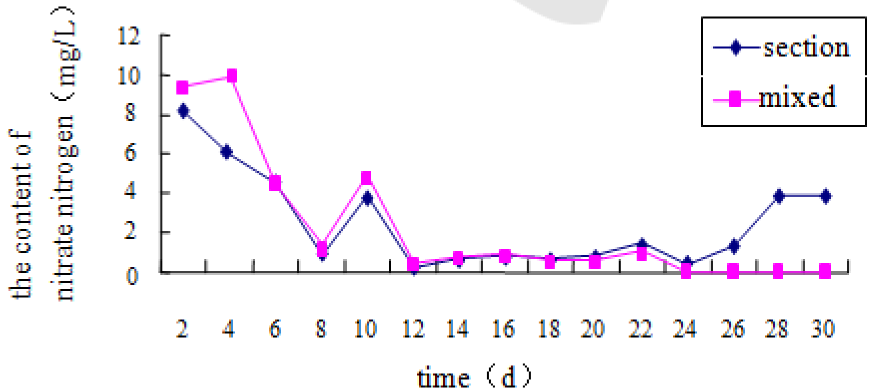

Figure 2. Change of nitrate content in column experiments.

4.2. Effect of different filling methods on nitritenitrogen concentration

Seen from Figure 3, during the first 20 days that two filling methods are operated in the reactor, the nitrite nitrogen concentration in these two methods almost remains the same with concentration of nitrite nitrogen in sectional filling method reaching around0.003mg/L and nitrite nitrogen concentration in mixed filling method remaining around 0.002mg/L, which complies with National groundwater environmental quality standard of Class III. On the 21st day, nitrite nitrogen concentration in sectional filling method increases significantly，reaching 2.04mg/L, and the concentration of nitrite nitrogen in the mixed filling method still maintains at a level of 0.03mg/L which has highlights the advantages. From this point， mixed filling method is more standard which can be utilized in the experiment.

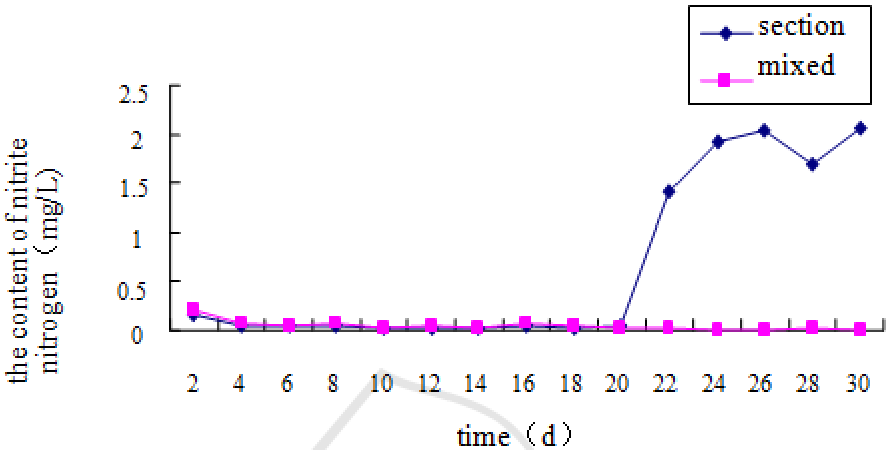

Figure 3. Change of nitrate content in column experiments.

During the whole experiment, the phenomenon of nitrite accumulation has always existed, especially during the orthogonal test nitrite accumulation is significant, while in the column experiment there is almost no nitrite accumulation. After analysis, what causes this difference might attributes to the different types of reactor. All of the reaction process of orthogonal test arecarried out in a conical flask. Nitrate reductase rates faster than nitrite reductase[5], so great amount of nitrate is reduced rapidly but nitrite accumulates rapidly in the conical flask. Only when the denitrification of nitrite accumulation finished, the amount of nitrite accumulation would gradually reduce in conical flask. Therefore, with the reduction of nitrate concentration, the reduction of nitrite nitrogen concentration has shown a delayed effect.It is completely different in column test case in which due to the influent nitrate solution runs slowly through the column bottom into the reaction column, giving sufficient time for denitrification and enabling the nitrite reductase could have sufficient time to reduce the by-products of nitrite, the accumulation of nitrite in the reaction system could be significantly reduced and thus in the effluent it shows that nitrite nitrogen concentration is very low[6].

But for the sectional filling column test in the late period of reaction, great amount of nitrite accumulation appears which might result from that sectional filling mode hinders the sustainable release of carbon source, leading to the lack of organic carbon release in the reactor and the accumulation of nitrite nitrogen.

4.3. The effect of different filling methods on ammonia nitrogen concentration

Figure 4 shows that in these two kinds of filling methods nitrogen accumulation trend are almost the same. In the first four days, due to the reaction processes completely, little ammonia is produced. As the denitrification of ammonia processes for a long time, the accumulation of ammonia becomes more and more obvious. The largest accumulation could reach 15mg/L which is 15 times more than the standard of groundwater. So when this reactor is utilized, the removal of ammonia should be considered which is conductive to the removal effects on nitrate.

Some of the accumulation of ammonia in effluent denitrification experiment comes from carbon source release (maize straw, sawdust), other comes from dissimilatory nitrate reduction to ammonium (DNRA) process. High organic carbon content in the environment is conductive to dissimilatory nitrate reduction to ammonium (DNRA) process[7]. Ammonia nitrogen content increases rapidly after sixth days, which might due to the release of a large number of organic carbon source. Under the condition of the existence of microorganisms, the release rate of ammonia nitrogen might also change. Therefore in the following experiments, it is necessary to take eliminating ammonia nitrogen content in water into consideration to meet the standard.

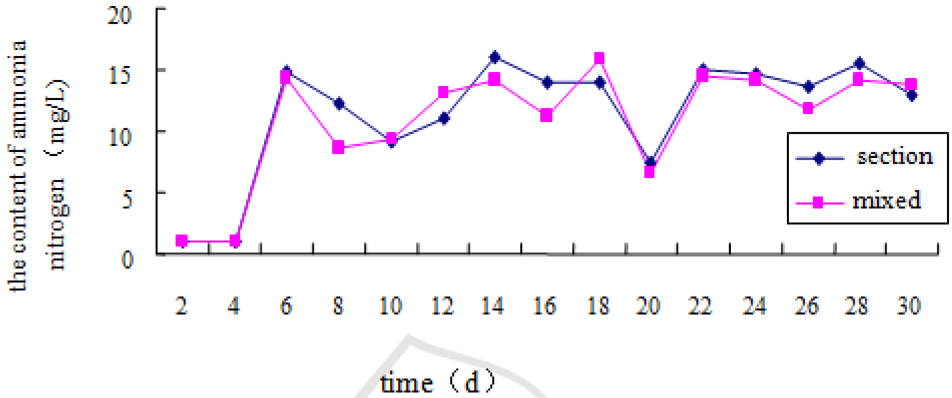

Figure 4. Change of ammonia content in column experiments.

4.4. Effect of different filling methods on pH

Seen from Figure 5, in the denitrification process, pH value is one of the important factors for the environmental pH can affect the growth and reproduction of microorganisms which enables different organisms havedifferent adaptive capacity in terms of various ranges of pH. In these two kinds of filling methods, pH has maintained neutral fundamentally in the denitrification process. That is to say that denitrification processed in neutral environmental condition.

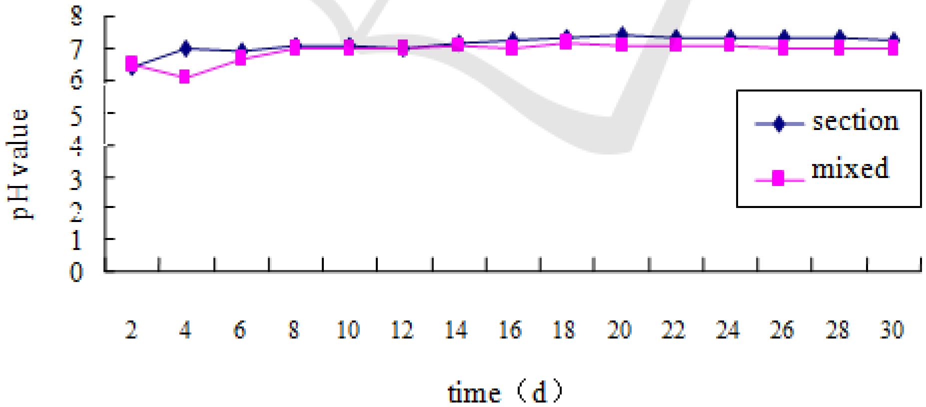

Figure 5. Change of pH in column experiments.

Too high or too low pH value would affect the denitrification reaction. Although denitrification reaction can also occurred when the pH value exceeds the optimum range, but this might cause the accumulation of toxic intermediate product (such as nitrite)[8]. As Figure 5 showed, in the whole reaction process, the pH value of effluent has maintained 6.0-7.5, suitable for denitrifying bacteria's growth and reproduction.

5. Conclusions

The column test of different filling methods operated on mixed filling materials has shown that two kinds of filling methods have different nitrate removal effects: the experiment that uses mixed filling method has a better and more stable removal effect with a sustainable removal rate of 95%.After twenty-fourth day the one used sectional filling method, nitrate removal rate begins to rebound. In the late period the removal rate drops to below 90%.As for the accumulation of by-products nitrite nitrogen in the reaction process, the mixed filling method helps it maintain at a low level, while when used sectional filling method, its accumulation increases rapidly in later period of reaction. At the same time, the accumulation of ammonia nitrogen in the column reaction has been maintained at a high level and the pH of the reaction system has been maintained between 7 to 8.

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