Scientific Research

Denitrification of Groundwater Using Walnut Shell as Solid Carbon Source

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Abstract: Removal of nitrate from groundwater and the factors affecting denitrification were studied in laboratory-scale columns packed with granular walnut shell. The experiment results indicated that walnut shell could achieve a great nitrate removal efficiency of 80%, and the concentration of NO_3^--N in effluent was below 3mg/L. During the experiment, pH and water temperature had been almost constant, and the concentration of NO_2^--N in effluent was low. One of the main factors affecting this reaction was HRT, and the best HRT was 24h. The denitrification of groundwater using walnut shell as solid carbon source conformed to the zero-order kinetics equation with a half-life of 14.8h and rate constant of 1.7509h^{-1}.

Keywords: Walnut Shell; Denitrification; Nitrate; Kinetics; Carbon Source

1 Introduction

Biological denitrification is one of the main methods to remediate the nitrate-polluted groundwater. Because of the diversity of denitrifying bacteria species, the mechanism of denitrification is varied . Up to the present study, the most widely used nitrogen removal process is the anaerobic denitrification process, whose mechanism is that heterotrophic denitrifying bacteria use organics as carbon source to transform the nitrate into nitrogen under anaerobic conditions[1]. In the groundwater, lack of organic carbon seriously affects the efficiency of heterotrophic denitrification, which hold many scholars' interest. Acetic acid and ethanol as liquid carbon were putted into the reactor, while greatly enhancing the denitrification, but the cost was too high, the addition was difficult to control, and practicability level was low[2]. The solid carbon source, such as sawdust, compost, cotton and paper, showed obvious advantages compared with liquid carbon source. They had high removal rate of nitrate and low cost, but their biological corrosion resistance were so poor that microbes could quickly deplete them. Thus the permeability of the reactor decreased and denitrification tended to be less effective[3-7]. Therefore, finding a better solid-phase organic carbon media for the remediation of nitrate pollution in groundwater has become a focus of research.

Walnut shell is the waste after the walnut kernel is taken. It not only has low cost and great production, but also has a fixed geometric shape. The main components of walnut shell are lignin, cellulose and hemicellulose, which can be consumed by denitrifying bacteria[8]. In this paper, walnut shell as the organic carbon source and denitrification reaction medium has been used to remediate the nitrate pollution of groundwater. The ultimate aim is to explore an efficient, economical, environmentally friendly ways to remediate the nitrate pollution of groundwater.

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2 Methods

2.1 Main materials and equipments

The experimental walnut shells, belonging to the pecan varieties, were bought from a Beijing water treatment materials factory, whose compressive resistance was 23.4kgf with the size range of 1-2mm.

The influent of column experiment was artificial wastewater. Potassium nitrate was guaranteed reagent (Eastern chemical plant). $MgSO_4 \cdot 7H_2O$, K_2HPO_4 and KH_2PO_4 were the buffering agents.

The main instruments were UV1200-visible spectrophotometer (Shanghai Mapada Instruments Co., Ltd) and Portable pH meter (pHTestr 30；Oakton).

2.2 Experimental design and operation

The PVC column (6.0cm in internal diameter and 60cm in length) was set up water distribution zone, reaction zone and the catchment areas. Their thicknesses were 5cm, 50cm and 5cm. The column was designed with four sampling ports spaced evenly along the length of the column. The ports were installed at 15cm (P1), 25cm (P2), 35cm (P3) and 45cm (P4) from the base of the column. Each port was fitted with a rubber septum to allow sampling with the aid of a syringe.

The artificial wastewater was pumped into the column by the peristaltic pump. The samples from the sampling ports and catchment areas were analyzed. Figure1 was the schematic of the column setup.

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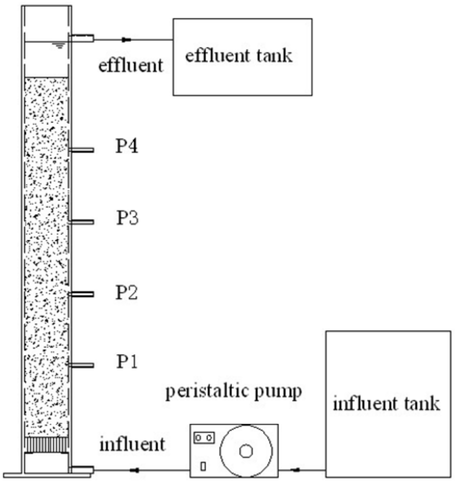

Figure 1. Schematic of the column setup

Walnut shells had been washed with distilled water and dried naturally. The column was soaked one day by suspension, which was from the denitrification segment in a sewage treatment plant in Beijing. The denitrifying bacteria was inoculated. The column reactor began to run and the initial hydraulic retention time (HRT) was 24h. Table 1 presented the operation parameters of the column reactor. The removal rate of nitrate and other related indicators were tested periodically.

Table 1 The operation parameters of the column reactor

Filler	Filling volume (cm^3)	Porosity (%)	Initial influent concentration of nitrate (mgL^{-1})	Initial HRT (h)
Walnut shell	1.41×10^3	53.9	35	24

2.3 Analytical method

Test method was in accordance with the “Water and Wastewater Monitoring Analysis Method” (Fourth Edition). Nitrate was tested by ultraviolet spectrophotometry. Nitrite was tested by N-(1-naphthyl)-ethylenediamine determination. Permanganate index was tested by acid method. pH was tested by a portable pH meter. Water temperature was tested by thermometer[9].

3 Results

3.1 Nitrate removal

At the beginning of the operation, the removal rate of nitrate was unstable. This was concerned with the growth of microorganisms and the adsorption of the filler. After 15 days, column reactor operated steady. Figure2 was the curve of the removal rate of NO_3-N and effluent NO_3-N concentration.

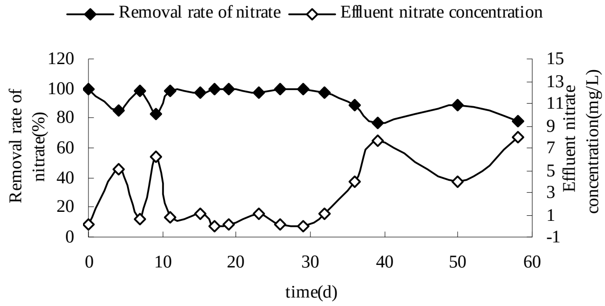

Figure 2. The curve of the removal rate of NO_3-N and effluent NO_3-N concentration

According to figure2, walnut shells had a great nitrate removal efficiency of 80%, and the effluent nitrate concentration was below 3mg/L. III water standards of the “Groundwater Quality Standard” GB/T14848-93 required the concentration of nitrate in the groundwater should be less than 20mg/L (The following also referred to as standard).

Walnut shell not only contains about 20-30% cellulose which is easy to be used by microbial, but also contains 50% hemicellulose and lignin which are not easy to be used by microbial[8]. Heterotrophic denitrifying bacteria mainly used the cellulose as an organic carbon source, and used the framework of forming with hemicellulose and lignin as a suspension biofilm carrier. The results showed that the denitrification efficiency in the column reactor was high.

After two months of operation, the sensory characteristics of walnut shells did not change significantly. Column porosity slightly decreased to 50.8%. From this description, walnut shells had some biotic resistance to avoid being disintegration. During the denitrification process, walnut shells could maintain a fixed geometric shape.

3.2 Permanganate index of the effluent

After 15 days, column reactor operated steady. The effluent permanganate index was tested regularly. Figure3 was the curve of the effluent $COD_{Mn.}$

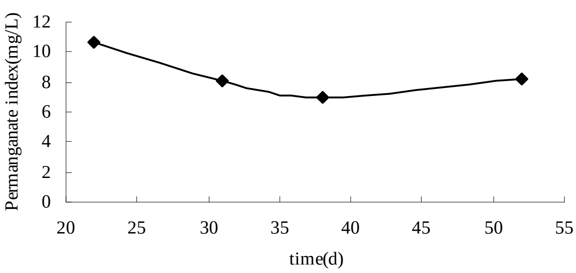

Figure 3. The curve of the effluent COD_{Mn}

The average value of the effluent permanganate index was beyond the standard requirement, was about 8.47mgO$_2$/L. According to figure3, after the thirtieth day, the curve presented obvious downward trend, and then went up significantly after the forty-fifth day. At the thirty-eighth day, the value of permanganate index reached its lowest. This was consistent with the curve of the removal rate of nitrate (figure2) in the same period. Thus, a positive correlation existed between the nitrate removal efficiency and carbon emission. With the increase of carbon emission, the removal rate of nitrate increased.

3.3 PH and Water Temperature

During the experiment, pH of the influent was between 6.5 and 7.5. pH of the effluent increased slightly and was between 7.0 and 7.5. The influent and effluent water was close to neutral. So the denitrification with walnut shells as the carbon source and reaction medium had little impact on groundwater pH. The effluent pH met the standards. Figure4 was the curve of pH.

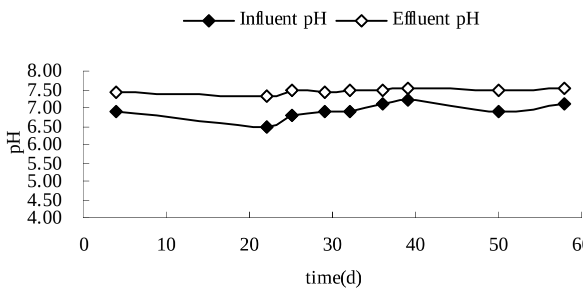

Figure 4. The curve of pH

Temperature of water maintained at 9-14℃. It was close to the actual groundwater temperature and greatly simulated the groundwater environment. It provided a more reliable reference for engineering. Figure5 was the curve of the removal rate of NO$_3$-N and water temperature. As it indicated, the water temperature changed obviously during 25-45d, but the removal rate of nitrate was stable in the same period. The removal rate of nitrate maintained at 80%. It was means that denitrification with walnut shells as the carbon source and reaction medium was not effected by the water temperature changes between 9-14℃.

3.4 The NO$_2$-N concentration of effluent

During the experiment, the effluent nitrite concentration was periodically monitored. And there was no nitrite accumulation phenomenon. Its concentration was in the range of 0.007-0.012mg/L and met the standards. Figure6 was the curve of effluent NO$_2$-N concentration.

It was found that the catchment areas sometimes bubbled.

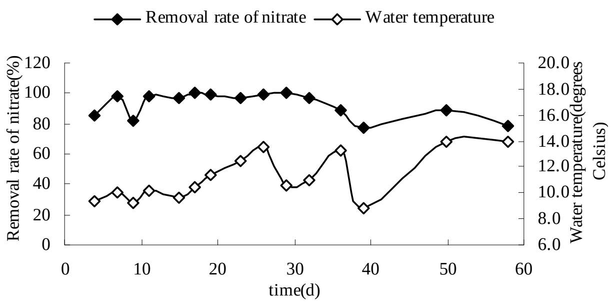

Figure 5. The curve of the removal rate of NO$_3$-N and water temperature

On the basis of the principle of anaerobic denitrification, the gas was nitrogen gas which was produced from the reduction of nitrate by denitrifying bacteria. Therefore, heterotrophic denitrification was more pronounced in the column reactor.

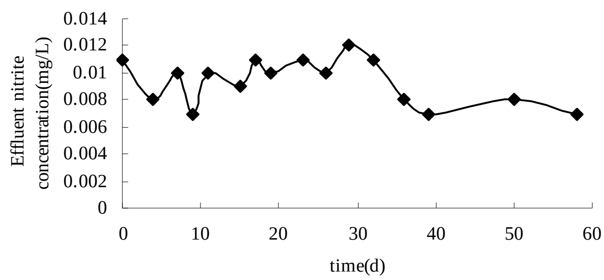

Figure 6. The curve of effluent NO$_2$-N concentration

3.5 The influence of operating conditions

3.5.1 The influence of HRT

The column reactor operated at HRT 12h, 24h and 48h respectively. Influent nitrate concentration was 35mg/L. The water temperature was 11.5±1.0℃. The influent pH was controlled at 7.0. The average values of the various indicators were contrasted for the optimum efficiency (figure7).

According to figure7, when HRT was 12h, the removal rate of nitrate was less than 40%, and the nitrate concentration in effluent was over 20mg/L. When HRT was 24h and 48h separately, the removal rate of nitrate was over 90%, and the nitrate concentration in effluent was less than 3.5mg/L.

When HRT was 12h, the nitrite accumulation phenomenon emerged. The effluent nitrite concentration was over 0.020mg/L and did not meet the standard. When HRT was 24h and 48h separately, the effluent nitrite concentration was less than 0.010mg/L and met the standard.

The value of effluent permanganate index was high. The minimum was 8.47mgO$_2$/L (HRT=24h) and the maximum was 15.95mgO$_2$/L (HRT=48h). It did not meet

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the standard.

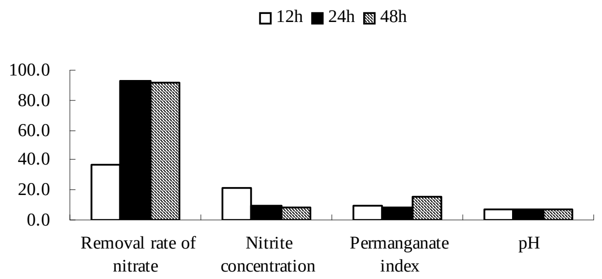

Figure 7. The effect of the performance of column reactor with HRT

Notes: Four indicators, including the removal rate of nitrate (%), effluent NO_2-N concentration (10^{-3}mg/L), effluent COD_{Mn} (mgO_2/L) and effluent pH, were contrasted.

The effluent pH almost kept constant among the three different HRT. The pH varied from 7.41 to 7.46 and the water quality was neutral.

In brief, when HRT was 12h, the removal rate of nitrate was low, the effluent permanganate index and effluent nitrite concentration were high. The effluent water quantity was bad. When HRT was 48h, although the removal rate of nitrate was high, the effluent permanganate index was also high which was about twice the 24h. When HRT was 24h, there were a high nitrate removal rate, a low effluent permanganate index and a low effluent nitrite concentration. Therefore, for the denitrification with walnut shells as the carbon source and reaction medium, the best HRT was 24h.

3.5.2 The influence of influent NO_3-N concentration

Influent nitrate concentration increased from 35mg/L to 50mg/L. HRT was 24h. The water temperature was 11.5±1.0℃. The influent pH was controlled at 7.0. The average values of the various indicators were contrasted for the optimum efficiency (figure8).

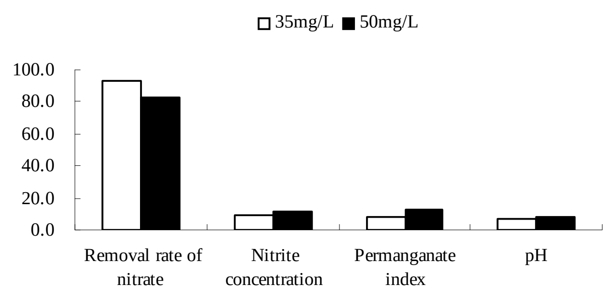

Figure 8. The effect of the performance of column reactor with influent NO_3-N concentration

Notes: Four indicators, including the removal rate of nitrate (%), effluent NO_2-N concentration (10^{-3}mg/L), effluent COD_{Mn} (mgO_2/L) and effluent pH, were contrasted.

According to figure8, the influent nitrate concentration increased from 35mg/L to 50mg/L. The removal rate of nitrate decreased slightly and still remained above 80%. The effluent nitrate concentration was less than 10mg/L. The effluent nitrite concentration increased from 0.009mg/L to 0.012mg/L, and they were below the limit by the standards. The effluent permanganate index increased from 8.47mgO_2/L to 12.16mgO_2/L. The effluent pH had little change and the value was still between 7.40 and 7.90.

Therefore, the influent NO_3-N concentration had little influence on the denitrification with walnut shells as the carbon source and reaction medium.

3.6 Kinetics of the denitrification

The operating conditions of column reactor were as follows: HRT was 24h, influent nitrate concentration was 50mg/L, influent pH was 7.0, temperature was 12.5℃. The samples were taken from the inlet, P1-P4 sampling ports and the outlet. The curve of nitrate concentration along column depth was drawn in figure9.

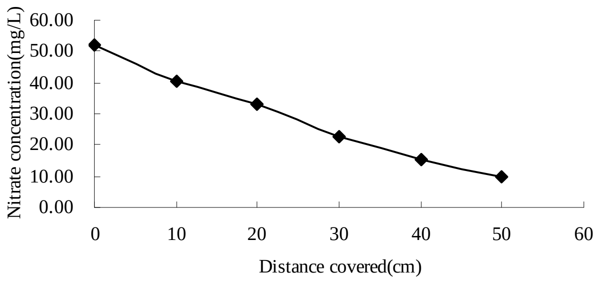

Figure 9. Profile of nitrate along the column

The concentration vs. distance profile (figure9) was converted to concentration vs. time profile (figure10). The time taken for the groundwater to travel upwards from the bottom of the column to the sampling ports was obtained from the flow rate using the following equation:

$$t = \frac{\pi r^2 h \varepsilon}{q} \quad (1)$$

Where r is the radius of the column (cm), h is the distance covered from the base of the column to the port (cm), ε is the porosity of the filling material of the column, and q is the flow rate of the groundwater through the column (cm^3/h).

From the figure10, c and t had a good linear relationship, R^2 was 0.9887, the reaction constant k was 1.7509. So this reaction coincided with zero-order kinetic model. c_0 was the influent nitrate concentration, then the kinetic equation was $c = c_0 - 1.7509t$. And the half-life was 14.8h.

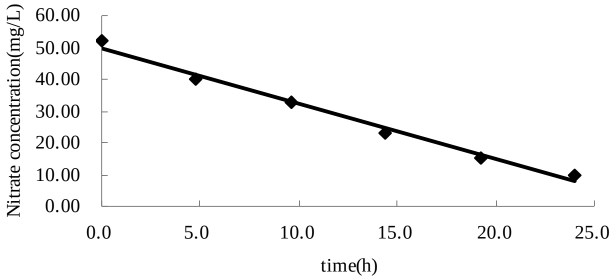

Figure 10. Regression curve of c - t of nitrate degraded by denitrification

4 Conclusions

- Walnut shells had a great nitrate removal efficiency of 80%, and the effluent nitrate concentration was below 3mg/L. After two months of operation, the sensory characteristics of walnut shells did not change significantly. Column porosity slightly decreased to 50.8%.
- During the experiment, the average value of the effluent permanganate index was beyond the standard requirement, was about 8.47mgO_2/L. The pH in effluent was close to neutral. There was no nitrite accumulation phenomenon. And the denitrification with walnut shells as the carbon source and reaction medium was not effected by the water temperature changes between 9-14℃.
- HRT had a greater impact on nitrate removal efficiency. When HRT was 24h, there were a high nitrate removal rate, a low effluent permanganate index and a low effluent nitrite concentration. Therefore, the best HRT was 24h.
- The nitrate concentration in influent increased from 35mg/L to 50mg/L. The removal rate of nitrate decreased slightly and still remained above 80%. The nitrate concentration in effluent was less than 10mg/L.
- The operating conditions of column reactor were as follows: 24h of HRT, 50mg/L of nitrate concentration in influent, 7.0 of pH in influent and 12.5℃ of temperature. Kinetics of the denitrification was studied. The experiment results indicated that c and t had a good linear relationship, R^2 was 0.9887, the reaction coincided with zero-order kinetic model. And the half-life was 14.8h.

Acknowledgement

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