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The denitrification treatment of low C/N ratio nitrate-nitrogen wastewater in a gas–liquid–solid fluidized bed bioreactor

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Abstract

A 12 l gas–liquid–solid three-phase fluidized bed bioreactor in which biomass supported on activated charcoal was used to remove nitrate-nitrogen from wastewater and its performance was considered. The effects of temperature, pH, C/N ratio, gas flow rate and hydraulic residence time (HRT) on nitrate-nitrogen reduction were investigated and discussed. The optimum operated conditions such as temperature of 20–35 °C, pH value of 6.5–7.5, HRT of 3 h, C/N of 0.95–1 and gas influx of 0.3 m^3/h were found. Under optimum operated conditions, the average removal ratios of COD and NO_x-N are higher than 92% and 96%, respectively. In addition, the radial and axial positions have little influence on the local profiles of COD and NO_x-N.

Keywords: Gas–liquid–solid three-phase fluidized bed bioreactor; Nitrate-nitrogen; Wastewater; Bio-denitrification

1. Introduction

After biochemical treatment of ammonia containing wastewater from the fertilizer production, the effluent with COD <50 mg/l and NH_4-N <10 mg/l and NO_x-N <500 mg/l can meet the national primary discharge standard of PR China for ammonia industry wastewater. But the nitrate-nitrogen in low C/N ratio wastewater, which was transformed from ammonia-nitrogen, still does rather serious harm to the environment [1–3]. It is very necessary to remove the nitrate-nitrogen from effluent. As a powerful tool for wastewater processing, bio-denitrification, which was used at municipal treatment plants to treat wastewater after ammonia was converted to nitrate via nitrification, has attracted biochemical and environmental scientists and engineers' attentions [4–8]. Especially, the bio-denitrification technology based on some new liquid–solid fluidized bed reactors was developed in recent years for the removal of nitrate-nitrogen from wastewater [9]. However, little is known about the bio-denitrification treatment of low C/N ratio nitrate-nitrogen wastewater in a gas–liquid–solid three-phase fluidized bed bioreactor, characterized by the higher operational flexibility, shorter reaction time and greater processing capability. Therefore, objective of the present study is to both develop a gas–liquid–solid three-phase fluidized bed bioreactor and acquire the optimum operated parameters for removing nitrate-nitrogen from wastewater.

2. Materials and methods

2.1. Reactor design and other apparatus

Experiments were performed in the apparatus shown in Fig. 1. The fluidized bed section (5), constructed from the plexiglass, had a 100 mm i.d. and was 1200 mm high. It was ended by a disengaging cap with 160 mm i.d. and a height of 200 mm. A growing medium, stored in reservoir (1), was pumped into the bottom of the bioreactor using a peristaltic pump (2) flux of which ranges from 600 to 10,000 ml/h. The nitrogen gas was introduced to the bed through a distributor with 0.1 mm diameter holes. The role of baffle plate separator (7) was to separate the carriers from the liquid in the effluent leaving the bioreactor and send the carriers back to the bioreactor. The liquid flow rate was measured with a rotameter (4) and was controlled by a cutoff valve (3). The flow rate of nitrogen gas, which is very convenient for fertilizer plant with air separation devices, was measured with a rotameter (8) and was control by a needle valve (9). The temperature controlled system (10) consisted of a coil with cold water and an electric heater coupled with a contact

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Nomenclature

COD	chemical oxygen demand (mg/l)
H	axial position from the distributor (m)
HRT	hydraulic residence time (h)
NH_4-N	ammonia-nitrogen (mg/l)
NO_2-N	nitrite-nitrogen (mg/l)
NO_3-N	nitrate-nitrogen (mg/l)
NO_x-N	summation of nitrite-nitrogen and nitrate-nitrogen (mg/l)
r	radial distance (m)
R	bioreactor radius (m)

thermometer. The pH was adjusted by a control system (11), consisting of a pH-meter and micropumps supplying base or acid as required.

2.2. Adaptations and immobilization

For the adaptation, a 5000 ml flask containing medium was seeded with activated sludge obtained from a local municipal wastewater treatment plant where no denitrification was carried out. The pH was controlled in the range 6.5–7 and the temperature was maintained at 30–35 °C. Air was introduced to the bottom of the flask. After a short preculture, the quantity of activated sludge increased gradually. Then the influx of air was stopped and magnetic stirring was added. Denitrifiction was carried out by heterotrophic bacteria with NO_3^- as its electronic acceptor under anoxybiotic condition. After 3–5 days, there were many bubbles in the flask, analyzing showed that the concentration of NO_3-N dropped to 15 mg/l. Adaptation was completed. Then the activated charcoal of 600 g with the average diameter of 0.2 mm was put into the flask for film-forming culture. The culturing was continued until the steady-state biomass loading on the activated charcoal was achieved. After 10 days, most free bacteria film was formed on the activated charcoal. At last, the activated charcoal was moved out and put into the fluidized bioreactor described above.

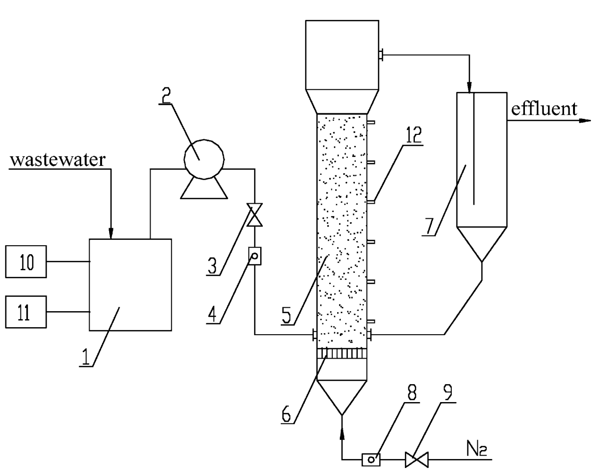

Fig. 1. Schematic diagram of the apparatus: (1) reservoir, (2) pump, (3) cutoff valve, (4) liquid rotameter, (5) fluidized bed, (6) distributor, (7) baffle plate separator, (8) gas rotameter, (9) needle valve, (10) temperature control system, (11) pH control system, (12) sample connection.

Table 1
Composition of the synthetic wastewater

Constituent	Concentration (mg/l)
COD	370–695
Nitrate	463.3
$MgSO_4$	10
$FeSO_4$	0.08
KH_2PO_4	2.5
$MnSO_4$	2.5
$CaCl_2$	1.8

2.3. The synthesized wastewater

The composition of the synthetic wastewater is shown in Table 1. The wastewater was formulated to simulate effluent generated at the fertilizer plant containing a high concentration of nitrate and low COD. Methanol was added to the medium as the carbon/energy substrate to give different C/N ratio, which is cheap for many fertilizer plants as by-product in carbamide production process.

2.4. Assays

COD was analyzed by dichromate method according to GB 11914-89 of PR China. Nitrate and nitrite were measured using the ion chromatography method by selecting Shim-pack IC-A3 as chromatographic column, 8.0 mM *p*-hydroxy benzoic acid and 3.2 mM bis-Tris as mobile phase, and CDD-6A, 3.2 mS/cm FS as conductivity detector. Liquor pH was analyzed using PHS-2 acidimeter.

3. Results and discussion

3.1. Effect of temperature on removal ratio of NO_x-N

The influences of temperature on the concentration of NO_3-N, NO_2-N and COD at solution pH value of 7.5, hydraulic residence time (HRT) of 3 h and gas influx of 0.3 m^3/h for initial nitrate-nitrogen concentration of 463.3 mg/l and COD of 486.5 mg/l are shown in Fig. 2. It is observed that temperature cannot exert great influence on the removal ratio of NO_x-N. The protection of the biofilm and extracellular polymer on bacteria is a major cause. Low temperature can inhibit the activity of intracellular enzyme and result in a low-level metabolism. Too high temperature maybe leads to protein denaturation. The optimum temperature for treating nitrate-nitrogen wastewater ranges from 20 to 35 °C.

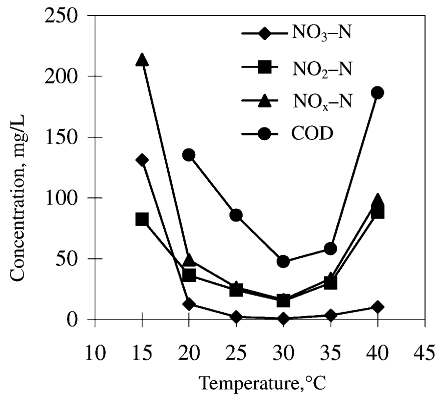

Fig. 2. Influences of temperature on concentration of NO_x-N and COD in effluent water.

3.2. Effect of pH on removal ratio of NO_x-N

pH is an important effect factor for the biological denitrification also. Fig. 3 illustrates the influences of pH values on removal ratio of NO_x-N at the same temperature of 30 °C, HRT of 3 h, gas influx of 0.3 m^3/h, nitrate-nitrogen concentration of 463.3 mg/l and COD of 486.5 mg/l. A significant influence of pH values on removal ratio of NO_x-N is observed. The removal ratio of NO_x-N reaches peak at solution pH value of 7.0 and the optimum pH is 6.5–7.5. However, it will be non-ideal for pH value higher than 8.0 or lower than 6.0. It is mainly attributed to the inhibitory effect of superacidity or superalkalinity on the activity of intracellular enzyme of bacteria. Additionally, the NO_2-N accumulation occurs when the pH values is higher than 8.0, and higher the pH values, more the accumulation of NO_2-N. This is probably because the activity of nitrite reductase was inhibited.

3.3. Effect of C/N ratio on removal ratio of NO_x-N

The typical results of the removal of NO_x-N as a function of various C/N at the fixed temperature of 30 °C, pH value of 7.5, HRT of 3 h, gas influx of 0.3 m^3/h and nitrate-nitrogen concentration of 463.3 mg/l are shown in Fig. 4. It can be seen that the concentration of NO_x-N in effluent decreases gradually, at the same time, COD increases with increasing in the ratio of C/N. Excessive added methanol as carbon source results in waste and makes the effluent COD too high. It is also observed that both the effluent NO_x-N and COD reach a satisfying level when the C/N ratio is 0.95–1.

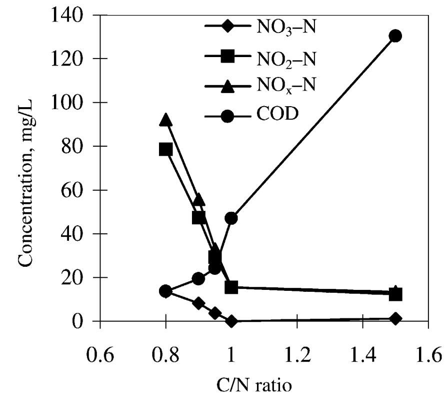

Fig. 4. Influences of C/N on concentration of NO_x-N and COD in effluent water.

3.4. Effect of HRT on removal ratio of NO_x-N

The influences of HRT on the removal of NO_3-N at the fixed nitrate-nitrogen concentration of 463.3 mg/l, COD of 486.5 mg/l, gas influx of 0.3 m^3/h, pH value of 7.5 and temperature of 30 °C are shown in Fig. 5. The HRT has a rather great effect on the removal of NO_3-N. The removal ratio of NO_x-N was higher but the operating charges would increase with increasing in the HRT. At HRT of 2 h, the effluent NO_3-N concentration almost dropped to 10 mg/l but the concentration of NO_2-N was still higher than 120 mg/l. Most NO_x-N had been removed when HRT was 3 h, corresponding to liquid flow rate = 4 l/h.

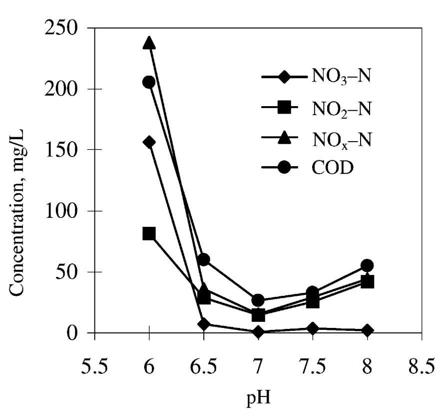

Fig. 3. Influences of pH values on concentration of NO_x-N and COD in effluent water.

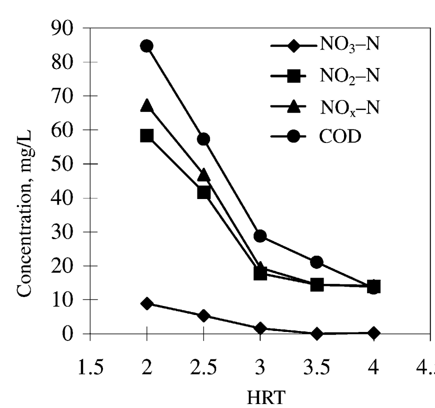

Fig. 5. Influences of Liquid flow rate on concentration of NO_x-N in effluent water.

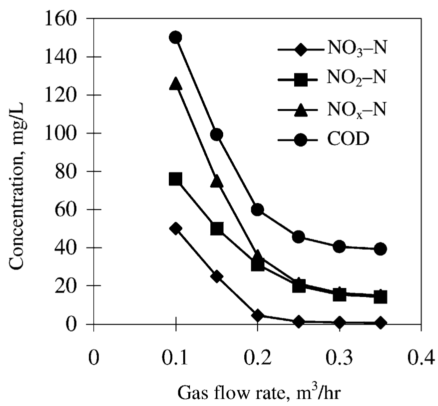

Fig. 6. Influences of gas flow rate on concentration of NO_x-N in effluent water.

3.5. Effect of gas flow rate on removal ratio of NO_x-N

Fig. 6 shows the variables of gas flow rate on the removal of NO_x-N at the same nitrate-nitrogen concentration of 463.3 mg/l, COD of 486.5 mg/l, HRT of 3 h, pH value of 7.5 and temperature of 30 °C. The gas influx is one of the important factors exerting great effect on the fluidized bed bioreactor. When the gas influx was smaller than 0.25 m^3/h, the carriers inside this bioreactor are gradually fluidized and suspended (called stationary fluidization region) with increasing in the gas influx, and the liquid–solid mass transfer coefficient and contact time were gradually improved, resulting in the decreases in the effluent NO_x-N and COD. When the gas influx reached the value of 0.25 m^3/h, the carriers inside this bioreactor are completely fluidized (called completely fluidization region), leading to the effluent COD <50 mg/l and NO_x-N <20 mg/l. With further increase in the gas influx, the quantity of the carriers carried from the test tube to the outer circulating tube increased, and a outer circulating fluidized bed was finally formed, the liquid–solid contact time was increased, thus resulting in the further decrease in the effluent NO_x-N and COD. So, the optimum gas flow rate was selected as 0.3 m^3/h.

3.6. Effect of the continuous bioprocess under the optimum operated conditions

Experiment was carried out at nitrate-nitrogen concentration of 463.3 mg/l, temperature of 30 °C, pH value of 7.5, HRT of 3 h, C/N of 0.95 and gas influx of 0.3 m^3/h. As can be seen from Fig. 7, under above optimum operated conditions the average removal ratio of NO_x-N and COD are respectively higher than 92 and 96% for more than 40 days, corresponding to the effluent COD <50 mg/l and NO_x-N <20 mg/l.

3.7. The local profiles of NO_x-N and COD under the optimum operated conditions

At the optimum operated conditions, the local profiles of NO_x-N and COD in the different radial and axial positions of this bioreactor were shown in Figs. 8 and 9. It is observed that the local distributions show little variation with the radial and axial positions of this bioreactor. It was mainly attributed to the well defined flow pattern, better dispersing effects and the higher mass transfer coefficients of this gas–liquid–solid three-phase fluidized bed bioreactor.

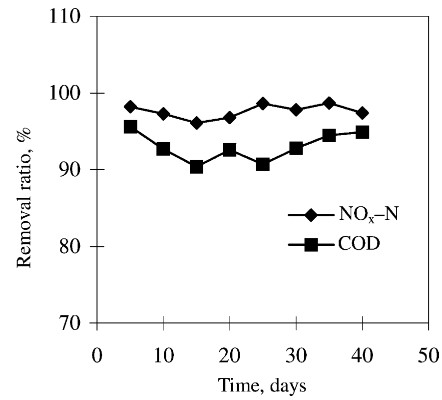

Fig. 7. Effect of bio-denitrification process on the optimum operated conditions.

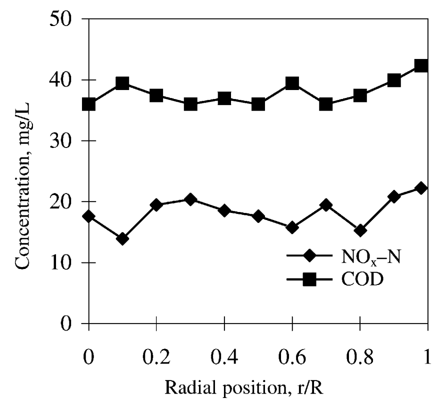

Fig. 8. Influences of radial position under the optimum operated conditions ($H = 0.47$ m).

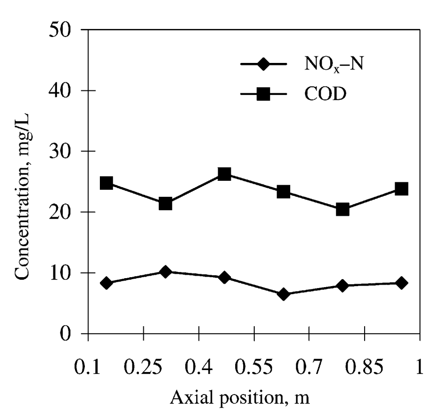

Fig. 9. Influences of axial position under the optimum operated conditions ($r/R = 0$).

4. Conclusions

Based on the present investigation, the following conclusions can be made:

1. The feasibility of gas–liquid–solid three-phase fluidized bed bioreactor for treating nitrate-nitrogen wastewater was verified.
2. The obtained strains after acclimatization had good process effect on low C/N ratio nitrate-nitrogen wastewater.
3. The optimum operated conditions of gas–liquid–solid three-phase fluidized bed bioreactor for treating nitrate-nitrogen wastewater are temperature of 20–35 °C, pH value of 6.5–7.5, HRT of 3 h, C/N of 0.95–1 and gas influx of 0.3 m^3/h. Under the optimum conditions, the average removal efficiencies of NO_x-N and COD are higher than 92 and 96%, respectively.

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