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Nitrification characteristics of PEG immobilized activated sludge at high ammonia and COD loading rates

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Abstract

Autotrophic nitrifiers and heterotrophic bacteria are all oxygen-consuming bacteria. In conventional active sludge, nitrification activities decrease dramatically with increasing COD and ammonia loading rate, as the presence of a large amount of carbonaceous substrates often prevents oxygen being used for nitrification, or high concentration ammonia can harm the metabolism of nitrifiers, which has a relative slow growth rate. In our study, PEG immobilized activated sludge can not only maintain high nitrification rate at high ammonia (more than 500 mg/L) and COD loading rate, but also simultaneously remove ammonia and COD. Experiments demonstrated that nitrifiers and heterotrophic bacteria can coexist in the PEG matrix and reactor to function normally. However, no obvious denitrification phenomena could be observed. Various operational conditions, such as DO, COD and ammonia loading rate, are investigated to study the reaction mechanism and nitrification characteristics of the immobilized activated sludge. The structure of the PEG gel is also discussed.

Keywords: Immobilized activated sludge; Nitrification; High ammonia nitrogen loading

1. Introduction

Lakes, marshes and reservoirs are enclosed water bodies, and they are usually used as main resources for domestic and industrial water supply. However, the relative difficulty of nitrogen and phosphorus removal from wastewater and their discharge without effective treatment into the water bodies cause eutrophication or serious eutrophication. How to effectively remove nitrogen from waste streams is a hot topic in the wastewater treatment field. Nitrification is an important step for nitrogen removal, and using immobilized bacteria to accomplish nitrification has the following advantages: compact structure, high efficiency and tolerating striking loading rates. Elimination of eutrophication requires a compact but highly efficient system. Nitrifiers immobilized in the substrates can retain in the reactor for unlimited period, favoring the growth of the autotrophic microbes [1]. However, in the ammonia nitrogen effluents, the presence of a large amount of organic substrates often prevents oxygen being used for nitrification of the immobilized bacteria,

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as nitrifiers have a slower respiration rate than the heterotrophs that consume organics [2–3]. This inadequate ammonia nitrogen and nitrifiers contact seriously inhibits nitrification rate.

In this paper, we utilize PEG immobilized activated sludge to treat a strong ammonia–nitrogen synthetic wastewater containing organic substrates. Results demonstrate that after acclimation, the immobilized activated sludge obtains high nitrification removal, ca. 94–98%, in treating strong ammonia nitrogen influents. Increasing ammonia nitrogen concentration in the influent, from 150 to 250 mg/L, then to 360 mg/L, leads to an increase of nitrification rate of immobilized activated sludge, from 32 to 34 mg N/L h, then to 38 mg N/L h, respectively. The presence of organic substrates in the influents does not influence the nitrification rates of the immobilized activated sludge. The nitrification characteristics of the immobilized activated sludge is evaluated, and the immobilized matrices is deduced as an evenly crosslinked structure without skin layer.

2. Materials and methods

Biological nitrification is carried out in an up-flow inner circulation aerated reactor, with 18 L operating volumes.

2.1. PEG immobilized activated sludge

PEG immobilized activated sludge is supplied by Hitachi Co. Ltd. Its general preparation procedure is as follows [4]: 2% concentrated activated sludge is suspended in 18% PEG pre-polymer solution containing 1% N,N′-methylene-bis-acrylamide (MBA) crosslinker is mixed with potassium persulfate initiator, and let the mixture stand for about 10 min at room temperature of about 25°C. An elastic gel, that is PEG immobilized activated sludge, is obtained. The gel is cut into 3 mm × 3 mm × 3 mm cubic pebbles and stored in synthetic ammonia wastewater in dark without aeration.

2.2. UIAR description and operation

In order to evaluate the characteristics of nitrite accumulation of the PEG immobilized bacteria, 18 L reactor made of acrylic glass is used which is fed with synthetic ammonia wastewater by variable speed peristaltic pumps. 12% of the effective volume of the reactor is filled with immobilized activated sludge. An inner circulation tube with two open sides is set in the center of the reactor. HRT is varied by adjusting the feed flow rate. Air is supplied through a sintered glass ball at the base of the reactor. The cubic pebbles (density = 1.02 g/cm^3) are lift up through the central tube to the top by aeration and drop to the bottom of the reactor because of gravity. Thus, inner circulation is formed, which ensures the complete mixing and contact of the synthetic wastewater and immobilized bacteria. A mesh (1 mm × 1 mm) at the reactor outlet is used to retain the immobilization particles and outflow of the treated water. Water temperature of the reactor is controlled by temperature controller.

2.3. Synthetic wastewater composition

Synthetic ammonia wastewater used in the system consists of NH_4Cl, Na_2HPO_4, $NaHCO_3$, NaCl, KCl, $CaCl_2$ and $MgSO_4$. Glucose is added as a carbon source. Different concentrations of the synthetic wastewater are fed to the reactor to evaluate the performance of the immobilized bacteria. Their compositions are listed in Table 1.

2.4. Analytical methods

DO and pH are measured daily. Temperature of the reactor is monitored using online probe. Samples taken are filtered with 0.45 μm filters and analyzed for NH_4^+-N, NO_3-N, NO_2-N. A Hach dr-4000/u SPECTROPHOTOMETER was employed for the measurements of NH_4-N (salicylate method at 655 nm), NO_2-N (diazotization method at 507 nm), and NO_3-N (chromotrophic acid method at 410 nm).

Table 1
The composition of the synthetic ammonia wastewater (150 L influent tank, mg/L)

Ammonia concentration	NH_4Cl	Na_2HPO_4	NaCl	KCl	$CaCl_2$	$MgSO_4$	$NaHCO_3$	$C_6H_{12}O_6$
150	573.6	174.1	77.2	36.0	27.1	61.6	1754.8	93.8
250	956.1	290.1	128.7	60.0	45.1	102.7	2924.7	140.6
350	1338	406.0	179.3	84.0	63.0	143.3	4094.7	140.6

3. Results and discussion

3.1. The acclimation of immobilized activated sludge to the synthetic wastewater

Before acclimation, the immobilized activated sludge has been stored in tap water without nutrient in dark for several months. The activity of the immobilized activated sludge is in dormant state.

The immobilized activated sludge volume is 12% of the working volume of the reactor. 40 mg/L ammonia nitrogen was fed continuously into the reactor at 27°C and HRT is fixed at 10 h. Aeration intensity is 1.2×10^2 m^3/m^3 h. Fig. 1 shows the time course of ammonia oxidation rate and pH changes in acclimation period.

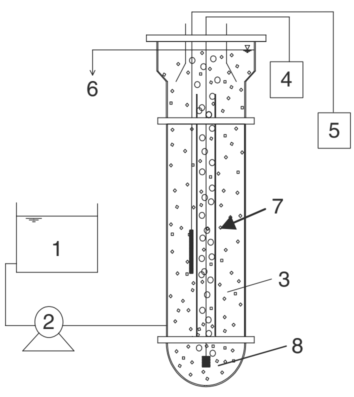

Fig. 1. Diagram of up-flow inner circulation reactor filled with immobilized activated sludge. 1. Influent tank; 2. Peristaltic pump; 3. Immobilized activated sludge; 4. Aeration pump; 5. Heater and temperature controller; 6. Effluent; 7. Inner circulation tube; 8. Sintered glass ball.

The initial ammonia oxidation rate of the immobilized activated sludge is 2.05 mg N/L-pellet h. The immobilized bacteria shows a slow increase in ammonia oxidation rate during initial acclimation stage, then reach its maximum value, 31.5 mg N/L-pellet h, after 13 days operation, its ammonia nitrogen removal efficiency rate is 94.6%. We increase the NH_4^+-N concentration to the level of 80 mg/L, a rapid decrease in nitrification rate of the immobilized bacteria, 16.3 mg N/L-pellet h, is observed. It reaches high level of the nitrification rate of 62 mg N/L-pellet h after 7 days operation, with ammonia nitrogen removal efficiency rate of 93.2%. This phenomenon demonstrates that the immobilized activated sludge begins to acclimate the synthetic wastewater and can rapidly recover its ammonia oxidation rate after an ammonia–nitrogen loading striking. After acclimation, the color of the immobilized activated sludge also changes, from initial dark to light yellow (see Fig. 2).

During acclimation, pH does not change much at initial stage, as nitrification takes place at

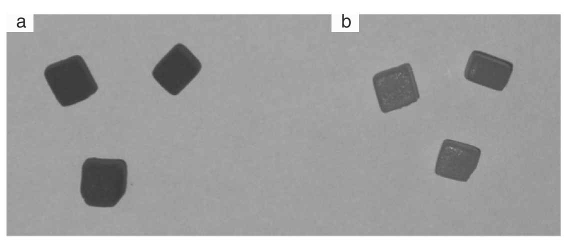

Fig. 2. The appearance of the immobilized activated sludge (a) before acclimation (dark) and (b) after acclimation (light yellow).

limited degree. With the recovery of nitrification activity of the immobilized activated sludge, pH values decrease gradually to 8.1. However, with a sudden increase of the feeding NH_4^+-N concentration, pH values increase firstly, and rapidly decrease. Correspondingly, its nitrification activity is suppressed, then recovered and increased.

3.2. The effect of feeding NH_4^+-N concentration on nitrification activity of the immobilized activated sludge

The effect of temperature on immobilized bacteria are masked when they are immobilized. Free ammonia is known to inhibit the growth and activity of nitrobacter and nitrosomonas at a concentration of 0.1–1.0 g/m^3 and 10–150 mg/m^3, respectively [5]. In this investigation, the performance of the acclimated immobilized activated sludge in treating high-concentration synthetic NH_4^+-N wastewater is studied in batch experiments (other conditions are fixed). The initial NH_4^+-N concentration is set as 100, 200, 300, 400, 500, 600, 700 and 800 mg/L, the nitrification curves of the immobilized activated sludge are illustrated in Fig. 3.

The concentration of free ammonia (FA) for the reactors (see Table 1) are calculated according to the following equation [6]:

$$FA = \frac{17}{14} \times \frac{[NH_4^+\text{-N}] \times 10^{pH}}{K_b / K_w + 10^{pH}} \quad (1)$$

(K_b: the ionization constant of ammonia equilibrium equation; K_w: the ionization constant of water; $[NH_4^+$-N$]$: the concentration of NH_4^+-N, mg/L).

In this study, the ranges of FA that completely inhibit nitrobacter and nitrosomonas are 25.7 and 60 mg/L, respectively. The maximum ammonia nitrogen treatment limit for the immobilized activated sludge is 500 mg/L. High level of nitrite build up is observed when the influent $[NH_4^+$-N$]$ is 100–400 mg/L.

3.3. The influence of COD on ammonia nitrogen removal

Wastewater is always composed of nitrogen compounds and organic substances. Even with pretreatment of COD removal, the effluent COD residue will also influence the nitrification activity of autotrophic nitrifiers. Autotrophic nitrifiers and heterotrophic bacteria are all oxygen-consuming bacteria, the rapid growth of the latter will inhibit respiration of the former.

The COD loading effect on nitrification activity of the immobilized activated sludge is investigated in batch experiments (other conditions are not changed), the result is shown in Figs. 4 and 5.

From Figs. 4 and 5, we can see that in the first 6 h of operation of the reactors, there are no obvious difference in nitrification activities and nitrification rates of the immobilized activated sludge with different COD loading, and less than 50% of nitrite nitrogen is built up. This may result from the sufficient oxygen supply and short operation time: Sufficient oxygen supply ensures degradation of COD and oxidation of ammonia nitrogen; heterotrophic bacteria may not have enough time to grow in short operation period.

We also test the influence of COD loading on the nitrification activity of the immobilized

Table 2
Free ammonia concentration for the reactors with various $[NH_4^+$-N$]$

$[NH_4^+$-N$]$ (mg/L)	100	200	300	400	500	600	700	800
FA (mg/L)	8.55	17.1	25.7	34.2	42.8	51.3	60	68.4

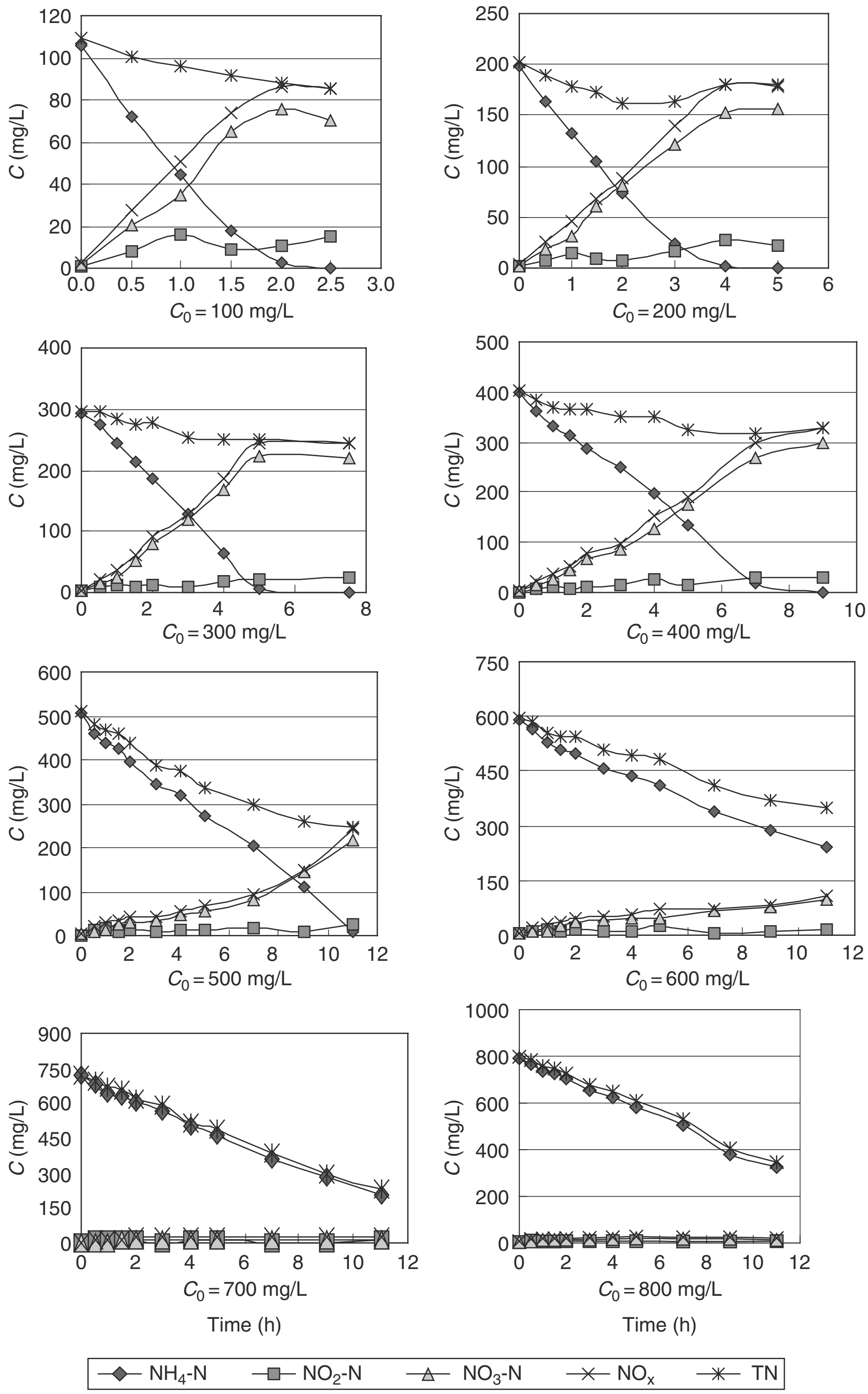

Fig. 3. Nitrification activity of the immobilized activated sludge treating different concentration of NH_4-N wastewater. DO = 5 mg/L.

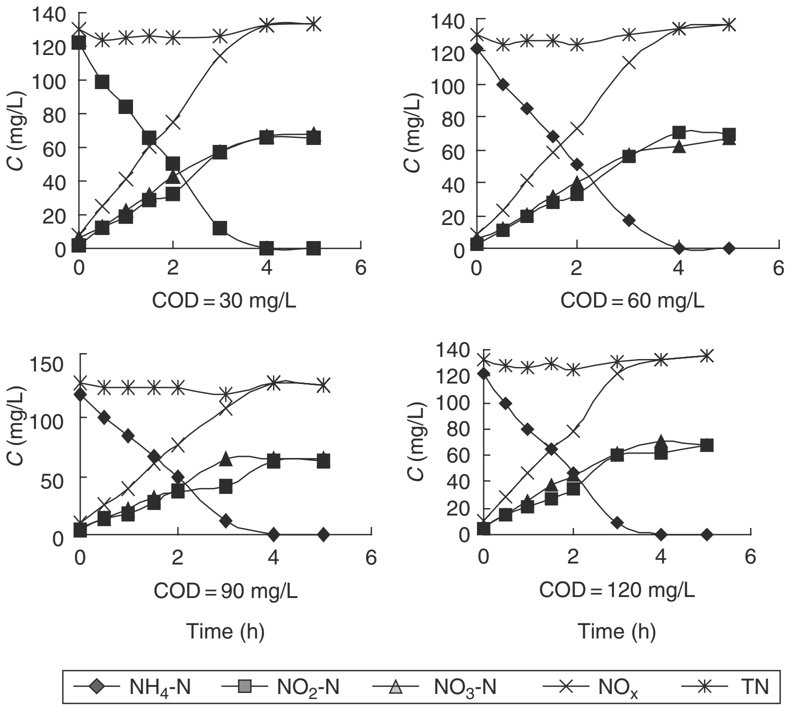

Fig. 4. The COD loading effect on nitrification activity of the immobilized activated sludge.

activated sludge in continuous feeding mode, and the result is presented in Fig. 6.

In the continuous feeding mode, the loading of COD also does not influence the nitrification activities obviously. With increasing of COD loading from 8 to 35 mg/L h, COD removal efficiency correspondingly decreases from 20 to 10%. This demonstrates that the existence of heterotrophic bacteria and COD loading rate increase do not

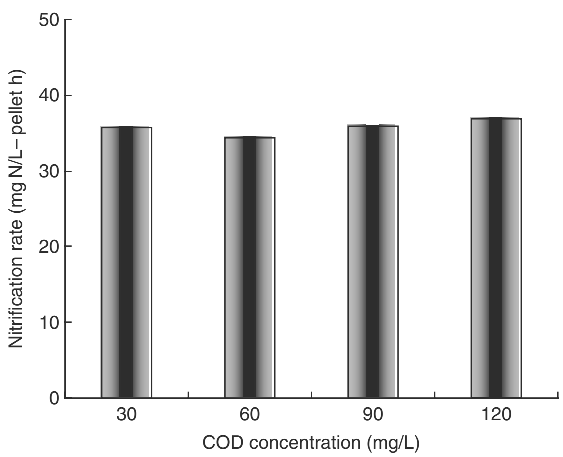

Fig. 5. Nitrification rates of the immobilized activated sludge under different COD loading.

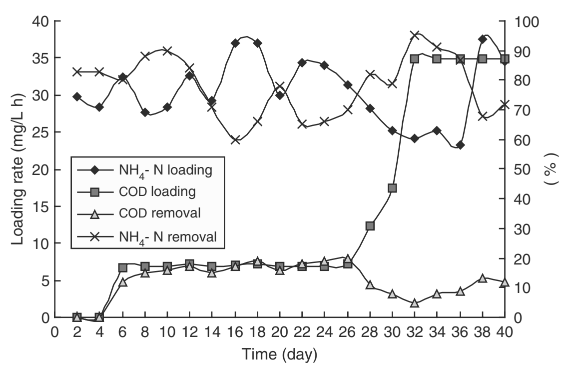

Fig. 6. COD and NH_4^+-N removal efficiency of the immobilized activated sludge.

affect the respiration of autotrophic bacteria. It is well accepted that heterotrophic bacteria consumes much more oxygen than nitrifiers to produce themselves, having fast growing rates. However, in our systems, COD removal efficiency is much slower than ammonia nitrogen. It can be explained by the reason: (1) the immobilized activated sludge has been acclimated with high strength inorganic ammonia nitrogen wastewater and exhibits high nitrification activity, then the majority of pores of the immobilized matrices are filled with nitrifiers. When the acclimated immobilized are used to treat ammonia nitrogen wastewater plus COD, the immobilized matrices have not space for heterotrophic to grow. Even some can grow and reproduce in small pores, its excess (burst out of the matrices surface) would be washed out of the reactor, as no return flow is designed in the system; (2) enough oxygen supply makes it feasible for nitrification and COD oxidation proceed simultaneously.

It should be noted that no denitrification is observed during the study. To eliminate the detrimental effect of dissolved oxygen on denitrification, O_2 in the reactor is lowered to 2–3 mg/L, and the nitrification or denitrification activities of the immobilized activated sludge are measured (see Fig. 7).

With decreasing of DO, NH_4^+-N and COD removal efficiency decrease correspondingly. However, no obvious denitrification is observed. Ammonia nitrogen in the influent is partially oxidized to nitrite and nitrate. In most cases, the immobilized bacteria exhibits denitrification activity treating ammonia nitrogen plus COD wastewater under low DO level. The denitrification mainly results from the formation of anoxic zone in immobilized matrix due to the diffusion limitation of DO to its core. The limitation of DO diffusion to deep layer is defined by the dense layer of immobilized matrix (asymmetrical structure), and denitrification is easy to take place. However, in our system, the immobilized matrix is formed by crosslinking of polymer with MBA evenly dispersed in aqueous solution. Then the obtained immobilized matrix has a homogeneous structure and evenly pores. Obviously, this kind of structure is unfavorable for the formation of anoxic zone in the matrix.

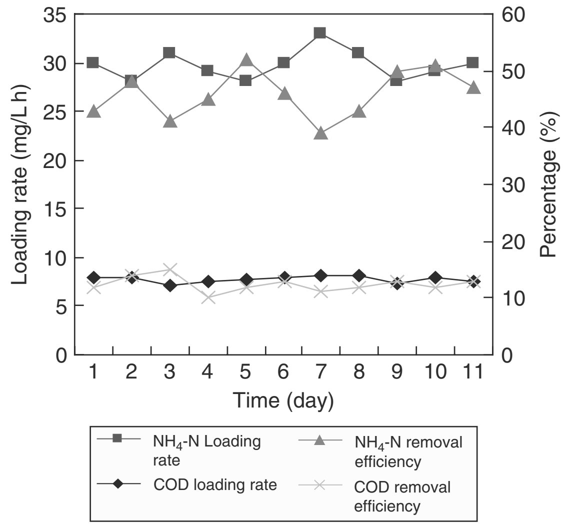

Fig. 7. COD and NH_4^+-N removal efficiency of the immobilized activated sludge at DO = 2 mg/L.

4. Conclusion

PEG immobilized activated sludge can tolerate strong strength of ammonia nitrogen wastewater, and it can oxidize more than 500 mg/L ammonia nitrogen to nitrite or nitrate. The existence of COD (0–35 mg/L h) does not obviously affect the nitrification activity of the immobilized bacteria: high ammonia nitrogen removal efficiency is maintained and partial removal of COD loading. However, denitrification does not take place in the study, as the immobilized matrix has evenly crosslinked structure and pores, unfavorable for the formation of anoxic zone in its core.

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