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Simultaneous methanogenesis and denitrification of aniline wastewater by using anaerobic–aerobic biofilm system with recirculation

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ABSTRACT

Wastewater containing highly concentrated nitrogenous and aromatic compounds, such as aniline, is difficult to degrade and very toxic to microorganisms, especially to nitrifier. In order to remove both carbon and nitrogen from aniline wastewater, recently two biofilm reactors equipped with anaerobic–aerobic cycle and internal recirculation have demonstrated some potential in treating the wastewater. In such system, ammonification, methanogenesis and denitrification reactions occurred simultaneously in one anaerobic reactor, followed by COD removal and nitrification in the aerobic reactor. The effect of recirculation ratio on COD and nitrogen removal using such reactor arrangement was therefore investigated in the present work. The results showed that recirculation had little impact on the overall COD removal or denitrification activity in the anaerobic reactor at any tested ratio, 96–98% of overall COD removal efficiency was achieved with a final effluent COD value below 200 mg/L. But nitrification and TN removal were strongly affected by recirculation. The nitrification rate reached a maximum of 0.48 kg N/(m^3 d) at recirculation ratio of 1 and complete nitrification was achieved at the recirculation ratios over 2. TN removal efficiency increased continuously and a sharp reduction of sludge production in the system was observed with increasing recirculation.

1. Introduction

Aniline is one of the most important industrially produced amines and widely used for the manufacture of polyurethanes, rubber, dyestuffs, pigments and pesticides. It is also used as an intermediate in the production of a wide range of synthetic organic chemicals including rubber additives, pharmaceuticals, drugs, photographic chemicals resins, varnishes, and herbicides [1]. The wide-scale production and use of aniline ensures that it is present in many effluents from the chemical industry. Aniline is one of the most harmful, toxic and least biodegradable organics. Therefore, for the environmental protection and safety of human beings, it is critical to treat the aniline waste prior to its disposal. The biodegradation of aniline at low concentrations or in aquatic environments has been reported by other research groups [2–5]. However, likely due to the reason that aniline compounds with an aromatic ring in the molecule are less biodegradable, few studies have shed light on efficient ways to treat highly concentrated aniline wastewater.

In addition to the removal of carbon, the organic nitrogen component must also be treated. First, the aerobic biodegradation of aniline involves removal of carbonaceous compounds by heterotrophic bacteria followed by ammonium ion release as a byproduct, subsequently, ammonium will be converted to nitrite or nitrate by autotrophic nitrifying bacteria. However, aniline is toxic to aerobic bacteria, especially to nitrifying bacteria. Shabbir et al. [3] found that nitrification can proceed when the aniline concentration drops below 3–4 mg/L. Then, the nitrified compounds require a denitrification step with a reductive substrate (e.g., biochemical oxygen demand [BOD]) as the electron donor. It would be ideal to use raw aniline wastewater as the carbon source for denitrification if toxicity issues to the denitrifying bacteria can be circumvented. However, to remove all the nutrients in the aniline wastewater, a traditional anaerobic/anoxic/oxic (A^2/O) system must be used, in which the appropriate conditions are established in each bioreactor to favor denitrification, methanogenesis, and nitrification [6–9].

Recently, the use of one single anaerobic reactor to carry out both denitrification and methanogenesis has been proposed, with inlet feeds for the inflow of organics and recirculation from an aerobic reactor [10–13]. This method offers several benefits, such as the lack of denitrifying reactor, reduction in treatment costs, removal of toxic compounds, creation of a better environment for

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subsequent nitrification, reduced sludge production and a source of phosphorus from the decomposition of aerobic bacteria. There have been many applications based on this idea, which have used an anoxic/oxic (AO) system to remove both the organic carbon and nitrogen in wastewater [14,15]. Borzacconi et al. [7] used a denitrifying/methanogenic upflow anaerobic sludge blanket (UASB) reactor combined with a nitrifying rotating biological contactor with effluent recycling. Im et al. [6] used a denitrifying/methanogenic biofilm reactor and a sequential activated sludge reactor to successfully remove both organic carbon and nitrogen from sanitary landfill leachate. Bernet et al. [8] found that a combined anaerobic–aerobic sequencing batch reactor (SBR) system, with effluent recycling, effectively removed organic carbon and nitrogen from piggery wastewater.

In this study, a laboratory-scale anaerobic–aerobic biofilm reactor system with direct aerobic effluent recycling was developed to simultaneously remove carbon and nitrogen from highly concentrated and toxic aniline wastewater. In addition, this system uses the portion of chemical oxygen demand (COD) in raw aniline wastewater as carbon source for denitrification. Inside the reactors, a small tube-chip type of suspended carrier was used to immobilize the microbes to achieve high biomass build-up and treatment efficiency. The raw wastewater was first treated anaerobically in order to remove majority of COD and decrease the toxicity. Then, ammonium was released by ammonification, and the anaerobic effluent will be introduced to the aerobic reactor to further remove the remaining COD and perform the nitrification reaction. Finally, the mixed liquid of aerobic effluent containing nitrite or nitrate and suspended sludge will be recirculated to the anaerobic reactor to finish the denitrification and reduce the sludge production. As the operation of recirculation maybe has adverse impact on the anaerobic reactor, more attention is focused on the effect of recirculation ratio (recirculation ratio is defined as the ratio of flux being recirculated from the aerobic reactor to that feeding the anaerobic reactor) on the performance of the system, such as COD removal, ammonification and nitrification rate, denitrification efficiency and sludge reduction.

2. Methods and materials

2.1. Aniline wastewater

The aniline wastewater was obtained from a chemical company in Korea. Its main constituents were 2-methyl-6-ethylaniline, *N*-ethyl diethanolamine, and 2,6-diethylaniline. The characteristics of the aniline wastewater were as follows: COD, 8000–10,000 mg/L; 5-day biological oxygen demand [BOD_5], 3000–4000 mg/L; NH_4^+–N, 20–40 mg/L; TN, 910–1280 mg/L; pH 10.5–11.4, in which more than 96% of nitrogen was present as the organic form. No nitrite or nitrate was detected in the raw wastewater. The pH was adjusted to 8.5–9 using HCl solution when the raw aniline wastewater was fed to anaerobic reactor.

2.2. Reactor system and operation

The reactor system consisted of two biofilm reactors connected in series, an anaerobic reactor followed by aerobic reactor, as shown in Fig. 1. The anaerobic reactor was a cylinderical tube with an inside diameter of 80 mm and a working volume of 2 L, and the aerobic reactor was a rectangular tank with a working volume of 3 L. The bio-carriers were small tube-chips made of a mixture of a polymeric substance and inorganic particles, with the following physical properties: outside diameter, 7 mm; length, 9 mm; wall thickness, 0.4 mm; density, about 0.97–0.98 g/cm^3; and surface area, about 800 m^2/m^3. The volumetric charge of the bio-carrier in the anaerobic and aerobic reactors was 45% and 60%, respectively. A mechanical stirrer with two impellers was used in the anaerobic reactor. The stirring speed was adjusted so that the top layer of the carriers (about 5–10% of the reactor volume) behaved as a self-floating packed bed, whereas the carriers in the remaining bottom part were fluidized. An increase in the stirring speed 4–6 times a day for 4 min per time was sufficient to prevent clogging in the sludge in the top packed bed. The sludge used in the anaerobic reactor was inoculated with 3.5 g SS/Lfrom a packed bed biofilm reactor which has successfully treated amine wastewater [17]; the aerobic sludge was inoculated with 1.5 g ML SS/L of the initial activated sludge from a municipal wastewater treatment plant.

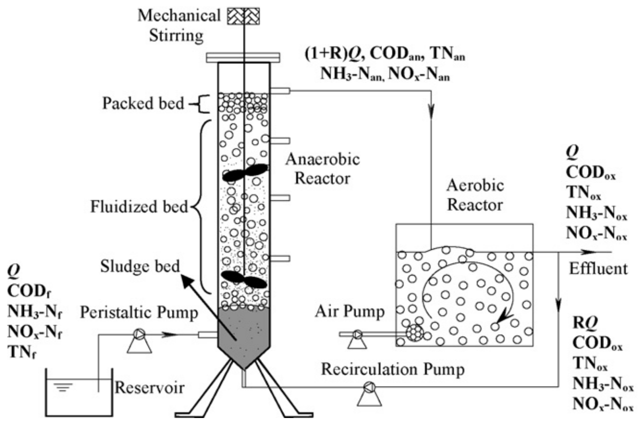

Fig. 1. Flow diagram of anaerobic/aerobic biofilm reactors

In such operation mode, the anaerobic reactor can be actually regarded as a hybrid reactor with sludge bed at the bottom and biofilm reactor at the top, especially the biofilm reactor was divided into two parts with packed bed and fluidized bed as shown in Fig. 1. The aerobic reactor was operated in a completely fluidized mode without sludge return, and the dissolved oxygen was kept over 3 mg/L by introducing sufficient amount of air. The temperature of the anaerobic reactor was maintained at 35 °C using a heating band and the aerobic reactor was maintained at 25 °C. The aniline wastewater was kept in a refrigerator at 4 °C before it was pumped to the bottom of the anaerobic reactor at a constant flow rate. The overflow from the top of the anaerobic reactor entered the aerobic reactor. A certain portion of the effluent from the aerobic reactor was recycled directly to the bottom of the anaerobic reactor, and the remainder was discharged. The pH of anaerobic and aerobic reactor was controlled at 7 and 8 using pH controller.

2.3. Measurement of reaction rate

In the present anaerobic–aerobic reactor system with recirculation, the flux of the feed was fixed at Q = 1 L/day for all experiments, the initial HRTs of anaerobic and aerobic reactor without recirculation were 2 days and 3 days, respectively. Our detailed investigation focused on the influence of the recirculation ratio (recirculation ratio is defined as the ratio of flux being recirculated from the aerobic reactor to that feeding the anaerobic reactor, R) on the performance of the reactors, especially on the simultaneous denitrification and methanogenesis in the anaerobic reactor. To evaluate the degradation performance of the present reaction system, expressions for various reaction rates (kg substrate/(m^3 d) were devised from mass balance in terms of the CODs and substrate concentrations measured at various points.

The removal rates of COD in the anaerobic and aerobic (oxic) reactors were measured using Eqs. (1) and (2), respectively:

$$-r_{an}(\text{anaerobic COD removal rate}) = \frac{(COD_f + RCOD_{ox} - (1+R)COD_{an})Q}{V_{an}} \tag{1}$$

$$-r_{ox}(\text{aerobic COD removal rate}) = \frac{(1+R)(COD_{an} - COD_{ox})Q}{V_{ox}} \tag{2}$$

where R is the recirculation ratio, COD is the COD concentration (kg/m^3), Q is flow rate of the input feed (m^3/d), and V is the reactor volume (m^3). The subscripts f, ox, and an in all equations represent the feed of anaerobic reactor, effluent from the aerobic reactor, and effluent from the anaerobic reactor, respectively.

The anaerobic ammonification rate (AR), which represents the rate of release of ammonia species from the organic compounds to the liquid phase during the anaerobic treatment, was obtained from Eq. (3), and the aerobic nitrification rate (NR) was measured using Eq. (4):

$$r_{AR}(\text{anaerobic ammonification rate, AR}) = \frac{((1+R)NH_3{-}N_{an}{-}NH_3{-}N_f{-}R \times NH_3{-}N_{ox})Q}{V_{an}} \tag{3}$$

$$-r_{NR}(\text{ammonia nitrification rate, NR}) = \frac{(1+R)(NH_3{-}N_{an}{-}NH_3{-}N_{ox})Q}{V_{ox}} \tag{4}$$

where NH_3–N and NO_x–N represent the nitrogen concentration in the ammonia and nitrate species in the liquid phase, respectively.

The rate of COD removal by denitrification in the anaerobic reactor, which was used as the electron donor for the reduction of nitrate, was obtained using Eq. (5). The rest of the COD can be considered to be removed by methanogenesis and can be estimated using Eq. (6).

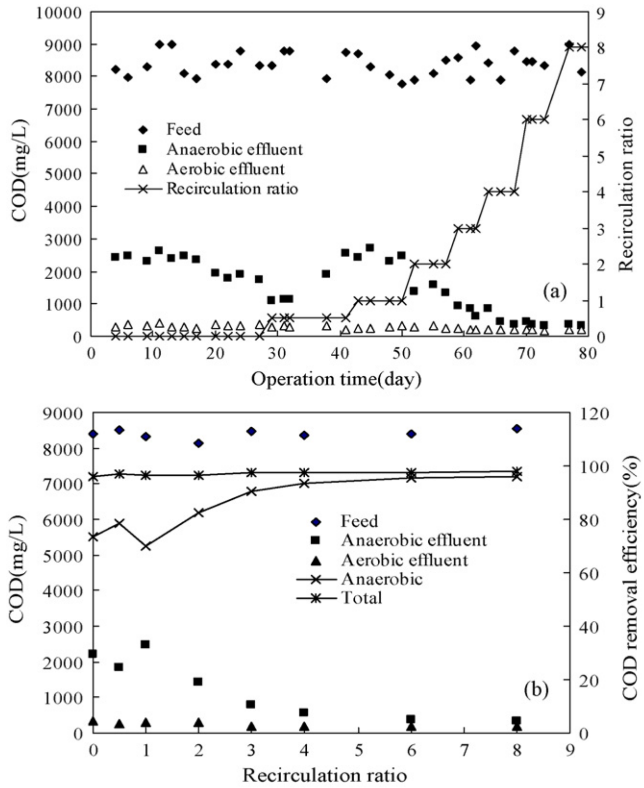

Fig. 2. Biodegradation performance of COD in the reaction system

$$-r_{\mathrm{DN}}(\text{COD removal rate by denitrification}) = \frac{3.5 \times (R \times \mathrm{NO}_x\text{–}\mathrm{N}_{\mathrm{ox}} - (1+R) \times \mathrm{NO}_x\text{–}\mathrm{N}_{\mathrm{an}})Q}{V_{\mathrm{an}}} \tag{5}$$

$$r_{\mathrm{CH}_4}(\text{COD removal rate by methanogenesis}) = -r_{\mathrm{an}} - (-r_{\mathrm{DN}}) \tag{6}$$

where the coefficient of 3.5 represents the equivalent COD for denitrifying 1 g nitrate obtained from the oxidation–reduction reaction stoichiometry and the results of R. Del Pozo's and V. Diez [14].

2.4. Analytical methods

BOD_5, COD and suspended solid/sludge (SS) in the feed, anaerobic effluent and aerobic effluent were measured according to standard methods [16]. The biomass attached on the bio-carriers was first desquamated by ultrasonic vibration for 15 min, and then the mixed liquid was filtered and dried at 105 °Cto measure the dry weight. NO_2–N and NO_3–N were analyzed by using Dionex-120 ion chromatography, NH_4 was measured using the Nesslerization method by reading absorbance at 425 nm, and TN was measured using Shimadzu TN analyzer. All the sample analysis was conducted every other day (or three times per week).

3. Results and discussion

3.1. Performance of COD removal

The results for COD removal in the anaerobic–aerobic system are shown in Fig. 2. With no recirculation, the initial HRTs of the anaerobic and aerobic reactor were 2 days and 3 days, respectively, which corresponded to an organic loading rate of about 4.2 kg COD/(m^3 d) exerted on the anaerobic reactor. Then, the HRTs of the anaerobic and aerobic reactor were decreased as the recirculation ration increased. As shown in Fig. 2(a), from operation day 1 to day 27, during which the recirculation ratio was kept at zero, there was a slow but continuous decrease in the effluent COD of the anaerobic reactor, to 1200 mg/L. When the recirculation ration was 0.5, the effluent COD was low. However, with a subsequent increase of the recirculation ratio to 1.0, the reactor performance began to deteriorate, with an increase of effluent COD to 2400 mg/L. As we shall see in Fig. 4(a), with recirculation ratio at 1, a higher concentration of nitrate is introduced into the anaerobic reactor liquid from the recycled aerobic effluent and a higher concentration of ammonia is released from organic nitrogenous compounds with improved biodegradation. High concentrations of ammonia and nitrate can have inhibitory effects on methanogenic bacteria. Chen et al. [17] reported that free ammonia at about 250–350 mg NH_3–N/L causes complete inhibition of methanogenesis in the treatment of aniline wastewater. Chen and Lin [18] also suggested that methanogenesis is inhibited by the presence of nitrate and nitrite because of the toxic effect of enzyme inhibition and/or changes in redox potential. In addition, Quevedo et al. [19] suggested from batch tests that this kind of inhibition was caused by the presence of intermediate denitrification products (NO_2^- and gaseous nitrogen oxides). With a further increase of the recirculation ratio beyond 1.0, the performance of the anaerobic reactor gradually improved, probably because the anaerobic bacteria were then acclimated to the toxic environment or because the toxic compounds were diluted and decreased to low levels with greater recirculation. Although the effluent COD values for the anaerobic reactor varied across a wide range, from 340 to 2400 mg COD/L, the next aerobic reactor behaved as a polishing reactor to reduce the COD further to a stable and low value between 180 and 330 mg/L, depending on the recirculation ratio. Higher recirculation produced lower values for the final effluent COD.

The average effluent CODs and removal efficiencies were calculated from Fig. 2(a) and are plotted as a function of the recirculation ratio in Fig. 2(b). With an increase in the recirculation ratio from 0 to 8, the effluent COD of the anaerobic reactor decreased from 2220 to 344 mg/L. However, the final COD of the aerobic reactor was less sensitive to the recirculation ratio, and showed a small decrease from 328 to 186 mg/L with increased recirculation. As a result of increased recirculation ratio, the efficiency of COD removal by the anaerobic reactor increased from 73.6% to 96.0%, which showed that the high level of recirculation had little adverse impact on anaerobic reaction, the reason was testified by the oxidation–reduction potential monitoring in the anaerobic reactor with less than −300 mV. But the overall COD removal efficiency of the system showed an increase of only <2%, from 96.1% to 97.8%. Therefore, the combination of anaerobic and aerobic biofilm reactors can effectively treat highly concentrated aniline wastewater. On one hand, the anaerobic reactor can reduce most of COD. On the other hand, the subsequent aerobic reactor behaves as a polishing reactor to ensure stable effluent quality. The anaerobic–aerobic system, with sufficient recirculation of the aerobic effluent to the anaerobic reactor, successfully tolerates the high organic loading impact of highly concentrated feed and reduces the inhibitory effects of toxic compounds on the biomass.

3.2. Effect of recirculation ratio on COD removal rate

As shown in Fig. 2, the COD removal efficiency of both the anaerobic and aerobic reactors increases accompanying increasing recirculation ratio. However, it cannot reflect the real performance of each reactor because the recycled liquid dilutes the COD concentration and changes the HRT of each reactor. Therefore, we measured the COD removal rate for each reactor using the reaction rate expressions in Eqs. (1) and (2); the results are shown in Fig. 3. The COD removal rate of the anaerobic reactor was 3.09 kg COD/(m^3 d) at zero recirculation. After a minimum value of 1.83 kg COD/(m^3 d) was reached at a recirculation ratio of 1, it increased gradually to 3.48 kg COD/(m^3 d) as the recirculation ratio approached 6. These results seem to be possible only when the rate is strongly inhibited by toxic materials. The results in Fig. 4(a) show that the ammonium concentration of the anaerobic reactor reaches the maximum at a recirculation ratio of 1, then gradually decreases

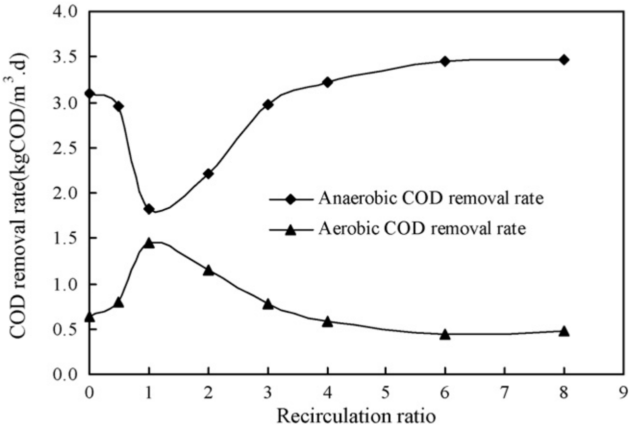

Fig. 3. Effect of recirculation ratio on the COD removal rate

and plateaus at a recirculation ratio of 6, indicating that the ammonium species is the toxic material in anaerobic COD removal. It is also interesting to observe that the anaerobic COD removal rate measured at a recirculation ratio of zero was much higher than that measured at a recirculation ratio of 1, although the effluent COD level was about the same. Recirculation brings the aerobic nitrified effluent back to the feed, which will increase the nitrate concentration in the anaerobic reactor. These results confirm that nitrated species also reduce the anaerobic COD removal rate.

In contrast to the anaerobic reactor, recirculation affects the COD removal rate in the aerobic reactor in the opposite way. The removal rate of the aerobic reactor reached the maximum at the point at which the anaerobic reactor reached the minimum, indicating that the aerobic reactor can complement the conversion of the anaerobic reactor when it suffers from poor performance. Although the anaerobic and aerobic reactors are differently affected by toxins and loading, the total COD removal efficiency is kept almost constant, with only a small increase in the total conversion, from 96.1% to 97.8%, while recirculation ratios increase from 0 to 8.

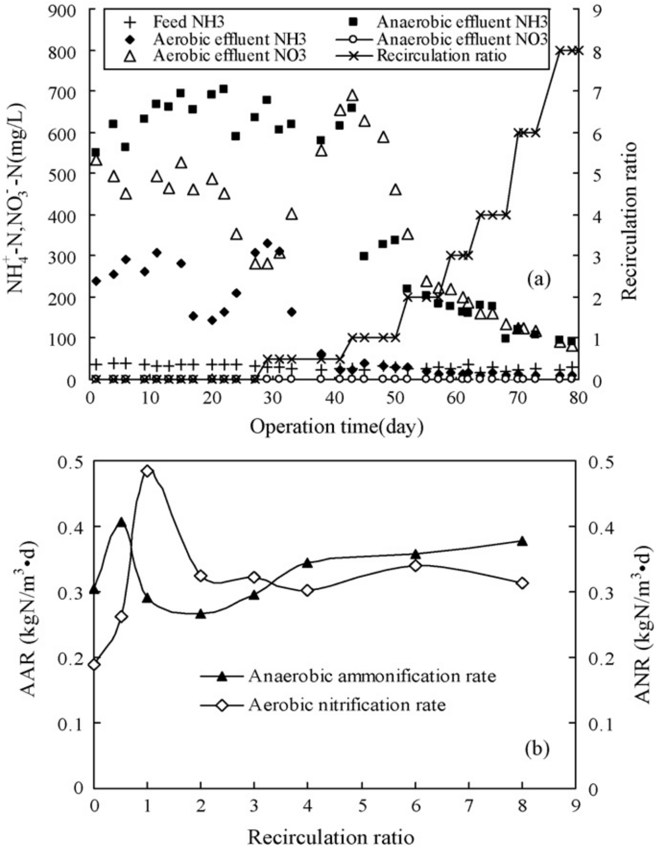

Fig. 4. Bioconversion of N species in the reaction system

3.3. *Ammonification and nitrification performance*

Because over 96% of nitrogen occurs in the organic form, the ammonium concentration in the liquid phase of the wastewater was very low, in the range of 20–40 mg/L. Therefore, large amounts of ammonium species will be released by ammonification during anaerobic decomposition. As shown in Fig. 4(a), the ammonium concentration in the anaerobic effluent increased sharply to 550–700 mg/L at zero recirculation, then gradually decreased as the recirculation ratio increased, as a result of diluted concentration caused by the recycled liquid. For aniline wastewater containing nitrogenous organics, the release of ammonium by anaerobic ammonification is necessary and preferable to sequential aerobic nitrification. The ammonium concentration of the aerobic effluent remained around 240 mg/L without recirculation, but it fast decreased to 31 mg/L at recirculation ratio of 1, and then decreased further to below 10 mg/L at recirculation ratio of 6. The nitrification efficiency of the ammonium ion was only 63% at zero recirculation, but almost complete nitrification was achieved at recirculation ratios greater than 2. The nitrate concentration of the aerobic effluent reached its highest level of over 600 mg/L at a recirculation ratio of 1. Then, it decreased because of the increased denitrification in the preceding anaerobic reactor, indicating that proper recirculation enhances the nitrification efficiency, which is attributable to the reduced inhibition to the nitrifiers by toxic materials (e.g., aniline molecules) as the result of anaerobic detoxification.

Fig. 4(b) shows the effects of the recirculation ratio on the anaerobic ammonification rate and the aerobic nitrification rate. With an increased recirculation ratio, the ammonification rate reached the maximum at a recirculation ratio of 0.5, then reached a minimum at a recirculation ratio of 2.0, after which it was monotonic, but slowly increased up to $R = 8$. The ammonification rate must be linked to the rate of COD removal in the anaerobic reactor because most of the elemental nitrogen exists as organic compounds. The ammonium ion is released from the organic compounds only when they are completely decomposed by anaerobic digestion. The ammonification rate shows more or less the same trend as the COD loading removal rate in Fig. 3. The nitrification rate in the aerobic reactor increased to a maximum of 0.48 kg N/(m^3 d) at a recirculation ratio of 1, after which it decreased and plateaued at a recirculation ratio of 2. These results can be compared with the aerobic effluent ammonium concentrations shown in Fig. 4(a), in which the ammonium concentration monotonically decreases from about 240 mg/L at zero recirculation to 170 mg/L at a recirculation ratio of 0.5 to 31 mg/L at $R = 1$, and finally levels off to less than 10 mg/L at $R = 6$. At recirculation ratios higher than 1, the ammonia concentration in the aerobic effluent was so low that the Monod Eq. (7) can be simplified to a first-order reaction and the nitrification rate is proportional to the effluent ammonia concentration. Thus, the nitrification rate should be proportional to the ammonium substrate concentration. In addition, the acclimation of the nitrifiers was another reason for the high nitrification rate. At circulation ratios of less than 1, the nitrification rate is inversely proportional to the ammonia concentration, which indicates that the nitrification rate is inhibited by high concentrations of ammonia.

$$r = \frac{kS}{K_S + S} \Rightarrow r = \frac{k}{K_S} S \quad (\text{when } S << K_S) \tag{7}$$

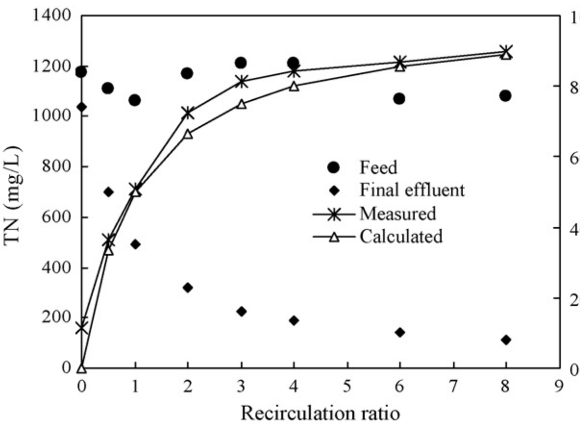

Fig. 5. Effect of recirculation ratio on TN removal

3.4. Effect of recirculation ratio on TN removal

In addition to improving anaerobic COD removal by using recirculation operation, we expected to simultaneously improve denitrification in the same anaerobic reactor. Eq. (8) shows the theoretical relationship between TN removal efficiency and the recirculation ratio, based on mass balance.

$$\text{TN\%} = \frac{\text{TN}_\text{f} - \text{TN}_\text{ox}}{\text{TN}_\text{f}} = \frac{R}{R+1} \qquad (8)$$

As shown in Fig. 4(a), the nitrite concentration of the anaerobic effluent remained zero at any recirculation ratio, which indicates that all the recycled nitrate/nitrite is completely reduced by denitrifying bacteria. The TN removal efficiency of the anaerobic–aerobic system is shown in Fig. 5. With an increasing recirculation ratio, the TN concentration in the aerobic effluent decreased. The TN removal efficiency reached 90% at recirculation ratios higher than 6. When the measured TN removal efficiency is compared with the calculated efficiency using Eq. (8), the measured values are a little higher than the calculated values. This difference is attributable to the additional uptake of $\text{NH}_4{}^+$–N during microbial growth in the anaerobic and aerobic reactors, and/or to the occurrence of simultaneous nitrification and denitrification in the aerobic biofilm reactor because of the anoxic micro-circumstances in the inner layer of the biofilm [11].

3.5. Denitrifying and methanogenic meactions in the anaerobic reactor

As pointed out earlier, both the denitrification of oxidized nitrogen and methanogenic degradation occur simultaneously in the one anaerobic biofilm reactor. Methanogenesis is more sensitive to substrate concentration than denitrification, because the average saturation constant (K_S) for methanogenic bacteria is 40–50 mg COD/L, which is higher than the 4 mg COD/L for the denitrification process. Therefore, there will be competition for the readily biodegradable substrates in the system. Fig. 6 shows the COD removal rate measured for the denitrification and methanogenesis reactions as a function of the recirculation ratio. The rate of COD removal by denitrification continued to increase as a result of increased recirculation ratio. This is reasonable because more and more nitrate species will be reduced with increased recycling from the aerobic effluent, and because greater amounts of volatile fatty acids (VFA), such as acetic and propionic acids, are produced by increased hydrolysis. VFA constitute a readily degradable carbon source for denitrification, causing an increase in the denitrification rate. Quevedo et al. [19] achieved denitrification activities of 1.65 g NO_3–N/(g VSS d) using acetic acid and 0.58 g NO_3–N/(g VSS d) with glucose. The rate of COD removal by methanogenesis showed a similar trend as the rate of total COD removal: Decease first followed by increase with increasing recirculation rate. The competition for substrate between denitrifying and methanogetic bacteria and the inhibitory effects of free ammonia and nitrite are the main causes [20]. By using batch tests, Quevedo et al. [19] observed that methanogenesis starts upon completion of denitrification. Our experimental condition may have been different: sufficient COD and continuous operation allowed methanogenesis and denitrification to occur simultaneously. Chen and Lin [18] observed no competition between these two kinds of biocommunities when methanol was used as the electron donor. The methanogenesis reaction was completely suppressed because the nitrite and nitrate concentrations were higher than 10 and 100 mg N/L, respectively. Very importantly, simultaneous methanogenesis and denitrification processes showed that the production of alkalinity by denitrification can prevent the acidification of the reactor that results from the accumulation of VFA. Since VFA produced by hydrolysis can promote the denitrification rate because their structure makes them readily accessible as substrate. We conclude that denitrifying and methanogenic bacteria that are in competition can be converted to a commensalistic relationship if the reaction system is designed and operated properly.

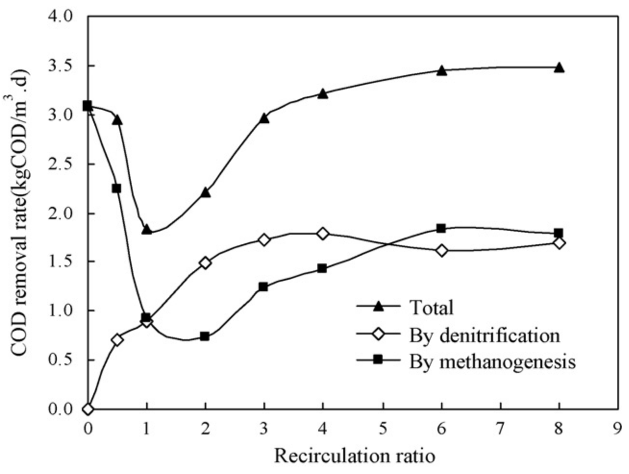

Fig. 6. Contribution of denitrification and methanogenesis to the COD removal

3.6. Sludge production in the anaerobic–aerobic system

It is well known that biofilm processes can reduce sludge production because the food chain is longer compared with that in activated sludge. Furthermore, in an anaerobic–aerobic combination, greater sludge reduction is expected because the recycled liquid is anaerobically digested. Therefore, less substrate will remain for the aerobic bacteria because anaerobic performance is enhanced by recirculation. As shown in Fig. 7, the biomass attached to the bio-carrier in the aerobic reactor initially increases and then remains constant as the recirculation ratio increases. The concentration of suspended sludge in the effluent of the aerobic reactor decreases while recirculation ratio increases. One reason for the decrease in the production of suspended sludge is the shortage of available substrates, attributable to the improvement in the anaerobic reactor caused by recirculation. Another reason is the greater reduction in biomass by anaerobic digestion with increased recirculation of the aerobic effluent biomass to the anaerobic reactor. The total biomass accumulated in the anaerobic reactor also increases with increasing recirculation ratios. This is probably because the increased recirculation enhances the denitrifying reaction, which has a higher sludge yield of about 0.3–0.5 kg SS/kg COD

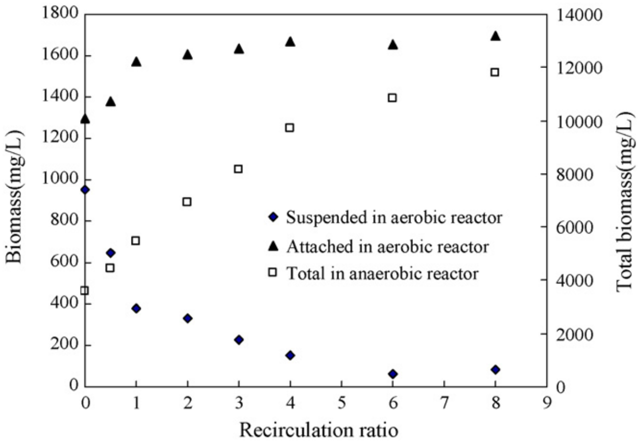

Fig. 7. Effect of recirculation ratio on biomass concentration

than the sludge yield of 0.1 kg SS/kgCOD observed for anaerobic methanogenic bacteria. However, judging from the final effluent biomass discharged from the biofilm system, the suspended biomass in the aerobic reactor decreased dramatically from 950 to 60 mg/L as the recirculation ratio increased from 0 to 6. This indicates that the anaerobic–aerobic biofilm system with recirculation can reduce the total sludge yield, probably because the recycled aerobic biomass decays through endogenous respiration or anaerobic digestion in the anaerobic reactor.

4. Conclusions

This study demonstrates that an integrated anaerobic and aerobic biofilm reactor system, with a high level of aerobic effluent recirculation to the anaerobic reactor, can effectively treat highly concentrated and toxic nitrogenous aniline wastewater, with the simultaneous removal of carbon and nitrogen. In this system, ammonification, methanogenesis, and denitrification reactions occur simultaneously in a single anaerobic biofilm reactor, and the aerobic reactor is used for further COD reduction and autotrophic nitrification. The effect of recirculation ratio on COD and nitrogen removal using such reactor arrangement was investigated. The results showed that recirculation of the aerobic effluent liquid to the anaerobic reactor had little impact on the overall COD removal or the denitrification activity of the anaerobic reactor, 96.1–97.8% of overall COD removal efficiency was achieved, with a final effluent COD value below 200 mg/L. Complete denitrification of the returned nitrite/nitrate was achieved at all recirculation ratios and a TN removal efficiency of more than 90% was achieved at recirculation ratios above 6. Enhancement of the detoxification and ammonification of the aniline molecules in the anaerobic reactor allowed the nitrification rate of the aerobic reactor to reach a maximum of 0.48 kg N/(m^3 d) at a recirculation ratio of 1, and complete nitrification was observed when the recirculation ratio exceeded 2. The anaerobic digestion of the directly recycled aerobic liquid also suggests that the suspended sludge in the final effluent decreased dramatically from 950 mg/L at zero recirculation to 60 mg/L at recirculation ratios above 6. Thus, the anaerobic–aerobic biofilm system with recirculation potentially facilitates sludge reduction.

The present work only proves that the feasibility of simultaneous methanogenesis and denitrification reactions can occur in one single anaerobic reactor by laboratory-scale experiments, but more work should be conducted for better understanding the mechanisms of reactions, ecological relations of microbiology and the sludge reduction; especially, the stability of anaerobic reactor at high level recirculations should be tested for longer term and more kinds of wastewater, pilot-scale experiment also was very necessary to carry out to test the applicability of this process.

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