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Sulfide removal by simultaneous autotrophic and heterotrophic desulfurization–denitrification process

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ABSTRACT

An anaerobic attached-growth bioreactor (AAGBR) of 3.52 L was operated for 510 days to treat sulfide-laden organic wastewater where nitrate and nitrite were introduced as electron acceptors. When the influent sulfide was kept at 200 mg S^{2-}-S/L and organic carbon was increased from 20 to 33.6 mg C/L, and the hydraulic retention time decreased from 41.4 to 2.67 h, the removal rates of sulfide and organic carbon reached 99.9% and 91.8% at the loading rates of 1800 mg S^{2-}-S/(L d) and 302.4 mg C/(L d), respectively. Simultaneously, the introduced electron acceptors of nitrate and nitrite were, respectively, removed by 99.9% and 99.9% at the loading rates of 472.5 mg NO_3^--N/(L d) and 180 mg NO_2^--N/(L d). Inside the AAGBR, both autotrophic and heterotrophic denitrification processes were noted to take place. When the influent organic carbon was increased from 20 to 33.6 mg C/L, the nitrate and nitrite consumed for heterotrophic denitrification accounted for 27.3% and 48.5%, respectively. This simultaneous autotrophic and heterotrophic desulfurization–denitrification process has provided a demonstration of the possibility to eliminate sulfide and organic carbon with the presence of nitrate and nitrite.

1. Introduction

Anaerobic reduction of sulfate or sulfite to sulfide has been adopted as a traditional microbial process to remove sulfate for several years [1–3]. This method may be problematic due to the fact that much sulfide is discharged to natural water bodies and much hydrogen sulfide gas (H_2S) is leaked into the atmosphere. Some types of industrial wastewaters also contain sulfide that has severe toxic effects on ecosystems even at very low levels [4]. Additionally, various toxicological effects of sulfide upon human health have also been described [5]. Many processes have been employed for sulfide-rich wastewater to remove sulfide. For instance, the precipitation process can remove sulfide with the aid of several kinds of heavy metals. Biogenic sulfides form insoluble complexes with heavy metals resulting in their precipitation [6–8]. In some cases, stripping can be also used as an alternative for eliminating H_2S toxicity [9,10]. As sulfide possesses a high oxygen demand [11], some chemical oxidants such as oxygen are also introduced to achieve oxidation of sulfide to sulfur [12]. Although physical-chemical methods for sulfide removal are effective, they are still costly and produce a great amount of chemical sludge. During past ten years, some bacterial species have been addressed able to oxidize sulfide coupled to sulfate reduction by sulfate reducing bacteria (SRB) [13–15]. Nevertheless, these bioprocesses are commonly confined to aerobic oxidation of sulfide.

Some denitrifying bacteria strains have been isolated to anaerobically oxidize inorganic sulfur compounds such as sulfide, sulfur, thiosulfate and sulfite by using nitrate as electron acceptor that is finally reduced to nitrogen gas [16–18]. The process employing these denitrifying bacteria is generally called autotrophic denitrification process and often used for treatment of low nutrition wastewater [19–21] and H_2S removal from biogas [22]. Recently, nitrite has been reported to replace nitrate as electron acceptor to remove sulfide in autotrophic denitrification process [23]. Bio-oxidation of sulfide to sulfur and sulfate in the presence of nitrate and nitrite can possibly occur based on the computation of Gibbs energy according to reactions given in Eqs. (1)–(6).

$$5S^{2-} + 2NO_3^- + 12H^+ \rightarrow 5S + N_2 + 6H_2O$$
$$\Delta G^\theta = -955\ \text{kJ/reaction} \quad (1)$$

$$5S + 6NO_3^- + 2H_2O \rightarrow 5SO_4^{2-} + 3N_2 + 4H^+$$
$$\Delta G^\theta = -2738\ \text{kJ/reaction} \quad (2)$$

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$$5S^{2-} + 8NO_3^- + 8H^+ \rightarrow 5SO_4^{2-} + 4N_2 + 4H_2O$$
$$\Delta G^\theta = -3693\,\text{kJ/reaction} \quad (3)$$

$$3S^{2-} + 2NO_2^- + 8H^+ \rightarrow 3S + N_2 + 4H_2O$$
$$\Delta G^\theta = -917\,\text{kJ/reaction} \quad (4)$$

$$3S + 6NO_2^- \rightarrow 3SO_4^{2-} + 3N_2 \qquad \Delta G^\theta = -2027\,\text{kJ/reaction} \quad (5)$$

$$3S^{2-} + 8NO_2^- + 8H^+ \rightarrow 3SO_4^{2-} + 4N_2 + 4H_2O$$
$$\Delta G^\theta = -2944\,\text{kJ/reaction} \quad (6)$$

To avoid sulfate secondary pollution, sulfide and nitrate can be degraded with the formation of element sulfur and nitrogen gas by autotrophic microorganisms in some processes [24]. However, when the organic carbon exists, the autotrophic microorganisms may be inhibited and organic carbon cannot be removed as well, which limits the widespread application of autotrophic denitrification.

In order to remove reductive sulfur compounds with the existence of organic carbon, the autotrophic denitrification and the heterotrophic denitrification could be combined together under mixotrophic conditions [25,26]. In the simultaneous autotrophic and heterotrophic denitrification process, both sulfide and organic carbon could be oxidized by nitrate without inhibition. The autotrophic denitrification can be also combined with the anaerobic ammonium oxidation for the treatment of baker's yeast effluent while sulfide is converted to sulfate rather than sulfur [27].

In wastewaters containing nitrogenous contaminants [28–30], nitrate and nitrite generated after nitrification can be circulated to sulfide-laden wastewater to promote the oxidation of sulfide. The sulfide-utilizing denitrification can remove sulfide and avoid emission of denitrification byproducts such as nitrous oxide [31–33]. Meanwhile, the nitrate and nitrite can be removed. It should be realized that little attention has been paid to the simultaneous removal of sulfide and organic carbon with the existence of nitrate and nitrite.

The objective of this work was to evaluate the biological removal of sulfide and organic carbon using nitrate and nitrite as electron acceptors under well-defined denitrifying conditions. The AAGBR cultivating autotrophic and heterotrophic microorganisms was under operation. Sulfide could be mostly oxidized to insoluble element sulfur and physically removed from effluents for reuse by sedimentation or slow rate sand filtration, while nitrate and nitrite introduced were converted to nitrogen gas that would not cause secondary pollution. Meanwhile the organic carbon compounds were removed by the simultaneous autotrophic and heterotrophic desulfurization–denitrification process. The ratio of autotrophic denitrification to heterotrophic denitrification in AAGBR was also investigated.

2. Materials and methods

2.1. Structure of AAGBR

The AAGBR of 3.52 L in column shape used was illustrated in Fig. 1. Constant temperature of $30 \pm 0.2\,^\circ$C inside the reactor was realized via temperature sensor connected with temperature controller (MWZK-02, China) and heating threads bonded around the reactor. Two peristaltic pumps were used to feed artificial wastewater from the bottom of the reactor into the system and another

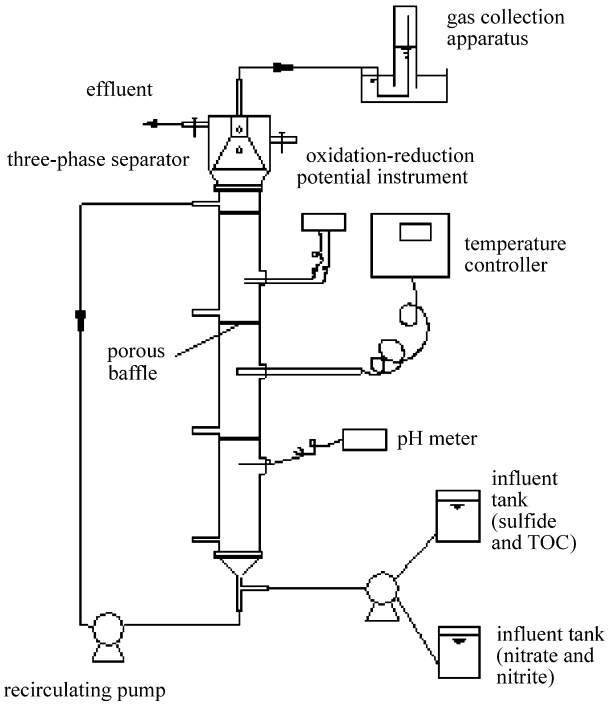

Fig. 1. Schematic diagram of AAGBR.

peristaltic pump was used to circulate water to achieve uniform mixing. On the top of the reactor, a three-phase separator was used to separate the biogas, sludge and effluent. Biogas was collected by water sealing tank. AAGBR was inoculated with 1.5 L of the sludge collected from a secondary sediment tank treating municipal wastewater, giving a biomass concentration of 15.19 MLVSSg/L. In order to increase the biomass inside the reactor, sponge cubes (8 mm × 8 mm × 8 mm) were applied as attached-growth media, which were washed with diluted hydrochloric acid, diluted sodium hydroxide solution and distilled water before use. The cubes and the active sludge attached on were held up in the reacting areas by three porous baffles in order not to block the circulating pipe. The oxidation-reduction potential (ORP) detector and the pH detector were inserted into the reactor to test ORP and pH.

2.2. Substrate

Artificial wastewater containing sodium sulfide as electron donor, glucose as organic carbon source, sodium bicarbonate as inorganic carbon source and potassium dihydrogen phosphate as phosphorus and potassium sources for bacteria growth was used as the feed to the reactor. Another solution containing potassium nitrate and sodium nitrite was fed to the reactor as electron acceptors. Two solutions were both diluted by tap water to supply other microelements nutrition for bacteria and the pH values were adjusted to 7.0 using 1 mol/L hydrochloric acid.

2.3. Analytical methods

To measure nitrate, nitrite and sulfate, liquid samples were filtrated with a 0.45 μm filter and injected into an ion chromatography (DIONEX ICS 3000, USA) equipped with an inhibitory type conductivity detector and an Ionpac column (AG4A AS4A-SC, 4 mm). The flow rate of carrier liquid was 1.0 mL/min. The sulfide was measured by the spectrophotometer (UV-2550, Japan). The wavelength and narrow slit width were maintained at 665 and 2.0 nm, respectively. Nitrogen gas was analyzed by gas

chromatography (Agilent 4890D, USA) equipped with a thermal conductivity detector and a molecular sieve column (5 Å). The temperatures of column, injector and detector were 60, 100 and 100 °C, respectively. Measurements for the concentrations of organic carbon (TOC) and inorganic carbon (IC) were taken by the TOC analyzing instrument (TOC-V_{CPH}, Japan) equipped with platinum catalyst quartz tube. The flow rate of oxygen gas was 130 mL/min and the furnace temperature was 680 °C. The images of microorganisms were taken by scanning electron microscope (HITACHI S-4700, Japan). ORP and pH values were measured by two pH meter models (pHs-3c, China). Sulfur was analyzed by a method described by Wang [34]. All the other items mentioned above were analyzed according to the standard methods [35].

3. Results and discussions

3.1. Startup of AAGBR

To start up the bioreactor, the influent without nitrite was fed semi-continuously for 90 days. The influent concentrations of sulfide, TOC, nitrate and IC were 200 mg S^{2-}-S/L, 20 mg C/L, 52.5 mg NO_3^--N/L and 113.7 mg C/L, respectively. To keep sulfur as the main product [24], the molar ratio of sulfide to nitrate in influent was maintained at 1.67. Initially, 1 L of influent was fed into the bioreactor within 30 min every 12 h. When the removal rates of all the contaminants reached 90%, the influent was added to 2 L every 12 h. The sludge in the suspended area entered the attached-growth area with upflowing streams and attached onto the sponge cubes. Little granular sludge remained in the suspended area. Thus the suspended area was used for diluting the influent to reduce the inlet shock.

When the removal rates of contaminants reached 90% again, the bioreactor was changed to operate under continuously feeding modes. And the effluent appeared turbid gradually with white sulfur particles suspended in solution. The amount of sulfur attached on the biofilm was analyzed at different stages under continuously feeding operation as shown in Fig. 2. The similar proportions of sulfur in the biofilm at different stages indicated that insoluble sulfur particles would not cumulate in the bioreactor. At higher sulfide loading rates, more sulfur was observed to be produced and discharged easily with the effluent. The proportion of abiotic sulfide oxidation was assessed by feeding the same wastewater into another similar bioreactor with no inoculation. The results indicated that about 20% of sulfide was oxidized abiotically while the nitrate, nitrite and TOC were not removed abiotically.

3.2. Degradation of sulfide

The influent concentrations of sulfide, nitrate, nitrite and IC were maintained constant at 200 mg S^{2-}-S/L, 52.5 mg NO_3^--N/L, 20 mg NO_2^--N/L and 113.7 mg C/L, respectively. And influent TOC increased from 20 to 33.6 mg C/L on day 171. The stepwise decrease

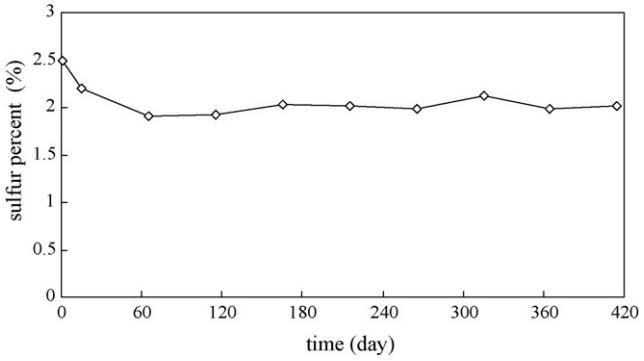

Fig. 2. Proportion of sulfur in the biofilm at different stages.

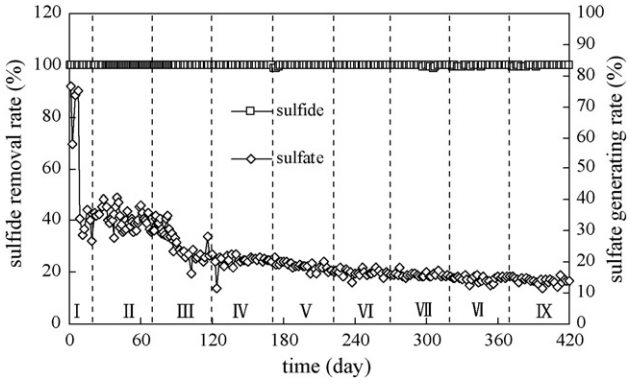

Fig. 3. Removal rate of sulfide and generating rate of sulfate as a function of time.

of hydraulic retention time (HRT) was performed to increase the loading rate of influent. The variation of HRT and substrates loading rates were shown in Table 1.

Fig. 3 revealed the degradation of sulfide and generation of sulfate in the bioreactor. The sulfide removal rate was found close to 100% for different HRTs. In view of 20% of sulfide being converted to sulfur under abiotic conditions, 160 mg S^{2-}-S/L (200 mg S^{2-}-S/L × 80% = 160 mg S^{2-}-S/L) of sulfide was used as electron donor for denitrification. The stoichiometry of Eqs. (1) and (4) indicated that 160 mg S^{2-}-S/L of sulfide could be converted to sulfur by 35 mg N/L of nitrate and nitrite (160 mg/L × 14 g/mol/(2 × 32 g/mol) = 35 mg N/L). And 140 mg N/L of nitrate and nitrite (160 mg/L × 2 × 14 g/mol/32 g/mol = 140 mg N/L) were needed for 160 mg S^{2-}-S/L of sulfide conversion to sulfate according to Eqs. (3) and (6). For the nitrate and nitrite average removal rates of 99.62% and 96.53% during various operating stages, 71.6 mg N/L (52.5 mg NO_3^--N/L × 99.62% + 20 mg NO_2^--N/L × 96.53% = 71.6 mg N/L) of nitrogen compounds accounted for denitrification. Considering that some portion of nitrogen compounds were also needed for heterotrophic denitrification, 71.6 mg N/L was closer to the

Table 1
Variation of substrates loading rates and HRT in AAGBR

Stage	Day	HRT (h)	S^{2-} (mg S^{2-}-S/(L d))	NO_3^- (mg NO_3^--N/(L d))	NO_2^- (mg NO_2^--N/(L d))	TOC (mg C/(L d))
I	1–20	41.4	115.9	30.4	11.6	11.6
II	21–70	25.1	190.9	50.0	19.1	19.1
III	71–120	16	300	78.7	30	30
IV	121–170	9.5	504.5	132.4	50.5	50.5
V	171–220	6.8	709.1	186.1	70.9	119.1
VI	221–270	5.3	900	235.7	90	151.2
VII	271–320	4.35	1104.5	289.9	110.5	185.6
VIII	321–370	3.7	1295.5	340.1	129.5	217.6
IX	371–420	2.67	1800	472.5	180	302.4

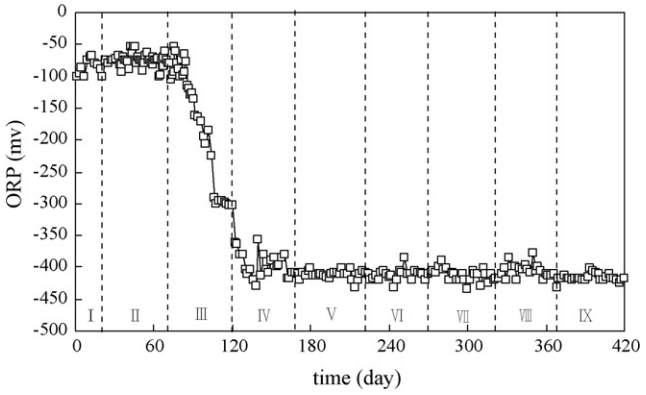

Fig. 4. ORP in AAGBR as a function of time.

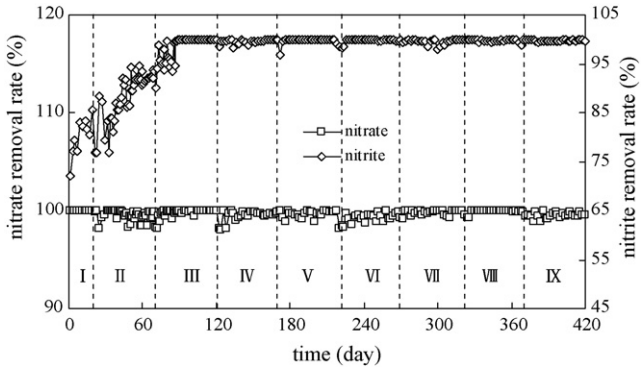

Fig. 5. Removal rates of nitrate and nitrite as a function of time.

theoretical value for oxidization of sulfide to sulfur. The generating rate of sulfate was defined in Eq. (7) and was demonstrated in Fig. 3. At the semi-continuously operating phase (30 min for water exchanging), the sulfur generated could not be discharged from the bioreactor during a short time and this could lead to the further oxidation of sulfur to sulfate. Hence, the sulfate concentration was relatively high during initial continuously operating phase and declined gradually with HRT decreasing. On the other hand, the sulfur could be rapidly discharged with effluent when the system was operated at high flow rate. Therefore shorter HRT should be more suitable for complete removal of sulfide from wastewater. The sulfate generating rate could reach as low as 11.61% when the volumetric loading rate of sulfide reached 1800 mg S^{2-}-S/(L d) at HRT of 2.67 h. 88.39% of influent sulfide converted to element sulfur indicated that the oxidization of sulfide to elemental sulfur predominated in the bioreactor. The element sulfur in effluent could be recovered by sedimentation [36] or slow rate sand filtration-sand scraping-extraction-distillation process [37]. Thus the sulfide removed from the wastewater would not bring secondary pollution to the environment.

$$\text{Generating rate of sulfate} = \frac{\text{sulfate} \times 100\%}{(\text{influent sulfide} - \text{effluent sulfide})} \quad (7)$$

The main component of biogas was found to be nitrogen gas with elementary H_2S and nitrous oxide (N_2O). The variation of ORP was strongly affected by the concentrations of reductive sulfur compounds in the bioreactor. The sulfur generated was difficult to be discharged and easily oxidized to sulfate at high HRT. Therefore, as illustrated in Fig. 4, the ORP in the bioreactor was high at −100 mV for HRT of 41.4 h and decreased to −426 mV for HRT of 2.67 h.

3.3. Degradation of nitrate and nitrite

Fig. 5 illustrated the removal rates of nitrate and nitrite. The nitrite removal rate appeared to be relatively low at HRT ranged from 41.4 to 25.1 h due to the inhibition of nitrite on microorganisms. However, as the microorganisms adapted the environment, the nitrite removal rate began to increase. As shown in Eqs. (1), (3), (4) and (6), 1 mol of nitrate used (5/8–5/2) mol of sulfide while 1 mol of nitrite used (3/8–3/2) mol of sulfide. As shown in the stoichiometry of Eqs. (8) and (9) [38], 1 mol of nitrate consumed 0.21 mol of glucose while 1 mol of nitrite consumed 0.125 mol of glucose. The nitrate required more sulfide and glucose than nitrite. Accordingly, the removal rate of nitrite was as high as that of nitrate even though the concentration of nitrite was lower. The removal rates of nitrate and nitrite were both 99.9% at loading rates of 472.5 mg NO_3^--N/(L d) and 180 mg NO_2^--N/(L d), respectively.

$$NO_3^- + 0.21C_6H_{12}O_6 \rightarrow 0.5N_2 + 0.75H_2O + HCO_3^- + 0.25CO_2$$
$$\Delta G^\theta = -509\,\text{kJ/reaction} \quad (8)$$

$$NO_2^- + 0.125C_6H_{12}O_6 \rightarrow 0.5N_2 + 0.5H_2O + 0.5HCO_3^- + 0.25CO_3^{2-}$$
$$\Delta G^\theta = -384\,\text{kJ/reaction} \quad (9)$$

3.4. Degradation of TOC

The removal rate of TOC and variation of pH in the bioreactor were revealed in Fig. 6. The TOC removal rate decreased sharply at each start of HRT changing for the influent shock load and increased gradually to a steady value when the microorganisms in AAGBR adapted to the environment at the end of each stage. Under mixotrophic conditions, the influent shock load had adversely impact on TOC degradation. But such impact became slight with the decrease of HRT. The TOC removal rates were maintained at 85% and 90% at steady-state conditions of stages I–IV and V–IX, respectively.

The organic carbon compounds disappeared as the amounts of sulfide, nitrite and nitrate decreased in the bioreactor. This simultaneous respiratory process could be explained in terms of the microbial diversity as shown in Fig. 7, where it could be possible to find communities of microorganisms carrying out the biological oxidation of glucose and sulfide using nitrate and nitrite as electron acceptors. The autotrophic denitrification took place together with heterotrophic denitrification in AAGBR. And the proportion of heterotrophic denitrification accomplished in the bioreactor

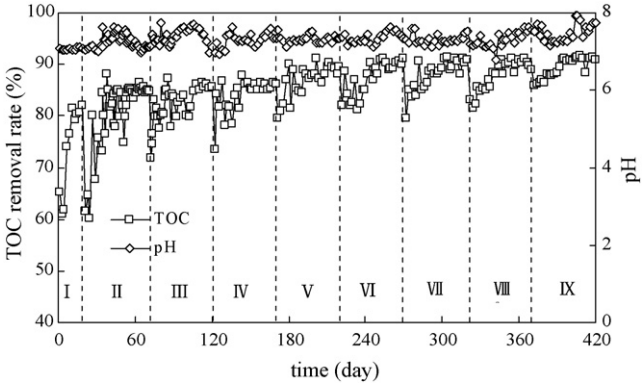

Fig. 6. pH value and removal rate of TOC as a function of time.

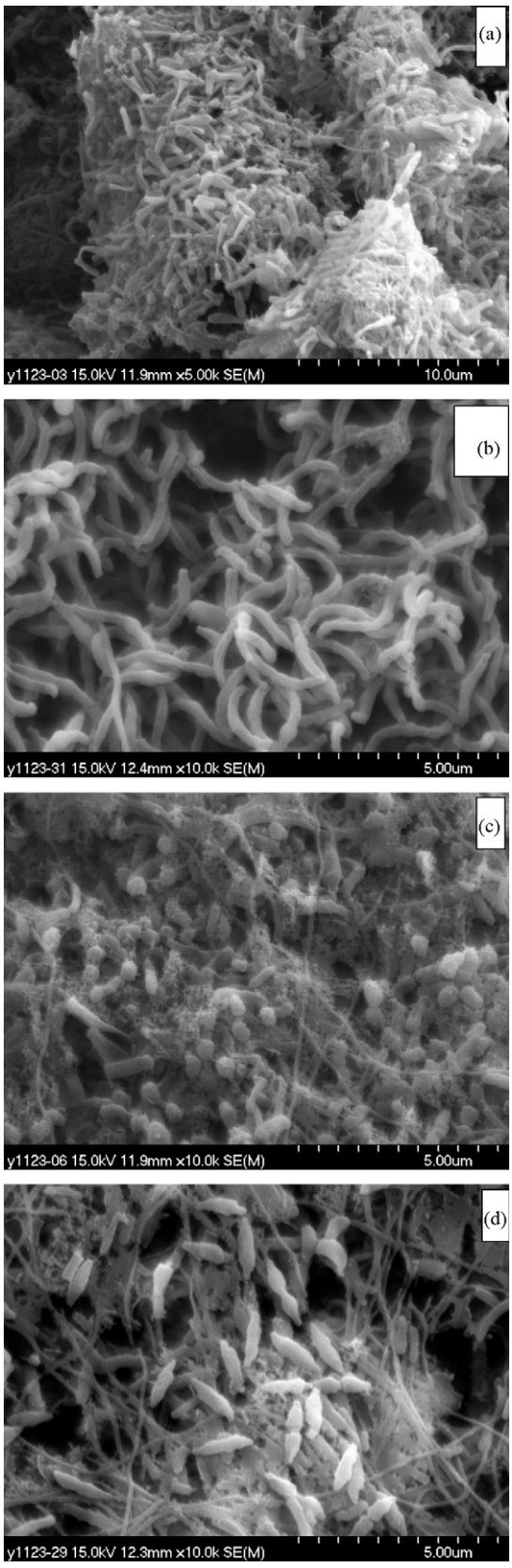

Fig. 7. Scanning electron microscopic images of microorganisms attached on media.

could be indicated by the consumption of nitrate and nitrite. TOC concentration was kept at 20 mg C/L during the stages I–IV and was increased to 33.6 mg C/L during the stages V–IX. In view of TOC removal rate of 85% at the stages I–IV, the amount of nitrate and nitrite consumed for heterotrophic denitrification was 19.73 mg N/L (20 mg/L × 85% × 2 × 14 g/mol/(0.335 × 6 × 12 g/mol) = 19.73 mg N/L) according to the stoichiometric reactions shown in Eqs. (8) and (9). The average removal rates of nitrate and nitrite at the stages I–IV were 99.7% and 99.8%, respectively and the total removed nitrogen (NO_3^-, NO_2^-) reached 72.3 mg N/L (52.5 mg NO_3^--N/L × 99.7% + 20 mg NO_2^--N/L × 99.8% = 72.3 mg N/L). Then the proportion of nitrate and nitrite consumed for heterotrophic denitrification was only 27.3% (19.73 mg N/L × 100%/72.3 mg N/L = 27.3%). The average removal rates of 99.8% and 99.9% for nitrate and nitrite were obtained with TOC removal rate increasing to 90% at the stages V–IX. Thus the amount of removed nitrogen used for heterotrophic denitrification was about 35.1 mgN/L (33.6 mg/L × 90% × 2 × 14 g/mol/0.335 × 6 × 12 g/mol = 35.1 mg N/L). Considering 72.38 mg N/L (52.5 mg NO_3^--N/L × 99.8% + 20 mg NO_2^--N/L × 99.9% = 72.38 mg N/L) of the total removed nitrogen, the proportion of nitrate and nitrite consumed for heterotrophic denitrification was 48.5% (35.1 mg N/L × 100%/72.38 mg N/L = 48.5%), which was higher than that at influent TOC of 20 mg C/L. Thus higher TOC was more advantageous for enhancing the proportion of heterotrophic denitrification in the desulfurization–denitrification process under mixotrophic conditions. As shown in Fig. 6, the effluent pH remained at about 7.5 for proton consumption during sulfur formation according to Eqs. (1) and (4).

The simultaneous autotrophic and heterotrophic desulfurization–denitrification process has been previously investigated, but these studies mainly focused on the conversion of reductive sulfur compounds to sulfate other than sulfur [39,40]. In addition, the sulfide removal using nitrite as electron acceptor was studied in the absence of organic carbon [23]. The AAGBR in this paper actualized the simultaneous removal of sulfide and TOC using nitrate and nitrite as electron acceptors, which opens a completely new approach to effective treatment of wastewater containing sulfide and organic carbon.

4. Conclusions

Based on the study of sulfide removal by the simultaneous autotrophic and heterotrophic desulfurization–denitrification process, main conclusions could be drawn as follows.

(1) Sulfide was removed up to 100% in the AAGBR when influent sulfide loading rate ranged from 115.9 to 1800 mg S^{2-}-S/(L d). At HRT of 2.67 h, 88.39% of influent sulfide was converted to element sulfur.
(2) Although TOC loading rate increased from 11.6 mg C/(L d) to 302.4 mg C/(L d) (HRT decreased from 41.4 to 2.67 h), a constant removal rate of 85%–92% could be obtained. The effect of influent shock load on TOC removal decreased with HRT decreasing. The proportion of nitrate and nitrite consumed for heterotrophic denitrification increased from 27.3% to 48.5%, when the influent TOC concentration was increased from 20 to 33.6 mg C/L. The higher influent TOC was more advantageous for heterotrophic denitrification proportion enhancement.
(3) The influent shock load had slight effect on the removal rates of nitrate and nitrite. The removal rates of nitrate and nitrite could both reach 99.9% when the loading rates increased from 30.4 to 472.5 mg NO_3^--N/(L·d) for nitrate and 11.6 to180 mg NO_2^--N/(L·d) for nitrite.

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