Biological sulfate removal from acrylic fiber manufacturing wastewater using a two-stage UASB reactor

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Received 11 January 2011; revised 11 March 2011; accepted 18 March 2011

Abstract

A two-stage UASB reactor was employed to remove sulfate from acrylic fiber manufacturing wastewater. Mesophilic operation (35±0.5°C) was performed with hydraulic retention time (HRT) varied between 28 and 40 hr. Mixed liquor suspended solids (MLSS) in the reactor was maintained about 8000 mg/L. The results indicated that sulfate removal was enhanced with increasing the ratio of COD/SO$_4^{2-}$. At low COD/SO$_4^{2-}$, the growth of the sulfate-reducing bacteria (SRB) was carbon-limited. The optimal sulfate removal efficiencies were 75% when the HRT was no less than 38 hr. Sulfidogenesis mainly happened in the sulfate-reducing stage, while methanogenesis in the methane-producing stage. Microbes in sulfate-reducing stage performed granulation better than that in methaneproducing stage. Higher extracellular polymeric substances (EPS) content in sulfate-reducing stage helped to adhere and connect the flocculent sludge particles together. SRB accounted for about 31% both in sulfate-reducing stage and methane-producing stage. Higher extracellular polymeric substances (EPS) content in sulfate-reducing stage helped to adhere and connect the flocculent sludge particles together. SRB and MPA were predominant in sulfate-reducing stage and methane-producing stage corresponding to the COD/SO$_4^{2-}$ ratio of 4.7. SRB and MPA were predominant in sulfate-reducing stage and methane-producing stage respectively.

Key words: a two-stage UASB reactor; sulfidogenesis; granule; fluorescence in situ hybridization (FISH)

DOI: 10.1016/S1001-0742(11)60772-9

Introduction

Many industries generate wastewater containing high sulfate concentrations. The damage caused by sulfate emissions is not direct, since sulfate is a non-toxic compound. However, high sulfate concentrations can unbalance the natural sulfur cycle (Lens et al., 1998). Wastewater containing sulfate is normally treated with physicochemical and biological methods. However, even though physicochemical methods are effective, the underlying limitations such as separation and appropriate disposal of the solid phase, relatively high cost and energy consumption limit their usage (Silva et al., 2002). Biologically, sulfate bearing wastewater is generally treated by anaerobic processes (Sarti et al., 2010; Wei et al., 2007; Sinbuathong et al., 2007). In the anaerobic digestion of industrial sulfate-rich wastewater, the sulfate-reducing bacteria (SRB) present a unique microbial group responsible for the noted sulfate reduction. Sulfate is the terminal electron acceptor and is reduced to sulfide, with reducing equivalents derived from the degradation of many organic compounds (Sinbuathong et al., 2007). The SRB can suppress methane-producing archaea (MPA) through competition for the same substrates such as hydrogen and acetate, and consequently result in a primary inhibition to MPA (Nielsen, 1987). Moreover, the SRB can convert sulfate into sulfide which can poison MPA and decrease methane production (Maree and Strydom, 1985). The chemical oxygen demand (COD)/SO$_4^{2-}$ ratio in influent significantly affected the metabolic pathways of SRB (Parkin et al., 1991), and early study indicated that the electron-flow to SRB decreases with increasing COD/SO$_4^{2-}$ ratio (Wang et al., 2008).

Acrylic fiber is one of the major synthetic fibers which are commonly used in the mass production of clothing. The chemical synthesis of acrylic fiber is carried out by polymerization of the acrylonitrile (AN) monomers. The quantity of acrylic fiber manufacturing wastewater is inclined to increase with the increment of acrylic fiber used, and the components of wastewater discharged are complicated and variable. The sulfate concentration ranges from 1380 to 2205 mg/L (Cheng et al., 2004). The biodegradability of the acrylic fiber manufacturing wastewater was very low; the ratio of BOD$_5$/COD was 0.1–0.2, and there were some biorefractory organic pollutants in the wastewater (Zhang et al., 2003). For wastewater treatment, most acrylic fiber manufacturing companies had adopted a conventional biological treatment system (Cheng et al., 2004) or followed by physicochemical methods of neutralization, coagulation and sedimentation.
(Na et al., 2005). However, high sulfate concentration and low BOD₅/COD value made its treatment difficult. Among different types of high-rate anaerobic reactors, the upflow anaerobic sludge blanket (UASB) reactor comprises a popular design with successful applications in different kinds of wastewater (Diamantis and Alexandros, 2007). This is mainly due to its simple design; easy construction and maintenance; low operating cost; and ability to withstand fluctuations in pH, temperature, as well as influent substrate concentration (Cronin and Lo, 1998; Álvarez et al., 2006; Tiwari et al., 2006). The development of the molecular biology tools has contributed to the detection, quantification, and identification of the microbial communities involved in the wastewater treatment. Of all the molecular techniques considered, fluorescent in situ hybridization (FISH) technique has been widely utilized to clarify the microbial community structure and dynamics owing to its visual, qualitative, and semi-quantitative characteristics (Zhao et al., 2007). However, studies on the molecular identification of the microbial communities in anaerobic treatment processes are quite limited (Nadas et al., 2010).

Two-stage anaerobic digestion process (Wei et al., 2007) can separate SRB and MPA in different reactors, and restrain the inhibition of methanogenesis caused by sulfide toxicity (Sae-Eum, 2007). The first stage is for sulfate reduction and the second for methanogenesis. In this work, a two-stage UASB reactor was employed to remove sulfate from acrylic fiber manufacturing wastewater and the FISH technique was applied to explore the microbial community. The objective of the work was to test the performance of sulfate removal and granule formation in the two-stage UASB reactor treating acrylic fiber manufacturing wastewater, and to evaluate the coexistence of SRB and MPA in the reactor by FISH.

1 Materials and methods

1.1 Wastewater characteristics

The acrylic fiber manufacturing wastewater was collected from a synthetic-fiber factory located at the city of Ningbo, China. The wastewater quality was quite complicated because it consisted of acrylonitrile monomer, vinyl acetate monomer, oligomers, DMAc (dimethyl acetamide), EDTA (ethylene diamine tetraacetic acid) and sulfate as Table 1 shown. The molecular formulae of acrylonitrile monomer and vinyl acetate monomer are shown in Fig. 1. The COD/SO₄²⁻ of raw wastewater was around 2.1. To test the COD/SO₄²⁻ effect on the performance of the reactor, we changed the COD/SO₄²⁻ via adding Na₂SO₄ or glucose. Extra 7.039, 1.998 and 0.685 g/L Na₂SO₄ was added to achieve the COD/SO₄²⁻ of 0.5, 1.1 and 1.6, respectively. Besides, extra 1.214, 2.826, 4.037 and 5.245 g/L glucose was added to achieve the COD/SO₄²⁻ of 2.7, 3.5, 4.1 and 4.7, respectively. To maintain the population balance of biological system, extra nutrient and mineral elements were added to the wastewater as follows: CaCl₂·2H₂O (0.08 mg/L), MgCl₂·6H₂O (0.08 mg/L), FeCl₂·4H₂O (0.05 mg/L), MnCl₂·4H₂O (0.15 mg/L), ZnCl₂ (0.05 mg/L), CuCl₂ (0.05 mg/L), CoCl₂·6H₂O (0.05 mg/L), NiCl₂·6H₂O (0.05 mg/L).

1.2 Experimental setup and startup

Figure 2 shows a flow chart of two-stage UASB reactor used in this study. The first stage was mainly for sulfate reduction while the second for methane production. Continuous operation was carried out during the whole experiment. The volume of sulfate-reducing stage and methane-producing stage were 11 and 30 L respectively. Temperature control was accomplished by water bath with water recirculation through the reactor’s double jacket. The study was conducted at mesophilic condition and at (35±0.5)°C. The seed sludge was inoculated from a full-scale UASB reactor treating brewing wastewater. NaOH was added to make influent pH value at 6.5. The mixed liquor suspended solids (MLSS) concentration in the two-stage UASB reactor was maintained at 8000 mg/L by extracting excess sludge.

1.3 Sample collection and preparation

Samples were withdrawn from the liquid media both at the beginning and the end of each treatment period. They were centrifuged at 6000 r/min for 30 min to remove microorganisms from the liquid medium. Clear supernatants were analyzed for COD, sulfate contents according to standard methods (APHA, 1999). Samples were analyzed in triplicate and average values were reported. ORP and pH measurements were done using the relevant probes and analyzers. Biomass concentrations were determined by filtering the washed salt-free samples through 0.45 μm membrane filter and drying in an oven at 105°C to constant weight.

The cooling extraction method, which is described as follows, was applied for the extraction of the extracellular polymeric substances (EPS) from the sludge. For the EPS analysis, 2 mL sludge were centrifuged, removed of supernatant, added with 10 mL of 0.85% NaCl solution and 60 mL formalin. The EPS in this mixed liquor was extracted with ultrasonication for 300 sec while being cooled in ice water. After being centrifuged at 12,000 r/min for 30 min, the supernatant was analyzed for polysaccharide and protein.

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Table 1 Characteristics of acrylic fiber manufacturing wastewater

<table>
<thead>
<tr>
<th>Item</th>
<th>Range</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylonitrile (mg/L)</td>
<td>2.99—3.51</td>
<td>3.33</td>
</tr>
<tr>
<td>Vinyl acetate (mg/L)</td>
<td>201.8—218.5</td>
<td>203.8</td>
</tr>
<tr>
<td>Oligomers (mg/L)</td>
<td>0.028—0.038</td>
<td>0.033</td>
</tr>
<tr>
<td>DMAc (mg/L)</td>
<td>85—115</td>
<td>100</td>
</tr>
<tr>
<td>pH</td>
<td>3.0—3.8</td>
<td>3.5</td>
</tr>
<tr>
<td>COD (mg O₂/L)</td>
<td>4378—4611</td>
<td>4528</td>
</tr>
<tr>
<td>NH₄⁺-N (mg N/L)</td>
<td>71—88</td>
<td>85</td>
</tr>
<tr>
<td>SO₄²⁻ (mg S/L)</td>
<td>2061—2262</td>
<td>2158</td>
</tr>
<tr>
<td>PO₄³⁻ (mg P/L)</td>
<td>0.015—0.021</td>
<td>0.018</td>
</tr>
</tbody>
</table>

5.245 g/L glucose was added to achieve the COD/SO₄²⁻ of 2.7, 3.5, 4.1 and 4.7, respectively. To maintain the population balance of biological system, extra nutrient and mineral elements were added to the wastewater as follows: CaCl₂·2H₂O (0.08 mg/L), MgCl₂·6H₂O (0.08 mg/L), FeCl₂·4H₂O (0.05 mg/L), MnCl₂·4H₂O (0.15 mg/L), ZnCl₂ (0.05 mg/L), CuCl₂ (0.05 mg/L), CoCl₂·6H₂O (0.05 mg/L), NiCl₂·6H₂O (0.05 mg/L).

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Fig. 1 Molecular formulae of acrylonitrile unit and vinyl acetate unit.
protein, which were regarded as the main parts of EPS materials. Polysaccharide was determined by a sulphuric acid-anthrone method and protein was analyzed according to the Lowry Folin method (Lowry et al., 1951).

1.4 FISH
The samples were fixed with freshly prepared 3.7% paraformaldehyde solution in PBS for 3 hr at 4°C. After centrifugation, the samples were washed twice with PBS and stored at −20°C in a storage buffer consisting of a 1:1 (V/V) mixture of PBS and 100% ethanol. Hybridization was performed according to the standard protocol described by Amann et al. (1990). The oligonucleotide probes used in this study are indicated in Table 2. Probes were labeled with fluorescein isothiocyanate (FITC). For each sample, total microscopic counts were performed by fixed samples stained with 4′,6-diamino-2-phenylindole (DAPI; Sigma, St. Louis, USA) at a final concentration of 0.1 mg/L for 10 min in the dark at 4°C. Cells stained with DAPI were defined as total cell counts. Dual staining with DAPI and fluorescently labeled rRNA probes allowed estimation of the proportions of bacteria and different bacterial groups to the total counts. A minimum of 1000 cells in at least 10 randomly chosen microscopic fields (1 mm × 1 mm) were scored.

2 Results and discussion

2.1 Sulfate reduction with different COD/SO_{4}^{2−} ratios
The competition between MPA and SRB for available substrates in anaerobic wastewater treatment systems where high-sulfate was present was significantly influenced by COD/SO_{4}^{2−} ratio of the substrate (McCartney and Oleszkiewicz, 1991). In general, low and high COD/SO_{4}^{2−} ratio should favor sulfidogenesis and methanogenesis respectively (Dar et al., 2008). However, there was some controversy between the applications of COD/sulfate ratios when applied to biological treatment of complex wastewater. In this case, the HRT of the two-stage UASB reactor was 34 hr. The COD/SO_{4}^{2−} ratio in raw wastewater was 2.1. The effect of eight different influent COD/SO_{4}^{2−} ratios (0.5, 1.1, 1.6, 2.1, 2.7, 3.5, 4.1 and 4.7 achieved by adding Na_{2}SO_{4} or glucose) on sulfate reduction and COD removal was discussed. The next phase did not start until the last one was performed steadily.

Figure 3a presents the sulfate removal regularity with different COD/SO_{4}^{2−} ratios. In general, sulfate removal was enhanced with increasing COD/SO_{4}^{2−}. When the COD/SO_{4}^{2−} was 0.5, the sulfate removal efficiencies in sulfate-reducing stage and whole process were 15% and 28%, respectively. With the COD/SO_{4}^{2−} being increased, both of sulfate removal were enhanced and kept at 57% and 65% respectively corresponding to the COD/SO_{4}^{2−} ratio of 2.1. Enhanced COD/SO_{4}^{2−} ratio by adding glucose as extra carbon source, the sulfate reduction could be improved further. Finally, the sulfate removal efficiencies in sulfate-reducing stage and whole process were kept at 90% and 92% respectively when the COD/SO_{4}^{2−} ratio was 4.7. SRB depended on both sulfate and carbon source. When the COD/SO_{4}^{2−} ratio was low, the growth of the SRB was carbon-limited. There was no enough electron donor provided for achieving sulfate reduction. What’s more, residual acrylonitrile in acrylic fiber manufacturing wastewater was toxic to SRB in the reactors. Both microbial activity and metabolism were inhibited by it, which in turn affected sulfate reduction largely. When glucose was added as extra carbon source, the problems mentioned above could be alleviated and higher sulfate removal efficiencies were achieved.

During the process, COD removal regularity with different COD/SO_{4}^{2−} ratios was tested simultaneously. As it was presented by Fig. 3b, when the COD/SO_{4}^{2−} ratio was

<table>
<thead>
<tr>
<th>Probe</th>
<th>Specificity</th>
<th>Sequence (5′ to 3′)</th>
<th>Reference</th>
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<tbody>
<tr>
<td>EUB338</td>
<td>Most bacteria</td>
<td>GCTGCTCCCGTAGGAGT</td>
<td>Amann et al., 1990</td>
</tr>
<tr>
<td>SRB385</td>
<td>Sulfate-reducing bacteria</td>
<td>CGGGTTCGCTGGTACCGG</td>
<td>Sandaa et al., 1999</td>
</tr>
<tr>
<td>ARC915</td>
<td>Archaea</td>
<td>GTGCTCCCCGCAATTCTT</td>
<td>Stahl and Amann, 1991</td>
</tr>
</tbody>
</table>

Table 2 Sequences and hybridization conditions of oligonucleotide probes
0.5, COD removal efficiencies in sulfate-reducing stage and whole process were 5% and 8% respectively. Then both of them increased with COD/SO$_4^{2-}$ ratio improved and could kept at 20% and 35%, respectively, corresponding to COD/SO$_4^{2-}$ ratio of 2.1. Glucose added as extra carbon source could enhance COD removal efficiencies. The final COD removal efficiencies in sulfate-reducing stage and whole process arrived at 35% and 71% respectively corresponding to the COD/SO$_4^{2-}$ ratio of 4.7. When the COD/SO$_4^{2-}$ was 0.5, the COD removal through sulfate-reducing stage and methane-producing stage accounted for 5% and 3% of total COD removal respectively. At this COD/SO$_4^{2-}$, sulfate concentration both in sulfate-reducing stage and methane-producing stage were high due to low sulfate removal efficiency mentioned above. So SRB could outcompete MPA (data presented in Section 2.4) which resulted in low COD removal efficiency. The COD consumed mainly for sulfate reduction. With COD/SO$_4^{2-}$ being improved to 4.7, the COD removal through sulfate-reducing stage and methane-producing stage accounted for 35% and 36% of total COD removal respectively. The sulfate concentration in methane-producing stage was low due to high sulfate removal efficiency in sulfate-reducing stage. So MPA outcompeted SRB in methane-producing stage (data shown in Section 2.4) due to sulfate limitation, which devoted to higher COD removal efficiency.

### 2.2 Sulfate reduction with different HRT

Hydraulic retention time (HRT) is a key parameter in two-stage UASB process treating acrylic fiber manufacturing wastewater, because not only treatment performance but also reactor volume is associated with it. Experiments were performed at fixed COD/SO$_4^{2-}$ ratio of 2.1 (raw wastewater). Figure 4 presents the sulfate removal regularity with HRT in two-stage UASB reactor treating acrylic fiber manufacturing wastewater. When the HRT was kept at 28 hr operated during the first five weeks, sulfate removal efficiencies in sulfate-reducing stage and whole process were 37% and 46% respectively. Both of them increased with prolonged HRT and were kept at 68% and 75% respectively when the HRT was no less than 38 hr. During the whole 35-week operation process, the sulfate removal efficiencies in methane-producing stage were much lower than that in sulfate-reducing stage. The ratio of sulfate reducing was approximately 7 to 68. The SRB could suppress MPA through competition for the same substrates such as hydrogen and acetate, which consequently resulted in primary inhibition to MPA. Moreover, the SRB could convert sulfate into sulfide which could poison MPA. Thereby, in the sulfate-reducing stage, SRB could outcom-
pete MPA and predominate in quantity. The growth of SRB was dependent on the carbon and sulfate concentration, whereas the growth of MPA was solely dependent on the concentration of carbon. In the methane-producing stage, sulfate concentration was low, and the growth of the SRB would be sulfate-limited. This enabled the MPA to outcompete the SRB, and made MPA predominate in quantity. Accordingly, sulfidogenesis mainly happened in the sulfate-reducing stage, while methanogenesis mainly happened in the methane-producing stage. The phase separation between sulfidogenesis and methanogenesis was achieved in the two-stage UASB reactor treating acrylic fiber manufacturing wastewater.

Figure 4b presents the COD removal regularity with HRT in two-stage UASB reactor treating acrylic fiber manufacturing wastewater. At first five weeks, the COD removal efficiencies in sulfate-reducing stage and whole process were 5% and 18%, respectively, corresponding to the HRT of 28 hr. With the HRT being increased, both of COD removal efficiencies were enhanced steadily and kept at about 32% and 51%, respectively, corresponding to the HRT of 38 hr. When the hydraulic retention time was prolonged further to 40 hours from the 31th to 35th week, little increment of COD removal both in sulfate-reducing stage and whole process was achieved. So the optimal HRT operated in two-stage UASB reactor treating acrylic fiber manufacturing wastewater was 38 hr. This was much longer than that operated in treating reactive dye bath wastewater (Chinwetkitvanich et al., 2000) and synthetic fruit wastewater (Diamantis and Alexandros, 2007), but agreed with Buzzini et al. (2006) that the use of UASB reactors in the treatment of complex effluents required long hydraulic retention time (Buzzini et al., 2006). On one hand, residual acrylonitrile in acrylic fiber manufacturing wastewater was toxic to microbes in the reactors. Both microbial activity and metabolism were inhibited by it, which in turn decelerated metabolic rate to organic pollutants in water. Therefore, long HRT was required to offset decreasing metabolic rate resulted from toxicity of acrylonitrile. On the other hand, oligomers existed in the wastewater belonged to biorefractory organic pollutants. The degradation rates to them were quite low and the process was time-consuming. This also needed long HRT to make sure there was enough contact time between microbes and oligomers.

2.3 Formation and characteristics of granule

Granulation in UASB reactors was important in the treatment of various industrial wastewater containing toxic substances due to their compact structure which protect the bacteria from inhibitory and toxic pollutants. What’s more, the aggregation and compaction of the microbial mass resulted in higher density and larger size of the granule, which had higher settling velocity. Up to now, the important role of extracellular polymeric substances (EPS) in the process of granulation had already been well established (Schmidt and Ahring, 1994; Morgan et al., 1990; Uyanik et al., 2002). The EPS was excreted by the microbial cells and exposed at their surfaces under suitable physiological conditions. Because of its position and chemical characteristics, the EPS affected the properties of the bacterial flocs and helped to adhere and connect the floculent sludge particles together.

At the beginning of the experiment, the inoculum was fine and flocculent (< 0.1 mm) rather than granular. Figure 5 reveals the relationships between organic and sulfate loading rates and EPS content at different COD/SO$_4^{2-}$ ratios. Generally, EPS content in sulfate-reducing stage was more than that in methaneproducing stage. At first seven weeks, the EPS content was around 0.7 g/g MLVSS in sulfate-reducing stage, and then the content dropped with decreasing sulfate loading rates. Since the 25th week, the EPS content start increasing with organic loading rates enhanced, and the most content was 0.774 g/g MLVSS appearing on the 44th week. After four weeks a lot of small granules with diameters of 0.5–1.0 mm were firstly found in sulfate-reducing stage reactor.

![Fig. 5 Relationships between organic and sulfate loading rates (a) and EPS content (b).](image-url)
Then the granules grew quickly and the diameters varied between 1.5 and 2.5 mm as Fig. 6a shown. As the EPS content dropped from the 8th week, the sizes of granules decreased slightly and were about 1.0–2.0 mm. However, the sizes grew bigger from the 27th week due to increasing EPS content and the final diameters varied from 2.0 to 3.0 mm shown as Fig. 6c. All of the granules were black and of irregular and uneven shape. In methane-producing stage reactor, the EPS content was approximately 0.2 g/g MLVSS throughout the whole process. Granules formed on the 15th week and the sizes which varied between 0.5 and 1.0 mm were kept constant during the following process (Fig. 6d).

Earlier study reported that high salinity greatly affected the physical and biochemical properties of activated sludge, and increased EPS concentration (Reid et al., 2006). At first seven weeks, the sulfate content and loading rate in sulfate-reducing stage were about 9175 mg/L and 24 kg/(m$^3$·day), respectively. To combat the salt inhibition, more EPS were secreted in this period. When the organic loading rates were large after the 25th week, the ratios of food to microorganisms were high. So the microorganisms were provided with sufficient foodstuffs and a great deal of EPS was produced. This agreed with other researchers that with plentiful foodstuffs, microorganisms were stimulated to produce more EPS in a relatively shorter time because of their increased anabolic activity (Francese et al., 1998; Zhou et al., 2003). High EPS content helped to adhere and connect the flocculent sludge particles together. Consequently, microbes in sulfate-reducing stage performed granulation better than that in methane-producing stage.

### 2.4 Quantification of microbial community composition

Fluorescence in situ hybridization (FISH) was employed to quantify the microbial community composition in the two-stage UASB reactor. Sludge was extracted from sulfate-reducing stage and methane-producing stage respectively on the 7th week and 42nd week. Figure 7 indicates that the abundances of bacteria, SRB and MPA were similar in sulfate-reducing stage and methane-producing stage at COD/SO$_4^{2-}$ ratio of 0.5. Bacteria, SRB and MPA accounted for about 75%, 31% and 20% respectively. When the COD/SO$_4^{2-}$ ratio was 4.7, ...
the microbial community composition in sulfate-reducing stage and methane-producing stage varied largely. From sulfate-reducing stage to methane-producing stage, bacteria decreased sharply from 67% to 24% while archaea increased from 27% to 71%. Sulfate reducing bacteria also dropped dramatically from 34% in sulfate-reducing stage to 10% in methane-producing stage. At COD/SO$_4^{2-}$ ratio of 0.5, sulfate content in methane-producing stage was high due to low sulfate removal efficiency in sulfate-reducing stage. There were enough sulfates for SRB to grow both in sulfate-reducing stage and methane-producing stage. Besides, sulfidogenesis mediated by SRB was thermodynamically more favorable than methanogenesis mediated by MPA. What’s more, hydrogen sulfide converted from sulfate by SRB could poison MPA. These all favored SRB growth and made SRB outcompete MPA in both stages. When the COD/SO$_4^{2-}$ ratio was 4.7, SRB and MPA were predominant in sulfate-reducing stage and methane-producing stage respectively. The sulfate content and COD/SO$_4^{2-}$ ratio in methane-producing stage were approximately 255 mg/L and 25.5. The growth of the SRB would be sulfate-limited, and it enabled the MPA to outcompete the SRB, and made MPA predominate in the reactor. This agreed with Mizuno et al. (2007) that at high COD/SO$_4^{2-}$, the MPA predominated while at lower COD/SO$_4^{2-}$ the SRB were more competitive (Mizuno et al., 1994). FISH results were also in accordance with the sulfate reduction shown in Section 2.1.

3 Conclusions

On the basis of the results on the sulfate removal from acrylic fiber manufacturing wastewater by a two-stage UASB reactor. The following conclusions could be drawn. Sulfate removal was enhanced with increasing COD/SO$_4^{2-}$. The sulfate removal efficiencies were 28% and 92% respectively corresponding to the COD/SO$_4^{2-}$ ratios of 0.5 and 4.7. At low COD/SO$_4^{2-}$, the growth of the SRB was carbon-limited. There was no enough electron donor provided for achieving sulfate reduction. The problem could be solved by adding glucose as extra carbon source to improve COD/SO$_4^{2-}$.

At fixed COD/SO$_4^{2-}$ ratio of 2.1, the optimal sulfate removal efficiency was 75% when the HRT was no less than 38 hr. Sulfidogenesis mainly happened in the sulfate-reducing stage, while methanogenesis in the methane-producing stage. The phase separation between sulfidogenesis and methanogenesis was achieved in the two-stage UASB reactor treating acrylic fiber manufacturing wastewater.

Microbes in sulfate-reducing stage performed granulation better than that in methane-producing stage. Higher EPS content in sulfate-reducing stage helped to adhere and connect the flocculent sludge particles together. At COD/SO$_4^{2-}$ ratio of 0.5, more EPS were secreted to combat salt inhibition because of high sulfate content. When the organic loading rates were large at high COD/SO$_4^{2-}$ ratios, microorganisms were stimulated to produce more EPS in a relatively shorter time because of their increased anabolic activity.

SRB accounted for about 31% both in sulfate-reducing stage and methane-producing stage at COD/SO$_4^{2-}$ ratio of 0.5. There were enough sulfates for SRB to grow both in sulfate-reducing stage and methane-producing stage. When the COD/SO$_4^{2-}$ ratio was 4.7, SRB dropped dramatically from 34% in sulfate-reducing stage to 10% in methane-producing stage. SRB and MPA were predominant in sulfate-reducing stage and methane-producing stage respectively.

Acknowledgments

This work was supported by the National Science and Technology Major Project (No. 2009ZX07529-004-2) and the National High Technology Research and Development Program (863) of China (No. 2009AA063901). The authors would like to thank the editor and the anonymous reviewers for their editing and review.

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