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Performance of oxidation-reduction potential-based hydrolysis and acidification process for high-strength antibiotic wastewater treatment

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ABSTRACT

This study used hydrolysis and acidification process under appropriate oxidation-reduction potential (ORP) condition to treat high-strength antibiotic wastewater. ORP was controlled at approximately −100 mV through air-flow regulation. Results showed that the appropriate ORP condition enhanced the physiological metabolic function of facultative hydrolytic and acidogenic bacteria, and aerated stirring improved the hydraulic condition. Acidification degree (AD) and effluent volatile fatty acid (VFA) reached 58.64% and 4,825 mg/L, respectively, at the shortest hydraulic retention time of 10 h and the maximum organic loading rate (OLR) of 20 kg COD/(m^3 d). Wastewater biodegradability was improved by approximately 17%, thus providing good substrate for post-aerobic treatment. Relatively stable effluent was achieved with the fluctuant influent, and COD and SS removal efficiencies were 15–30% and 90–95%, respectively. The change in VFA lagged behind the AD in the effluent, indicating that AD could better represent the effects of hydrolysis and acidification process. The height of the reactor for stable VFA production increased as the OLR increased.

Keywords: Antibiotic wastewater; Hydrolysis and acidification; Oxidation-reduction potential; Biodegradability

1. Introduction

With the advantages of simplicity, high efficiency, economy, stability, and satisfactory application results, aerobic and anaerobic biological wastewater treatment technologies have been widely used globally. Aerobic wastewater treatment consumes significant amounts of energy, whereas anaerobic wastewater treatment normally requires a long hydraulic retention time (HRT). Considerable attention is being directed toward the technology of facultative bacteria application in wastewater treatment for its extensive usage, stability, and low energy demand [1,2]. This technology could synchronously transform and biodegrade organic contaminants, especially when treating highly poisonous and refractory wastewater.

Given the limitation of the antibiotic production process, numerous antibiotics, by-products, and high-strength sulfate remain in the waste fermentation liquid [3]. These residues are highly poisonous and refractory compounds to be treated [4]. When the aerobic

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treatment process is applied, the process falls short of being cost-effective, and the tolerance to poisonous substrate is weak. However, when the anaerobic treatment process is adopted, the primary inhibition and sub-inhibition induced by sulfate-reducing bacteria may result in volatile fatty acid (VFA) accumulation, and consequently affect the stability or even cause the failure of the whole system [5].

Hydrolysis and acidification are conducted by facultative hydrolytic and acidogenic bacteria, which are completely different from strictly anaerobic bacteria in terms of physiological ecology and metabolizability. Studies on hydrolysis and acidification have focused on supplying substrate to methane-producing bacteria (MPB). Conditions that are favorable to hydrolytic and acidogenic bacteria, such as short HRT and low pH, may generally inhibit MPB. The activity of MPB will be significantly suppressed when pH is below 5.5 [6–8]. Fermentation type and end products mainly depend on the nature of substrate and operating conditions [9], especially pH and organic loading rate (OLR), but are only slightly influenced by temperature. During the acidification of gelatin-rich wastewater, Yu et al. found that acidification degree (AD) only slightly increased with temperature, from 56.4% at 20˚C to 72.6% at 55˚C, and temperature only slightly affected the end products. By contrast, AD increased from 32% at pH 4.0 to 71.6% at pH 6.5. The operation at pH of 4.0–5.0 favored the production of propionate, whereas that at pH of 6.0–7.0 encouraged the production of acetate, butyrate, and i-butyrate. Hence, temperature control may not be essential, but pH control is important for producing a stable effluent composition from an acidogenic reactor [7]. The pH of the hydrolysis and acidification system may vary during acidification; the system can buffer itself toward a pH value in the range of 5.0–7.0 without control [10]. Lettinga emphasized that the complete acidification of wastewater would be detrimental to the granulation of anaerobic sludge and recommended partial acidification of 20–40% and HRT of 6–24 h for anaerobic treatment [11]. Facultative and anaerobic bacteria are capable of removing toxicity and refractory organic substrate, which can result in the cleavage of aromatic and heterocyclic hydrocarbons with short HRT, wide pH range, and low temperature [12]. Thus, such bacteria enable efficient pretreatment for further biological treatment. Therefore, this study aimed to maximize VFA production through the oxidation-reduction potential (ORP)-based hydrolysis and acidification process for high-strength refractory antibiotic wastewater treatment to improve the biodegradability of antibiotic wastewater further and to provide good substrate for post-aerobic treatment. The performance of the process was mainly evaluated in terms of VFA accumulation, AD, and biodegradability improvement.

2. Materials and methods

2.1. Experimental setup

Fig. 1 shows a diagram of the ORP-based hydrolysis and acidification system used in this study. The system was a modified steel UASB (1,300 × 1,300 × 2,500 mm) without a three-phase separator. The effective volume was 3.8 m^3. To reduce the adsorption to sludge by micro air bubbles and to improve the mixing effect, perforated pipes were used to generate big bubbles at the bottom. An ORP electrode was fixed in the middle. Nine sampling ports were installed along the height to collect samples for VFA and sludge measurements, and a filling layer was arranged in the upper with an overflow weir in the top. The biological reaction was limited to the hydrolysis and acidogenesis stage and did not develop into methanogenesis. In addition, the obligate anaerobic MPB were inhibited by dissolved oxygen, and no or perhaps considerably less methane was produced. Thus, no biogas collector was equipped.

2.2. Characteristics of feed wastewater

The feed wastewater was directly obtained from an antibiotic wastewater treatment plant, and its characteristics were tabulated in Table 1. The quality of

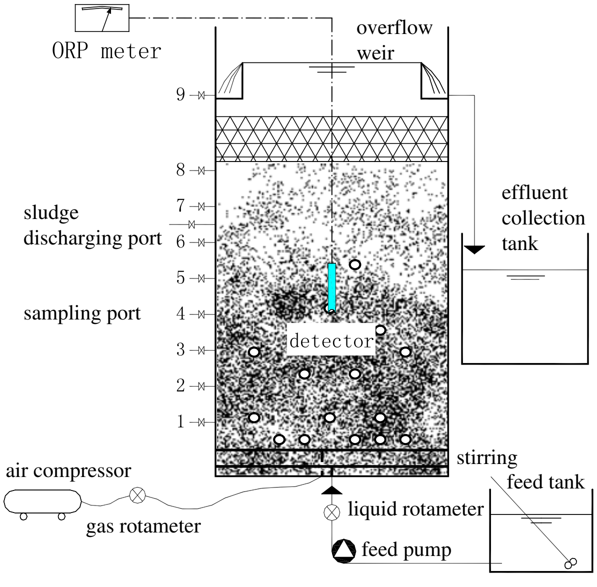

Fig. 1. Diagram of the ORP-based hydrolysis and acidification system.

Table 1
Characteristics of feed wastewater

pH	COD ($mg\ L^{-1}$)	BOD_5/COD	SS ($mg\ L^{-1}$)	VSS/SS	SO_4^{2-} ($mg\ L^{-1}$)	Total dissolved solids (TDS) ($mg\ L^{-1}$)	*T* (℃)
4.5–5.0	6,500–22,000	0.33–0.40	2,500–13,200	0.87–0.95	790–5,250	1,920–11,580	30–35

the antibiotic wastewater violently fluctuated with high sulfate content, and numerous biological poisonous inhibitory matters remained in it. VSS/SS was as high as 90%. The BOD_5/COD value (0.35) contained analytical error induced by large multiple-fold dilution during the analysis process, such that biodegradability should be much worse.

2.3. Sludge inoculation

The reactor was inoculated with sludge from a sludge thickener of the aforementioned antibiotic wastewater treatment project. Prior to inoculating, it was elutriated to remove the inorganic particles and then concentrated by gravity settling for 24 h. The inoculation sludge concentration was 25,680 mg/L with VSS/SS of 76%, and the inoculation ratio was 100%.

2.4. Analytical methods

Once the pseudo-steady state was reached under a certain HRT, all the analytical tests were conducted. COD, BOD_5, SS, and VSS were all performed according to Standard Methods [13]. Before COD and BOD_5 measurements, 0.45 μm pore-sized filters were used. SO_4^{2-} concentrations were analyzed by the EDTA titration method. The pH values were measured with the pH meter (model PHS-25, LeiCi, Shanghai, China), and ORP was monitored online with the ORP meter (model PHSJ-3F, LeiCi, Shanghai, China). The total VFA was assayed by the distillation method as acetic acid [14]. Prior to total VFA measurement, the samples were acidified with H_2SO_4 (1:1).

AD is one of the main focus points in this study. It can be quantified using the percentage of the influent COD converted to total VFA (Si). The quantity of total VFA was converted to theoretical equivalent in mg COD/L (Se), using the COD equivalent 1.066 for acetic acid [15]. AD was defined by the following formula:

$$\text{Acidification degree } (\%) = (\text{Se}/\text{Si}) \times 100 \quad (1)$$

2.5. Experimental design

No control on wastewater temperature and pH was found. ORP was controlled near −100 mV (±20 mV) by air-flow adjustment. After dilution wastewater was fed during the first week, high-strength antibiotic wastewater was directly fed. The continuous-flow pattern was adopted in the experiment, and OLR was gradually increased by gently decreasing HRT from 24 to 8 h. A pseudo-steady state must be reached for each HRT condition before OLR was elevated. Pseudo-steady state was defined by stable (±5% confidence level) COD, SS, VFA concentration, and AD in the effluent. The activity and precipitation of sludge in the bottom of the reactor were better than those in the upper part [16]. Thus, the excessive sludge was periodically removed from the sludge-discharging port located in the upper part to avoid sludge accumulation, and to keep sludge active in the system.

3. Results and discussion

3.1. Effluent VFA and AD at different HRT periods

VFA was the final hydrolysis and acidification product for various substrates. Short-chain fatty acids (SCFA) were the main products at a long HRT, such as acetate. Long-chain fatty acids could not be converted into SCFA and remained in effluent at a short HRT, such as caprylic acid [17]. During the acidification of mid- and high-strength dairy wastewater tested by Yu et al. the acidification rate, namely, VFA formation rate, only slightly increased from 0.259 to 0.261 g/(gVSS d), whereas AD obviously dropped from 44.5 to 33.1% when the influent COD increased from 12,000 to 20,000 mg/L at HRT of 12 h [6].

Fig. 2 shows that both effluent VFA concentration and AD displayed similar increasing trends when HRT was decreased. During the period that HRT was decreased from 18 to 14 h, they markedly increased, which meant that the reactor obtained good hydrolysis and acidification effect. The increasing rate of AD tended to drop when HRT was shortened from 14 to 10 h, and AD and effluent VFA concentration both reached the largest values of 58.64% and 4,825 mg/L,

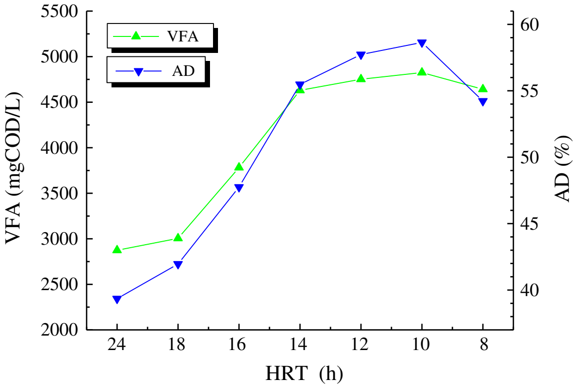

Fig. 2. VFA production and effluent AD at different HRT periods.

respectively. However, both of them began to decrease when HRT was reduced to 8 h, which indicated that the maximum AD was obtained with the maximum OLR of 20 kg COD/(m^3 d) at HRT of 10 h.

During the period that HRT was decreased from 24 to 18 h, the increasing rate of AD was higher than that of effluent VFA concentration, which was mainly caused by organism synthesis using a part of effluent VFA. However, when HRT was shortened from 10 to 8 h (overloaded OLR), the decreasing rate of AD was higher than that of effluent VFA concentration, because the entrapped VSS continued to be hydrolyzed and acidified to produce VFA. Therefore, the decrease of effluent VFA concentration lagged behind that of AD, indicating that AD could more properly represent the performance of hydrolysis and acidification process. AD of antibiotic wastewater at maximum OLR of 20 kg COD/(m^3 d) was close to that of easily hydrolyzed and acidified dairy wastewater at maximum OLR of 23 kg COD/(m^3 d) and HRT of 12 h in CSTR, namely, 61% [18]. On one hand, the physiological metabolizability of facultative hydrolytic and acidogenic bacteria was enhanced by appropriate ORP condition; on the other hand, it benefited from the stirring of aeration by perforated pipes in the bottom part with the low upflow velocity of 0.22 m/h at the maximum OLR and without methane production. Aeration by perforated pipes improved the hydraulic condition, promoted the wastewater–biomass contact, intensified the transport of substrate into the biomass, and thus enhanced the treatment efficiency of the system.

Hydrolysis and acidification reaction is the result of enzymatic reactions. Thus, it is the key factor that offers preferable environment for enzyme synthesis. Although, the acidification rate was enhanced by increasing OLR, the increasing rate of AD began to drop until the maximum OLR was reached. When HRT was shortened to 8 h, the production rate of extracellular hydrolytic enzymes was clearly lower than the dilution rate, and enzymes were insufficient for high OLR, thus decreasing AD.

3.2. *VFA concentration at different heights of the reactor*

Variations of VFA concentration at different heights of the reactor at pseudo-steady states were illustrated in Fig. 3. The four different HRT periods were 24, 16, 10, and 8 h.

Fig. 3 shows that when HRT decreased, the height of the reactor for stable VFA concentration production simultaneously increased. At HRT of 24 h, the maximum VFA concentration was reached at sampling port 2 and remained constant thereafter, whereas at HRT as short as 10 h, namely, at the maximum OLR, the maximum VFA concentration was not reached until at sampling port 8. This result indicated that hydrolysis and acidification reaction was conducted by the whole volume of the reactor. The sludge bed zone below the sampling port 4 was the main reaction field for VFA production, where the sludge concentration was over 40,000 mg/L. Evidently, VFA production rates in this field were much higher than those in the upper part. Comparisons of the four curves below sampling port 4 showed that VFA concentration decreased when OLR increased, which demonstrated that VFA concentration was negatively correlated with OLR. This result was mainly caused by the biological poisonous inhibition of antibiotic wastewater, as well as the dilution of the extracellular hydrolytic enzymes under high OLR.

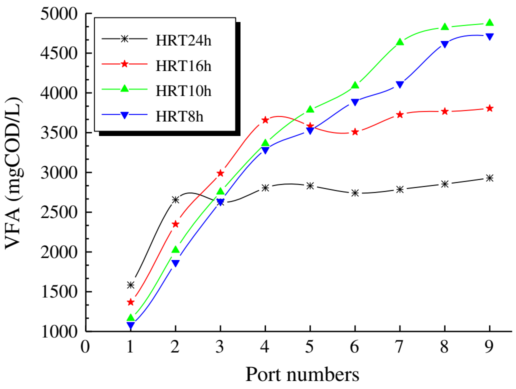

Fig. 3. Profile of VFA concentration along the reactor height.

3.3. Improvement of biodegradability of antibiotic wastewater

The readily biodegradable organic substrate in wastewater is the substantial base for biological treatment, and it is the key factor that determines treatment efficiency and effluent quality. Small-molecule VFAs generated by the cleavage of large-molecule refractory compounds in the hydrolysis and acidification process comprise the substantial base that enhances wastewater biodegradability.

Twenty days of operating results under HRT of 10 h is shown in Fig. 4. The biodegradability of antibiotic wastewater was greatly improved, and the effluent BOD_5/COD was enhanced by approximately 17%. In addition, the improvement was closely correlated to the influent biodegradability. When the influent BOD_5/COD was 33% on operating day 128, the rising BOD_5/COD was only 14%; however, while the influent BOD_5/COD was 40% on operating day 132, the effluent BOD_5/COD was enhanced by 20%. The phenomenon in which the effluent BOD_5/COD did not decrease but rather increased sufficiently demonstrates the reduction or elimination of toxicity. Thus, the system exhibited strong capacity to buffer toxicity and high OLR.

3.4. Removals of COD and SS

The hydrolysis and acidification process mainly focused on the transformation of the chemical structure and characteristic of contaminants, rather than on their removal [9,12]. COD removal was mainly ascribed to the entrapment by the sludge bed and the precipitation of large influent organic particulates, and most of it was colloid COD and suspended COD. To deal with the VSS accumulation problem, Zeeman et al. applied the upflow anaerobic solid removal reactor and removed 65 and 98% of suspended COD for the pretreatment of raw sewage and waste activated sludge, respectively [19]. However, in the ORP-based hydrolysis and acidification process, most of the suspended COD was hydrolyzed and acidified into VFA in the effluent, thus improving biodegradability.

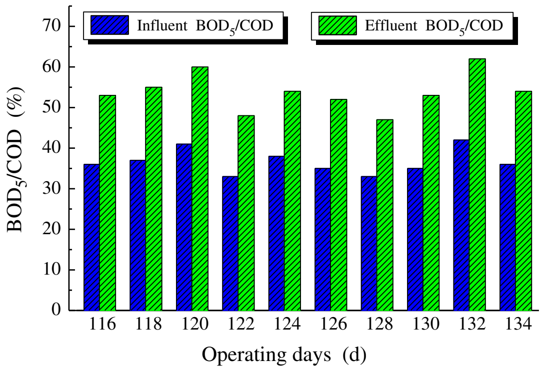

Fig. 4. Biodegradability improvement of antibiotic wastewater.

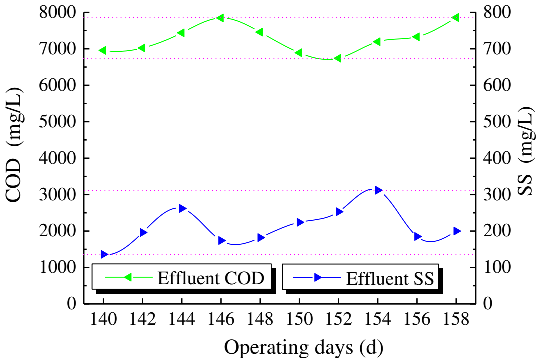

Fig. 5. Effluent COD and SS concentrations.

Twenty days of operating results under HRT of 10 h is shown in Fig. 5. The results showed that the effluent quality was relatively stable even with fluctuating influent (Table 1), and the effluent COD and SS were 7,000–8,000 mg/L and 150–300 mg/L, respectively, with removal efficiencies of 15–30% and 90–95%. This result was close to the COD removal efficiency of 10–40% for food wastewater treatment by hydrolysis and acidification process [9]. The filling field strengthened the entrapment of SS and reduced effluent SS but slightly contributed to VFA production.

4. Conclusions

From the abovementioned study and analysis, the following conclusions can be drawn:

(1) The appropriate ORP condition (−100 mV) enhanced the physiological metabolizability of facultative hydrolytic and acidogenic bacteria, and aerated stirring improved their hydraulic condition. Both of them promoted the organic transport between substrate and organisms and enhanced the hydrolysis and acidification effect of high-strength antibiotic wastewater.

(2) AD and effluent VFA reached 58.64% and 4,825 mg/L at the shortest HRT of 10 h and the maximum OLR of 20 kg COD/(m^3 d). This study showed that AD could more properly represent the effect of hydrolysis and acidification process.

(3) The sludge bed in the bottom was the main field for VFA production, and the height of the reactor for stable VFA production increased when OLR increased. VFA concentration was negatively correlated with OLR in the sludge bed.
(4) The biodegradability of antibiotic wastewater was improved by approximately 17%, offering good substrate for post-aerobic treatment.
(5) The effluent quality was relatively stable with fluctuating influent. COD and SS were 7,000–8,000 mg/L and 150–300 mg/L with the removal efficiencies of 15–30% and 90–95%, respectively.

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