Biological treatment of high-pH and high-concentration black liquor of cotton pulp by an immediate aerobic-anaerobic-aerobic process

Miao Lihong, Li Furong and Wen Jinli

ABSTRACT

In this study, an immediate aerobic-anaerobic-aerobic (O/A/O) biological process was established for the treatment of black liquor of cotton pulp and was tested by both laboratory-scale batch experiment and pilot-scale continuous experiment. The effects of the hydraulic retention time (HRT) were studied, as were the alkaliphilic bacteria number, the culturing temperature and the concentration of black liquor on COD (chemical oxygen demand) removal. The total COD (COD$_{\text{tot}}$) removal rate of the novel O/A/O process, for a black liquor with influent COD$_{\text{tot}}$ over 8,000 mg/L and pH above 12.8, was 68.7 ± 4% which is similar with that of the traditional acidic-anaerobic-aerobic process (64.9 ± 3%). The first aerobic stage based on alkaliphilic bacteria was the crucial part of the process, which was responsible for decreasing the influent pH from above 12 to an acceptable level for the following treatment unit. The average generation time of the alkaliphilic bacteria in the black liquor was about 36 minutes at 40°C in a batch aerobic activated sludge system. The efficiency of the first aerobic stage was affected greatly by the temperature. The COD$_{\text{tot}}$ removal at 55°C was much lower in comparison with the COD$_{\text{tot}}$ removal at 45°C or 50°C. Both the laboratory-scale batch experiments and the pilot-scale continuous experiment showed that the COD$_{\text{tot}}$ removal rate could reach about 65% for original black liquor with a pH of about 13.0 and a COD of 18,000–22,000 mg/L by the immediate O/A/O process. The first aerobic stage gave an average COD$_{\text{tot}}$ removal of 45.5% at 35°C (HRT = 72 h) at a volume loading rate of 3.4 kg COD m$^{-3}$ d$^{-1}$.

Key words | aerobic-anaerobic-aerobic process, alkaliphilic bacteria, biological treatment, black liquor

INTRODUCTION

The black liquor of cotton pulp is a highly contaminated digestion wastewater generated in the process of cotton cooking with caustic soda. It contains a high concentration of organic matter (i.e. lignin, cellulose, semicellulose and their decomposition products under high alkalinity and high temperatures). The black liquor exhibits some distinct properties, including high temperature, high pH, and high COD. Usually, biological method is the most economical solution for organic wastewater. However, high pH and salinity could severely inhibit biological treatment of industrial wastewater (Intrasungkha et al. 1999; O’Neill et al. 2000).

Two kinds of processes have been applied in the black liquor treatment of cotton pulp production in China. In the first process, waste sulfuric acid solution is added to the black liquor until the pH is adjusted to 2–3. The lignin in the pulp effluent black liquor is thus recovered by acidulation precipitation. The pretreated wastewater is subsequently adjusted to a neutral pH followed by biological treatment. In the second process, the black liquor is initially adjusted to a neutral pH by adding acid, and then subjected to biological and physical-chemical treatments such as flocculation. Both of these two processes have some
distinct shortcomings including complexity and costliness (because of a great requirement for acid). Moreover, the high concentration of SO$_4^{2-}$ brought by waste acid solution inhibits the follow-up anaerobic process. Besides, the coagulation-flocculation process produces enormous sludge, which is difficult to handle or discard. Therefore, a cost-effective method for treating black liquor is required. On the other hand, biological method has been applied in textile wastewater treatment, whose water quality is similar to black liquor, as an efficient and low-cost means (Banat et al. 1996). There were also some reports on black liquor treatment by fungus (Marwaha et al. 1998; Fuming et al. 1999).

Soda lakes and soils, as well as non-saline alkaline environments, are inhabited by a group of microorganisms known as alkaliphilic bacteria (Kleinsteuber et al. 2001; Tiago et al. 2004), which grow optimally at pH above 9 (Krlwich & Guffanti 1989; Ventosa & Nieto 1995; Horikoshi 1999). These microorganisms have been applied in many fields including production of extremophilic enzymes and wastewater treatment (Nogi et al. 2005; Oie et al. 2007).

The object of this study was to develop an immediate aerobic-anaerobic-aerobic biological process based on the alkaliphilic bacteria for treating the high-pH and high-concentration black liquor of cotton pulp.

**MATERIALS AND METHODS**

**Factory wastewater and activated sludge**

Three types of cotton pulp black liquor were provided by Hubei Jinhuan Co., Ltd. (China) for this study: low-consistency black liquor (COD 3,000 ± 1,000 mg/L, pH 12.5 ± 0.2), median-consistency black liquor (COD 7,500 ± 1,500 mg/L, pH 12.7 ± 0.3), and high-consistency black liquor (COD 19,000 ± 4,000 mg/L, pH 13.1 ± 0.4).

The aerobic activated sludge acclimation method: the sediment sludge of the black liquor sump in the cotton pulp plant (Hubei Jinhuan) was collected and mixed with a suspension of the soil (from the plant surrounding area) in order to increase the content of alkaliphiles. The mixing volume ratio of the sludge versus the soil suspension (containing 10% soil) was 10:1. Then the black liquor was added (lower-consistency black liquor primarily, higher-consistency black liquor afterwards, the concentration of black liquor increased gradually during the process of acclimation). The mixture was aerobic cultured at 30–40°C with air aeration until the pH fell below 9.5, and then the aeration was stopped. The supernatant was discarded, and the precipitated sludge was kept. This process was repeated 3–5 times. The time for acclimated aerobic sludge to treat median or high consistency black liquor (reduce its pH to 9.5) was 15–45 hours, while the time for unacclimated aerobic sludge was 40–90 hours. The acclimated sludge was used in lab-scale batch and pilot-scale continuous experiments.

Anaerobic activated sludge was acclimated from the sludge of the sludge thickener of a biological treatment station at the cotton pulp plant (Hubei Jinhuan Co., Ltd.). The originally collected sludge was washed to remove the scum and grit and a MLSS of 15,000 mg/L was achieved. Median-consistency black liquor three times of the volume of the sludge was added and thoroughly mixed with the sludge. The mixture was placed overnight and gas was generated the next day because of the good activity of the sludge. Thirty percent of the black liquor was renewed per day. After one week, the gas production increased markedly and the COD loading rate reached 0.5 kg COD m$^{-2}$ d$^{-1}$. Then the anaerobic sludge can be put to normal use.

The second aerobic stage sludge was also acclimated from the sludge of the sludge thickener of the biological treatment station at Hubei Jinhuan Co., Ltd. The reaction conditions of the second aerobic stage in pilot-scale continuous experiments were similar to those of the aerobic reactor in the biological treatment station. Therefore, the inoculating sludge could be used directly without acclimation.

**Laboratory-scale batch experiments**

The aerobic treatment of black liquor in the lab employed several 1-L micro-bioreactors with compressed air micro-pore aeration and bath temperature controls. The aeration rate was regulated based on the concentration of dissolved oxygen in the reactor, which was controlled at 4–6 mg/L. The MLSS in the reactor maintained constant around 4,000 mg/L and 10,000 mg/L in the treatments of the median-consistency black liquor and the high-consistency...
black liquor, respectively, at 40°C. The experiments using 1L micro-bioreactors included the effects of degradation time on the pH and the COD removal of black liquor, the effects of temperature and concentration of black liquor on COD removal in aerobic treatment, and the effects of acid adjustment process on biological treatment of black liquor.

The determinations for the generation time of the alkaliphilic bacteria and the effect of the degradation time of the first aerobic stage on COD removal were carried out using a 500 mL flask holding a reaction volume of 250 mL. Acclimated aerobic activated sludge was inoculated into fresh median-consistency black liquor with a pH of 12.8 and a COD of 7,732 mg/L. The mixture with a MLSS of 4,000 mg/L was cultivated in a constant temperature shaker with an agitation speed of 180 rpm and a temperature of 40°C and sampled regularly to determine the alkaliphilic bacteria numbers.

For the anaerobic treatment of wastewater, liquid transfers were made in an anaerobic incubator and anaerobic incubation was done in an enclosed 1 L plastic bottle that was statically incubated in a thermostat.

In the acidic-anaerobic-aerobic process, the first aerobic stage was replaced by a pH adjustment (acidification), in which pH was adjusted by HCl to a final pH of 9.3. In the O/A/O process, the first aerobic stage needed a hydraulic retention time (HRT) of 24 hours. Both of these two processes included an anaerobic stage (72 hours) and a second aerobic stage (50°C, 20 hours).

**Pilot-scale continuous experiments**

The effective volume of the first aeration tank was 1,000 L. The inoculation quantity of the first stage aeration sludge was 300 L. The acclimation process was described above and followed the pattern of discontinuous running beforehand and long running afterward. After the continuous running had been achieved, the inflow rate was elevated progressively with the pH of the reactor always controlled below 9.5. The acclimation process ended basically when the COD loading rate reached 2.5 kg COD m$^{-3}$ d$^{-1}$ or so. The anaerobic stage employed a UASB reactor with an effective volume of 150 L (Figure 1). The inoculation quantity of the anaerobic sludge was 40 L. The effective volume of the second aeration tank was 50 L. The inoculation quantity of the second stage aeration sludge was 15 L. The MLSS in the second aeration tank was about 4,000 mg/L. All of these containers were made of PVC material.

High-consistency black liquor was introduced from the inlet pressure pipelines of the black liquor biological treatment station into the first aeration tank, aerated with...
compressed air by pore aerator installed in the bottom of the tank. The inflow rate of the first aerobic treatment stage maintained at about 10–15 L per hour. The effluent of the first aeration tank flowed automatically into the first settler and, after liquid-solid separation, most of the supernatant was discharged directly and flowed automatically into the UASB reactor (with an influx rate of 0.8–1 L/h or so), then flowed into the second aeration tank. Most of the activated sludge on the bottom of the two settlers was recycled by a pump. The sludge recycle ratio was 90%. The MLSS of return sludge was kept at about 12,000 mg/L by discharging the residual sludge irregularly. The wastewater flux and the air flux were measured separately by a rotameter, and the volume ratio between the water and the air was adjusted to about 1:10. The experiment’s reactors were placed in a thermostatic room with the atmospheric temperature kept at 35 ± 2°C.

**Analyses**

COD$_{tot}$, BOD$_5$, total alkalinity, ammonia nitrogen (NH$_3$-N), and total Kjeldahl nitrogen (TKN) concentrations were measured using the standard methods of the National Environmental Protection Agency of China (NEPA 1989). Mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) were measured according to the standard methods of APHA (1998). The soluble COD (COD$_{sol}$), suspended COD (COD$_{sno}$), and colloidal COD (COD$_{col}$) were measured according to Vogelaar et al. (2002).

The alkaliphilic bacteria numbers (CFU/mL) were determined by a plate counting method. The alkaliphilic bacteria from the black liquor were cultured on plates with a medium of original black liquor containing 2% agar. The plates were incubated at 40°C for 48 hours and the colonies were counted.

**RESULTS AND DISCUSSION**

**Lab-scale batch experiments**

**Effects of degradation time on the pH and the COD removal of black liquor**

The acclimated aerobic activated sludge was inoculated to the original black liquor with a pH of 12.4 and a COD$_{tot}$ of 7,556 mg/L. The mixture was cultured in a micro-bioreactor at 40°C. The total COD and the pH were assayed at 3-hours intervals. The results showed that the pH and the COD were reduced simultaneously in the course of degradation. The pH decreased quickly from 12.4 to below 10.0 in 7 hours, and the final pH of the mixture was about 9 after 18 hours. The maximal COD$_{tot}$ removal rate was about 40% (Figure 2).

The aerobic activated sludge utilized in the treatment of the printing and dyeing industrial wastewater (pH 9.10–12.59) has been reported to disperse and become inhibited when the influent pH was above 11.1, which could not be avoided even if the HRT was over 24 hours under an influent pH of 11.6 (Baohong et al. 2002). But our results indicated that the aerobic activated sludge for the treatment of black liquor had not been influenced, even by an influent pH above 12. The possible reason for the rapid decrease of the black liquor’s pH was that alkaliphilic bacteria grew and produced a large amount of CO$_2$. This CO$_2$ reacted with the survival OH$^-$ in the black liquor and formed the anion of HCO$_3^-$, keeping the effluent pH at 9–10.

\[
\text{NaOH} + \text{CO}_2 \rightarrow \text{NaHCO}_3
\]  

The results of counting the alkaliphilic bacteria number indicated that it increased quickly in the beginning and entered into the logarithm period subsequently. The number of alkaliphiles reached the maximum after 3 hours, dropped rapidly to the order of 10$^8$ per millilitre, and then maintained at this level (Figure 3). In the logarithm period, the total number of alkaliphilic bacteria increased 10 times in 2 hours. The average generation time of alkaliphilic bacteria growing in black liquor (initial pH = 12.8, initial

![Figure 2](https://iwaponline.com/wst/article-pdf/60/12/3275/447463/3275.pdf)
COD = 7,732 mg/L) was about 36 minutes at 40°C by calculations. The dominant alkaliphilic bacteria isolated from the aerobic activated sludge had been classified into the genus of *Bacillus* and *Paracoccus* by ARDRA analysis and 16S rDNA sequences (Jinli et al. 2007).

**Effects of temperature and concentration of black liquor on COD removal in aerobic treatment**

The acclimated aerobic activated sludge was inoculated into fresh black liquor. The mixture was cultured in a micro-bioreactor for 24 hours aeration at 30°C and 50°C. The effects of temperature on the black liquor effluent in different fractioned COD, CODtot removal, total alkalinity, NH₃-N, TKN, lignin, MLSS, and MLVSS were measured. The different characteristics of black liquor before and after aeration are presented in Table 1. The results showed that the major component of black liquor COD was CODsol. The CODss and CODcol together composed only 8.1% of CODtot. The removals of black liquor CODtot were 41 ± 3% and 36 ± 4% at 30°C and 50°C, respectively. The MLVSS decreased from 4.50 g/L at 30°C to 3.35 g/L at 50°C. Total alkalinity (according to the CaO) of the black liquor increased slightly after the aerobic treatment.

The effects of the culturing temperature and the concentration of black liquor on CODtot removal by aerobic activated sludge were tested further. The black liquor (COD = 17,452 mg/L, pH = 13.0) and the aerobic activated sludge acclimated at different temperatures were mixed separately. The mixtures were cultured for three days in micro-bioreactors at 40°C, 50°C, and 55°C, after which 44%, 35%, and 21% CODtot removals were achieved, respectively (Figure 4). The results showed that the CODtot removal was affected greatly by the temperature. The COD removal rate declined notably when the treatment temperature was above 50°C. The COD removal rate at 55°C remained lower than that at 50°C, even when the retention time were prolonged. And the COD removal rate at 50°C was always lower than that at 45°C. The concentration of the black liquor had no significant effect on the CODtot removal rate under normal temperatures.

It has been reported that high-temperature aerobic processes have a particular advantage over other processes in treating high-strength wastewater that can support

*Table 1* | The water quality characteristics of influent black liquor and effluent after treated at 30°C and 50°C by aerobic-activated sludge for 24 hours

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Influent black liquor</th>
<th>30°C</th>
<th>50°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>12.6 ± 0.1</td>
<td>9.3 ± 0.1</td>
<td>9.6 ± 0.1</td>
</tr>
<tr>
<td>CODtot (mg/L)</td>
<td>6758 ± 304</td>
<td>3971 ± 227</td>
<td>4296 ± 235</td>
</tr>
<tr>
<td>CODss (mg/L)</td>
<td>208 ± 21</td>
<td>333 ± 36</td>
<td>362 ± 45</td>
</tr>
<tr>
<td>CODcol (mg/L)</td>
<td>6208 ± 312</td>
<td>3377 ± 206</td>
<td>3646 ± 283</td>
</tr>
<tr>
<td>CODtot removal (%)</td>
<td>342 ± 36</td>
<td>261 ± 30</td>
<td>288 ± 28</td>
</tr>
<tr>
<td>Total alkalinity (mg/L)</td>
<td>2052 ± 45</td>
<td>2461 ± 50</td>
<td>2425 ± 52</td>
</tr>
<tr>
<td>NH₃-N (mg/L)</td>
<td>40.4 ± 1.8</td>
<td>3.3 ± 0.2</td>
<td>2.8 ± 0.2</td>
</tr>
<tr>
<td>TKN (mg/L)</td>
<td>187.57 ± 9.58</td>
<td>151.31 ± 9.36</td>
<td>148.16 ± 9.62</td>
</tr>
<tr>
<td>Lignin (g/L)</td>
<td>1.88 ± 0.21</td>
<td>1.56 ± 0.18</td>
<td>1.52 ± 0.20</td>
</tr>
<tr>
<td>MLSS (g/L)</td>
<td>–</td>
<td>5.56 ± 0.9</td>
<td>4.20 ± 0.9</td>
</tr>
<tr>
<td>MLVSS (g/L)</td>
<td>–</td>
<td>4.50 ± 0.8</td>
<td>3.35 ± 0.8</td>
</tr>
</tbody>
</table>
autothermal operations (LaPara & Alleman 1999; Daniel et al. 2007) or hot wastes from industries such as pulp and paper producers (Barr et al. 1996; Tripathi & Allen 1999). However, it has also been reported that aerobic biological wastewater treatment at high temperatures has produced biomass that flocculates poorly or not at all. The COD$_{filt}$ and COD$_{tot}$ values were markedly higher in effluents at higher temperatures (Suvilampi et al. 2005; Vogelaar et al. 2002). Our experiments indicated that the alkaliphilic bacteria communities in the black liquor at high temperatures were generally less abundant than those in the black liquor at normal temperatures. More components of the black liquor could be metabolized by bacteria communities under normal temperatures than under higher temperatures. So the aerobic activated sludge played its biodegradation role better under normal temperatures. The final COD removal percentage was only related to the properties of the black liquor and the activated sludge, while high temperatures could cause alterations of the microbial communities in the activated sludge.

**Effect of pH on anaerobic biological treatment**

Acclimated anaerobic activated sludge was mixed with the original black liquor (pH = 12.3, COD = 2,521 mg/L) according to a ratio (V/V) of 1:1. Meanwhile, the activated sludge was mixed with the aerobic effluent of the black liquor (pH 9.7) according to a ratio (V/V) of 1:0.7 as a control. The two mixtures were cultivated constantly at 37°C. The effect of the starting pH on the anaerobic treatment was checked, and the results indicated that the anaerobic hydrolysis speed was relatively low when the starting pH of mixture was above 10 (using the original black liquor). This effect was reflected by the fact that the pH of the mixture dropped slowly and remained above 9.0, even 72 hours later. However, when the starting pH of the mixture was about 9.3 (using the aerobic effluent), the pH of the mixture dropped quickly and fell to about 8.4 in 24 hours, and the mixture was hydrolyzed thoroughly in 48 hours. These results obviously indicated that the starting pH of wastewater was crucial for the efficacy of the anaerobic process and that the aerobic effluent of the black liquor could be treated directly by anaerobic activated sludge.

**Effect of the degradation time of the first aerobic stage on COD$_{tot}$ removal**

To investigate the effect of the degradation time of the first aerobic stage on COD$_{tot}$ removal, the black liquor (pH = 12.8, COD = 8,707 mg/L) was subjected to the O/A/O process and various degradation time intervals for the first aerobic stage were tested respectively. In all these parallel experiments (O/A/O processes), the anaerobic stage lasted four days and the second aerobic stage were maintained at 37°C for 20 hours. The results showed that the COD removal rates of the anaerobic stage and the second aerobic stage decreased with the prolongation of degradation time of the first aerobic stage, and the total COD removal rates were remained invariably at 61%–65% (Table 2). Therefore, to maximize the efficacy of the anaerobic treatment, it was appropriate to prolong the retention time for the anaerobic stage and to shorten that for the first aerobic stage. By using this strategy, the running cost of wastewater treatment was reduced.

**Effect of acid adjustment process on biological treatment of black liquor**

Two processes (acidic-anaerobic-aerobic and O/A/O) were compared at the level of the COD$_{tot}$ removal for raw black liquor. The results showed that the acidic-anaerobic-aerobic and the O/A/O processes resulted in COD$_{tot}$ removal rates of 64.9 ± 3% and 68.7 ± 4%, respectively (Table 3). There was no significant difference between the efficacies of the two methods, but the O/A/O process was more economical than the acidic-anaerobic-aerobic process.
There were reports that the COD removal rate could reach 58%–64% when the influent COD concentration of cotton pulp wastewater was within 1,200–1,800 mg/L range and the pH was 8.4–8.6. The COD loading rate could reach 1.8–2.8 kg m$^{-3}$ d$^{-1}$, but the biodegradability (BOD$_5$/COD) of the pulp digestion wastewater could not be raised by hydrolytic acidification (Yang & Wang 1999).

The COD removal rates for cotton pulp digestion at a nearly neutral pH were similar to the results of cotton pulp digestion with a pH of more than 12. In theory, the total COD removal rate for wastewater bio-treatment was mainly determined by the wastewater’s components. The neutralization by adding acid could not alter the composition of wastewater’s components such as lignin, and thus could not increase the COD removal rate.

**Pilot-scale continuous experiments of the aerobic-anaerobic-aerobic process**

This experiment was performed in a black liquor treatment plant, and the black liquor came directly from the cotton pulp production. Anaerobic and aerobic activated sludge came from the treatment plant and was acclimated for about 25 days. The MLSS in the first stage aeration tank was measured to be about 12,000 mg/L after sludge acclimation. The experiment lasted two months, during which time the system ran stably.

At the beginning of the experiment, the pH and the COD$_{tot}$ of the influent were about 13.0 and 18,000–22,000 mg/L, respectively (Figure 5). Since the consistency of the black liquor was varied with time, the flow rate of the black liquor was regulated based on the measured pH. The inflow rate of the first aerobic treatment stage maintained at about 10–15 L per hour. The pH in the first aerobic tank was maintained at 9.0–9.2. In the first aerobic treatment stage, the wastewater contained a high content of utilizable nutrients. The first aerobic process ran at a constant flow with HRT of 72 hours, and after 60 days of continuous operation achieved an average COD$_{tot}$ removal rate of 45.5% and an average BOD$_5$ removal rate of 71.4%, corresponding to a volume loading rate of 3.4 kg COD m$^{-3}$ d$^{-1}$.

After the first stage sedimentation, an effluent of about 0.8–1 L/h entered the anaerobic phase. In the anaerobic

### Table 2 | Effect of the degradation time of the first aerobic stage on the efficacy of the followed anaerobic and second aerobic processes

<table>
<thead>
<tr>
<th>Degradation time of the first aerobic stage</th>
<th>pH</th>
<th>COD (mg/L)</th>
<th>pH</th>
<th>COD (mg/L)</th>
<th>pH</th>
<th>COD (mg/L)</th>
<th>pH</th>
<th>COD (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>10.3</td>
<td>8237 ± 415</td>
<td>9.7</td>
<td>7299 ± 408</td>
<td>9.5</td>
<td>6760 ± 330</td>
<td>9.3</td>
<td>6135 ± 321</td>
</tr>
<tr>
<td>II</td>
<td>8.6</td>
<td>4455 ± 431</td>
<td>8.4</td>
<td>3938 ± 376</td>
<td>8.3</td>
<td>3800 ± 366</td>
<td>8.1</td>
<td>3620 ± 328</td>
</tr>
<tr>
<td>III</td>
<td>9.2</td>
<td>3392 ± 251</td>
<td>9.1</td>
<td>3194 ± 259</td>
<td>9.2</td>
<td>3142 ± 238</td>
<td>9.2</td>
<td>3021 ± 202</td>
</tr>
<tr>
<td>COD$_{tot}$ Removal (%)</td>
<td>61 ± 3</td>
<td>63 ± 3</td>
<td>64 ± 3</td>
<td>65 ± 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

I: effluent of the first aerobic stage; II: effluent of the anaerobic stage; III: effluent of the second aerobic stage.

### Table 3 | Comparison of the acidic-anaerobic-aerobic process and the O/A/O process

<table>
<thead>
<tr>
<th>Process phases</th>
<th>acid-aerobic-aerobic process</th>
<th>O/A/O process</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>COD (mg/L)</td>
<td>pH</td>
</tr>
<tr>
<td>--------------------------------------------</td>
<td>------------------------------</td>
<td>---------------</td>
</tr>
<tr>
<td>Influent black liquor</td>
<td>12.8</td>
<td>8707 ± 360</td>
</tr>
<tr>
<td>Addition of HCl</td>
<td>9.3</td>
<td>–</td>
</tr>
<tr>
<td>Effluent of first aeration</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Starting of anaerobic culture</td>
<td>8.5</td>
<td>–</td>
</tr>
<tr>
<td>Effluent of anaerobic culture</td>
<td>7.7</td>
<td>3904 ± 454</td>
</tr>
<tr>
<td>Effluent of second aeration</td>
<td>9.2</td>
<td>3052 ± 292</td>
</tr>
<tr>
<td>COD$_{tot}$ Removal percentage (%)</td>
<td>–</td>
<td>64.9 ± 3</td>
</tr>
</tbody>
</table>
Figure 5 | Operation period for O/A/O process of treating black liquor in the pilot-scale experiment.
stage, the pH of wastewater decreased slightly to about 8.9. The COD and the BOD5 were reduced to 8,000–10,000 mg/L and 650 mg/L, respectively. The volume loading rate was only 0.4 kg COD m$^{-3}$ d$^{-1}$, and the COD removal rate was just 23.3%. There are two main reasons for the low COD loading and COD removal at the anaerobic stage: (1) After the first aerobic treatment, the BOD/COD of the wastewater fell from 0.35 to 0.18, indicating poor biodegradability. (2) Although the influent pH covered the basic needs of the anaerobic treatment, the total alkalinity of the wastewater was still too high and might inhibit the anaerobic treatment.

The effluent from the anaerobic stage entered the second aerobic phase entirely. In the second aerobic stage, the biodegradable matter in the wastewater had been essentially metabolized, and the average COD$_{tot}$ removal rate was 16.3%. The BOD$_5$ of the ultimate effluent was low to about 30 mg/L, and the BOD$_5$ removal rate stayed above 95%. The effluent COD$_{tot}$ of the three stages were 10,000–12,000, 8,000–10,000, and 6,000–8,000 mg/L, respectively. The effluent COD$_{tot}$ of the second aerobic stage was still high, mainly due to the remaining lignin (biological resistant COD).

Throughout the experimental runs, the influent flow rates and the circumstance temperatures were regulated, enabling a stable and continuous operation of the test device. The O/A/O process achieved an average COD$_{tot}$ removal rate of 65% and a BOD$_5$ removal rate of 95%. The biodegradable COD of the black liquor had been almost fully utilized.

CONCLUSIONS

In this paper, we reported an immediate aerobic-anaerobic-aerobic (O/A/O) process based on alkaliphilic bacteria and had particular advantages in the treatment of high-pH and high-concentration black liquor. The COD$_{tot}$ removal rate of the novel O/A/O process is similar to that of traditional acidic-anaerobic-aerobic process in lab-scale batch experiments, yet the O/A/O process seemed to be more economical.

The average generation time of alkaliphilic bacteria in black liquor was about 36 minutes at 40°C. The degradation capacity of the aerobic activated sludge was greatly affected by temperature. The total COD removal rates at different temperature were 44% (40°C), 35% (50°C) and 21% (55°C) in the batch experiments, respectively.

In the O/A/O process, the retention time of the first aerobic stage seemed to be insignificant for the final COD removal efficiency. The parallel O/A/O experiments with different retention time for the first aerobic stage all achieved a similar COD$_{tot}$ removal rate. On the other hand, a pH below 10 for the starting influent was shown to be significant for the efficacy of the anaerobic process.

The O/A/O process was carried out successfully by pilot-scale continuous experiments. The system was operated stably for two months and the O/A/O process achieved an average COD$_{tot}$ removal rate of 65% and a BOD$_5$ removal rate of 95%. For black liquor with an initial COD$_{tot}$ of 20,000 ± 2,000 mg/L and a pH of 13.1 ± 0.4, the first aerobic stage achieved an effluent COD$_{tot}$ of 11,000 ± 1,000 mg/L and a pH of 9.1 ± 0.1, corresponding to a volume loading rate of 3.4 kg COD m$^{-3}$ d$^{-1}$.

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