TREATMENT OF P-CRESOL WITH A RECIRCULATING UASB REACTOR USING THE CONCEPT OF KINETIC CONTROL

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ABSTRACT

A series of batch Biochemical Methane Potential (BMP) tests and an Upflow Anaerobic Sludge Bed (UASB) bioreactor were conducted to investigate the biodegradability of p-cresol. The inhibition of microbes caused by substrate accumulation due to shock loading, recirculating pump turn-off and thermal shock were also studied. The results showed that the microbial activity was inhibited or even poisoned in the high concentration range (1000 mg/L) of p-cresol. However, the volumetric loading of the reactor could be maintained relatively high at 8.0 kgCOD/m³.day, if the recirculation of effluent was used to maintain the substrate concentration in the reactor within a suitable range. The concept of so-called kinetic control was proved to be a critical strategy for the treatment of the inhibitory substrate. The results of shock loading, recirculation cessation and thermal shock tests all showed that the concentration control in the reactor would be of vital importance for the treatment of inhibitive compounds with biological processes, and the critical concentration of the highest degradation rate could be estimated with a modified Haldane equation derived from the batch BMP data.

KEYWORDS

UASB; BMP; recirculation; inhibition; shock loading; thermal shock.

INTRODUCTION

As the chemical industry grew rapidly in recent years, numerous chemicals were released to the environment. With inherent refractoriness, some chemicals not only exhibit resistance to the conventional biological treatment processes, but also present toxicity to the microbes. p-Cresol represents one of the major constituents in the coal gasification wastewater; the concentration is at the range of 1000 mg/L, and the toxic nature of p-cresol limits its biodegradability (Blum et al., 1986).

The concept of kinetic control was employed in this study. The results of both batch BMP and the reactor operation data showed that p-cresol would inhibit or even poison the microbial activity in the high concentration range (1000 mg/L). However, the volumetric loading could be maintained at a relatively high range with effluent recirculation to provide suitable in-tank concentration. The batch BMP test is an appropriate method to estimate the appropriate concentration of the highest degradation rate. Other operation problems, such as thermal shock, were connected to the substrate inhibition. Thus that the concentration control would be a vital parameter for the treatment of the inhibitive compounds with biological processes.

EXPERIMENTAL

The UASB bioreactor employed in this study consisted of plexiglass column with the height of
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180c I and internal dialeter of l0cI. Tbe top end of coluln was connected to a 30cI high expanded column with 30cm diameter; this expanded column decreased the upflow velocity and promoted better settling of suspended solids. A 15cm external diameter concentric plexiglass water jacket was installed to maintain a constant temperature of 35°C ± 1°C. The empty volume of the reactor was 21.3 litres. The gas produced was measured by the liquid displacement apparatus which had an automatic releasing electromagnetic valve and counter; the displacement volume was calibrated with a Shinagawa wet gas-meter. Fig. 1 illustrates a schematic diagram of the UASB bioreactor as described above.

The feeding solution consisted of p-cresol and glucose as carbon source, KH2PO4 (114mg/L as P), NH4Cl (220mg/L as N) and trace mineral salts (Cheng, 1984, except the multi-vitamin ethanol extracts) were added as nutrient; NaHCO3 was also added to provide 2000 mg/L alkalinity.

The anaerobic transfer apparatus used in the batch BMP tests is shown in Fig. 2. The operation procedures were those modified from Owen et al. (1978); the nutrient composition used in the batch tests also followed Owen.

The analytical methods adopted in this study followed the Standard Methods except the following items:
Gas production in the batch tests was measured with glass syringe (Owen et al., 1978). Gas composition was analyzed by Hitachi 164 Gas Chromatograph using a 12' x 1/4'' stainless column packed with Porapak Q & Porapak T. p-Cresol was analyzed by Varian 5060 Liquid Chromatograph (30cm x 4mm Micropak MCH-5 column; eluent: 50% CH3CN (1% acetic acid) and 50% H2O (1% acetic acid); detector: Varian UV50 (280nm)) (Chao and Suatoni, 1982) or Varian 3700 Gas Chromatograph (Column: SP1240DA, 2M).

RESULTS AND DISCUSSION

Acccllatjon and Operation of the DASB Bjoreactors

The UASB bioreactor was seeded with anaerobic sludge taken from a pulp-mill wastewater lagoon. During the start-up period, the anaerobic sludge was withdrawn from the UASB reactor and investigated with a series of BMP batch tests. The results shown as Fig. 3 indicate that the degradability of p-cresol with this bottom sludge was relatively high compared with Blum et al. (1986) and Fedorak et al. (1986). However, the microbial activity was inhibited in the higher concentration range (more than 500 mg/L).

According to the conventional concept of anaerobic digestion, methanogenic reaction is the rate-limiting step and the time-consuming procedure. Acclimation of Methanosarcina species should be enhanced by high strength of biodegradable substrates, such as glucose, acetic acid and methanol which were fed into the continuous-flow UASB. After 113 days of start-up, 200 mg/L of p-cresol was fed along with glucose substrate. Hydraulic retention time of 24 hours was maintained throughout the first operation stage of UASB process. The operation data indicated that the acclimation of the sludge was quite slow compared with the batch BMP data; it seemed that the degradation rate of p-cresol was slower in the presence of high concentration of glucose and which would further be proved with the batch BMP test and the anaerobic metabolic pathway of p-cresol. However, the removal efficiency of p-cresol increased gradually when the glucose concentration was decreased stepwise.

The degradability of p-cresol was getting higher and higher after the decrease and cessation of the addition of glucose, and the volumetric loading of reactor was augmented.

Fig. 1. Schematic of UASB bioreactor.
Fig. 2. The anaerobic transfer apparatus for batch BMP test.
Treatment of p-cresol with a UASB reactor

As the loading increased, the gas production rate became greater gradually and increased up to a high value of 7.25 kg COD/m$^3$. day via the increase of influent concentration and the maintenance of constant HRT. The removal efficiency of both p-cresol (Fig. 4) and COD was maintained relatively high in the duration of the operation; the operation data of the first stage is shown in Table 1.

**TABLE 1: Upgrading Performance of UASB Reactor with Increasing Concentration in the First Duration**

<table>
<thead>
<tr>
<th>run</th>
<th>date (mg/L)</th>
<th>p-cresol influent</th>
<th>p-cresol effluent</th>
<th>%Removal</th>
<th>HRT (days)</th>
<th>Volumetric Loading (kg COD/m$^3$. day)</th>
<th>p-Cresol C.O.D</th>
<th>Gas Production Rate (L/day)</th>
<th>% Methane</th>
<th>% Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>332–347</td>
<td>1000</td>
<td>0</td>
<td>100</td>
<td>1.0</td>
<td>2.52</td>
<td>1.0</td>
<td>25.7</td>
<td>67</td>
<td>91.7</td>
</tr>
<tr>
<td>2</td>
<td>348–357</td>
<td>1500</td>
<td>0</td>
<td>100</td>
<td>0.97</td>
<td>3.89</td>
<td>1.55</td>
<td>41.9</td>
<td>66</td>
<td>95.3</td>
</tr>
<tr>
<td>3</td>
<td>358–390</td>
<td>2000</td>
<td>0</td>
<td>100</td>
<td>1.0</td>
<td>5.04</td>
<td>2.0</td>
<td>52.4</td>
<td>66</td>
<td>92.1</td>
</tr>
<tr>
<td>4</td>
<td>391–401</td>
<td>2500</td>
<td>0</td>
<td>100</td>
<td>1.04</td>
<td>6.05</td>
<td>2.4</td>
<td>62.7</td>
<td>64.8</td>
<td>90.1</td>
</tr>
<tr>
<td>5</td>
<td>402–408</td>
<td>3000</td>
<td>1.4</td>
<td>99.9</td>
<td>1.04</td>
<td>7.25</td>
<td>2.88</td>
<td>79</td>
<td>62.7</td>
<td>91.6</td>
</tr>
</tbody>
</table>

As the loading increased, the gas production rate increased gradually and reached a high value of 80 L/day, which corresponded to the volumetric loading of 7.25 kg COD/m$^3$. day with HRT of 1.04 days and influent concentration of 3000 mg/L. Owing to the high turbulence evoked by the rising bubble, the solids concentration in the sludge blanket increased substantially, and the recirculating pump was turned off due to the clogging problem. As the influent concentration of p-cresol increased abruptly from about 400 mg/L directly to 3000 mg/L, the gas production rate dropped down rapidly and the effluent p-cresol reached 1700 mg/L within the duration of 1 HRT, and the bioactivity of microbes was seriously inhibited. After the replacement of reactor liquor with the effluent of the other UASB, 200 mg/L of p-cresol was refed; however, both the gas production and the p-cresol degradation were almost zero, which indicated that the microbes were poisoned because of the presence of high concentration of p-cresol, and the UASB unit needed to be restarted.

In the restart period, 500 mg/L glucose was fed along with 200 mg/L p-cresol to maintain the bioactivity of microbes.
Microbial activity but not to retard the p-cresol degradation. The better acclimation is shown in Fig. 5 which was compared with the first stage of the operation (Fig. 4). In order to avoid the concentration inhibition caused by the mechanical trouble, the influent was kept within 1000 mg/L of p-cresol except during the period of shock loading tests, and the loading was promoted via the shortening of HRT. The operation data of the second stage are shown in Table 2.

**Table 2: Upgrading Performance of UASB Reactor with decreasing HRT in the Second Duration**

<table>
<thead>
<tr>
<th>run</th>
<th>date</th>
<th>influent</th>
<th>Effluent</th>
<th>p-cresol (mg/L)</th>
<th>Removal (%)</th>
<th>HRT (days)</th>
<th>Volumetric Loading (kg COD/m³-day)</th>
<th>Gas Production Rate (L/day)</th>
<th>% Methane</th>
<th>% Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>604-608</td>
<td>1000</td>
<td>0</td>
<td>100</td>
<td>0.9</td>
<td>0.2</td>
<td>1.11</td>
<td>28.0</td>
<td>65</td>
<td>92.3</td>
</tr>
<tr>
<td>2</td>
<td>638-642</td>
<td>1000</td>
<td>0</td>
<td>100</td>
<td>0.72</td>
<td>0.37</td>
<td>1.38</td>
<td>34.9</td>
<td>65</td>
<td>88.0</td>
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<tr>
<td>3</td>
<td>657-661</td>
<td>1000</td>
<td>1.0</td>
<td>99.9</td>
<td>0.55</td>
<td>0.5</td>
<td>1.83</td>
<td>46.1</td>
<td>65</td>
<td>87.8</td>
</tr>
<tr>
<td>4</td>
<td>739-741</td>
<td>1000</td>
<td>1.0</td>
<td>99.9</td>
<td>0.42</td>
<td>0.4</td>
<td>2.36</td>
<td>59.4</td>
<td>65</td>
<td>86.1</td>
</tr>
<tr>
<td>5</td>
<td>746-752</td>
<td>1000</td>
<td>6.0</td>
<td>99.4</td>
<td>0.35</td>
<td>0.1</td>
<td>2.83</td>
<td>71.8</td>
<td>65</td>
<td>87.8</td>
</tr>
</tbody>
</table>

**Kinetic Control in UASB Bioreactor**

To control the substrate concentration within an appropriate range was a critical control strategy for treating inhibitive compounds such as phenolics. Lower concentration of substrate decreased the rate of the reaction with limited loading, while a too high concentration of p-cresol would contribute to microbial inhibition; it even could cease the biodegradation. The serious effect elicited by the recirculation cessation in the first stage was a perceptible evidence of this kind of inhibition.

In the second stage of the operation, the concept of so-called "Kinetic Control" was introduced. The substrate concentration in the UASB reactor was maintained within a suitable range via the recirculation of the effluent, and the batch BMP test was employed to obtain the control parameters for the reactor operation.

Three sets of sludge were taken from the reactor during the different operation periods, and conducted with the BMP tests to investigate the variation of microbial activity in the duration of the operation. The highest rate R* and the corresponding critical concentration S* estimated from the initial specific reaction and gas production rate by modified Haldane inhibition model (Edwards, 1970) could be used as the control factor for the UASB operation. Both p-cresol degradation (Fig. 6 and 7) and gas production showed that the microbial activity increased with the duration of the operation. However, the biodegradativity to the high concentration of p-cresol did not increase, but even became worse after a period of operation, which was the same as the results of the recirculating UASB treating phenol (Cheng and Ma, 1988).

![Fig. 6. The p-cresol degradation in the first BMP test.](https://iwaponline.com/wst/article-pdf/24/5/133/102009/133.pdf)

![Fig. 7. The p-cresol degradation in the second BMP test.](https://iwaponline.com/wst/article-pdf/24/5/133/102009/133.pdf)
Treatment of p-cresol with a UASB reactor

Modified Haldane Equation

\[ R = \frac{R_{\text{max}} \cdot S \cdot \exp\left(-\frac{S}{K_i}\right)}{S + K_s} \]

- \( R \): Specific reaction rate (mg-cresol/g VSS . day) or Specific gas production rate (ml/g VSS . day)
- \( R_{\text{max}} \): Maximum reaction rate or Maximum gas production rate
- \( S \): p-cresol concentration (mg/L)
- \( K_s \): the saturation constant
- \( K_i \): the inhibition constant

**TABLE 3. THE MODIFIED HALDANE MODEL AND THE CORRESPONDING UASB DATA**

<table>
<thead>
<tr>
<th>Run</th>
<th>p-Cresol (mg/L)</th>
<th>HRT Recirculation (days)</th>
<th>VSS Gas Production (g)</th>
<th>pH</th>
<th>Gas Production (ml/gVSS/day)</th>
<th>p-cresol</th>
<th>( K_s )</th>
<th>( K_i )</th>
<th>( S^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>543</td>
<td>185</td>
<td>0.88</td>
<td>5</td>
<td>213</td>
<td>15</td>
<td>3.9</td>
<td>19.6</td>
<td>41</td>
</tr>
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<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>670</td>
<td>0</td>
<td>0.87</td>
<td>5</td>
<td>185</td>
<td>21.4</td>
<td>9.0</td>
<td>118</td>
<td>75</td>
</tr>
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<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>950</td>
<td>130</td>
<td>0.87</td>
<td>5</td>
<td>164</td>
<td>25.9</td>
<td>121</td>
<td>158</td>
<td>100</td>
</tr>
</tbody>
</table>

The results showed that the degradation rate of p-cresol would be slower if the concentration was increased to over 500 mg/L, and the inhibition occurred in the higher concentration range. At the critical concentration \( (S^*) \), the highest degradation rate fell down in the range of 100 to 200 mg/L. If the in-tank concentration of p-cresol was adjusted around \( S^* \) level with the feed concentration and appropriate recirculation rate of the treated effluent, the performance of UASB reactor would achieve the highest reaction rate. The plug-like flow in UASB reactor also accomplish high efficiency of p-cresol degradation. The so-called "kinetic control" strategy did successfully perform in another UASB system to treat 2000mg/L phenol with short hydraulic retention time of 6 hours and an extremely high volumetric loading at 20 kgCOD/m^3.day (Cheng and Ma, 1988). The same strategy will be expected to increase the volumetric loading of p-cresol.

A purposeful shut-down of recirculation pump was used to investigate the inhibition effect due to concentration built up. As recirculation stopped, the inlet concentration increased to the influent level at once, and the gas production rate would drop down significantly.
which could be concluded from the kinetic model in Fig. 8. Fig. 9 shows that the p-cresol in the sludge bed built up as soon as the recirculation stopped and reached almost to the influent level within 10 hours, the gas production rate was only 21% of the original value, and the microbial activity was seriously inhibited. To prevent the sludge deterioration in the high concentration p-cresol environment, the recirculation was resumed after 17 hours of cessation. However, the high effluent p-cresol did not provide meaningful dilution to the influent concentration. The inlet p-cresol maintained over 500 mg/L and effluent p-cresol still went up; the process was not restored. Later the influent was stopped to lower the in-tank concentration for two days in order to recover the original microbial activity. Nevertheless, the gas production rate after refeeding was only 60% of the original value; it meant that some microbes were poisoned in the duration of recirculation cessation. As time went by, the substrate accumulation occurred and the gas production rate lessened gradually; the loading needed to be lowered down to prevent the microbial inhibition.

Effect of Shock Loading on the UASB Reactor

The substrate accumulation and the further inhibition would be a consequence of shock loading, however, the degree of inhibition depended on the overall microbial activity and the extent of the shock loading. Several sets of shock loading tests were conducted to investigate this kind of inhibition.

In case I, the reactor was operated under its permissible loading and the magnitude of the shock loading was still in the reasonable range; the reactor would maintain its good performance. The gas production rate increased proportionally to a stable value, and the effluent p-cresol increased a little bit during the initial stage and then dropped down to the original value. Nevertheless, the residual p-cresol in the sludge bed bottom rose to a certain extent and the reactor maintained its good performance.

In case II, a small scale increase of loading was applied to a reactor which was operated at its march loading. The gas production rate would keep up its original value, however, the p-cresol in the effluent, sludge bed and the inlet built gradually to a certain extent according to the magnitude of shock loading. If the loading was sustained, the raise of gas production and the further concentration dropping down would be the consequence of the increase of biomass and the microbial activity. On the other hand, the reactor would recover its performance if the pulse shock loading was stopped.

![Fig. 10. Effect of shock loading (case III)](image)

![Fig. 11. Effect of step shock loading (case III)](image)

As the applied shock loading was far beyond the microbial activity in case III, the inhibition caused by the substrate accumulation would occur. In the early stage, the inlet concentration was maintained under the inhibitive range through the dilution of recirculated effluent, while the gas production would sustain the original rate or increase a little bit, which depended on the overall microbial activity. As time went on, the substrate concentration in the effluent and the sludge bed built up, and the inlet concentration would increase as a consequence of effluent deterioration. If the pulse shock was applied and the loading resumed to the original value before the inlet concentration was built up to inhibit the microbial activity, the reactor would recover its good performance as soon as the loading dropped down. When the step shock was undertaken, the inlet concentration would build up to the inhibitive range and the gas production rate dropped down rapidly due to microbial inhibition. Fig. 10 shows the reactor performance when the loading was augmented from 3 to 4.5 kg COD/m³·day with increase of influent p-cresol from 1000 to 1500 mg/L. As soon as the inlet concentration reached around 500 mg/L p-cresol, the abrupt decrease of gas production rate and the increase of both effluent and sludge bed concentration meant that the microbial activity was inhibited.
Comparing with the inhibition model in Fig. 8, the symptom of concentration inhibition was proven again with certain significance. However, it seemed that the reactor could maintain the good performance via the suitable operation strategy. When the shock loading was applied, the increase of gas production rate would be a good parameter whether the reactor could withstand the shock or not. The expected effluent and inlet concentration were calculated from the material balance of gas production rate and the recirculation ratio. It could be predicted that if the reactor would suffer from the substrate inhibition via the inhibition model (Fig. 8) and the calculated data, then the suitable measure would be adopted. Resuming the original loading as in case II is a good method; lowering the extent of shock loading is another way. Fig. 11 shows the reactor performance when 100% increase of loading was applied from 3 up to 6 kg COD/m$^3$.day; the gas production data indicate that the loading was beyond the microbial activity, and the inlet concentration built up to over 400 mg/L in 12 hours, which nearly reached the margin of inhibition. The loading was lowered down to 45% increase; the stable gas production rate and the dropping down of concentration indicated the good performance of the reactor. Nevertheless, it could be a feasible means to prevent the reactor from inhibition at the time of shock loading via the increase of recirculation ratio. The expected effluent was estimated from the material balance of gas production rate and the applied loading, and the recirculation ratio which would keep the inlet concentration under the inhibition was calculated with influent and expected effluent concentration. In this manner, the reactor could be operated in the same way as in case II and no inhibition would occur.

**Temperature Effect on UASB Process**

Conventional anaerobic processes were operated at thermophilic or mesophilic temperature to maintain the methanogenic activity. Relatively lower temperature of an anaerobic system would decrease the biodegradation rate and contribute to the substrate accumulation in the reactor. Therefore, the inhibitive p-cresol deteriorated the performance of UASB system.

![Fig. 12. Thermal effect on the p-cresol degradation rate with incubation temperature of 35, 27.5 and 20°C.](image)

![Fig. 13. Responses of effluent p-cresol and gas production rate of UASB when temperature changed from 35°C to 21°C.](image)

A series of BMP tests at different temperatures were employed to investigate the effects of temperature drop to the degradation of p-cresol. The anaerobic sludge was withdrawn from the reactor treating 650 mg/L of p-cresol with volumetric loading of 1.84 kgCOD/m$^3$.day. Two sets of batch test with concentration of 100 and 200 mg/L were conducted in 35, 27.5 and 20°C incubation chambers. The p-cresol degradation in terms of incubation time is shown in Fig. 12. It indicates that the temperature effect was pronounced on the degradation of p-cresol. Relationship between the p-cresol degradation rate ($R_\text{p}$) and temperature ($t$) was evaluated as the following equation and the results are shown in table 4.

$$R_\text{p} = R_\text{p}_0 \times e^{a \cdot t}$$

In this study, the temperature factor $a$ is estimated as 1.087, that is comparative to the reference (Table 5). The larger $a$ value attained more sensitively to temperature change.

Process response of the drop in temperature is illustrated in Fig. 13. After 30 hours of temperature change from 35°C down to 21°C, the p-cresol concentrations increased gradually in the inlet, the sludge bed #1 section and the effluent respectively. The maximum effluent concentration reached 333 mg/L p-cresol, while the inlet concentration attained 558 mg/L that
was on the margin of p-cresol inhibition (500 mg/L in BMP test, Fig. 8). At the same time, the biogas production rate decreased to 40% of the original rate at 35°C. To prevent the further deterioration of the reactor, the operation temperature was restored to 35°C. Then the gas production rate increased significantly. The effluent concentration decreased to the original level after 20 hours. According to the response of gas production rate and effluent p-cresol concentration, this UASB system was very sensitive to the thermal shock.

CONCLUSIONS

It was definitely important to maintain appropriate in-tank concentration of inhibitive p-cresol in order to prevent the substrate inhibition and to provide high bioactivity in the reactor. The concept of kinetic control with recirculation of effluent to dilute the high inhibitive concentration could be applied to promote the removal efficiency of the inhibitive substrate. The batch BMP test is an appropriate method to evaluate the bioactivity of the sludge and to estimate the critical concentration of highest activity for the optimization of the UASB operation.

The temperature factor $e = 1.087$ meant that the p-cresol degradation was very sensitive to the thermal shock, and the slower degradation rate at the lower temperature could cause the p-cresol accumulation in the UASB bioreactor and the further inhibition of the microbes. It is suggested that the automatic monitoring and control devices should be provided to shutdown the feed when the heating system is damaged.

REFERENCE


