Treatment of coke plant wastewater by SND fixed biofilm hybrid system

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Received 23 February 2006; revised 26 April 2006; accepted 8 May 2006

Abstract

In this article, coke plant wastewater was treated by a simultaneous nitrifying and denitrifying (SND) fixed biofilm hybrid system. The results showed that suitable parameters of the system were important for the performance of the bio-degradation system. The chemical oxygen demand (COD) removal efficiency in this system was satisfactory, higher than 94%, and ammonia nitrogen was higher than 95%. The effluent COD concentration could meet the discharge standard, except for very few situations. The results showed that a sufficient carbon source was important for making ammonia nitrogen concentration meet the discharge standard. Then the TN removal efficiency in this system can be brought higher than 94%. Dissolved oxygen (DO) is very important to the performance of the SND bio-degradation system, and the suitable DO is about 3.5–4.0 mg/L at the forepart of reactor. In addition, the performance of the system was almost not affected by pH value. The results show that the system is feasible to treat coke plant wastewater.

Key words: coke plant wastewater; SND fixed biofilm; ammonia nitrogen; COD; carbon source

Introduction

Coke plant wastewater is a kind of typical industrial wastewater, which is difficult to biodegrade. In practical industry, the composition and the amount of coke plant wastewater greatly varies from one factory to another, depending on the quality of raw coal, the operation parameters, and so on. Because of the presence of refractory and biologically inhibitory organic compounds, such as PAHs and high ammonia content (Stamoudis and Luthy, 1980; Luthy et al., 1983; Grady, 1990; Wen et al., 1991), coke plant wastewater is very harmful to human health. At present, domestic coke plant wastewaters are mainly treated by conventional activated sludge system. This system is unsatisfactory in removing high concentration of ammonia nitrogen and refractory compounds, because the nitrifying bacteria are difficult to live in a suspended growth system. Aimed at this problem, many researchers tried to improve the reactor structure (Zhang et al., 1998; Li et al., 2001; Jiang, 1993; Sutton et al., 1999), devise new technological process (Shu, 1990), cultivate efficient bacteria (Hong et al., 1999; Hyungseok, 1999) and so on, to meet the discharge standards.

In the past decades, extensive work had demonstrated that biological nitrogen removal process was always carried out in more-than-two separate reactors, such as anoxic/aerobic (A/O) system and anaerobic/anoxic/aerobic (A/A/O) system. In recent years, many studies had demonstrated the phenomenon of non-assimilation loss of nitrogen (Hong et al., 1999). Some researchers also found that, in a special environment, denitrification could also be achieved in aerobic condition, i.e., aerobic denitrification (Kong and Li, 2004; Christine and Sabine, 1998; Robertson et al., 1988). The main evidence was the loss of total nitrogen (TN).

One of the problems in biological nitrogen removal of coke plant wastewater is the lack of carbon resource, which acts as electron donor in denitrification. The unavailable organic carbons in coke plant wastewater further reduce the ratio of organic carbon to nitrogen. Moreover, alkalinity is needed in aerobic reactor to compensate the alkalinity consumption by nitrification. Simultaneous nitrifying and denitrifying (SND) phenomenon were reported in some research recently. In the process, nitrifying and denitrifying reactors were finished in one reactor. Obviously, different microenvironments were needed to inoculate different bacteria. The only way was by controlling the operational parameters temporally or spatially. The sequencing batch reactor was one example for SND; in which aerobic and anaerobic conditions were kept according temporal schedules (Yu et al., 1997). The present studies on SND were mostly focused on sequencing batch reactor. But in the reactors, the particle size of sludge was too small and easily be penetrated by dissolved oxygen (DO). High DO could inhibit the denitrifying process, which would result in bad performance.

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The objective of this study was to investigate the feasibility of SND process via different microenvironments spatially. In order to insure the retention time of nitrobacteria, and enhance the biofilm ability to resist the shock, packing media were used. On the basis of the characters of the SND system, the organic pollutants and nitrogen removal rates were studied. The major influential factors were also investigated, and the optimum operational conditions were selected.

1 Materials and methods

Experiments were conducted to study the degradation efficiency of the SND fixed-biofilm hybrid system. The flow sheet is shown in Fig.1. The dimensions of the main reactor was 1800 mm×500 mm×750 mm, and the effective volume was 1800 mm×500 mm×500 mm. The aerators were arranged only near the inlet of the reactor, so the main reactor was divided into three sub-reactors in the ratio of 4:13:1. The sub-reactors were pre-aerated region, biofilm reaction region and post-aerated region in order. A secondary sedimentation tank was applied to discharge water with better quality. The volume of sedimentation tank was 54 L.

Except a few tests, the influent was collected from the conventional coke plant wastewater treatment plant of Baosteel Chemical Factory in Shanghai, China. The wastewater quality is shown in Table 1. During most tests, the wastewater quality varied in terms of COD and NH$_3$-N concentrations.

In coke plant wastewater, phosphorus was not present in sufficient amount, so phosphorus from an external source should be added. According to the ratio of N:P=5:1, KH$_2$PO$_4$ was dosed into the influent. The seeding sludge for the system was obtained from the aerobic pond of Quyang Wastewater Treatment Plant in Shanghai and some sewer anaerobic sludge.

Soluble COD, pH, organic-N, NH$_3$-N, NO$_2$-N, and NO$_3$-N were measured in accordance with methods as described in standard methods for the examination of water and wastewater (Hong et al., 1999). TN includes NO$_2$-N, NO$_3$-N and KN (NH$_3$-N and organic-N).

2 Reactor start-up and operation

2.1 Reactor acclimation

Start-up of the reactor was accomplished by a progressive increase in the loading rate. The initial influent COD and NH$_3$-N concentrations were kept below 200 mg/L and 30 mg/L respectively, avoiding the irrecoverable impact on the microorganisms. After stable operation was achieved, the COD load was increased appropriately. The performance of the reactors improved with the acclimation time. And the reactor was operated at 13–20°C. The hydraulic retention time (HRT) was kept at about 36 h, and the DO in the pre-aerated region was maintained at 4.0–4.5 mg/L. In the acclimation, NaHCO$_3$ was also dosed into the influent, controlling the pH value in the range of 6.0–7.0.

During the acclimation period, the color of the biofilm in the back region changed to be darken. At the day 50, the organic pollutants and ammonia nitrogen were biodegraded effectively. The removal efficiencies were above 70% for COD and 80% for NH$_3$-N, indicating that the nitrifying and the denitrifying bacteria were acclimated.

2.2 Selection of the operational parameters

Because the reactor studied herein was a hybrid system, the affecting factors and their influencing regulars were very complex. In order to find out the rough regularity simply, orthogonal method was adopted. Based on the previous studies, HRT, the influent COD and NH$_3$-N concentrations, pH and DO were selected as the studied factors. The orthogonal layout is shown in Table 2. Herein the C column was arranged as an error column.

In this test, the COD removal rate was chosen as the index, and the nitrogen removal would be studied in follows. The influent in this test was synthetic. The pH was adjusted by NaHCO$_3$.

Table 3 shows the extreme difference analyst of the COD removal efficiencies. It could be concluded that, DO was the most remarkable factor to the system, and the extreme difference of DO was as high as 54.62%. According to

![Fig. 1 Experimental set-up for SND fixed biofilm hybrid system. (1) Storage tank; (2) pH meter; (3) influent pump; (4) air pump; (5) aerator; (6) main reactor; (7) fixed biodegrading area; (8) secondary sedimentation tank; (9) DO meter; (10) flowmeter.](image)

Table 1 Influent water quality

<table>
<thead>
<tr>
<th>Index</th>
<th>COD$_{c}$</th>
<th>BOD$_5$</th>
<th>NH$_3$-N</th>
<th>Organic-N</th>
<th>Cyanide</th>
<th>Phenol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (mg/L)</td>
<td>900–2000</td>
<td>350–800</td>
<td>150–420</td>
<td>30–90</td>
<td>2–7</td>
<td>80–120</td>
</tr>
</tbody>
</table>

The data were offered by the plant in October 2004.
the extreme differences in Table 3, the important order of those studied factors was DO > pH > influent COD concentration. In addition, the results also showed that, the influence of NH$_3$-N concentration on COD removal was small (4.38%), even lower than the error column (5.90%). In other words, the effect of other factors might be more remarkable than NH$_3$-N concentration.

From Table 3, it could be founded that, DO and pH both had a maximum, i.e., a optimum value. The COD removal rate increased with HRT proportionally when the HRT was relatively short. Until HRT was longer than a special value, the influence of it would be very small.

Depending on the orthogonal tests, the optimum operational conditions could be settled tentatively as HRT 44.1 h, DO 3.5–4.0 mg/L, pH 8.

Further, the system was operated at the above optimal conditions continuously for 25 d, with coke plant wastewater used as influent. The results are shown in Fig. 2. The result indicated that the first four days was an adapting period. After this, the average COD removal rate was higher than 92%, and the effluent content of COD was basically adequate for discharge.

In a conclusion, the SND biofilm hybrid system was feasible to remove the organic pollutants in coke plant wastewater.

### 3 Results and discussion

Coke plant wastewaters are harmful because of their high ammonia content. So the efficiency of nitrogen removal is of the same importance.

#### 3.1 Hydraulic retention time (HRT)

Nitrifying bacteria are autotrophic microorganisms, which reproduce themselves much slower than heterotrophic microorganisms. In this respect, the total HRT should significantly impact on nitrogen removal, especially in this SND hybrid system. According to the orthogonal tests, keeping pH 7.5–8.5, DO in pre-aerated region at 3.5–4.0 mg/L, the HRT impact was further explored. The steady-state performances of the hybrid process with seven different HRT levels are shown in Fig. 3. Average performance of every HRT was obtained from eight measurements in 4 d, with the system operated under the same condition.

The curves in Fig. 3 shows that, when the HRT < 40.1 h, the NH$_3$-N removal rate increased in proportion to the HRT. Raising the HRT from 40.1 h to 48.4 h, the NH$_3$-N removal almost remained stable, while TN and COD removal rate both increased to a certain extent. It could be inferred that denitrifying rate was raised obviously.

When the HRT was kept too low, higher flow velocity could result in higher transfer rate. On the other hand, the microorganisms were shocked and their activities decreased. At a serious condition, they might be washed out. If the transfer rate of DO higher than its consumption rate by aerobic nitrifying bacteria, the residual DO would be brought to denitrifying section. The anaerobic bacteria were inhibited and denitrifying rate decreased. Then the

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**Table 2 Designed orthogonal layout**

<table>
<thead>
<tr>
<th>Level</th>
<th>HRT (h)</th>
<th>COD (mg/L)</th>
<th>Error column</th>
<th>DO (mg/L)</th>
<th>pH</th>
<th>NH$_3$-N (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Level 1</td>
<td>32.5</td>
<td>880–920</td>
<td></td>
<td>6.5–7.5</td>
<td>6</td>
<td>120–140</td>
</tr>
<tr>
<td>Level 2</td>
<td>44.1</td>
<td>1580–1620</td>
<td></td>
<td>2.0–2.5</td>
<td>7</td>
<td>30–50</td>
</tr>
<tr>
<td>Level 3</td>
<td>24.8</td>
<td>1280–1320</td>
<td></td>
<td>3.5–4.0</td>
<td>8</td>
<td>200–240</td>
</tr>
<tr>
<td>Level 4</td>
<td>56.3</td>
<td>550–590</td>
<td></td>
<td>0.5–1.0</td>
<td>9</td>
<td>70–90</td>
</tr>
<tr>
<td>Level 5</td>
<td>61.6</td>
<td>1955–2000</td>
<td></td>
<td>5.0–5.5</td>
<td>5</td>
<td>340–360</td>
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**Table 3 Analysis of orthogonal result (%)**

<table>
<thead>
<tr>
<th>Level</th>
<th>HRT</th>
<th>COD</th>
<th>Error column</th>
<th>DO</th>
<th>pH</th>
<th>NH$_3$-N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Level 1</td>
<td>50.78</td>
<td>48.17</td>
<td>47.80</td>
<td>49.12</td>
<td>46.73</td>
<td>50.27</td>
</tr>
<tr>
<td>Level 2</td>
<td>53.87</td>
<td>54.07</td>
<td>53.70</td>
<td>47.17</td>
<td>49.49</td>
<td>47.86</td>
</tr>
<tr>
<td>Level 3</td>
<td>41.31</td>
<td>53.77</td>
<td>48.17</td>
<td>76.69</td>
<td>59.81</td>
<td>51.62</td>
</tr>
<tr>
<td>Level 4</td>
<td>52.94</td>
<td>42.58</td>
<td>50.53</td>
<td>22.07</td>
<td>54.06</td>
<td>49.02</td>
</tr>
<tr>
<td>Level 5</td>
<td>52.86</td>
<td>53.15</td>
<td>51.56</td>
<td>56.71</td>
<td>41.66</td>
<td>52.24</td>
</tr>
<tr>
<td>Extreme difference</td>
<td>12.56</td>
<td>11.49</td>
<td>5.90</td>
<td>54.62</td>
<td>18.15</td>
<td>4.38</td>
</tr>
</tbody>
</table>

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![Fig. 2 COD removal efficiency at the optimal conditions.](image1)

![Fig. 3 Influence of HRT on the system performance.](image2)
balance between nitrification and denitrification was destroyed.

As shown in Fig. 3, when the HRT was raised to 61.6 h, the performance of the system decreased again. It might be that the biofilm needed refresh continually due to the decrepitude of microorganisms. Too long HRT might slower the update periods of biofilm.

In order to keep the NH$_3$-N concentration meet the effluent standard, HRT should be kept in the range of 40.1–56.3 h in this study, and to COD concentration. HRT should be approximately 48.4 h. The corresponding removal rate was above 95% and 93% respectively. But the effluent TN and NO$_3$-N content needed to be further removed.

### 3.2 Dissolved oxygen (DO)

DO is an important factor to biological degradation process, not only for the COD removal as shown in orthogonal tests, but also for the NH$_3$-N removal. It has been verified that different bacteria have different suitable range of DO. In this SND study, DO was supplied by spot-aerated way, and the nitrifying and denitrifying were carried out in different local areas simultaneously. The desired aerobic and anaerobic microenvironments were realized through only the DO consumption by nitrifying bacteria and mass transfer. Thus it could be seen, the pre-aerated volume of airflow was of great importance.

Fig. 4 shows the removal efficiencies in different DO levels by SND system. And the HRT was kept at 44.1 h, pH in the range of 7.5–8.5.

The effects of DO on the removal of NH$_3$-N and TN differed, as shown in Fig.4. With the increase of DO from 2 to 4 mg/L, the NH$_3$-N removal rate rose from 33.10% to 95.22%, then the rate tended to be stable until the DO concentration rose to 6 mg/L. For the TN removal, there was an obviously turning point. At this point, the DO was 4 mg/L, and the TN removal efficiency reached its maximum, 82.87%. At the same point, the COD removal efficiency also reached the highpoint, 93.64%. However, higher DO brought the two efficiencies down notably. The main reason might lie in the particularity of SND process. The aerobic, anoxic and anaerobic conditions existed in different local areas simultaneously. The aerobic and anaerobic bacteria and mass transfer. Thus it could be seen, the pre-aerated volume of airflow was of great importance.

With the DO test, it could be found that, compared with those multi-stepped process, the SND hybrid system’s ability to resist the shock of DO was strengthened, and the feasible DO range was widened greatly. The system could adjust the proportion of its different microenvironments by itself, according to the wastewater quality.

### 3.3 Carbon source

During the HRT and DO tests, the effluent TN concentrations were never below 50 mg/L, even at the optimal HRT and DO condition. The results indicated poor denitrifying effect of coke plant wastewater. One of the possible reasons was that the carbon source was not present in sufficient amount in the wastewater. What is more, extensive studies (Zhang, 1996; Xu, 1994) show that the quality of many existing carbon sources in coke plant wastewater was bad and could not be used by microorganisms, which further worsened the problem. In theory, deoxidizing 1 g of NO$_3$-N to N$_2$ needs 3.7 g COD. The study on coke plant wastewater by Srqên Brqvnd (1994) showed that the wastewater could be denitrified fully only when the influent COD/NH$_3$-N>8. Many similar work (Chen, 1994; Zhang, 1989) also indicated that only when COD/NH$_3$-N>6–7, the external carbon source could be left out of account. All those studies evidenced the poor availability of the organic matter in coke plant wastewater.

Denitrifying bacteria were well known as heterotrophic microorganisms, so deficient carbon source might become the limitary substrate to them. Although the bacteria could make use of the internal carbon source to obtain energy under the low COD/NH$_3$-N ratio condition, but the denitrification was only about 1/10 of the normal denitrifying reaction (Wen, 1989).

In this study, methanol was used as external carbon source, and dosed in continuous way. The dosing point was 1300 mm away from the inlet. In the operation, the parameters were settled as, HRT around 44.1 h, DO between 3.5–4.0 mg/L, and pH in the range of 7.5–8.5. The results are shown in Table 4.

The removal efficiencies and the effluent concentrations of different types of nitrogen are also quoted in Fig.5.

Denitrifying bacteria used organic matters as electron donor, and NO$_3$-N as electron acceptor. With the supplement of methanol as carbon source, the denitrifying effect was improved and the effluent NO$_3$-N concentration decreased greatly. However, it could be found that more methanols not always meant better denitrifying perfor-

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**Fig. 4** Influence of pre-aerated volume on the system performance.
No. 2 Treatment of coke plant wastewater by SND fixed biofilm hybrid system

Table 4 Effects of external carbon source on the performance

<table>
<thead>
<tr>
<th>Methanol amount (g/h)</th>
<th>NH₃-N (mg/L)</th>
<th>COD (mg/L)</th>
<th>TN (mg/L)</th>
<th>Effluent NOₓ-N (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Influent</td>
<td>Effluent</td>
<td>Influent</td>
<td>Effluent</td>
</tr>
<tr>
<td>0.0</td>
<td>282.28</td>
<td>11.76</td>
<td>1653.23</td>
<td>98.82</td>
</tr>
<tr>
<td>0.4</td>
<td>270.85</td>
<td>10.84</td>
<td>1609.75</td>
<td>95.91</td>
</tr>
<tr>
<td>0.6</td>
<td>308.77</td>
<td>12.66</td>
<td>1544.91</td>
<td>91.64</td>
</tr>
<tr>
<td>0.8</td>
<td>287.45</td>
<td>12.80</td>
<td>1824.07</td>
<td>111.31</td>
</tr>
<tr>
<td>1.0</td>
<td>281.92</td>
<td>11.01</td>
<td>1531.51</td>
<td>93.22</td>
</tr>
<tr>
<td>1.2</td>
<td>315.03</td>
<td>43.93</td>
<td>1472.90</td>
<td>149.91</td>
</tr>
<tr>
<td>1.4</td>
<td>282.29</td>
<td>148.49</td>
<td>1445.82</td>
<td>389.39</td>
</tr>
<tr>
<td>1.6</td>
<td>283.10</td>
<td>178.75</td>
<td>1403.26</td>
<td>593.89</td>
</tr>
</tbody>
</table>

Influent COD concentration did not include the COD brought by methanol.

Fig. 5 Effect of external carbon source on the removal performance (a) and nitrogen in effluent (b).

3.4 pH and alkalinity

Microorganisms are very vulnerable and sensitive to the pH value of water. The preferential ranges for ammonia oxidizing bacteria and nitrate oxidizing bacteria are about 7.5–8.5 and 6.5–7.5 respectively. To denitrifying bacteria, the preferential range was 6.5–7.5. If the pH value was higher than 8, the denitrifying bacteria would be inhibited.

In normal treatment systems of coke plant wastewater, nitrifying and denitrifying reactions were placed in separate reactors. In the aerobic section, alkalinity was usually added to compensate its loss due to the nitrification. Otherwise, with the progress of nitrification, the pH of water would drop distinctly. Li (1999) studied the treatment of coke plant wastewater by an A/A/O system. It was proved that the alkalinity supplement amount had a great influence on the performance. The results also showed that, to keep the effluent adequate for discharge, the needed alkalinity rose with the increase of influent NH₃-N content.

On the other hand, denitrifying reaction produces amount of alkalinity, which might compensate the alkalinity loss to some extent. One of the important advantages of SND system was just the alkalinity cancellation compensation between the two reactions, and the supplement might be omitted.

In order to explore the effects of pH on the SND system, the pH in wastewater was adjusted by NaHCO₃. The results are plotted in Fig.6, it can be seen SND system showed high ability to sustain the pH fluctuates. In the range of pH 6.5–8.5, both NH₃-N and TN were removed satisfactorily. Only when the pH>9 or pH<6, the blight emerged. It also could be found during the study that, the system had excellent ability to resist the pH shock. After the pH dropped from 9 to the preferential range, the performance improved quickly. This advantage could simplify the operation and bring down the operating costs.

In addition, the optimal pH for COD removal was in accordance with the results of orthogonal tests, which was pH=8 as shown in Fig.6b.

During the test, the effluent pH values were also mea-

Influent COD concentration did not include the COD brought by methanol.

There were two possible results. With the increase of the concentration of substrate, heterotrophic bacteria propagated fast, so they became dominant bacteria, the bloom of heterotrophic bacteria might result in an inhibitory effect on nitrifying bacteria. On the other side, the heterotrophic bacteria might consume most of the dissolved oxygen chemicals, which were also needed by nitrobacteria to grow. The nitrifying bacteria were competitively inhibited.

Due to the hybrid character, poor nitrifying might destroy the balance of the system, and brought down the denitrifying rate in succession. Poor denitrification would further result in less consumption of carbon, which could worsen the nitrification. In summary, although an external carbon source could help the TN removal and improve the effluent quality effectively for coke plant wastewater; excessive amount might bring the whole system into a vicious circle.

In this study, the desired amount of external methanol was 0.8–1.0 g/h. Under this condition, the TN removal efficiencies were raised above 93%, and the effluent NOₓ-N reduced lower than 3 mg/L.

Thus it could be inferred that, in SND hybrid system, nitrifying and denitrifying were two interacting progress. And there should be an optimal balance point to the performance of the system as a whole. Compared with COD and DO, carbon source seemed more important to the TN removal from coke plant wastewater.

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During the test, the effluent pH values were also mea-
Fig. 6 Influence of pH value on NH$_3$-N removal (a), COD removal (b) and TN removal (c).

Fig. 7 Contrast of the pH value of influent and effluent.

4 Conclusions

The following conclusions could be drawn from the present investigation:

The SND fixed biofilm hybrid system was an effective process to treat the coke plant wastewater.

With the orthogonal tests, the optimal operational parameters were settled preliminarily. That was HRT 44.1 h, DO 3.5–4.0 mg/L, pH 8. Keeping the parameters at the optimal conditions, the average COD removal efficiency during 25-d continuous run was higher than 92%.

As the nitrogen removal efficiencies were concerned, the influencing factors were investigated one by one. For HRT, in order to keep the effluent qualities meet discharge standard, 40.1–56.3 h were needed for NH$_3$-N removal. To COD removal, HRT should about 48.4 h. The corresponding removal rate was above 95% and 93% respectively. DO was proved as an important parameter to the SND system in the investigation. And there existed a turning point for COD and TN removal. The DO at the turning point was 4 mg/L, and the TN removal efficiency reached its maximum, 82.87%. The COD removal efficiency reached the highpoint, 93.64%, under the same condition. And higher DO brought the two efficiencies down notably. Coke plant wastewaters were typical for their high ammonia content, accompanied by low ratio of carbon to nitrogen. And without any external carbon source, the effluent TN and NO$_x$-N content were difficult to be brought down fully. But excessive amount might bring the whole system into a vicious circle. In this study, the desired amount of external methanol was 0.8–1.0 g/h. In this condition, the TN removal efficiencies were raised above 93%, and the effluent NO$_x$-N reduced lower than 3 mg/L. As for the pH, in this study, the feasible range was widened remarkably as 6.5–8.5. And the system showed strong ability to resist shock. To the SND hybrid system, the alkalinity supplement might be omitted, which could reduce the operating costs greatly.

More work should be done on the aspects of microorganism analysis and identification in the system. The mechanism of nitrogen removal and biodegradation of organic matters might be studied in depth.

Acknowledgements: The authors are grateful for Prof. Zhao X Y of Chemical Department, School of Science, Tongji University and Feng Y Y of School of Biological Engineering, Tongji University for their guidance. The authors would also like to thank the Baosteel Corporation, Shanghai, China for the collaboration with this study and its financial support.

References


Li C J, Geng Y, Zhou Q et al., 2001. SMSBR characters in removing the organic matter and nitrogen in coke plant


