Effect of hydraulic retention time on ABR tail water treatment by contact oxidation process under low oxygen condition

Xiaolong Huang¹², Chunhong Shi¹²³, Zhenbao Wang¹² and Kai Jiang¹²

¹ School of Energy and Environmental Engineering, University of Science and Technology Beijing, Beijing 100083, China;
² Beijing Key Laboratory of Resource-oriented Treatment of Industrial Pollutants, Beijing 100083, China.
³ sch22@163.com

Abstract. Biological contact oxidation process of low dissolved oxygen was applied to the treatment of ABR tail water, which were pretreatment effluent for Island sewage. The reactor was built and filled with polyurethane suspension filler as carrier for biofilm growth in laboratory. The dissolved oxygen in the reactor is kept at 1.3-1.8mg/L to distinguish between traditional method which is 2.5-3.5mg/L. Influence of hydraulic retention time(HRT) on ABR tail water treatment by the process was studied. Results show that the system has good effect on removal of COD and TN under this condition. When HRT is among 4h to 12h, the removal rate of COD can be maintained at 80-90%. From period 1 to period 3, the removal rate of NH₄⁺-N and TN at the end of each period can be recovered to a higher level, and the average removal rate after stabilization is 99% and 67% respectively which can come up to first grade of the national standard GB18918-2002. It is remarkable that when HRT is 4h, the removal rate of NH₄⁺-N and TN showed a significant decrease trend, the concentration of effluent was 14.79mg/L and 19.5mg/L, respectively.

1. Introduction
Integrated sewage treatment equipment with small scale is usually used to treat island sewage with decentralized characteristics. The process composition generally includes anaerobic reaction zone, contact oxidation zone and precipitation zone, which contact oxidation is the most critical part. Effects of filler type, hydraulic retention time(HRT), temperature, pH and hydraulic load on the denitrification in contact oxidation process have been studied systematically[1-4]. The dissolved oxygen (DO) of traditional contact oxidation process should be maintained at 2.5-3.5 mg/L[5, 6]. Keep high levels of aeration will lead to the consumption of too much power, this is conflicted with the present situation on the island, which is short for energy and the supplement of electricity is inconvenient. In order to solve this problem, the effect of treatment with low dissolved oxygen is proposed[7]. However, research in this aspect is not sufficient and systematic. In this study, the contact oxidation reactor was set up in the laboratory which using polyurethane suspension filler as the carrier, and the effect of HRT on the treatment with low dissolved oxygen will be researched in this article.
2. Experiment

2.1. Experiment method
The activated sludge was inoculated into the reactor for quick start. The sludge was obtained from the aerobic section of the A2/O process of the Gaobeidian sewage treatment plant. The indexes of sludge were SV: 13%, MLSS: 1231mg/L, SVI: 105.6mL/g, and the sludge activity was good. After the reactor has been started successfully, the effect of HRT on effluent indicators was investigated in the case of DO = 1.3-1.8mg/L. Experimental cases are shown in table 1.

| Case number | HRT (h) | DO (mg/L) | Temperature(℃) |
|-------------|---------|-----------|----------------|
| Case1       | 12      | 1.3-1.5   | 24±2           |
| Case2       | 8       | 1.3-1.5   | 24±2           |
| Case3       | 6       | 1.3-1.5   | 24±2           |
| Case4       | 4       | 1.3-1.5   | 24±2           |

Experimental device is shown as figure 1. The cylindric reactor was made of plexiglass, 500 mm high, 150 mm in diameter, with an effective volume of 8L. The reactor was packed with polyurethane suspension fillers which fill rate was 75%. The inlet and outlet were set in the bottom and the top of the reactor. The device inlet was achieved by a peristaltic pump. In order to realized the smaller range of temperature variation in tropical climate of the South China Sea Islands, the temperature of the system was maintained at 24 ± 2 ℃ by heating rod.

Figure 1. Experimental device.
① Water storage tank; ② Peristaltic pump; ③ Air pump; ④ Water inlet/Sludge pipe; ⑤ Air flow meter; ⑥ Water outlet; ⑦ Aerator; ⑧ Filler area

The water quality of the inlet and outlet of the reactor was checked every two days. Detection indicators include COD, NH₄⁺-N, TN, DO, pH. The analytical methods and instruments is shown as table 2.

2.2. Experiment materials
After the reactor was started successfully, the influent was changed to ABR tail water which was pre-treatment process of contact oxidation. The water quality of ABR tail water is shown as table 3.
Table 2. Analytical methods and instruments.

| Analysis projects | Analytical methods                                         |
|-------------------|------------------------------------------------------------|
| COD               | Spectrophotometry of Rapid Resolution using Potassium Dichromate |
| NH₄⁺-N           | Nessler’s reagent spectrophotometric method                 |
| TN                | Alkaline persulfate digestion spectrophotometric method   |
| DO                | Multi-parameter water quality analyzer(HQ40d, HACH, USA)  |
| pH                | Multi-parameter water quality analyzer(HQ40d, HACH, USA)  |

Table 3. Water quality of ABR tail water.

| Index         | Range       | Average |
|---------------|-------------|---------|
| pH            | 7.01-7.93   | 7.47    |
| COD/(mg/L)    | 66.41-225.87| 124.26  |
| TN/(mg/L)     | 16.94-71.45 | 32.16   |
| NH₄⁺-N/(mg/L) | 10.22-55.74 | 27.35   |
| TP/(mg/L)     | 3.24-6.15   | 4.89    |

Polyurethane suspension filler was purchased from a packing plant in Beijing. The filler is a square body which has 20mm length of side, the specific surface area is 1000-1200m²/m³ and the porosity is more than 99%.

3. Results and discussion

3.1. Influence of HRT on COD removal efficiency

Figure 2 demonstrates the variation of COD concentration and removal efficiency in the influent and effluent. Figure 2 showed that under the operation of period 1 (HRT=12h), COD concentrations of the influent and effluent were 79.54-149.82mg/L, 10.17-91.56mg/L respectively while the average COD removal rate is 78.42%. It can be seen that in first period of the experiment, the COD of influent changed obviously, the removal rate also corresponds to a significant fluctuation. The fifth day of influent COD rose from 79mg/L to 148mg/L, the removal rate dropped rapidly to 38%. This indicates that the condition of biofilm growth was not good enough at this part, the system was less adaptable to changes of water quality. With the increase of system operating time, effluent COD removal rate rose to 86% on the seventh day, that indicates the microorganisms on the biofilm have adapted to the influent changes.

Under the operation of period 2 (HRT=8h), COD concentrations of the influent and effluent were 117.98-146.12mg/L, 14.04-36.68mg/L respectively while the average COD removal rate is 81.66%. As can be seen from the figure 2, with HRT shortened from 12h to 8h, COD removal rate always maintained at 85% which changes smoothly. When HRT dropped to 6h, COD removal rate remained at a very high level. Under the operation of period 4 (HRT=4h), COD concentrations of the influent and effluent were 66.41-225.87mg/L, 11.18-31.46mg/L respectively while the average COD removal rate is 82.95%. It is noteworthy that the water quality of the period 4 has been a significant fluctuation, the lowest COD was 66mg/L, the highest reached 225mg/L, but the COD removal rate has been very stable.

On the whole, under the condition of low oxygen, the contact oxidation process has a strong effect on the removal of COD. With the HRT changing from 12h to 4h, the COD removal rate of the effluent is stable, indicating that the effect of HRT on decarburization is non-significant.
3.2. Influence of HRT on NH$_4^+$-N removal efficiency

Figure 3 showed that under the operation of period1(HRT=12h), NH$_4^+$-N concentrations of the influent and effluent were 10.22-55.74mg/L, 0.14-13.86mg/L respectively while the average NH$_4^+$-N removal rate is 83.98%. It can be seen from the figure3 that the removal rate of NH$_4^+$-N in the period1 basically changed with the change of influent NH$_4^+$-N concentration. When the device was running for 3 days to 11 days, the influent NH$_4^+$-N decreased from 54mg/L to 24mg/L, and the removal rate of NH$_4^+$-N decreased from 96% to 74%. With the influent ammonia nitrogen stabilized at 25mg/L, NH$_4^+$-N removal rate stabilized at 80% gradually. When HRT was reduced to 8 h, the removal rate of NH$_4^+$-N was rapidly reduced from 84% to 32% at day 27. After 10 days of continuous operation, the removal rate of ammonia nitrogen gradually recovered to more than 90% and maintain a high level. Under the operation of period3(HRT=6h), the change of NH$_4^+$-N removal rate is similar to period 2, which has undergone the process of decreasing first and then increasing. However, the recovery time of this period is 15 days. It can be seen that, the system can still maintain a high removal rate of NH$_4^+$-N at the terminal of period when HRT is shortened to lower level. It is shown that the nitrifying bacteria in the contact oxidation reactor still have strong activity under the condition of low oxygen, because the large porosity and specific surface area of the filler make the transfer efficiency of oxygen very high. However, when HRT is decreased to 4h, the removal rate of ammonia nitrogen continues reduced to 20% at day 95. It is shown that under this condition, the activity of nitrifying bacteria is greatly reduced in the system due to the rapid propagation of heterotrophic bacteria with large hydraulic load. Excessive consumption of oxygen causes the nitrification rate to be inhibited.

Figure 3. Effect of HRT on NH$_4^+$-N removal efficiency.
3.3. Influence of HRT on TN removal efficiency

Figure 4 demonstrates the variation of TN concentration and removal efficiency in the influent and effluent. Figure 4 showed that under the operation of period 1 (HRT = 12h), TN concentrations of the influent and effluent were 16.94 - 71.45 mg/L, 4.5 - 46.11 mg/L respectively while the average TN removal rate is 46.82%. It can be seen that in first period of the experiment, with the influent TN concentration gradually stabilized at 35 mg/L, TN removal rate gradually increased to about 50%. At the end of period 2 and period 3, the TN removal rate of the effluent from the reactor can rise to 60% - 70% due to the simultaneous nitrification and denitrification (SND) phenomenon in the contact oxidation process. The microorganisms are present in the form of a fixation on the filler which is beneficial to the growth of different dominant species and the accumulation of biofilm thickness is more conducive to the formation of aerobic/anaerobic microdomains [8-10]. The presence of anaerobic microdomains allows the denitrification of bacteria to multiply to achieve the purpose of denitrification.

It can be seen from the figure 4 that the denitrification effect of period 1 is not as good as that of period 2 and period 3 because of too long HRT makes the organic carbon source is insufficient, resulting in denitrification rate is inhibited. When HRT is 4h, the inhibition of nitrification led to the effect of nitrogen removal is also gradually reduced to 20%-30% at day 91.

![Figure 4. Effect of HRT on TN removal efficiency.](image)

3.4. Scanning electron microscope observation of filler surface

Scanning electron microscope (SEM) was used to observe the situation of biofilm growth on filler. Figure 5 shows the SEM photograph of filler before biofilm formation. It can be found that there are a lot of voids in the polyurethane suspension filler and the surface is smooth.

![Figure 5. SEM photograph of filler before biofilm formation(×50).](image)

![Figure 6. SEM photograph of filler after biofilm formation(×300).](image)
Figure 6 shows the SEM photograph of filler after biofilm formation. It can be seen clearly from the graph that dense biofilm was formed on the surface of the filler. The biofilm is covered by fibrous material as a framework, and the extracellular polymeric substances secreted by microorganisms wrap these fibrous skeletons together to form a translucent membrane. It can be seen clearly from Figure 7 that Filamentous bacteria and Long bacilli are the main biological membrane. Filamentous bacteria grow out of the biofilm, a large number of sludge floc adsorbed on the surface of filamentous bacteria and then increase the biomass on the filler greatly. At the same time, there are some microorganisms belong to algae category, such as Chlorella vulgaris, Achnanthes and Pinnularia.

![Figure 6](image1.png)

**Figure 7.** Microorganisms on biofilms.

(a) Long bacilli  (b) Filamentous bacteria  (c) Chlorella vulgaris  (d) Achnanthes and Pinnularia

4. Conclusions

In this experiment, polyurethane suspension fillers were padded in the contact oxidation reactor and the dissolved oxygen was limited to 1.3-1.8mg/L in order to maintain a hypoxic background. The experimental results reflect that the system has good effect on removal of COD and TN under this condition. When HRT is among 4h to 12h, the removal rate of COD can be maintained at 80-90%. In this range, HRT has little effect on COD removal. At the beginning of each period, changes of hydraulic load will lead to the removal rate of NH$_4^+$-N and TN in a state of fluctuation. However, with the increase of running time, the removal rate of NH$_4^+$-N and TN is gradually stable and achieved a high level, which can come up to first grade of the national standard GB18918-2002. It is remarkable that when HRT is 4h, the removal rate of NH$_4^+$-N and TN showed a significant decrease trend, the concentration of effluent was 14.79mg/L and 19.5mg/L, respectively. Effect of this treatment can not meet the requirements under this condition, so suitable HRT for this treatment process can not be less than 6h. This study shows that the contact oxidation process has high decarburization and denitrification performance under low oxygen condition, and has obvious economic benefit compared with the traditional contact oxidation process.
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Reference
[1] Zhumei J, Xiwu L and Xianning L 2007 J Technology of Water Treatment 5 33-37
[2] Zhiyong W, Zhencheng X, Qingwei G, Zhengwei X, Yongliang Z and Fuquan P 2009 J Environmental Science & Technology 60 55-62
[3] Yang L 2012 J Environmental Engineering 30 41-43.
[4] Xianhui Z 2010 J Industrial Safety and Environmental Protection 9 25-29
[5] Weizhong W, Yong L, Qing Z, Caijie Wei and Jianlong W 2010 J International Journal of Environment & Pollution 38 223-234
[6] Weizhong W, Yong L, Qing Z and Jianlong W 2010 J International Journal of Environment & Pollution 38 223-234
[7] Bernat N 2001 J Journal of Environmental Engineering 127 266-271.
[8] Yang S and Yang F 2011 J Journal of Hazardous Materials 195 318-323
[9] Guibing Z, Yongzhen P, Shuyun W, Shuying W and Shiwei X 2007 J Journal of Environmental Sciences 19 1043-1048.
[10] Bing W, Wei W, Hongjun H and Haifeng Z 2012 J Journal of Environmental Sciences 24 303-308