Pilot-scale anaerobic/anoxic/oxic/oxic biofilm process treating coking wastewater

Xin Zhou, a,b Yaxin Li, b* Yi Zhao b and Xiuping Yue b

Abstract

BACKGROUND: Biological treatment efficiency of coking wastewater is rather poor, especially for chemical oxygen demand (COD) and ammonia-nitrogen (NH\textsubscript{4}+ -N) removal due to its complex composition and high toxicity.

RESULTS: A pilot-scale anaerobic/anoxic/oxic/oxic (A\textsuperscript{2}/O\textsuperscript{2}) biofilm system has been developed to treat coking wastewater, focusing attention on the COD and NH\textsubscript{4}+ -N removal efficiencies. Operational results over 239 days showed that hydraulic retention time (HRT) of the system had a great impact on simultaneous removals of COD and NH\textsubscript{4}+ -N. At HRT of 116 h, total removal efficiencies of COD and NH\textsubscript{4}+ -N were 92.3% and 97.8%, respectively, reaching the First Grade discharge standard for coking wastewater in China. Adequate HRT, anoxic removal of refractory organics and two-step aerobic bioreactors were considered to be effective measures to obtain satisfactory coking effluent quality using the A\textsuperscript{2}/O\textsuperscript{2} biofilm system. The correlation between removal characteristics of pollutants and spatial distributions of biomass along the height of upflow bioreactors was also revealed.

CONCLUSION: The study suggests that it is feasible to apply the A\textsuperscript{2}/O\textsuperscript{2} biofilm process for coking wastewater treatment, achieving desirable effluent quality and steady process performance.

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Keywords: anaerobic/anoxic/oxic/oxic(A\textsuperscript{2}/O\textsuperscript{2}); biofilm bioreactor; coking wastewater; removal efficiency; hydraulic retention time(HRT)

INTRODUCTION

As one of the largest coke producing countries in the world, China has currently approximately 45% of worldwide total production. Over one-third of national coke production was supplied from Shanxi Province in North China. According to statistics, 51.87 million tons of coking wastewater are discharged annually, accounting for 30% of the overall emissions of industrial wastewater in the whole province. This figure will rise further in the coming years with the development of the coal and coking industry in Shanxi.

Coking wastewater, generated from coal conversion processes such as coal coking, coal gas purification and liquefaction, and the refining of coal by-products in coke plants, is a complex industrial wastewater characterized by a large amount of organic matters, suspended solids, ammonia and other toxic compounds such as phenols and cyanide, leading to harmful effects on water environment and human health without proper treatment. Therefore, pollution control of coking wastewater has become an important topic for industrial wastewater treatment.

Biological treatment has been widely used as an efficient and cost-effective method for coking wastewater treatment until now, while physico-chemical methods generally are considered as options for pre- or post-treatment of wastewater. Since the 1970s and 1980s, a wide range of biological treatment reactors and processes have been developed and researched in North America, China, South Korea, Australia, and Spain. These processes included conventional activated sludge (CAS), fixed biofilm system, hybrid system, oxic/anoxic (O/A) process, anaerobic/anoxic/oxic (A\textsuperscript{2}/O\textsuperscript{2}) process, anoxic/oxic (A/O) process, sequencing batch reactor (SBR), biological fluidized-bed reactor (FBR), membrane bioreactor (MBR), and membrane bioreactor (MBR).

Unfortunately, the biologically treated effluents from these processes do not meet the stringent effluent standard in China for COD ≤ 100 mg L\textsuperscript{-1} and NH\textsubscript{4}+ -N ≤ 15 mg L\textsuperscript{-1}, although phenols and cyanide in the effluents are lower than regulation limits. For NH\textsubscript{4}+ -N removal, the activity of autotrophic nitrifying bacteria was depressed by high concentrations of organics and ammonia as well as other highly toxic or inhibitory compounds, leading to poor nitrification in a single oxic bioreactor; in addition, it is difficult to retain sufficient nitrifying bacteria in the system, especially in the CAS process, due to their slow reproduction at low biomass concentration and shorter sludge age. In terms of chemical oxygen demand (COD) removal, a great variety of refractory compounds in the coking wastewater involving mono- and polycyclic aromatics hydrocarbons (PAHs) and heterocyclic aromatic hydrocarbons containing nitrogen, oxygen and sulfur are difficult to biodegrade causing COD...
concentrations higher than 200–250 mg L\(^{-1}\) in the final effluent even though a very long hydraulic retention time (HRT) is maintained in the single-aerobic system.\(^6\) The high toxicity and complicated composition of coking wastewater seem to be the main factors preventing meeting the discharge standards for both COD and NH\(_4\)\(^+\)-N in coking effluent.

Compared with other activated sludge processes, attached growth systems with fixed biofilm maintain a very long sludge retention time and higher biomass to achieve process efficiency and stability without poor sludge settle-ability problems in the presence of highly toxic compounds. The aerobic process with anaerobic and anoxic treatment units enhanced the degradation of refractory carbonaceous organics, and autotrophic nitrifying bacteria were easily developed within two-step aerobic reactors: COD was removed in the first aerobic reactor and NH\(_4\)\(^+\)-N was removed in the second aerobic reactor under the lower organic loading and toxicity. Accordingly, the objective of this present study is to characterize the performance of a novel four-stage anaerobic/anoxic/oxic/oxic (A\(^2\)/O\(^2\)) combined biofilm process\(^35\) for simultaneous removal of carbon and nitrogen from coking wastewater at varying HRTs. Removal characteristics of COD, NH\(_4\)\(^+\)-N and NO\(_3\)\(^-\)-N as well as spatial distribution in microbial biomass within the upflow biofilm reactors are also reported.

**MATERIALS AND METHODS**

**Experimental setup**

The experiment was carried out in a pilot-scale combined system, consisting of four up-flow fixed biofilm bioreactors: anaerobic (A\(_1\))–anoxic (A\(_2\))–oxic (O\(_1\)) and oxic (O\(_2\)) (in Fig. 1) located at a coking plant of Tongshida Co. Ltd in Linfen, Shanxi Province. The working volumes of the four reactors were, respectively, 3, 4.8, 4.8 and 4.8 m\(^3\). Reactors A\(_1\), A\(_2\) and O\(_2\) were packed with ceramsite and Reactor O\(_1\) was packed with polypropylene media. Characteristic parameters of carriers are listed in Table 1. Sampling ports were installed at different heights of the packing layer in Reactors A\(_1\), A\(_2\) and O\(_2\). Bio-contact oxidation reactor (O\(_1\)) and biological aerated filter (BAF) (O\(_2\)) were supplied with air by the compressor. Backwashing of the filter at regular intervals was also required to avoid clogging of the carriers.

**Wastewater and seed sludge**

The seed sludge for anaerobic/anoxic reactors and aerobic reactors of the A\(^2\)/O\(^2\) system was, respectively, obtained from the anoxic tank and aerobic aeration tank of a coke-plant wastewater treatment facility of Tongshida Co. Ltd. During the experiment, raw coking wastewater was collected from the wastewater tank. The influent coking wastewater in this study (Table 2) was rather complex and poorly degraded (BOD\(_5\)/COD ratio: 0.16–0.25) with a low carbon source (COD/NH\(_4\)\(^+\)-N ratio: 3–5). K\(_2\)HPO\(_4\) was added into the influent tank to provide sufficient nutrients for normal growth of the microorganisms. pH and alkalinity were controlled through the addition of NaHCO\(_3\) solution into the second aerobic reactor to compensate the loss of alkalinity due to nitrification. The final effluent pH was maintained above 7.0 and the alkalinity was not less than 80 mg L\(^{-1}\) (as CaCO\(_3\)).

**Table 1.** Characteristic parameters of carriers

<table>
<thead>
<tr>
<th>Specification</th>
<th>Hollow plastic balls</th>
<th>Ceramic particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Ball</td>
<td>Granular</td>
</tr>
<tr>
<td>Specific surface area (m(^2) m(^{-3}))</td>
<td>236</td>
<td>3900</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>≥90%</td>
<td>≥55%</td>
</tr>
<tr>
<td>Hydrochloric acid soluble rate (%)</td>
<td>&lt;0.22</td>
<td>&lt;0.22</td>
</tr>
<tr>
<td>Sodium hydroxide soluble rate (%)</td>
<td>≤15.0</td>
<td>≤15.0</td>
</tr>
<tr>
<td>Diameter (mm)</td>
<td>50</td>
<td>3–7</td>
</tr>
</tbody>
</table>

**Table 2.** Characteristics of influent coking wastewater

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Average value</th>
<th>SD, standard deviation</th>
<th>Number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>–</td>
<td>8.3</td>
<td>0.3</td>
<td>32</td>
</tr>
<tr>
<td>BOD(_5)</td>
<td>mg L(^{-1})</td>
<td>303</td>
<td>61</td>
<td>24</td>
</tr>
<tr>
<td>COD</td>
<td>mg L(^{-1})</td>
<td>1195</td>
<td>297</td>
<td>30</td>
</tr>
<tr>
<td>NH(_4)(^+)-N</td>
<td>mg L(^{-1})</td>
<td>228.2</td>
<td>55.5</td>
<td>32</td>
</tr>
<tr>
<td>Phenol</td>
<td>mg L(^{-1})</td>
<td>255</td>
<td>117</td>
<td>5</td>
</tr>
<tr>
<td>Cyanide</td>
<td>mg L(^{-1})</td>
<td>8</td>
<td>2</td>
<td>5</td>
</tr>
</tbody>
</table>

**Figure 1.** Schematic diagram of pilot-scale A\(^2\)/O\(^2\) biofilm system.
During the pilot experiment, which lasted for 239 days, four different long-term steady-state experimental runs (R1 – R4) were carried out after 40-day system start-up period. Operating conditions for experimental periods are listed in Table 3. Throughout the whole experimental period, influent wastewater temperature was in the range 25–35 °C, DO concentrations in the aerobic reactors were kept between 4 and 5 mg L\(^{-1}\) and nitrifying recirculation ratio from Reactor O2 to Reactor A2 was controlled at 3, which was the optimum for denitrification of the A2/O2 system, based on previous studies.

**Operating conditions**

During the pilot experiment, which lasted for 239 days, four different long-term steady-state experimental runs (R1 – R4) were carried out after 40-day system start-up period. Operating conditions for experimental periods are listed in Table 3. Throughout the whole experimental period, influent wastewater temperature was in the range 25–35 °C, DO concentrations in the aerobic reactors were kept between 4 and 5 mg L\(^{-1}\) and nitrifying recirculation ratio from Reactor O2 to Reactor A2 was controlled at 3, which was the optimum for denitrification of the A2/O2 system, based on previous studies.

**Analytical methods**

Temperature, pH, dissolved oxygen (DO) and alkalinity were measured daily. COD, NH\(_4^+\)-N, NO\(_3^−\)-N and alkalinity in the influent and effluent of each single bioreactor were analyzed according to standard methods.\(^{35}\) Temperature and pH were measured with a pH meter (WTW Multi340i). DO was measured using a portable DO meter (YSI-500). The biofilm biomass of each bioreactor was analyzed as detailed by Zhang and Li.\(^{37}\) Specified amounts of packing media from sampling ports within reactors were immediately soaked with 20% ammonia water and boiled for 15 min, the retained liquid was poured out and the procedure repeated. The packing media were also flushed with distilled water. The liquid and leachate were collected into a large vessel and mixed together. A small volume was taken from the vessel to measure MLSS/MLVSS according to standard methods,\(^{36}\) representing biomass concentrations of biofilm attached to the packing media. The average biomass of each bioreactor was calculated from

\[
ML(V)SS = \sum M_{ij} \cdot h_i + \sum M_{2j} \cdot h_2 + \ldots + \sum M_{nj} \cdot h_n
\]

where \(ML(V)SS\) is mixed liquor (volatile)suspended solids, \(M_{ij}\) is the biomass at the specified height of the packing layer in the bioreactor, and \(h_i\) is the full height of the packing layer in the bioreactor.

**RESULTS AND DISCUSSION**

**Overall performance of A2/O2 system**

Figure 2 shows the profile of COD concentration in the influent and effluent and the removal efficiency of the A2/O2 system during the experimental periods. As shown in Fig. 2, the COD concentration in the final effluent from the system was maintained below 300 mg L\(^{-1}\), although the COD at the influent varied between 758 and 1873 mg L\(^{-1}\). This indicated the ability of the multi-stage biofilm system to withstand organic loading shocks. As the HRT was increased from 43.5 h to 116 h, average COD removal efficiency was improved from 75% to 92%, and the corresponding lowest effluent COD value was 98 mg L\(^{-1}\) for R3, which met the requirements of the first level of the coking wastewater discharge standards (GB8978 – 1996). However, it was also observed that COD removal dropped slightly when HRT was further lengthened to 174 h from 116 h. One possible reason was that a too low hydraulic load rate (HLR) resulting from extremely long HRT could aggravate the clogging of carriers without sufficient washing out of biofilm, weakening the renewal of the biofilm growth. Furthermore, lower influent organic loading rate (OLR) also led to a reduction in COD removal capacity. In general, it was concluded that proper selection of HRT played an important role in COD removal efficiency. Longer system retention times helped to eliminate more refractory organic compounds from the coking wastewater.

Figure 3 illustrates the profile of NH\(_4^+\)-N concentration in the influent and effluent and removal efficiency of the A2/O2 system during the experimental periods. Effluent NO\(_3^−\)-N is also given in the same figure demonstrating the nitrification performance. As shown in Fig. 3, the impact of HRT on ammonia removal was much more evident than on organics removal. Generally, NH\(_4^+\)-N removal efficiency increased with increased HRT. There was no obvious removal of NH\(_4^+\)-N at a short HRT of 43.5 h at R1, while NH\(_4^+\)-N concentration in the effluent was sharply decreased with sufficiently long HRT. NH\(_4^+\)-N removal efficiency reached 89–99% when HRT was extended to more than 87 h. As NH\(_4^+\)-N was converted to NO\(_3^−\)-N via nitrification under aerobic conditions, effluent NO\(_3^−\)-N concentration was directly correlated with the degree of NH\(_4^+\)-N removal. It was clear that little NO\(_3^−\)-N was produced in the effluent due to no nitrification at R1, while levels as high as 95 mg L\(^{-1}\) NO\(_3^−\)-N at R4 indicated complete nitrification. Nitrification was performed by nitrifying bacteria whose growth rate was slower than heterotrophic bacteria. Therefore, the longer HRT favored reproduction and heightened activity of nitrifying bacteria due to sufficient degradation of organic matter and nitrification inhibitory compounds.

Figures 2 and 3 show that it was necessary to maintain longer total system HRT to achieve better process efficiency during steady operation. In our study, the optimal HRT was 116 h for simultaneous carbon and nitrogen removals from the coking wastewater.

**Removal efficiency in each bioreactor of A2/O2 system**

To clearly identify the performance within each unit of the A2/O2 system, COD and NH\(_4^+\)-N removal efficiencies of each

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**Table 3.** Operating conditions for experimental periods

<table>
<thead>
<tr>
<th>Period</th>
<th>HRT(_{Total}) (h)</th>
<th>HRT(_{A1}) (h)</th>
<th>HRT(_{A2}) (h)</th>
<th>HRT(_{O1}) (h)</th>
<th>HRT(_{O2}) (h)</th>
<th>Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>43.5</td>
<td>7.5</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>0–63</td>
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<tr>
<td>R2</td>
<td>87</td>
<td>15</td>
<td>24</td>
<td>24</td>
<td>24</td>
<td>64–120</td>
</tr>
<tr>
<td>R3</td>
<td>116</td>
<td>20</td>
<td>32</td>
<td>32</td>
<td>32</td>
<td>121–190</td>
</tr>
<tr>
<td>R4</td>
<td>174</td>
<td>30</td>
<td>48</td>
<td>48</td>
<td>48</td>
<td>191–238</td>
</tr>
</tbody>
</table>

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Figure 2. Influent and effluent COD concentrations and COD removal during operational periods.

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**Figure 3.** NH\(_4^+\)-N concentration in the influent and effluent and removal efficiency of the A2/O2 system during the experimental periods.
bioreactor during different operating periods are presented in Figs 4 and 5. As shown in Fig. 4, COD was removed to varying degrees by each single bioreactor at the various HRTs. In Reactor A1, COD removal varied between 5.4 and 11.6% for different HRTs due to transformation of the macromolecular structure rather than degradation of the refractory organics through hydrolysis-acidification of the anaerobic pretreatment, leading to improved biodegradability of wastewater.7,14 Obviously, most organics were removed by subsequent treatment units. More than 50% COD removal occurred in Reactor A2 for both R3 and R4, while anoxic removal of COD was lower than oxic removal, accounting for 81.2% and 69.2% of the overall COD removal for R1 and R2, respectively. The differences in distribution of COD removal depended mainly on the process efficiency of Reactor A2. During the first two runs, COD was poorly utilized as carbon source for denitrification in the absence of sufficient electron acceptors (NO\textsubscript{3}-N) because of limited nitrification; consequently, COD was reduced only through aerobic reactions. In contrast, COD was removed in the anoxic bioreactor through denitrification when the nitrification capacity of the system was fully developed during the last two periods. The result demonstrated that the final effluent COD could meet the first grade discharge standard (below 100 mg L\textsuperscript{-1} in Fig. 2) when 55–60% of overall COD removal in the system was contributed by the anoxic bioreactor. Previous studies\textsuperscript{38–40} also found that large amounts of refractory or inhibitory compounds, which were non-biodegradable or slowly degradable under aerobic or anaerobic conditions, were effectively utilized as carbon sources under NO\textsubscript{x}-N-reducing conditions, resulting in lower effluent COD concentration than other biological processes but without recycling of nitrified effluent.\textsuperscript{3,6,12} As for a two-step aerobic process, COD removal in Reactor O1 was always higher than Reactor O2 at various loadings owing to the higher organic volumetric loading rate in the first aerobic reactor. Extremely low levels of SS in the effluent through media filtration in Reactor O2 (BAF) also encouraged lower COD values.

Unlike the profile of COD removal, NH\textsubscript{4}+-N was almost totally removed in the aerobic bioreactors. In the anaerobic and anoxic reactor, ammonification of nitrogenous compounds gave rise to an increase in NH\textsubscript{4}+-N. It was observed that NH\textsubscript{4}+-N removal contributed by Reactor O1 was always lower than that by Reactor O2 for each period. It is most likely that nitrifiers grow more slowly than heterotrophic bacteria in Reactor O1 due to the high OLR and toxic and inhibitory substances, while nitrifying bacteria became dominant in Reactor O2 at the low level of organic compounds and toxicity. Hence, on the basis of NH\textsubscript{4}+-N removal efficiency, a two-step aerobic process with a single separate nitrifying reactor might retain more nitrifying bacteria and perform more favorable nitrification than a single aerobic system.

**Profile of pollutant concentration in biofilm reactors**

Figure 6(a) and 6(b) show profiles of COD, NH\textsubscript{4}+-N and NO\textsubscript{3}-N along the height of Reactors A2 and O2, respectively, at an HRT of 116 h. In Fig. 6(a), it is evident that sudden drops in both COD and NO\textsubscript{3}-N occurred at 0.2 m height of the packing layer due to denitrification quickly performed at the bottom of the anoxic reactor in the presence of abundant NO\textsubscript{x}-N and organic substrates, while their concentrations were changed slightly above 1 m height. About 25 mg L\textsuperscript{-1} NO\textsubscript{3}-N were depleted through full denitrification. Instead, NH\textsubscript{4}+-N concentration increased with the height of the packing layer due to transformation of organic nitrogen and cyanide compounds (CN\textsuperscript{-}) under the anaerobic conditions.\textsuperscript{40}
In Fig. 6(b), similarly to Reactor A2, COD was removed chiefly in the lower part of the packing layer at 0.6 m of Reactor O2 where its concentration dropped from 145 mg L$^{-1}$ to 114 mg L$^{-1}$, while a large decrease of NH$_4^+$ concentration took place in the upper part of the reactor, implying competition between heterotrophic and nitrifying bacteria. At the bottom of the packing layer, heterotrophic bacteria were probably more active than nitrifying bacteria due to the high organic concentration. COD gradually decreased at increasing height and meanwhile, NH$_4^+$ concentration decreased rapidly from 27 mg L$^{-1}$ to 7.8 mg L$^{-1}$ at a height of 1.2 m, indicating that nitrifying bacteria became dominant at the low content of organics, causing continuous accumulation of NO$_3^-$.

**CONCLUSIONS**

A pilot-scale A$^2$/O$^2$ biofilm process treating real coking wastewater was investigated to study the feasibility of simultaneous removal of COD and NH$_4^+$-$N$. Long-term operating results showed the great impact of HRT on the overall treatment efficiency. The system removed 92.3% COD and 97.8% NH$_4^+$-$N$ at an HRT of 116 h, reaching the First Grade of the discharge standard for coking wastewater in China. In the A$^2$/O$^2$ biofilm system, the combination of anaerobic acidification, anoxic degradation, aerobic oxidation and biofilm filtration was responsible for the maximum COD removal. A two-step aerobic biofilm reactor was favorable to efficient NH$_4^+$-$N$ removal. There was an obvious correlation between pollutant removal characteristics and spatial distribution of microbial biomass at the different heights of up-flow bioreactors.

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