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

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Abstract

BACKGROUND: Biological treatment efficiency of coking wastewater is rather poor, especially for chemical oxygen demand (COD) and ammonia-nitrogen ($\text{NH}_4^+\text{-N}$) removal due to its complex composition and high toxicity.

RESULTS: A pilot-scale anaerobic/anoxic/oxic/oxic (A^2/O^2) biofilm system has been developed to treat coking wastewater, focusing attention on the COD and $\text{NH}_4^+\text{-N}$ 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 $\text{NH}_4^+\text{-N}$. At HRT of 116 h, total removal efficiencies of COD and $\text{NH}_4^+\text{-N}$ 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^2/O^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^2/O^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^2/O^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.¹ 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,^{2–4} 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,^{5,6} leading to harmful effects on water environment and human health without properly 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-^{5,7} or post-treatment of wastewater.^{8–11} 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),^{3,6,12} fixed biofilm system,^{13–15} hybrid system,¹⁶ oxic/anoxic (O/A) process,^{17,18} anoxic/oxic process (A/O),^{19,20} anaerobic/anoxic/oxic

(A^2/O) process,^{21–23} anoxic/oxic/oxic (A/O^2) process,^{24–26} sequencing batch reactor (SBR),^{5,27} biological fluidized-bed reactor (FBR)^{28–30} and membrane bioreactor (MBR).^{31,32}

Unfortunately, the biologically treated effluents from these processes do not meet the stringent effluent standard in China for $\text{COD} \leq 100 \text{ mg L}^{-1}$ and $\text{NH}_4^+\text{-N} \leq 15 \text{ mg L}^{-1}$, although phenols and cyanide in the effluents are lower than regulation limits. For $\text{NH}_4^+\text{-N}$ 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,³³ 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,²³ 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^{7,23,34} are difficult to biodegrade causing COD

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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 NH₄⁺-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 NH₄⁺-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 (A²/O²) combined biofilm process³⁵ for simultaneous removal of carbon and nitrogen from coking wastewater at varying HRTs. Removal characteristics of COD, NH₄⁺-N and NO₃⁻-N as well as spatial distribution in microbial biomass within the upflow biofilm reactors are also reported.

Table 1. Characteristic parameters of carriers

Specification	Hollow plastic balls	Ceramic particles
Type	Ball	Granular
Specific surface area (m ² m ⁻³)	236	3900
Porosity (%)	90%	≥55%
Hydrochloric acid soluble rate (%)	≤0.22	≤0.22
Sodium hydroxide soluble rate (%)	≤15.0	≤15.0
Diameter (mm)	50	3–7

Table 2. Characteristics of influent coking wastewater

Parameter	Unit	Average value	SD, standard deviation	Number of samples
pH	–	8.3	0.3	32
BOD ₅	mg L ⁻¹	303	61	24
COD	mg L ⁻¹	1195	297	30
NH ₄ ⁺ -N	mg L ⁻¹	228.2	55.5	32
Phenol	mg L ⁻¹	255	117	5
Cyanide	mg L ⁻¹	8	2	5

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 (A₁)–anoxic (A₂)–oxic (O₁) and oxic (O₂) (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 m³. Reactors A₁, A₂ and O₂ were packed with ceramsite and Reactor O₁ 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 A₁, A₂ and O₂. Bio-contact oxidation reactor (O₁) and biological aerated filter (BAF) (O₂) 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 A²/O² 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 (BOD₅/COD ratio: 0.16–0.25) with a low carbon source (COD/NH₄⁺-N ratio: 3–5). K₂HPO₄ 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 NaHCO₃ 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 CaCO₃).

Figure 1. Schematic diagram of pilot-scale A²/O² biofilm system.

Table 3. Operating conditions for experimental periods

Period	HRT _{Total} (h)	HRT _{A1} (h)	HRT _{A2} (h)	HRT _{O1} (h)	HRT _{O2} (h)	Days
R ₁	43.5	7.5	12	12	12	0–63
R ₂	87	15	24	24	24	64–120
R ₃	116	20	32	32	32	121–190
R ₄	174	30	48	48	48	191–238

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, NH₄⁺-N, NO₃⁻-N were analyzed weekly. COD, NH₄⁺-N, NO₃⁻-N and alkalinity in the influent and effluent of each single bioreactor were analyzed according to standard methods.³⁶ 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

$$ML(V)SS = \frac{\sum M_{1i} \cdot h_1 + \sum M_{2i} \cdot h_2 + \dots + \sum M_{ni} \cdot h_i}{h_1 + h_2 + \dots + h_i} \quad (1)$$

where *ML(V)SS* is mixed liquor (volatile)suspended solids, *M_{ni}* 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

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

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 NH₄⁺-N concentration in the influent and effluent and removal efficiency of the A²/O² system during the experimental periods. Effluent NO₃⁻-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, NH₄⁺-N removal efficiency increased with increased HRT. There was no obvious removal of NH₄⁺-N at a short HRT of 43.5 h at R₁, while NH₄⁺-N concentration in the effluent was sharply decreased with sufficiently long HRT. NH₄⁺-N removal efficiency reached 89–99% when HRT was extended to more than 87 h. As NH₄⁺-N was converted to NO₃⁻-N via nitrification under aerobic conditions, effluent NO₃⁻-N concentration was directly correlated with the degree of NH₄⁺-N removal. It was clear that little NO₃⁻-N was produced in the effluent due to no nitrification at R₁, while levels as high as 95 mg L⁻¹ NO₃⁻-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 NH₄⁺-N removal efficiencies of each

Figure 3. Influent $\text{NH}_4^+\text{-N}$ and effluent $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$ concentrations and $\text{NH}_4^+\text{-N}$ removal during operational 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 oxalic 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 ($\text{NO}_3^-\text{-N}$) 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^{-1} in Fig. 2) when 55–60% of overall COD removal in the system was contributed by the anoxic bioreactor. Previous studies^{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 $\text{NO}_x^-\text{-N}$ -reducing conditions, resulting in lower effluent COD concentration than other biological processes but without recycling of nitrified effluent.^{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, $\text{NH}_4^+\text{-N}$ was almost totally removed in the aerobic bioreactors. In the anaerobic and anoxic reactor, ammonification of nitrogenous compounds gave rise to an increase in $\text{NH}_4^+\text{-N}$. It was observed that $\text{NH}_4^+\text{-N}$ 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

Figure 4. COD removal for each bioreactor in the total removal of the system during operational periods.

Figure 5. $\text{NH}_4^+\text{-N}$ removal for each bioreactor in the total removal of the system during operational periods.

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 $\text{NH}_4^+\text{-N}$ 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, $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ 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 $\text{NO}_3^-\text{-N}$ 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 $\text{NO}_x^-\text{-N}$ and organic substrates, while their concentrations were changed slightly above 1 m height. About 25 mg L^{-1} $\text{NO}_3^-\text{-N}$ were depleted through full denitrification. Instead, $\text{NH}_4^+\text{-N}$ concentration increased with the height of the packing layer due to transformation of organic nitrogen and cyanide compounds (CN^-) under the anaerobic conditions.⁴⁰

Figure 6. Profile of COD, $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ along the height of carrier layer in (a) Reactor A₂, (b) Reactor O₂.

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 $\text{NH}_4^+\text{-N}$ 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, $\text{NH}_4^+\text{-N}$ 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 $\text{NO}_3^-\text{-N}$.

Microbial biomass of A²/O² system

Biomass concentrations in each biofilm reactor at the different heights of the A²/O² system for Day 144 during the R₃ period are summarized in Table 4. Average biomass calculated using Equation (1) for fixed biofilm reactors A₁, A₂, O₁ and O₂ were 9.2 g L⁻¹, 8.5 g L⁻¹, 11.4 g L⁻¹ and 8.1 g L⁻¹, respectively. High biomass concentrations within biofilm reactors could be 4 to 6 times greater than conventional activated sludge systems (2–2.5 gMLSS L⁻¹), indicating high treatment efficiency of high-strength wastewater. It was observed that the amount of biomass gradually decreased from the bottom to the top

Table 4. Biofilm biomass at the different heights of reactors in the A²/O² system

	Reactor A ₁		Reactor A ₂			Reactor O ₁	Reactor O ₂			
	1 ^a	2 ^a	1 ^a	2 ^a	3 ^a		1 ^a	2 ^a	3 ^a	4 ^a
MLSS (g L ⁻¹)	10.6	8.7	9.9	8.6	8.4	11.4	15.8	9	7.9	6
MLVSS (g L ⁻¹)	8.7	6.2	6.7	6.2	5.7	9.2	9	5	3.2	2.5

^a Representing sampling ports at different heights in Figure 1.

of the packing layer depending on the removal characteristics of the particular pollutants concentration (Fig. 6(a) and 6(b)) in the up-flow biofilm reactors. Unlike suspended growth reactors, an obvious vertical distribution pattern of microbial biomass caused by the plug-flow characteristic in the upflow attached growth bioreactors⁴¹ developed along the height of the packing layer due to the competition between the different microbial groups for space, oxygen and organic carbon.⁴¹ Thus, the multi-stage biofilm reactors were able to create a favorable growing microenvironment for the different microbial groups (heterotrophic bacteria, ammonia oxidizers and nitrite oxidizers) responsible for process performance and stability. As the total biomass could not entirely represent the quantity of these functional bacteria and the activity of microorganisms, further work will be required.

CONCLUSIONS

A pilot-scale A²/O² biofilm process treating real coking wastewater was investigated to study the feasibility of simultaneous removal of COD and $\text{NH}_4^+\text{-N}$. Long-term operating results showed the great impact of HRT on the overall treatment efficiency. The system removed 92.3% COD and 97.8% $\text{NH}_4^+\text{-N}$ at an HRT of 116 h, reaching the First Grade of the discharge standard for coking wastewater in China. In the A²/O² 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 $\text{NH}_4^+\text{-N}$ removal. There was an obvious correlation between pollutant removal characteristics and spatial distribution of microbial biomass at the different heights of upflow bioreactors.

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