



A Combination of Anaerobic and Aerobic Treatment for Ammonia-laden Coke Plant Effluent: The Pilot Study

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Abstract. In the study, a two-stage system of anaerobic and aerobic treatment was developed to treat coke plant effluent containing abundant ammonia (796-2161 mg/L) and a high COD level (4511-16690 mg/L) with well-acclimated heterogeneous microbial cultures. Overall reduction for COD was between 90% and 96%, and for NH₃ was approximately 60%. The COD reduction in range of 43-71% was achieved in anaerobic unit while it reached 65-91% in aerobic unit. The pilot plant was able to consistently reduce phenols and total cyanide to below 0.5 and 1 mg/L, respectively. The nitrate-nitrogen in the eventual effluent gradually remained stable around 100 mg/L. When experimental temperature varied between 21°C and 31°C, higher temperature greatly improved the nitrification and COD reduction in the aerobic unit but slightly reduced COD removal in the anaerobic unit. Longer HRT maximized COD reduction in anaerobic unit at the cost of aerobic COD reduction and nitrification efficiency in the aerobic unit although total COD removal remained consistent.

Keywords: Anaerobic, Aerobic, Coke plant, Ammonia

1. Introduction

Coke Plant Effluent (CPE) is produced in the integrated steel plants at coke-oven gas-cleaning operations, and is laden with ammonia (Grady, 1990; Wen et al., 1991; Littleton and Ren, 1992; Li et al., 2003). The main organic components of CPE includes phenols and nitrogenous heterocyclic compounds which are difficult for conventional activated sludge process to purify to meet the discharge requirement. Following anaerobic reactions including partial scission of polycyclic or heterocyclic rings and cleavage of long chains, these persistent and toxic substances can be converted into intermediates readily oxidized by the subsequent activated sludge process (Yu et al., 1996). Moreover, biological denitrification reaction is able to rapidly take place only when the dissolved oxygen (DO) level is low than 0.5 mg l⁻¹ (Brond and Sund, 1994; Liu et al., 1996). Therefore, a combination of acidogenic, anoxic, aerobic

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treatment (A₁-A₂-O) for the type of wastewater frequently could achieve the desired results (Chuang and Ouyang, 2000; Li et al., 2003; Mosquera-Corral et al., 2003). In this process, the anaerobic unit mainly uses its first phase, i.e., hydrolysis and acidogenesis, as a pretreatment (Fang and Yu, 2000; Li et al., 2003). In the anoxic unit, organic compounds were oxidised by nitrate while nitrate is reduced to nitrogen gas and discarded from the system. Finally, the pollutants such as COD and ammonia were further oxidized in the aerobic unit. A fraction of the treated effluent was commonly required to return to anoxic unit to enhance the denitrification reaction. The efficiency of A₁-A₂-O system is greatly influenced by a wide variety of variables, including chemical nature of wastewater, hydraulic retention time (HRT), pH, temperature, etc. (Nutt et al., 1984).

Since the presupposition of biological denitrification reaction is low DO level (Brond and Sund, 1994; Liu et al., 1996), it seems possible to integrate anaerobic reactor with anoxic reactor in one unit to perform degradation of persistent or toxic organic compounds and denitrification of nitrate simultaneously, which simplifies the process to a certain extent. In this study, a combined anaerobic/aerobic process is developed to treat the CPE. The main objective of the study is to evaluate the performance of the pilot scale treatment system and examine the effect of Hydraulic Retention Time (HRT), temperature and shock load on treatment performance. Thereinto, anaerobic unit effects a full series of anaerobic reactions including hydrolysis, acetogenesis and methanogenesis as well as the denitrification of nitrate which is formed from the oxidation of the ammonia in aerobic unit and brought back by the recycled eventual effluent.

2. Materials and Methods

2.1 Wastewater

The ammonia-laden wastewater was collected from effluent of skimming/settling tanks that skimmed oil and remove suspended solids from raw wastewater in the existing wastewater treatment plant (WWTP). An appropriate amount of phosphoric acid (10 % w/v) was added to provide the required phosphorus nutrient (approximately COD: P =500: 1) in the wastewater. The pH was adjusted to within 8.5 and 8.9 using hydrochloric acid (10% w/v). The wastewater characteristics were summarized in Table 1.

Table 1 Characteristics of Coke Plant Effluent Used in This Study

Target	Concentration	Target	Concentration
pH	8.5 - 8.9	Total cyanide	20.8 - 31
COD	4511 - 16690	Petroleum oil	52 - 95
Phenols	440-1607	Ammonia	796 - 2161

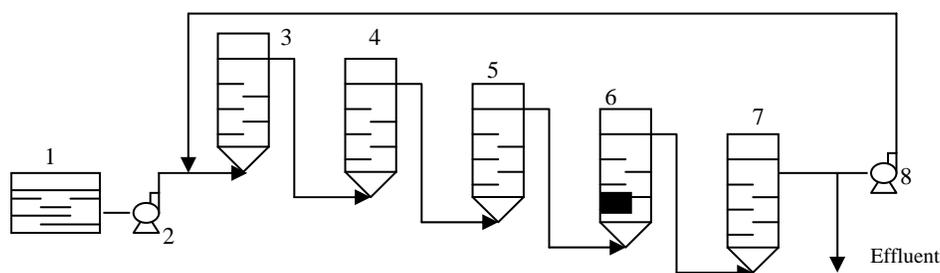
¹The unit of all items are mg/L except that of pH.

2.2 Pilot-scale biological treatment system

The pilot plant included a feed tank, anaerobic reactor 1, anaerobic reactor 2, anaerobic reactor 3, aerobic reactor and clarifier, as illustrated in Figure 1.

The effective working volumes of these reactors were 60, 22, 22, 22, 45 and 13 L, respectively. The metering pump transferred the wastewater from the feed tank at a controlled rate to the anaerobic reactor 1. The effluent flowed by gravity from anaerobic reactor 1 over the settler located on its top to the bottom of anaerobic reactor 2

and then to the bottom of anaerobic reactor 3 for further anaerobic treatment. In each anaerobic reactor, a mixer was used to agitate the water to keep all the suspended solids in suspension. The clarified effluent from the anaerobic reactor 3 flowed by gravity to the aerobic reactor to receive aerobic treatment. The effluent from the aerobic reactor flowed by gravity to clarifier. The settled sludge in the clarifier was pumped to the aerobic reactor to enhance the biological reaction. Part of the ultimate effluent was also recycled to the anaerobic reactor 1 for dilution and to enhance the denitrification reaction.



1. Feeding tank; 2. Metering pump; 3. Anaerobic unit 1; 4. Anaerobic unit 2; 5. Anaerobic unit 3; 6. Aerobic unit; 7. Clarifier; 8. effluent-returning pump.

Figure 1 Schematic illustration of the pilot-scale anaerobic/aerobic treatment system

2.3 Acclimation of biological systems

To speed up the acclimation process, the sludge from the anaerobic reactor of some existing WWTP was used to seed the anaerobic reactor systems of the pilot plants, approximately 96 % of their volumes. At the initial stage of the acclimation period, the wastewater with a COD value varying between 5,000 and 11,000 mg/L was used to feed the anaerobic systems. Only 50 mL wastewater was used on the first day of acclimation and the feed rate was increased slowly day by day. The pH and COD of the anaerobic reactor samples were analyzed daily to check the progress of the anaerobic reaction. After 20 days of manual feeding, the feed rate had increased to 1 L/d. The feed pumps were then used to pump the feed to the anaerobic reactors intermittently and the wastewater was diluted 10-fold by tap water. The pumping frequency increased gradually and the pumping rate was set at 1.2 l/hour. The feed concentration was raised gradually and reached 100% after 40 days of pump feeding operation.

Aerobic sludge was collected from the existing treatment plant for seeding the aerobic reactor of the pilot plant. The reactor was filled with the seed sludge to approximately 80% full when the effluent from the anaerobic reactor 3 started to overflow. The aerobic reactor was filled up gradually and the effluent flowed by gravity to the clarifier that followed.

2.4 Operation of combined treatment systems

From the beginning, the feed was transferred at a controlled rate of 0.5 L/h into the anaerobic reactor 1. On day 32, the feed rate was modified to 0.3 L/h to prolong the Hydraulic Retention Time and to enhance the biological treatment. Activated carbon of 260 grams in all was added to the aerobic tank in 8 batches in the first 14 days. An air pump was used to introduce air into the diffusers in the aerobic reactor where the dissolved oxygen was controlled to

above 3 mg/L. In the course of sequential running, NaHCO_3 was automatically supplemented to the aeration reactor to control pH in the range of 7.5-8.5 and to compensate the loss of alkalinity due to nitrification of ammonia. The daily temperature was also recorded to examine the effect of temperature on the treatment performance. The plant was operated round the clock for 50 days. The analyses for pH, COD, ammonia-nitrogen levels in the feed tank, effluent from anaerobic reactor 3 and eventual effluent from clarifier were conducted on a daily basis. Besides, the concentration of total cyanide, nitrate-nitrogen, petroleum oil and phenols was randomly monitored. The analyses of the wastewater followed standard methods (CSEPA, 1998).

3. Results and Discussion

The characteristics of CFE in this study were shown in Table 1. As a result of oil-skimming pretreatment, the concentration of petroleum oil was lowered to about 52-95 mg/L. However, the wastewater still contained high-strength organic matters, indicated as a COD level of 4511-16690 mg/L, which partially comprised medium concentration of phenols, 440-1607 mg/L. The effluent also contained plenty of ammonia which amounted to 796-2161 mg/L and was far higher than those reported in other literatures (Chakraborty and Veeramani, 2002; Li et al., 2003; Mosquera-Corral et al., 2003).

Although the ammonia-blowing pretreatment could be used to improve the performance of the biological treatment system significantly and reduce the oxygen demand for oxidation of ammonia to nitrate accordingly, the capital cost and the operating cost for the ammonia still are significant and limit its wide application. In contrast, biological treatment process is still the preferred option from the viewpoint of efficiency and economy. Since the concentrations of COD and ammonia were high, in the order of 15,000 mg/L and 1500 mg/L respectively, it was desirable and advantageous to use the treated effluent to dilute the feed to detoxify and enhance the biological treatment. In the study, the return ratio of recycle flow to feed was controlled at 2.5: 1.

The evolution of COD, ammonia and pH level in the feed tank, effluent from anaerobic reactor 3, and ultimate effluent was illustrated in Figure 2. Over the whole experimental periods, the overall reduction for COD was between 90% and 96% which was higher than that reported by Li et al. (2003), 85%, and for ammonia was approximately 60% which was lower than that reported by Li et al. (2003), 98%. It seemed that anaerobic/aerobic treatment process maximized the organic compounds rather than ammonia. This was mainly attributed to the existence of full anaerobic fermentation that consumed too much carbon sources and influenced the supply of electron donor for biological nitrification reaction.

The pilot-scale anaerobic/aerobic treatment system seemed to perform well in the sequential running because the COD and ammonia concentrations in the eventual effluent remained the roughly same levels. Thereinto, the anaerobic system appeared to be very robust in resisting shock load (high concentrations of COD and ammonia) under the conditions used. Many toxic or refractory organic compounds, such as azo dyes, benzenes, polynuclear aromatic hydrocarbons (PAHs), heterocyclic compounds and chlorinated organic pesticides, have been found to be degraded to simple organic acids, alcohol, etc., rather than CO_2 and H_2O under anaerobic conditions (Evans and Fuchs, 1988; Heider et al., 1998), which limited the COD reduction of anaerobic process. In the study, the COD reduction in anaerobic unit varied in ranges of 43-71%. In contrast, the COD reduction reached 65-91% in aerobic unit, which assured the stability of eventual effluent.

Since the nitrification took place merely under the aerobic conditions, ammonia reduction in the aerobic unit could be roughly looked on as the total nitrification efficiency. In this study, nitrification efficiency or ammonia

reduction of about 60% was obtained. Regarding pH, when pH in the feed tank and effluent from the anaerobic reactor 3 remained consistent, the pH in treated effluent fluctuated acutely mainly because the nitrification of nitrate consumed a large number of alkalinity.

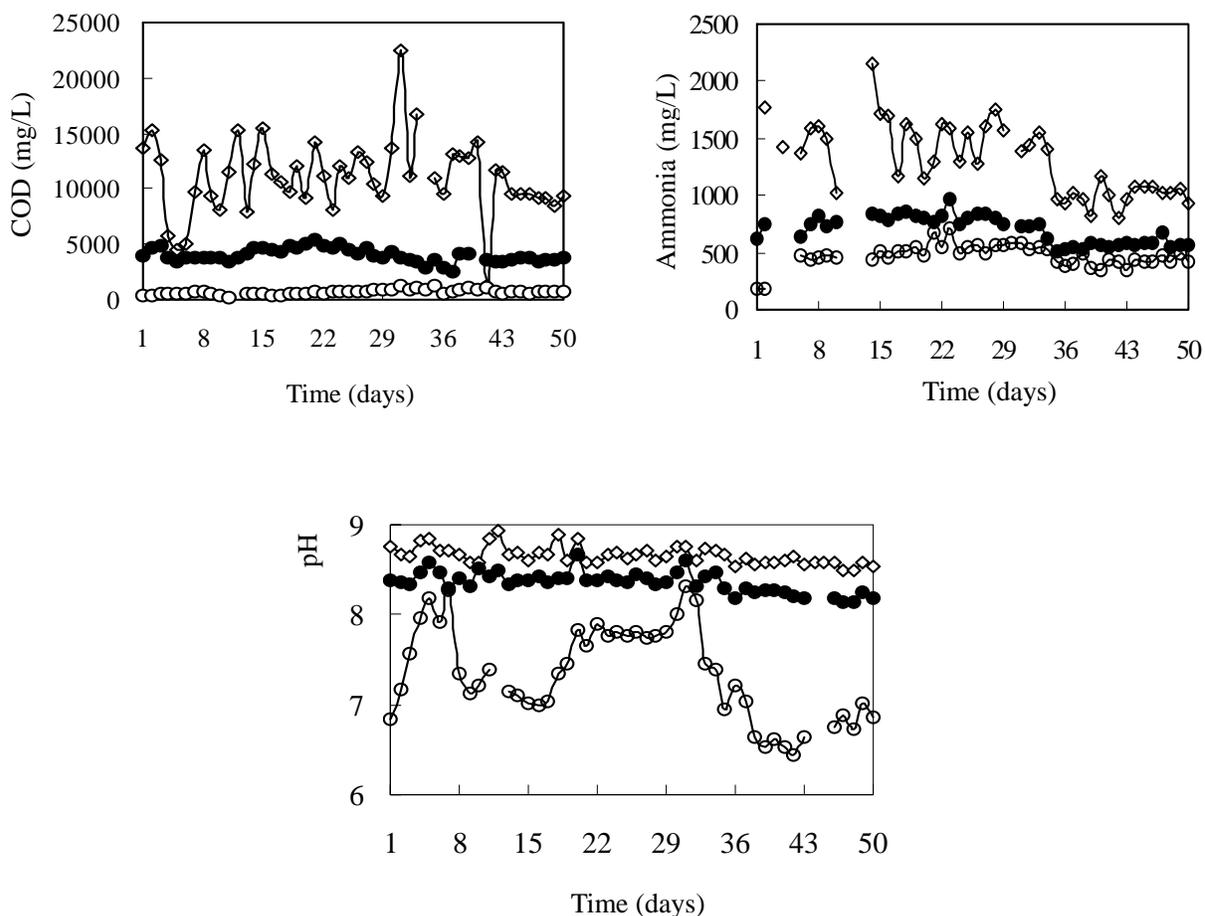


Figure 2 Evolution of COD, ammonia and pH levels in the feed tank (\diamond), effluent from the anaerobic reactor 3 (\bullet) and treated effluent (\circ).

It seemed that the pilot plant was also able to consistently reduce phenols and total cyanide, as demonstrated in Figure 3. With the progress of sequential running, the concentration of phenols and total cyanide in the eventual effluent approximated 0.5 mg/L and 1 mg/L, respectively, and corresponding overall reductions exceeded 99% and 95%, respectively. Over 98% of petroleum oil was also removed from the system. Because these toxic organic compounds in the ultimate effluent still were able to threaten the natural waterbody, however, some chemical treatment, such as lime treatment/aeration, carbon treatment or peroxide treatment to polish the effluent, was still required to polish the ultimate effluent further.

The evolution of nitrate-nitrogen concentration in the eventual effluent was shown in Figure 4. With the development of continuous treatment, the nitrate-nitrogen in the eventual effluent gradually fell to around 100 mg/L.

In consideration of ammonia-nitrogen in the eventual effluent, the overall nitrogen reduction of the pilot plant amounted to roughly 40% in the end of running.

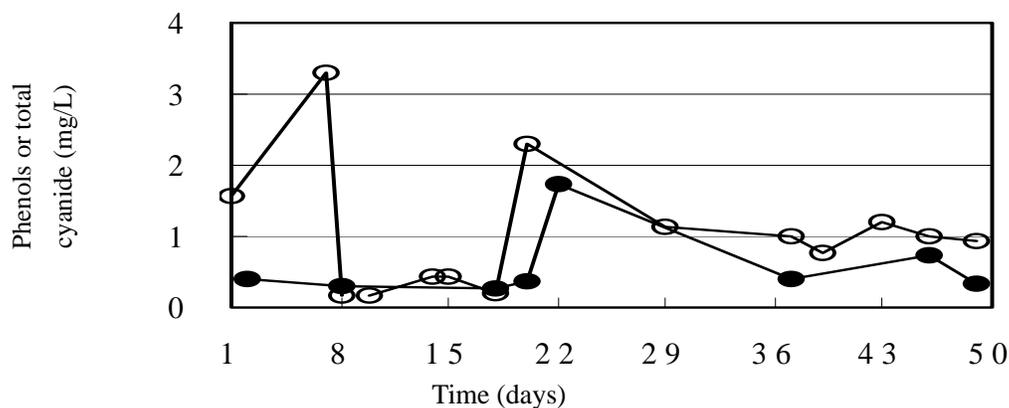


Figure 3 Evolution of phenols (●) and total cyanide (○) levels in the treated effluent.

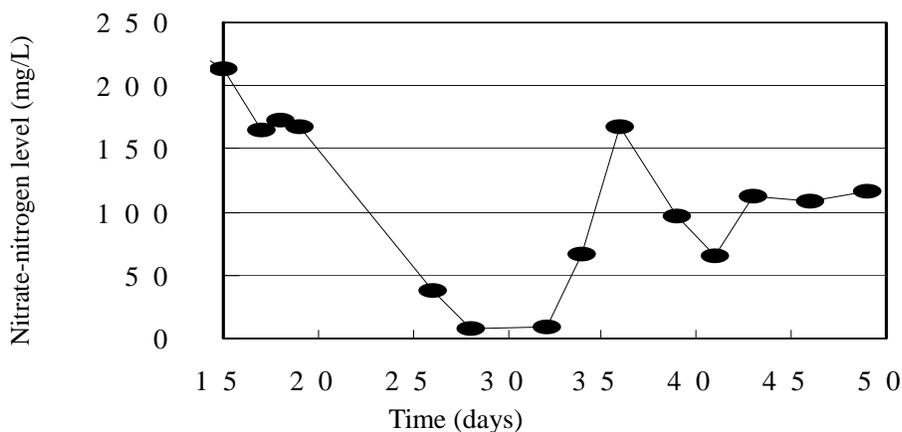


Figure 4 Evolution of nitrate-nitrogen level in the ultimate effluent.

Temperature often restricted the microbial activity and lowered the degradation efficiency accordingly (Nutt et al., 1984). In the study, the effect of temperature on performance of anaerobic and aerobic unit was analyzed in Figure 5-6. Each unit of the pilot plant seemed very sensitive to the temperature change. Higher temperature greatly improved the nitrification reaction in the aerobic unit: the average ammonia reduction was divided into two evident sections at 26°C and 60% ammonia reduction. Likewise, the temperature played different roles in performance of anaerobic and aerobic unit in spite of roughly invariant total COD removal, 92-96%, at all temperatures. With the increase of temperature from 21°C to 31°C, the average COD reduction in anaerobic unit gradually dropped from 71% to 59% while that in aerobic unit gradually went up from 73% to 86%.

HRT has been found to have a significant influence on the performance of an A₁-A₂-O system (Qian et al., 1994;

Yu et al., 1997), and was also investigated in respect of COD and ammonia in the work. When the feed rate was reduced by approximately 50% to increase the biological treatment time, its effect on treatment performance was summarized in Table 2. Under the experimental conditions, total COD removal remained consistent while there was a little rising in COD removal of anaerobic unit and a little falling in that of aerobic unit. It implied that longer HRT would maximize the degradation capability of anaerobic process at the cost of aerobic degradation including COD reduction and nitrification efficiency. Longer HRT had a side effect on the nitrification reaction possibly due to the shortage of electron donor following longer anaerobic treatment, which was also demonstrated by Mosquera-Corral et al. (2003). It was thus of the key importance to control the anaerobic progress to reserve the carbon source for the subsequential treatment process.

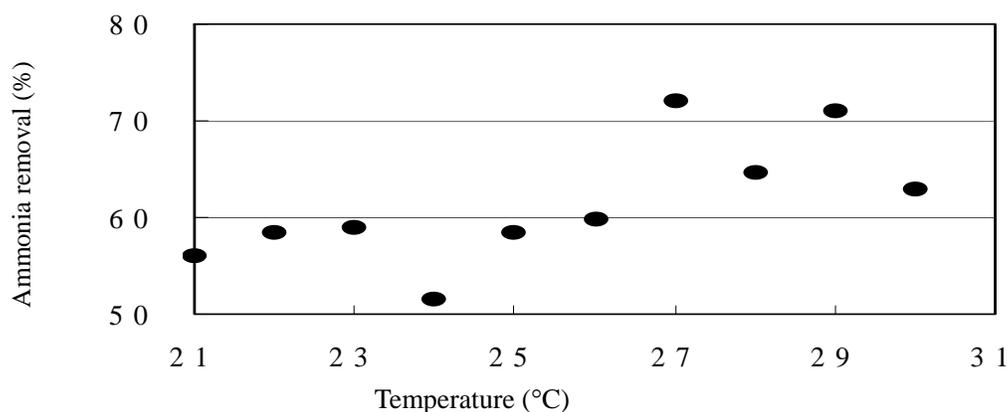


Figure 5 Effect of experimental temperature on the nitrification performance of aerobic unit

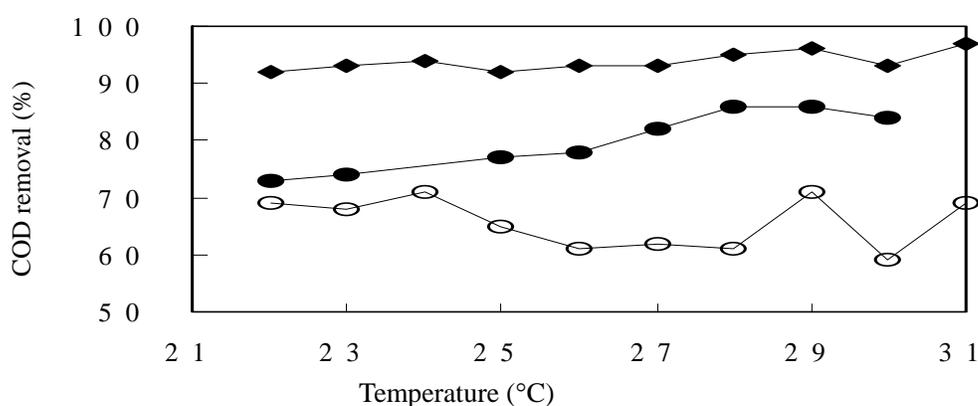


Figure 6 Effect of experimental temperature on the COD removal of pilot scale system. anaerobic unit (○), aerobic unit (●) and total COD removal (◆).

Table 2 Effect of hydraulic retention time (HRT) on the performance of treatment stages and pollutant removal

Periods	Total HRT (d)	Average reduction efficiency (%) for			
		COD			Ammonia
		Anaerobic	Aerobic	Total	
Day 15-32	9.25	61	84	94	62
Day 33-50	15.42	67	77	93	59

4. Conclusion

The implication of the success of the pilot trials is that the installation and operation of the combined anaerobic/aerobic process might be an option for the treatment of ammonia-laden and high-strength CPE. In comparison with A₁-A₂-O system, the anaerobic/aerobic process had the advantage of more effective COD reduction, and its disadvantage is low ammonia removal efficiency. It is possible to treat the wastewater to meet the discharge requirement using the combined biological treatment process along with some post-treatments.

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