



Treatment of Short-chain Nonylphenol Polyethoxylates by the Technique of Combing Biological Contact Oxidation with an Anoxic/oxic Membrane Bioreactor

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ABSTRACT

The technique of combing biological contact oxidation with an anoxic/oxic membrane bioreactor was designed for the treatment of short-chain nonylphenol polyethoxylates (SC-NP_nEO, n<3). The temperature (T), dissolved oxygen (DO) and hydraulic retention time (HRT) were selected as influence factors by an orthogonal experiment of three factors and three levels. Degradation effect of NPEO₀₋₅ and other components were selected as the evaluation index for the orthogonal experiment, evaluating the influence degree of each parameter to the degradation of the target pollutant, and determining the optimum condition of the system operation. The results showed that the removal rate of COD and NH₄⁺-N was stable at more than 85%, and the average removal rate of NPEO₀₋₅ was remained above 98%. The optimum operation parameters of the system were achieved as temperature of 33 °C, DO of 5mg/L, HRT of 24h. The largest influence factor to the degradation of total NPEO₀₋₅ was DO, followed by temperature and HRT. These results showed the technique of combing biological contact oxidation with an anoxic/oxic membrane bioreactor had good sludge retention capacity and shock load resistance capacity and efficient degradation of SC-NP_nEO and water pollutants, has broad application prospects.

Keywords: Anoxic/oxic, Biological degradation, Contact oxidation, Membrane bioreactor, Short-chain nonylphenol polyethoxylates.

1. INTRODUCTION

Short-chain nonylphenol polyethoxylates (SC-NP_nEO, n<3, such as NP₁EO, NP₂EO, etc.) and nonylphenol (NP) were the degradation products in nature of nonylphenol polyethoxylates (NP_nEO), which is the current global most commonly used nonionic surfactants [1-3]. SC-NP_nEO and NP have high biological toxicity, accumulation of biological chain, and they are difficult to be further degraded [4-6]. Thus, the final harmless degradation of SC-NP_nEO is the key to the treatment of NP_nEO [7-9].

The methods of degradation of NP and SC-NP_nEO are mainly divided into physical and chemical methods and biological methods mainly at present. Physical and chemical methods mainly include chemical oxidation, physical and chemical adsorption and photo degradation, and the biological degradation of organic pollutants has been widely used [10-11]. So the biological degradation is still one of the most important ways to remove it.

Y. L. Huang *et al.* used biological contact oxidation process for micro polluted raw water of nitrogen removal

treatment. The results showed that when the dissolved oxygen was 3.0~4.0 mg/L in the water temperature of 25 °C, the removal rate of NH₄⁺-N, NO₃⁻-N, TN and COD_{Mn} could reach 73%, 80%, 77% and 28%. The effect of nitrogen removal was achieved the quality standard of surface water class III [12]. Okayasu *et al.* studied on activated sludge on the degradation of NP_nEO and found that under anoxic conditions NPEO₁₋₂ had high conversion rate of NP, and part of SC-NP_nEO under oxic conditions could be further degraded, and the decomposition rate of NP (0.089~0.17g/gVSS·d) decomposition rate was higher than NP₂EO (0.019~0.038g/gVSS·d) [13]. In particular, under the conditions of repeated operation of anoxic and oxic two processes, NP₂EO and NP₁EO were likely to be completely transformed into NP. The above studies indicated that the Anoxic/Oxic (A/O) process may be an effective method for the degradation of SC-NP_nEO and NP.

As a kind of efficient water treatment process, biological contact oxidation had features of both activated sludge method and biological membrane method. Now, it is widely used for the treatment of domestic sewage and industrial

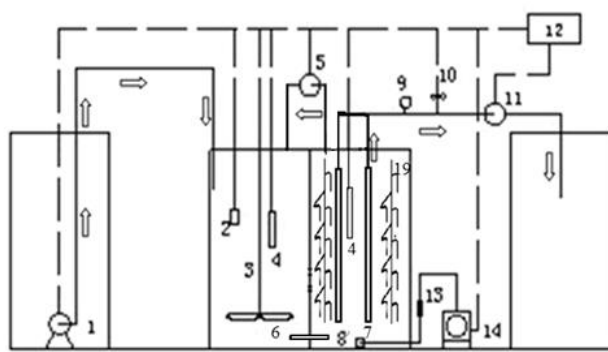
wastewater with larger surface area, higher sludge concentration and higher oxygen utilization rate [14].

Study combines the A/O-MBR and the biological contact oxidation, the operation parameters, including temperature (T), dissolved oxygen (DO) and hydraulic retention time (HRT), were selected as influence factors, in an orthogonal experiment of three factors and three levels. Chemical oxygen demand (COD), ammonia nitrogen (NH₄⁺-N), NP, NP₁EO, NP₂EO and other indicators during the degradation process were monitored to investigate the effect of the system on the removal of pollutants and the system stability.

2. EXPERIMENT SECTION

2.1 Experimental system

Figure 1 was the schematic diagram of the A/O-MBR biological contact oxidation system.



1 influent pump; 2 liquid level indicator; 3 stirrer; 4 heater; 5 circulating pump; 6 connected valve; 7 membrane module; 8 aeration pipe; 9 vacuum meter; 10 solenoid valve; 11 outlet pump; 12 control panel; 13 air flow meter; 14 air compressor; 15 raw water tank; 16 anoxic tank; 17 oxic tank; 18 effluent tank; 19 suspended filler

Figure 1. Schematic diagram of the system

The system reactor is composed of anoxic tank and oxic tank. The effective volume was 10L, respectively. Influent was pumped into anoxic tank 16 by influent pump 1 (peristaltic pump), and then streamed through connected valve 6 to oxic tank 17. Oxic tank 17 and anoxic tank 16 used circulating pump 5 to achieve internal circulating sludge, water streamed from outlet pump 11 to the membrane module 7 inside oxic tank 17. Water level was controlled by liquid level indicator 2 inside the anoxic tank 16. As outlet pump worked, liquid level approached the lowest level, influent pump 1 began to pump raw water to anoxic tank 16. When it reached the highest level, influent pump 1 stopped working.

Membrane module 7 was vertically placed in oxic tank 17 (Shanghai Snape, PVDF flat membrane, membrane pore size of 0.1 μ m, effective filtration area 0.1 m²). Besides membrane module were suspended filler 19, in the bottom of oxic tank 17 was an aeration pipe 8. Used air compressor 14 to aerate the sludge in oxic tank 17, aeration rate was determined by air flow meter 13. System worked in intermittent mode, the pump 11 worked 5 min, stop for 1 min, solenoid valve 10 opened when outlet pump 11 stopped pumping to make membrane module 7 connecting to atmosphere that can reduce negative pressure in membrane.

2.2 Experimental simulation of sewage

Simulation sewage took glucose (300 mg/L), starch (300 mg/L) as the main C source, urea (54 mg/L) for the N source, KH₂PO₄ (35 mg/L) for the P source. Adding pH buffer NaHCO₃ (120mg/L), CaCl₂ (6 mg/L), inorganic salts (FeSO₄·7H₂O of 0.55 mg/L, MgSO₄·7H₂O of 6 mg/L, MnSO₄·H₂O of 6 mg/L) for microbial growth. In addition, during the sludge acclimation stage and SC-NP_nEO degradation stage, added NP_nEO (n \approx 2) to replace the original part of the C source to become surfactant sewage.

2.3 Experiment

The experiment carried out for 180 d and could be divided to 3 periods as initiating period (Run1), sludge acclimation period (Run2) and critical parameter optimization of system period (Run3). The initial mixed liquor suspended solids (MLSS) was 3000 mg/L. Anoxic tank and oxic tank temperature (T) was 18 $^{\circ}$ C. DO in anoxic tank and oxic tank were 0.3 mg/L and 2~4 mg/L, respectively. HRT initially was set as 12h and pH of system was approximating to 7.0.

Run1 (1~20 d) used artificial domestic sewage (COD:N:P \approx 100:5:1) to cultivated activated sludge. The COD was about 500 mg/L.

Run 2 (21~73 d) used artificial nonionic surfactants to acclimated activated sludge. Added simulate sewage NP_nEO (n \approx 2) to replace part of C source, gradually increased NP_nEO (n=2) dosage with interval of about 15 days, the dosage change were 20mg/L, 40mg/L, 60mg/L, 80mg/L. After the accession, keep COD to around 500mg/L.

Run 3 (74~180 d), the simulation of NP_nEO in sewage (n \approx 2) was 80mg/L. The main technological parameters of this experiment are temperature, DO and HRT, and the three factors and three levels of orthogonal test L₉(3³) (e.g., Table 1) to optimize the system operation parameters.

Table 1. Factors' value of orthogonal experiment

Level	A T($^{\circ}$ C)	B DO(mg/L)	C HRT(h)
1	26	2.0	24
2	33	3.5	16
3	40	5.0	8

Influent was the artificial simulated sewage in raw water tank. The mixed liquor from anoxic tank and oxic tank were centrifuged under 5000 rpm about 5 min. The supernatant was used to measure the water quality parameters and the lower layer sludge was used to determination of the concentration of mixed liquid sludge. The effluent is the membrane effluent.

COD measurement used the standard method of water and wastewater testing in the USA [15]. NH₄⁺-N measurement used OPP method [16]. Temperature was measured by thermometer directly. NP_nEO (n \approx 2) concentration of influent and effluent measured by Waters 2695 high performance liquid chromatography (Waters, USA, configuration 2487 UV detector). 4-NP and NP_nEO (average of n is 2, n=2) standard products were brought by TCI (Shanghai) Chemical Industry Development Co., LTD.

3. RESULTS AND DISCUSSION

3.1 COD removal

From Figure 2, fluctuation of influent concentration was in the range of 350~550mg/L during the orthogonal experiment. The COD in anoxic and oxic supernatant were maintained at about 50mg/L firstly. Then concentration of supernatant both were increased to approximate 200mg/L which might be because of the metabolism affected by rising temperature. While concentration of COD in influent and supernatant changed, effluent concentration remained stable, below 50mg/L. Because a lot of microorganisms grew on the filler, improved the ability of degradation of organic by activated sludge greatly, also enhanced the system's ability to resist shock load. The retention and filtration of the membrane and the membrane filter cake layer have adsorption and closure effect on suspended particles, colloids and dissolved organic matter, etc., made the system removal of COD to maintain at a high level.

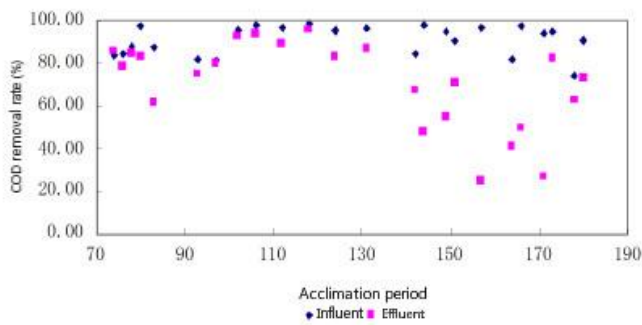


Figure.2 Changes of removal rate of COD

3.2 NH₄⁺-N removal

E.g., Figure 3 was the change of ammonia nitrogen concentrations and removal rate in the process of experiment and the orthogonal experiment. During acclimation period (influent ammonia nitrogen 2.82~6.80 mg/L), the fluctuations were large. In anoxic tank, the amount of ammonia nitrogen in supernatant was about 4 mg/L, compared with influent, the difference was not big, even higher than the influent concentration. As the ammonia nitrogen were converted to nitrate and nitrite mainly occurred in oxic stage, so the concentration of ammonia nitrogen in the supernatant of oxic tank was significantly decreased, ammonia concentration was mostly lower than 1mg/L, hovering in the 0.33mg/L. The retention of the membrane made the nitrification bacteria and the nitrite bacteria stayed, and the filler provided a good adsorption, growth and degradation environment, enhanced the nitrification capacity of the system. That made the removal rate of ammonia nitrogen had been maintained at a high level during the acclimation period, the average removal rate was 92.65%. This showed that the system had a strong nitrification capacity.

After optimizing the parameters of the orthogonal experiment, the system still had high degradation ability, the removal rate remained at about 95% despite the fluctuation of influent ammonia nitrogen concentration. When the temperature was 40°C, the removal rate was lower than 90%,

and the effluent concentration of 0.66mg/L was higher than that of the previous data, which may be that the temperature exceeded the optimum temperature, the growth of activated sludge was affected, so the degradation effect of ammonia nitrogen was reduced.

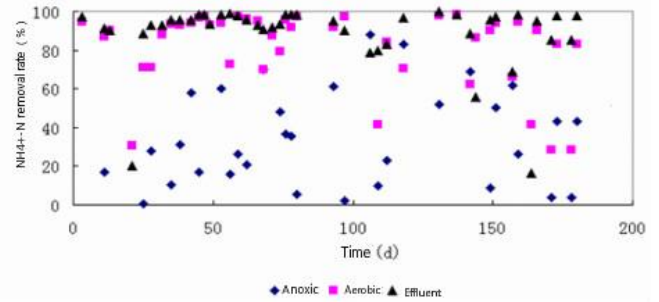


Figure 3. Changes of removal rate of NH₄⁺-N

3.3 Degradation of SC-NPnEO in A/O-MBR- contact oxidation system

The concentration of total NPEO₀₋₅ was composed of NP, NP₁EO, NP₂EO and organic compound. With the total NPEO₀₋₅ concentration we could know the overall situation of short chain nonylphenol degradation. Table 2 listed effects of total NPEO₀₋₅ removal under different operation parameters. The effect of dissolved oxygen was more significant compared with temperature. When the dissolved oxygen was 5mg/L, the total NPEO₀₋₅ concentration of effluent was the smallest, under the condition of 2mg/L nearly had double concentration. As a second important influence factor, the total NPEO₀₋₅ removal efficiency was the best at 33°C. The hydraulic retention time of the system was the most least obvious degradation effect. From table 2, removal efficiency was best when the hydraulic retention time was the longest (24h). It showed under this condition, the longer the hydraulic retained, the longer sludge degraded total NPEO₀₋₅. And NP and NP₁EO degradation effect was not good, NP and NP₁EO degraded by NPEO₂₋₅ might be the reasons. Considered all the factors of total NPEO₀₋₅ operation, the optimum parameters: dissolved oxygen of 5mg/L, temperature of 33°C, HRT of 24h.

Table 2. Analysis of orthogonal experiments for overall NP in effluent

Experiment number	Factors			Effluent NPEO ₀₋₅ (mg/L)
	T (°C)	DO (mg/L)	HRT (h)	
1	26	2	24	1.214
2	26	3.5	16	1.132
3	26	5	8	0.822
4	33	2	16	0.678
5	33	3.5	8	0.620
6	33	5	24	0.513
7	40	2	8	1.207
8	40	3.5	24	0.412
9	40	5	16	0.388
1	1.056	1.033	0.713	
2	0.604	0.721	0.733	
3	0.669	0.574	0.833	
R	0.452	0.459	0.170	

4. CONCLUSIONS

An A/O-MBR-contact oxidation method was carried out for short-chain nonylphenol polyethoxylates degradation experiment and effect on system was evaluated to optimize the operation parameters. Through the analysis of the removal effect on conventional pollutants and short-chain nonylphenol ethoxylates degradation effect, the following results were achieved:

(1) COD removal rate was average at 85% in system, during sludge incubation period was above 95%. $\text{NH}_4^+\text{-N}$ average removal rate was 92%. The total NPEO₀₋₅ average degradation rate was above 98%.

(2) The operation parameters were selected as evaluation index for orthogonal experiment. For total NPEO₀₋₅, the largest influence factor was dissolved oxygen, followed by temperature and hydraulic retention time. The influence of critical parameters on contaminants removal was different, but the microorganism in system had good degradation stability.

(3) The optimum operation parameters of the A/O-MBR-contact oxidation system were temperature of 33 °C, dissolved oxygen of 5mg/L and HRT of 24h.

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