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Treatment of 2-phenylamino-3-methyl-6-di-*n*-butylaminofluoran production effluent by combination of biological treatments and Fenton's oxidation

DING Wei[1], GAO Ying-xin[2], YANG Min[2,*], DING Ran[2] , ZHANG Yu[2]

1. College of Resource and Environmental Engineering, East China University of Science and Technology, Shanghai 200237. E-mail: great@ecust.edu.cn
2. SKLEAC, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

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Abstract

High strength refractory organic stream is produced during the production of 2-phenylamino-3-methyl-6-di-*n*-butylaminofluoran (One Dye Black 2, abbr. ODB 2), a novel heat-sensitive material with a promising market. In this study, a combination of acidification-precipitation, primary biological treatment, Fenton's oxidation and another biological treatment was successfully used for the removal of COD from 18000–25000 mg/L to below 200 mg/L from the ODB 2 production wastewater in a pilot experiment. A COD removal of 70%–80% was achieved by acidification-precipitation under a pH of 2.5–3.0. The first step biodegradation permitted an average COD removal of 70% under an hydraulic residence time (HRT) of 30 h. By batch tests, the optimum conditions of Fenton's oxidation were acquired as: Fe^{2+} dose 6.0 mmol/L; H_2O_2 dose 3000 mg/L; and reaction time 6 h. The second step biological treatment could ensure an effluent COD below 200 mg/L under an HRT of 10 h following the Fenton's treatment.

Key words: 2-phenylamino-3-methyl-6-di-*n*-butylaminofluoran; ODB 2 wastewater; Fenton's oxidation; activated sludge; heat-sensitive material

Introduction

2-Phenylamino-3-methyl-6-di-*n*-butylaminofluoran (commercially called as One Dye Black 2, or ODB 2), appeared recently as a promising heat-sensitive material (ESCO, 2003). With an annual output of about 3000 t in the world, the production of ODB 2 is speculated to increase at an annual rate of 25% in the next decade (Yang, 2004). A waste stream characterized with a high COD concentration but a low BOD ratio is produced during the production of OBD 2, making it difficult to treat the waste stream with a simple biological process. It is urgent to establish a high efficient treatment process with a reasonable cost for the ODB 2 production wastewater.

Many advanced oxidation processes (AOPs) were employed to improve the bio-degradability of wastewater containing bio-refractory organic compounds (Bertanza *et al*., 2001). Among these AOPs, Fenton's oxidation, which could produce high oxidative OH radicals, is very attractive because of its simplicity, high efficiency, and low cost (Walling, 1975; Merz and Waters, 1947; Antonio *et al*., 2004). By coupling with a biological treatment facility, it could be used for treating most kinds of wastewater containing bio-refractory organic substances at a reasonable cost (Steensen, 1997; Bertanza *et al*., 2001; Gao and Yang, 2004).

In this study, a pilot plant with a capacity of 2 m^3/d and consisting of successive acidification-precipitation, primary biological treatment, Fenton's oxidation, and another biological treatment was constructed for the treatment of ODB 2 wastewater based on preliminary batch test results. Experiments were conducted to investigate the effects of operational conditions on the performance of the treatment system. The results derived from the pilot study could provide valuable information for engineering purpose.

1 Material and methods

1.1 Characteristics of ODB 2 wastewater

Chemical structure of ODB 2 is shown in Fig.1. Wastewater was taken from an ODB 2 producing line and its characteristics are shown in Table 1. It contains high concentrations of TDS (total dissolved solids), sulfate, and COD. The ratio of BOD (biochemical oxygen demand) to COD was <12%.

1.2 Reagents

H_2O_2 (27.5%), ferrous sulfate (90%), sodium hydroxide (95%), and all of the other reagents were purchased from Beijing Chemical Company, Beijing. All of the chemicals

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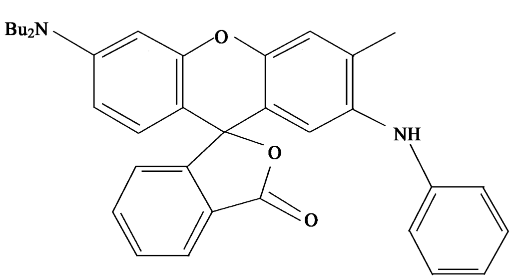

Fig. 1 Chemical structure of ODB 2.

Table 1 Characteristics of ODB 2 waste stream

Item	COD (g/L)	SO_4^{2-} (g/L)	TDS (g/L)	SS (g/L)	BOD (g/L)	pH
Average	12.40	15.28	20.9	2.23	1.51	10.5
Max.	23.89	40.89	63.4	3.71	2.35	12.0
Min.	11.98	11.20	18.0	0.50	0.56	9.0

used for treatment tests were industrial grade and used without further purification. The chemicals used for analysis were analytical grade.

1.3 Sample analysis

Hydrogen peroxide was determined iodometrically. The pH and DO were measured with a portable pH meter (pH14M, TOA, Japan) and DO meter (DO10 TOA, Japan), respectively. The COD was determined with a portable COD meter (Hach, USA), and the MLSS (mixed liquor suspended solids) was analyzed according to Standard Methods (APHA, 1998).

1.4 Pilot treatment system

The pilot plant was built in Shouguang Fukang Pharmaceutical Co., Ltd located in Shouguang City, Shandong Province, based on preliminary batch test results. As shown in Fig.2, the pilot system with an average capacity of 2 m^3/d mainly consisted of acidification-precipitation, primary biological treatment, Fenton's oxidation, and another biological treatment. Acidification-precipitation was used for the removal of part of organic compounds that precipitate at a pH of 2.5–3.0. After neutralization, a continuously-flow activated sludge process was used for the primary biological treatment, and an SBR (sequenced batch reactor) was used for the second step biological treatment. The two biological steps were separated by a continuous Fenton's oxidation process.

The primary biological treatment was used to remove biodegradable organics for reducing the addition of Fenton's regent. After primary biological process, Fenton's oxidation was employed to remove the residual COD as well as to improve the bio-degradability of the biologically treated effluent for further biological treatment. The MLSS in the two biological reactors were 4000–6000 mg/L and 3000–6000 mg/L, respectively.

The Fenton's reactor was operated at a pH of 3.0 with continuous additions of H_2O_2 and Fe^{2+}, followed by a neutralization-sedimentation combination.

The optimum conditions of Fenton's oxidation during the pilot experiment were determined by preliminary batch tests. A series of 1 L wastewater samples were added in beakers, followed by adjusting the pH to 3 with NaOH or H_2SO_4. The scheduled Fe^{2+} dosage was achieved by adding the necessary amount of solid $FeSO_4{\cdot}7H_2O$, and a given volume of 30% (w/w) H_2O_2 solution was added to start up the Fenton's oxidation. After mixed for a given time with a jar tester, the solutions were neutralized with NaOH solution, and settled for 1 h. The supernatant was taken for batch biological treatment tests under the following conditions: MLSS about 3500 mg/L; dissolved oxygen 2–3 mg/L.

2 Results and discussion

2.1 Pretreatment of ODB 2 wastewater

In the preliminary experiments, the effect of pH on wastewater stability was investigated by changing pH from 12 to 2, and it was found that part of organic components in wastewater precipitated at a pH of 2.5 to 3.0, resulting in a decrease of COD for about 70%–80%. It is speculated that the ODB wastewater might contain quite a lot of acidic organic compounds, which precipitated under the acidic condition. Based on this result, acidification was selected as the pretreatment method before biological treatment to reduce the operational cost. Variation of COD removal during the acidification-sedimentation pretreatment is shown in Fig.3. Over a period of 1 month, the acidification-precipitation process in the pilot system kept a COD removal of 70%–80%, producing an effluent COD in a range 3000–4500 mg/L from an influent COD range 18000–25000 mg/L. The result demonstrates that the acidification-precipitation treatment was an effective method for the OBD 2 wastewater.

2.2 Primary biological treatment

In spite of the low BOD to COD ratio, quite amount of COD in the ODB 2 waste stream could be removed through biodegradation after activated sludge was acclimated to

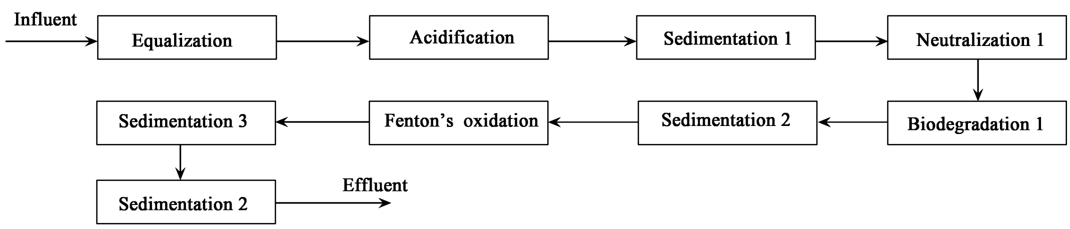

Fig. 2 Schematic diagram of ODB 2 treatment system.

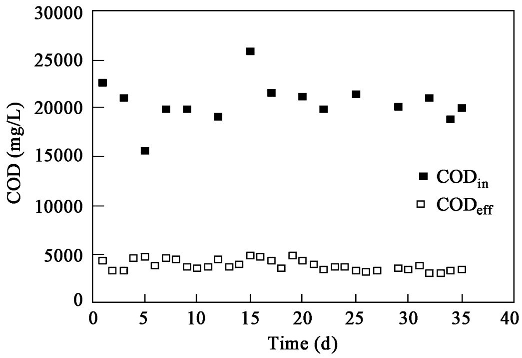

Fig. 3 COD removal through acidification-precipitation treatment.

wastewater. Before the startup of the pilot experiment, sludge in the system was acclimated to wastewater for 45 d. Fig.4 shows the COD removal performance of the primary biological treatment reactor during the stable state.

The primary biological treatment was divided into 3 phases based on hydraulic residence times (HRTs). An average COD removal of about 70% was achieved at HRTs of 40 h and 30 h. The MLSS varied in a range between 4000–6000 mg/L, and the F/M (COD/MLSS) ratio was 0.15–0.25 d^{-1}. The COD removal, however, decreased to below 60% when the HRT was decreased to 24 h and the F/M ratio was increased to 0.30–0.35 d^{-1}. So, the HRT of 30 h was suitable for the primary biological treatment of the waste stream.

2.3 Optimization of Fenton's oxidation conditions

Although the conditions for Fenton's oxidation have been investigated by many researchers, most of the previous studies mainly focus on the COD removal performance by Fenton's oxidation itself (Kang *et al.*, 2002; Lunar *et al.*, 2000; Kuo, 1922). In this study, the improvement of biodegradability of the waste stream was focused, and batch biodegradation tests following Fenton's oxidation were systematically performed to determine the optimum doses of Fe^{2+} and H_2O_2 for the pilot treatment. The COD removal by Fenton's oxidation and corresponding biodegradation are shown in Figs.5 and 6, respectively.

The COD was reduced from 1400 to 400 mg/L by direct

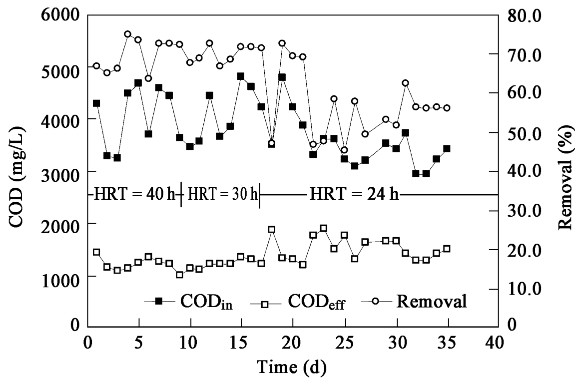

Fig. 4 COD removal of the primary biological treatment.

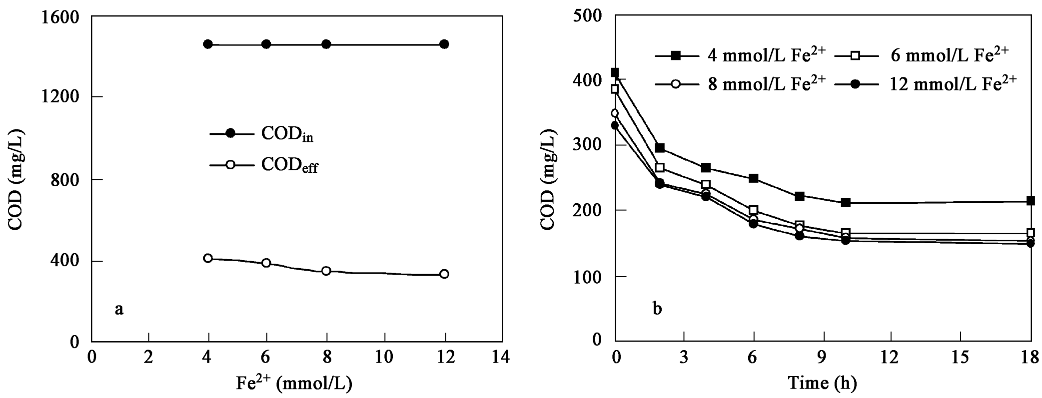

Fig. 5 Effect of Fe^{2+} dose on COD removals. (a) Fenton's oxidation; (b) biodegradation. $[H_2O_2]_0$ = 3000 mg/L; pH = 3.0; T = 25°C; Fenton's oxidation = 6.0 h.

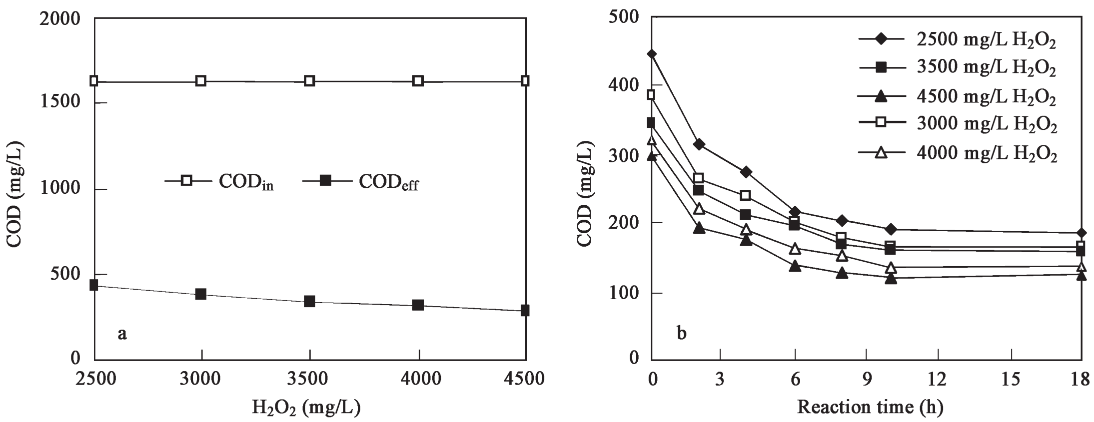

Fig. 6 Effect of H_2O_2 dose on COD removals. (a) Fenton's oxidation; (b) biodegradation. $[Fe^{2+}]_0$ = 6 mmol/L; pH = 3.0; T = 25°C; Fenton's oxidation = 6.0 h.

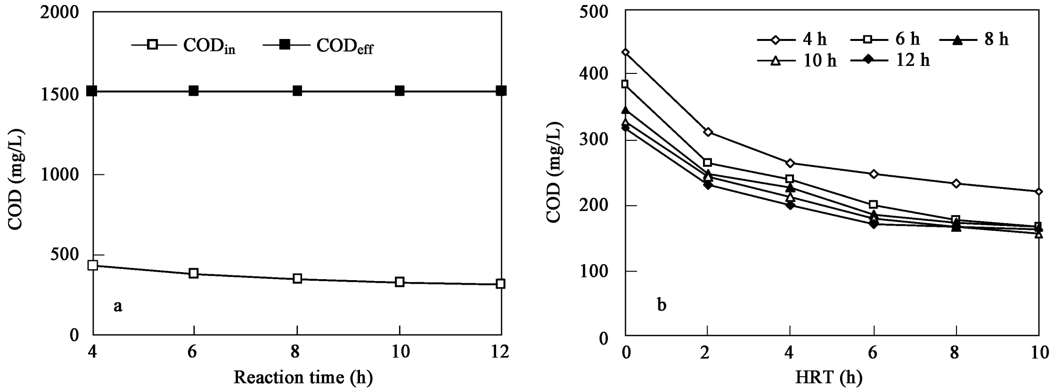

Fig. 7 Effect of oxidation time on COD removals. (a) Fenton's oxidation; (b) biodegradation. $[H_2O_2]_0$ = 3000 mg/L; $[Fe^{2+}]_0$ = 6.0 mmol/L; pH = 3.0; T = 25°C.

Fenton's treatment over a Fe^{2+} dose range 4–12 mmol/L, and an H_2O_2 dose range 2500–4500 mg/L. It is clear that the COD removal by direct Fenton's treatment almost did not change with the changes of Fe^{2+} and H_2O_2 doses. However, there existed an optimum Fe^{2+} dose (6 mmol/L) for the successive biological treatment (Fig.5). The COD removal by the biological treatment increased with the increase of H_2O_2 dose (Fig.6). However, 3000 mg/L of H_2O_2 was sufficient to ensure an effluent COD of 200 mg/L. In the same time, both Figs.5 and 6 show that a time of 10 h was necessary for performing biological treatment.

Figure 7 shows the effects of Fenton's oxidation and bio-oxidation times on the COD removal. The COD removal by direct Fenton's treatment was not affected in a reaction time range 6–12 h. However, the biological treatment performance was affected markedly by Fenton's oxidation time. A Fenton's oxidation of 6 h was necessary to achieve an effluent COD below 200 mg/L through successive Fenton's oxidation and biological treatment.

2.4 Fenton's oxidation performance of the pilot system

In the pilot system, the Fenton's treatment was performed under the following conditions: H_2O_2 3000 mg/L; Fe^{2+} 6.0 mmol/L; and HRT 6 h, and the performance of the Fenton's treatment is shown in Fig.8. Through the treatments of acidification-precipitation and the primary bio-oxidation, the effluent COD was decreased from 18000–25000 mg/L to 1200–1800 mg/L. Following further treatment with Fenton's oxidation, the COD was reduced to 250–390 mg/L. The second step biological treatment with the SBR resulted in an effluent COD below 200 mg/L under the following conditions: HRT 10 h; MLSS 3000–6000 mg/L; DO 3–4 mg/L.

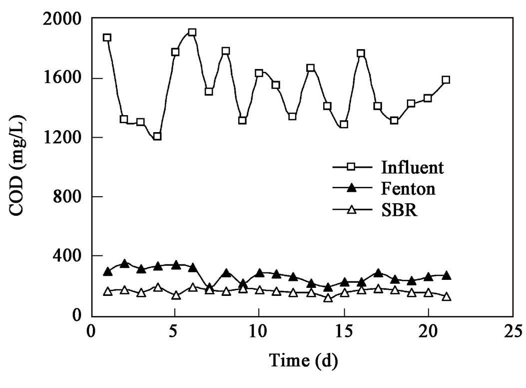

Fig. 8 COD removals by Fenton's oxidation and SBR.

3 Conclusions

The present study demonstrated that the high concentration of COD in the ODB 2 wastewater could be removed by a combination of acidification-precipitation, two steps of biological treatments enhanced by Fenton's oxidation. Acidification pretreatment under a pH of 2.5–3.0 permitted a COD removal of 70%–80%. The primary biological treatment permitted an average COD removal of 70% under an HRT of 30 h. The second step biological treatment could ensure an effluent COD below 200 mg/L following Fenton's treatment with an Fe^{2+} dose of 6.0 mmol/L, an H_2O_2 dose of 3000 mg/L, and an reaction time of 6 h.

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