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Evaluation of the correlation between ammonia nitrogen and *p*-toluidine using sequencing batch reactor treating synthetic *p*-toluidine wastewater

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Abstract: This paper presents lab-scale experiment carried out to evaluate the correlation between ammonia nitrogen (NH_3-N) and *p*-toluidine using sequencing batch reactor treating synthetic *p*-toluidine wastewater. The profiles of NH_3-N and *p*-toluidine were traced under the concentration of sucrose in the influent varied from 0 to 500 mg/L, aerated airflow varied from 0.6 to 1.2 L/min and temperature varied from 10 to 25℃, respectively. The results showed that the concentration of NH_3-N turned from increase to decrease when *p*-toluidine was nearly completely biodegraded, so the profile of NH_3-N could clearly indicate the endpoint of *p*-toluidine biodegradation. And the profile of NH_3-N was not influenced by the sucrose in the influent, aerated airflow and temperature. It is showed that using ammonia nitrogen as monitoring and control parameter is feasible and reliable and has promising application in amine wastewater treatment by SBR.

Keywords: sequencing batch reactor; correlation; ammonia nitrogen; *p*-toluidine; biodegradation

Introduction

The activated sludge process has been traditionally applied to treat industrial wastewater, but the nature of such discharges often causes operational problems in continuous flow systems. The sequencing batch reactor (SBR) has been widely used for the treatment of inhibitory wastewater. It can work with suspended or attached biomass. SBR-type bioreactor operates under five well-defined phases: fill, react (biodegradation), settle, draw and idle. The standard operation mode consists in fixing the duration of each phase according to a programmed strategy. The duration of these phases is typically determined by an expert operator based on experience and exhaustive testing in the laboratory with a pilot plant. However, SBR is usually controlled with a steady-state sequential approach, in which it is difficult to adjust the operational and control conditions to dynamic influent loading and system state variations, and always led to tremendous energy and resources consumption for meeting the effluent standards and increasing the system operation performances. To overcome the problems discussed above, several operation modes have been presented using dissolved oxygen (DO) concentration (Buitrón *et al.*, 2005; Nguyen *et al.*, 2000), the electric conductivity(Serralta *et al.*, 2004), the carbon dioxide evolution rate(CER) (Buitrón *et al.*, 1993), the oxygen uptake rate(OUR) (Third *et al.*, 2004; Vives *et al.*, 2003), oxidation-reduction potential(ORP)(Gao *et al.*, 2003), pH (Peng *et al.*, 2003, 2004) and so on to control parameters. The reduction of the cycle time of the SBR volume by using the automated system increases the quantity of water that can be treated (or, alternatively, less volume would be needed for a same water flow).

p-Toluidine is one of the important industrially produced amines. It is a useful intermediate in the production of dyestuffs, pesticides and drugs. Thus, a variety of industrial effluents have *p*- toluidine as a major constituent. Discharge of *p*- toluidine to the environment must be controlled as *p*-toluidine is toxic and also exerts additional oxygen demand due to nitrification reaction involved during biodegradation. And because the mass of *p*- toluidine and other contaminants in wastewater were fluctuant, so the automated control was important for treating these waters efficiently. Biological conversion of aniline involves first, carbonaceous removal by heterotrophic bacteria releasing ammonia nitrogen as the end product (Gheewala and Annachhatre, 1997). And the amounts of NH_3-N released were stoichiometric to the amounts of aniline added (Liu *et al.*, 2002). So it was hypothesized the course for *p*-toluidine biodegradation has the similar characteristics. Therefore, the NH_3-N concentration maybe correlates with the concentration of *p*-toluidine in the course of *p*-toluidine biodegradation. The objective of this study was to explore the correlation between ammonia nitrogen and *p*-toluidine using sequencing batch reactor treating synthetic *p*-toluidine wastewater. In this paper, the profiles of NH_4-N and *p*-toluidine were studied while the duration of *p*-toluidine aerobic biodegraded in SBR at different conditions.

1 Materials and methods

1.1 Wastewater and pilot reactor

Synthetic wastewater was prepared with ordinary tap water and *p*- toluidine (AR grade) and

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complemented with the following composition (per liter of wastewater): NH_4Cl (75 mg/L), KH_2PO_4 (25 mg/L), $NaHCO_3$(375 mg/L), $MgSO_4$(250 mg/L), yeast extract paste (12.5 mg/L). The concentration of *p*-toluidine and sucrose (0—500 mg) were diluted as experiment needed.

A cylindrical vessel with 1.3 L working volume was used as the pilot SBR system. The volume exchange in each cycle was 0.8 L thus the exchange ratio in the reactor was about 61.5%. The SBR was operated in a fill-react-settle-draw-idle mode and repeated continuously. The fill and draw phases were immediate. The time of react, settle and idle phases were 8 h, 2 h and 1.5 h, respectively. After the fill phase finished, there was a still phase about 30 min without both aerated and stirred. Air was provided by an air pump through a diffuser placed at the bottom of the reactor. The aerated airflow was ranged from 0.6 to 1.2 L/min controlled by a flowmeter as experiment needed. An automatic temperature controller was used to maintain the temperature of the reactor at the temperatures needed.

The inoculated activated sludge was coming from the aeration tank of a municipal activated sludge treatment plant. After about 30 d, the biomass was acclimated to degrade about 330 mg/L *p*-toluidine present in the influent. The biomass in SBR was kept about 6000 mg/L of mixed liquor suspended solids (MLSS) and about 5300 mg/L of mixed liquor volatile suspended solids(MLVSS).

1.2 Analyses

During all the operational study, raw and treated wastewaters were analyzed for NH_3-N, *p*-toluidine and the sludge for MLSS, MLVSS according to standard methods (AHPA, 1998). A model TOC 5000 (Shimadazu, Japan) was used to determine the TOC of raw and treated wastewater.

1.3 Experimental strategy

After microorganisms were acclimated to the *p*-toluidine concentration in the influent of about 330 mg/L, the profiles of NH_3-N, TOC and *p*-toluidine were determined during the aerated phase under different operating conditions. In this paper, the influences of concentration of sucrose in the influent, aerated airflow and operational temperatures on the profiles of *p*-toluidine, TOC and NH_3-N were investigated. Every operating condition was conducted several cycles to let the reactor come to stable. In the experiment 1, the initial sucrose concentrations in the influents were 0, 125, 250, 500 mg/L in four runs, respectively. The aerated airflow and reactor temperature were controlled at 0.6 L/min and 25 ± 0.5℃. In the experiment 2, the aerated airflows were 0.6, 0.9 and 1.2 L/min, respectively. The initial sucrose concentration in the influent and the reactor temperature were 500 mg/L and 25 ±0.5℃. In the experiment 3, the reactor temperature was controlled at 10, 20 and 25℃, respectively. The initial sucrose concentration in the influent and the aerated airflow were 500 mg/L and 0.9 L/min, respectively. In all experiments, the concentration of *p*-toluidine was about 330 mg/L in the influent.

2 Results and discussion

2.1 Profiles of *p*-toluidine, TOC and NH_3-N with different initial sucrose concentrations in the influent

The profiles of *p*-toluidine, TOC and NH_3-N with four concentrations sucrose in the influents were traced(Fig.1). As Fig.1b shows, with the concentration of sucrose in the influent increased, the time for *p*-toluidine nearly completely biodegraded increased. It is because of the competition between *p*-toluidine and sucrose. During biodegradation of *p*- toluidine, the concentration of NH_3-N increased quickly. When *p*-toluidine was biodegraded below 1 mg/L, the concentration of NH_3-N turned from increase to decrease (Fig.1a). So the point where the maximum concentration of NH_3-N in the profile means that *p*-toluidine was almost biodegraded. The variation of NH_3-N was the results of the biodegradation of *p*-toluidine and nitrification. While *p*- toluidine was biodegraded, the NH_3-N was being released. For the inhibition of *p*-toluidine and sucrose to nitrifier, so the NH_3-N was accumulated. When the *p*-toluidine was almost biodegraded, the nitrification became dominant and the concentration of NH_3-N began to decrease. With the concentrations of sucrose in the influents increased, the times of the NH_3-N concentration peaks appeared delayed, which was consistent with the time

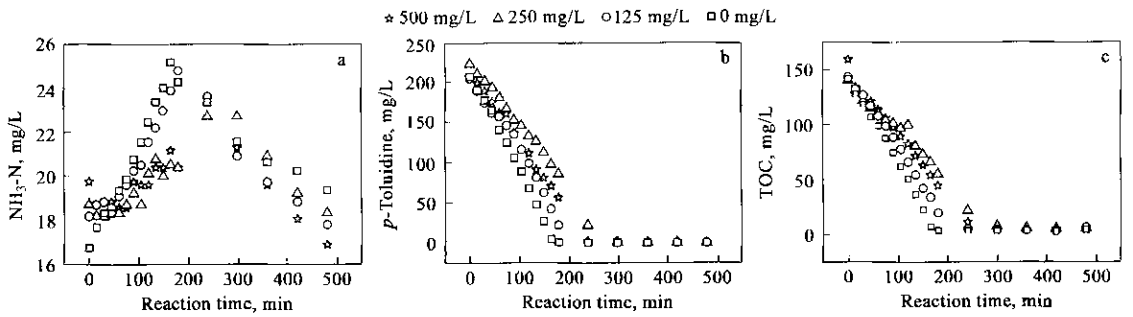

Fig.1 Profiles of NH_3-N, *p*-toluidine and TOC during aerated phase under different initial sucrose concentrations in the influent

that the *p*- toluidine biodegraded delayed. The maximum of the NH_3-N concentration was also influenced by the sucrose concentration in the influent. With the sucrose concentration increased, the maximum of NH_3-N was decreased. It is because when the heterotrophic bacteria degraded the sucrose, they also used some NH_3-N for growth and reproduction. The TOC profiles(Fig.1c) show that the TOC was biodegraded under 10 mg/L when the concentration of NH_3-N turned from increase to decrease. It is because that the microorganisms were fully acclimated to *p*-toluidine so the sucrose and *p*-toluidine were biodegraded simultaneously. It was illuminated that using NH_3-N as control parameter to indicate the endpoint of biodegradation of *p*-toluidine is feasible and reliable under the initial second substrate concentrations in the influents were greatly different.

2.2 Profiles of *p*-toluidine and NH_3-N under different aerated airflows

The aerated airflow directly influences the concentration of DO in the reactor. And the concentration of DO influences the rates of biodegradation and nitrification greatly. The high DO concentration will enhance the metabolic activity of ammonia-oxidizing bacteria (Wang and Yang, 2004). To investigate the influence of aerated airflow on the profiles of NH_3-N and *p*- toluidine, three runs were conducted under various aerated airflows (Fig.2). As Fig.2b shows the time for *p*-toluidine biodegraded under 1 mg/L delayed from about 250 min to 100 min when the aerated airflow increased from 0.6 to 0.9 L/min. While the aerated airflow changed from 0.9 to 1.2 L/min, the time for biodegraded *p*-toluidine barely reduced. When the aerated airflow increased from 0.6 to 0.9 L/min, the concentration of NH_3-N in the reactor decreased greatly and the time for the maximum of NH_3-N appeared was delayed from about 250 to 100 min. However, while the airflow was changed from 0.9 to 1.2 L/min, the concentration of NH_3-N in the reactor increased a little and the time for the maximum of NH_3-N appeared advanced a little. The results illuminated when the aerated airflow was 0.6 L/min DO was the limiting factor, so when the aerated airflow was 0.9 L/min the rates of *p*-toluidine biodegradation and nitrification enhanced greatly. While the aerated airflow was above 0.9 L/min, the limiting factor was not DO but the activity of bacteria. Therefore, increasing the aerated airflow did not increase the efficiency for the remove of *p*-toluidine and NH_3-N. Although the rates of nitrification and *p*-toluidine biodegradation varied wildly under different aerated airflows, all the profiles of NH_3-N have the point that the concentration of NH_3-N was maximum. At these points the concentrations of NH_3-N were turned from increase to decrease. These points were accurately coincided with the end of the biodegradation of *p*-toluidine.

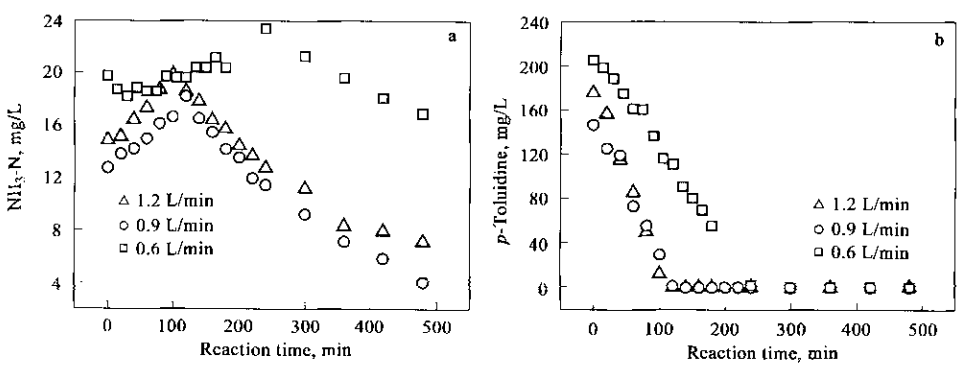

Fig.2 Profiles of NH_3-N, and *p*-toluidine during aerated phase under different aerated airflows

2.3 Profiles of *p*-toluidine and NH_4-N at different temperatures

Three runs were conducted at 10, 20, 25℃, respectively. As Fig.3b shows, the biodegradations of *p*-toluidine were nearly finished in about 100 min at 20, 25℃, and while at 10℃ the time for *p*-toluidine completely biodegraded was about 300 min. The rate of *p*-toluidine biodegradation at 10℃ was only one third of the rates at 20 and 25℃. As Fig.3a shows, the nitrification rate decreased greatly with the temperature decreased. It is because that nitrifying bacteria grow slowly and are sensitive to environmental conditions, the growth and activity of nitrifiers are greatly influenced by temperature (Martin *et al.*, 2005). The rate of nitrification at 20℃ was much lower than that at 25℃ and the nitrification nearly stopped at 10℃. This observation was in accordance with the classical temperature influence found in the literature that the nitrification rate increased by two to three times as temperature increased by 10℃ over the range of 5—30℃ (Rittmann and McCarty, 2001). At 25℃ the maximum concentration of NH_3-N was about 18 mg/L, while at 10, 20℃ the maximum concentration of NH_3-N was about 28 mg/L. The time for the maxima of the NH_3-N concentrations at 10, 20, 25℃ was about 300, 100 and 100 min, respectively. They

were accordant with the time needed for the *p*-toluidine concentration decreased 1 mg/L. Although the influence of temperature on nitrification was much greater than that on the biodegradation of *p*-toluidine, the profiles of NH_3-N could still clearly indicate the point where the *p*-toluidine was almost biodegraded accurately.

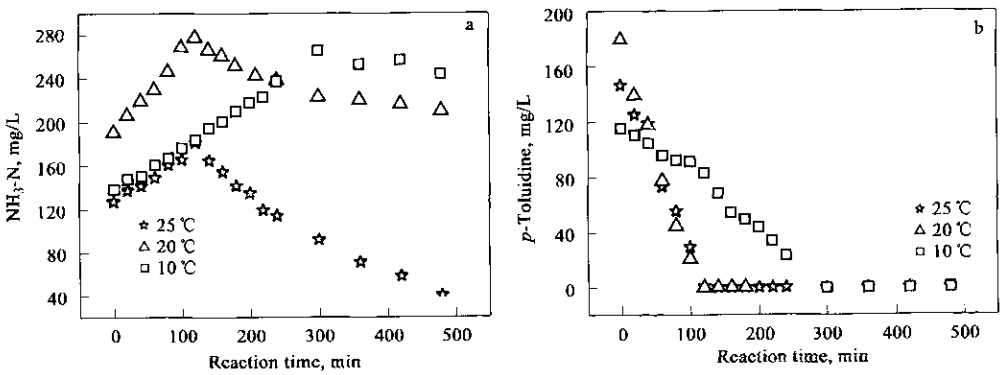

Fig.3 Profiles of NH_3-N, and *p*-toluidine during aerated phase at different temperature

3 Conclusions

According to the results, the profile of NH_3-N clearly indicated the end of *p*-toluidine biodegradation under different conditions. The time when the concentration of NH_3-N turned from increase to decrease means the *p*-toluidine was biodegraded nearly completely. Therefore, the length of aerobic phases can be controlled by monitoring the profile of NH_3-N in SBR treatment of synthetic *p*-toluidine wastewater.

When the sucrose concentration varied from 0 to 500 mg/L the profile of NH_3-N could clearly indicate the endpoint of biodegradation for *p*-toluidine and organic substance. The fluctuation of initial second substrate(sucrose in this experiment) concentrations in the influents did not influence the application of using NH_3-N as control parameter.

The profile of NH_3-N could reliably indicate the endpoint of biodegradation for *p*-toluidine when the acrated airflow was varied from 0.6 L/min to 1.2 L/min and the temperature varied from 10 to 25℃. It is illuminated that using NH_3-N as control parameter to indicate the endpoint of biodegradation of *p*-toluidine is feasible and reliable under different aerated airflow and temperature.

Using NH_3-N as control parameter can help increasing the efficiency of the treatment process and reducing the energy and resources consumption by automatically optimizing the time required to effectively treat the *p*-toluidine wastewater. This control strategy maybe has promising application in amine wastewater treatment with SBR.

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