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Technical Note

Comparison of polyurethane foam and biodegradable polymer as carriers in moving bed biofilm reactor for treating wastewater with a low C/N ratio

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ABSTRACT

This paper presents a comparison between two different materials used as carriers: inert polyurethane (PU) foam and biodegradable polymer polycaprolactone (PCL) particles for the removal of organics and nitrogen from wastewater with a low C/N ratio using moving bed biofilm reactors. The results, during a monitoring period of four months, showed that TOC and ammonium removal efficiency was higher in reactor 2 filled with PU carriers than in reactor 1 filled with PCL carriers (90% and 65% in the former, compared with 72% and 56% in the latter at an hydraulic retention time of 14 h). Reactor 1 showed good behavior in terms of total nitrogen removal as the biodegradable polymer was an effective substrate providing reducing power for denitrification. From three-dimensional excitation–emission matrix analysis, it was shown that the effluent from reactor 1 contained mainly protein-like and soluble microbial product-like substances.

1. Introduction

The removal of total nitrogen (TN), i.e., ammonium, nitrate, and nitrite, is an increasingly important goal in municipal and industrial wastewater treatment plants. Practical and cost-effective biological nitrogen removal technologies are needed, especially in older plants with limited space for expansion. The moving bed biofilm reactor (MBBR), which combines suspended growth and attached growth processes by adding free-floating biofilm carriers into the aeration tank, is a highly effective biological treatment process and has attracted significant interest in the field of wastewater treatment (Rusten et al., 1997; Rouse et al., 2007; Di Trapani et al., 2008). Typical advantages of the MBBR system are the low head loss, no filter channeling, no need for periodic back washing and sludge recycle, and a large surface area for colonization and high specific biomass activity (Odegaard, 2006; Guo et al., 2010). To date, the MBBR has been successfully employed to treat sewage and industrial wastewater and upgrade small wastewater treatment plants (Andreottola et al., 2000; Loukidou and Zouboulis, 2001; Yang et al., 2009). Di Trapani et al. (2010a) compared the traditional activated sludge system and the MBBR for treating sewage wastewater. Their results showed that good treatment performance of the MBBR system was obtained in terms of removal of organics and ammonium. Chen et al. (2008) used a MBBR with anaerobic–aerobic processes to treat landfill leachate using polyethylene carriers. The anaerobic reactor played a major role in COD removal (92–95% at an organic loading rate of 4.1–15.7 kg COD m^{-3} d^{-1}) due to the fact that methanogenesis, and the aerobic MBBR was involved in the removal of ammonium (>97% at a hydraulic retention time (HRT) of more than 1.25 d).

The biofilm carriers used in these systems have included polyethylene, granular activated carbon, sand and diatomaceous earth. The polyurethane (PU) carrier is an ideal growth medium with high porosity for microorganism immobilization, good mechanical strength and low cost (Chae et al., 2008; Kim et al., 2009). Deguchi and Kashiwaya (1994) reported that the nitrification and denitrification rate coefficients of the PU suspended biological growth reactor were 1.5 and 1.6 times, respectively, higher than those of a conventional activated sludge reactor.

The biological process is economical for wastewater treatment, but it is often ineffective for treating wastewater with a low C/N ratio due to a shortage of carbon sources for denitrification (Aslan and Turkman, 2003; Boley and Muller, 2005). With the application of more stringent nutrient discharge criteria, the demand for external carbon sources for enhanced denitrification is increasing. In recent years, new biodegradable polymers including polycaprolactone (PCL), poly butylene succinate and poly lactic acid as solid organic carbon sources have been developed (Boley et al., 2000; Honda and Osawa, 2002; Walters et al., 2009). Compared to the traditional

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soluble organic carbon sources, the solid organic substances, also acting as biofilm carriers themselves, are accessible for denitrification only by enzymatic attack. Therefore, the process is simple and the risk of overdosing or insufficient carbon dosing can be avoided (Boley and Muller, 2005). For a better understanding of the role that solid carbon sources play in bioreactors, further research is necessary.

The objective of the present study was to investigate the efficiency of suspended carrier biofilm technology by comparing two different materials as carriers: inert PU foam and biodegradable polymer PCL particles for the removal of organics and nitrogen from wastewater with a low C/N ratio. The characteristics of nitrogen removal and the structure of the microorganisms attached the two types of carriers were evaluated.

2. Materials and methods

2.1. Experimental setup and carriers

Two MBBRs, one (reactor 1) filled with PCL carriers and another (reactor 2) filled with PU carriers, were set up on a laboratory scale. Each reactor contained a 6.0 L aeration zone and a 3.5 L settling zone. Air was diffused in order to supply oxygen to the microbial mass for biological activity and to mix the carriers. The supplied airflow was controlled at a rate of 160–180 L h^{-1}. The reactors were operated at 19–27 °C, from March to July, 2010. Table 1 shows the characteristics of the PCL and PU carriers. It was obvious that the PU foam had a high specific surface area and water retention ratio due to high porosity.

2.2. Wastewater and experimental procedure

Synthetic wastewater was prepared by dissolving glucose, NH_4Cl, KH_2PO_4 and trace elements in tap water. It consisted of 192–406 mg COD L^{-1}, 44 ± 5 mg NH_4 L^{-1}, 3.2 ± 1.2 mg total phosphorus (TP) L^{-1}, 10 ± 3 mg nitrate NO_3 L^{-1} (from tap water) and 0.1% (v/v) of a trace nutrient solution containing the following (g L^{-1}): $MgSO_4{\cdot}7H_2O$, 2.5; $CaCl_2$, 1.5; $FeSO_4{\cdot}7H_2O$, 0.28, $MnCl_2{\cdot}4H_2O$, 0.13; $ZnSO_4{\cdot}7H_2O$, 0.12; $CoCl_2{\cdot}6H_2O$, 0.004; H_3BO_3, 0.003; $Na_2SeO_3{\cdot}5H_2O$, 0.003. The pH value was 7.7 ± 0.2.

Wastewater was continuously fed to the reactor using a peristaltic pump. The operation of the two MBBRs was started by inoculating activated sludge taken from an oxic tank at the Qinghe municipal wastewater treatment plant, Beijing. The initial sludge concentration was 2.5 g total suspended solids (TSS) L^{-1}. The MBBRs were in continuous operation in parallel for 4 months. The variations in operational parameters are listed in Table 2. The long-term operational period was divided into three phases. The first step was the start-up period and consisted of decreasing the HRT stepwise from 40, to 24 and to 16, and then to 14 h in both systems. Then the two MBBRs were operated at a HRT of 14 h and the COD/TN ratio of the influent was maintained at approximately 4.2. Finally, in the third phase, the influent COD/TN ratio was increased by increasing the COD concentration to investigate the effect of COD/TN ratio on TN removal. Treatment performance was monitored by following NH_4, NO_2 and NO_3, as well as TN, TOC and pH values in the effluent three to five times a week. The structure of the biofilm attached to the carriers and the used PCL and PU carriers after being washed with deionized water were examined by a scanning electron microscope (SEM, JSM-6700F, JEOL, Japan).

Table 1
Characteristics of the PCL and PU carriers.

Parameters	PCL	PU
Diameter (mm)	3.5–4	8–10
Height (mm)	3	8–10
Density (kg L^{-1})	1.08–1.12	0.3–0.5
Specific surface area	0.346 m^2 g^{-1}	900 m^2 m^{-3}
Filling ratio (%) on volume basis	16.7	20
Dry weight (g) per piece	0.0245	0.0936
Wet weight (g) per piece	0.0274	0.673

2.3. Batch experiments

On 90th day, about 70 mL of PCL and PU carriers with biofilm were taken from the two MBBRs for batch experiments to determine the kinetics of organics and nitrogen removal at 26 ± 2 °C. Before these experiments, the carriers were gently rinsed with deionized water to remove residual dissolved compounds in the reactors.

Aerobic batch experiments were performed in two 500 mL Erlenmeyer flasks filled with PCL and PU carriers, respectively. Approximately 200 mL of synthetic wastewater (glucose, NH_4Cl and trace elements solution diluted in tap water) containing 20 mg L^{-1} of TOC, 42 mg L^{-1} of NH_4 and 15 mg L^{-1} of NO_3 were added to the flasks. Aeration was supplied though an air diffuser installed in the bottom of the reactor. Supernatant samples were taken periodically to determine the concentrations of TOC and nitrogen compounds (NH_4, NO_3 and NO_2). The specific ammonium oxidation rate (SAOR, g N g volatile suspended solid (VSS)$^{-1}$ d^{-1}) was calculated by the decreasing slope of ammonium concentration with time and divided by the initial VSS concentration.

2.4. Analytical methods

TOC was evaluated by a TOC analyzer (multi N/C 2100, Analytik Jena, Germany). COD, TN, NH_4, NO_3, NO_2 and TP contents were determined according to Chinese SEPA Standard Methods (SEPA, 2002). Dissolved oxygen (DO) was measured by a DO meter (JPSJ-605, Rex, China).

The biofilm attached to the PCL carriers was removed by ultrasonic treatment for 5 min and 2 kW L^{-1}at a frequency of 40 kHz. The sludge samples were centrifuged at 5000 rpm for 15 min. The pellets were heated at 105 and 550 °C to measure TSS and VSS, respectively. An assessment of the biofilm attached to the PU carrier was carried out which also considered the biomass in the pores. To evaluate the TSS on the support carriers, a sample of carrier elements was taken from the reactor, dried at 105 °C for 24 h and weighed. This value was then compared with an average "zero" weight of the fresh carrier, thus obtaining TSS amount attached to the PU carriers (Di Trapani et al., 2010b). The extracellular polymer substances (EPS) in the biofilm were extracted using the formaldehyde–NaOH method (Liu and Fang, 2002).

Three-dimensional excitation–emission matrix (EEM) fluorescence spectroscopy was used to characterize the dissolved organic matter in the effluent of the two systems. Fluorescence EEM measurements were conducted using a Hitachi F-7000 fluorescence spectrophotometer. The spectrometer used a xenon excitation source, and excitation (Ex) and emission (Em) slits were set to a 10 nm band-pass. Ex wavelength was set at 200–450 nm and Em at 250–500 nm, applying a bandwidth of 2 nm for both. The scanning speed was set at 1200 nm min^{-1}.

3. Results and discussion

3.1. Performance of the two MBBRs

Fig. 1 illustrates the variation in effluent TOC, ammonium and nitrate as well as TN removal in the two systems during the whole operation period. After one month of operation, the MBBRs were