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Insight into the roles of tightly and loosely bound extracellular polymeric substances on a granular sludge in ammonium nitrogen removal

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HIGHLIGHTS

- Ammonium, nitrite and nitrate nitrogen were present in the LBEPSs and TBEPSs.
- LBEPSs and TBEPSs had a greater ability to adsorb ammonium nitrogen.
- LBEPSs had higher adsorption (retention) of nitrite and nitrate nitrogen.
- LBEPSs had greater mass transfer resistance.

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ABSTRACT

To explicitly understand the function of extracellular polymeric substances in the treatment of ammonium-nitrogen-rich wastewater using aerobic granular sludge, the three forms of nitrogen (ammonium, nitrite and nitrate nitrogen) contained in tightly and loosely bound extracellular polymeric substances were analyzed. The three forms of nitrogen were monitored in the tightly and loosely bound extracellular polymeric substances in aerobic granular sludge after adsorption. The ammonium nitrogen contained in the extracellular polymeric substances was distributed in both the tightly and loosely bound forms and decreased gradually as the aeration time increased. Ammonium nitrogen remained in the tightly bound extracellular polymeric substances even after aeration was complete. The nitrite and nitrate nitrogen species in the extracellular polymeric substances were mainly present in the loosely bound extracellular polymeric substances. The sources of the three nitrogen forms detected in the extracellular polymeric substances differed relative to the different nitrogen forms.

1. Introduction

Several properties of aerobic granular sludge (AGS), including good sludge settling, a high sludge concentration, highly efficient solid-liquid separation and promotion of long-term microorganism, are advantageous, explaining its widespread use in sewage treatment, especially the treatment of wastewater containing hazardous substances (Lv et al., 2014) and high levels of ammonium nitrogen (Wang et al., 2012).

As a result of the secretion of microorganisms, extracellular polymeric substances (EPSs) contain large amounts of proteins (PN), polysaccharides (PS) and other substances and widely exist in the sludge floc and granular sludge. EPSs play very important roles in microbial aggregates (Liu et al., 2010); sludge flocculation, settlement and dewatering performance (Li and Yang, 2007); carbon/nutrient storage (More et al., 2014); protection of cells (Li and Yu, 2014); and maintaining the formation and stability of granular sludge. Additionally, because cells exchange material with the outside environment, EPSs affect metabolism and substrate removal. Researchers have primarily focused on the role of EPSs in enhancing the removal of biological phosphorus (Li et al., 2015). Few studies have evaluated the nitrogen content in EPSs (Chen et al., 2015; Lin et al., 2012), and those that have only evaluated ammonium nitrogen. The detected ammonium concentration is often lower than the theoretical concentration predicted for the ammonium nitrogen removal process. This result was attributed to several phenomena, of which the adsorption behavior

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was viewed as an important process. As a result, researchers began to focus on the adsorption of ammonium nitrogen in activated sludge, biofilms and granular sludge (Bassin et al., 2011; Schwitalla et al., 2008; Temmink et al., 2001). The adsorption studies mainly focused on the batch adsorption process, and there is a lack of direct and effective information on the continuous adsorption process. A previous study by the author revealed that EPSs contained large amounts of ammonium, nitrite and nitrate nitrogen (Yan et al., 2016) and provided a new way to directly study the adsorption of ammonium nitrogen.

EPSs have a dynamic two-layer structure consisting of tightly bound EPSs (TBEPSs) in the inner layer of cells and loosely bound EPSs (LBEPSs) in the outer layer (Li and Yang, 2007). Because of the difference in the composition and location of components, their effect on the flocculation of sludge, surface properties and dewatering performance are different (Ahmed et al., 2007; Basuvaraj et al., 2015; Li and Yang, 2007). Although TBEPSs contain more PN and PS, LBEPSs have a greater performance impact on sludge flocculation, sedimentation and dewatering. Understanding the distribution of ammonium nitrogen and its transformation products in LBEPSs and TBEPSs will further understanding of the role of LBEPSs and TBEPSs in ammonium adsorption by sludge as well as the role of EPSs in biological nitrification and denitrification.

The purpose of this study was to determine the concentrations of ammonium, nitrite and nitrate nitrogen in LBEPSs and TBEPSs at the beginning of aeration and throughout the whole aeration process during AGS treatment of ammonium-nitrogen-rich wastewater and then to analyze the role of LBEPSs and TBEPSs in ammonium biotransformation. This study furthers understanding of the roles of LBEPSs and TBEPSs in ammonium removal by granular sludge.

2. Materials and methods

2.1. Reactor set-up and operation

The test device was a cylindrical sequencing batch reactor (SBR) composed of organic glass (Fig. S1) and with a height of 85 cm, an inner diameter of 9 cm, an effective volume of 4.2 L, and an exchange ratio of 50% by volume. The SBR was controlled by a time controller with a cycling time of 4 h; six cycles were performed each day. Each cycle consisted of influent of 5 min, aeration for 198 min, sedimentation for 5 min, draining for 2 min, and idling for 30 min. The temperature was not intentionally controlled in the continuous flow experiment. A flow meter was used to control the flow rate of air at 1.19 vvm. The dissolved oxygen (DO) content was 6–8 mg/L.

2.2. Experimental wastewater and sludge

Artificial wastewater was used as the experimental water, glucose and sodium acetate were used as carbon sources, and ammonium chloride was used as a nitrogen source. The detail characteristics of the sewage were as follows: 170–290 mg/L chemical oxygen demand (COD), 270–330 mg/L NH_4^+-N, pH 7.2–8.0, 10 mg/L $CaCl_2 \cdot 2H_2O$, 20 mg/L $MgSO_4 \cdot 7H_2O$, and 0.5 ml/L trace elements (Yan et al., 2014).

The inoculated AGS was obtained from an ongoing lab-scale SBR system (Yan et al., 2014), and the original AGS concentration, particle size distribution and contaminant removal characteristics are shown in Tables 1 and 2.

Table 1
AGS characteristics.

Sludge properties	Numerical value	Particle size (mm)	Percentage mass content (%)
MLSS ($g.L^{-1}$)	6.28 ± 0.19	>1.7	33.62
SVI ($ml.g^{-1}$)	50.08 ± 0.74	1.4–1.7	9.08
		1.0–1.4	14.35
		0.85–1.0	0.51
		0.5–0.85	5.75
		<0.5	42.44

Table 2
Characteristics of influent and effluent for AGS.

Parameters	Characteristics of effluent and influent	
	Average influent	Average effluent
COD ($mg.L^{-1}$)	226.79 ± 41.07	34.70 ± 12.85
Ammonium nitrogen ($mg.L^{-1}$)	301.16 ± 18.84	2.17 ± 1.56
Nitrite nitrogen ($mg.L^{-1}$)	0.050 ± 0.029	108.04 ± 28.30
Nitrate nitrogen ($mg.L^{-1}$)	0.04 ± 0.02	135.77 ± 23.90
pH	7.47 ± 0.27	7.03 ± 0.53

2.3. Adsorption experiments

Sludge mixture samples were collected from the reactor at 2 min before the end of the aeration, and the samples were divided into four equal parts. The samples were centrifuged (336g, 5 min), and the supernatant was discarded. Then, the sludge pellets were used in the adsorption experiment. Three pellets were each placed into 500 mL beakers. Solutions of NH_4Cl (199.80 mg/L), $NaNO_3$ (100.33 mg/L), and $NaNO_2$ (94.63 mg/L) were added to separate beakers, and the mixtures were brought to the initial volume (S1, S2 and S3). The pH was adjusted to 7.5 by adding 0.05 mol/L NaOH or 10% sulfuric acid. Afterwards, the solutions were placed on magnetic stirrers for 210 min, along with the fourth sample, a blank. LBEPSs and TBEPSs were extracted and analyzed for their nitrogen contents.

2.4. LBEPS and TBEPS extraction method

Samples of the mixed solution inside the SBR were collected 2 min after the start of aeration, at different times during the aeration reaction and 2 min before the end of the aeration. Then, the samples were centrifuged (336g, 5 min), and diluted with deionized water to the original volume. LBEPSs and TBEPSs were extracted according to procedures in the literature (Yan et al., 2015).

2.5. Analytical procedure

Analysis of the ammonium nitrogen, nitrite nitrogen, nitrate nitrogen, pH, COD, mixed liquor suspended solids (MLSS), and sludge volume index (SVI) were performed in accordance with standard methods (APHA, 1998). The measurement of DO was carried out using a DO meter (inoLab Oxi 7310, WTW Company, Germany). PS and PN were determined according to procedures described in the literature (Frølund et al., 1996; Lowry et al., 1951).

3. Results

3.1. Quantitative analysis of TBEPSs and LBEPSs

The PN and PS concentrations in the TBEPSs and LBEPSs are shown in Table 3. The main component of the EPSs was PN; the main component of the TBEPSs was also PN, consistent with other