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Effects of magnetic nanoparticles on aerobic granulation process

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HIGHLIGHTS

- Magnetic NPs shortened the granulation time and enhanced the granules stability.
- MNPs affected the secretion and functional bands of extracellular polymer substrates.
- The hydrophobicity of granular sludge was correlated with the concentration of MNPs.

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ABSTRACT

A novel granulation strategy by introducing magnetic nanoparticles (MNPs) into activated sludge system was investigated in this study. The study of the physicochemical characteristics (appearances, sizes, sludge volume index, and chemical oxygen demand) demonstrated that MNPs could decrease the granulation time and improve the retention of biomass, meanwhile enhanced the compact structure of the granules. The secretion and functional groups especially O—H and C=O of extracellular polymeric substances (EPS) also had significant changes under the long-term influence of MNPs. The contents of proteins (PN) and polysaccharides (PS) in R2 (with MNPs) were 95.7523 mg/gVSS and 43.7129 mg/gVSS, while in R1 (without MNPs) they were 85.7523 mg/gVSS and 32.8632 mg/gVSS, respectively. The contact angles of sludge against water dramatically increased with the increase of MNPs concentration, which means that the addition of MNPs could improve the sludge surface hydrophobicity, playing a positive role in the aggregation process.

1. Introduction

Aerobic granular sludge (AGS) technology has been extensively investigated during recent decades in the laboratory level and even has been scaled-up and implemented for industrial and municipal wastewater treatment under the product name of Nereda (Pronk et al., 2015). As dense microbial aggregates, aerobic granules have better settling ability, higher biomass levels, and better adaptation to shock loadings and unfavorable environmental conditions compared with conventional activated sludge system (Adav et al., 2008a; Abdullah et al., 2013; Dai et al., 2015). Granules have excellent settling properties, therefore Nereda does not require a separate time-consuming decant phase like conventional SBR's. Furthermore, all the biological treatment processes take place simultaneously in the granules, requiring only one tank. Moreover, AGS technology was assigned to treat various types of high-strength wastewaters (Corsino et al., 2016; Ramos et al., 2016) or wastewater with high levels of toxicity (Li et al., 2015; Wei et al., 2015). Especially, the excellent simultaneous nitrification and denitrification capacity makes AGS more attractive (Yilmaz et al., 2008). The limiting factor of the popularity and applications of aerobic granules is mainly the long start-up time. Yilmaz et al. (2008) reported that aerobic granulation process took 170 days to treat synthetic wastewater. Shi et al. (2011) obtained 0.8 mm granules after 60 days of operation. Such a long start-up time is a major drawback for aerobic granules to be a worldwide application technology in wastewater treatment.

Granulation is affected by a number of operational parameters, and one of the most essential factors is the manipulation of organic loading rate (OLR), serving as selective pressure which pushes microbes to aggregate (Peyong et al., 2012). Meanwhile, hydrodynamic turbulence caused by up flow aeration also influences the formation structure and stability of granules (Liu and Tay, 2002). Meanwhile, granular sludge is considered to be formed because of the aggregation of multiple smaller colonies (Verawaty et al., 2012) and the attachment of layering of cells to certain surface functional points (Sun et al., 2016). Consequently, adding of

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specific carriers which the microorganisms in sludge are preferred to adhere to is beneficial for the growth of granules. Yu et al. (2009) observed that the reactor seeded with EPS-free pellets led to fast granulation with larger particle size and more compact structure. Moreover, the aerobic granular sludge reactors with crushed aerobic granules and floccular sludge can accelerate granule formation (Pijuan et al., 2011;Verawaty et al., 2012). These findings suggest that adding some kinds of matrixes for adsorbing microorganisms could enhance granule formation.

Recently, man-made nanoparticles (NPs) have been widely used in many aspects of human life. Among these artificial NPs, magnetic nanoparticles (MNPs) have appealed to much attention because of their unique magnetic features and important applications in biomedicine and therapeutics (Liu et al., 2009b). And among various magnetic nanoparticles, iron oxides, such as magnetite (Fe_3O_4) or magnemite (γ-Fe_2O_3) were considered as ideal candidates for these bio-relate applications owing to their good biocompatibility and stability in physiological conditions and low cytotoxicity (Liu et al., 2009a). Moreover, the large specific surface area of NPs leads to high surface energies, so MNPs may have a tendency to aggregate so as to minimize the surface energies (Wu et al., 2008), which means the aggregation of nanoparticles may contribute to the aggregation of sludge as a core or the nanoparticles may be combined with the charged particles on the surface of activated sludge. Therefore, MNPs could be assumed to be an appropriate candidate to shorten the start-up time of granulation process. Limbach (2008) found that large amounts of cerium oxide NPs could be adsorbed by activated sludge in a waste water treatment plant (WWTP). Wang et al. (2012) proposed that the applied magnetic field decreased the full granulation time by stimulating the secretion of extracellular polymeric substances (EPS), and Yan et al. (2015) showed that the existence of metal ions reduced zeta potential of EPS which helped the adhesion among granules. In addition, the adsorption to activated sludge was the major mechanism for NPs removal in conventional activated sludge systems. However, few researches investigated the interaction mechanism between magnetic NPs and sludge granulation process.

Since MNPs could not only be attracted by each other, but also be adsorbed by sludge bacteria as well. A novel start-up strategy was investigated in this study by adding MNPs to optimize the cultivation of aerobic granular sludge. Size distribution, biomass concentration and nutrient removal performance were monitored for several months, which allowed assessing the effectiveness of the strategy in reducing the granulation time and maintaining the activity of aerobic granular. The influence of MNPs on the secretion as well as functional groups of EPS was further investigated. Furthermore, the general physiological activity and morphology of aerobic granules were studied to confirm the effects of MNPs on the sludge bacteria. Through the investigation about the mechanism of the MNPs on granular sludge, the theoretical support may be helpful to the use of nanoparticles to enhance the properties of granular sludge.

2. Materials and method

2.1. Magnetic nanoparticles

The MNPs were synthesized by a modified solvothermal reaction (Liu et al., 2009a; Ni et al., 2013). In brief, 4.0 mmol $FeCl_3$ and 0.68 mmol trisodium citrate were first dissolved in 20 mL ethylene glycol, followed by adding 1.20 g NaAc with stirring. The mixture was stirred vigorously for 30 min and then sealed in a Teflon-lined stainless-steel autoclave (50 mL capacity). The autoclave was heated at 200 °C for 10 h and cooled to room temperature. The black products were washed with ethanol and deioned water for several times.

2.2. Seed sludge and Synthetic wastewater

The reactors were inoculated with 1.5 L of conventional activated sludge (MLSS of 3.425 g/L, SVI of 43.17 mL/g) which was taken from the secondary clarifier of Jinan No. 2 Municipal Wastewater Treatment Plant, China. Synthetic wastewater primarily consisted of ammonium chloride, glucose and sodium acetate, sodium bicarbonate (used to adjust pH at a level of 7.5–8.5) and other necessary trace nutrients according to (Ni et al., 2013). The chemical oxygen demand (COD) was kept fixing at 500 mg/L according to the influent water standard of the sewage treatment plant in China during the experiment. On account of that glucose-fed granules had a larger mean diameter than acetate-fed granules but had a filament-dominant outer surface (Tay et al., 2001), glucose and sodium acetate contributed 50% of total COD, respectively, while NH_4^+-N was stepwise increased from 100 to 400 mg/L when the removal efficiency of NH_4^+-N was more than 90%.

2.3. Parent sequencing batch reactor operation

The experiments were performed in two 3.5 L parent SBRs with volumetric exchange ratio of 50%, named R1 and R2. The reactors were worked at 21 ± 2 °C with four cycles each day. Each cycle (6 h) consisted of 12 min of influent filling, 336 min of aeration, 9 min of settling and 3 min of effluent withdraw. The influent pH was adjusted to 7.5 by adding 4 M NaOH or 4 M HCl. The settling time of two reactors was decreased from 6 to 3 min after two weeks as this abatement of settling time was beneficial to the granule formation. Air bubbles were supplied by diffusers located at the reactor bottom, providing a flux of compressed air of $0.10 m^3/h$ controlled by separated gas flowmeters. The control check (R1) without adding magnetic iron oxide nanoparticles was served as the control, while an influent of 50 mg/L magnetic iron oxide nanoparticles was added to another reactor (R2).

2.4. EPS extraction

The contents and changes of EPS were examined by ultraviolet spectrophotometer (TU-1810, China). The extraction of EPS from granules was operated by means of cation exchange resin extraction (Dowex) according to the method developed by Frolund and Palmgren (1996). The proteins and carbohydrates present in the extract were determined according to reference methods (Gaudy, 1962; Lowrry et al., 1951).

2.5. SEM and FTIR

The scanning electron microscopy (SEM) and energy dispersive X-ray were used to investigate the surface morphologies and elemental compositions of aerobic granules in parent reactors. The aerobic granules were fixed in 2.5% glutaraldehyde for 12 h and then washed three times by phosphate buffer solution. Afterwards, the samples were dehydrated orderly by 50%, 70%, 80%, 90%, 95% and 100% ethanol solution for 10 min, and washed three times by *tert*-butyl alcohol, followed by frozen drying and metal spraying. The samples were examined by SEM (S-570, Japan) coupled with EDX (Oxford INCA X, Japan). FT-IR spectra of the EPS from two different long-time reactors were recorded on a FT-IR spectrometer (Avatar 370, USA) to identify and evaluate the functional groups that might be involved in the aerobic granules process. Before analysis, the biomass was freeze-dried and then grounded to powder.

2.6. XPS

The morphologies and crystalline structure of the sludge were examined by energy dispersive X-ray spectroscopy (EDS, INCAx-