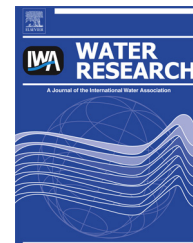




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The influence of multivalent cations on the flocculation of activated sludge with different sludge retention times

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ABSTRACT

The mechanism governing the flocculation of activated sludge (AS) with different sludge retention times (SRTs) was studied in this paper. AS samples were cultivated in 8 lab-scale reactors with SRTs of 5 d, 7.5 d, 10 d, 12.5 d, 15 d, 20 d, 30 d, and 40 d. The bulk solution, loosely bound extracellular polymeric substances (LB-EPS), tightly bound EPS (TB-EPS), and pellet were extracted for all 8 AS samples. There was a clear trend that the effluent turbidity decreased as the SRT increased, and we deduced that this is because AS samples with longer SRTs have lower interaction energy barriers and lower LB-EPS content. Furthermore, the concentrations of multivalent cations (especially trivalent cations) in the pellets were found to be closely correlated to the AS flocculability, total interaction energy (W_{tot}), and LB-EPS content. The multivalent (especially trivalent) cations possess greater binding ability, and this ability to bind tightly to AS in large quantities is responsible for the superior flocculability of AS samples with longer SRTs. Hence, the concentrations of multivalent cations in the pellets are an important indicator of AS flocculability. We deduced that variations in the quantities of multivalent cations that tightly bind with the AS rather than remaining in the influent are the core reason behind observed fluctuations in the AS flocculability with different SRTs.

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1. Introduction

Activated sludge (AS) systems are the most widely used biological wastewater treatment process (Sanin et al., 2006). One of the key elements to the successful operation of an AS system is the efficient solid–liquid separation achieved by bioflocculation.

The sludge retention time (SRT) is not only considered one of the most important operating parameters but also one of the most complicated elements to manipulate due to its widespread effects on the AS system (Maharajh, 2010). The SRT affects the performance, including the removal of slowly biodegradable organics, nitrogen, and phosphorus. In addition, AS flocculation is also considerably influenced by the

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SRT. A higher content of pin-point flocs is often found to be related to a shorter SRT, and a minimum SRT is required for acceptable bioflocculation (Maharajh, 2010). It is a commonly accepted idea that AS flocculation, sedimentation, and dewaterability improve considerably with a longer SRT (Chao and Keinath, 1979; Liao et al., 2006; Sanin et al., 2006; Li and Yang, 2007; Xie and Yang, 2009).

The extracellular polymeric substances (EPS) content also has a significant influence on the bacterial surface characteristics and flocculability (Liu et al., 2007). However, the exact role the EPS content plays in AS flocculation is currently still under debate (Masse et al., 2006). For example, Wilén et al. (2003) suggested that increased amounts of total extracted EPS are negatively correlated to AS flocculability, whereas another study showed exactly the reverse trend (Ng and Hermanowicz, 2005); meanwhile, Liao et al. (2001) found that the surface properties, hydrophobicity, surface charge, and EPS composition, rather than EPS quantity, govern bioflocculation. Recently, researchers separated EPS into two parts, loosely bound EPS (LB-EPS) and tightly bound EPS (TB-EPS), and found that LB-EPS had a negative effect on bioflocculation and sludge-water separation and also that both the flocculability and LB-EPS content of AS decreased as the SRT increased (Li and Yang, 2007; Yang and Li, 2009; Wu et al., 2011).

Due to the high negative charge density of EPS, cations also play an important role in AS flocculation (Wilén et al., 2008). The theories pertaining to the role of cations in AS flocculation are divalent cation bridging (DCB) theory (include the alginate theory) and Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (Sobeck and Higgins, 2002). According to DCB theory, divalent cations serve as bridges that connect negatively charged functional groups within the EPS and this helps to promote AS flocculation. Therefore, it is a well accepted idea that divalent cations are much more beneficial to AS flocculation than monovalent cations, and a ratio of divalent:monovalent cations exceeding 1:2 (expressed on an equivalent basis) is necessary for good bioflocculation (Higgins and Novak, 1997). The classical DLVO theory was first proposed to describe the stability of colloidal suspensions in colloid chemistry, and the theory takes into account attractive energy (the van der Waals force (W_A)) and repulsive energy (the electric double layer (W_R)) (Yen, 1999). Later, Lewis acid–base interactions (W_{AB}) were also added to the extended DLVO theory; thus, the total interaction energy (W_{tot}) in the extended DLVO theory is the sum: $W_{tot} = W_R + W_A + W_{AB}$ (Wu et al., 1999). Both DLVO theory and extended DLVO theory have been widely used in different fields including aggregation of sludge flocs (Zita and Hermansson, 1994; Liu et al., 2007, 2010; Chia et al., 2011).

Al^{3+} and Fe^{3+} are widely adopted in wastewater treatment plants (WWTPs) as coagulating agents because of their remarkable effects in promoting AS flocculation (Subramanian et al., 2010). Limited information indicates that there is a connection between the flocculation and the content of trivalent cations in the AS, and that trivalent cations contribute to a better effluent quality (Murthy and Novak, 2001; Park et al., 2006). Despite the importance of trivalent cations to bioflocculation, the role that trivalent ions such as Al^{3+} and Fe^{3+} play in AS flocculation has been investigated far

less than the roles of monovalent and divalent cations, yet researchers have suggested they may contribute greater floc stability due to their higher charge valence (Park et al., 2006; Maharajh, 2010). However, too high concentration of aluminum and iron is detrimental for the activated sludge flocculation, because their precipitate could block the transfer between microorganisms and their surroundings, and the impact is more severe for iron, due to its ability to form oxygen reactive species which could attack the molecules of microorganisms (De Freitas and Meneghini, 2001; Philips et al., 2003; Agridiotis et al., 2007).

Recent studies have shown that both longer SRTs and lower contents of LB-EPS are beneficial to AS flocculation; furthermore, they indicated that higher contents of multivalent cations also have some relationship with the bioflocculation. Thus, it is reasonable to speculate that the relationships between the abovementioned phenomena will definitely be helpful in understanding AS flocculation. In this study, we have found a relationship between the SRT, the LB-EPS content, the concentrations of multivalent cations, and the AS flocculation, and this has provided a new perspective on the mechanisms governing AS flocculation with different SRTs.

2. Materials and methods

2.1. AS cultivation

The AS used in this study was cultivated in 8 parallel sequencing batch reactors (SBRs), and each of them had a volume of 4 L. The reactors were seeded with AS from Qu Yang WWTP with a nitrogen and phosphorus removal process in Shanghai, China. Each reactor was equipped with a paddle mixer operating at 100 rpm to prevent the AS from settling; air was introduced through stone air diffusers in order to maintain the dissolved oxygen (DO) in the range of 2–3 mg/L; and the temperatures of the reactors were maintained at 20 ± 1 °C. SRTs of 5 d, 7.5 d, 10 d, 12.5 d, 15 d, 20 d, 30 d, and 40 d were achieved by wasting of the AS at the end of the last phase of aeration.

The SBRs were operated at a cycle time of 4 h; thus, 6 cycles were performed each day. Each cycle was divided into six phases: 1) mixing + filling (anaerobic) for 20 min; 2) mixing + aerating (aerobic) for 120 min; 3) mixing (anoxic) for 30 min; 4) mixing + aerating (aerobic) for 30 min; 5) settling for 30 min; and 6) decanting for 10 min. The chemical oxygen demand (COD) values of the influent and effluent for the 8 reactors are shown in Table S1, and the COD:N:P ratio of the influent was maintained at 100:7.5:1.5. Glucose, NH_4Cl , and KH_2PO_4 were the carbon, nitrogen, and phosphorus sources, respectively. The types and concentrations of feeding micronutrients (including iron) for the reactor with the SRT of 15 d were in accordance with the protocol that was given by Liao et al. (2001); and the ratios of micronutrient concentrations between all 8 reactors were the same as the ratios of their influent CODs; thus, the micronutrient concentrations were higher in the AS with shorter SRTs. The pH of all reactors was controlled in the range of 6.8–7.2 by adding $NaHCO_3$ to the influent. After 80 d of operation under good conditions,

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