



Role of extracellular polymeric substances in enhancement of phosphorus release from waste activated sludge by rhamnolipid addition



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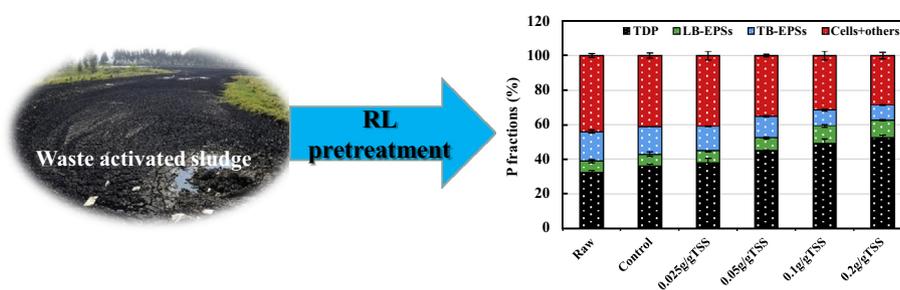
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HIGHLIGHTS

- RL pretreatment was successfully developed to enhance P release from WAS.
- The cumulative $\text{PO}_4^{3-}\text{-P}$ was better fitted with pseudo-first-order kinetic model.
- This was the first time to explore the role of EPSs in P-release from WAS.
- Changes of metal elements, P fractions and species in EPSs had been investigated.
- Release contributions of P from EPSs/ (cells + others) to liquid had been identified.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigated the role of extracellular polymeric substances (EPSs) in enhanced performance of phosphorus (P) release from waste activated sludge (WAS) by adding rhamnolipid (RL). Results showed that compared to WAS without pretreatment, the released $\text{PO}_4^{3-}\text{-P}$ increased with RL addition from 0 to 0.2 g/g TSS (total suspended solid), and increased by 208% under the optimal condition (0.1 g RL/g TSS and 72-h fermentation time). The cumulative $\text{PO}_4^{3-}\text{-P}$ was better fitted with pseudo-first-order kinetic model. Moreover, the contents of metal ions increased in liquid but decreased in EPSs linearly with RL addition increasing, and WAS solubilizations were positively correlated with the released metal ions. The enhanced total dissolved P mainly came from cells and others (69.39%, 2.27-fold higher than that from EPSs), and $\text{PO}_4^{3-}\text{-P}$ was the main species in both liquid and loosely bound EPSs, but organic P should be non-negligible in tightly bound EPSs.

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1. Introduction

Phosphorus (P) is well known to be one of the most important nutrients to all life (e.g. plants, animals and bacteria) (Cordell et al., 2009; Rittmann et al., 2011; Tan and Lagerkvist, 2011).

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However, the main P source, phosphate rock, is non-renewable, and it has been reported that P demand will outstrip supply after the year of 2035 (Cordell et al., 2009). Thus, it is one of urgent challenges all over the world to develop new strategies for P-recovery from secondary resources, especially the renewable feedstock. Waste activated sludge (WAS), as the by-product of wastewater treatment plants (WWTPs), may be one potential and attractive P resource (12.0% P of dry sludge, by weight) (Xu et al., 2015; Xie et al., 2011). In 2013, 6.25 million tons dry sludge have been produced in China, and its production is still increasing with urbanization and population growth (Yang et al., 2015a, 2015b). Thus, WAS may be one kind of potential P source to recover P, and to further establish a sustainable P-circulation. It has been reported around 40% of P is bound biologically (11% in the primary sludge and 30% as physiological P in the biomass of WAS) and approximately another 50% is inorganic P in WAS (Petzet et al., 2012; Xu et al., 2015). Therefore, it is the first step to release P from WAS for P-recovery (Zhang et al., 2014; Zhang et al., 2013).

Recently, there are some reported literatures aim to achieve P release from sludge ash (Tan and Lagerkvist, 2011; Guedes et al., 2014; Kalmykova and Karlfeldt Fedje, 2013). However, few efficient methods have been developed to release P from WAS directly because of low solubilization and difficult polymeric substrates deconstruction. Some literatures have reported that addition of surfactants could easily and effectively destroy polymeric matrix and facilitate the release of extracellular polymeric substances (EPSs) from WAS flocs (Sheng et al., 2010; Zhou et al., 2013). And the performances of surfactants (such as linear alkylbenzene sulphonates (LCA) and sodium dodecylbenzene sulfonate (SDBS)) on P release from WAS have been reported (Dereszewska et al., 2015; Jiang et al., 2007). However, both the kinetic modeling of P-release from WAS and the mechanism of surfactant action have not been investigated. Meanwhile, SDBS and LCA were synthetic surfactant and difficult to be biodegrade, their accumulation will present a potential risk for eco-system and human health (Zhou et al., 2013), while recycling either the liquid or solid produced from WAS treatment process. As a special bio-surfactant, rhamnolipid (RL) has been found its secretion in WAS fermentation process and self-utilization in situ to improve efficient solubilization of WAS (Zhou et al., 2013), and may be positive for P release from WAS.

It is well known that microbial EPSs are major components of the WAS floc matrix (Yan et al., 2015; Li and Yang, 2007; Zhou et al., 2015), normally accounting for 80% of the total mass (Zhou et al., 2015). EPSs were composed by large amounts of organic compounds such as proteins (PNs), polysaccharides (PSs), humic acid (HA), nucleic acid, and phospholipid (Liang et al., 2010; Yan et al., 2015), especially PNs and PSs, accounting for 50–72% of EPSs (Wei et al., 2015; Li and Yang, 2007). EPSs in WAS suspension and floc matrix can be regarded as a dynamic double-layered structure of loosely bound EPSs (LB-EPSs) diffused from the tightly bound EPSs (TB-EPSs), which surrounds the cells (Zhou et al., 2015; Li and Yang, 2007; Yan et al., 2015). The physicochemical properties and special location of EPSs make them serve as an important role for maintaining the structure and function of microbial aggregate (Hou et al., 2015; Li and Yang, 2007; Yan et al., 2015; Zhou et al., 2015). Thus, it is postulated that EPSs can make a certain influence on P-release from WAS. To authors' knowledge, until now, no information has been available for the role of EPSs characteristics during the P-release process from WAS.

In this study, the effects of RL pretreatment on P release was explored. In order to identify the role of EPSs on the improvement of P release under different RL addition, the changes of WAS solubilization and metal ions, P fractions and species in both EPSs and liquids were investigated. Meanwhile, the release contributions of P from EPSs and/or cells and others (C&O) had been identified.

Based on the experimental results, a possible pathway for enhanced P-release process was proposed. The outcome of this study will establish some fundamentals that permit on the exploration of novel P release technique and further improvement of P recovery from WAS, as well as the role of EPSs in P release from WAS.

2. Methods

2.1. Source of WAS and RL

The WAS used in this study was taken from the secondary sedimentation tank of Taiping Municipal Wastewater Treatment Plant, Harbin, China. The WAS firstly was thickened by gravitational sedimentation for 24 h at 4 °C, then screened with a 1 mm sieve to remove impurities, finally stored at 4 °C prior for later use and test. The main characteristics were: total suspended solid (TSS) 23.58 ± 0.49 g/L, volatile suspended solid (VSS) 14.43 ± 0.43 g/L, total chemical oxygen demand (TCOD) 22.71 ± 0.50 g/L, soluble chemical oxygen demand (SCOD) 231 ± 34 mg/L, NH_4^+ 53.42 ± 9.06 mg/L, PO_4^{3-} 159.72 ± 5.72 mg/L and total phosphorus (TP) 501.41 ± 21.45 mg/L and pH 6.51 ± 0.02 .

The bio-surfactant RL was purchased from Victex Company, China, and the purity was 80%, which was a blend of RhaC₁₀C₁₀ (C₂₆H₄₈O₉, *m/z* 503) and RhaRhaC₁₀C₁₀ (C₃₂H₅₈O₁₃, *m/z* 649).

2.2. Batch experiments

To investigate the effects of RL pretreatment and the role of EPSs on P release from WAS, 15 batch laboratory-scale anaerobic fermentation experiments were set up, which were conducted in 500 mL serum bottles filled with 300 mL raw WAS each. The addition levels of RL were 0, 0.025 g/g TSS, 0.05 g/g TSS, 0.1 g/g TSS and 0.2 g/g TSS, respectively. Nitrogen gas was introduced to the reactors for 10 min to remove oxygen, then the reactors were capped, sealed, and stirred in an air-bath shaker (100 rpm) at 35 ± 1 °C for 5 days. All the fermentation experiments were carried out in triplicate.

2.3. EPSs extraction

In this work, the EPSs were extracted at 12-h fermentation time to investigate the role of EPSs on P release under different RL levels. A heat method was used to extract the EPSs of WAS and the detailed procedures could be found in the previous literatures, which was modified appropriately (Li and Yang, 2007; Yan et al., 2015). The specific method were: firstly, 10 mL samples was centrifuged at 4000g for 10 min, the supernatant was filtered with 0.45 μm cellulose nitrate membrane filters, and the filtrate was serviced as dissolved matters. Secondly, the residue in centrifuge tube was treated according to the EPSs extraction method for LB-EPSs. And the filtrate was serviced as the LB-EPSs. Finally, after LB-EPSs extraction, the residue in centrifuge tube was treated according to the EPSs extraction method for TB-EPSs. And the filtrate was regarded as the TB-EPSs.

2.4. Analytical methods

Sludge samples collected from reactors were centrifuged at 10,000 rpm for 10 min, then supernatant samples were filtered by 0.45 μm cellulose nitrate membrane filters, finally filtrated samples were stored at 4 °C prior to analysis. P analysis scheme were: molybdate reactive phosphorus (MRP, free PO_4^{3-}) measurements were performed by the molybdenum blue method of APHA (2005), total dissolved phosphorus (TDP) and TP were measured

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