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Effects of potassium peroxymonosulfate on disintegration of waste sludge and properties of extracellular polymeric substances

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ABSTRACT

Effects of peroxymonosulfate (PMS) oxidation on disintegration degree (DD) and extracellular polymeric substances (EPS) properties of waste activated sludge were investigated. A combined approach of fractionation procedure and parallel factor (PARAFAC) analysis was applied to characterize EPS of sludge. Results indicated that PMS oxidation effectively broke sludge particles, resulting in DD in total nitrogen of 39.8% at 10 mg PMS (g SS)$^{-1}$. After PMS treatment, EPS increased significantly and mostly transferred to slime layer rather than loosely bound EPS (LB-EPS), and the ratio of slime to tightly bound EPS was correlated significantly with PMS dosage. With increasing PMS dosage, polysaccharides in EPS increased, while proteins in EPS and DNA in slime EPS increased firstly and then decreased. PARAFAC analysis of excitation-emission matrix spectra showed that tryptophan-like substances in both slime and LB-EPS were greatly influenced by PMS oxidation, and humic-like fluorophores in slime EPS were positively correlated with PMS dosage.

1. Introduction

Waste activated sludge (WAS) massively generated from municipal and industrial wastewater treatment plants (WWTPs) has become a pressing environmental problem in recent years. In China, the total amount of wet WAS (80% water content) was estimated to be 33.6 million tons in 2015 (ChinaWater.net, 2013), accounting for 17.4% of the total amount of municipal solid waste. The hazardous substances present in WAS, such as pathogens and toxic chemicals, can be harmful to the environment if it is inappropriately disposed of Li et al. (2009). The conventional sludge disposal methods, such as landfill and incineration, both created a burden for society because of their footprint requirements, operational costs, and strict regulations for human health and environmental protection (Nguyen et al., 2014). From an economic standpoint, treatment and disposal of WAS account for 25–65% of the total operating costs of WWTPs (Nguyen et al., 2014; Wu et al., 2014). The increased strict restrictions in disposal, as well as requirements in reuse of sludge, have made sludge treatment more challenging and costly (Cho et al., 2012; Zhou et al., 2014). Therefore, various methods and strategies have been developed to decrease the amount of sludge production (Ye et al., 2012b; Park et al., 2013; Wu et al., 2014; Zhou et al., 2014; Fang et al., 2015; Kim et al., 2015; Liu et al., 2015).

To reduce WAS production, chemical oxidation technologies by using oxidant, such as ozone, potassium ferrate, potassium permanganate and Fenton reagent, have been developed and were proved to be an effective way to achieve a high disintegration degree (DD) of WAS (Chu et al., 2009; Yang et al., 2012; Ye et al., 2012a, 2012b; Wu et al., 2014). With chemical oxidation, sludge disintegration was achieved by the destruction of sludge flocs and/or the disruption of microorganism cells (Chu et al., 2009; Ye et al., 2012a; Yang et al., 2013). Intracellular compounds in cells were released, and organic structures were oxidized and converted into small molecular compounds (Wu et al., 2014). Chemical oxidation also improved settleability and dewaterability of WAS (Ye et al., 2012b; Zhen et al., 2012a), and enhanced cumulative biogas production for the subsequent anaerobic sludge digestion (Wu et al., 2015).

The physicochemical and biological properties of WAS, including flocculability, settleability, dewaterability and disintegrating characteristics, are closely related to the presence and

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forms of extracellular polymeric substances (EPS) (Ye et al., 2012b; Zhen et al., 2012a). EPS are metabolic products accumulating on bacterial cell surface, and constitute up to 80% of the activated sludge mass (Abelleira et al., 2012; Ye et al., 2012b). Activated sludge has a dynamic multilayered EPS structure consisting of soluble EPS (slime EPS), loosely bound EPS (LB-EPS) and tightly bound EPS (TB-EPS) (Wang et al., 2009b; Wu et al., 2014). Although interacted weakly with cells, slime EPS have a crucial effect on microbial activities and surface characteristics of the sludge (Wu et al., 2014). TB-EPS are reported to be responsible for cell adhesion and attachment in the inner flocs structure through strong interactions, while sludge cells in the outer region of flocs are entangled by weak interactions through LB-EPS (Liu et al., 2010). Therefore, EPS and its fractions, reflecting structural and functional integrity of activated sludge aggregates, were used as an indicator of sludge disintegration (Liu et al., 2015). Wu et al. (2014) reported that after potassium permanganate addition, EPS were efficiently released into supernatant, and the release of LB-EPS was much higher than slime EPS and TB-EPS. Ye et al. (2012b) also observed much higher release of LB-EPS than TB-EPS for sludge disintegration by potassium ferrate. Although studies mentioned above are very helpful to understand effects of chemical oxidation on EPS properties of WAS, investigations on migration and transformation of EPS are still required to elucidate mechanisms of sludge disintegration by oxidants.

Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) is a stable oxidants with peroxymonosulfate (PMS) as its active species, and generates sulfate radicals (SO_4^{-}) with higher oxidation potential (2.5–3.1 eV) comparable to hydroxyl radicals (2.8 eV) (Anipsitakis and Dionysiou, 2003; Shi et al., 2012). Using $SO_4^{-}\cdot$ for wastewater treatment shows advantages over ozonation, chlorination and H_2O_2 oxidation, such as it is safe, non-toxic, stable at room temperature and easy to handle due to the solid state of Oxone (Shi et al., 2012; Ren et al., 2015). However, to date, information on sludge disintegration with PMS was hardly found in literatures. Therefore, DD based on soluble COD (SCOD) and total nitrogen (TN), flocs size, and EPS fractions were selected as parameters to explore the feasibility of applying PMS oxidation to sludge disintegration. Influences of PMS oxidation on components and properties of slime EPS, LB-EPS and TB-EPS of WAS were also examined by three-dimensional excitation-emission matrix (EEM) fluorescence spectroscopy and chemical analysis. The application of three-dimensional EEM to investigating effects of oxidants on EPS fractions and properties could be useful for better understanding sludge disintegration mechanisms because of the high sensitivity and good selectivity of EEM technology (Wang et al., 2009a). The parallel factor (PARAFAC) analysis was also adopted to decompose EEM into individual fluorescent components. The results obtained in this study are expected to provide some insights into EPS properties during sludge disintegration process by chemical oxidation.

2. Materials and methods

2.1. Waste activated sludge

The WAS used in this study was collected from sludge return line of Bailonggang WWTP in Shanghai, China. The WWTP treats about 2,000,000 $m^3\ d^{-1}$ of municipal wastewater using anaerobic-anoxic-aerobic process. The collected samples were transferred to the laboratory within 1 h, and aerated for 1 h before experiment to remove released organic substances. All experiments were accomplished within 24 h to avert sludge transformation. The main characteristics of sludge samples were as follows: suspended solid (SS) of 11,513 ± 398 mg l^{-1}, volatile SS (VSS) of 6240 ± 154 mg l^{-1}, SCOD of 40 ± 12 mg l^{-1}, TN of 5.96 ± 2.32 mg l^{-1} and pH of 7.32 ± 0.15.

2.2. Experimental procedure

A series of tests were conducted in a bench-scale reactor equipped with thermostat and magnetic stirrer with a sample volume of 500 ml. In each test, the sludge disintegration reaction was initiated immediately by adding different dosages of potassium PMS (Ansin Chemicals Co., China). The mixture was continuously homogenized at 300 rpm for 150 min. A 15 ml sample was withdrawn and tested after filtration by 0.45 μm vinyl cellulose membrane. All analyses were carried out in triplicate, and blank tests with the same treatment were done along with these experiments. All the experiments were carried out at 20.0 ± 0.1 °C.

2.3. Estimation of sludge disintegration degree

The DD of WAS was determined as the portion of soluble matters generated by pretreatment, expressed as the increment ratio of SCOD in released COD (Yang et al., 2012; Wu et al., 2014). Considering the oxidation and mineralization of the released organic substances by residual oxidants (Chu et al., 2009; Ye et al., 2012a; Yang et al., 2013), TN was also selected as an index to estimate DD value in this study. The DD_{COD} and DD_{TN} of sludge were calculated using Eqs. (1) and (2):

$$DD_{COD} = (COD_S - COD_{S0})/(COD_T - COD_{S0}) \tag{1}$$

$$DD_{TN} = (TN_S - TN_{S0})/(TN_T - TN_{S0}) \tag{2}$$

where, COD_S and TN_S are concentrations of released COD and TN for sludge samples treated by PMS (mg l^{-1}), respectively; COD_{S0} and TN_{S0} are concentrations of COD and TN for untreated sludge samples (mg l^{-1}), respectively; COD_T and TN_T are the total releasable COD and TN in the sludge (mg l^{-1}), and were obtained via an alkaline hydrolysis procedure in which the initial sludge samples were mixed with 0.5 M NaOH at room temperature for 24 h (Ye et al., 2012b; Wu et al., 2014). The samples used for TN_S determination were sealed during alkaline hydrolysis procedure, and neutralized with hydrochloric acid before opening to prevent ammonia escaping under alkaline conditions.

2.4. Analytical methods

2.4.1. Extraction procedure of EPS from mixed liquor

The EPS extraction protocol in this study was modified based on the research of Zhen et al. (2013). In brief, 50 ml of sludge suspension was firstly centrifuged at 8000 g for 15 min at 4 °C, and the supernatant was slime EPS. The sludge pellet left in the centrifuge tube was suspended and diluted to its original volume by adding 0.05% NaCl solution. The sludge suspension was vibrated by a laboratory shaking tables for 1 min at temperature of 50 °C, and followed by centrifugation at 8000 g for 10 min at 4 °C. The organic matter in the supernatant was regarded as LB-EPS. The pellet left in the centrifuge tube was diluted by NaCl solution again and placed in a water bath at 60 °C for 30 min. The mixed liquor was centrifuged at 8000 g for 15 min at 4 °C, and the collected supernatant was TB-EPS. The sludge sample left was pellet.

2.4.2. Three-dimensional EEM fluorescence spectroscopy

The three-dimensional EEM measurements were conducted using a luminescence spectrometry (RF-5301pc, Shimadzu, Japan). The EEM spectra were collected with the scanning emission spectra (Em) from 220 to 500 nm at 5 nm intervals by varying the excitation wavelengths (Ex) from 220 to 500 nm at 5 nm sampling intervals. The Ex and Em slits were maintained at 5 nm and the scanning speed was set at super. To solve the overlap problem of fluorescence