Water Research 88 (2016) 728–739

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Influence of wastewater sludge treatment using combined peroxyacetic acid oxidation and inorganic coagulants re-flocculation on characteristics of extracellular polymeric substances (EPS)

Weijun Zhang [a, *], Bingdi Cao [b], Dongsheng Wang [a, b, **], Teng Ma [a], Hua Xia [a], Dehong Yu [c]

[a] School of Environmental Studies, China University of Geosciences, Wuhan 430074, Hubei, China
[b] State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
[c] School of Chemistry and Environmental Engineering, Wuhan Institute of Technology, 430073 Hubei, China

A R T I C L E I N F O

Article history:
Received 27 August 2015
Received in revised form
21 October 2015
Accepted 25 October 2015
Available online 30 October 2015

Keywords:
Activated sludge
Peracetic acid
EPS
Oxidation
Chemical flocculation

A B S T R A C T

Extracellular polymeric substances (EPS) are highly hydrated biopolymers and play important roles in bioflocculation, floc stability, and solid-water separation processes. Destroying EPS structure will result in sludge reduction and release of trapped water. In this study, the effects of combined process of peracetic acid (PAA) pre-oxidation and chemical re-flocculation on morphological properties and distribution and composition of EPS of the resultant sludge flocs were investigated in detail to gain insights into the mechanism involved in sludge treatment. It was found that sludge particles were effectively solubilized and protein-like substances were degraded into small molecules after PAA oxidation. A higher degradation of protein-like substances was observed at acid environments under PAA oxidation. Microscopic analysis revealed that no integral sludge floc was observed after oxidation with PAA at high doses. The floc was reconstructed with addition of inorganic coagulants (polyaluminium chloride (PACl) and ferric chloride ($FeCl_3$)) and PACl performed better in flocculation due to its higher charge neutralization and bridging ability. Combined oxidative lysis and chemical re-flocculation provide a novel solution for sludge treatment.

1. Introduction

The management of wastewater sludge, now often referred to as biosolids, accounts for a major portion of the cost of the wastewater treatment process and represents significant technical challenges. Dewatering is a vital part of sludge treatment, which has proven to be an efficient method to reduce transportation and disposal costs (Neyens et al., 2004). Except for the sludge characteristics, dewatering efficiency is mainly dependent on the selection of dewatering devices and conditioning chemicals.

Extracellular polymeric substances (EPS) are high molecular-weight biopolymers originating from bacterial secretion, cell lysis and hydrolysis, leakage of exocellular constituents, and adsorbed organic matter from the surrounding wastewater. The total mass of EPS (EPS and water held within the EPS-structure) has been found to represent up to 80% of the mass of activated sludge (Liu and Fang, 2003). Houghton et al. (2001) reported that there existed a certain EPS mass at which the sludge dewaterability reached a maximum. In addition, EPS content was also observed to greatly affect floc charge and floc stability (Mikkelsen and Keiding, 2002). Higgins and Novak (1997) demonstrated that sludge dewaterability correlated well with

Abbreviations: 3D-EEM, Three-dimensional excitation emission matrix; ASTP, Advanced sludge treatment processes; AMW, Apparent molecular weight; DOC, Dissolved organic carbon; EPS, Extracellular polymeric substances; HPSEC, High performance size-expulsion chromatography; LB, Loosely bound; MBR, Membrane bioreactor; MW, Molecular weight; NOM, Natural organic matter; PAA, Peracetic acid; PACl, Polyaluminium chloride; PN, Proteins; PS, Polysaccharides; SI, Supporting information; SEPS, Soluble EPS; SRF, Specific resistance to filtration; TB, Tightly bound; TOC, Total organic carbon; TSS, Total suspended solid; VSS, Volatile suspended solids.

* Corresponding author.
** Corresponding author. School of Environmental Studies, China University of Geosciences, Wuhan 430074, Hubei, China.
E-mail addresses: zhwj_1986@126.com (W. Zhang), wgds@rcees.ac.cn (D. Wang).

http://dx.doi.org/10.1016/j.watres.2015.10.049
0043-1354/

Table 1
Characteristics of activated sludge.

Indicator	Moisture content (%)	pH	VSS/TSS	CST (s)	$d_{0.5}$ (μm)	Zeta potential (mV)	SCOD (mg/L)
Value	98.3	7.5	0.75	320	62	−15.2	130

the ratio of protein and polysaccharide in sludge EPS. Consistent with the findings of Murthy and Novak (1999), proteins (PN) generally play a more important role in sludge flocculation and dewatering than polysaccharides (PS) whereby a high PN concentration is detrimental for dewatering process. More recent studies have demonstrated that the spatial distribution of EPS was important to sludge settling, bioflocculation and, dewatering properties (Mikkelsen and Keiding, 2002; Zhang et al., 2015). Li et al. (2006) used a modified heat extraction method to separate the loosely bound (LB) EPS and tightly bound (TB) EPS fractions from sludge floc. Sludge settleability and dewaterability were found to be much more strongly correlated with the concentration of LB-EPS than with the concentration of TB-EPS, and excessive LB-EPS was always related to poor bioflocculation and sludge-water separation performance (Li and Yang, 2007; Yang and Li, 2009). Yu et al. (2008) fractionated sludge flocs into five layers (supernatant, slime, LB-EPS, TB EPS and pellet) with combined ultrasound and centrifugation treatments. It was found that sludge dewaterability in terms of specific resistance to filtration (SRF) correlated well with protein content in the supernatant, slime, and LB-EPS, while no correlation was shown between organic composition in the pellet and the sludge floc as a whole.

It is essential to precondition sludge particles with chemicals before dewatering to improve operating performance of sludge dewatering devices. Addition of traditional chemical conditioners (inorganic salt coagulants and organic polymers) can agglomerate fine sludge colloids to form large flocs through charge neutralization and bridging. These can then be more easily separated from water (Niu et al., 2013; Zhang et al., 2014). Considering the high water binding capacity of EPS, traditional chemical conditioners are ineffective in the destruction of EPS and the promotion of the partial release of water inside sludge particles. Therefore, many advanced sludge treatment processes (ASTP) have been developed to improve solid-water separation performance and facilitate handling and ultimate disposal. ASTP can break the floc structure and solubilize EPS components, consequently reducing sludge volume to be disposed and the final cake moisture content in dewatering process (Neyens et al., 2004). Established ASTP include (photo)Fenton oxidation (Tokumura et al., 2007; Liu et al., 2013; Neyens and Baeyens, 2003), acid/alkaline (Zhu et al., 2013), thermal hydrolysis (Neyens et al., 2004) and enzymatic treatments (Ayol, 2005), or their integrated processes.

Peracetic acid (PAA) is a strong disinfectant with a wide spectrum of antimicrobial activity. Due to its bactericidal, virucidal, fungicidal, and sporicidal effectiveness as demonstrated in various industries, the use of PAA as a disinfectant for wastewater effluents has been attracting attention (Kitis, 2004). Su et al. (2004) demonstrated that PAA was very effective at dissolving EPS and oxidizing cells, promoting the release of biopolymers, thereby reducing sludge volume. Sludge solubilization efficiency in PAA oxidation was enhanced in the presence of ultrasonic treatment. In addition, organic materials showed a higher biodegradability after PAA treatment. Sun et al. (2011) found that PAA and microwave treatment exhibited a significant synergetic effect in sludge solubilization, whereby the protein and polysaccharide content in the sludge supernatant was significantly increased.

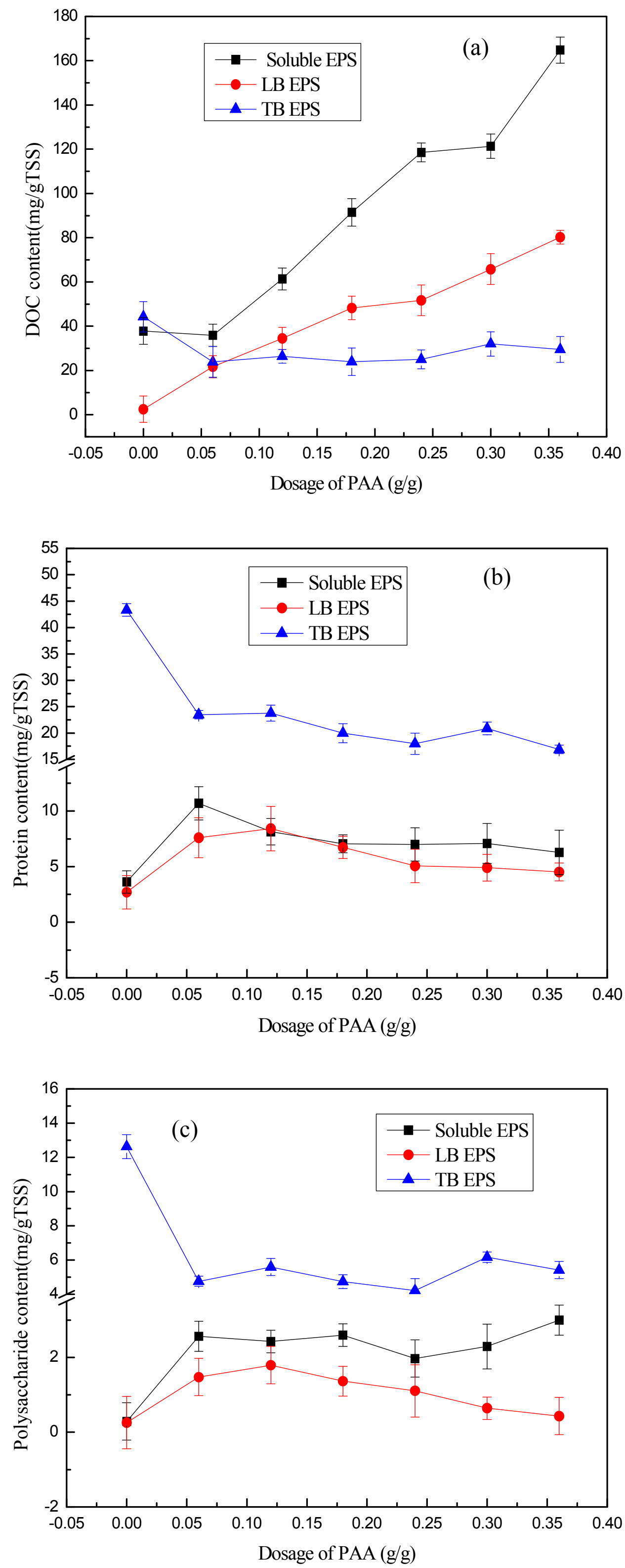

Fig. 1. Effects of PAA dosage on content of different EPS fractions (a) and their protein (b) and polysaccharide (c) (Initial sludge pH was 7).