Water Research 134 (2018) 101–114

Contents lists available at ScienceDirect

Water Research

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

Unraveling the catalyzing behaviors of different iron species (Fe^{2+} vs. Fe^0) in activating persulfate-based oxidation process with implications to waste activated sludge dewaterability

Guangyin Zhen [a, b, *], Xueqin Lu [c, **], Lianghu Su [d], Takuro Kobayashi [e], Gopalakrishnan Kumar [f], Tao Zhou [g], Kaiqin Xu [e], Yu-You Li [c], Xuefeng Zhu [a], Youcai Zhao [g]

[a] *Shanghai Key Lab for Urban Ecological Processes and Eco-Restoration, School of Ecological and Environmental Sciences, East China Normal University, Dongchuan Rd. 500, Shanghai 200241, PR China*
[b] *Shanghai Institute of Pollution Control and Ecological Security, 1515 North Zhongshan Rd. (No. 2), Shanghai 200092, PR China*
[c] *Department of Civil and Environmental Engineering, Graduate School of Engineering, Tohoku University, Sendai, Miyagi 980-8579, Japan*
[d] *Nanjing Institute of Environmental Sciences, Ministry of Environmental Protection, 210042, Nanjing, PR China*
[e] *Center for Material Cycles and Waste Management Research, National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba, Ibaraki 305-8506, Japan*
[f] *Department of Environmental Engineering, Daegu University, Jillyang, Gyeongsan, Gyeongbuk, Republic of Korea*
[g] *The State Key Laboratory of Pollution Control and Resource Reuse, Tongji University, Shanghai 200092, PR China*

ARTICLE INFO

Article history:
Received 9 December 2017
Received in revised form
27 January 2018
Accepted 30 January 2018
Available online 3 February 2018

Keywords:
Waste activated sludge
Dewatering
Persulfate-based oxidation process
Iron catalysts
Extracellular polymeric substances

ABSTRACT

Dewatering of waste activated sludge (WAS) is of major interest in its volume reduction, transportation and ultimate disposal. Persulfate-based oxidation process is a newly developed option for enhancing WAS dewaterability through the generation of powerful sulfate radicals ($SO_4^-\cdot$). However, the enhancement in WAS dewaterability by persulfate differs with the species of iron catalysts used. In this study, two types of iron catalysts (i.e. Fe^{2+} vs. Fe^0) were employed to initiate the persulfate ($S_2O_8^{2-}$), and the catalyzing behaviors and the underlying principles in enhancing WAS dewaterability were investigated and compared. The Fe^{2+} exhibited the high effectiveness in catalyzing the decomposition of persulfate to sulfate radicals ($SO_4^-\cdot$), inducing the greater improvement in WAS dewatering. The WAS dewaterability (indicated by dry solids content after filtration) increased with the added $S_2O_8^{2-}/Fe^{2+}$ dosages, with the dry solids content reaching up to 5.1 ± 0.8 wt% at $S_2O_8^{2-}/Fe^{2+}$ dosages of 1.2/1.5 mmol/g-VS after only 30 s' filtration, roughly 1.8-fold increase than raw WAS (1.8 ± 0.1 wt%). In contrast, the influence of the persulfate oxidation when activated with Fe^0 on WAS dewaterability was statistically insignificant. The WAS dewaterability remained nearly unchanged (i.e. dry solids content of 2.0 ± 0.0 wt %), irrespective of the employed $S_2O_8^{2-}/Fe^0$ dosages. Further analysis demonstrated that the WAS dewaterability negatively corresponded to loosely bound extracellular polymeric substances (LB-EPS) and tightly bound EPS (TB-EPS). The abundant $SO_4^-\cdot$ from $S_2O_8^{2-}/Fe^{2+}$ system could effectively disrupt the gel-like EPS matrix, break apart the cells and subsequently arouse the release of the water inside EPS and cells, facilitating water-solid separation. In the case of $S_2O_8^{2-}/Fe^0$, the dissolution of Fe^0 particles was the rate-limiting step, due to the formation of oxide iron layer near Fe^0 metallic surface, which resulted in the slow $SO_4^-\cdot$ production and thus hardly promoted WAS dewaterability. The pH adjustment could accelerate Fe^0 dissolution and enhance the dewatering performance of $S_2O_8^{2-}/Fe^0$ process to a certain degree, but the effect was unsatisfactory. Additionally, the observations regarding the dissolved organic matters and ammonium collectively revealed that except for enhancing WAS dewatering, $S_2O_8^{2-}/Fe^{2+}$ oxidation could concurrently degrade COD and ammonia from WAS filtrate, lighten the burden of the subsequent

---

* Corresponding author. Shanghai Key Lab for Urban Ecological Processes and Eco-Restoration, School of Ecological and Environmental Sciences, East China Normal University, Dongchuan Rd. 500, Shanghai 200241, PR China.
** Corresponding author.
E-mail addresses: gyzhen@des.ecnu.edu.cn (G. Zhen), luxueqin0220@126.com (X. Lu).

https://doi.org/10.1016/j.watres.2018.01.072

sewage treatment facilities and reduce operational expense. Hence, from an environmental and economic perspective, the $S_2O_8^{2-}/Fe^{2+}$ system possesses much greater promise for WAS dewatering.

1. Introduction

The management of waste activated sludge (WAS) accounts for approximately 50–60% of the operating cost of the wastewater treatment plant (WWTP) and has become one of the main concerns (Appels et al., 2008). To reduce the expenses of the subsequent transport and disposal, WAS needs to be dewatered deeply and effectively. To date, the dewatering of such sludge still poses a huge technical challenge to water industry. The water content of WAS is usually in the range of 95–99%, and it is still up to 75–80% even after mechanical dewatering. For decades, the development of high-performance techniques for deep dewatering of WAS has been being a high research priority in research communities. To improve the WAS dewaterability, a wide variety of methods including ultrasonication (Feng et al., 2009), microwave irradiation (Liu et al., 2016a), bioleaching (Murugesan et al., 2014), hydrothermal process (Wang et al., 2017), electrolysis/electrocoagulation (Gharibi et al., 2013; Visigalli et al., 2017), Fenton peroxidation (Neyens et al., 2004; Zhen et al., 2014b), and the addition of nanoparticles (Ju et al., 2016; You et al., 2017) have been suggested. However, the WAS dewatering is not so easy and the effective dewatering process requires the rapid destruction of the rigid structures of cell walls and extracellular polymeric substances (EPS) in sludge flocs, facilitating the release of bound water (Kim et al., 2016).

In a previous study, Zhen et al. (2012c) proposed a sulfate radical ($SO_4^-\cdot$)-based oxidation process to condition the WAS for the enhancement of dewaterability. Persulfate ($S_2O_8^{2-}$), through the activation by heat, UV light or transition metals (Fe^{2+}, Co^{2+}, etc.), is capable of generating powerful sulfate radicals with high redox potential for one-electron transfer ($E^0(SO_4^-\cdot/S_2O_8^{2-}) = 2.43\ V_{SHE}$, Eq. (1)) (Wardman, 1989). The $SO_4^-\cdot$ is able to destroy the particular functional groups of fluorescing substances (e.g. aromatic protein-, tryptophan protein-like matters, etc.) in EPS, breakdown the linkages in the polymeric backbone and rupture bacterial cells, resulting in the liberation of EPS-bound water and intracellular materials from cells and subsequently improved dewaterability (Zhen et al., 2012a,b; 2013a,b). This process using ferrous iron (Fe^{2+}) as the catalyst demonstrated a sufficiently marked enhancement of the WAS dewaterability with up to 88.8% capillary suction time (CST) reduction within only 1 min under 1.2 mmol-$S_2O_8^{2-}$/g-VSS, 1.5 mmol-Fe^{2+}/g-VSS, and pH 3.0–8.5 (Eq. (1)) (Zhen et al., 2012c). Compared with some other activators, Fe^{2+} in the form of ferrous salts (e.g. $FeSO_4\cdot 4H_2O$) owns more advantages of low-cost, nontoxicity, easy storage/use, convenient operation and very fast reaction rate; consequently, it can be a cost-efficient and attractive alternative for improving dewaterability from the perspective of process engineering. Because of the superior features and good performances, Fe^{2+}-activated persulfate ($S_2O_8^{2-}/Fe^{2+}$) oxidation process has gained great attention most recently and been extensively investigated for the disintegration and dewatering of WAS (Liu et al., 2016b; Oncu et al., 2015; Ren et al., 2015; Shi et al., 2015a,b; Song et al., 2016a; Waclawek et al., 2015; Zhen et al., 2013b, 2017).

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^-\cdot + Fe^{3+} + SO_4^{2-} \quad (1)$$

As an alternative, zero-valent iron in the form of powder (Fe^0, ZVI) (Sahinkaya et al., 2015) can also be used as the catalyst in place of Fe^{2+} (Li et al., 2016; Song et al., 2016b; Zhou et al., 2015). In this process, the surface of Fe^0 corrodes spontaneously under aerobic or anaerobic conditions releasing Fe^{2+} and/or H_2, in accordance with Eqs. (2) and (3) (Liang and Lai, 2008); also, persulfate could directly react with Fe^0 to generate Fe^{2+}, in accordance with Eq. (4) (Liang and Lai, 2008). Then, the resulting Fe^{2+} catalyzes $S_2O_8^{2-}$ to produce $SO_4^-\cdot$, just like in $S_2O_8^{2-}/Fe^{2+}$ process (Eq. (1)). Meanwhile, the ferric ions (Fe^{3+}) produced from $S_2O_8^{2-}/Fe^0$ process can be further reduced into Fe^{2+} at the ZVI metallic surface following Eq. (5) (Bremner et al., 2006; Kallel et al., 2009; Liang and Lai, 2008), realizing the catalyst Fe^{2+} regeneration and recycling.

$$Fe^0 + 0.5O_2 + H_2O \rightarrow 2Fe^{2+} + 4OH^- \quad (2)$$

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + 2OH^- + H_2 \quad (3)$$

$$S_2O_8^{2-} + Fe^0 \rightarrow Fe^{2+} + 2SO_4^{2-} \quad (4)$$

$$Fe^0 + 2Fe^{3+} \rightarrow 3Fe^{2+} \quad (5)$$

The use of Fe^0 could reduce sulfate radical consumption by excess Fe^{2+} and avoid the introduction of other anions. $S_2O_8^{2-}/Fe^0$ process would be thus efficient in water treatment with selected organic contaminants as targets (Kambhu et al., 2017; Oh et al., 2010; Xiong et al., 2014); but the performance might be discounted more or less when utilized for the dewatering of high-solid WAS containing complex and even unknown components. One of main reasons for this problem is the relatively complex radical pathways of $S_2O_8^{2-}/Fe^0$ process (Eqs. (2)–(5)) and the major step that is contributing to $SO_4^-\cdot$ production may shift with operating conditions and sludge characteristics. Therefore, whether or not Fe^0 can substitute for or even be comparable with ferrous salts for the activation of persulfate to sulfate radicals in WAS dewatering still needs clarifying. In addition, Fe^0 corrosion according to Eqs. (2) and (3) could be a vital, even not the sole factor governing WAS dewatering performance. It has been observed that acidic conditions ($pH \leq 4.0$) could promote the corrosion of Fe^0 and the release of Fe^{2+} in H_2O_2/Fe^0 system, accelerating sludge disintegration (Sahinkaya et al., 2015) or the removal of phenolic compounds (Kallel et al., 2009). The enhanced Fe^0 corrosion and Fe^{2+} release under acidic conditions may be advantageous to $S_2O_8^{2-}/Fe^0$ process as well.

The objectives of this study were to (i) compare the catalyzing behaviors and potentials of two types of iron catalysts (i.e. Fe^{2+} vs. Fe^0) to disintegrate and enhance WAS dewaterability in persulfate-based oxidation process; (ii) investigate the physiochemical characteristics of WAS (i.e. sludge solubilization/disintegration, different EPS fractions, particle size, chemical states of several elements, morphology, etc.) under different pretreatment conditions to unravel the underlying dewatering mechanisms; and (iii) evaluate several possible strategies in increasing Fe^0 corrosion and WAS dewatering efficiency by $S_2O_8^{2-}/Fe^0$ process.

2. Materials and methods

2.1. Materials

Waste activated sludge (WAS) used in the present study was