Water Research 140 (2018) 232–242

Contents lists available at ScienceDirect

Water Research

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

Citric acid assisted Fenton-like process for enhanced dewaterability of waste activated sludge with *in-situ* generation of hydrogen peroxide

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ARTICLE INFO

Article history:
Received 17 January 2018
Received in revised form
14 April 2018
Accepted 23 April 2018
Available online 24 April 2018

Keywords:
Waste activated sludge
Sludge dewaterability
Nano zero-valent iron
Citric acid
Extracellular polymeric substances
Fenton-like process

ABSTRACT

Fenton's reagent has been widely used to enhance sludge dewaterability. However, drawbacks associated with hydrogen peroxide (H_2O_2) in Fenton's reagents exist, since it is a hazardous chemical and shows carcinogenicity, explosivity, instability, and corrosivity. Moreover, initial acidification and subsequent neutralization are needed as optimal conditions for homogeneous Fenton conditioning and final filtrate discharge. In this study, a Fenton-like process for the enhanced dewaterability of waste activated sludge with *in-situ* generation of H_2O_2 and without extra pH adjustment was firstly proposed, namely citric acid (CA)-assisted oxygen activation in an air/nano zero-valent iron (nZVI) system and chemical re-coagulation with polydiallyldimethylammonium chloride (PDMDAAC). Using the response surface methodology (RSM), the optimal doses of CA, nZVI, and PDMDAAC were determined to be 13, 33, and 9 mg g^{-1} dry solids (DS), respectively. This composite conditioner showed a good dewatering capability compared with the raw sludge, e.g. the capillary suction time decreased from 130.0 to 9.5 s. The enhanced sludge dewaterability was further confirmed by laboratory-scale diaphragm filter press dewatering tests, which produced a lower cake moisture content compared with the raw sludge, and the final pH of the filtrate was close to neutrality. The citric acid promoted the production of H_2O_2 and Fe(II)/Fe(III) species, the degradation of protein in tightly-bound extracellular polymeric substances, and the decomposition of protein-N in the solid phase of sludge, resulting a greater conversion of bound water to free water. The results of electron spin resonance indicated that the hydroxyl radicals were mainly responsible for the decomposition of proteinaceous compounds. The subsequent chemical re-coagulation with PDMDAAC can make the zeta potential of sludge samples less negative, reduce the repulsive electrostatic interactions, and agglomerate the smaller particles into larger aggregates, thus enhancing sludge dewaterability.

1. Introduction

The conventional wastewater treatment plant (WWTP) produces large amounts of waste activated sludge (containing more than 99 wt% of water). Sludge dewatering is to reduce sludge volume by water separation and save costs for the subsequent transportation, incineration, and handling (Qi et al., 2011). Sludge composition, i.e. extracellular polymeric substances (EPS), is one of the key factors affecting sludge dewaterability (Zhang et al., 2016). The removal of bound water (the sum of the interstitial, surface and internal water) is another important factor governing sludge dewatering (He et al., 2017). The traditional flocculants fail to decompose EPS structure and release bound water to free water (Neyens et al., 2004). Numerous studies reported that Fenton process was effective for sludge dewatering through solubilizing EPS components (Yu et al., 2016; Dai et al., 2017; Liang et al., 2015; Zhang et al., 2014), with hydroxyl radicals generated via the reaction between Fe(II) and hydrogen peroxide (H_2O_2). However, drawbacks of Fenton conditioning exist due to the use of hazardous chemicals, i.e. H_2O_2, which is carcinogenic, explosive, instable, and corrosive in nature, thus posing a big threat to the ecological system

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https://doi.org/10.1016/j.watres.2018.04.051
0043-1354/

Abbreviations

BSA	Bovine serum albumin
CA	Citric acid
CST	Capillary suction time
DMPO	5,5-dimethyl-1-pyrroline N-oxide
DS	Dry solids
EDTA	Ethylenediaminetetraacetic acid
EPS	Extracellular polymeric substances
ESR	Electron spin resonance
FTIR	Fourier transform infrared spectroscopy
G	Gauss
k	Reaction rate
LB-EPS	Loosely-bound extracellular polymeric substances
nZVI	Nano zero-valent iron
PAM	Polyacrylamide
PDMDAAC	Polydiallyldimethylammonium chloride
ROS	Reactive oxygen species
RSM	Response surface methodology
R^2	Regression coefficient
SB-EPS	Soluble extracellular polymeric substances
TB-EPS	Tightly bound extracellular polymeric substances
TS	Total solids
VS	Volatile solids
WWTP	Wastewater treatment plant
W_c	Water content of the vacuum-filtered sludge cake
W_1	Weight of sludge cake after filtration
W_2	Weight of sludge cake dried at 105 °C overnight
XPS	X-ray photoelectron spectroscopy
ZVI	Zero-valent iron

and causing difficulty in storage and transportation (Neyens et al., 2004). Other oxidants, such as peroxymonosulfate and persulfate, have been investigated to replace H_2O_2 to decompose EPS and enhance sludge dewatering, however, the prices of peroxymonosulfate and persulfate were much higher than H_2O_2 (Liu et al., 2016). Moreover, initial acidification and/or subsequent neutralization with chemicals are necessary for Fenton conditioning and the final filtrate discharge. Initial acidification at pH of 3 is often needed for Fenton oxidation to prevent iron precipitation (Neyens et al., 2004). Zhang et al. (2015) also reported that acidification and Fenton oxidation showed a synergistic effect in improving sludge dewaterability. Subsequent neutralization with alkaline additives such as red mud (Zhang et al., 2014) and lime (Yu et al., 2016) was also necessary for the final filtrate discharge. The urgent need for a stable, low-cost, and environmental-friendly oxidant without initial acidification and/or subsequent neutralization drives the sustained research on a new oxidant for sludge dewatering.

Researchers have reported that molecular oxygen is a green and cost-effective oxidant (Huang et al., 2015; Mu et al., 2017). The molecular oxygen activated with nano zero-valent iron (nZVI) can be used to degrade organic pollutants for wastewater treatment, with the generation of reactive oxygen species (ROS) (i.e. •OH and $\bullet O_2^-$) (Shen et al., 2017). Generally, nZVI induced molecular oxygen activation process takes place as follows: Firstly, nZVI reacts with O_2 to generate H_2O_2 via a two-electron molecular oxygen reduction, accompanying with the Fe^{2+} release (Eq. (1)) (Joo et al., 2004). Subsequently, the released Fe^{2+} also reacts with O_2 to generate H_2O_2 through a sequential single-electron molecular oxygen activation pathway (Eqs. (2) and (3)) (Noradoun and Cheng, 2005). The *in-situ* generated H_2O_2 then reacts with Fe(II) to produce •OH (Eq. (4)) (Joo et al., 2004). The major drawback of this route for the generation of ROS from the molecular oxygen activated with nZVI is the narrow working pH of acidic conditions. Ferric ions would precipitate under neutral or alkaline pH values in form of iron hydroxides and then existed as an iron-oxides film on the surface of nZVI, thus hindering Fe(II) release and ROS generation (Qin et al., 2015). This drawback could be overcome by introducing ligands to chelate Fe(II) so as to maintain the dissolution of Fe(II) and generate the subsequent ROS at neutral or weakly alkaline pH (Cui et al., 2017).

$$O_2 + Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2O_2 \quad (1)$$

$$O_2 + Fe^{2+} \rightarrow \bullet O_2^- + Fe^{3+} \quad (2)$$

$$\bullet O_2^- + Fe^{2+} + 2H^+ \rightarrow H_2O_2 + Fe^{3+} \quad (3)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^- \quad (4)$$

The addition of ligand can promote Fenton-like reaction at neutral or weakly alkaline pH through chelating iron ions and maintain the dissolved iron concentration at a sufficient level (Cui et al., 2017). A variety of ligands have been reported to chelate ferrous/ferric ions in Fenton-like process to promote the generation of reactive oxygen species (i.e. •OH) for the removal of organic pollutants and contaminants (Gong et al., 2016; Shen et al., 2017). The organic ligands such as ethylenediaminetetraacetic acid and nitrilotriacetic acid are recalcitrant in nature and show poor biodegradability, thus causing secondary environmental pollution, while the inorganic ligand such as polyphosphate may cause problems for subsequent phosphorus removal (Cui et al., 2017). Citric acid (CA) is an environmental-friendly tricarboxylic acid. The environmentally benign CA has been used for pollutants degradation and shows superiority due to its larger molecular size, greater accessibility to iron center, and slighter consumption during the degradation process (Gong et al., 2016). When the citric acid (CA) was used as a ligand, the citric acid could chelate both ferrous and ferric ions (Cui et al., 2017; Gong et al., 2016; He et al., 2016). Firstly, nZVI reacts with O_2 to generate H_2O_2, accompanying with the release of Fe^{2+} (Eq. (1)). After this, by the addition of the citric acid to the reactive media, the ferrous ions are chelated by the citric acid (Eq. (5)) and are not precipitated as iron oxides. In a following step, the Fe(II)(Cit) complex is oxidized to a Fe(III)(Cit) complex allowing the formation of additional hydroxyl radicals (Eqs. (6)–(8)).

$$Fe(II) + Cit \rightarrow Fe(II)(Cit) \quad (5)$$

$$Fe(II)(Cit) + O_2 \rightarrow Fe(III)(Cit) + \bullet O_2^- \quad (6)$$

$$Fe(II)(Cit) + \bullet O_2^- + 2H^+ \rightarrow Fe(III)(Cit) + H_2O_2 \quad (7)$$

$$Fe(II)(Cit)_{(sol)} + H_2O_{2(sol)} \rightarrow Fe(III)(Cit)_{(sol)} + \bullet OH + OH^- \quad (8)$$

Fenton oxidation can degrade EPS and release bound water so as to enhance dewaterability (Neyens et al., 2004). Furthermore, better filtration and separation performance could be achieved when pre-oxidation treatment was followed by coagulation with inorganic coagulant or organic polymer. Therefore, the combination of pre-oxidation process with organic polymers can effectively agglomerate sludge tiny flocs and improve sludge filterability when simultaneously releasing bound water (He et al., 2016).