Bioresource Technology 181 (2015) 247–253

Contents lists available at ScienceDirect

Bioresource Technology

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

Insights into the respective role of acidification and oxidation for enhancing anaerobic digested sludge dewatering performance with Fenton process

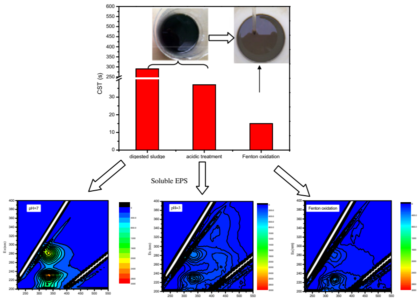
Weijun Zhang, Peng Yang, Xiaoyin Yang, Zhan Chen, Dongsheng Wang *

State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18, Shuangqing Road, Beijing 100085, China

HIGHLIGHTS

- Proteins were effectively removed from sludge bulk after acidification treatment.
- Acidification and Fenton oxidation showed a significant synergetic effect.
- Oxidation played a more important role than coagulation in Fenton conditioning.
- Extracellular polymers degradation was the major mechanism of sludge conditioning.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 September 2014
Received in revised form 28 December 2014
Accepted 3 January 2015
Available online 7 January 2015

Keywords:
Anaerobic digested sludge
Dewaterability
Extracellular polymeric substances
Fenton oxidation

ABSTRACT

Digested sludges generally exhibit poorer dewaterability than activated sludges. This study investigated the effects of acidification and oxidation on EPS properties and dewaterability of anaerobic digested sludge in Fenton treatment in order to unravel the underlying mechanism of sludge conditioning. The results indicated that sludge dewatering property was improved after acidification treatment. Meanwhile, fluorescence analysis revealed that the protein-like substances were effectively removed from sludge bulk after acidification treatment. Acidification and Fenton oxidation showed a significant synergetic effect in enhancing sludge dewatering process. Solubilization and decomposition of bound EPS occurred synchronously during Fenton conditioning. Oxidation process is very likely to play a more important role in sludge conditioning than Fenton coagulation. According to pilot test, Fenton treatment performed much better in cake moisture content reduction than chemical conditioning with traditional inorganic coagulants. Additionally, full-scale application of Fenton conditioning will not have detrimental effects on performance of wastewater treatment system.

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. Reducing the amount of sludge produced and improving the dewaterability are hence of paramount importance to cut transportation and disposal cost (Niu et al., 2013; Zhai et al., 2012). Activated sludges are generally hard to dewater due to high content organic materials (Yuan et al., 2011). It was reported that extracellular polymeric substances (EPS) accounted for 60–80% of total sludge mass (Liu and Fang, 2003; Vaxelaire and Cézac, 2004). The distribution and abundance of EPS have a significant

---

* Corresponding author. Tel./fax: +86 10 62849138.
E-mail address: wgds@rcees.ac.cn (D. Wang).

http://dx.doi.org/10.1016/j.biortech.2015.01.003
0960-8524/

influence on sludge dewatering property (Liu and Fang, 2003). Houghton et al. (2001) stated that sludge dewaterability was mainly affected by the EPS content, and there was an optimum level of EPS at which the sludge exhibited maximum dewaterability. In addition, EPS also had an influence on charge properties, moisture content of dewatered sludge cake and floc stability and so on (Mikkelsen and Keiding, 2002). Of main components in EPS, protein-like substances were believed to play more important in sludge dewatering than polysaccharide and humic acid (Liu and Fang, 2003). Murthy and Novak (1999) suggested that high protein content was detrimental to sludge dewatering.

Prior to dewatering most sludges are always conditioned with chemicals in order to improve performance of sludge dewatering devices. Addition of traditional chemical conditioners (inorganic salt coagulants and organic polymers) can agglomerate the small fines and compress EPS structure of the sludge colloids to form large flocs through charge neutralization and bridging, which can be more easily separated from the water (Niu et al., 2013). It was noted that EPS are highly hydrated and are able to bind a large volume of water (Houghton et al., 2001), but traditional chemical conditioners are ineffective to remove the bound and intercellular water in sludge flocs (Neyens et al., 2004). In recent years, many advanced sludge treatment (AST) processes have been developed in order to improve sludge dewatering and to facilitate handling and ultimate disposal (Neyens and Baeyens, 2003a). Neyens et al. (2004) demonstrated that AST improve the sludge dewaterability through decomposing and/or changing EPS properties to reduce bound water content. Established AST methods include photo-Fenton/Fenton oxidation (Neyens and Baeyens, 2003a), acid/alkaline treatment (Neyens et al., 2004), thermal treatment (Neyens and Baeyens, 2003b) and enzymatic treatment (Ayol, 2005) or their integrated processes. Fenton oxidation is known to be dependent on in situ producing a non-selective strong hydroxyl radical which can effectively destruct various refractory organic matters at ambient condition (Neyens and Baeyens, 2003a). Many studies reported that Fenton reagents are able to break activated sludge floc and solubilize EPS, promoting the conversion from bound water to free water (Neyens and Baeyens, 2003a,b; Neyens et al., 2004; Pham et al., 2010). In addition, the ferric hydroxo complexes produced from Fenton process could act as coagulants to further enhance dewatering performance of biosludge (Neyens and Baeyens, 2003a). Liu et al. (2012) found that sludge conditioning with combined Fenton's reagent and skeleton builders was an efficient mean to achieve deep dewatering. Fenton treatment resulted in partial destruction of EPS and decrease in sludge floc size. Then lime and Portland cement were added to serve as skeleton builders to transmitted the stresses to the internal parts of flocs and provide channels for water release under high pressures (Liu et al., 2013).

As mentioned above, many previous studies reported that sludge (activated or digested) flocculation and dewaterability could be greatly improved via peroxidation treatment, but the responsible mechanism is not fully understood. Therefore, the objectives of this paper were to: (1) get more comprehensive insights into the respective role of acidification and oxidation in anaerobic digested sludge conditioning with Fenton reagents; (2) investigate the effects of acidification and Fenton oxidation on solubilization and chemical properties of digested sludge EPS in detail; (3) examine the dewatering or drying performance of digested sludge after Fenton conditioning through pilot test; (4) evaluated the potential impacts of Fenton conditioning on influent quality and operation of wastewater treatment plant was also evaluated. In addition, the present study is able to provide information on improvement of digested sludge treatment and management with Fenton process in practical application.

2. Methods

2.1. Source and properties of digested sludge

Sewage sludge was obtained from anaerobic digested reactors of the biggest wastewater treatment plant in Beijing city. It treats approximately 1,200,000 m^3 of wastewater daily by anaerobic/anoxic/oxic process. Sample was stored at 4 °C after sampling. The sludge characteristics can be found in Table 1. All the chemicals used in this study were of analytical grade. 98% Sulfuric acid and sodium hydroxide (Sinopharm Chemical Reagent, China) was used to adjust pH of the sludge samples. Ferrous sulfate ($FeSO_4 \cdot 7H_2O$) and hydrogen peroxide (H_2O_2, 30 wt.%) were purchased from Sinopharm Chemical Reagent of China.

2.2. Sludge conditioning with Fenton oxidation

A 200 mL of sludge sample was added in a 500 Erlenmeyer flask. The beaker was placed in thermostatic bath (25 ± 1 °C). And then appropriate amounts of ferrous sulfate heptahydrate salt ($FeSO_4 \cdot 7H_2O$) were added in the beaker at varying pH values. An aliquot of H_2O_2 (30% (w/v)) was spiked in the sludge sample under vigorous stirring using a magnetic stirrer. Finally, the reaction was stopped by raising the pH of the solution to 7 after 2 h stirring. The suspension was centrifuged at 5000*g* for 15 min, and the supernatant was used for TOC and fluorescence analysis later. Each experiment was performed in duplicate.

2.3. Analytical methods

2.3.1. Dewatering test

The dewaterability of the sludge flocs was measured with a capillary suction time (CST) instrument (Model 319, Triton, UK) equipped with an 18 mm diameter funnel and Whatman No. 17 chromatography-grade filtration paper. In addition, centrifugal dewatering test was conducted to get a further understanding into the effects of Fenton treatment on dewatering efficiency. The sludge conditioned with Fenton reagents was transferred and centrifuged at 5000*g* for 30 min, and then the moisture content of sediments was measured according to standard method.

2.3.2. Three-dimensional excitation emission matrix (3-DEEM) spectra analysis

The sample was diluted with Milli Q water until concentration of DOC was below 10 mg/L. 3-DEEM spectra were measured by a Hitachi F-4500 fluorescence spectrophotometer with an excitation range from 200 to 400 nm at 10 nm sampling intervals and an emission range from 280 to 500 nm at 10 nm sampling interval. The spectra were recorded at a scan rate of 12,000 nm/min, using excitation and emission slit bandwidths of 10 nm. Each scan had 37 emission and 27 excitation wavelengths. As stated by Sheng and Yu (2006), pH had significant effect on EEM analysis, so solution pH was adjusted to be neural prior to analysis in order to remove the interference.

2.3.3. Other indicators

Zeta potential and turbidity was measured using Zetasizer2000 (Malvern Instruments Ltd, Malvern, UK) and 2100 N Turbidimeter (Hach, USA) respectively. The dissolve organic carbon (DOC) in the filtrate was analyzed using TOC analyzer (Shimadzu, Kyoto, Japan). pH was measured by a pHS-3C (Shanghai, China) pH meter, which was calibrated using pH 7.01 and pH 9.18 buffers. The sludge floc size was determined by using Mastersizer 2000 (Malvern, UK). The $d_{0.5}$ value mean that 50% of the particles measured were less than or equal to the size stated. Other sludge