Water Research 146 (2018) 19–29

Contents lists available at ScienceDirect

Water Research

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

Enhancement of anaerobic digestion sludge dewatering performance using in-situ crystallization in combination with cationic organic polymers flocculation

Qiandi Wang [a], Weijun Zhang [a, b, *], Zhaoyi Yang [c], Qiongying Xu [d], Peng Yang [d], Dongsheng Wang [b, c, d]

[a] School of Environmental Studies, China University of Geosciences, Wuhan, 430074, Hubei, China
[b] Hubei Provincial Engineering Research Center of Systematic Water Pollution Control, Wuhan, 430074, Hubei, China
[c] State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China
[d] Faculty of Materials Science and Chemistry, China University of Geosciences, Wuhan, 430074, Hubei, China

ARTICLE INFO

Article history:
Received 21 June 2018
Received in revised form
18 August 2018
Accepted 4 September 2018
Available online 6 September 2018

Keywords:
Anaerobic digestion sludge
Cationic organic polymers
Dewaterability
Floc morphology
In-situ magnesium ammonium phosphate crystallization

ABSTRACT

Anaerobic digestion (AD) has been widely used in sludge treatment for biogas recovery, organic fraction stabilization, and sludge reduction. However, after AD, sludge filterability is extremely deteriorated due to the release of biopolymers and the formation of fine particles. AD sludge is generally rich in nutrients, mainly ammonium nitrogen and phosphates, that result from biopolymer degradation. We designed a conditioning process that combines the in-situ crystallization of magnesium ammonium phosphate (MAP), as a skeleton builder, with organic polymer flocculation. We show that crystallized MAP can bind with extracellular polymeric substance fractions to increase sludge floc density. The molecular structure and electrical charge of organic polymers importantly influence sludge particle flocculation and aggregation. We found that cationic polyacrylamides form flocs that aggregate with branching structures which are characterized by a larger size and a more compact structure. Simultaneous crystallization and flocculation produced by a magnesium–organic polymer gel improved AD dewaterability more than the separate addition of magnesium ions and organic polymers. The method of sludge conditioning that we propose was tested by extensive use in different AD sludge conditioning protocols. The method reduces the ammonium nitrogen load in AD liquor and increases the suitability of the biosolids for use as land fertilizer.

1. Introduction

Waste activated sludge (WAS) is the major byproduct of wastewater treatment plants (WWTPs) and disposing of it is increasingly challenging. Standards governing effluent treatment have become more stringent, and population growth and industrial expansion have increased the quantity of wastewater that must be treated. Annual production of sludge cake with moisture content of 80% had exceeded 30 million tons in China by 2015 and is expected to reach 50 million tons by 2020. Sludge must be disposed of cost-effectively and safely. Sludge management accounts for 30%–60% of the total operating cost of a WWTP (Zhao and Kugel, 1996; Zhao et al., 2015; Wang et al., 2016), which makes it important to develop effective methods to recover energy and useful nutrients from sludge in order to reduce operating costs and increase the environmental sustainability of wastewater treatment (Tay and Show, 1997; Tay et al., 2000).

Activated sludge is a heterogeneous colloidal system that consists mainly of microbial cells, extracellular polymeric substances (EPS), and inorganic minerals. EPS are produced by microorganisms and account for 60%–80% of total sludge mass (Liu and Fang, 2003; Vaxelaire and Cézac, 2004). EPS are complex high-molecular-weight polymers and include polysaccharides, proteins, humic substances, and nucleic acids. EPS can form gelatinous networks to which microorganisms adhere and which increase water retention and protect microorganisms against harmful pollutants. EPS are

---

* Corresponding author. School of Environmental Studies, China University of Geosciences, Wuhan, 430074, Hubei, China.
E-mail address: zhangweijun@cug.edu.cn (W. Zhang).

https://doi.org/10.1016/j.watres.2018.09.015

conducive to floc formation and increase flocculation of sludge particles (Cetin and Erdincler, 2004; Mikkelsen and Keiding, 2002). The EPS fraction influences floc stability, settleability, and dewaterability. Sludge particles are always negatively charged due to the ionization of anionic functional groups (such as phosphate and carboxyl groups) in EPS, which results in electrostatic repulsion between sludge particles and maintains the stability of the colloidal system.

Many studies have demonstrated the crucial effects of EPS on sludge dewaterability. Higgins and Novak (1997) showed that sludge dewaterability was strongly influenced by the proportions of protein and polysaccharides in EPS. Proteins exerted a more significant influence on sludge dewaterability than polysaccharides, and a high protein: polysaccharide ratio was detrimental to dewaterability. This observation agreed with Murthy and Novak's (1999) findings. EPS in sludge were characterized by regionalization: the outer EPS fraction had a loose structure (loosely bound EPS, LB-EPS) and the inner EPS fraction had a more compact structure (tightly bound EPS, TB-EPS). Li and Yang (2007) showed that a higher LB-EPS content weakened the bonds between cells, resulting in poor settleability and dewaterability. The higher protein content of LB-EPS also adversely affected sludge dewaterability (Yu et al., 2008). Zhang et al. (2015) found that the composition of soluble EPS (S-EPS) and LB-EPS changed over time, while TB-EPS and pellets, mainly composed of protein-like substances, were more stable. Sludge filtration performance is related to S-EPS, while bound water content is primarily affected by bound EPS; a higher concentration of bound EPS is related to an increase in bound water (Yuan et al., 2017).

Anaerobic digestion (AD) has been used to treat biosolids for more than a century. It has the advantages of reducing solids, stabilizing the organic fraction, and producing biogas. Over half the WWTPs in the European Union use anaerobic digestion in sludge treatment, and China has recently encouraged large and medium WWTPs to preferentially use AD (Wu et al., 2014). There are typically four stages of AD: solubilization, hydrolysis, acidogenesis, and methanogenesis. Solubilization of biopolymers is widely accepted as the rate-limiting stage of AD because of poor biodegradability due to the biofilm that protects EPS and the cell walls or membranes (Zhao et al., 2015; Peng et al., 2016). Extensive thermal, mechanical, chemical, and biological methods of hydrolysis have been developed to accelerate the AD rate (Wang et al., 2013; Li et al., 2016; Lee et al., 2014). EPS, sludge floc morphology, and sludge chemistry change greatly after AD. Proteins and polysaccharides are released into the sludge during hydrolysis and are then converted into methane, carbon dioxide, and humic substances. The ammonium nitrogen and phosphate content of the sludge liquor dramatically increases due to the conversion of biopolymers. In addition, anaerobic digestion liquor can be highly alkaline. Degradation of EPS can decrease flocculation activity and reduce the size of sludge particles. Thus, in most cases, sludge dewaterability and filterability will deteriorate after AD.

Various technologies have been developed to improve sludge dewaterability, including photo-Fenton/Fenton oxidation technology (Liu et al., 2013; Tokumura et al., 2007), thermal hydrolysis, acid and alkali treatment (Zhu et al., 2013), heat treatment (Neyens et al., 2004), enzymatic treatment (Chen et al., 2015; Thomas et al., 1993), and combinations of these processes. These technologies can give good dewaterability, but most of them are difficult to use in practice. Deep dewatering has been widely used in China to reduce sludge volume and to alleviate the pressure on WWTPs caused by the rapid increase in sludge production. Deep dewatering requires chemical conditioning of the sludge and high-pressure filter press equipment, such as a plate and frame filter press or a diaphragm filter press. Inorganic coagulants (aluminum salts and iron salts) are used as chemical conditioners in high-pressure filter press deep dewatering because they bind with the EPS fraction through electrostatic neutralization, and the hydrolysis products of inorganic coagulants increase floc strength through skeleton building (Cao et al., 2016). However, both aluminum salts and iron salts greatly reduce the alkalinity of the sludge through the hydrolytic reaction, which is unfavorable for the subsequent use of the anammox process to treat filtrates containing high concentrations of ammonium nitrogen, and adversely affect subsequent sludge disposal, such as land use.

AD sludge bulk is characterized by high levels of ammonium nitrogen and phosphates. This observation led us to design an innovative sustainable conditioning process which combines the in-situ crystallization of magnesium ammonium phosphate (MAP), as a skeleton builder, and organic polymer flocculation without reducing alkalinity. We monitored floc formation and cake morphology under chemical conditioning and optimized this conditioning process. The distribution and chemical composition of EPS in AD sludge were investigated to provide an understanding of the underlying mechanisms of in-situ crystallization and cationic organic polymer flocculation.

2. Materials and methods

2.1. Source of anaerobic digestion sludge and reagents

Anaerobic digestion sludge was obtained from the Xiaohongmen WWTP in Beijing, which reclaims 600 000 tonne/d wastewater using an anaerobic–anoxic–oxic process and a membrane filter system. The waste activated sludge is thermally hydrolyzed at 160 °C for 30 min in a high-pressure reactor (Cambi, Norway). Characteristics of the raw sludge are shown in Table 1.

All analytical reagents were purchased from Sinopharm Chemical Reagent Co., Ltd in China. Three kinds of commercial polyacrylamide (PAM) with a molecular of 9 000 000, cationic PAM (CPAM), non-ionic PAM (NPAM) and anionic PAM (APAM), were purchased from SNF Flocculant Co., Ltd. And CPAM has a charge density of 50%. They were dissolved in ultrapure water to prepare a 0.2% (w/w) solution. The Mg-CPAM gels were created by dissolving CPAM (0.7%, w/w) in different concentrations (1%, 2%, 5%, and 7%, w/w) of an $MgCl_2$ solution.

2.2. Experimental procedures

2.2.1. Magnesium ammonium phosphate crystallization

Sludge samples of 100 mL were used in the experiments. The pH optimization experiments were performed under the molar ratios of $Mg^{2+}:NH_4^+ = 0.5$ and $Mg:P = 1:1$. HCl and NaOH were used to set pH at 6.5, 7, 7.5, 8, 8.5, 9, and 9.5. Then the MAP conditioner was added at the set pH value. The molar ratios of $Mg^{2+}:NH_4^+$ and Mg:P in sludge were respectively set to 0.025, 0.125, 0.25, 0.375, 0.5, 0.625, 0.75 and 1:0.5, 1:0.8, 1:1, 1:1.2, 1:1.5 by adding $MgCl_2$ and K_2HPO_4. Sludge samples were reacted for crystallization using a magnetic stirrer at a gradient of velocity of $112.08 s^{-1}$ for 120 min.

2.2.2. Flocculation

Sludge samples of 200 mL were used for flocculation. A MY-3000M variable-speed jar tester (Meiyu) was used with 50 × 40 mm flat paddle impellers. A rapid mix for 30 s at a gradient of velocity of $112.08 s^{-1}$ was followed by a slow stir at a gradient of velocity of $17.37 s^{-1}$ for 10 min. The flocculants (CPAM, APAM, NPAM and Mg-CPAM gel) were added using a graduated pipette and the samples were agitated. After mixing, the conditioned sludge was allowed to settle in the beaker for 30 min.