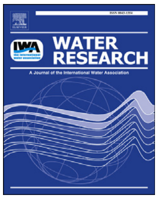
Water Research 130 (2018) 281–290

Contents lists available at ScienceDirect

Water Research

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



Understanding the impact of cationic polyacrylamide on anaerobic digestion of waste activated sludge

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ARTICLE INFO

Article history:
Received 20 June 2017
Received in revised form
15 November 2017
Accepted 4 December 2017
Available online 5 December 2017

Keywords:
Cationic polyacrylamide
Waste activated sludge
Anaerobic digestion
Methane production

ABSTRACT

Previous investigations showed that cationic polyacrylamide (cPAM), a flocculant widely used in wastewater pretreatment and waste activated sludge dewatering, deteriorated methane production during anaerobic digestion of sludge. However, details of how cPAM affects methane production are poorly understood, hindering deep control of sludge anaerobic digestion systems. In this study, the mechanisms of cPAM affecting sludge anaerobic digestion were investigated in batch and long-term tests using either real sludge or synthetic wastewaters as the digestion substrates. Experimental results showed that the presence of cPAM not only slowed the process of anaerobic digestion but also decreased methane yield. The maximal methane yield decreased from 139.1 to 86.7 mL/g of volatile suspended solids (i.e., 1861.5 to 1187.0 mL/L) with the cPAM level increasing from 0 to 12 g/kg of total suspended solids (i.e., 0–236.7 mg/L), whereas the corresponding digestion time increased from 22 to 26 d. Mechanism explorations revealed that the addition of cPAM significantly restrained the sludge solubilization, hydrolysis, acidogenesis, and methanogenesis processes. It was found that ~46% of cAPM was degraded in the anaerobic digestion, and the degradation products significantly affected methane production. Although the theoretically biochemical methane potential of cPAM is higher than that of protein and carbohydrate, only 6.7% of the degraded cPAM was transformed to the final product, methane. Acrylamide, acrylic acid, and polyacrylic acid were found to be the main degradation metabolites, and their amount accounted for ~50% of the degraded cPAM. Further investigations showed that polyacrylic acid inhibited all the solubilization, hydrolysis, acidogenesis, and methanogenesis processes while acrylamide and acrylic acid inhibited the methanogenesis significantly.

1. Introduction

Biological wastewater treatment is widely used in the world, but large amounts of waste activated sludge (WAS) are produced, which is a big problem faced by wastewater treatment plants (WWTPs) nowadays (Chen et al., 2016; Wang et al., 2012; 2017a; Zhao et al., 2016a; 2017b). WAS would readily cause secondary pollution if it is treated and disposed inappropriately. However, WAS also contains high concentrations of carbon and nutrient substrates, which makes it a useful resource for energy recovery (Li et al., 2016a, 2016b; Wang et al., 2017b; 2017c, 2017d; Xie et al., 2016a). As anaerobic digestion is able to effectively reduce sludge volume, stabilize sludge characteristic, kill pathogenic microorganisms, and produce renewable energy, methane, it is considered the most promising method for WAS treatment and widely implemented in real situations (Jenicek et al., 2012; Xu et al., 2017).

As a major byproduct of wastewater treatment, WAS not only contains organic compounds such as protein, carbohydrate, and polyhydroxyalkanoates, but also concentrates a variety of pollutants present in wastewaters and biological/chemical additives

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https://doi.org/10.1016/j.watres.2017.12.007
0043-1354/

added during wastewater treatment and sludge dewatering processes (Chen et al., 2014; Luo et al., 2016; Li et al., 2016a, 2016b; Qi et al., 2011; Yi et al., 2017). It is known that sludge anaerobic digestion includes several biological conversions (e.g., solubilization, hydrolysis, acidogenesis, and methanogenesis) executed by a series of microbes such as hydrolytic microorganisms, acid-producing microorganisms, hydrogenogens, and methanogens (Appels et al., 2008; Zhao et al., 2016b). Thus, these concentrated pollutants and additives might affect these bio-conversions, thereby affecting the performances of sludge anaerobic digestion.

Cationic polyacrylamide (cPAM), a linear water-soluble polymeric compound with a high molecular weight and cationic charges, is widely used in enhancing solid-liquid separation through charge neutralization and interparticle bridging (Aguilar et al., 2005; Moussas and Zouboulis, 2009). In WWTPs, cPAM is usually applied in wastewater pretreatment, leading to cPAM accumulation in WAS (Xia et al., 2005). Moreover, in small-scale WWTPs where digesting WAS in-situ in WWTPs is not economically feasible and in some developing counties like China where most of the WWTPs has not already been configured with anaerobic digesters, WAS is first required to be dewatered and then gathered together for further treatment (Duan et al., 2012; Guendouz et al., 2008; Zhai et al., 2012). As cPAM is substantially added into floc during mechanically dewatering process, cPAM contents in such sludges are inevitably at high levels. It was reported that cPAM level in dewatered sludge was in the range 2.5–10 g/kg dry sludge (Chu et al., 2002; Thornton et al., 2001).

Due to the significant level of sludge cPAM, its impact on sludge anaerobic digestion raised concerns in the past years. For example, Chu et al. (2003) found that compared with the control, 15 and 40 g/kg of cPAM resulted in 22% and 37% of methane yield reduction during anaerobic digestion, respectively. The increased size of the sludge caused by particle aggregation, which limited the disintegration rate of WAS, was considered the main reason for the deterioration of methane reduction (Campos et al., 2008; Chu et al., 2005; Dentel and Gossett, 1982). Recently, cPAM has been demonstrated to be degradable during anaerobic digestion (Chang et al., 2001; Dai et al., 2014). Furthermore, it could be utilized as nitrogen source to stimulate methanogenesis and even as a carbon source to produce volatile fatty acids (Dai et al., 2015; Haveroen et al., 2005). It is reported that cPAM could be anaerobically biodegraded via a series of biochemical processes (Bao et al., 2010; Chang et al., 2001; Dai et al., 2014, 2015; Haveroen et al., 2005). Long-chain cPAM is first transformed into short-chain cPAM by ectoenzymes. Then short-chain cPAM is activated by either ectoenzymes or amidases and hydrolyzed to acrylamide, acrylic acid, and polyacrylic acid. The generated acrylic acid and polyacrylic acid can be further bio-converted to pyruvic acid and acetyl-CoA, which are finally used to produce methane via acetic acid, hydrogen, and carbon oxidize. Despite these significant advances, details of how cPAM affects the process of anaerobic digestion of WAS are still poorly understood.

Since cPAM is degradable in the anaerobic digestion, it could be utilized as nitrogen and carbon sources to produce methane directly, but it is unknown whether cPAM has a lower biochemical methane potential on a unit VSS basis, as compared with other sludge compositions such as protein and carbohydrate. Previous studies demonstrated that cPAM slowed the sludge disintegration process, but the potential effect of cPAM on other processes of anaerobic digestion such as hydrolysis, acidogenesis, and methanogenesis have never been documented. Moreover, cPAM and its degradation metabolites such as polyacrylic acid, acrylic acid, and acrylamide would co-exist in the digestion system (Chang et al., 2001; Dai et al., 2015; Haveroen et al., 2005), thus the toxicity of cPAM and its degradation metabolites to the bio-conversion processes involved in anaerobic digestion is also needed to be comprehensively identified.

This work therefore aims to deeply understand the underlying mechanism of how cPAM affects methane production during anaerobic digestion of sludge. Firstly, the influence of cPAM at different dosages on methane production during WAS anaerobic digestion was investigated. Then, details of how cPAM affects the methane production were explored. Till now, most of the reported studies on WAS anaerobic digestion focused on the enhancement of methane yield, ignoring the effect of pollutants and additives such as cPAM contained in WAS Stuckey and Mccarty, 1978, Wang et al., 2013, Xie et al., 2016b, Zhang et al., 2011. To the best of our knowledge, this is the first work revealing the underlying mechanisms of cPAM inhibiting methane production during sludge digestion system. The findings obtained would not only fill a knowledge gap regarding cPAM's impact on sludge digestion but also could guide engineers to develop strategies to mitigate cPAM's negative impact in the future.

2. Materials and methods

2.1. WAS and cPAM

To minimize the background of cPAM in WAS, the WAS used in this study was obtained from the secondary sedimentation tank of a WWTPs with sludge retention time of 20 d in Changsha, China, where cPAM-based wastewater pretreatment was not implemented. Before use, the sludge was concentrated by settling at 4 °C for 24 h and screened with a 1 mm sieve to remove impurities. Its main characteristics are as follows: pH 6.9 ± 0.1, total suspended solids (TSS) 24655 ± 625 mg/L, volatile suspended solids (VSS) 16728 ± 342 mg/L, soluble chemical oxygen demand (COD) 82 ± 6 mg/L, total COD 21100 ± 420 mg/L, total carbohydrate (as COD) 1998 ± 120 mg/L, total protein (as COD) 11715 ± 90 mg/L, and ammonium nitrogen (NH_4^+-N) 22.4 ± 3 mg/L. The cationic PAM used in this study was purchased from Chongqing Reagent Company, which had a molecular weight of 6–8 million Da with a 30% charge density, and with a residual acrylamide content less than 10 mg/kg.

2.2. Methane production during WAS anaerobic digestion in the presence of different cPAM levels

This batch experiment was carried out in 5 replicate reactors, and each had a working volume of 1 L. A 4 L WAS was divided equally and added into the 5 reactors. Then different volumes of flocculant solution (0.3% w/w) were added into those reactors to achieve the predetermined dosage at the beginning of the experiment, followed by 200 rpm of stirring for 5 min and 50 rpm for 20 min. The predetermined dosages of cPAM addition were 0, 3, 6, 12, and 24 g/kg TSS, respectively. Afterwards, 400 mL of inoculum, which was collected from a laboratory anaerobic sludge digester, was equally divided and added to these five reactors. The TSS, VSS, and total COD concentrations of inoculum were respectively 12610 ± 360, 10120 ± 240, and 16500 ± 400 mg/L. Each reactor was diluted with Milli-Q water to 1 L, resulting in 0, 59.2, 118.3, 236.7, or 473.4 mg/L of initial cPAM in these digesters. Besides, one control reactor was also performed to assess the productivity of methane from the inoculum alone. This control reactor contained 80 mL of inoculum and 920 mL of Milli-Q water without either WAS or cPAM addition. All reactors were flushed with nitrogen gas for 5 min to remove oxygen. Finally, all reactors were capped with rubber stoppers, sealed, and placed in an air-bath shaker (150 rpm) with medium temperature of 35 ± 1 °C. The pH value in all reactors was controlled at 7.0 ± 0.1 in the whole digestion period by adding 4 M hydrochloric acid or 4 M sodium hydroxide with automatic