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Cleavage of the main carbon chain backbone of high molecular weight polyacrylamide by aerobic and anaerobic biological treatment

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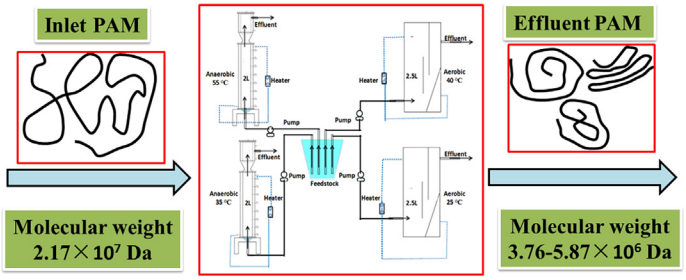
HIGHLIGHTS

- PAM over 2 × 10^7 Da was reduced to less than one-third of its original size after biological treatment.
- Both aerobic and anaerobic treatment were effective in the hydrolysis of large molecular weight PAM.
- Thermophilic anaerobic treatment was more efficient in degrading PAM.

GRAPHICAL ABSTRACT



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ABSTRACT

High molecular weight partially hydrolyzed polyacrylamide (PAM) can be bio-hydrolyzed on the amide side group, however, solid evidence regarding the biological cleavage of its main carbon chain backbone is limited. In this study, viscometry, flow field-flow fractionation multi-angle light scattering (FFF-MALS), and attenuated total reflectance-Fourier transform infrared (ATR-FTIR) analysis were used to investigate the biodegradability of PAM with a nominal molecular weight of 2 × 10^7 Da (Da) in two suspended aerobic (25 and 40 °C) and two upflow anaerobic blanket reactors (35 and 55 °C) operated for 470 d under a hydraulic residence time (HRT) of 2 d. Both anaerobic and aerobic biological treatment reduced the viscosity from 2.02 cp in the influent to 1.45–1.60 cp, and reduced the molecular weight of PAM using FFF-MALS from 2.17 × 10^7 Da to less than one-third its original size. The removals of both the amide group and carbon chain backbone in the PAM molecule were further supported by the FTIR analysis. In comparison with the other conditions, thermophilic anaerobic treatment exhibited higher efficiency for PAM biodegradation. Batch test excluded the influence of temperature on the molecular weight of PAM over the range 25–55 °C, suggesting that cleavage of the main carbon chain backbone was attributed to biological degradation. Our results suggested that high molecular weight PAM was biodegradable, but mineralization did not occur.

1. Introduction

Partially hydrolyzed anionic polyacrylamide (PAM) with a molecular weight of more than 10^6 Da and hydrolysis degree of around 25% (Fig. 1) can increase viscosity and tolerate high mechanical

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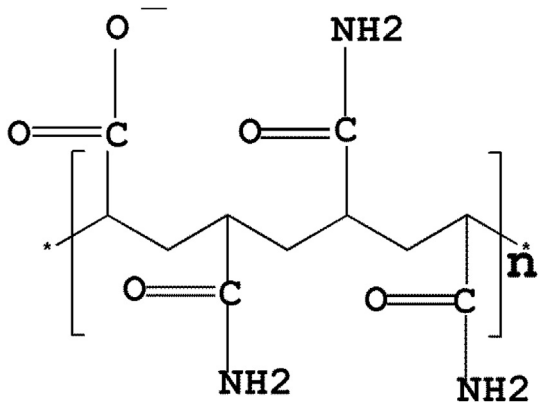

Fig. 1. Molecular structure of high molecular weight partially hydrolyzed polyacrylamide.

forces, and is widely used in oilfields for enhanced oil recovery (EOR) (Wever et al., 2011). To date, 32 pilot and large-scale applications of EOR in China and USA have reported performance data worldwide (Sheng, 2014), with the oil recovery rate increasing by 20% after adoption of EOR in the Daqing Oilfield, China (Olajire, 2014). Currently, oil recovery accounts for 57% of PAM consumption in China (Qian, 2010). Due to its high molecular weight and solubility, PAM used during EOR has been considered refractory to biodegradation (Suzuki et al., 1978), and not easily removed from oilfield produced water through conventional treatment (Pi et al., 2015). Thus, many studies have investigated the biodegradability of residual PAM in produced water from the perspective of environmental safety in case of discharge to the natural environment.

It has been reported that PAM biodegradation occurs more easily on the amide side group than cleavage of the main carbon chain backbone (Guezennec et al., 2015; Kay-Shoemake et al., 1998b). PAM can be used as a nitrogen source to stimulate the growth of sulfate-reducing bacteria (Grula and Sewell, 1982; Grula et al., 1994) and methanogens (Haveroen et al., 2005) under anaerobic conditions. In addition, aerobic-mixed bacteria from soil can hydrolyze the amine group of hydrolyzed PAM to release ammonia (Kay-Shoemake et al., 1998a; 1998b).

Although *Bacillus* sp. (Bao et al., 2010; Wen et al. 2010), *Acinetobacter* sp. (Matsuoka et al., 2002), and *Clostridium* sp. (Ma et al., 2010). isolated from oil recovery processes and soil samples reportedly use PAM as sole carbon sources, other studies showed that PAM is unable to serve as the sole carbon source for microbial growth (Chu et al., 2003; Kay-Shoemake et al., 1998a) and that the carbon backbone of PAM would not be cleaved through biological degradation (Haveroen et al., 2005). These contradictory results could relate to the physical properties of the polymers studied (molecular weight, copolymers, degree of hydrolysis, and history) as well as the differences in experimental conditions (Caulfield et al., 2002). The lack of conclusive results and suitable approaches for the characterization of PAM, especially for carbon chain, might also be an important factor affecting the observed biodegradation (Guezennec et al., 2015). To date, solid evidence regarding the cleavage of the main carbon chain backbone of high molecular weight PAM in biological wastewater treatment systems remains limited.

In this study, two suspended aerobic reactors (25 and 40 °C) and two upflow anaerobic blanket reactors (35 and 55 °C) were constructed and operated for 470 d to investigate biodegradability of PAM under different conditions. Viscometry, flow field-flow fractionation multi-angle light scattering (FFF-MALS), and attenuated total reflectance-Fourier transform infrared (ATR-FTIR) analysis were used to characterize the molecular weight and functional group change of PAM. The results of this study will hopefully provide important information for the risk assessment and management of PAM in water environments.

2. Materials and methods

2.1. Experimental setup and reactor operation

The PAM polymer (Table S1) with a nominal molecular weight of 2×10^7 Da and hydrolysis degree of 24% was provided by SNF SAS ZAC de Milieux (Andrezieux-42163, France). The molecular weight determined by FFF-MALS was 2.17×10^7 Da, and the viscosity in a 200 mg/L polymer solution (4 g NaCl/L, 25 °C) was 2.02 cp. Nutrient solution was prepared by dissolving nutrients in tap water at the following composition: starch 24.72 g/L, NH_4Cl 2.87 g/L, NaH_2PO_4 0.48 g/L, NaCl 240 g/L, HBO_3 50 mg/L, $MnSO_4 \cdot 4H_2O$ 40 mg/L, $ZnSO_4 \cdot 7H_2O$ 40 mg/L, $Na_2MoO_4 \cdot 4H_2O$ 20 mg/L, $CuSO_4$ $5H_2O$ 10 mg/L, $CoCl_2$ 10 mg/L, KI 10 mg/L, and $NiCl_2$ 10 mg/L. The PAM stock solution was prepared by adding 1.2 g or 2.4 g of PAM powder into a beaker containing 4 L of tap water under stirring for 12 h. The solution was then diluted in a bucket containing 8 L of tap water, and stirred with a mechanical stirrer for 2 d at 200 rpm. Synthetic wastewater was acquired by diluting the nutrient solution (100 mL) into the bucket, and then used to feed the reactors. Starch was added as a carbon source to promote bacterial growth.

The water-jacketed aerobic reactors had a 2 L aeration tank and a 0.5 L sediment tank. Air was supplied to the aeration reactors to provide oxygen and mixing. One reactor was operated at 25 ± 1 °C (Aerobic 25 °C) and another at 40 ± 1 °C (Aerobic 40 °C). The two upflow anaerobic sludge blanket reactors, one mesophilic (35 ± 1 °C, Anaerobic 35 °C) and one thermophilic (55 ± 1 °C, Anaerobic 55 °C), were manufactured with a working volume of 2 L. Activated sludge from the Qinghe Municipal Wastewater Treatment Plant, Beijing, was used as the seed sludge for the aerobic reactors (initial concentration, 2000 mg/L), and digestion sludge from the Gaobeidian Municipal Wastewater Treatment Plant, Beijing, was used as the seed sludge for the anaerobic reactors (initial concentration, 2000 mg/L). A schematic diagram of the experimental set up is illustrated in Fig. 2.

A HRT of 2 d was used for the four reactors. The reactors were operated for 470 d and the whole experiment was divided into two phrases: Phase I with the PAM concentration of 100 mg/L (from days 0–185) and Phase II with PAM concentration of 200 mg/L (from days 186–470).

Influent and effluent water samples were taken twice a week after filtration for chemical oxygen demand (COD), PAM concentration, and viscosity analyses. Effluent samples were taken every two to three months for molecular weight analysis, and were kept at 4 °C after centrifugation. Biomass samples were taken for the measurement of mixed liquor suspended sludge (MLSS).

Sludge samples for microbial community structure analysis were collected on days 183, 407, and 470, and centrifuged at 10,000 rpm for 10 min at 4 °C. Genomic DNA was extracted from the samples with a FastDNA® SPIN kit for soil (Qbiogene, Solon, OH, USA) according to the manufacturer's instructions, and then checked by spectrophotometric analysis on a NanoDrop ND-1000 (Nanodrop, USA) and stored at −20 °C before use.

The COD, ammonia nitrogen, and MLSS contents were determined according to standard methods (APHA, 2005). Chlorination of the amide nitrogen under acidic conditions forms colloids that can be measured by turbidity method (Scoggins and Miller, 1979). The PAM concentration was measured based on the principle and the brief overview described in supplemental material. The