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Effects of different electron acceptors on the methanogenesis of hydrolyzed polyacrylamide biodegradation in anaerobic activated sludge systems[☆]

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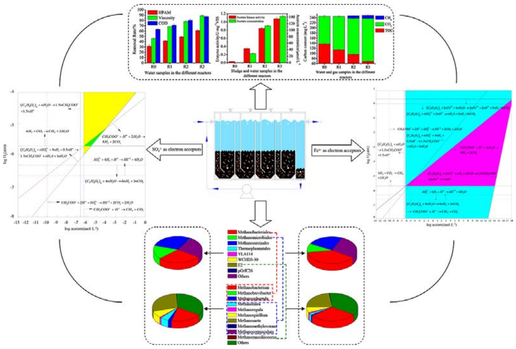
GRAPHICAL ABSTRACT



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ABSTRACT

The type of electron acceptor was a crucial factor in regulating the methanogenic process of anaerobic hydrolyzed polyacrylamide (HPAM) degradation. The combined methods of biodegradation experiments and thermodynamic calculations were applied to explore the effects of different electron acceptors on methanogenic HPAM degradation. Under the conditions of without electron acceptor, SO_4^{2-}, Fe^{3+}, SO_4^{2-} and Fe^{3+} as electron acceptors, HPAM biodegradation ratio reached 31.56%, 41.48%, 49.4% and 61.1%, acetate production reached 0.0532, 28.28, 112.7 and 141.95 $mg{\cdot}L^{-1}$, CH_4 production reached 0.024, 0.3015, 9.446 and 11.78 $mg{\cdot}L^{-1}$, respectively. The synergistic effect of SO_4^{2-} and Fe^{3+} further promoted methanogenic HPAM biotransformation. Archaeal community analysis revealed that *Methanobacteriales*, *Methanomicrobiales* and *Methanosarcinales* were dominant. Thermodynamic opportunity windows of methanogenesis with Fe^{3+} as electron acceptor are 35 times larger than that with SO_4^{2-} as electron acceptor. It indicated that acetoclastic methanogenesis was dominant and hydrogenotrophic methanogenesis was inhibited in the methane-producing process of anaerobic HPAM degradation.

1. Introduction

Hydrolyzed polyacrylamide (HPAM) is a water soluble polymeric compound with high molecular weight and is composed of acrylamide monomers. HPAM-flooding technology was applied to improve the oil recovery in subsurface. Meanwhile, a large amount of HPAM-containing wastewater was produced (Yan et al., 2016). It caused a series of problems for the underground water and the surrounding ecological

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environment. Current methods for treating HPAM-containing wastewater include biodegradation (Li et al., 2016), enzymatic degradation (Gilbert et al., 2017), photocatalytic degradation (Gu et al., 2016), membrane intercept (Wang et al., 2011) and flocculation (Zeng et al., 2007). Low-cost, environmentally friendly biodegradation technologies play a crucial role in the treatment of HPAM-containing wastewater (Zhao et al., 2016a). Meanwhile, methanogenic HPAM degradation is an important biological process in polymer-flooding oilfields or anoxic environments contaminated with HPAM (Li et al., 2015).

The type of electron acceptor is a crucial factor in regulating the extent and rate of methanogenic petroleum degradation in subsurface (Head et al., 2003). CH_4 as a major final product is generated under CO_2-reducing condition. Electron acceptors supply and methane production are of importance to exploit crude oil and recover heavy oil in subsurface through microbial engineering interventions (Head et al., 2003). Microorganisms provide biodegradation potential for eliminating the pollutants in hydrosphere, atmosphere and biosphere. Thermodynamic feasibility as a metric was applied to evaluate the potential biodegradation pathways (Finley et al., 2009). The concept of "windows of opportunity" was developed to evaluate the feasibility of biodegradation pathways whereby hydrocarbons were converted to methane (Dolfing et al., 2008; Dolfing et al., 2009). Moreover, compared with the experimental yields for aromatic hydrocarbons and methane, thermodynamic cell yields of biodegradation were also predicted through oxygenase activation reactions, energy and electron balances (Vanbriesen, 2001).

Biological hydrolysis of HPAM proceeds through several metabolic pathways linked to enzyme activity (Dai et al., 2015). A series of biochemical reactions involved in biological pathways are violently rate-limiting due to enzyme control, and these rate-limiting reactions also have large absolute values of Gibbs free energy changes (Shelley et al., 1996). Because HPAM can be utilized as energy, nitrogen and carbon sources by microorganisms (Bao et al., 2010; Dai et al., 2014; Yan et al., 2016), their biodegradation pathways also contain violently rate-limiting steps. However, the rate-controlling reaction steps have not been fully determined in the methane-producing process of anaerobic HPAM degradation.

There exist three major issues: (i) What are the effects of different electron acceptors on the anaerobic degradation efficiencies of HPAM? (ii) How many opportunities for methanogenesis of anaerobic HPAM degradation in the presence of different electron acceptors? (iii) What is the limiting step for anaerobic HPAM degradation in the presence of different electron acceptors?

The objectives of the study were to (i) explore the effects of different electron acceptors on HPAM biodegradation efficiencies, Total organic carbon (TOC) reduction, CO_2 and CH_4 productions, acetate kinase activity and archaeal community structure and (ii) draw thermodynamic opportunity windows for evaluating the feasibility of methanogenesis of anaerobic HPAM degradation in the presence of different electron acceptors.

2. Materials and methods

2.1. Materials

2.1.1. Wastewater ingredients

HPAM with an average molecular weight (MW) of 2.2×10^7 was supplied by Dongying Changan Polymer Group Co., Ltd. located in Shandong Province of China. The components of the wastewater pumped into the four reactors of R0, R1, R2 and R3 are shown in Table 1. The concentration of HPAM is approximately $500\ mg \cdot L^{-1}$ in the wastewater of Gudong Oil Production Plant, located in Shandong, China. So the initial concentration of HPAM was selected at $500\ mg \cdot L^{-1}$ in this study. The maximum microbial quantity of 9.6×10^7 CFU mL^{-1} and the maximum HPAM biodegradation efficiency of 61.5% occurred at $200\ mg \cdot L^{-1}$ SO_4^{2-} and $230\ mg \cdot L^{-1}$ Fe^{3+} in anaerobic activated sludge system. In addition, the number of the required electrons of SO_4^{2-}-reducing and Fe^{3+}-reducing reaction should be equal in the study of Section 3.5. Therefore, the concentrations of SO_4^{2-} and Fe^{3+} were selected at 200 and $228\ mg \cdot L^{-1}$, respectively. The microelements for microorganism growth were added (Dai et al., 2015). $NaHCO_3$ was added to balance the initial pH of wastewater in the range of 7–7.5. The final pH of effluent ranged from 6.5 to 6.8.

Table 1
The components of the wastewater pumped into the four reactors of R1, R2, R3 and R4.

Ingredients	Concentrations ($mg \cdot L^{-1}$)			
	R1	R2	R3	R4
HPAM	500	500	500	500
SO_4^{2-} (Na_2SO_4)	0	200	0	200
Fe^{3+} ($FeCl_3$)	0	0	228	228
$NaHCO_3$	405	405	405	405
$MgCl_2 \cdot 6H_2O$	100	100	100	100
$CaCl_2$	50	50	50	50
$(NH_4)_6Mo_7O_{24}$	15	15	15	15
$CuCl_2 \cdot 5H_2O$	5	5	5	5
$NiCl_2 \cdot 6H_2O$	5	5	5	5
$ZnCl_2$	5	5	5	5
$MnCl_2 \cdot 4H_2O$	5	5	5	5
$CoCl_2 \cdot 6H_2O$	5	5	5	5
H_3BO_3	5	5	5	5
$AlCl_3$	2.5	2.5	2.5	2.5

2.1.2. Seed sludge

The seed granular sludge was obtained from the wastewater treatment station of Gudong Oil Production Plant in Shandong, China. The seed sludge contained abundant microorganisms and it had a good biodegradation potential for HPAM. The average particle size of seed sludge is 1–2 mm. The concentrations of total suspended solid (TSS) and volatile suspended solid (VSS) are approximately 6900 and $5100\ mg \cdot L^{-1}$, respectively.

2.2. Experimental system

Four anaerobic baffle reactors (ABRs) were designed to simulate the anaerobic environment. The flow diagram of experimental system is shown in Fig. 1. The simulated wastewater without SO_4^{2-} and Fe^{3+} was pumped into the reactor of R0. The simulated wastewater containing SO_4^{2-} was pumped into the reactor of R1. The simulated wastewater containing Fe^{3+} was pumped into the reactor of R2. The simulated wastewater containing SO_4^{2-} and Fe^{3+} was pumped into the reactor of R3. Operating and starting-up conditions of the ABR were described elsewhere in the literature (Zhao et al., 2016a). The capacity of each reactor is 35.5 L. The reactor has four compartments. Hydraulic retention time (HRT) and reflux ratio were set to 24 h and 10:1, respectively. 17 L seed granular sludge was added to the reactor. In the first stage of starting-up process, $50\ mg \cdot L^{-1}$ HPAM and $450\ mg \cdot L^{-1}$ glucose served as the carbon source for sludge domestication. After 7 days of domestication, HPAM and COD removal ratios reached 50% and 60%, respectively. After that, HPAM concentration was increased and glucose concentration was decreased with the gradient of $50\ mg \cdot L^{-1}$. When HPAM and COD removal ratios reached stability, the gradient of domestication was changed. In the final stage of starting-up process, HPAM concentration reached $500\ mg \cdot L^{-1}$ and HPAM served as the sole carbon source. After 70 days starting-up stage, HPAM and COD removal ratios reached above 50% and 60%, respectively. Operation of the ABRs achieved stability and anaerobic activated sludge achieved maturity after acclimatization.

2.3. Sample analysis

The concentration of HPAM was quantified by the starch-cadmium