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Kinetics and thermodynamics of biodegradation of hydrolyzed polyacrylamide under anaerobic and aerobic conditions ☆

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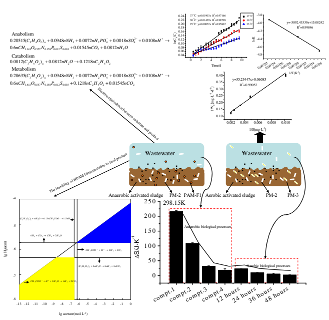
HIGHLIGHTS

- HPAM biodegradation kinetics were established in the activated sludge system.
- Thermodynamic entropy changes (ΔS) were calculated in biochemical treatment system.
- Thermodynamic windows of opportunity for the HPAM biodegradation were drawn.
- The feasibility of the HPAM biodegradation to final product was demonstrated.
- Growth-process equation confirmed electron equivalence between substrate and product.

GRAPHICAL ABSTRACT



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ABSTRACT

Kinetics and thermodynamics of hydrolyzed polyacrylamide (HPAM) biodegradation in anaerobic and aerobic activated sludge biochemical treatment systems were explored to determine the maximum rate and feasibility of HPAM biodegradation. The optimal nutrient proportions for HPAM biodegradation were determined to be 0.08 $g\cdot L^{-1}$ $C_6H_{12}O_6$, 1.00 $g\cdot L^{-1}$ NH_4Cl, 0.36 $g\cdot L^{-1}$ NaH_2PO_4 and 3.00 $g\cdot L^{-1}$ K_2HPO_4 using response surface methodology (RSM). Based on the kinetics, the maximum HPAM biodegradation rates were 16.43385 $mg\cdot L^{-1}\cdot d^{-1}$ and 2.463 $mg\cdot L^{-1}\cdot d^{-1}$ in aerobic and anaerobic conditions, respectively. The activation energy (E_a) of the aerobic biodegradation was 48.9897 $kJ\cdot mol^{-1}$. Entropy changes (ΔS) of biochemical treatment system decreased from 216.21 $J\cdot K^{-1}$ to 2.39 $J\cdot K^{-1}$. Thermodynamic windows of opportunity for HPAM biodegradation were drawn. And it demonstrated HPAM was biodegraded into acetic acid and CO_2 under laboratory conditions. Growth-process equations for functional bacteria anaerobically grown on polyacrylic acid were constructed and it confirmed electron equivalence between substrate and product.

1. Introduction

HPAM-containing oilfield wastewater is a type of relatively complex and special sewage that can cause a series of environmental problems whether through reinjection or discharge. High viscosity and strong emulsification of the wastewater lead to difficulties in its treatment (Guezennec et al., 2015). Treatment

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methods generally involve mechanical degradation (Shao et al., 2005; Al Hashmi et al., 2013), chemical oxidation (Caulfield et al., 2002; Zhou et al., 2015), biodegradation (Kay-Shoemake et al., 1998a,b; El-Mamouni et al., 2002; Bao et al., 2010) and new technologies that combine these methods (Lu and Wei, 2011; Pi et al., 2015). The effect of treatment has improved to some extent. Physical/chemical methods have some drawbacks, such as secondary pollution problems and substantially increased costs. Therefore, environmentally friendly, low-cost biological treatments play an important role in the field of HPAM-containing wastewater treatment.

Most of the previous studies have focused on the methods of improving HPAM biodegradation. Yan et al. (2016) investigated HPAM biodegradation in a sequencing batch biofilm reactor, and the HPAM removal ratio reached 54.69%. After anaerobic/aerobic coupling biodegradation, the HPAM removal ratio reached 90%, and HPAM with a relative molecular mass of approximately 2.2×10^7 was biodegraded into small molecule segments of approximately 3.5×10^3 (Sang et al., 2015). HPAM-containing oilfield wastewater was treated by biological processes combined Fenton oxidation, and the maximum removal rate of COD_{Cr} and HPAM reached 94.61% and 91.06%, respectively (Pi et al., 2015). A zero-valent iron/EDTA/air chemical oxidation/sequencing batch activated sludge system for treatment of the wastewater had a total HPAM removal rate of 96% (Lu and Wei, 2011). Other research revealed HPAM was a source of either carbon or nitrogen for microorganisms, and the metabolic pathways of HPAM biodegradation occurred under both anaerobic and aerobic conditions. Kay-Shoemake et al. (1998a,b) showed that soil microorganisms utilized HPAM as a sole N-source and hydrolyze the amide group by amidase, which converted HPAM into ammonia and organic acids. Cross-linked PAM stimulated the activity of microorganisms and the generation of methane under anaerobic conditions in the absence of a nitrogen source (Haveroen et al., 2005). Wen et al. (2010) reported two strains isolated from oil contaminated soil and activated sludge that used PAM as their sole carbon source. Bao et al. (2010) inferred the biodegradation mechanism of microbial enzymes. An amide enzyme hydrolyzed amino into carboxyl and microorganisms attacked the methyl group at the end of the side chain. Finally, the methyl group was oxidized to acid under the catalysis of a single oxygenase. The chain skeleton of HPAM formed acetic acid, propionic acid, butyric acid, isobutyric acid, valeric acid and isovaleric acid from different positions of fracture (Dai et al., 2014). In addition, Dai et al. (2015) also interpreted metabolic pathways for the biological hydrolysis of PAM from the perspective of enzymes.

However, four major issues exist: (i) How is the maximum biodegradation rate of HPAM determined? (ii) What does the model of kinetics for HPAM biodegradation conform to under anaerobic and aerobic conditions? (iii) Can HPAM be degraded completely by microorganisms? (iv) How many opportunities exist for reactions to be carried out?

Kinetics for utilization of different substrate was also researched. Pala-Ozkok et al. (2013) studied the effect of sludge age on acetate utilization kinetics. The maximum growth rate was observed to change from 3.9/d to 8.5/d when the sludge age was decreased from 10 d to 2.0 d. Orhon et al. (2009) found that peptone biodegradation at different sludge ages under aerobic conditions conformed to Monod kinetics. The kinetics of aerobic biodegradation of hydroquinone and catechol were successfully described by a Haldane model (Pramparo et al., 2012). First-order exponential and sigmoidal models were used for the two different stages in biochemical methane potential tests (Fernández-Rodríguez et al., 2014). In addition, Battley (1998) studied the thermodynamics of microbial growth by calculating ΔS and free energy change. In the same way, the kinetics and thermodynamics can be used to calculate the maximum rate and feasibility for HPAM biodegradation under anaerobic and aerobic conditions.

The objectives of this study were to (i) build the kinetics models of HPAM biodegradation in anaerobic and aerobic activated sludge biochemical treatment systems, (ii) investigate the effects of temperature on the HPAM biodegradation rate constant and determine E_a, (iii) calculate ΔS and demonstrate the feasibility of the biodegradation process from HPAM to CH_4 and CO_2 and (iv) construct growth-process equations for functional bacteria anaerobically grown on polyacrylic acid and confirm electron equivalence between substrate and product.

2. Materials and methods

2.1. Materials

2.1.1. Wastewater composition

The average molecular weight of HPAM in the sample was approximately 2.2×10^7, and it was 10% hydrolyzed. The HPAM wastewater in this study was dispensed to simulate the wastewater of Gu Liu joint station, located in Dongying, China. The composition of the wastewater is shown in Table 1. The optimal nutrient proportions were added as reported in Section 3.1, and microelements were added as nutriments for microorganism growth (Ren et al., 2008). $NaHCO_3$ was used to regulate the pH value between 7.0 and 7.5.

2.1.2. Inoculated sludge

The inoculated granular sludge used as inoculum was obtained from Gu Liu joint station, where one of the treatment stations of HPAM-containing wastewater is located. The sludge was selected for its high activity. This inoculum contained dominant bacteria, and it adapted to the wastewater. The main characteristics of inoculated sludge were: 1–2 mm average particle size, 1.76 $mg \cdot L^{-1}$ total phosphorus (TP), 3.97 $mg \cdot L^{-1}$ total nitrogen (TN), 32.54 sludge volume index (SVI) and 14.89 $mg \cdot L^{-1}$ volatile suspended solid (VSS).

2.1.3. Functional bacteria

The three strains of bacteria for HPAM biodegradation were isolated from production water after polymer flooding. Partial sequencing revealed that the closest matches, determined by a BLAST search, corresponded to *Bacillus cereus* strain FM-4 EU794727 (95% similarity, PM-2), *Bacillus* sp. M7-23 EU706321 (95% similarity, PM-3) and *Rhodococcus* strain EF028124.1 (99% similarity, PAM-F1). The GenBank accession numbers of PM-2, PM-3 and PAM-F1 are JN713901, FJ598437 and KC476501.1, respectively (Bao et al., 2010; Sang et al., 2015).

2.1.4. Experimental set-up

Inoculated sludge was cultivated as anaerobic and aerobic activated sludge in an anaerobic baffle reactor (ABR) and a

Table 1
The ingredients of the wastewater.

Ingredients	Concentrations ($mg \cdot L^{-1}$)	Ingredients	Concentrations ($mg \cdot L^{-1}$)
HPAM	500	NaCl	10
$C_6H_{12}O_6$	80	$CoCl_2 \cdot 6H_2O$	5
NH_4Cl	1000	$MnCl_2 \cdot 4H_2O$	5
NaH_2PO_4	360	$AlCl_3$	2.5
K_2HPO_4	3000	$(NH_4)_6Mo_7O_{24}$	15
$NaHCO_3$	405	H_3BO_3	5
$CaCl_2$	50	$NiCl_2 \cdot 6H_2O$	5
$MgCl_2 \cdot 6H_2O$	100	$CuCl_2 \cdot 5H_2O$	5
$FeCl_2$	25	$ZnCl_2$	5