

Aerobic and anaerobic biodegradability of a flocculant polymer

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Abstract Flocculant polymers are used to improve the efficiency of separation processes used in wastewater treatment. The subsequent fate and effects of these additives are uncertain, however, with some previous reports indicating them to be biodegradable while others indicate complete recalcitrance. The biodegradability of a common flocculant polymer was therefore evaluated, using both aerobic and anaerobic batch assays. Knowledge of the polymer's chemical composition also allowed degradation stoichiometries to be calculated for complete biodegradation and also for incomplete degradation to several hypothesized end products. Results showed conclusively that the polymer was subject to partial degradation by both aerobic and anaerobic cultures. Measured oxygen consumption under aerobic conditions, and gas production under anaerobic conditions, both indicate that the partial destruction of pendant cationic moieties occurs, but that the polymer's CH₂ backbone remains essentially intact. These results allow seemingly contradictory previous reports to be explained. The findings are relevant to the environmental fate of these polymers as well as certain treatment process effects.

Keywords Biodegradation; flocculant; polyacrylamide; polymer

Introduction

Water-soluble, cationic polyelectrolytes are used extensively in wastewater treatment plants worldwide, primarily to improve the processes of thickening and dewatering. The use of these polymers is essential in attaining the solids concentrations now called for, given the limited options available for ultimate disposal. Given the large amounts utilized (over 5×10^7 kg/yr in the U.S. alone), attention should be directed at the possible treatment effects and environmental fate of these substances. If the polymers are aerobically degradable, for example, they will decompose when land-applied or when recirculated into secondary treatment in a supernatant, filtrate, or centrate. If anaerobically degradable, they will be transformed into lower molecular weight byproducts when wastewater solids (sludges or biosolids) are disposed of in landfills; otherwise, their long-term presence could serve to bind colloidal materials and thereby retard the degradation of other organics. Polymers usage prior to thickening processes may remain with the collected solids to be stabilized by anaerobic digestion, and possibly be degraded there. If the polymer is non-degradable, it could hinder the digestion of the thickened solids, analogous to a phenomenon that has been demonstrated when using inorganic coagulants for the enhancement of clarification processes (Gossett *et al.*, 1978; Dentel and Gossett, 1982).

Accordingly, and as part of a broader project investigating the overall fate and effects of flocculant polymers, this paper describes recent research to determine the aerobic and anaerobic biodegradability of a typical flocculant polymer.

Previous research

Flocculant polymers used to enhance settling, thickening, and dewatering processes in wastewater treatment are invariably cationic in charge and are derivatives of polyacrylamide. These products are difficult to synthesize, dispense, characterize, and quantify due primarily to their high molecular weight and tenacious adsorptivity. As a result, prior work

concerning polymer interactions with microbial processes paints an inconsistent picture.

Previous work regarding polymer effects in biological systems has provided seemingly contradictory results. Suzuki *et al.* (1978) observed that both polyacrylamide (PAM) and sodium polyacrylate (PAA) were only slightly biodegradable under aerobic conditions, based on size exclusion chromatography (SEC) and total organic carbon (TOC) measurements. They also reported only slight aerobic biodegradation of PAM at high concentrations, even after ozone degradation (decreasing the molecular weight from 280,000 to 840). This suggested that the resistance of PAM to biodegradation results from not only the high molecular weight but also the molecular structure of the polyacrylamide "backbone" linkage.

Mourato and Gehr (1983) found that a polyDADMAC (diallyldimethylammonium chloride) polymer was not degraded by a mixed aerobic culture, but a quaternized AM/AETAC copolymer showed some oxygen consumption. The amount of consumed oxygen reported appears to be less than would have been required for complete degradation but consistent with the amount required for partial degradation. However, the result was uncertain due to possible degradation of ethanol used in solubilizing the polymer. Neither polyDADMAC nor the quaternized AM/AETAC inhibited the degradation of glucose. A *Pseudomonas* species was claimed to degrade both polymers and several others as well, but it appears that nitrification could have been responsible for the observed oxygen consumption, and carbonaceous COD balances are not apparent.

A later report by Saponkanaporn and Gehr (1989) indicated that aerobic biodegradation of an AM/AETAC copolymer occurred as evidenced by size exclusion chromatography (SEC). The results suggested that bacteria are capable of utilizing this polymer as a carbon source, and converting it to CO₂. Although oxygen consumption was not measured in this research, TOC was completely removed by the end of experiment. Nevertheless, these results could be questioned since the disappearance of polymer (and TOC) from solution could have been due to the adsorption of polymer onto microbial surfaces in the inoculum. Controls without inoculum would not only lack microbial activity, but also the surface area due to microbial presence and growth.

Schumann and Kunst (1991) used anionic and cationic ¹⁴C-labeled polyacrylamides in bench-scale activated sludge units (10-L aeration volume, 5-L settling volume, 12-hr HRT) and, based on subsequent fate and location of the marked carbon, concluded that neither polymer was significantly degraded (less than 2%). Overall COD destruction of the synthetic feed substrate exceeded 95%, suggesting that the polymer was not toxic to the microbial population (although no control reactor appears to have been included in the experiments). Most cationic polymer was removed from solution by attachment to the solid phase (>80% with continuous dosing of polymer to the system, 98% with an impulse dose). Similar results were obtained in anaerobic assays using 500-mL batch digestions: neither polymer was anaerobically degraded to a significant extent. The cationic polymer was primarily (88.5%) associated with the solid phase, and only 2.2% of the ¹⁴C was in the gas phase. However, the manner in which the polymer was labeled in this study restricted degradation information to the main [-CH₂-] chain and immediately adjacent carbon atoms (Schumann, 1990).

Gula *et al.* (1994) investigated the effects of acrylamide-based polymers on sulfate reducing bacteria, which are strict anaerobes. It was concluded that polyacrylamide and partially hydrolyzed polyacrylamide (i.e. a copolymer of polyacrylamide and polyacrylic acid) stimulated this population's growth. Polyacrylic acid, however, was somewhat toxic and the cationic polymer strongly inhibited growth. These results are open to question because growth was inferred from an increase in the optical density of the microbial suspension, and polymer degradation from viscosimetric changes. These traits, however,

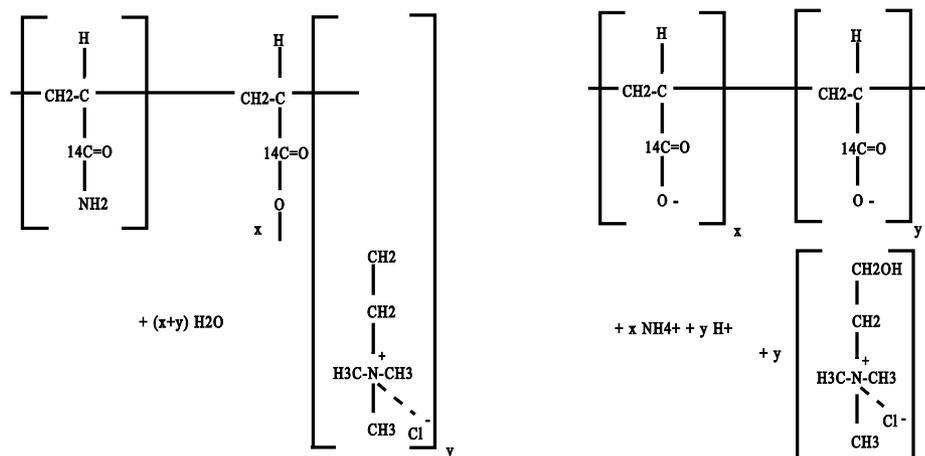


Figure 1 Hypothetical reaction showing complete hydrolysis of an AM/AETAC copolymer resulting in PAA, ammonium, and trimethylaminoethanol. Radioactively marked carbons, shown as ^{14}C , are not released from the polymer structure

may also be correlated with the degree of flocculation brought about by each polymer. It was also noted that a partially hydrolyzed polyacrylamide marked at the carboxylic carbon (immediately adjacent to the main $[-\text{CH}_2-]$ chain) exhibited negligible release of the marked carbon after anaerobic incubation. As in the study of Schumann and Kunst (1991), retention of this carbon shows recalcitrance of the polyacrylic backbone. As illustrated in Figure 1, deamination and ester hydrolysis could occur, as well as further degradation of the dimethylaminoethanol, without release of the marked ^{14}C . Lower molecular weight amines formed by this means may be more amenable to anaerobic degradation than they would be in an aerobic environment (c.f. Rothkopf and Bartha, 1984; Fitzsimons *et al.*, 1997).

Grula *et al.* (1994) also studied the biodegradation of PAM-based polymers by aerobic soil bacteria. Anionic, nonionic, and cationic varieties were included, although the specific structure of the cationic monomer was not indicated. The nonionic and anionic polymers were shown to provide the sole source of nitrogen for several species of *Pseudomonas* isolated from soil. The nitrogen was obtained by hydrolysis of the amide groups from the pendant acrylamide, apparently using an amidase enzyme similar to the type commonly found in pseudomonads. The backbone $[-\text{CH}_2-]$ chain was not believed to be degraded to any extent. These investigators reported that “the cationic polymer did not support growth of any strain, under any conditions tested. Indeed, it appeared to be highly toxic.”

Larson *et al.* (1997) studied the biodegradability of acrylic acid oligomers and polymers by mixed populations of activated sludge microorganisms. It was shown that monomers and dimers of acrylic acid could be completely degraded to carbon dioxide, and that oligomers of up to seven units could be partially degraded. Degradation of polymers of higher molecular weights (1,000-4,500) dropped off sharply. The degradation of polyacrylic acid is relevant to this study because ester hydrolysis and deamination of common wastewater solids flocculants (essentially, stripping of pendant groups from the polymer backbone) will leave polyacrylic acid as the residual polymer. Since the molecular weights of the flocculants are over 10^6 , the polyacrylic acid formed would not be biodegradable. Physical effects such as shear may lead to some polymer degradation over long time periods (Barvenik, 1994).

Kay-Shoemaker *et al.* (1998a,b) confirmed amidase induction and activity in the presence of PAM and its use as a sole source of nitrogen during microbial growth. However, the

carbon in the PAM was not available to the aerobic soil microorganisms. Since both acrylic acid and acrylamide monomers were observed both to be readily degradable and utilizable as sources of carbon, this demonstrated that PAM's $[-CH_2-]$ backbone was not degraded. Thus the deamination of a PAM polymer ultimately results in a PAA polymer of the same chain length. These researchers reported that mechanical shear or UV radiation can reduce the molecular weight of PAM, but not to the extent that allowed remaining fragments to be utilized as a carbon source. Their smaller, non-degradable PAM molecules were reported to have molecular weights of 3000–4000.

Research concerning acrylamide polymers in anaerobic environments is thus limited. However, as with aerobic systems, evidence suggests that hydrolysis and deamination of pendant structures are possible, but with the polyacrylamide backbone remaining intact. Toxicity again may hinge on whether the added polymer is exposed to inert surfaces onto which it can bind without impairing microbial activity. If the polymer binds with organic colloidal material of enzymes, indirect effects on the anaerobic process would accrue.

Procedures

Biochemical oxygen demand (BOD) was used in evaluating polymer biodegradability under aerobic conditions. The BOD procedure as described in *Standard Methods* (APHA, 1995) was used for initial biodegradation assays. Primary clarifier effluent was used as seed for samples of polymer solutions. All samples were run in triplicate at $20\text{ C} \pm 1\text{ C}$. Glucose-glutamic acid standards were run with each test as a check solution. Nitrification inhibitor was not used in these BOD tests, but subsequent respirometer studies confirmed that no nitrification occurred within the test period. Calculation of BOD values was performed according to *Standard Methods* (APHA, 1995). Statistical tests for analysis of variance and trends in sets of means were performed on all applicable BOD data (Crow *et al.*, 1960). Indicated confidence intervals are at the 95% level.

To simulate an anaerobic environment, a batch bioassay technique, known as the serum bottle test (Owen *et al.*, 1979), was performed. The seed used is from an anaerobic digester, the containers are maintained anaerobically at 35C, and gas production is measured over time. The polymer used was Percol (or Zetag) 787, a commonly used and representative cationic derivative of polyacrylamide. Supplied by Ciba Geigy (formerly Allied Colloids), it is a dry product copolymer of acrylamide and acryloyloxyethyltrimethylammonium chloride (AM/AETAC), at approximately 45/55 mole percent respectively ($x = 0.45$ and $y = 0.55$ in Figure 1).

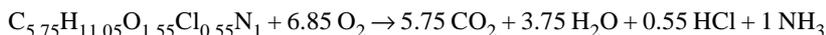
Serum bottles were prepared by combining the polymer as test substrate, plus an anaerobic seed culture (inoculum), and a defined media solution as described by Owen *et al.* (1979). The defined media contained necessary inorganic nutrients, pH and redox buffering components, and a redox indicator, resazurin, to visually indicate reduced conditions. After preparation, it was kept in a sealed flask to prevent introduction of oxygen. Prior to use, it was inoculated with 200 mL of biosolids from a full-scale anaerobic digester.

In order to determine the anaerobic biodegradability of the polymer itself, serum bottle tests were prepared with a polymer solution employed as the substrate. Serum bottles with only the inoculum and water samples were required for controls. Ingredients were added to serum bottles under anaerobic conditions. Subsamples were then withdrawn for COD and other analyses. The serum bottles were quickly flushed with the gas mixture, equilibrated in the shaker bath or incubator at 35C for one hour, then equilibrated with atmospheric pressure. A simple manometer assembly was used to measure gas production during incubation. At the conclusion of the test, the bottles were removed from the incubator or shaker bath for content analysis such as COD. Further details on the serum bottle and analytical procedures are also given in Raudenbush (1994) and Chang (1999).

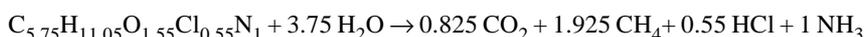
Theoretical stoichiometries for polymer degradation

Given the chemical formula for any substrate, the initial amount present, and the anticipated net reaction (or set of reactions) for its biodegradation, the amount of oxygen consumption can be determined for aerobic degradation, or the predicted amount of gas production can be determined for anaerobic degradation.

For the polymer used in these studies, the chemical formula for each monomer was used in determining a mole-fraction weighted overall composition. With 45% acrylamide, $\text{CH}_2\text{CHCONH}_2$, and 55% AETAC, $\text{CH}_2\text{CHCOO}(\text{CH}_2)_2\text{N}^+(\text{CH}_3)_3\text{Cl}^-$, the formula is $\text{C}_{5.75}\text{H}_{11.05}\text{O}_{1.55}\text{Cl}_{0.55}\text{N}_1$, giving an overall oxidation reaction of



and, for anaerobic degradation,



These two equations were then used to determine expected oxygen consumption and gas production for aerobic and anaerobic degradation, respectively.

Reactions were also formulated for possible degradation paths that did not result in destruction of the polymer $[-\text{CH}_2-]$ chain, and the corresponding stoichiometries calculated. These reactions assumed that degradation left a remaining organic portion consisting of polyacrylic acid (PAA); polyacrylamide/polyacrylic acid (PAM/PAA); polyacrylic acid and trimethylamine (PAA + TMA); PAM + TMA; polyacrylic acid and quaternary tetramethylammonium chloride (PAA + QTMA); PAM + QTMA; PAA/AETAC; or PAM/AETAC.

A final correction that can be determined is the effect of converting some of the carbon into new biomass. This requires an energy balance to find the maximum fraction of substrate usable for this purpose while providing sufficient energy. Details are given in Chang (1999). This correction is not included here since it does not significantly affect the final results or conclusions.

Calculated stoichiometric predictions of oxygen consumption and gas production are given in Table 1. These were then compared to experimental results.

Results

Aerobic degradability

Table 2 presents the BOD_5 values for the polymer solution samples tested. These values are not averages of replicates. All values were similar, even though tests were run on three different dates. The consistency of results suggests that the rate of oxygen consumption was relatively low at the experiments' termination, i.e. any biodegradation was completed.

From this data, the average BOD_5 for Percol 787 solution is 0.32 ± 0.01 mg/g. Table 1 shows that the value is consistent with partial polymer degradation, leaving trimethylamine and a non-fragmented backbone of either polyacrylamide or polyacrylic acid and ammonia. The initial hydrolysis step may occur abiotically given sufficient time or an alkaline pH

Table 1 Theoretical values of oxygen consumption and gas production for biodegradation of an Am/AETAC polymer (Percol 787) to varying extents

Measured parameter (mL/mg of polymer used)	Organic portion of polymer remaining				
	None	PAA or PAM/PAA	PAA+TMA or PAM+TMA	PAA+QTMA or PAM+QTMA	PAA/AETAC or PAM/AETAC
Aerobic oxygen consumption	1.58	0.89	0.32	0.13	0.00
Anaerobic gas production	0.93	0.45	0.18	0.09	0.00

Table 2 BOD₅ values of 0.05% polymer solutions

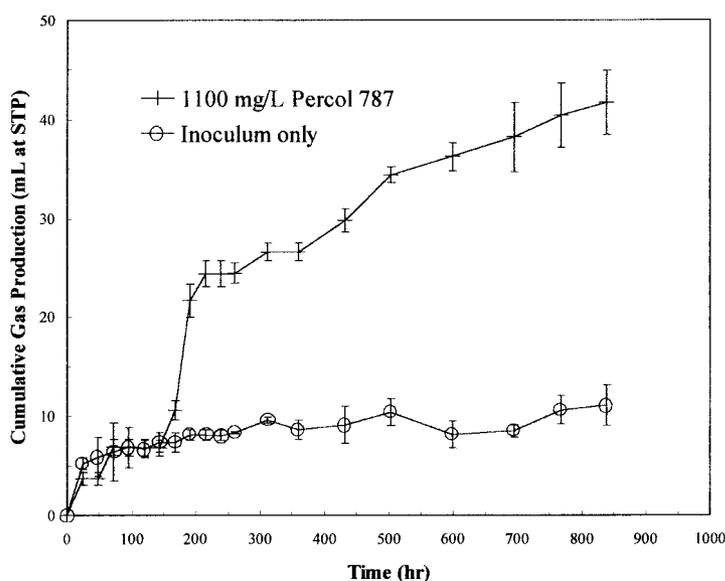
Test series	Concentration used (mg/L)	Polymer BOD ₅ (mg/mg)
I	10	0.336
	10	0.302
II	15	0.300
	20	0.314
III	10	0.314
	10	0.328
		0.326

(Aksberg and Wagberg, 1989), and this consumes no oxygen. The subsequent steps are oxidative (Figure 1), and unseeded samples showed no oxygen consumption. Tertiary amines such as TMA are reported to be resistant to aerobic biodegradation (Rothkopf and Bartha, 1984).

Anaerobic degradability

The serum bottle tests showed significant gas production. Figure 2 presents the results as cumulative gas production over time. Data were corrected to standard temperature and pressure.

The increase in gas production in samples with Percol 787 present was statistically significant (t-test, $P < 0.001$). The graph clearly shows that an acclimation period was required prior to degradation of the Percol polymer, with no significant difference from the inoculum samples (at $P = 0.05$) until 6 days into the incubation. At that point, a period of rapid gas generation is evident in Figure 2. When the experiment was terminated after 840 hours, net gas production due to the polymer was 29.8 ± 4.9 mL, or 0.34 ± 06 mL/mg polymer, and it is evident that some gas production was ongoing. Stoichiometric calculations predict gas production from complete polymer biodegradation to be 0.93 mL/mg, and 0.45 mL/mg if degradation of only the AETAC pendant group occurs (Table 1). The amount of gas produced rules out other hypothesized degradation reactions because the amount of gas exceeds the maximum amount possible.

**Figure 2** Cumulative gas production vs. time for 1100 mg/L Percol 787 solution

Discussion

These results show that the AM/AETAC polymer is partially degradable under both aerobic and anaerobic conditions. In both cases, it appears that the cationic pendant group is removed by ester hydrolysis, which leaves an acrylamide or acrylate monomer within the main polymer chain. The removed portion is completely degraded anaerobically, but not aerobically. In the latter case, the residual component appears to be trimethylamine. TMA has a characteristic “fishy” odor and, if released in significant amounts, may lead to some health concerns.

The partial degradation seen in these tests is consistent with previous reports suggesting the biodegradability of flocculant polymers. However, previous research has established the recalcitrance of the polyacrylic acid backbone resulting from this partial degradation. Prior investigations in which the backbone was radioactively marked thus showed no release of the marked carbon, leading to the mistaken conclusion that no biodegradation occurred.

The transformation of the cationic polymer to a nonionic or anionic one due to ester hydrolysis may have some interesting implications. The hydrolytic release of the pendant group may occur with many common flocculant polymers possessing an ester in the position immediately adjacent to the main alkyl chain. Others possess amide linkages which may be less susceptible. Loss of cationicity is likely to eliminate the flocculant capabilities of the polymer. If used to enhance mechanical thickening, a polymer may be degraded in subsequent digestion and increase the polymer demand for dewatering or impair the effectiveness of the polymer. The ammonia released during the partial degradation of the polymer may increase ammonia concentrations in centrates, filtrates or other flows.

Subsequent experiments have confirmed the findings reported here by additional analyses. However, further work is called for in order to determine if there are specific effects accruing from the byproducts of biodegradation that have been indicated in this research.

Conclusion

The pendant groups of the AM/AETAC polymer are hydrolyzed and partially degraded under both aerobic and anaerobic biotic conditions. The removed portion is completely degraded anaerobically, but not aerobically. The remaining acrylamide or acrylate polymer chain is not significantly degraded.

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