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Combining photolysis and bioprocesses for mineralization of high molecular weight polyacrylamides

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Abstract

The influence of ultraviolet photolysis as a pretreatment to the aerobic and anaerobic biological mineralization of a ^{14}C-polyacrylamide was assessed using a series of radiorespirometry bioassays. The polyacrylamide studied was non-ionic with molecular weights ranging between 100,000 and 1 million. Aerobic and anaerobic biomineralization of the unphotolysed (raw) polyacrylamide was found to be only 0.60% and 0.70%, respectively, after 6 weeks of incubation, and hence indicative of the natural recalcitrance of polyacrylamide to microbial degradation. The effectiveness of UV irradiation in the physical breakdown of the polyacrylamide chain into oligomers was demonstrated by the shift in the molecular weight distribution and the positive correlation between the time of irradiation and the degree of its biological mineralization. The molecular weight fraction below 3 kD, which represents only 2% of the raw polyacrylamide, was increased to 41, 60 and 80% after 12, 24 and 48 hours of photolysis, respectively. This in turn, yielded, after 6 weeks of incubation, an aerobic mineralization of 5, 17 and 29% of 150 mg/L polyacrylamide, respectively, and an anaerobic mineralization of 3, 5 and 17%, respectively. Biomass acclimation substantially improved the specific initial rate of biomineralization of the photolysed polyacrylamides, but not the overall percentage of polyacrylamides mineralized.

Abbreviations: COD – chemical oxygen demand, dpm – disintegration per minute, FID – flame ionization detector, kD – kilodalton, MW – molecular weight, PAM – polyacrylamide, rxr – reactor, TCD – thermal conductivity detector, UV – ultraviolet, VSS – volatile suspended solids

Introduction

Polyacrylamides (PAM) are high molecular weight (MW) synthetic polymers. They can be synthesized as cationic, anionic, non-ionic or amphoteric polymers. Linear PAM are water-soluble. PAM are widely used as flocculents in wastewater treatment, as flooding agents for petroleum recovery, as soil stabilizing agents and to strengthen paper (Seybold 1994). This widespread use of PAM has created certain concern over the possible harmful effects on humans and the environment. PAM have been reported to be non-toxic to the ecological system (Rothwell 1974). In contrast, the toxicity of the acrylamide monomer was a major concern. Acrylamide is reported to be a neurotoxin to humans (McCollister et al. 1964). The residual acrylamide (monomer) content of PAM may range from 0.05 to 5% (Croll et al. 1974). Nevertheless, acrylamide has been reported to be mineralized by microorganisms (Croll et al. 1974; Brown et al. 1980; Shanker et al. 1990), while PAM are quite resistant to biodegradation (Montgomery 1968; Grula & Huang 1981; Kay-Shoemake et al. 1998). PAM may therefore accumulate and persist in the environment. Kay-Shoemake et al. (1998) showed that PAM could be utilized as a nitrogen source via inducible amidase

activity and transformed in polyacrylates, but could not serve as a carbon source. Grula et al. (1994) also showed that PAM could serve as an electron source to sulfate reducing bacteria, but not as a carbon source. This recalcitrance was most probably related to both the high molecular weight and, in some cases, cross-linking, thus making them inaccessible to microbial attack. Therefore, it appears that the initial breakdown of PAM macromolecules is a prerequisite for microbial degradation. Thus far, biological breakdown of a ^{14}C-polyacrylate by white-rot fungus had yielded only 5% mineralization (Sutherland et al. 1997). The use of white-rot fungus was based on its ability to secrete lignin breakdown enzymes. PAM, however, have been reported to be easily broken down by physical-chemical factors (such as high temperature, light, hydrogen peroxide, salts and ions of transition metals, such as Fe^{3+} and Cu^{2+}) (Kheradmand et al. 1990; Tolstikh et al. 1992). The efficacy of photolysis depends on both the chemical structure and the strength of the chemical bonds of the PAM. Sensitivity to light has been observed for these polymers. For instance, Smith et al. (1996) observed that simple exposure to sunlight decreased the viscosity of PAM solutions. Yet, this may only be caused by some fractionation of the polymer, but not its degradation to acrylamide monomer (Ver Vers 1999). Nevertheless, it is expected that higher energy UV radiation (at wavelength well below 300 nm) would break PAM more effectively (McKellar & Allen 1979).

The overall objective of this study was to evaluate the degradability of PAM through a photolytic-biological process. UV photolysis of PAM was used as a pretreatment to aerobic and anaerobic biological processes. Breaking down PAM into fragments with lower MW through photolysis, may increase its bioavailability, and in turn improve its biodegradability. Radiolabelled PAM was used in the study for the biodegradation effectiveness to be appraised out of any doubt.

Material and methods

Chemicals

The polymer used in this study, a neutral synthetic PAM with MWs ranging between 100,000 and 1 million daltons, and the monomeric acrylamide were supplied by SNF Floerger S.A., Saint-Étienne, France. The radiolabelled acrylamide monomer [1-^{14}C] was supplied by American Radiolabeled Chemicals Inc., St. Louis, MO, USA. The radiolabelled PAM was synthesized using the radiolabelled monomer by SNF S.A. Specific activities of the acrylamide and the PAM were 119 and 0.165 μCi/mg, respectively.

Photolysis of polyacrylamide

To investigate photolysis (i.e., breakdown) by UV irradiation, a PAM solution (0.21% w/v) was transferred to quartz glass cells and exposed to UV irradiation in a photoreactor (RPR-100 Rayonet, Hamden, CT, USA). The photoreactor was fitted with a merry-go-round apparatus (Southern New England Co, Hamden, CT) equipped with sixteen 254-nm mercury arc lamps (25 watt each). Control experiments were carried out in tubes filled with the above solution and covered with aluminum foil. The temperature of the reactor was maintained at 40–42 °C by allowing a stream of air through the apparatus during irradiation. Light intensity at 254 nm ($2.4\ 10^{-6}$ einstein/mL.h) was measured using ferrioxalate actinometry (Hatchard and Parker 1956). Four different durations of photolysis (time of exposure to UV) were examined: 12, 24, 48 and 72 hours.

Molecular weight distribution

The MW size distribution of PAM was determined before and after each photolytic treatment. Size distribution was assessed by ultrafiltration with different molecular weight cut-offs (500 to 3 kD: Centricon® Amicon Canada Ltd., Oakville, Ontario; 1 kD: Microsep™ Pall Gelman, Ann Arbor, MI, USA). For this, 1-mL of a ^{14}C-PAM solution was added to each ultrafiltration tube and centrifuged according to the manufacturer's instructions (Beckman, model J2-21M, CA, USA). The filtrate of each tube was then analyzed for its radioactive content. The size distribution was obtained by dividing each filtrate radioactivity by the original radioactivity of the sample before ultrafiltration.

Sources of microorganisms

Aerobic biomass originated from the municipal wastewater treatment plant of the city of Ste-Catherine (Quebec, Canada). Anaerobic biomass originated from the anaerobic reactor treating the wastewater of Champlain Industries, Cornwall (Ontario, Canada), a food processing company.

Mineralization bioassays

The biological mineralization of PAM and its photolytic by-products was investigated using radiorespirometric bioassays. The bioassays were prepared as follows: a series of 120-mL serum bottles were filled with 20 mL of culture medium and 10 mL of either aerobic or anaerobic biomass (corresponding to a biomass concentration of 0.8 and 6 mg volatile suspended solids (VSS)/mL in the culture liquid, respectively). The culture medium contained (in mg/L): sucrose, 2000; K_2HPO_4, 2260; KH_2PO_4, 800; $NaHCO_3$, 3700; $KHCO_3$, 4400; $MgSO_4$, 200; $FeCl_2.4H_2O$, 4; H_3BO_3, 0.10; $ZnCl_2$, 0.10; $CuCl_2.2H_2O$, 0.08; $MnCl_2.4H_2O$, 1.0; $(NH_4)_6Mo_7O_{24}.4H_2O$, 1.0; $AlCl_3$, 0.06; $CoCl_2.6H_2O$, 0.30; $NiCl_2.6H_2O$, 0.2; $CaCl_2.2H_2O$, 30; Na_2WO_4, 0.15; $MgCl_2.6H_2O$, 20; Na_2SeO_3, 0.10; $Na_2C_{18}H_{14}O_8N_2$ (EDTA), 1.0; HCl, 10. pH was in the neutral range. The initial concentration of PAM was 150 mg/L in the culture liquid, for an initial radioactivity of 10^5 disintegrations per minute (dpm). The aerobic microcosms were flushed with pure oxygen to create an aerobic environment, while nitrogen gas was used to purge the headspace of the anaerobic microcosms in order to maintain anaerobic conditions. Serum bottles were incubated at 20 ± 2 °C with shaking at 150 rpm (G24 Shaker, New Brunswick Scientific, Edison, NJ, USA). The microcosms were sampled regularly with subsequent flushing using pure oxygen such as aerobic conditions were maintained, or nitrogen gas to keep anaerobic conditions. Mineralization of PAM was measured by counting the radioactivity of $^{14}CO_2$ produced and trapped in 1 mL KOH (0.1 N) using a Liquid Scintillation Analyzer (Packard Tri-Carb model 2100 TR, Downers, IL, USA).

$^{14}CH_4$ was analyzed with a gas chromatograph (GC, SRI, Model SRI8610C, Torrance, CA, USA) with a thermal conductivity detector (TCD) in tandem with a radioactivity detector (GC-RAM, INUS Systems, Pine Brook, NJ, USA), and a flame ionization detector (FID) in parallel. The SRI 8610C GC had the following configuration: the TCD was set at 100 °C and the FID was set at 150 °C, and the oven was set at 60 °C. Each detector was connected to a separate column (2-m stainless steel 1/8-inch outer diameter packed with Porapak Q packing) (Supelco, Bellafonte, PA, USA). Helium was used as carrier gas with flow rates of 23 mL/min for the TCD-GC-RAM and of 20 mL/min for the FID. The detection limit for CH_4 is 20 ppmv using the FID and 800 ppmv using the TCD. The GC-RAM detector was connected in tandem to the TCD with a heated transfer line. $^{14}CH_4$ samples passed through a CuO column heated at 750 °C for the conversion to $^{14}CO_2$ before reaching the ionization chamber for the detection of radioactive counts. Signals of $^{14}CO_2$ gas were acquired and integrated by the Peak Simple II software (SRI, Torrance, CA, USA). For gas analysis, 0.5 mL of the gas samples were injected onto the GC system with simultaneous integration of peaks using the PeakSimpleII software (SRI). The instrument was calibrated with $^{14}CO_2$ which was prepared by acidifying ^{14}C-$NaHCO_3$ (American Radiolabeled Chemicals Inc., St. Louis, MO, USA) with HCl. The amount of radioactivity in this ^{14}C-$NaHCO_3$ was separately determined on a scintillation counter (Packard Tri-Carb model 2100 TR, Downers, IL, USA).

Acclimation of aerobic biomass in continuously-fed reactor

The aerobic bioreactor used for biomass acclimation to PAM, consisted of a glass column (60-cm height, 6-cm inner diameter) with a working volume of 1.55 L, including an integrated decanter, accounting for 20% of the liquid volume. The reactor was inoculated with municipal activated sludge (5.4 g VSS/L). Air was bubbled at the base of the column (85 and 130 L air/L_{rxr}.d) to provide aeration and mixing. The system was operated at 22–25 °C with a constant influent flow rate (ca. 265–280 mL/L_{rxr}.d, i.e., a hydraulic residence time of 3.7 days). The influent solution contained (mg/L): photolysed PAM (photolysis time given on Table 1), 100; sucrose, 1400; KH_2PO_4, 800; K_2HPO_4, 2300; $NaHCO_3$, 3700; $KHCO_3$, 4400; $MgSO_4.7H_2O$, 200; $FeSO_4.7H_2O$, 3.25; $ZnSO_4.7H_2O$, 0.2; $MgSO_4.7H_2O$, 5; $NiSO_4.7H_2O$, 0.12; EDTA, 0.75; $CuSO_4$, 0.08; $MnSO_4.H_2O$, 0.65; H_3BO_3, 0.06; $(NH_4)_6Mo_7O_{24}.4H_2O$, 0.2; $AlK(SO_4).12H_2O$, 0.03; $Co(NO_3)_2.6H_2O$, 0.25; Na_2SeO_4, 0.02. The solution was essentially devoid of nitrogen as PAM was meant to be the N-source. The organic loading rate was kept at 0.4 ± 0.05 g chemical oxygen demand (COD)/L_{rxr}.d, for the duration of the experiment. The biomass content of the reactor remained fairly constant (around 3.1 ± 0.2 g VSS/L_{rxr}), independent of the operating conditions. The pH fluctuated between 7.5 and 8.0.

Table 1. Impact of the biomass acclimation in a continuous aerobic bioreactor, to the rate and the extent of mineralization of polyacrylamides photolysed 24 h

In-reactor phase	Period (d)	Initial specific rate of PAM biomineralization* (mg/gVSS.d)	Normalized mineralization (after 7 weeks) (%)
I (fed PAM photolysed 72 h)	21–120	21	11 (0.5)**
II (fed PAM photolysed 48 h)	121–239	25	10 (0.5)
III (fed PAM photolysed 24 h)	240–331	31	14 (2)
Unacclimated biomass		2	17 (2)

*Estimated by linear regression on the two first weeks data (standard deviation of the first 2-weeks of data, on the order of 10%).
**Values in parentheses represent standard deviation of triplicate analysis.

Results

Molecular weight distribution

Comparison of the MW distribution of the photolysed PAM to that of the raw (unphotolysed) macromolecule, as shown in Figure 1, clearly indicated the effectiveness of UV irradiation in the physical breakdown of the PAM macromolecule and a positive correlation between the time of irradiation and the degree of degradation. With photolysis, there is an obvious shift in the MW distribution. The highest percentage of the raw PAM (average percentage ± standard deviation, 72 ± 7%) was found in the 100–500 kD fraction. After photolysis, the MW distribution shifted to lower size fractions. For instance, the 3 kD fraction, which represented only 2 ± 0.5% of the raw PAM, accounted for 41 ± 6, 60 ± 8, 80 ± 6 and 92 ± 4% after 12, 24, 48 and 72 hours of photolysis, respectively. In the latter photolysis assay, the MW distribution was extended down to a cut-off of 1 kD. After 72 hours of photolysis, the MW distribution contained 79 ± 4% fragments less than 1 kD and 13 ± 4% fragments between 1 and 3 kD (data not shown).

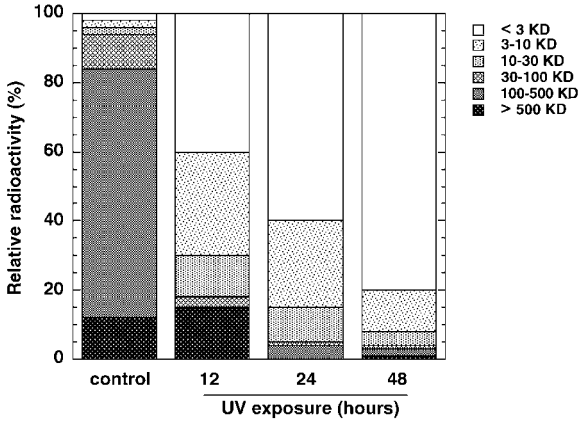

Figure 1. Molecular weight distribution of the polyacrylamide after 12, 24, and 48 hours of UV exposure.

Influence of photolysis on mineralization of the polyacrylamide

The results of the influence of photolysis on the aerobic and anaerobic mineralization of PAM are presented in Figures 2 and 3, respectively. Aerobic and anaerobic mineralization of the unphotolysed PAM was found to be only 0.60% and 0.70%, respectively. This indicates the recalcitrance of PAM to microbial degradation, as expected. UV photolysis of PAM increased biological mineralization under both aerobic and anaerobic conditions. A positive correlation was observed between the time of photolysis (i.e., 12, 24 and 48 hours), and the percentage of PAM mineralized. However, the kinetics of aerobic mineralization were faster than the kinetics of anaerobic mineralization. After 6 weeks of incubation, the 12-, 24- and 48-hour photolysis periods yielded an aerobic mineralization of 5 ± 0.05, 17 ± 2 and 29 ± 2%, respectively, compared to 3 ± 0.2, 5 ± 0.3 and 17 ± 2% mineralization obtained under anaerobic conditions, respectively.

Increase of the aerobic biodegradation rate by acclimation of biomass

To acclimate the biomass to PAM, the aerobic bioreactor was fed for 310 days with photolysed PAM. The acclimation period consisted of three phases, differentiated by the duration of photolysis (Table 1). The PAM loading rate was constant for the duration of the experiment: 25 ± 5 mg/L_{rxr}.d. At the end

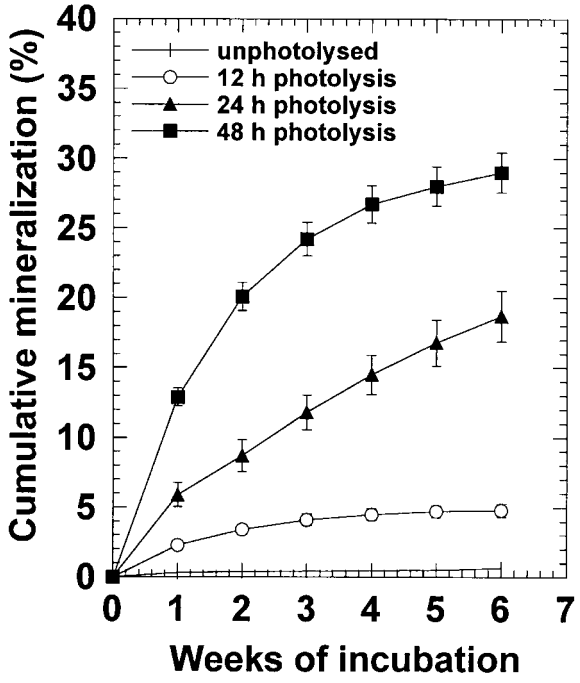

Figure 2. Influence of photolysis on the aerobic mineralization of polyacrylamide (% of poly-^{14}C-1-acrylamide initial radioactivity recovered as $^{14}CO_2$).

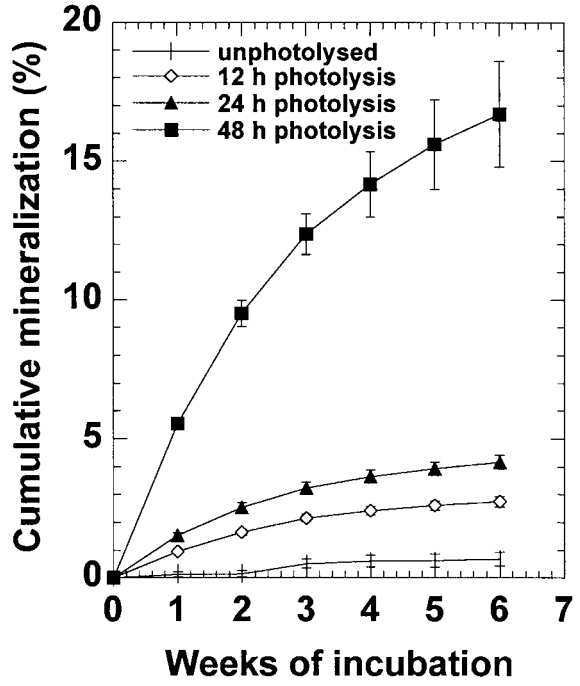

Figure 3. Influence of photolysis on the anaerobic mineralization of polyacrylamide (% of poly-^{14}C-1-acrylamide initial radioactivity recovered as $^{14}CO_2$).

of each phase, a biomass specimen was withdrawn from the reactor and tested for its capacity to mineralize the photolysed PAM, in microcosms spiked with ^{14}C-labeled PAM. All tests were performed with the same PAM photolysed for 24 h, for the sake of comparison. The results are presented in Table 1. Initial specific rate were calculated using the radioactivity data from the first two weeks, and converted in PAM-equivalents. Biomass became acclimated to acrylamide oligomers, since the specific rates of biomineralization increased by one order of magnitude as compared to that of unacclimated biomass. However the biodegradability level did not change much, remaining between 10 and 16%, which is comparable to values obtained previously with unacclimated biomass.

Discussion

Only a small fraction of the raw (unphotolysed) PAM was microbially-mineralized after a 38-day incubation, under both aerobic conditions (0.60%) and anaerobic conditions (0.70%). This is probably due to the presence of residual acrylamide because complete polymerization is never attained. The acrylamide content was no more than 0.05% by weight (data from the manufacturer). Additionally, the fraction of oligomers below 3 kD, some of which may be biodegradable, accounted for 2% of the raw PAM. The recalcitrance of acrylamide polymers to microbial degradation was expected based on the literature (Montgomery 1968; Ress et al. 1998; Kay-Shoemake et al. 1998). Similarly, anaerobic treatment of ^{14}C-polyacrylate yielded, after an incubation period of 6 months, mineralization of only 2.5% (Ress et al. 1998). The mechanism of recalcitrance is linked to the high MW of these polymers, thus making them inaccessible to microbial attack (Alexander 1994). Our research has shown that combining photolysis by UV irradiation with aerobic or anaerobic biotreatment resulted in improved mineralization of PAM over the unphotolysed PAM. This mineralization was attributed to the effectiveness of UV light in breaking down (photolysis) the acrylamide polymer into oligomers, which were more accessible to bacterial attack, as was assessed by the MW distributions. The mechanism of break down (i.e., photolysis) is probably due to the oxidation of PAM by the hydroxyl radicals ($OH^{\cdot}$), formed by UV irradiation of water. $OH^{\cdot}$ radicals are extremely reactive and frequently used in advanced oxidation processes

to destroy many undesirable chemicals in the environment. Furthermore, a positive correlation was observed between the length of photolysis (i.e., 12, 24 and 48 hours), the degree of the breakdown and thus the percentage of the mineralized PAM.

It is virtually impossible for acrylamide to be generated from UV photolysis of PAM. Theoretically, monomers such as propionamide or propionic acid may form (Wallace & Wallace 1995). Consequently, photolysis products that were mineralized by the aerobic or anaerobic cells were likely composed of more than one monomer. However, the mineralization percentages obtained were notably lower than the MW fraction below 3 kD. This suggests that oligomers which are susceptible to microbial degradation are less than 3 kD. This agrees with the observation of Kay-Shoemake et al. (1998), who found that PAM above 3000 kD could not be assimilated by microorganisms. For comparison, the literature has reported only mineralization of di- and trimer acrylates (Kawai 1993, 1995). That the molecular size is the limit to the microbial activity, is suggested by the mineralization results by acclimated biomass. Although biomass acclimation (probably by enrichment in bacteria able to degrade the acrylamide oligomers) resulted in an increased specific rate of mineralization of identically UV-irradiated PAM, the biomineralized fraction remained unchanged.

The aerobic processing of the photolysed PAM resulted in a higher mineralization of 29%, measured as $^{14}CO_2$, as compared to the $^{14}CO_2$ recovery of 17% under anaerobic conditions. This might be partially explained by the production of other carbon-containing end-products by the anaerobic degradation of PAM oligomers as compared to the aerobic degradation. $^{14}CH_4$ was analyzed in a few radiorespirometric assays with the 72 hour-photolysed PAM. Results (not shown) indicated a conversion of 8 to 10% of radioactivity as $^{14}CH_4$.

However biodegradation was incomplete in all conditions tested, as the size reduction efficacy of UV was limited, although the irradiation time applied was relatively long. UV are only 4% of the solar irradiation. The sunlight wavenlengths practically are above 300 nm and much less energetic than that used in this study. Thus, attenuation of PAM in natural environments by sunlight and indigenous microorganisms still has to be confirmed.

Conclusions

This investigation demonstrated that the combination of UV irradiation followed by aerobic or anaerobic treatment resulted in increased PAM biomineralization, as compared to biomineralization without photolysis. Using radiolabelled compounds, this is the first time that PAM mineralization was convincingly demonstrated, in contrast to the use of other methods that rely solely on polymer depletion or biomass activity. UV light effectively decreased the MW distribution of the PAM, and it is hypothesized that this made the oligomers more susceptible to bacterial attack. In fact as the time of photolysis increased, the MW size distribution shifted to lower size fractions, and a greater percentage of PAM was mineralized.

The key to efficient treatment of complex and large compounds is often the use of a combination of different processes, either physical or biological. UV treatment alone could not achieve complete destruction, ending up with oligomers, but it did increase carbon mineralization in a subsequent biological treatment. However biodegradation was incomplete, as the size reduction efficacy of UV was limited.

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