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Biodegradation and sorption properties of polydisperse acrylate polymers

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Abstract

Polyacrylate (PA), which is widely used in disposable diapers, is synthesized by polymerization and cross-linking of acrylate. During the synthesis, 3–6% of the polyacrylate polymers is not incorporated into the absorbent material, but remains soluble. If the soluble PA is mobilized from a landfill, it could enter the groundwater. Therefore, the biodegradation and adsorption properties of soluble polymers contained in PA are determined in this study. The soluble PA is highly polydisperse, and the fraction tested has a weight-average molecular-weight of 16,700 and a range extending from 10^3 to 10^5. Sand-column tracer tests show that about 1% of the polyacrylate is unadsorbed, but the remainder has a retardation factor that averages at least 58. Biodegradation kinetics are determined in completely mixed biofilm reactors having a methanogenic consortium grown on glucose. The polyacrylate fraction, as well as glucose and acrylate, are removed and mineralized to CO_2. The Monod parameters for the polyacrylate are: maximum specific rate of substrate utilization = 0.0016 gC/g biomass-day, and half-maximum-rate concentration = 0.79 gC/m^3. Although these kinetics are much slower than for glucose and acrylate, significant degradation and mineralization are observed.

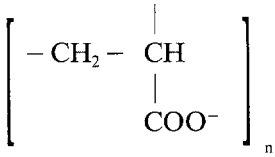
Introduction

Biodegradation of synthetic polymers comprised of biodegradable monomers usually is enhanced by high water solubility of the polymer and the presence of extracellular enzymes able to cleave the polymers to membrane-permeable subunits. When water-soluble polymers are present in soils or aquifers, a third factor affects degradation: the sorption of the polymer to solids. Although sorption slows the advective transport of the polymer and gives a greater contact time, it also reduces the liquid-phase concentration, which may slow biodegradation kinetics.

An important example of the interactions of biodegradation and sorption is found in the polymers of acrylate ($CH_2 = CHCOO^-$, molecular weight = 71 g/mole), which are used as super-absorbent materials in diapers, surgical pads, and feminine hygiene products. Over 136 metric tons of polyacrylate polymers are used annually (Martin et al. 1987). Since disposable diapers alone constitute about 2% of the solid waste stream in the United States (Lehrburger 1988), the fate of these acrylate

polymers is of importance, especially in landfills and the groundwater beneath landfills.

Polyacrylates are formed by addition polymerization of acrylate monomers. The double bonds of the acrylate are broken, and single bonds connect the subunits with the following repeating structure



in which n is the number of monomeric subunits. Acrylic acid is a weak acid, having a pK_a of 4.25 (Merck 1989). The electron-donating nature of the polymeric carbon backbone makes the carboxylic groups less acidic, and the pK_a values are 1 to 2 units higher than for acrylic acid (Miller 1968). When dissolved in fresh water near neutral pH, polyacrylates are partially ionized, which causes the polymer chains to uncoil and behave as semi-linear chains.

The polyacrylates used in diapers, termed PA, are composed of long, lightly cross-linked polymers that can swell to enormous volumes as they absorb liquids. However, during the manufacture of PA, 3 to 6% of the polyacrylate is not incorporated into the cross-linked polymers. These unincorporated polymers are called the mobile fraction, because they are water soluble, which makes them susceptible to transport and to biodegradation. The mobile fraction of PA also is characterized as being polydisperse, which means that the soluble polymers have a large range of molecular weights. Whereas some of the mobile fraction can be as small as dimers and trimers, the molecular weight can be as high as 10^7 g/mole, or n approximately equal to 140,000.

Although our literature review identified that many polymers undergo biodegradation via initial hydrolytic, oxidative, or reductive cleavage (e.g., Gottschalk 1986; Zaikov and Livshits 1987; Morita and Watanabe 1977; Kawai et al. 1977), we found no information on PA. Therefore, the purpose of our research project was to determine the biodegradability of the mobile fraction of PA and how its sorption and polydispersed nature affect the biodegradation. This paper reports on studies that characterize the sorption of a PA mobile fraction to aquifer sand and its anaerobic biodegradation kinetics. A companion paper (Rittmann et al. 1992) investigates how degradation and sorption interact during transport through an anaerobic sand medium.

Materials and methods

Polyacrylate

The Procter & Gamble Co. provided four fractions of soluble polyacrylate with and without ^{14}C-label. Fractions had been prepared by fractional precipitation of PA passing a Whatman 40 filter paper (98% retention at 8 μm). Successive addition of 0.4 N NaBr and methanol to the filtrate yielded three precipitates and a final liquid that was reduced to a dry solid by evaporation.

Procter & Gamble also provided molecular weight distributions obtained using size-exclusion chromatography. Figure 1 presents the molecular weight distributions for the three labelled fractions obtained as precipitates, as well as for the whole sample before fractional precipitation. Table 1 summarizes the distributions, which demonstrate the polydisperse nature of the soluble PA. Although the weight-averaged molecular weights decreased with successive fractional precipitations, each precipitate contained polymers covering 1.5 to 2.5 orders of magnitude in molecular weight. In general, the spread in molecular weights decreased as the average molecular weight decreased through successive precipitations.

We performed the detailed experimentation on the fraction having an average molecular weight of 16,700. It exhibited the polydispersed nature of soluble PA, but had relatively little of the very high molecular weight polymers that adsorbed very strongly to the laboratory equipment, creating difficulties in obtaining mass balances.

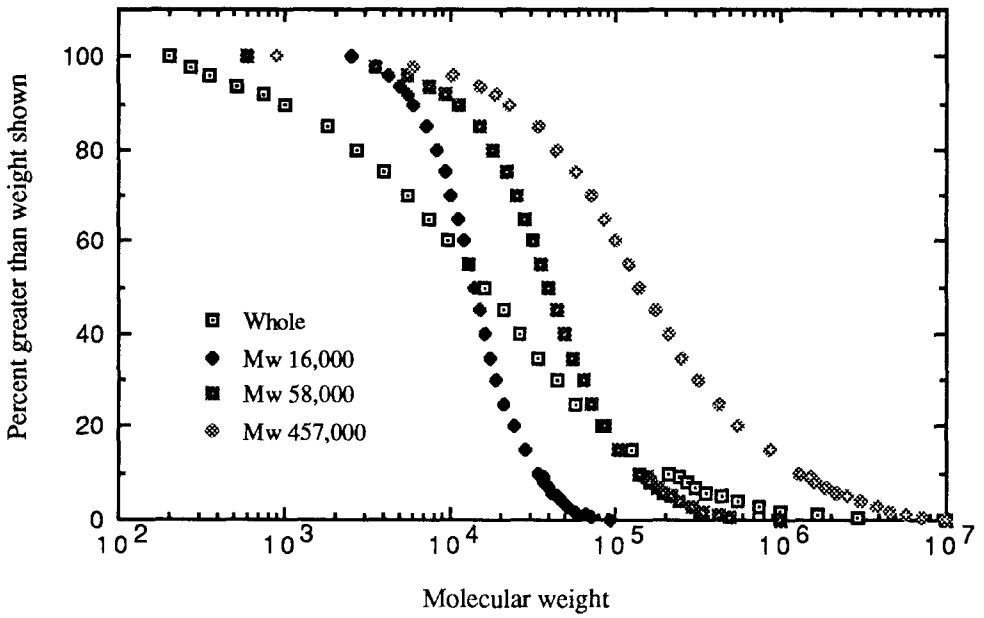


Fig. 1 Molecular weight distributions of the ^{14}C-labelled polyacrylates. The distributions were provided by the Proctor & Gamble Company.

Other substrates

Reagent-grade glucose and acrylate also were used as substrates and/or tracers. Both were obtained with and without ^{14}C-label.

Adsorption experiments

Adsorption characteristics of fraction M_w 16,700 were obtained in a once-through column system. The column was made of glass, had an inside diameter of 2.5 cm, and had a working length of 3 cm between the stainless-steel screens (72.5 μm nominal opening size). The end caps were made of TFE teflon and were machined to be conical on the inside. All tubing was 1/16-inch TFE teflon. The injection port for the tracer was constructed by sealing the side port of a TFE teflon T fitting with a rubber septum. Feeding was from a reservoir and through a constant-head regulator, both made of glass.

The medium was Borden sand taken from the Canadian Forces Base at Borden, Ontario (Curtis et al. 1984). A subsample of the original sand was obtained by sieving between U.S. mesh sizes 60 and 140, which gave a grain-size range of 0.106 to 0.250 mm. Grain size analysis of the subsample (by

Table 1. Summary of molecular weight distributions for the ^{14}C-labelled polyacrylate fractions.

Weight-averaged molecular weight, M_w	90% > molecular weight	10% > molecular weight	Ratios	
			10% >/M_w	10% >/90% >
457,000	255,000	1,300,000	2.84	5.10
58,200	11,000	142.000	2.44	12.9
16,700	6,000	34,000	2.04	5.67
<200	nd	nd	nd	nd

nd – not determinable.

sieving) gave a median size of 0.152 mm and a uniformity coefficient of 1.06. The specific surface area was 0.8 m^2/g (Curtis et al., 1984). The particle density was determined to be 2.59 g/cm^3 by water displacement. The bulk density for the sand as packed into the column was 1.60 g/cm^3, giving a porosity of 0.36. The percent organic carbon, determined by the Walkley-Black method (American Society of Agronomy and Soil Science Society of America, 1965) was 0.16%, a very low value typical of a clean, well-sorted sand (Hassett et al. 1980).

In order to preclude any biological activity during adsorption experiments, two precautions were taken. First, all components of the experimental system, including the water and sand, were autoclaved prior to each test. Second, all tests were performed in a constant-temperature room held at 5 ± 1 °C.

Extreme care was taken to achieve uniform, air-bubble-free conditions in the system. The packing procedure began by bringing all materials to 5 °C. Then, all the components on the influent side of the system were assembled. The column was filled with synthetic groundwater (described below) until it was 1/2 full. Care was taken to ensure that no air bubbles were trapped under the bottom screen. Sterilized sand and groundwater were mixed in a beaker and stirred to eliminate all air bubbles. A 10-ml automatic pipet was used to transfer the sand slurry to the column, where it was distributed evenly over the bottom of the column. The excess water was slowly drained out the bottom, and the sides were gently tapped to uniformly settle and pack the sand. This procedure was repeated until the column was full. Then, the top end cap was inserted in such a manner that no air bubbles were trapped on the screen. The effluent tubing was connected, and water flow (upflow) was initiated. The height of the constant-head regulator was adjusted to give a steady flow of 2 ml/min.

A synthetic groundwater was used as the solvent for the abiotic studies. Its composition was (in mg/l): $CaCl_2$, 110; $CaSO_4$, 272; KNO_3, 34; $NaHCO_3$, 336; $MgCl_2$, 38 and $FeCl_3$, 6.6. The composition was chosen to represent a typical midwestern U.S.A. groundwater having an alkalinity of 200 mg/l as $CaCO_3$ and a hardness of 340 mg/l as $CaCO_3$.

The tracer studies used acrylate or fraction M_w 16,700. With a constant flow rate of 2 ml/min, the pore water velocity was 0.019 cm/sec, giving a 2.6-min liquid detention time in the sand bed. The total liquid detention time in the sand, end caps, and tubing between the injection and sampling ports was 3.5 min. A small volume of ^{14}C-labelled tracer was injected instantaneously into the steady flow. Effluent samples were collected in scintillation vials at time intervals of 0.25–10 minutes. Effluent tracer concentrations were assayed for radioactivity.

After tracer tests were performed with fraction M_w 16,700, the sand was drained and extruded from the column using a special circular tool that fit snugly in the column. As the sand was pushed from the column, 0.75-cm slices (i.e., 1/4th of the total length) were cut off and collected. The sand was extracted sequentially three times with 20 ml of Scintiverse E scintillation cocktail (70% xylene and 30% Triton X, by volume), and the cocktail was analyzed for radioactivity.

The experimental retention time, θ_e, was computed by the residence-time distribution method of Levenspiel (1972) for tracer exiting the column during the experiment. For k discreet measurements,

$$\theta_e = \frac{\sum_{i=1}^{k} \theta_i C_i \Delta\theta_i}{\sum_{i=1}^{k} C_i \Delta\theta_i} \quad (1)$$

in which C_i = tracer concentration for measurement i, θ_i = average retention time of measurement i, and $\Delta\theta_i$ = time between measurements (i - 1) and i. The retardation factor was computed for the exiting tracer (R_e) from

$$R_e = \theta_e/\theta_t \quad (2)$$

in which θ_t = theoretical liquid retention time, 3.5 minutes.

Because much of the tracer did not exit the column when fraction M_w 16,700 was tested, a retar-

dation factor for the adsorbed tracer (R_a) was computed by comparing the fractional distance (f_d) the centroid of sorbed tracer traveled within the column to the number of pore volumes that had passed through the column (P_v)

$$R_a = \frac{P_v}{f_d} \tag{3}$$

The fractional distance was computed from

$$f_d = \frac{\sum_{j=1}^{4} (PE)_j d_j}{100\, L_c} \tag{4}$$

in which PE_j = percent of the total extracted tracer found in segment j, d_j = the distance from the inlet to the center of segment j, and L_c = length of the column = 3 cm.

The percent of total tracer exiting the column (M_e) was determined by calculating the area under the C_t versus θ_t curve,

$$M_e \sum_{i=1}^{k} \left\{ \frac{(C_i + C_{ti})}{2} \Delta\, \theta \right\} Q \frac{100}{M_T} \tag{5}$$

in which M_T = total tracer mass injected (in dpm) and Q = the flow rate (in ml/min).

Biodegradation kinetics

The kinetics for the anaerobic biodegradation of glucose, acrylate, and fraction M_w 16,700 were determined in an anaerobic, completely mixed biofilm reactor, which is an anaerobic modification of the set-up used for kinetic characterization by Rittmann et al. (1986). The reactor was constructed of tubular glass with an inside diameter of 2.5 cm and length of 3 cm. Glass beads, 3-mm in diameter, were used as the attachment medium. Air-tight end caps precluded air entry, and teflon screens supported the glass beads. The three sample ports accepted Luer tip syringes. The reactor was covered with aluminum foil to exclude light. The temperature for the biodegradation experiments was 21 ± 2 °C.

Peristaltic pumps fed the system at a rate of approximately 1 ml/min and recycled the effluent at approximately 72 ml/min. The high recycle ratio provided a nearly completely mixed flow regime and uniform biofilm distribution. The flow direction was alternated weekly to make the biofilm distribution more uniform. Tubing was chosen to resist O_2 permeation. Tygon, Teflon, and Viton tubing were adequate and used in different places, as appropriate.

Table 2 describes the feed solution, which provided necessary nutrients for the growth of a methanogenic consortium. Glucose, at a feed concentration of 10 mg/l, served as the primary substrate for the consortium of fermenting and methanogenic microorganisms. Buffering to keep the pH at 7.0 was provided by $NaHCO_3$, KH_2PO_4, and K_2HPO_4. Sodium sulfide was added in excess to reduce the feed solution and scavenge any oxygen entering the feed system. Every four days, medium was prepared according to carefully controlled procedures. Clean, 8-l aspirator bottles were filled with distilled water and the proper amounts of the first ten ingredients in Table 2. The filled bottle and a gas-dispersion apparatus were autoclaved. Glucose and the vitamins were added to the hot solution. N_2 gas was bubbled through the hot solution for 2 hours to strip O_2. Then the sulfide was added, and the resazurin turned clear. The solution was sealed and cooled overnight before being connected to the reactor system by sterilized tubing.

The reactor was inoculated with an inoculum from another anaerobic biofilm reactor in the laboratory. Only the recycle flow was applied for 24 hours. Then, feed flow was initiated. Periodically, glucose removal and conversion to CO_2 (described below) were measured. After almost 5 months of continuous operation, the effluent soluble ^{14}C stabilized at about 10% of the influent soluble ^{14}C. This signified that the system had approached steady state and could be used for kinetic experiments.

Kinetic data were collected in special short-term experiments (Rittmann et al. 1986) that gave a range of substrate concentrations and corresponding fluxes. In order to minimize problems of adsorption of polyacrylates to the tubing, the effluent

recycle line was disconnected, and the system was run as a once-through reactor having a flow rate of 1 ml/min. Samples were taken from the feed reservoir and from sampling ports located at the inlet and outlet of the column. These samples were analyzed for ^{14}C (described below). During the tests, known amounts of the unlabelled substrate were added to give the desired concentration, and sufficient amounts of the ^{14}C-labelled substrate was added to give adequate quantification. Influent concentrations were varied over a wide range (2 to 3.5 orders of magnitude) to give the required full response of substrate flux versus reactor concentration (Rittmann et al. 1986).

The kinetic parameters were estimated by the curve-matching method of Rittmann et al. (1986). That technique requires several sets of experimental values for the substrate flux (J_{exp}) and the substrate concentration at the biofilm/liquid interface (S_s). These were computed from the following equations, derived by Rittmann et al. (1986):

$$J_{exp} = \frac{(S_0 - S)\,Q}{Va} \tag{6}$$

$$S_s = \bar{S} - \frac{L\,J_{exp}}{D} \tag{7}$$

$$\bar{S} = \frac{S_0 - S}{ln\,(S_0/S)} \tag{8}$$

$$L = \frac{DR_e^{0.75}\left(\frac{\mu}{\varrho D}\right)^{0\,67}}{5.7\,v} \tag{9}$$

$$Re = \frac{2\varrho d_p v}{(1 - \varepsilon)\mu} \tag{10}$$

in which

- V = void volume of the reactor
- a = specific surface area of the reactor
- Re = Reynolds number
- μ = absolute viscosity of the feed solution
- ϱ = density of the feed solution
- d_p = diameter of the glass beads
- v = superficial flow velocity
- ε = porosity of the reactor
- S_0 = influent substrate concentration
- S = effluent substrate concentration
- $\bar{S}$ = log-mean substrate concentration
- L = thickness of effective diffusion layer for mass transport resistance to the biofilm surface
- D = molecular diffusion coefficient for the substrate
- Q = volumetric flow rate

Ordered pairs of log (J_{exp}) and log (S_s) were plotted and matched with the family of curves giving the solution to the biofilm rate equations (Rittmann et al. 1986).

Sampling and analytical methods

All samples for radioactivity analysis were collected in syringes that were specially prepared to prevent adsorption of labelled AGM materials. To remove any residual ^{14}C, syringes and filter holders were scrupulously cleaned with soap and water,

Table 2. Composition of the anaerobic feed solution.

Component	Concentration, mg/l
NH_4Cl	58.2
KH_2PO_4	85.5
K_2HPO_4	64.8
$CaCl_2 \cdot 2H_2O$	2.0
$MnCl_2 \cdot 4H_2O$	0.2
$FeCl_2 \cdot 4H_2O$	6.2×10^{-3}
$NaHCO_3$	8.4
$MgCl_2 \cdot 6H_2O$	16.9
$Na_2MoO_4 \cdot 2H_2O$	0.1
Resazurin	0.9
$Na_2S \cdot 9H_2O$	30.0
Glucose	10.0
Vitamin stock solution	1.25 ml/l
Biotin	2.0
Folic acid	2.0
Pyridine-HCl	10.0
Riboflavin	5.0
Thiamine	5.0
Nicotinic acid	5.0
Pantothenic acid	5.0
Vitamin B_12	0.1
p-Amino benzoic acid	5.0
Thioctic acid	5.0

rinsed with acetone, and rinsed with distilled water. Prior to sampling, the filter holders and syringes were "blocked" by exposing them to the unlabelled substrate being tested. Blocking means that the filter surface was saturated with substrate, so that no further sorption occurred. This equipment preparation yielded consistent measures by preventing adsorptive losses of ^{14}C during sample handling.

Samples were collected and divided in such a manner that soluble organic carbon, CO_2, and cellular carbon could be distinguished. Three blocked syringes were filled with 0.1 ml of Carbosorb (containing strong base) and attached to each sample port. Flow was diverted first to the effluent port, and the syringe was filled at the feed flow rate. Syringes at the inlet and feed reservoir subsequently were filled in the same manner. The full syringes were shaken to mix the Carbosorb. One ml was injected into a scintillation vial without further amendment, and this sample contained all three ^{14}C species. Another 1-ml sample was injected into a scintillation vial containing 2 drops of concentrated sulfuric acid. The acid was used to drive off CO_2, and this second vial contained ^{14}C in cells and soluble organic matter. A blocked filter holder and 0.45-μm membrane filter were attached to the syringe, 0.3 ml was wasted, and 1 ml of sample was added to a vial containing 2 drops of concentrated sulfuric acid. This sample contained only soluble organic ^{14}C. After the vials had been shaken to drive off CO_2, 9 ml of Fisher Scintiverse E scintillation cocktail was added to each vial. The vials were counted in a Hewlett-Packard Tricarb Model 1600 CA liquid scintillation counter for 12 minutes or to a 95.5% confidence level, whichever came first.

Biofilm thickness, L_f, was determined at the end of experimentation by analyzing 20 glass beads from each of three different sections of the reactor. The beads were weighed, dried, and reweighed. Since a biofilm is approximately 99% water, the biofilm thickness was computed by

$$L_f = \frac{W}{\varrho\, m\, A\, (0.99)} \tag{11}$$

in which W = weight of evaporated water, ϱ = density of water at 21°C, A = surface area of one bead, and m = number of glass beads.

The dried beads were further investigated to determine the biomass density, X_f. The dried beads were placed in prepared HACH COD (Chemical Oxygen Demand) vials, agitated with a vortex mixer, and digested at 160 °C for 2 hours in a HACH COD reactor. A spectrophotometer was used to assess the absorbance, which was converted to COD by an equation given by HACH. The density was computed from

$$X_f = \frac{COD\ (mg) \times 0.706\ (mg\ cell\ mass/mg\ COD)}{mAL_f} \tag{12}$$

in which 0.706 assumes that cells have the chemical formula $C_5H_7O_2N$.

Results and discussion

Adsorption

Figure 2a presents the breakthrough curve for acrylate, which was used as a conservative tracer, when 0.0l6 mg of acrylate was instantaneously injected. The results were nearly identical for an injection of 0.16 mg. The experimental retention time was 3.6 minutes, giving a retardation factor of 1.04. The retardation near 1.0 and the nearly 100% mass recovery in the effluent ($M_e > 98\%$) demonstrate that adsorption of the acrylate monomer was negligible and that the experimental system performed satisfactorily.

Figure 2b is the breakthrough curve for fraction M_w 16,700. The shape of the curve in Figure 3 and its θ_c value, 4.0 minutes, are quite similar to those of Figure 2. Thus, the material exiting the column resembled acrylate in that it had a retardation factor of only 1.15. However, only 1.2% of the added ^{14}C exited the column in 5.8 liquid retention times. Most of the polyacrylates in fraction M_w 16,700 were strongly adsorbed and had retardation factors well in excess of 5.8.

Experiment also were carried out at pH = 7.0, and the results were virtually the same as shown in

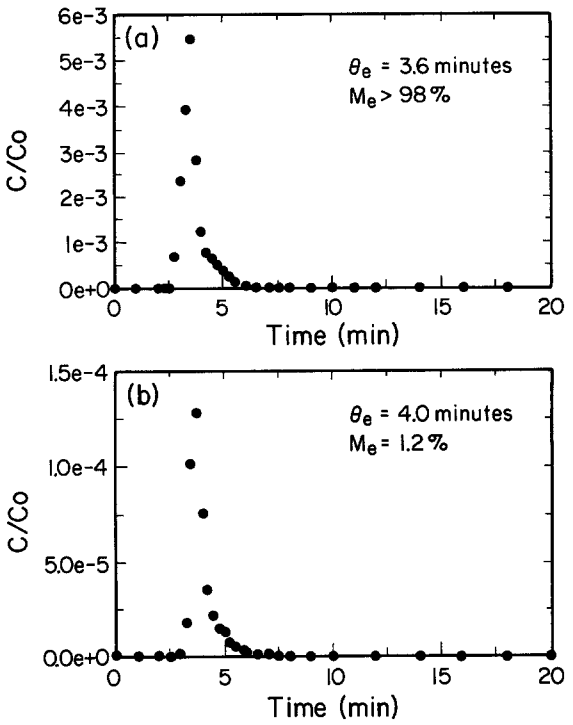


Fig. 2. Breakthrough curves for (a) acrylate at pH = 5.0 and an injection of 0.016 mg of ^{14}C-acrylate, and (b) fraction M_W 16.700 at pH = 5.0.

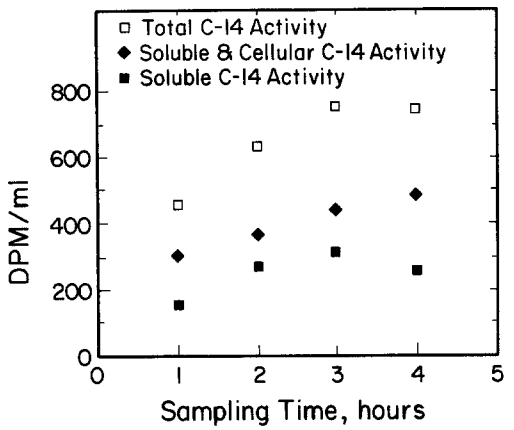


Fig. 3. Typical data from a short-term biodegradation experiment. These results are for glucose fed at 10 mg/l (4 mg C/l) and a flow rate of 1 ml/min. The influent soluble radioactivity was 953 dpm/ml.

Figure 2. This lack of a pH effect suggests that adsorption was not electrostatically controlled (the pK_a of the polymer should be between 5 and 6), but was driven by the hydrophobic nature of the polymer. Thus, the larger polymers probably were the one most strongly adsorbed.

At the end of the experiment with fraction M_w 16,700, the sand was extruded and extracted. All of the retained ^{14}C was found in the first half of the column, and 98% remained in the first quarter. The average retardation factor for the adsorbed tracer (R_a) was computed from Equation 3 to be 58. Thus, the polydisperse nature of fraction M_w 16,700 has some molecules that are unretarded, while the majority of the polymers are strongly retarded. Presumably, the unretarded molecules are the smallest ones. Figure 1 shows that the smallest 1.2% of fraction M_w 16,700 has an apparent molecular weight less than about 3,500, which is a polymer with n approximately equal to 50. Since the molecular weight distribution extends almost to 10^5, the retardation factors for some of the materials undoubtedly are much larger than 58. In fact, the average retardation factor for the retained material probably is greater than 58, since the computation in equation 3 assumes that the material in the first quarter travelled to the mid-point of that segment. The more likely situation is that the majority of the mass had not travelled that far.

Biodegradation kinetics

Biodegradation kinetic parameters were estimated for glucose, acrylate, and fraction M_w 16,700 in series of short-term tests that yielded ranges of substrate concentration and flux. Figure 3, which gives the results for one glucose experiment, illustrates the typical data from the short-term tests. The data labelled soluble organic ^{14}C represents the substrate concentration. The difference between total ^{14}C activity and soluble and cellular ^{14}C activity is the $^{14}CO_2$. The difference between soluble and cellular ^{14}C and soluble ^{14}C activities is the ^{14}C in suspended biomass. In all cases, the effluent substrate concentration reached a plateau, which indicated that all mechanisms (biodegradation, adsorption, desorption, advection, and dispersion) had reached steady state. The steady state values were used to compute J_{exp} and S_s. The appendix

Table 3. Carbon partitioning for steady states with a feed carbon concentration of approximately 1 mg/l.

Substrate	Percentage of influent *14C*			
	Effluent soluble C	Effluent CO_2 – C	Effluent cell – C	Soluble C removed
Glucose	10	35	2	90
Acrylate	89	9	0	11
Fraction M_w 16,700	95	5	0	5

shows how those computations were made for the example of Figure 3.

Table 3 compares the results for one feed concentration, approximately 1 mg/l. The data show that all input substrates were removed and oxidized to CO_2 to some extent by the methanogenic consortium. Biodegradation of glucose was substantially greater than for the other substrates, and acrylate was biodegraded about twice as fast as fraction M_w 16,700 under these conditions.

The Monod kinetic parameters for each substrate were determined by the curve-matching technique of Rittmann et al. (1986) for ordered pairs of J_{exp} and S_s. To use the method, two biofilm parameters (X_f and L_f) and three transport parameters (D, D_f, and L) had to be estimated for each substrate. X_f and L_f were the same for all substrates, since the same reactor was used for all experiments. Their values, determined at the end of kinetic experimentation, were: X_f = 13.5 g biomass/cm^3 and L_f = 105 μm. The molecular diffusion coefficient, D, was computed from the Wilke-Chang relationship (Perry & Green 1984), the molecular weight of the substrate, and an association factor of 2.26. For fraction M_w 16,700, the number averaged molecular weight, M_N = 10,700, was employed. The diffusion coefficient in the biofilm, D_f, was computed as 0.8 D (Williamson & McCarty 1976). L was computed from equation 9 and the flow conditions of the short-term experiments. Table 4 lists the transport parameters used for each substrate.

Figure 4 presents the experimental data and the best-fit curves of log S_s versus log J_{exp}. Table 5 lists the best-fit Monod kinetic parameters: q_{max} = maximum specific rate of substrate utilization, and K = half-maximum rate concentration. In each case, the experimental data defined the classic biofilm kinetic response: J_{exp} is a first-order function of S_s at low S_s, but it gradually shifts to a lower reaction order at higher S_s. The kinetic parameters quantify the general observation that glucose has much faster kinetics than do the other substrates. The maximum rate of degradation is 10 times faster for glucose than for acrylic acid and about 400 times faster than for fraction M_w 16,700. The difference is accentuated for low concentrations, as glucose also has the lowest K value. Thus, the first-order rate coefficient, q_{max}/K, shows an even greater advantage than does q_{max}: the first-order coefficient for glucose is 18 times that of acrylic acid and 5,500 times that of fraction M_w 16,700.

That glucose had substantially faster kinetics than acrylate can be expected, since glucose was the primary substrate for the methanogenic consortium and is a highly labile compound for anaerobic biodegradation. Nonetheless, acrylate was biode-

Table 4. Transport parameters.

Substrate	M_n	D, cm^2 s^{-1}	D_f, cm^2 s^{-1}	L, μm
Glucose	180	6.55×10^{-6}	5.24×10^{-6}	200
Acrylate	72	1.08×10^{-5}	8.64×10^{-6}	236
Fraction M_w 16,700	10,700	4.73×10^{-7}	3.78×10^{-7}	83

graded significantly by the anaerobic biofilms, which exhibited no lag or acclimation periods.

The relatively slow kinetics for fraction M_w 16,700, compared to acrylate, probably are related to its polymerized nature, but two factors demonstrate that slow diffusion was not the cause of the reduced kinetics for fraction M_w 16,700. First, the curve-matching method explicitly included mass-transport resistance inside the biofilm and to the biofilm surface. Second, we varied M_n from 72 to 10,700 (with D, D_f, and L varying accordingly) and found that the best-fit parameters for q_{max} and K did not change. This insensitivity to mass transport occurred because the degradation kinetics were slow enough to be completely rate limiting. Thus, the q_{max} and K estimates for fraction M_w 16,700 are especially robust, since they are not affected by transport resistances.

Conclusions

The adsorption and biodegradation characteristics of a polydisperse mixture of soluble PA, fraction M_w 16,700, were evaluated experimentally.

Sand-column tracer tests showed that 1.2% of fraction M_w 16,700 was virtually unadsorbed, but the remaining material was strongly retained by the sand and had a retardation that averaged at least 58, but probably included values much higher. Strong adsorption was correlated to polymers having an apparent molecular weight greater than about 3,500.

Biodegradation kinetics were determined for glucose, acrylate, and fraction M_w 16,700 by performing a series of short-term experiments in biofilm reactors in which a mixed methanogenic consortium had been grown on glucose. Removal of the soluble substrate and production of CO_2 were observed in each case. Although glucose had much faster kinetics, acrylate and fraction M_w 16,700 showed significant biodegradation. The first-order rate coefficients (in m^3/g biomass-day) were 11 for

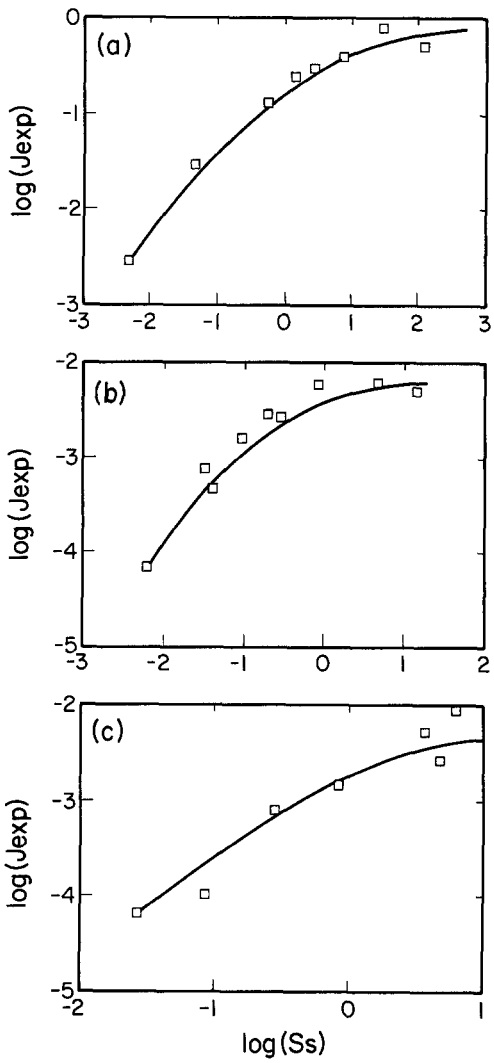


Fig. 4. Experimental data and best-fit curve for (a) glucose, (b) acrylate and (c) fraction M_w 16,700. S_s is in mgC/l and J_{exp} is in C/m^2-day.

Table 5. Best-fit kinetic parameters.

Substrate	q_{max}, gC/g biomass-day	K, gC/m^3	q_{max}/K, m^3/g biomass-day
Glucose	0.66	0.060	11
Acrylate	0.066	0.11	0.60
Fraction M_w 16,700	0.0016	0.79	0.002

glucose, 0.60 for acrylate, and 0.002 for fraction M_w = 16,700.

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Appendix – sample calculation

The sample calculation is for a feed concentration of 10 mg/l glucose, which corresponds to the data in Figure 3.

Influent Concentrations: 10 mg glucose/l, 4 mgC/l, 953 dpm/ml

Effluent Soluble Concentrations: 286 dpm/ml, 3 mg glucose/l, 1.2 mg C/l

$$\bar{S} = \frac{S_0 - S}{ln\,(S_0/S)} = \frac{4\,mg\ C/l - 1.2\,mg\ C/l)}{ln\,(4/1.2)} = 2.33\,mg\ C/l$$

$$J_{exp} = \frac{(S_0 - S)\,Q}{Va} = \frac{(4\,mg\ C/l - 1.2\,mg\ C/l) \times 1\,cm^3/\text{min}}{14.73\,cm^3 \times 12/cm} \times \frac{10^{-3}\,l/cm^3}{60\,\text{sec/min}}$$

$$= 2.64 \times 10^{-7}\ \text{mgC/cm}^2\text{-sec}$$

$$(= 0.228\ \text{gC/m}^2\text{-day})$$

$$\bar{S}_1 = \bar{S} - \frac{L\,J_{exp}}{D} = 2.33\,mg\ C/l - \frac{0.02\,cm \times 2.64 \times 10^{-7}\,mg\ C/cm^2\text{-sec}}{6.55 \times 10^{-6}\,cm^2/\text{sec} \times 10^{-3}\,l/cm^3}$$

$$= 1.52\,\text{mg C/l}$$