

Controlled Release of the Herbicides 2,4-D and Dichlobenil from Alginate Gels

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Synopsis

The herbicides 2,4-D[(2,4-dichlorophenoxy)acetic acid] and dichlobenil (2,6-dichlorobenzonitrile) were individually incorporated into 1.6–2.8-mm alginate gel beads by using calcium chloride and barium chloride as gellants. The release rate of each herbicide from the beads into water was greatly influenced by drying and the choice of gellant cation. Slowest release was obtained with dried samples that were gelled with barium chloride. At the slowest rates, release of 2,4-D was complete in 14 days, while only 59% of the less-soluble dichlobenil was released in 150 days.

INTRODUCTION

There is a growing realization that conventional application of agricultural chemicals is often wasteful, and can cause toxicity problems in nontarget species. Delivery from controlled-release formulations is a promising concept, and many advances have been made in recent years.¹ Synthetic and naturally occurring polymers are the cornerstone of this technology. Alginate gels were selected as matrices for studying the utility of controlled release in certain agricultural applications because of the biodegradability of these gels and the ease of incorporation of pesticides using an aqueous system at ambient temperature.

Alginic acid, a linear polysaccharide derived from brown seaweeds (Phaeophyceae), is composed of polymannuronic and polyguluronic acid units.² The sodium salt is water-soluble and is used in a variety of industrial, pharmaceutical, and food applications. Tough gels containing up to 99% water can be prepared from dilute solutions of sodium alginate by reaction with cations such as H⁺, Ba²⁺, Pb²⁺, Cu²⁺, Zn²⁺, and Ca²⁺.

Scher³ reported the use of alginate gel discs for the controlled release of an insect juvenile hormone. Barrett⁴ formulated the herbicide diquat dibromide with alginate for aquatic weed control, and Mitchell⁵ used the gelling action of alginic acid to obtain slow fertilizer release. Alginates have also been used in several encapsulation processes,^{6–10} but release rate data were not reported.

This article reports a laboratory process for the individual incorporation of 2,4-D [(2,4-dichlorophenoxy)acetic acid] and dichlobenil (2,6-dichlorobenzonitrile) into alginate gel beads, and the release profiles of each herbicide from the gels into water. These compounds were selected because both are effective in aquatic weed control¹¹ and because their water solubilities span a wide range (900 and 18 ppm, respectively).¹² Beads were gelled with Ca²⁺ and Ba²⁺, and studied in their "hydrated" (as initially isolated) and dried states.

EXPERIMENTAL

Materials

Sodium alginate, obtained from MCB Manufacturing Chemists, Inc., had a bulk density of 43 lb/ft³ and viscosities of 400 cps at 1% and 3500 cps at 2% (Brookfield LVF at 60 rpm). The 2,4-D [99.7% by high-performance liquid chromatography (HPLC)] was from Eastman Kodak Co. Dichlobenil was obtained at 97% purity from Aldrich Chemical Co. and recrystallized twice from methanol (mp 144.5–146°C). (Names of companies or commercial products are given solely for the purpose of providing specific information; their mention does not imply recommendation or endorsement by the U.S. Department of Agriculture over others not mentioned.)

Each herbicide was powdered and sieved to pass a 60-mesh screen. Water was purified by passage through deionizing resins and activated charcoal. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Preparation of Alginate Gel Beads

Alginate gel beads containing herbicide dispersed throughout (not encapsulated) were prepared by use of the apparatus shown in Figure 1. A herbicide/alginate mixture was prepared by adding 8.0 g of herbicide and 3.0 g of sodium alginate to 189.0 g of water while mixing with a propeller-type stirrer. A uniform dispersion of the herbicide in the alginate solution resulted after about 30 min. This mixture (pH 4.0 with 2,4-D; 7.0 with dichlobenil) was added dropwise into 400 mL of gellant solution [0.25M CaCl₂ (pH 5.4) or 0.25M BaCl₂ (pH 4.4)] so that, over a 5-min period, a 42–62 g quantity was transferred. The rate of addition could be increased by applying slight air pressure to the apparatus, and stopped by hose clamps placed on the rubber tubing. The weight of formulation transferred could be read directly off the balance. Each droplet was gelled immediately at its surface as it entered the gellant solution and formed a distinct, spherical bead. An additional 5 min residence time was given to the batch so that total time in the gellant solution was 5–10 min. By this time, each bead was gelled throughout.

The gellant solution was separated from the beads by filtration through a funnel equipped with a coarse fritted disc, and the filtrate was saved. The hydrated beads were rinsed with 50 mL of deionized water and placed in sealed jars. Liquid resulting from gel syneresis was removed from each jar periodically, added to the filtrate from the same batch, and the resulting solution was analyzed for herbicide content by HPLC.¹³

After a period of time (21 days for 2,4-D and 7 days for dichlobenil), a portion of each sample was dried. Samples could be dried just after preparation, but the waiting period selected allowed the hydrated beads to stabilize in weight. The 2,4-D/alginate beads (5 g) were dried for 75 min in a rotary evaporator using water aspirator vacuum and a 45°C bath. The dried beads were hard, white spheres with a rough surface. The dichlobenil/alginate beads (13 g) were spread out on aluminum foil and air dried for 24 h, then desiccated over CaCl₂ for 24 h. The resulting granules were irregularly shaped but fairly uniform in size (Figure 2).

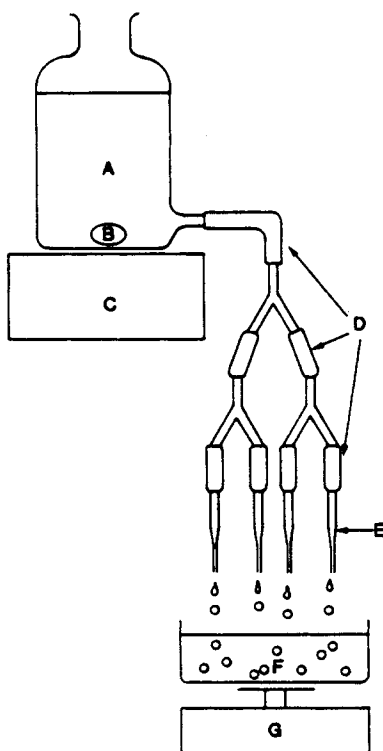


Fig. 1. Apparatus used to prepare herbicide/alginate gel beads. (A) 250-mL aspirator bottle; (B) stir bar; (C) magnetic stirrer; (D) rubber tubing, 6.4 mm ID; (E) disposable Pasteur pipets, 146 mm length, 1.3 mm ID orifice; (F) 190 × 100 mm crystallization dish containing gellant solution; (G) top-loading balance.

Analysis of Samples

Herbicide content of these products was determined by material balance calculations for all of the 2,4-D and for the hydrated dichlobenil samples. The herbicide concentration was taken as the amount contained in the original

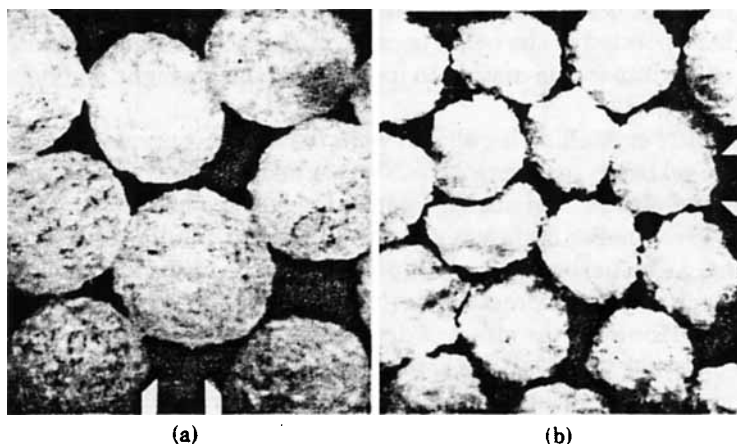


Fig. 2. Light micrographs of Ca-gelled dichlobenil/alginate beads: (a) hydrated; (b) dried. 1 mm between markers.

mixture less the amount lost in processing (determined by HPLC analysis of the solutions). The dichlobenil content of the dried beads was determined from the % *N* analyses.

Determination of Controlled-Release Properties

2,4-D/alginate beads. For each sample (two replicates), a quantity of beads accurately weighed and containing about 40 mg of 2,4-D was added to 1 L of water in a 1.9-L mason jar. The solution would, therefore, become about 40 ppm (w/v) in 2,4-D when the entire amount had been released into the water. Temperature was $25 \pm 3^\circ\text{C}$. Water samples (about 1 mL) were removed periodically after swirling the jars, and analyzed by HPLC.¹³ Excess samples were returned to the jars to minimize volume change.

Dichlobenil/alginate beads. Also done in duplicate, an accurately weighed quantity of beads from each sample containing about 13-mg dichlobenil was added to 1 L of water [about a 13 ppm (w/v) solution if totally released] in an Erlenmeyer flask (1-L) with screw cap. The flasks were swirled to mix the contents at least once a week, and before each sampling. Water samples were removed for HPLC analysis,¹³ with the cap only slightly ajar to minimize loss of the somewhat volatile herbicide. Excess samples were returned to the flasks. Temperature for the duration of the experiment was $20 \pm 3^\circ\text{C}$.

At the conclusion of the experiment at 150 days, the beads were removed and extracted with an acetonitrile (50%)–water (50%) solution (3×100 mL) at 60°C for 5 h. The extracts were combined and analyzed by HPLC to determine the amount of dichlobenil that remained incorporated in each sample.

RESULTS AND DISCUSSION

Tables I and II give data on properties of hydrated and dried alginate beads containing 2,4-D and dichlobenil, respectively.

A considerable amount of syneresis occurred, as can be seen from the loss of product weight with time. Greatest loss was during the first day, after which there was a leveling off. This loss of herbicide into gellant solution and syneresis liquid amounted to about 7% of the weight of 2,4-D originally formulated, but only to about 0.1% of the less-soluble dichlobenil. Some calcium and barium were incorporated in the beads because of reaction with the alginate. The higher wt % of barium is due mainly to its higher atomic weight and does not indicate more reactivity.

The pure crystalline herbicides were readily incorporated by this process into alginate gel beads that were 2.55–2.78 mm in diameter. The hydrated beads were tough and elastic, and slightly wet at the surface because of syneresis. Dried beads were smaller and were generally easier to handle because they were free-flowing. The herbicide content of the dried beads was higher than one would usually choose for a practical agricultural application where good coverage is needed. However, the effect of drying on release rate could best be determined by comparing beads of the same batch, so that a portion of each was dried (thereby concentrating the herbicide). Comparisons of release profiles of the samples are approximate, because differences in size, shape, and concentration may affect release properties. Data from bead preparation and herbicide release were found to have good reproducibility.

TABLE I
Properties of 2,4-D/Alginate Beads

Gellant	Formulation wt (g)	Product wt ^a (g)		Wt loss on drying (%)	Bead wt ^b (mg)	Bead size ^c (mm)	Herbicide content (%)	Analyses (%)	
		Days						Ca	Ba
		1	7						
Hydrated									
Ca ²⁺	42.0	18.0	15.6	81	9.9	2.70	10.8	0.76	—
Ba ²⁺	42.6	20.1	18.2	82	11.1	2.70	9.3	—	2.64
Dried									
Ca ²⁺	—	—	—	—	1.7	1.59	56.6	3.83	—
Ba ²⁺	—	—	—	—	1.8	1.61	52.7	—	14.48

^a After removal of liquid due to synthesis.

^b Average weight of 20 beads.

^c Average size of 20 beads lined up in a row.

TABLE II
Properties of Dichlobenil/Alginate Beads

Gellant	Formulation wt (g)	Product wt (g)		Wt loss on drying (%)	Bead wt (mg)	Bead size (mm)	Herbicide content (%)	Analyses (%)	
		Days						Ca	Ba
		1	7						
Hydrated									
Ca ²⁺	60.7	26.4	24.4	84	9.3	2.55	9.9	0.90	—
Ba ²⁺	62.2	31.6	29.1	85	11.4	2.78	8.5	—	2.71
Dried									
Ca ²⁺	—	—	—	—	1.7	1.88	63.3	4.64	—
Ba ²⁺	—	—	—	—	1.9	1.83	54.5	—	16.93

A total of 97–110% of the 2,4-D and 91–104% of the dichlobenil was accounted for at the conclusion of the experiments. This variability resulted principally from using small weights of samples whose herbicide contents were not determined with high accuracy. A small amount of dichlobenil may have escaped during sampling for HPLC because of its volatility. Data for Figures 3 and 4 were normalized to 100% based on the highest amount released, plus the amount extracted at the conclusion of the experiment, if any.

Figure 3 shows the release profiles for the 2,4-D/alginate beads and the solubility profile for unformulated 2,4-D (the same particle size as incorporated in the beads). Hydrated beads released the relatively water-soluble 2,4-D as fast as the unformulated material dissolved, so that there was no slow release obtained. By 2 days, more than 96% of the 2,4-D in these samples was in solution. The dried beads, however, did give slower release. The Ca-gelled sample released for 4–6 days; the Ba-gelled sample released for 14 days.

The variety of release rates obtained with the dichlobenil/alginate samples are shown in Figure 4. Unformulated dichlobenil dissolved completely by 41 days under the experimental conditions. Hydrated beads gave slow release, and had exhausted their herbicide content by about 90 days. The Ca- and Ba-gelled, hydrated samples gave almost identical release profiles.

Significantly slower release rates were obtained from the dried beads. When the experiment was terminated at 150 days, the Ca-gelled sample had released 84% and the Ba-gelled sample had released 59% of their dichlobenil content into solution. A sample that was prepared using a 5-min drop time plus 1-min additional residence (1–6 min total) in the CaCl_2 solution gave results identical to the longer-gelled sample. This suggests that even shorter gel time, possibly with higher CaCl_2 concentration, would be practical.

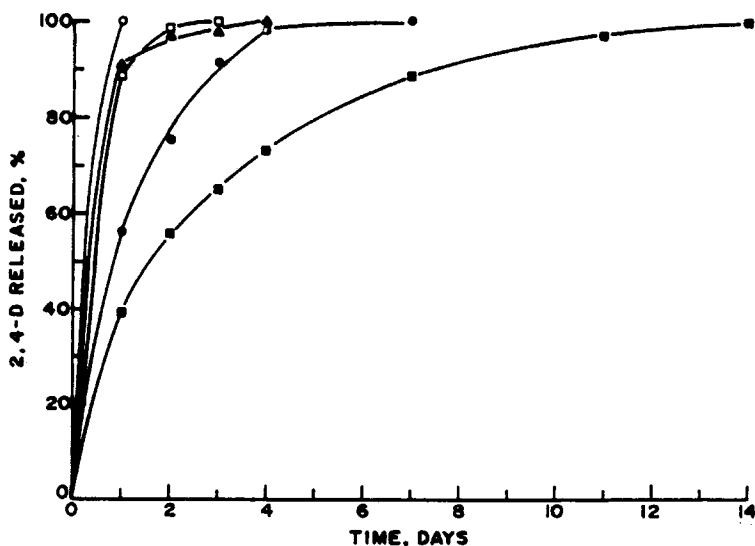


Fig. 3. Release of 2,4-D into water: (▲) unformulated, crystalline 2,4-D; (○) Ca-gelled, hydrated; (□) Ba-gelled, hydrated; (●) Ca-gelled, dried; (■) Ba-gelled, dried.

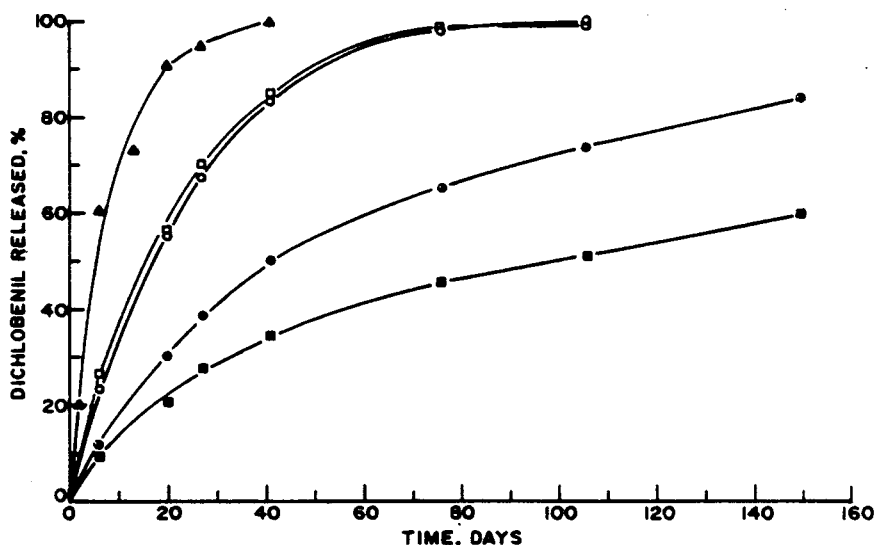


Fig. 4. Release of dichlobenil into water: (▲) unformulated, crystalline dichlobenil; (○) Ca-gelled, hydrated; (□) Ba-gelled, hydrated; (●) Ca-gelled, dried; (■) Ba-gelled, dried.

CONCLUSIONS

A measure of control over the release rate of 2,4-D or dichlobenil from alginate gel beads has been demonstrated. By virtue of its greater water solubility, 2,4-D was released much faster than dichlobenil, which was still being released from some samples after 150 days in water. Hydrated beads released herbicide faster than did the same beads after drying. No appreciable differences in release rates were noted for Ca- and Ba-gelled, hydrated beads. However, for dried beads, use of barium ion as gellant gave significantly slower release of both herbicides. Apparently, the dried barium alginate gel matrix has lower water permeability, which slows the dissolution and diffusion of the compounds incorporated within.

The laboratory-scale alginate gel process described should be useful in sample preparation for the study of controlled-release herbicides. It is easy to use under very mild, aqueous conditions and employs common laboratory equipment. Alginate solutions are compatible with a wide variety of bioactive materials. Experience has shown that liquids and emulsions, as well as solids, can readily be incorporated in the gel beads. It is even possible to prepare hydrated beads that will float in water by mixing air bubbles into the herbicide/alginate mixture by rapid stirring prior to gelation. Investigation is underway on the effects of fillers and other adjuvants on gel properties and release rates.

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