

# Controlled Release of Pesticides into Water from Clay–Polymer Formulations

Z. Gerstl,\* A. Nasser, and U. Mingelgrin

Institute of Soil, Water and Environmental Sciences, ARO, Volcani Center, P.O. Box 6,  
Bet Dagan 50-250, Israel

The release of alachlor and atrazine into aqueous solution from controlled-release formulations (CRFs) prepared from alginate and pectin, with and without the addition of clay minerals, was studied. The rate of release of the incorporated herbicides was a function of both the properties of the herbicide and the composition of the CRF. The rate of release of herbicides was related to their aqueous solubility; the greater the solubility of a compound, the more rapid its release from a CRF. The rate of release of the chemicals from pectin-based CRFs was generally greater than from alginate-based CRFs. This seems to be related to the relatively large number of methoxy groups in the pectin, which hinders the gelation process and results in a more porous matrix than in the case of alginate. The addition of sodium montmorillonite to these CRFs was found to have a profound inhibitory effect on the release of alachlor. This was attributed to the sorption of the herbicide to the clay mineral. Other clays generally had little or no effect on the rate of release of the active ingredient. Bead radius was observed to have a profound effect on release rates; the smaller the radius, the greater the release rate. Release rates conformed to the Higuchi equation for a diffusion controlled release mechanism from a porous polymer in which the active ingredient is present in excess of its solubility.

**Keywords:** *Controlled release; alachlor; atrazine; herbicides; clay; alginate; pectin; diffusion*

## INTRODUCTION

To ensure adequate pest control for a suitable period, pesticides are applied in concentrations greatly exceeding those required for control of the target organism, thus increasing the likelihood of runoff or leaching and pollution of surface or ground water (Guyot, 1994). The use of controlled-release formulations (CRFs) can, in many cases, supply the active ingredient (ai) at the required rate for pest control while decreasing the total amount of chemical needed, thereby decreasing the risk to the environment. The advantages of CRFs are longer duration of efficacy for rapidly degraded compounds, reduction in the amount of material required for pest control, decrease in the risk of environmental pollution, savings in manpower and energy by reducing the number of applications required in comparison to conventional formulations, increased safety for the farmer or pesticide applicator, and a general decrease in nontarget effects.

Much of the work carried out to date on agricultural CRFs has concentrated on devices using substrates such as starch, kraft lignin, and alginate, although several commercially available microencapsulated formulations of pesticides are available. Riggle and Penner (1988) reported on the controlled release of three herbicides from a pine kraft lignin formulation and found that at the higher lignin rate, mobility of the pesticides, when leached in soil columns, was somewhat retarded. Melhretter et al. (1974) studied the release of 2,4-D from several starch formulations and found them to exhibit

desirable release rates. Boydston (1992) found reduced leaching of norflurazon and simazine in soil columns when they were applied in starch-based granules as compared to the commercial products. Schreiber et al. (1978, 1993) and Gish et al. (1994) have shown the efficacy of starch-encapsulated EPTC, butylate, and atrazine in relation to their commercial formulations. Gish et al. (1994) and Schreiber et al. (1993) have also shown that these formulations are beneficial in that they significantly reduce atrazine leaching. The greenhouse and field test of starch-based CRFs have been summarized by Schreiber et al. (1993).

Alginate has also received attention for use in CRFs. Vollner (1990) found that carbofuran leaching from soil columns was slower than that of the nonformulated material when applied in barium–alginate granules. Hussain et al. (1992) studied the release of thiobencarb into static water from calcium–alginate beads using kaolinite as a filler and found that the rate of release of the herbicide was much higher from the commercial formulations and that increasing the proportion of kaolinite in the CRF reduced the rate of release of the herbicide. In a subsequent study, Gan et al. (1994) reported that use of the alginate–kaolinite-based formulation for thiobencarb resulted in lower concentrations of the parent compound in rice plants and fish in a rice paddy system, thus reducing the potential impact on nontarget organisms. The use of alginate together with linseed oil and kaolin as a filler for the controlled release of metribuzin and alachlor was reported by Pepperman and Kuan (1993, 1995). They found that the rate of release of metribuzin from alginate-based formulations increased greatly in the absence of linseed oil. Similar results were found for alachlor, for which

\* Author to whom correspondence should be addressed (telephone 972-3-9683446; fax 972-3-9604017; e-mail vwzevg@volcani.agri.gov.il).

**Table 1. Selected Properties of the Pesticides Studied**

compound	log $K_{ow}$	solubility (mg/L)	vapor pressure (mPa)
alachlor	2.77	240	1.9
atrazine	2.47	33	0.04
trifluralin	4.55	0.3	14.7

it was further found that the size of the beads had no appreciable effect on the rate of release.

The addition of clay to alginate gels is expected to decrease the rate of release of trapped or included molecules both as a result of sorption of the compound by the clay and due to increased tortuosity within the gel. The objective of this study was to prepare clay- and polymer-based CRFs for agrochemicals. These CRFs are based on readily available natural materials, require a simple preparation procedure, and produce nontoxic degradation products. In the present paper the various CRFs will be compared with regard to the rate of release of the ai into water. An accompanying paper reports the behavior of the CRFs in soil (Gerstl et al., 1998).

## MATERIALS

The alginate used for our studies was purchased from Fluka (Buchs, Switzerland; sodium alginate for immobilization of microorganisms, No. 71238). The pectin (Unipectine range 3 g), derived from fruit, was obtained from Sanofi Bio-Industries, France, and had a degree of esterification of 18–30%.

The following clays were studied: sodium montmorillonite (Fisher Scientific, Fair Lawn, NJ), kaolinite (Supreme, English China Clays, St. Austell, U.K.), and two commercial attapulgites, Minugel and Diluex, which differ primarily in their particle size distribution (Floridon Inc., GA).

The following pesticides were studied: alachlor [2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide]; atrazine [6-chloro-*N*-ethyl-*N*-(1-methylethyl)-1,3,5-triazine-2,4-diamine]; and dicamba (3,6-dichloro-2-methoxybenzoic acid). Technical grade and formulated products (dicamba, Banvel 4S, 602 g/L; alachlor, Alanex 48EC, 480 g/L; atrazine, Atranex 50WP, 500 g/kg) were provided by Agan Chemicals, Ashdod, Israel. Relevant physicochemical properties of the chemicals are presented in Table 1. All reagents were of analytical grade and purchased from Merck (Darmstadt, Germany). Solvents were all of HPLC grade purchased from BioLab Ltd., Israel.

## EXPERIMENTAL PROCEDURES

**Preparation of Polymer-Based Beads.** Mixtures of polymer, clay, and ai (3:4:2 ratio) were prepared in water to a final polymer concentration of 3%. The suspension was mixed until uniform and then slowly added dropwise to a 0.5 M CaCl<sub>2</sub> solution from a Pasteur pipet attached to a peristaltic pump. The spherical beads formed were left in the CaCl<sub>2</sub> solution for 4 min to ensure complete gelling and then separated from the solution in a Büchner funnel, rinsed twice with distilled water, and air-dried in a fume hood overnight. By changing the aperture of the pipet through which the suspension was added to the CaCl<sub>2</sub>, it was possible to control the size of the beads formed.

The loading of the ai in the beads was determined by shaking the beads overnight with 0.1 M sodium citrate and then extracting the ai into a 1:1 mixture of hexane and ethyl acetate. Determination of the ai was by gas chromatography with a nitrogen specific detector.

In the CRF containing a mixture of alachlor, atrazine, and dicamba, the weight ratio of the herbicides was 1:0.9:0.1, respectively. The ratio of clay, polymer, and active ingredients was 4:3:2, respectively, and water was added to the mixture to give 3% polymer. Analysis of the active ingredients was carried out by bead disintegration as above using HPLC instead of GC-NPD.

**Release of the ai to Water.** The rate of release of the active ingredients from the various CRFs was determined in

a closed system shown in Figure 1. A number of beads were suspended on a stainless steel net in a glass beaker containing distilled water. The solution in the beaker was stirred by a magnetic stirrer while at the same time it was circulating through an HPLC UV-vis detector. The change in solution concentration was determined by the recorder tracing of the detector output.

Proper operation of this system requires that the concentration of the released material in the external solution should always remain within the linear range of the detector and that sink conditions apply. This means that the amount of ai in the formulation should be such that even if 100% of the material is released, the final solution concentration should not exceed 10% of its aqueous solubility. If this condition is met, then the external solution concentration can be disregarded and we can assume that release is not affected by the presence of ai in the external solution until practically all of the ai has been released from the bead.

In the case of mixtures, the solution in the beaker was not circulated through the detector; instead, at various times 0.2 mL samples were taken for analysis by HPLC. The periodic removal of such small subsamples was assumed not to have any influence on the release pattern.

**Sorption of Alachlor by Clay Minerals.** A solution of 100 ppm alachlor was equilibrated with the clay minerals in a 4% suspension. After 24 h, the suspension was centrifuged and the alachlor remaining in the clear supernatant was extracted into ethyl acetate. Analysis was by GC as described below.

**Chromatographic Analysis.** Analysis of the various pesticides was carried out on a Varian 3300 GC equipped with an NP detector. A DB-5 megabore column (0.53 mm i.d. × 30 m) from J&W Scientific was used with nitrogen as the carrier gas at a flow rate of 10 mL/min.

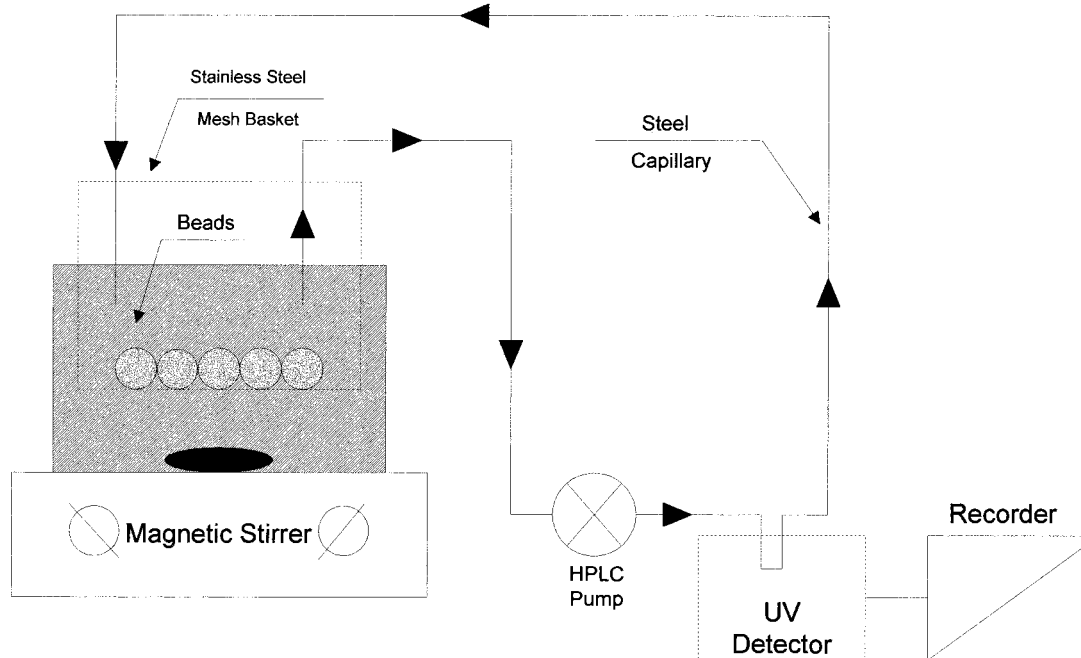
Analysis of the herbicides in the mixed ai CRFs was carried out on a Perkin-Elmer HPLC with a model 235C photodiode array detector set to 230 nm and using a Merck C18 column. The mobile phase for all three compounds was water/methanol (20:80).

**Scanning Electron Microscopy (SEM).** The internal pore network of polymer-based CRFs was studied using SEM to help elucidate the release mechanism. The beads were freeze-dried as this method causes a minimum in deformation of the internal structure of the beads upon drying. The beads were dissected with a surgical blade after freezing. The dried beads were coated with a 20 nm layer of gold and observed in a JOEL SEM model JSM-T330A.

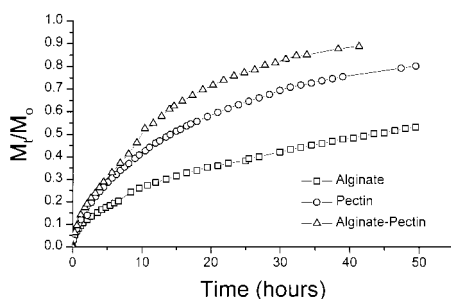
## RESULTS AND DISCUSSION

A simple laboratory test was designed to help quantify the rate of release of the active ingredients from the CRFs under controlled environmental conditions. The release rates are presented as  $M_t/M_0$  versus time, where  $M_0$  is the amount of ai in the CRF beads at time 0 and  $M_t$  is the amount of ai released up to time  $t$ .

**Effect of Type of Polymer on Release Rates.** The rate of alachlor release is greatly influenced by the nature of the polymer composition (Figure 2). Pectin beads release 70% of their content after 40 h, whereas alginate-based beads and alginate/pectin beads release, after the same period of time, 40 and 88%, respectively. During the drying stage of their preparation, alginate beads retained their spherical shape, whereas pectin-based beads seemed to collapse inward, giving a platelet-type shape. The addition of alginate to pectin increased the bead's mechanical resistance to shrinkage during drying and helped the beads formed to retain their spherical shape, yet the rate of release from the combined polymer beads was greater than from either of the individual polymer ones.



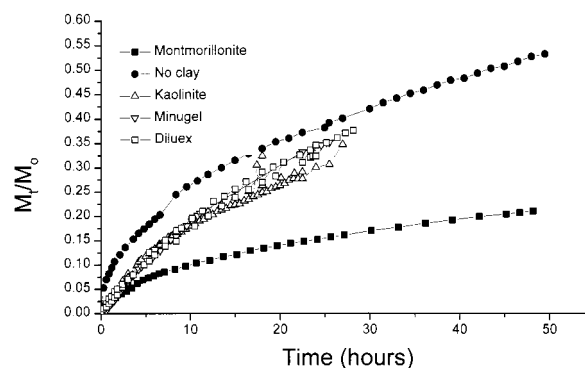
**Figure 1.** Schematic diagram of the system used for measuring the rate of release of the active ingredients into aqueous solutions.



**Figure 2.** Rate of release of alachlor from polymer-based CRFs.

In both polymers, gelation occurs due to interaction between the multivalent cation and the  $\text{COO}^-$  moiety of the sugar units comprising the polymer (Glicksman, 1982; Thom et al., 1982). In the pectin employed in our study the degree of esterification was 18–30%, resulting in a considerable density of methoxy groups, which hinders interaction between the  $\text{Ca}^{2+}$  and the remaining carboxyl units. This reduces the extent of gelation (and mechanical strength) of the pectin-based beads in comparison to the alginate-based ones, resulting in a looser and more porous structure, thus, the greater release rate from the pectin-based CRF. Addition of alginate to pectin increases the mechanical strength of the beads but also results in a higher rate of release of the alachlor than from either polymer by itself. In alginate gels the  $\text{Ca}^{2+}$  cation can bind only to identical structural units (either D-mannuronic or L-guluronic acid). The presence of pectin with a different sugar (D-galacturonic acid) can result in steric interferences reducing the extent of gelation in alginate (Thom et al., 1982; Toft, 1982). The result is a structure with more and larger pores than in beads of either polymer by itself.

**Effect of Clay on the Rate of Release.** The release of alachlor from clay-containing preparations is presented in Figure 3. The results show that the addition of clay to alginate reduces the rate of release of alachlor. Two distinct groups of preparations can be observed,



**Figure 3.** Rate of release of alachlor from alginate-based CRFs as affected by the incorporation of different clay minerals.

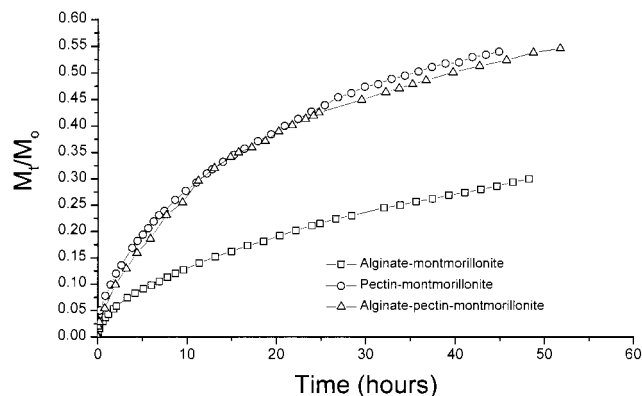
**Table 2. Removal of Alachlor from Solution by Different Clay Minerals**

clay	% alachlor remaining in solution
montmorillonite (Fisher)	28.0
kaolinite (Supreme)	98.5
attapulgite (Minugel)	101
attapulgite (Diluex)	110

montmorillonite (Fisher), which greatly reduces the rate of release, and all the other clays, for which the inhibitory effect is much smaller.

The results of alachlor sorption by the different clay minerals are presented in Table 2 and clearly show that montmorillonite strongly sorbs the herbicide, whereas the other clays show no signs of appreciable sorption. Sodium montmorillonite is known to swell and thus increase its interlayer spacing or even disperse in aqueous solutions. This will allow alachlor to reach the large internal surface area of the clay. In kaolinite with almost no internal surface area or in attapulgite, where the internal channels have fairly small diameters, alachlor is not retained. The strong interaction of the herbicide with montmorillonite obviously retards its release from clay-polymer beads (Nasser et al., 1997). The apparent increase in concentration of alachlor in





**Figure 4.** Rate of release of alachlor from polymer-based CRFs as affected by the incorporation of montmorillonite.

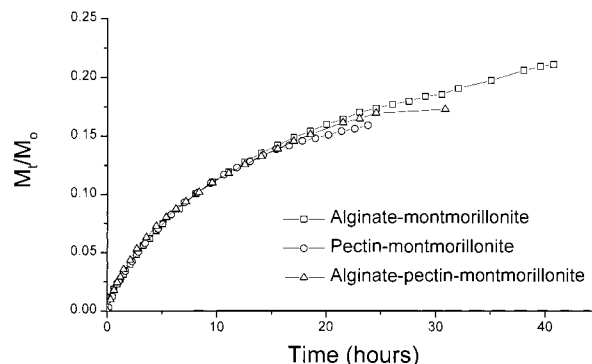
solution upon addition of Diluex may result from water uptake by the fibrous mineral in its internal pores, which are  $\sim 0.4$ – $0.6$  nm in size. These pores can exclude alachlor as they are impervious even to small polar molecules such as methanol and ethanol (Barrer and Mackenzie, 1954).

The reduction in the rate of release of alachlor from clay–alginate beads in the absence of sorption is most likely due to the effect the clay has on the internal pore network of the bead matrix. Increased tortuosity, resulting from a disruption of the normally ordered eggshell configuration of the polymer fibers by the clay particles, could account for the noted decrease in the rate of release.

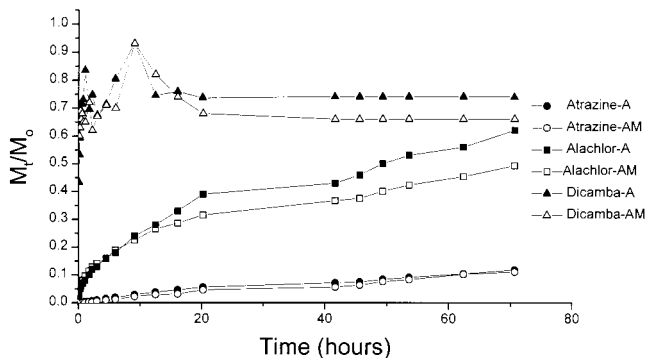
**Effect of Montmorillonite on the Release of Alachlor from Different Polymers.** Alachlor release from polymer-based beads was in the order alginate + pectin > pectin > alginate (Figure 4). The addition of montmorillonite reduces the rate of release of alachlor with all of these polymers but not to the same extent, and the order of release became alginate + pectin = pectin > alginate (Figure 4). As in the case of alginate, the mechanism for reduced rate of release is believed to be due to both interaction of the alachlor with the clay and increased tortuosity resulting from a disruption of the pore network in the presence of the clay.

**Effect of Solubility on the Rate of Release of Herbicides from Polymer-Based Beads.** The physicochemical properties of the ai will have a strong influence on the rate of release from polymer-based beads. Probably the most important property in this respect is the aqueous solubility of the ai. Polymer-based beads were prepared with atrazine, a herbicide with a relatively low solubility of  $\sim 30$  mg/L, approximately one-eighth that of alachlor. The release curves for atrazine are presented in Figure 5, where we see that the release of atrazine from the beads is not influenced by the nature of the polymer and the amount of material released is less than that observed in the case of alachlor.

The dominant mechanism of release of the ai from the polymer–clay-based beads is diffusion through the matrix of the beads to the external solution (Pepperman and Kuan, 1995). The overall diffusive flux depends on the concentration gradient between the solution within the bead and the external solution. Given the lower solubility of atrazine, this gradient is much lower and hence the slower rate of release. It would seem that the rate of release is reduced to such an extent that other factors, such as pore size and tortuosity, no longer have a significant effect on the rate of release.



**Figure 5.** Rate of release of atrazine from polymer–clay-based CRFs.

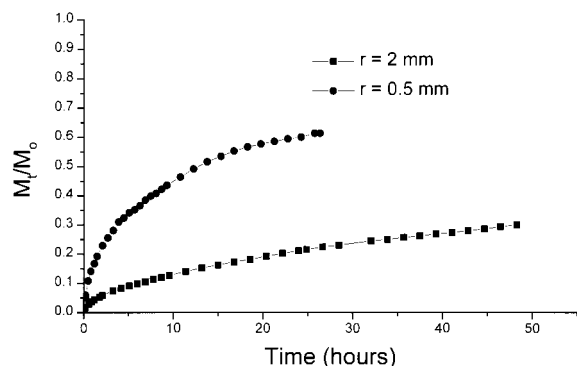


**Figure 6.** Rate of release of alachlor, atrazine, and dicamba from alginate-based CRFs with (AM) and without (A) incorporated montmorillonite.

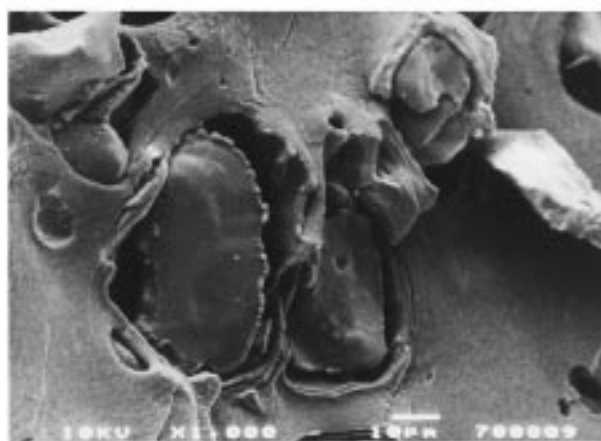
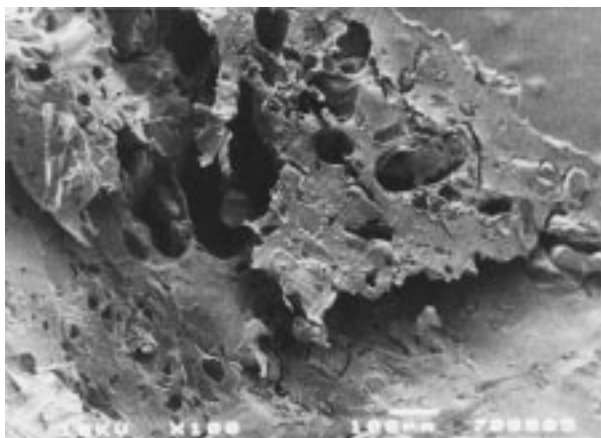
Release curves for the three active ingredients from beads containing a mixture of alachlor, atrazine, and dicamba, a herbicide with a much higher solubility (6500 mg/L), are presented in Figure 6, where we can readily observe the effect of compound solubility on release rates. It is interesting to note that the presence of clay has little effect on the release of any of the compounds in this case. Dicamba, the most soluble compound, is released from the beads extremely rapidly. Alachlor, with a much lower solubility, is released at a much slower rate, and after 70 h, only  $\sim 50\%$  of the compound has been released to the solution. Atrazine release is the slowest, as expected from its low solubility, and after 70 h, only  $\sim 10\%$  of the atrazine has diffused out of the beads. The three compounds chosen are all used for weed control on corn. Controlled release of the compounds from a mixed formulation such as the one presented here would provide weed control over a very long period of time. Initial weed control would be by dicamba followed by alachlor with long-term control by atrazine.

**Effect of Bead Radii on Rate of Release.** CRFs can be prepared in almost any shape. The shape and size of a CRF will have a profound effect on the rate of release of the ai. The CRFs prepared according to the present method are spherical in shape, and so the radii of the beads are expected to greatly influence release rates (Trimmell and Shasha, 1990; Wing et al., 1990).

Alginate–clay beads were prepared with different radii, and the release of the ai was determined. The results, presented in Figure 7, show quite clearly the inverse relationship between radius and the rate of release of alachlor. After 12 h, 50% of the alachlor has been released from the small radius beads, whereas only



**Figure 7.** Rate of release of alachlor from alginate-montmorillonite-based CRFs of different diameters.

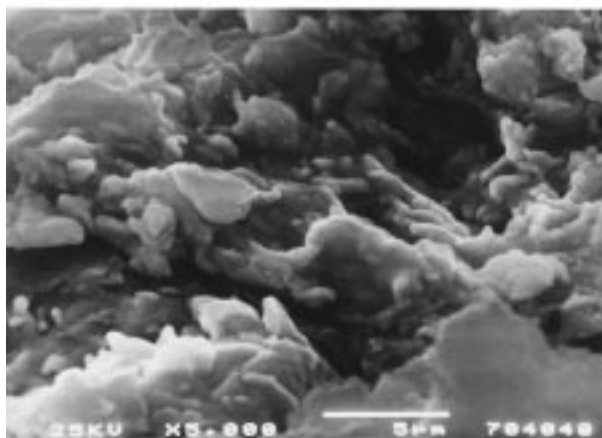
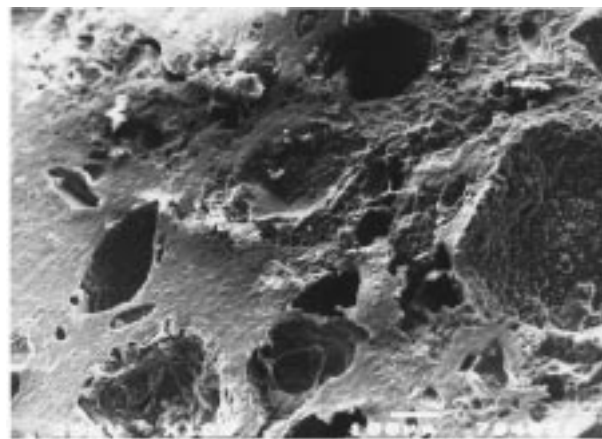


**Figure 8.** Scanning electron micrographs of an alginate-alachlor bead cross section.

~12% of the material has been released from the larger sized beads.

**SEM.** Figure 8 presents micrographs of alginate-alachlor beads at different magnifications. At a magnification of  $\times 100$ , the porous nature of the polymer-based beads, in which the large number of pores do not form a continuous network, is visible. The pores are of different diameters (up to  $200 \mu\text{m}$ ), and at increased magnification ( $\times 1000$ ) one can see the polymer structure near the pore walls and note their uniformity and homogeneity. Increasing the magnification to  $\times 5000$  does not provide any evidence for the presence of concentrations of solid alachlor, even though it is present in appreciable quantities (~10 wt %).

In Figure 9 micrographs of the alginate-montmorillonite beads are presented, and it is evident that the



**Figure 9.** Scanning electron micrographs of an alginate-montmorillonite-alachlor bead cross section.

porous nature of the bead is similar to that of the bead without the clay but that the overall porosity is somewhat reduced. The polymer-clay structure near the pore walls is less homogeneous and rougher than in the clay-free bead. At  $\times 5000$  magnification the polymer coating of the clay particles is evident, as is the resultant coarse structure of the micropores. The observed structure results in increased tortuosity and diffusion path lengths in the bead. The distribution of alachlor again seems to be uniform in these beads.

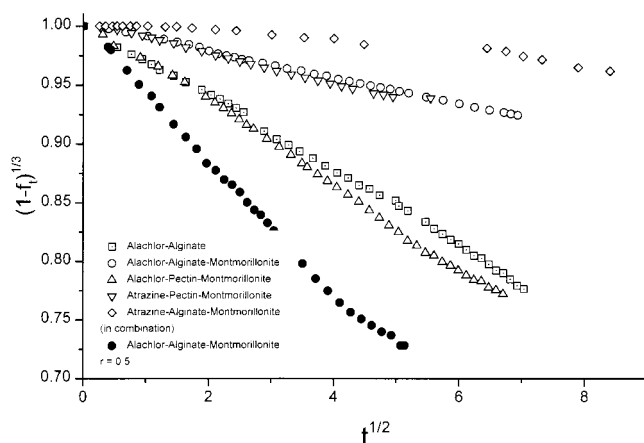
SEM observations of pectin and pectin-alginate beads (with and without montmorillonite) show results similar to those obtained for alginate and alginate-montmorillonite beads as far as porosity and alachlor distribution in the beads and the effect of the presence of the clay on these factors are concerned.

**Fitting of a Mathematical Model.** The polymer and clay-polymer CRFs can be classified as monolithic devices in which the active material, well in excess of its solubility, is evenly distributed in a polymer matrix. Higuchi (1963) developed a model for the diffusive release of a drug from a porous matrix when the drug is present in excess of its solubility. In this pseudo-steady-state system we assume that the dissolution of the ai does not influence the release rate; that is, the release is diffusion controlled with dissolution being relatively rapid. For a system with a finite sink where the bulk solution concentration is not zero, a kinetic equation, having a cubic form, has been derived (Cobby et al., 1974)

$$f_t = M_t/M_0 = 3K_r t^{1/2} - 3(K_r t^{1/2})^2 + (K_r t^{1/2})^3 \quad (1)$$

**Table 3. Polymer–Clay Preparations Studied, Their Release Rates, and 50% Release Times**

herbicide	polymer	clay	radius (mm)	loading (%)	$K_r$ (h <sup>-1</sup> )	$r^2$	$T_{50\%}$
alachlor	alginate		1.75	11.7	0.0309	0.997	44
alachlor	pectin		1.75	13.9	0.0570	0.982	13
alachlor	alginate–pectin		1.75	9.7	0.0755	0.959	7
alachlor	alginate	montmorillonite	1.75	14.9	0.0109	0.997	357
alachlor	alginate	kaolinite	1.75	6.9	0.0215	0.941	92
alachlor	alginate	Minugel	1.75	7.5	0.0304	0.972	46
alachlor	alginate	Diluex	1.75	6.9	0.0237	0.927	76
alachlor	pectin	montmorillonite	1.75	11.6	0.0341	0.996	37
alachlor	alginate–pectin	montmorillonite	1.75	9.4	0.0327	0.993	40
atrazine	alginate	montmorillonite	1.75	11.8	0.0121	0.992	290
atrazine	pectin	montmorillonite	1.75	12.4	0.0120	0.989	295
atrazine	alginate–pectin	montmorillonite	1.75	10.0	0.0119	0.987	300
alachlor/comb.	alginate	montmorillonite	1.75	1.94	0.0237	0.980	76
alachlor/comb.	alginate		1.75	2.74	0.0299	0.988	48
atrazine/comb.	alginate	montmorillonite	1.75	0.43	0.0036	0.908	3274
atrazine/comb.	alginate		1.75	0.74	0.0036	0.908	3274
alachlor	alginate	montmorillonite	0.5	6.6	0.0558	0.996	14

**Figure 10.** Higuchi plot for selected CRFs. Diameter for all CRFs is 1.5 mm unless indicated otherwise.

where  $f_t$  is the fraction of material released to time  $t$  and  $K_r$  is the release rate constant.

This expression can be written in a linear form as

$$(1 - f_t)^{1/3} = 1 - K_r t^{1/2} \quad (2)$$

By plotting the left-hand side of the above expression as a function of the square root of time, a linear plot with slope  $K_r$  is obtained (Figure 10).

The release constant,  $K_r$ , is defined as

$$K_r = (1/C_{a0}r_0)[D_m(2C_{a0} - C_{as})C_{as}]^{1/2} \quad (3)$$

where  $C_{a0}$  is the weight of the ai per unit volume of bead (sphere),  $C_{as}$  is the equilibrium solubility of the ai in the dissolution fluid,  $D_m$  is the diffusion coefficient of the ai in the bead (including the effect of porosity and tortuosity), and  $r_0$  is the bead radius.

Calculation of the diffusion constant,  $D_m$ , from the release rate  $K_r$  is possible, but the uncertainty in the values of  $C_{a0}$  and  $r_0$  make the results of questionable value. Nonetheless, the values calculated for  $D_m$  range from  $\sim 5 \times 10^{-4}$  to  $\sim 7.5 \times 10^{-6}$  cm<sup>2</sup>/s and are in general agreement with the diffusion coefficients of similarly sized molecules from alginate beads as reported in the literature (Hideo et al., 1984; Hannoun and Stephanopoulos, 1986; Oyaas et al., 1995a,b).

In a recent study on 2,4-D release from lignin-based CRFs (Hannoun and Stephanopoulos, 1986), 50% release times of 2,4-D ranged from  $\sim 4$  to 20 days, not very different than those observed for alachlor release (be-

tween several hours and over two weeks, depending on the CRF chosen; Table 3). The  $T_{50\%}$  for alachlor from an alginate CRF is  $\sim 45$  days. The addition of the various clays increases the  $T_{50\%}$  to  $\sim 78 \pm 20$  days, whereas addition of montmorillonite increases it to 357 days. For atrazine release from an alginate–montmorillonite CRF the  $T_{50\%}$  is 295 days. Interestingly, when combined together with dicamba in an alginate–montmorillonite CRF the  $T_{50\%}$  values for alachlor and atrazine are 63 and 3274 days, respectively. It is not immediately clear why such differences are observed, especially for atrazine.

Davis et al. (1997) studied the release of several herbicides from a series of commercial and slow-release formulations. They reported that after 24 h, 51% of the initial mass of alachlor was leached from a clay–alginate preparation [the type of clay was not reported; however, previous publications by one of the authors (Pepperman and Kuan, 1993) lead us to believe it is kaolinite], whereas we found release of 12, 28, and 35% of the initial mass of alachlor from montmorillonite–alginate, clay (other than montmorillonite)–alginate, and alginate preparations, respectively. The lower rates observed in the present study may be due to the methods employed for studying release. Davis et al. (1997) used a flow-through system in which the external solution was constantly leached, providing a larger concentration gradient with the internal solution of the preparation than would be obtained in our system where the external solution concentration increased with time. The addition of linseed oil to the clay–alginate formulation reduced the amount of alachlor released after 24 h to 12% as it provided a partitioning medium for the herbicide within the clay–alginate bead. The addition of montmorillonite (as opposed to kaolinite) to the alginate polymer resulted in a similar reduction in release rates of the active ingredients.

As mentioned previously, the advantage of CRFs may be in reduced leaching or reduced degradation in soils. The ability of various preparations described here to favorably influence these processes is presented in an accompanying paper Gerstl et al. (1998).

**Conclusions.** The use of clay and clay–polymer combinations for the preparation of CRFs was studied. In a series of laboratory experiments the release of the active ingredients into aqueous solution from the different preparations was determined.

It was found that the rate of release of the incorporated herbicides was a function of both the properties



of the herbicide and the composition of the CRF. The rate of release of herbicides was related to their aqueous solubility; the greater the solubility of a compound, the more rapid its release from the CRFs. The rate of release of the chemicals from pectin-based CRFs was generally greater than from alginate-based CRFs. This observation seems to be related to the internal pore structure of the CRFs. After gelling, pectin-based CRFs exhibited larger and wider pores than did alginate-based CRFs. The addition of clays to the CRFs generally had little or no effect on the rate of release of the ai with the exception of sodium montmorillonite, the addition of which was found to have a profound slowing effect on the release of alachlor. This was attributed to the sorption of the herbicide to the clay mineral and to plugging of the pores in the polymer matrix by the well-dispersed clay.

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