Controlled Release of Carbofuran from an Alginate–Bentonite Formulation: Water Release Kinetics and Soil Mobility

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The insecticide–nematicide carbofuran was incorporated in alginate-based granules to obtain controlled-release (CR) properties. The basic formulation [sodium alginate (1.61%)–carbofuran (0.59%)–water] was modified by addition of sorbents. The effect on carbofuran release rate, caused by the incorporation of natural and acid-treated bentonite (0.5 and 1.0 M H_2SO_4) in alginate formulation, was studied by immersion of the granules in water under shaking. The time taken for 50% of the active ingredient to be released into water, t_{50}, was longer for those formulations containing natural bentonite (6.1 h) or acid-treated bentonite (9.0 and 11.7 h for 0.5 and 1.0 M H_2SO_4 treatments, respectively) than for the preparation without bentonite (4.7 h). It appears from the results that the release of carbofuran from the various formulations is controlled by a diffusion mechanism according to the *n* values obtained, which were close to 0.5 in all cases. The mobility of carbofuran from alginate-based CR formulations was investigated by using soil columns packed with a clay soil (53% clay and 0.08% organic matter). Two alginate-based CR formulations containing natural bentonite or acid-treated bentonite (0.5 M H_2SO_4) were compared to technical grade carbofuran. The use of alginate-based CR formulations resulted in a reduction of the leached amount of carbofuran compared with the total amount of pesticide leached using the technical product (50 and 75% for CR granules containing natural and acid-treated bentonite, respectively). Alginate-bentonite CR formulations might be efficient systems for reducing carbofuran leaching in clay soils, which would reduce the risk of groundwater pollution.

Keywords: *Carbofuran; controlled release; bentonite; soil; sorption; leaching*

INTRODUCTION

Carbofuran [2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate] is a systemic insecticide–nematicide for soil and foliar treatments, which has been identified as potential leacher by using the groundwater ubiquity score (GUS) modeling technique (Gustafson, 1989). In addition, carbofuran is of environmental concern because of its acute toxicity (Tomlin, 1994) (e.g., for the rat, LD_{50} parameter is equal to 8 mg kg^{-1}).

The vast agricultural use of pesticides in southern Spain has important implications for the contamination of the groundwater system, which is used both for human consumption and for crop irrigation. Areas such as Almería (southeastern Andalucía) have low rainfall and intensive horticultural production based on plastic greenhouses, so this contamination of aquifer systems is an increasingly serious problem. Water analyses have shown pesticide residues in the Almeria wells, including the insecticide carbofuran at levels >0.5 μg L^{-1} (Parrilla et al., 1994; Chiron et al., 1995).

The mechanisms by which pesticides enter drinking water are mainly related to their physical–chemical properties, the methods by which the pesticides are used, and the environmental factors (Gustafson, 1993). The pollution of groundwater with pesticides is effected through runoff, leaching, and improper application.

Improper application and/or inappropriate disposal exarcebate the problem. The use of controlled-release (CR) formulations has an important potential in reducing the use and impact of pesticides in the environment. Natural and biodegradable polymers used in larger particle sized formulations or devices such as gels, cross-linked polymers, and composites represent an important trend in the preparation of CR systems of pesticides (Wilkins, 1995). Alginates have been used as matrices for CR of pesticides by several workers. Connick et al. (1984) have described a series of alginate–kaolin-based 2,6-dichlorobenzonitrile CR formulations. In aquatic release experiments, the authors reported that the sustained release of active ingredient becomes longer as kaolin concentration is increased. Pepperman et al. (1991) have described a series of alginate–kaolin-based metribuzin CR formulations. In a water release study, the authors reported little effect on release due to alginate type or to various organic adsorbents. Greater control of release rates could be obtained with the addition of charcoal or linseed oil to the formulations, although this resulted in some irreversible adsorption (Pepperman and Kuan, 1993).

Fernández-Pérez et al. (1998) reported that the addition of natural bentonite to alginate-based formulations reduced the rate of release of diuron in water. The authors also demonstrated that much greater control of diuron release rates could be obtained with the addition of acid-treated bentonite without irreversible adsorption. Moreover, this behavior seems to be in agreement with the result obtained in batch sorption

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experiments with bentonite samples and diuron, in which the sorption capacity of acid-treated bentonite for diuron was much greater than that obtained with natural bentonite.

In the present study, we consider the potential use of a native clay from the region, such as bentonite—a natural silicate with a lamellar structure containing montmorillonite as a major constituent—as a modifying agent in CR formulations of carbofuran. This material has been previously studied and characterized by the present authors (González-Pradas et al., 1991).

A second important aspect to consider in CR technology of pesticides is the study of their behavior in soils. Carbofuran is applied to foliage at 0.25–1.0 kg of active ingredient (ai)/ha for the control of insects and mites or to the seed furrow at 0.5–4.0 kg of ai/ha for the control of soil-dwelling nematodes or broadcast at 6–10 kg of ai/ha for the control of nematodes (Tomlin, 1994). Therefore, as carbofuran is used in a wide range of soil environments to control a variety of pests, it could be a good model compound to assess the value of the special formulations used in this study in reducing losses in soil.

Ali and Wilkins (1992) investigated the factors influencing release and distribution of carbofuran from granules on the basis of an lignin matrix system into soils. They reported that the study helps to quantify the effect of the soil environment on the release of carbofuran from the slow release formulation and, thus, it could be useful in the design and application of such methods.

The objectives of the present work were (i) to evaluate the effect of incorporation of natural and acid-treated bentonite into alginate-based formulations on the rate of carbofuran release and (ii) to evaluate the capacity of alginate—bentonite encapsulated CR formulations to reduce leaching of carbofuran.

MATERIALS AND METHODS

Chemicals. The materials used as sorbents for this series of experiments were a natural bentonite (98% montmorillonite, containing sodium as exchange ion) from Almería (Spain) (crushed to a particle size of <0.15 mm), previously studied by the present authors (González-Pradas et al., 1983), and two acid activated bentonite samples.

Acid activation of the bentonite was carried out in a boiling solution of H_2SO_4 (concentrations of 0.5 and 1.0 mol L^{-1}) for 1 h. In all cases the resulting samples were heated at 105 °C to constant weight. Chemical composition and textural properties of the samples were also previously studied by the present authors (González-Pradas et al., 1991). The two products so obtained and the natural bentonite are designated in the text B-0.5, B-1.0, and B, respectively.

Bentonite samples were analyzed by using standard methods. Sample pH was determined in a 1:2.5 (g/g) clay/water suspension using a glass electrode (Jackson, 1982); surface area was determined from N_2 adsorption isotherms using a surface analyzer from Micromeritics, model II-2370; cation exchange capacity (CEC) and exchange acidity were calculated by using the barium acetate method (Primo-Yúfera and Carrasco-Dorrién, 1981). All of these properties of the bentonite samples are shown in Table 1.

Analytical grade carbofuran (99.0%) was obtain from Riedel-de Haën (Seelze, Germany). Technical grade carbofuran (75.0%) was kindly supplied by Industrias Afrasa S.A. (Valencia, Spain). Solvents used in the mobile phase for HPLC determinations were HPLC grade acetonitrile (Riedel-De Häen) and water, demineralized Milli-Q quality (Millipore Corp., Milford, MA). Chemical products used in the preparation and evaluation of CR formulations were sodium alginate

Table 1. Characteristics of the Sorbents

sample[a]	pH	surface area (m² g⁻¹)	CEC (mequiv/100 g)	exchange acidity (mequiv/100 g)
B	8.31	72.7	65.6	22.3
B-0.5	2.78	183.0	76.9	67.4
B-1.0	2.68	298.8	73.7	71.7

[a] B, natural bentonite; B-0.5, acid-treated bentonite with 0.5 M H_2SO_4 solution; B-1.0, acid-treated bentonite with 1.0 M H_2SO_4 solution.

Table 2. Percentage (by Weight) of Component and pH of Dispersions Containing Carbofuran

sample[a]	carbofuran	sodium alginate	B	B-0.5	B-1.0	water	pH[b]
CA	0.59	1.61				97.80	8.20 (0.03)
CAB	0.92	1.61	2.65			94.82	7.92 (0.06)
CAB-0.5	0.92	1.61		2.65		94.82	4.26 (0.09)
CAB-1.0	0.92	1.61			2.65	94.82	4.16 (0.05)

[a] CA, carbofuran—alginate formulation; CAB, carbofuran—alginate—bentonite formulation; CAB-0.5, carbofuran—alginate—acid-treated bentonite with 0.5 M H_2SO_4 formulation; CAB-1.0, carbofuran—alginate—acid-treated bentonite with 1.0 M H_2SO_4 formulation. [b] Values in parentheses represent the standard deviation.

(medium viscosity = 3500 cP for 2% solution) and tripolyphosphate (90–95%) obtained from Sigma Chemical Co. (St. Louis, MO) and calcium chloride (95%) from Panreac (Barcelona, Spain).

Preparation and Evaluation of CR Formulations. The CR formulations were based on the gelling properties of the alginate in the presence of divalent cations. Formulations containing 16.1 g kg⁻¹ sodium alginate (A), natural bentonite (B), acid-treated bentonite samples (B-0.5 and B-1.0), and technical carbofuran (C) were made up in water (as shown in Table 2) and vigorously stirred for 1 h.

The alginate mixtures were dropwise added to a 300 mL gellant bath of 0.25 M CaCl₂ using the apparatus described by Connick (1982). The resulting beads were allowed to gel in the 0.25 M CaCl₂ solution for a total of 5 min, and then they were filtered and allowed to dry first at room temperature and then in an oven (40 °C) to constant weight. The products so obtained will be designated in the text CA, CAB, CAB-0.5, and CAB-1.0.

The actual concentration of carbofuran in the dry products was determined by dissolving the granules in a 0.03 M tripolyphosphate solution following an extraction into a water/methanol (80:20) mixture. The resulting extract was filtered and the insecticide concentration determined by high-performance liquid chromatography (HPLC). The HPLC operating conditions were as follows: separation by isocratic elution was performed on a 150 × 3.9 mm Nova-Pak LC-18 bonded-phase column (Waters, Millipore Corp.); sample volume, 20 µL; flow rate, 1.0 mL min⁻¹; and mobile phase, acetonitrile/water mix (55:45). Carbofuran was analyzed at 276 nm. External standard calibration was used, and three replicates were carried out for each formulation.

Experiment Carried out in Water. Release Experiments. An accurately weighed quantity of granules containing ~8.0 mg of carbofuran for each sample (three replicates) was added to 0.5 L of distilled water and placed into stoppered conical flasks. Flasks were shaken in a thermostated bath at 25 ± 0.1 °C. At different time intervals, 1-mL aliquots were removed for determination of carbofuran by HPLC using the method above-described, and unused sample portions were returned to the flasks.

In the final stage of the study, granules were removed from each flask to determine the amount of carbofuran that had remained incorporated in the granules. To normalize the release profile curves, the total amount of carbofuran released plus the extracted carbofuran remaining in the granules will be considered to be 100% of the active ingredient initially present in the granules.

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Table 3. Characteristics of the Soil Selected

soil property		sorption parameter	
pH (H$_2$O)	8.44	K_d (L kg^{-1})	1.47
organic matter (%)	0.08	r	0.98
clay content (%)	53.00		
CEC (mequiv/100 g)	10.63		
field capacity (% v/v)	38.00		
water saturation (% v/v)	52.00		

Experiments Carried out in Soil. The mobility of carbo-furan from alginate-based CR formulations was investigated by using soil columns. Two alginate-based CR formulations (CAB and CAB-0.5) were compared to the technical grade carbofuran. Sorption experiments were also carried out for determining the sorption capacity of the soil for carbofuran.

Static Experiments. Soil Characterization and Sorption Studies. The soil investigated was a Luvic Xerosol from the Almería region (southeastern Spain) used as an amended soil in greenhouses. Air-dried soil samples, particle size <2 mm, were analyzed according to standard methods. The pH was determined in a 1:2.5 soil/water suspension using a glass electrode (Jackson, 1982). Organic matter content was determined by using the Walkley–Black method (Walkley and Black, 1934), clay content by using the hydrometer method (Black et al., 1982), and CEC by using the barium acetate method (Primo-Yufera and Carrasco-Dorrién, 1981). Water saturation and field capacity were determined following the guidelines of Hall et al. (1977). All of these characteristics are shown in Table 3.

The sorption experiments were carried out as follows: 0.01 M CaCl$_2$ aqueous solutions containing initial carbofuran concentrations (C_0) between 1.45 and 23.45 mg L^{-1} were used. Aqueous suspensions of the samples were prepared by adding 25 mL of each carbofuran solution to 3.0 g of soil. They were then placed in several stoppered conical flasks and shaken in a thermostated shaker bath at 25 ± 0.1 °C. Preliminary experiments were conducted for various time intervals to determine when sorption equilibrium was reached. The time required for equilibrium to be reached between carbofuran sorbed and carbofuran in solution was 12 h. Following the equilibrium period, the adsorption systems were centrifuged at 9250g for 10 min, and the concentration of carbofuran in the supernatant solutions, C, was determined by HPLC using the method above-described. The amount of carbofuran sorbed (X) was calculated from the difference between the initial (C_0) and equilibrium pesticide solution concentrations (C). Blanks containing no carbofuran and three replicates of each sorption point were used for each series of experiments.

Mobility Experiments. (a) Column Preparation. Soil columns were prepared by splitting a poly(vinyl chloride) (PVC) pipe (7 cm internal diameter, 26 cm length) longitudinally and applying 2-mm-thick silicone ridges around the inside of the column at 5-cm increments to minimize boundary flow. The two parts of each column were then put together and sealed with waterproof adhesive paste. Nylon mesh with an effective pore diameter of 60 μm and lined with a layer of fiberglass wool was sealed to the bottom of each column to prevent displacement of the soil from the columns and to minimize the dead-end volume (Fleming et al., 1992). Each column contained, from the bottom to the top, a layer of acid-washed sand (1 cm) and soil (20 cm). The soil, screened through a 2-mm sieve, was added to the column in small increments to minimize particle size segregation, obtaining a final bulk density of 1.43 g cm^{-3}. This bulk density resulted in a column pore volume of ~0.16 L. Prior to application of the insecticide treatments, the columns were saturated with distilled water via capillarity and then left to drain for 24 h.

(b) Application of Insecticide to the Soil Columns. The insecticide–nematicide treatments were applied at a rate of 6.5 kg of ai ha^{-1}. This rate is commonly used for the control of nematodes in greenhouse soils and is enough to achieve adequate surface coverage. Each insecticide treatment, technical grade carbofuran and alginate-based CR formulations (CAB and CAB-0.5), was applied to duplicate soil columns. Technical

Table 4. Indicative Parameters of Controlled-Release Products (Dry Granule) Containing Carbofuran

sample[a]	carbo-furan[b] (%)	Ca^{2+} (%)	yield[c] (%)	av wt (mg/granule)	encap effic[d] (%)
CA	10.82 (0.12)	17.2 (0.20)	4.5	0.76 (0.08)	84.82
CAB	9.40 (0.19)	35.8 (0.98)	8.1	1.05 (0.12)	85.01
CAB-0.5	10.39 (0.21)	30.4 (0.52)	7.6	1.16 (0.10)	86.53
CAB-1.0	10.05 (0.12)	32.5 (0.73)	7.9	1.13 (0.05)	87.12

[a] CA, carbofuran–alginate formulation; CAB, carbofuran–alginate–bentonite formulation; CAB-0.5, carbofuran–alginate–acid-treated bentonite with 0.5 M H$_2$SO$_4$ formulation; CAB-1.0, carbofuran–alginate–acid-treated bentonite with 1.0 M H$_2$SO$_4$ formulation. [b] Values in parentheses represent the standard deviation [c] Yield = weight of dry product × 100/weight of formulation processed. [d] Encapsulation efficiency = (amount of pesticide in dry product/amount of pesticide in formulation processed) × 100.

grade carbofuran was applied following the next method: a methanol solution containing 10 mg of carbofuran was added to 50 g (0.5 cm) of acid-washed sand. The washed sand/insecticide mixture was left to dry overnight at room temperature before being added to the top of each column. After application of the pesticide, an additional 0.5 cm of washed sand was added to the top of the column. The alginate-based CR formulations (CAB and CAB-0.5) were evenly distributed on the sand layer. After that, an additional 1 cm of acid-washed sand was added to the top of the column.

(c) Leaching and Leachate Collection. The leaching solution used in all experiments was 0.01 M CaCl$_2$. This was done to simulate the soil solution and to prevent dispersion of the soil during the leaching procedure (Johnson and Pepperman, 1995). Leaching solution (1500 mL) was applied at a flow rate of 8 mL h^{-1} using a Gilson Minipuls 3 peristaltic pump (Gilson Medical Electronics, Middleton, WI). The time and volume of each leachate were recorded. Aliquots were taken from the leachates, passed through 0.5-μm PTFE filters, and injected directly into the HPLC system. At the end of the leaching procedure, the columns were allowed to drain for 48 h.

(d) Column Analysis. The columns were split vertically, and the soil was removed in 5-cm increments. Each fraction was dried at room temperature and homogenized. Subsamples of soil (10 g) were extracted in an ultrasound bath for 15 min with 25 mL of a methanol/water mixture (80:20), filtered through Whatman No. 42 paper, and analyzed by HPLC, as described above. The extraction efficiency was ~96%.

RESULTS AND DISCUSSION

CR Formulations. The characteristics of the algi-nate-based CR granules containing carbofuran are presented in Table 4. The granules were generally spherical in shape, and the white powder technical grade carbofuran was readily incorporated in the algi-nate matrix. The addition of bentonite to the alginate formulations led to larger and heavier granules that were more spherical and dried with less aggregation. It is also interesting to note from the data in Table 4 that inexpensive bentonite effectively increased gran-ules yields and reduced the amount of alginate in the final product, permitting us, in this way, to obtain a cheaper formulation.

Release Kinetics in Water. The cumulative release of carbofuran from alginate-based CR granules and the solubility profile for the technical grade carbofuran are shown in Figure 1. As can be seen, 99.0% of technical grade product is dissolved in <4 h, whereas at least 48 h is needed to release 93.0% of active ingredient from the alginate-based CR formulation CAB-1.0. For all formulations, a decline in the release of pesticide with time was observed. This result is probably due to an increase in the distance through
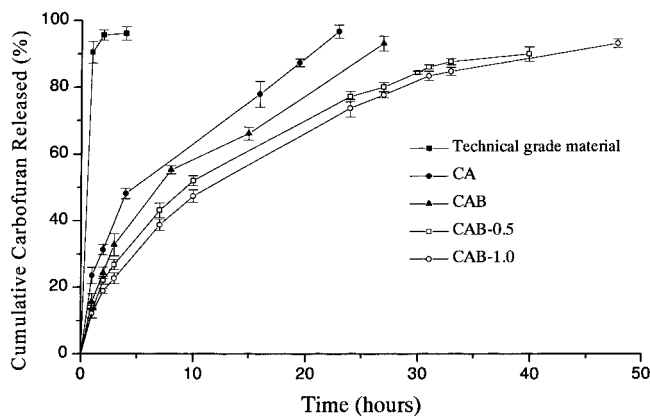
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Figure 1. Cumulative release of carbofuran from granules into static water (error bars represent the standard deviation of three replicates).

Figure 2. Sorption isotherm of carbofuran on the soil (error bars represent the standard deviation of three replicates).

Table 5. Constants from Fitting the Empirical Equation $M_t/M_0 = Kt^n$ to Release Data of Carbofuran into Static Water

product[a]	K^{b} (h^{-n})	n	r	t_{50} (h)
CA	0.23 ± 0.015	0.50 ± 0.06	0.996^{c}	4.73
CAB	0.16 ± 0.003	0.63 ± 0.01	0.999^{c}	6.10
CAB-0.5	0.14 ± 0.007	0.58 ± 0.02	0.996^{c}	8.98
CAB-1.0	0.12 ± 0.003	0.58 ± 0.01	0.999^{c}	11.71

[a] CA, carbofuran−alginate formulation; CAB: carbofuran−alginate−bentonite formulation; CAB-0.5, carbofuran−alginate−acid-treated bentonite with 0.5 M H_2SO_4 formulation; CAB-1.0, carbofuran−alginate−acid-treated bentonite with 1.0 M H_2SO_4 formulation. [b] These values represent the standard errors. [c] Significant at the 0.001 probability level.

which dissolved molecules have to diffuse as the depleted zone advances to the center of the matrix. In diffusion-controlled matrix systems this usually means that the release is proportional to the square root of time (Baker, 1987).

The release data were analyzed by applying the empirical equation proposed by Ritger and Peppas (1987)

$$M_t/M_0 = Kt^n \qquad (1)$$

where M_t/M_0 is the percentage of active ingredient release at time t, K is a constant that incorporates characteristics of the macromolecular network system and the active ingredient, and n is a diffusional parameter that is indicative of the transport mechanism. The values of K and n obtained from the initial 60% of released carbofuran, together with the correlation coefficients, were obtained using the curve fitting utility of Fig.P software (version 6.0 c, Biosoft, 1992) and are presented in Table 5. As can be seen, the release profiles of carbofuran formulations fit well to the empirical equation, as shown by the values obtained for the correlation coefficients given in Table 5. The n values range from 0.50 for the CA formulation up to 0.63 for the CAB formulation. Values of n close to 0.5 are indicative of Fickian diffusion in spherical monolithic matrices; that is, the release is diffusion-controlled (Ritger and Peppas, 1987). The complexity of the heterogeneous system involved, together with the capacity of bentonite samples to interact with the diffusion agent, could explain some deviation from the n value as indicated above.

From the constants in Table 5, the t_{50} values (the time taken for 50% of the carbofuran to be released) were
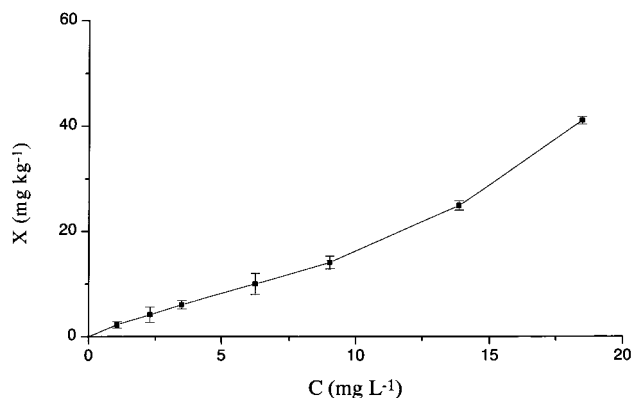
calculated for the alginate-based CR granules. These values are also shown in Table 5. The t_{50} values range from 4.73 h for the CA formulation to 11.71 h for the CAB-1.0 formulation. The CR granules can be ranked in order of increasing t_{50} values as follows:

$$CA < CAB < CAB\text{-}0.5 < CAB\text{-}1.0$$

The t_{50} values obtained could be explained if we take into account one of the factors that affect the diffusion process, that is, the sorption capacity of the modifying agents, natural and acid-treated bentonite. The extent of interaction between the modifying agents and the pesticide will affect the release of carbofuran from the alginate-based granules. This aspect could be quantified with sorption experiments of carbofuran with natural and acid-treated bentonite. A high sorption capacity would result in a slower release of pesticide.

Previous studies in which batch sorption experiments were carried out with natural and acid-treated bentonite as sorbents and carbofuran as solute showed that the sorption capacity (K_f) of the acid-treated bentonite B-1.0 for carbofuran ($K_f = 13.5$ mg kg^{-1}) was higher than that obtained with the B-0.5 bentonite sample ($K_f = 8.5$ mg kg^{-1}). In the same study it was also reported that the sorption capacities of the acid-treated bentonite samples were higher than that obtained with natural bentonite ($K_f = 0.48$ mg kg^{-1}) (Martinez-López, 1997). Sulfuric acid treatments stronger than 1.0 M to the bentonite resulted in lower efficiencies of pesticide sorption due to the partial destruction of the bentonite structure (González Pradas et al., 1988). The results obtained seem to be in agreement with the fact that granules containing natural bentonite as modifying agent (CAB) produce a slower release rate compared with that without bentonite (CA). In addition, the incorporation of the B-1.0 sample produces the slowest value of t_{50}. The variety shown for t_{50} values in Table 5 might be useful for selecting the most appropriate formulation depending on the environmental factors.

Experiments Carried out in Soil. *Static Studies. Sorption Studies.* Figure 2 shows the sorption isotherm of carbofuran on the soil. According to the slope of the initial portion of the curve, this isotherm may be classified as L type of the Giles classification (Giles et al., 1960), which suggests that the soil has a medium affinity for carbofuran and also that there is no strong competition from the solvent for sorption sites. To evaluate the sorption capacity of the soil for carbofuran, the experimental data points were fitted to the Henry

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Table 6. Mean of Values of Extracted Carbofuran from the Soil Segments and Total Percentages of Carbofuran Recovered from the Granules, Soil, and Leachates

	mg kg^{-1}		
depth (cm)	technical grade material[a]	CAB[b]	CAB-0.5[b]
0–5	0.40 (0.07)	0.22 (0.06)	0.25 (0.08)
5–10	0.08 (0.01)	0.15 (0.02)	0.10 (0.02)
10–15	0.08 (0.02)	0.12 (0.03)	0.06 (0.01)
15–20	0.05 (0.01)	0.07 (0.01)	0.05 (0.01)
% carbofuran recovered			
in soil	1.70	1.39	1.29
in leachate	75.40	38.05	18.55
in granules		18.89	43.45

[a] Values in parentheses represent the standard deviation. [b] CAB, carbofuran–alginate–bentonite formulation; CAB-0.5, carbofuran–alginate–acid-treated bentonite with 0.5 M H_2SO_4 formulation.

equation (Voice et al., 1983)

$$X = K_d C \tag{2}$$

where X is the amount of insecticide sorbed per kilogram of sorbent (mg kg^{-1}), K_d is a parameter related with the solute partitioning between the sorbent and the solvent (L kg^{-1}), and C is the equilibrium solution concentration (mg L^{-1}).

The K_d value obtained was 1.47 L kg^{-1}, value of the same order of those shown in the literature, 0.29 L kg^{-1} on Riverhead soil (0.023% organic matter) and 0.35 L kg^{-1} on Valois soil (0.035% organic matter) (Dowling et al., 1994). These values represents a low ability of the soils with low organic matter for retain carbofuran molecules in its structure.

Mobility Studies. The amount of carbofuran recovered per kilogram in each portion of the columns is presented in Table 6. In addition, the total percentages of carbofuran recovered in the soil, leachate, and granules referred to the total amount of insecticide applied in the experiments are also indicated in Table 6.

As can be seen, 1.7% of the insecticide is recovered in the soil when carbofuran is applied as technical product, whereas 75.4% of the total amount applied is present in the leachate. The presence of this high amount of carbofuran in the leachate was expected according to the low value of K_d obtained from the sorption isotherm. When carbofuran was applied as alginate-based CR formulations (CAB and CAB-0.5), the amount of active ingredient remaining in the soil tended to decrease with depth. In addition, the amount of carbofuran recovered in the leachates was less in the soil columns treated with alginate-based CR formulations than in those treated with technical grade product (38.1% for the treatment with CAB granules and 18.5% for the columns treated with CAB-0.5 granules).

The characteristics of release of carbofuran from alginate-based CR formulations in soil under dynamic conditions are related to those obtained in water under static conditions; that is, the release of carbofuran from the alginate-based CR formulation CAB-0.5 (56.6% in 8 days) is slower than that observed for the alginate-based CR formulation CAB (81.1% in 8 days). In addition, the release of carbofuran from CAB and CAB-0.5 granules in the soil is much slower than that observed in water. The time taken for 56.6% of the active ingredient to be released from alginate-based CR formulation CAB-0.5 in water under static conditions was 14.5 h, and the time taken for 81.1% of the active
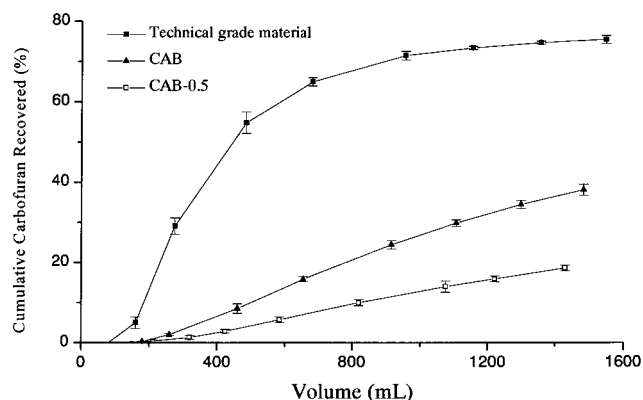

Figure 3. Cumulative carbofuran leached from technical product, CAB and CAB-0.5, formulations applied in the soil (error bars represent the standard deviation of two replicates).

ingredient to be released from CAB granules in water was 13.2 h. This fact might be explained if we consider that an occlusion of the formulation surface by soil particles takes place, as well as a slower diffusion within the soil as compared to water (Ali and Wilkins, 1992; Wilkins, 1989). Soil water solutes may also retard movement of pesticides into the aqueous phase (Sharm et al., 1985; Connick et al., 1984). The granules recovered from the soil did not show any signs of disintegration or major degradation at the end of the experiment. The integrity of the CR granule is an important feature of nonerodible CR formulations, as unpredictable fracture formation and breakage would increase the release surface of the matrix and, thus, the amount of active ingredient released. Increasing the surface concentration of a nonbound form of a soil insecticide–nematicide is important from an efficacy standpoint. Evidence from the above-discussed water release studies and the breakthrough data indicate that the carbofuran present in the CR granules will be gradually and completely released. Some irreversible adsorption has been reported in other papers (Pepperman and Kuan, 1993).

The cumulative carbofuran leached from soil columns treated with technical grade carbofuran and alginate-based CR formulations (CAB and CAB-0.5) is shown in Figure 3. Significant differences were noted in the leaching patterns of the formulations investigated. The ranking of the formulations investigated in terms of percentage leached was as follows:

CAB-0.5 (18.6%) < CAB (38.1%) <
technical grade product (75.4%)

For the technical grade product, carbofuran was first detected in the leachate at ~0.16 L (equivalent to one pore volume). The amount of leached carbofuran increased steadily over time to ~75.4% of the total applied by the termination of the experiment. For the alginate-based formulations CAB and CAB-0.5, carbofuran was detected later in the leachate (0.18 L for CAB and 0.21 L for CAB-0.5). The amount leached from CAB formulation increased to 38.1% of that applied by the termination of the leaching procedure. Carbofuran present in the CAB-0.5 formulation was leached to a much smaller extent, with a total amount leached of 18.6%. It can be appreciated (Figure 3) that the use of alginate-based CR formulations reduces leaching of carbofuran to a very acceptable level during the greater part of the experiment compared to the technical grade product. Prevention of pesticide leaching should focus

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on reduction of breakthrough from the soil columns. According to the results obtained from the study with the CAB and CAB-0.5 granules, it is possible that CR formulations could be of benefit in this respect, because they reduce the rate of carbofuran released to the soil. This fact results in a reduction of the potential environmental hazard of carbofuran.

Conclusions. The use of untreated bentonite and acid-treated bentonite samples as modifying agents of an alginate−carbofuran formulation reduces the release rate of carbofuran in comparison with the technical product and the alginate formulation without bentonite. It appears from the results that the release of carbofuran from the various formulations is controlled by a diffusion mechanism according to the *n* values obtained, which are close to 0.5 in all cases. The release of the active ingredient from alginate-based CR granules in water is affected not only by the addition of natural bentonite to the alginate−carbofuran-based formulations but also, and to a greater extent, by the addition of the acid-treated bentonite sample (B-1.0). The use of alginate-based CR formulations resulted in a reduction of the leached amount of carbofuran compared with the total amount of pesticide leached using the technical product (50 and 75% for CR granules containing natural and acid-treated bentonite, respectively). Alginate−bentonite CR formulations might be efficient systems for reducing carbofuran leaching in clay soil, which would reduce the risk of groundwater pollution.

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