

Use of Bentonite and Activated Carbon in Controlled Release Formulations of Carbofuran

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Controlled release systems (CRS), unlike the conventional formulations, facilitate a gradual and controlled discharge of the pesticides, reducing the losses by evaporation and leaching and minimizing pesticide pollution. In this study, carbofuran—an insecticide–nematicide identified as a groundwater pollutant—was incorporated in alginate-based granules to obtain controlled release properties. The effect on carbofuran release rate caused by the incorporation of bentonite, activated carbon, and different mixtures of both sorbents in alginate basic formulation was studied by immersion of the granules in water. The water uptake, sorption capacity of the sorbent, permeability, and time taken for 50% of the active ingredient to be released into water, T_{50} , were calculated by the comparison of the preparations. T_{50} values were higher for those formulations containing bentonite and/or activated carbon (T_{50} values range from 14.76 h for the alginate formulation containing only bentonite as the sorbent to 29.5 weeks for the alginate formulation containing only activated carbon as the sorbent) than for the preparation without these sorbents (11.72 h). On the basis of a parameter of an empirical equation used to fit the insecticide–nematicide release data, it appears that the release of carbofuran from the various formulations into water is controlled by a diffusion mechanism. The sorption capacity of the sorbents for carbofuran was the most important factor modulating carbofuran release. In addition, it was observed that there is a linear correlation of the T_{50} values and the content of activated carbon in dry granules.

KEYWORDS: Carbofuran; controlled release; activated carbon; bentonite; sorption

INTRODUCTION

Contamination of groundwater of agricultural origin is an environmental and public health concern throughout the world, because groundwater is a major source of water for different uses, including drinking water. Pesticides from the carbamate group have been found in the environment, especially in aquatic habitats where many of these pesticides have a high potential of contamination (1–3).

Carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-ylmethylcarbamate) is a systemic carbamate insecticide–nematicide for soil and foliar treatments (4), which has been identified as a potential leacher by using the groundwater ubiquity score modeling technique (5). In addition, carbofuran is known to be a more persistent insecticide than other carbamate or organophosphorus insecticides (6). Getzin (7) reported that the half-life of carbofuran in soil ranged from 3 to 50 weeks, and the degradation rate was found to be from seven to 10 times faster in alkaline soils (pH 7.9) than in acidic or neutral soil (pH 4.3–6.8). This has resulted in carbofuran being widely detected in groundwater (1, 2, 8, 9) and in surface water (3, 10).

The use of controlled release formulations (CRFs) has an important potential in reducing the use and impact of pesticides in the environment. Controlled release (CR) pesticide formulations have several advantages in relation to standard formulations, including increased safety to the user and nontarget organisms, a reduction in the amount of the pesticide applied, and a diminution in leaching potentials (11–13). Many different types of CR systems have been developed for their use in agriculture (14, 15), including those that use a natural polymer like alginate as a matrix for CR of pesticides (16–18). The use of natural polymers in the preparation of CR systems is of special interest due to the possible biological degradation of the matrices and the relatively low cost of some of the raw materials (19).

Several modifying agents have been used in CR systems to obtain different release profiles, including those that use natural and activated clays, humic acid, or linseed oils (17, 20–23). The present study evaluates the potential use of a natural bentonite (sorbent with a low sorption capacity), an activated carbon (sorbent with a high sorption capacity), and different mixtures of both sorbents as modifying agents in alginate-based CRFs of carbofuran. With the use of these materials, we intend to reach a higher variety of carbofuran release profiles. This

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fact would permit us to extend those profiles obtained in a previous paper where activated bentonites were used as modifying agents (21). Bentonite is a layer silicate mineral containing montmorillonite as a major constituent. This material has been previously studied and characterized (24), and it was used as an inorganic model compound to study the interactions between the soil inorganic fraction and the pesticides (25). Commercial activated carbons are usually derived from natural materials such as coconut shell, wood, or coal and are manufactured to produce precise surface properties. The activated carbon adsorption process has been used as an effective method to remove residual pesticides and other hazardous chemicals in raw water during drinking water treatment (26, 27).

The objective of the present work was to evaluate the effect of incorporation of bentonite, activated carbon, and different mixtures of both sorbents into alginate-based formulations on the rate of carbofuran release. We also intend to obtain a deeper understanding of the release mechanism of the insecticide from the investigated formulations. Therefore, CR formulations were prepared incorporating the carbofuran-bentonite-activated carbon mixtures into alginate granules by using calcium chloride as the gellant. The release rate of active ingredient from alginate-based CR granules was studied using a static immersion water test. The factors influencing the CR of carbofuran were examined by studying the interactions between the active ingredients and the sorbents. In addition, the correlation between the characteristic release parameter (T_{50}) and the granules properties such as the content of activated carbon (Q) was studied.

MATERIALS AND METHODS

Chemicals. The sorbent materials used were a natural bentonite (98% montmorillonite, containing sodium as exchange ion) from Almería (Spain), crushed to a particle size <0.15 mm, previously described by González-Pradas et al. (24), and a commercial powdered activated carbon from Panreac S.A. (Barcelona, Spain). In both cases, the samples were heated at 105 °C to constant weight. The materials are labeled in the text as B and C, respectively.

Technical grade carbofuran (75.0%) was kindly supplied by Afrasa, S.A. (Valencia, Spain). Solvents used in the mobile phase for high-performance liquid chromatography (HPLC) determinations were as follows: HPLC grade acetonitrile from Merck (Darmstadt, Germany) and water, demineralized milli-Q quality from Millipore (Billerica, United States). Chemical products used in the preparation and evaluation of CR formulations were as follows: sodium alginate (medium viscosity, 3.5 kg m⁻¹ s⁻¹ for 2% solution) and tripolyphosphate (90–95%) obtained from Sigma Chemical Co. (St. Louis, MO) and calcium chloride (95%) from Panreac S.A. (Barcelona, Spain).

Physicochemical Analysis of Bentonite and Activated Carbon. Bentonite and activated carbon samples were analyzed by standard methods. The density was determined using a pycnometer of He from Micromeritics, model AccuPyc 1330. The specific surface area and microporous volume were determined from N₂ adsorption isotherms using a surface analyzer from Micromeritics, model II-2370. The pore size distribution, for pores on a range of mesoporous and macroporous, was determined from intrusion and extrusion of mercury porosimetry, using a porosimeter of Hg from Micromeritics, model Autopore III. The sample pH was determined in experimental sorption conditions for blanks containing no carbofuran using a glass electrode (28). All of these characteristics of the bentonite and activated carbon samples are shown in Table 1.

Preparation of CRFs. The CRFs prepared were based on the gelling properties of the alginate in the presence of divalent cations. Formulations containing different percentages of technical grade carbofuran (Ca), sodium alginate (A), bentonite (B), and/or activated carbon (C) were made up in water (as shown in Table 2) and vigorously stirred for 1 h. The pH was measured in these formulations, and the values obtained are also shown in Table 2.

Table 1. Characteristics of the Sorbents

sample	pH	density (g cm ⁻³)	surface area (m ² g ⁻¹)	volume (mL g ⁻¹)		
				microporous	mesoporous	macroporous
B	8.60	2.35	70.27	0.028	0.100	0.458
C	7.65	1.79	727.27	0.286	0.197	1.766

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

formulation	technical carbofuran (%)	Na- alginate (%)	B (%)	C (%)	water (%)	pH
CaA	0.33	1.32			98.35	7.40 (0.13) ^a
CaAB	1.43	1.24	4.46		92.86	7.97 (0.03)
CaABC ₁₀	1.61	1.40	4.22	0.79	91.98	8.38 (0.05)
CaABC ₂₀	1.61	1.40	3.47	1.54	91.97	8.58 (0.07)
CaABC ₃₀	1.61	1.40	2.70	2.30	92.00	8.84 (0.02)
CaABC ₄₀	1.61	1.40	2.00	3.07	91.92	9.06 (0.05)
CaAC ₆₅	1.61	1.40		5.00	91.99	9.62 (0.06)

^a Values in brackets represent the standard deviation. Abbreviations: CaA, carbofuran-alginate; CaAB, carbofuran-alginate-bentonite; CaABC₁₀, carbofuran-alginate-bentonite-10% of activated carbon in dry formulation; CaABC₂₀, carbofuran-alginate-bentonite-20% of activated carbon in dry formulation; CaABC₃₀, carbofuran-alginate-bentonite-30% of activated carbon in dry formulation; CaABC₄₀, carbofuran-alginate-bentonite-40% of activated carbon in dry formulation; CaAC₆₅, carbofuran-alginate-activated carbon.

The alginate mixtures (100 g) were dropwise added to a 300 mL gellant bath of 0.25 M CaCl₂ using the apparatus described by Connick (29). The resulting beads were allowed to gel in the 0.25 M CaCl₂ solution for a total of 20 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 labeled in the text as CaA, CaAB, CaABC₁₀, CaABC₂₀, CaABC₃₀, CaABC₄₀, and CaAC₆₅.

The average diameter of dry granules was determined using a Stereoscopic Zoom Microscope from Nikon, model SMZ1000, provided with a camera PixellINK (Megapixel FireWire Camera) model PL-A662.

Analysis of Carbofuran and Calcium in Granules. The actual concentration of carbofuran in the dry products was determined by dissolving 5 granules in a 0.03 M tripolyphosphate solution (5 mL) following an extraction into a water:methanol (80:20) mixture (100 mL) using an ultrasound bath for 15 min. The resulting extract was filtered using nylon filters (0.45 μm), and the pesticide concentration was determined by HPLC. The HPLC operating conditions were as follows: separation by isocratic elution was performed on a 150 mm × 3.9 mm Nova-Pack LC-18 bonded phase column from Waters (Milford, United States); sample volume, 20 μL; flow rate, 1.0 mL min⁻¹; and the mobile phase, an acetonitrile–water mix (55:45). Carbofuran was analyzed at 276 nm, its wavelength of maximum absorption. External standard calibration was used, and three replicates were carried out for each formulation. The calcium content was also determined in the extract by atomic absorption spectrometry using a 1100 B Perkin-Elmer spectrometer.

Water Uptake Tests. The water uptake was measured for granules using the method of Franson and Peppas (30). Granules were immersed in water using stoppered conical flasks and shaken in a thermostatic bath at 25 ± 0.1 °C. Then, they were removed periodically (for intervals, see the Results and Discussion section). The excess water was blotted from the surface of the granules using filter paper, and after that, granules were weighed. Three replicates (10 granules in each replicate) were carried out. The granules were then allowed to dry, first at room temperature and then in an oven (40 °C) to constant weight, so the water uptake (g/g dry granule) could be calculated.

Sorption Studies. The sorption experiments were carried out as follows: aqueous solutions containing initial carbofuran concentrations (C₀) ranging between 2 and 234 mg L⁻¹ were prepared. Amounts of

Table 3. Characteristics of CR Granules Containing Carbofuran

formulation	carbofuran (%)	Ca ²⁺ (%)	average weight (mg/granule)	average diameter (mm/granule)	encapsulation efficiency ^a (%)
CaA	7.05 (0.12) ^b	10.73 (1.12)	0.43 (0.05)	0.67 (0.05)	70.05
CaAB	11.71 (0.15)	4.86 (0.37)	1.11 (0.09)	1.01 (0.06)	93.13
CaABC ₁₀	12.42 (0.32)	4.16 (0.46)	1.97 (0.13)	1.25 (0.03)	93.91
CaABC ₂₀	12.63 (0.27)	4.39 (0.42)	2.22 (0.06)	1.35 (0.05)	94.98
CaABC ₃₀	12.86 (0.21)	5.02 (0.40)	2.42 (0.08)	1.54 (0.02)	94.71
CaABC ₄₀	12.95 (0.13)	4.64 (0.31)	2.26 (0.04)	1.64 (0.03)	95.17
CaAC ₆₅	12.89 (0.29)	4.34 (0.34)	2.33 (0.03)	1.82 (0.07)	95.86

^a Encapsulation efficiency = (amount of pesticide in dry product/amount of pesticide in formulation processed) × 100. ^b Values in brackets represent the standard deviation.

3.0 g of bentonite sample or 0.05 g of activated carbon sample and 25 or 250 mL, respectively, of a carbofuran solution were placed in stoppered conical flasks and shaken in a thermostated bath at 25 ± 0.1 °C. Preliminary experiments were conducted for various time intervals to determine when the sorption equilibrium was reached. The time required for equilibrium to be reached between carbofuran sorbed and carbofuran in solution was 14 and 24 h for sorption of the carbofuran on bentonite and activated carbon, respectively. After they were shaken, the solutions were centrifuged and the concentration of carbofuran in the supernatant was determined by HPLC using the method described above. The carbofuran sorbed was calculated from the difference between initial and final solution concentrations. Blanks containing no carbofuran and three replicates of each sorption point were used for each series of experiments.

Desorption experiments were carried out for activated carbon by adding 125 mL of water to the stoppered conical flasks containing the highest initial carbofuran concentration ($C_0 = 234 \text{ mg L}^{-1}$), after the removal of the 50% sorption supernatant. This system was again shaken for a 24 h period to establish the new equilibrium. This treatment was also followed by centrifugation and determination of the new equilibrium concentration in the supernatant. The amount of carbofuran desorbed in the first rinse was calculated. This process was repeated seven times. Blanks containing no carbofuran were used for each case, and all desorption experiments were carried out in triplicate.

Water Release Kinetics. An accurately weighed quantity of dry CR granules containing about 8.0 mg of carbofuran was added for each sample (three replicates) to 500 mL of distilled water and placed into stoppered conical flasks. The systems were shaken in a thermostated bath at 25 ± 0.1 °C. At different time intervals, aliquots of 1 mL were removed for determination of carbofuran by HPLC using the method described above; unused sample portions were returned to the flasks.

RESULTS AND DISCUSSION

CRFs. Characteristics of alginate-based CR granules containing carbofuran are presented in **Table 3**. The granules were generally spherical in shape, and the technical grade carbofuran was readily incorporated in the alginate matrix, obtaining granules of size between 0.67 and 1.82 mm. The pesticide content of the dried granules is adequate for a practical agricultural application where good coverage is needed. The addition of activated carbon to the alginate formulation led to larger granules. In all granules containing bentonite and/or activated carbon, the encapsulation efficiency was higher than 93.13%, the higher values corresponding to the formulations prepared with a higher percentage of activated carbon (95.86% for CaAC₆₅).

Water Uptake. The water uptake of the granules vs time is shown in **Figure 1**. Water uptake curves were characterized by a fast initial uptake of water by the granules, after which an apparent equilibrium or a slow water uptake was observed. In granules containing bentonite and/or activated carbon (CaAB, CaABC₁₀, CaABC₂₀, CaABC₃₀, CaABC₄₀, and CaAC₆₅), the higher values of water uptake corresponded to the formulations prepared with a higher percentage of activated carbon. The lower

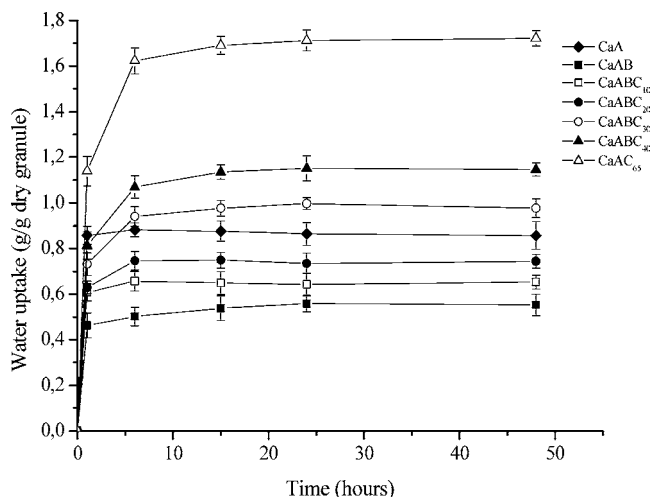


Figure 1. Water uptake of carbofuran granules over time (error bars represent the standard deviation of three replicates).

density of the activated carbon in comparison with the bentonite (**Table 1**), together with the higher percentage of activated carbon in granules, may be responsible for the higher water uptake. The addition of activated carbon to the alginate formulation generates a greater percentage of microporosity and produces an increase in the specific surface area of the granules. The presence of a higher amount of microporosity in granules could increase the amount of water uptake by formulations containing activated carbon as the modifying agent. The extent of swelling of the bentonite and/or activated carbon determines the volume occupied in the matrix and the area that can interact with the diffusing molecules of pesticide. Thus, water uptake and intensity of interactions of the carbofuran with either bentonite and/or activated carbon could affect the diffusion through the granules, and hence, the release of the active ingredient.

Sorption Studies. The sorption isotherms of carbofuran on the bentonite and activated carbon samples studied are shown in **Figure 2**. According to the slope of the initial portion of the curves, the isotherm corresponding to the sorption of carbofuran on the bentonite sample (**Figure 2a**) shows a decreased slope in the initial portion of the curve and may be classified as L type of the Giles classification (31). This suggests that the bentonite sample has a medium affinity for carbofuran and that no strong competition from the solvent for sorption sites occurs. However, the isotherm corresponding to the sorption of carbofuran on the activated carbon (**Figure 2b**) may be classified as H type of the Giles classification, which suggests that the sample of activated carbon has a high affinity for this pesticide. The curve tends to define a plateau, suggesting the formation of a complete monolayer of carbofuran molecules covering the adsorbent surface.

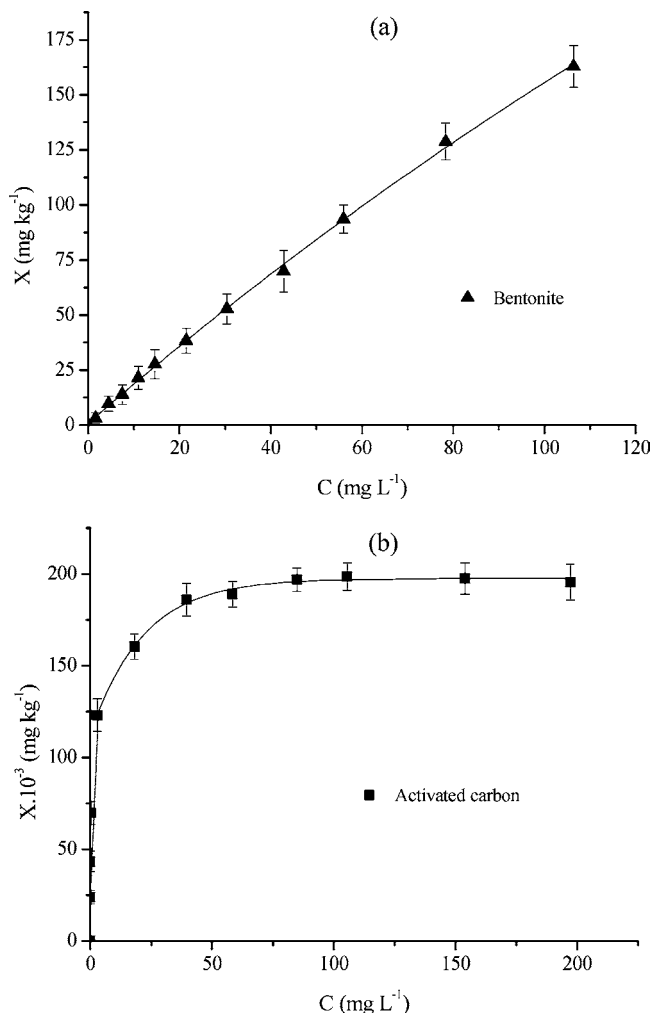


Figure 2. Sorption isotherms for carbofuran on bentonite (a) and activated carbon (b) samples (error bars represent the standard deviation of three replicates).

Table 4. Freundlich Coefficients, K_f and n_f , for the Sorption of Carbofuran on the Sorbents Samples

sample	K_f (mg kg ⁻¹)	n_f	r
bentonite	2.26 ± 0.02 ^a	0.93 ± 0.01	0.999 ^b
activated carbon	99.40 × 10 ³ ± 1.04	0.15 ± 0.02	0.993 ^b

^a These values represent the 95% confidence limits. ^b Significant at the 0.001 probability level.

The sorption isotherms in **Figure 2** were compared using the K_f parameter of the Freundlich equation (32). The linear form of this equation is

$$\log X = \log K_f + n_f \log C \quad (1)$$

where X is the amount of carbofuran sorbed (mg kg⁻¹ of sorbent), C is the equilibrium solution concentration (mg L⁻¹), and K_f and n_f are constants that characterize the sorption capacity of the pesticide. The constant K_f is the amount of pesticide sorbed for an equilibrium concentration of 1 mg L⁻¹, and n_f is a measure of the intensity of adsorption and reflects the degree to which adsorption is a function of the concentration (33). The K_f and n_f values were calculated from the least-squares method applied to the linear form of the Freundlich equation, and their values are summarized in **Table 4**. The correlation coefficients (r) were in all cases greater than 0.99, the correlation being significant at $p = 0.001$.

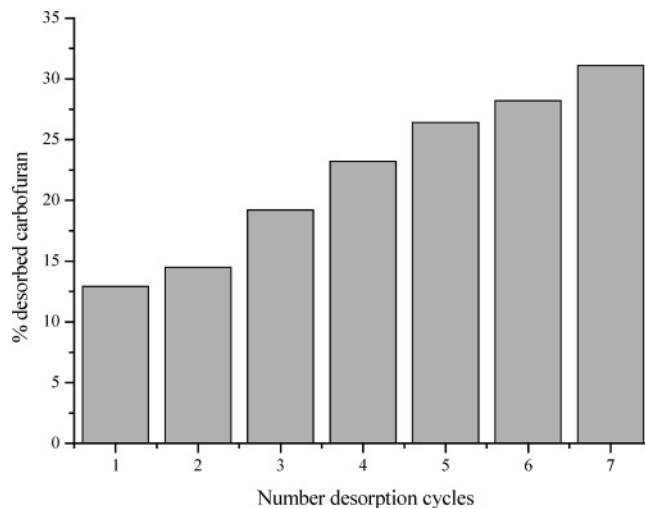


Figure 3. Percentage of desorbed carbofuran after seven desorption cycles.

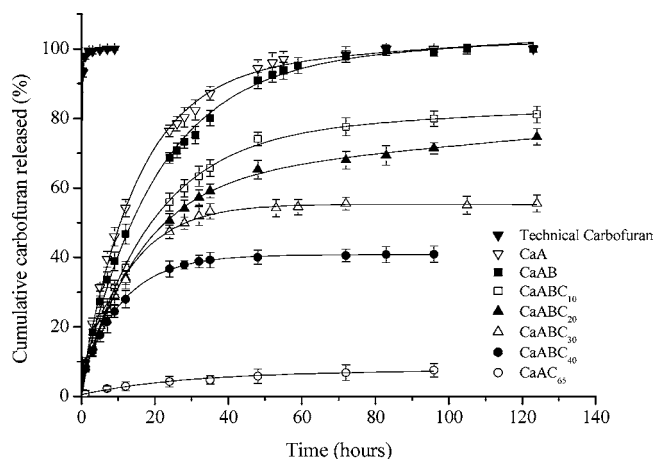


Figure 4. Cumulative release of carbofuran from granules into static water (error bars represent the standard deviation of three replicates).

As can be seen from **Table 4**, the K_f value for sorption of carbofuran on activated carbon is approximately 10⁴ times greater than that obtained for the sorption of carbofuran on a bentonite sample. The higher porosity and surface area (**Table 1**) of the activated carbon as compared with that obtained for the bentonite sample could explain to the higher sorption capacity of activated carbon sample for carbofuran. The high surface area of activated carbon origins a greater sorption takes place, that is, a higher sorption capacity of activated carbon for carbofuran.

The accumulated percentage of desorbed carbofuran from the activated carbon, after seven desorption cycles, is presented in **Figure 3**. As it can be seen from this figure, although the period of time employed is not enough for the total desorption of carbofuran to the solution, the percentage of carbofuran desorbed is higher when the number of desorption cycles increases, from 12.9% of desorbed carbofuran after the first cycle to 31.1% in the seventh cycle.

Release Studies. The cumulative release of carbofuran from alginate-based CR granules and the solubility profile for technical grade carbofuran are shown in **Figure 4**. As can be seen, 100% of technical grade product is dissolved in less than 5 h, while it takes at least 83 h to release the same percentage of active ingredient from the alginate-based CR formulation CaA. For the formulations containing bentonite and/or activated carbon as modifying agent, 100% of carbofuran is released in

Table 5. Constants from Fitting the Higuchi Equation to Release Data of Carbofuran in Water and Matrix Permeability Parameter

formulation	$K_H \times 10^2 \text{ (h)}^{-1/2}$	r	$P \times 10^4 \text{ (mg h}^{-1} \text{ mm}^{-1})$
CaA	5.62 ± 0.007^a	0.999 ^b	0.68 ± 0.003
CaAB	5.03 ± 0.013	0.999 ^b	1.55 ± 0.009
CaABC ₁₀	3.71 ± 0.008	0.999 ^b	1.26 ± 0.005
CaABC ₂₀	3.14 ± 0.015	0.999 ^b	0.97 ± 0.011
CaABC ₃₀	2.15 ± 0.020	0.991 ^b	0.44 ± 0.014
CaABC ₄₀	2.03 ± 0.013	0.996 ^b	0.34 ± 0.010
CaAC ₆₅	0.26 ± 0.011	0.997 ^b	0.0028 ± 0.008

^a These values represent the standard error. ^b Significant at the 0.001 probability level.

96 h for formulation CaAB, while it takes the same time to release 7.54% of active ingredient from the alginate-based CR formulation CaAC₆₅.

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 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 (34). Formulations such as those here studied could be described as systems containing finely divided solute particles, which are uniformly dispersed within the matrix phase. Higuchi originally analyzed analogous systems, such as drugs dispersed in a stationary matrix, e.g., semisolid ointment. The application of the model proposed by this author, involves that, (i) a pseudo-steady state exists, (ii) the active ingredient particles are small as compared to the average distance of diffusion, (iii) the diffusion coefficient is constant, and (iv) a perfect sink condition exists in the external media. In these conditions, the following equation was derived for spherical monoliths systems, assuming Fickian diffusion ($y = kt^{1/2}$) (35, 36):

$$\left[\frac{1 - \left(1 - \frac{M_t}{M_0}\right)^{2/3} - \frac{2}{3} \frac{M_t}{M_0}}{2} \right]^{1/2} = K_H t^{1/2}; K_H = \left(\frac{1}{C_0 r^2 P} \right)^{1/2} \quad (2)$$

where M_t/M_0 is the fraction of active ingredient released at time t and K_H is a constant that depends on the radius of the sphere (r), the initial concentration of the active ingredient (C_0), and the permeability of the matrix (P). The K_H values and correlation coefficients were obtained by applying the model proposed by Higuchi to release data, using the curve-fitting utility of Fig. P software (version 6.0 c, Biosoft, 1992). These values are presented in **Table 5** together with values of P . For all formulations containing bentonite and/or activated carbon as a modifying agent, the values of permeability decrease when the percentage of activated carbon increases. A similar variation was observed for K_H values according to the likeness between the values of C_0 and r of the granules.

To simplify the analysis curves from three-dimensional devices, the release data were analyzed by applying the empirical equation proposed by Ritger and Peppas (37):

$$M_t/M_0 = Kt^n \quad (3)$$

where M_t/M_0 is the percentage of active ingredient released 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, which is indicative of the transport mechanism.

Table 6. Constants from Fitting the Empirical Equation $M_t/M_0 = Kt^n$ to Release Data of Carbofuran in Water

formulation	$K \times 10^2 \text{ (h)}^{-n}$	n	r	$T_{50} \text{ (h)}$
CaA	12.6 ± 0.002^a	0.56 ± 0.009	0.995 ^b	11.72
CaAB	10.7 ± 0.005	0.57 ± 0.013	0.996 ^b	14.76
CaABC ₁₀	8.7 ± 0.006	0.57 ± 0.017	0.998 ^b	21.35
CaABC ₂₀	8.3 ± 0.004	0.56 ± 0.011	0.997 ^b	25.33
CaABC ₃₀	8.2 ± 0.007	0.54 ± 0.020	0.996 ^b	27.04
CaABC ₄₀	7.9 ± 0.006	0.50 ± 0.016	0.995 ^b	40.42
CaAC ₆₅	0.91 ± 0.008	0.47 ± 0.021	0.998 ^b	$\sim 5 \times 10^3$

^a These values represent the standard error. ^b Significant at the 0.001 probability level.

The values of K and n obtained from the initial 90% of maximum released carbofuran, together with the correlation coefficients, were obtained using the curve-fitting utility of Fig. P software and are presented in **Table 6**. 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 6**. The n values range from 0.47 for the CaAC₆₅ formulation up to 0.57 for the CaAB and CaABC₁₀ formulations. Values of n close to 0.43 are indicative of Fickian diffusion in spherical monolithic matrices (37). The complexity of the heterogeneous system involved together with the capacity of the bentonite and activated carbon samples to interact with the diffusion agent could explain some deviation from the n value above indicated.

The T_{50} values (the time taken for 50% of the carbofuran to be released) calculated from K and n constants ranged from 11.72 h for the CaA formulation to approximately 5×10^3 hours for the CaAC₆₅ formulation (**Table 6**). The alginate-based CRFs can be ranked in order of increasing T_{50} values as follows: CaA < CaAB < CaABC₁₀ < CaABC₂₀ < CaABC₃₀ < CaABC₄₀ < CaAC₆₅.

The lowest value of T_{50} corresponds to the CaA granule, which means that this CR preparation produces the fastest carbofuran release in water. The addition of bentonite and/or activated carbon to the basic alginate formulation reduces the rate of release, the formulations with a higher percentage of activated carbon producing a slower release rate as compared to the CaAB formulation. For a soil system, the same trends in release rate of the pesticide might be expected, although the specific conditions of the soil should be taken into account to evaluate this release rate.

The water uptake of the granules was shown to be fast as compared with the release of carbofuran. Therefore, it is proposed that the diffusion of active ingredient through the alginate matrices is the rate-controlling step, rather than the swelling of the granules in water and the dissolution of active ingredients under the present conditions. In this way, the T_{50} values obtained could be explained if we take into account two factors that affect the diffusion process, that is, the sorption capacity of modifying agents and the matrix permeability (36).

In relation to the first factor, the sorption capacity, the extent of interaction between the modifying agents and carbofuran will affect the release of carbofuran from the alginate-based granules. This aspect has been quantified with sorption experiments of carbofuran with bentonite and activated carbon samples. A higher sorption capacity would result in a slower release of pesticide. As related above, sorption experiments show that the sorption capacity (K_f) of the activated carbon sample for carbofuran ($K_f = 99.4 \times 10^3 \text{ mg kg}^{-1}$) was much higher ($\times 10^4$) than that obtained with the bentonite sample ($K_f = 2.26 \text{ mg kg}^{-1}$). The results obtained seem to be in agreement with the fact that granules containing bentonite and/or activated carbon

as modifying agents (CaAB, CaABC₁₀, CaABC₂₀, CaABC₃₀, CaABC₄₀, and CaAC₆₅) produce a slower release as compared with that without modifying agent (CaA). In addition, the incorporation of a high amount of activated carbon produces an increase in T_{50} values; that is, it produces a slower release of the carbofuran. Fernández-Pérez et al. (21) studied the release of carbofuran into aqueous solution from CRFs prepared from alginate, with and without the addition of natural and activated clay minerals. They reported that the addition of acid-treated bentonite to the CRFs was found to have a decrease on the release of carbofuran. This was attributed to the sorption of the pesticide to the activated bentonites. The T_{50} values for carbofuran CRFs ranged from 8.98 (carbofuran/alginate/acid-treated bentonite with 0.5 M H₂SO₄) to 11.71 h (carbofuran/alginate/acid-treated bentonite with 1.0 M H₂SO₄). These T_{50} values are lower than the values obtained for CaABC₁₀ (T_{50} = 21.35 h), CaABC₂₀ (T_{50} = 25.33 h), CaABC₃₀ (T_{50} = 27.04 h), and CaABC₄₀ (T_{50} = 40.42 h), probably due to the higher sorption capacity of activated carbon for carbofuran as compared with acid-treated bentonites. The higher variation of T_{50} values might be useful for selecting the most appropriate formulation depending on the soil environments, especially to avoid the carbofuran tendency to leach. This would be solved by giving the soil the appropriate concentration of carbofuran (38), using the suitable carbofuran CRF. In addition, the highest T_{50} values obtained for the formulations with higher contents of activated carbon would be appropriate in those applications, such as soil carbofuran treatments, where it is necessary to have a higher efficiency period of the carbofuran (39, 40).

In relation to the second factor, a lower matrix permeability value would result in a slower release of carbofuran. The alginate-based CRF studied containing bentonite and/or activated carbon as modifying agents can be ranked in order of increasing P values as follows: CaAC₆₅ < CaABC₄₀ < CaABC₃₀ < CaABC₂₀ < CaABC₁₀ < CaAB. This variation order is the same than that obtained when the rate release of granules was analyzed.

To know the factors that affect the release rate of carbofuran from bentonite and/or activated carbon-alginate granules, the T_{50} values, obtained from formulations that in our experimental conditions reached the 50% of active ingredient released, were correlated with the content of activated carbon in dry granules (Q). As related above, the content of activated carbon is the most influential factor that affects the release rate of carbofuran.

Figure 5 shows the plot of the T_{50} values vs the Q values of the granules. The analysis indicates that T_{50} values are well-correlated with the Q values for formulates CaAB, CaABC₁₀, CaABC₂₀, and CaABC₃₀.

The higher the Q values of the formulations, the higher the interactions of carbofuran with the activated carbon are. This fact produces a higher T_{50} value, which means a slower release of the nematicide.

The equations of linear correlation and correlation coefficient were obtained by applying the least-squares method to the data.

$$T_{50} = 40.22 \times Q + 15.96 \quad (r = 0.971) \quad (p = 0.03) \quad (4)$$

From the linear correlation obtained, the release of carbofuran from system of a similar structure to those used in our experiments could be readily predicted from the Q values used in the formulations prepared.

Ali and Wilkins (41) studied factors influencing release of carbofuran from CR granules based on byproduct lignin modified with poly(vinyl chloride) into soil and water. They showed that the characteristics of release into soil conditions were related to those obtained by release into water and that

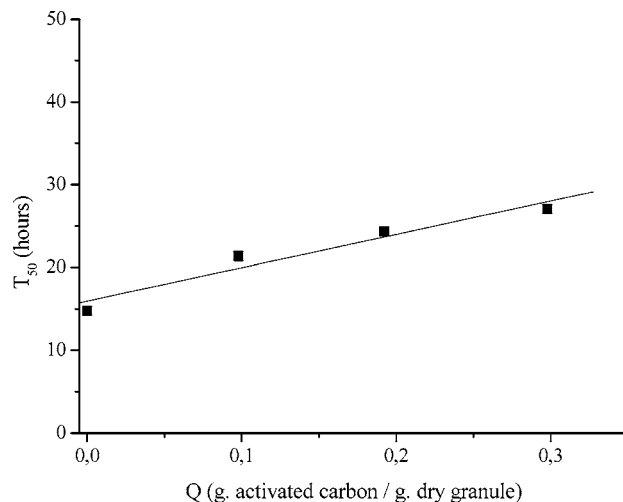


Figure 5. Correlation study with T_{50} and the content of activated carbon (Q) of carbofuran granules.

the release kinetics fitted a model that was generally valid for all of the environments studied. Using the model proposed by these authors, we will know the behavior of the alginate formulations prepared by us in soils; therefore, this study might be useful for selecting the most appropriate formulation, depending on the environmental factor that affects carbofuran release and mobility in soils. T_{50} values in soil for alginate formulations range from 33.05 h for CaA to 113.98 h for CaABC₄₀ formulation.

In conclusion, experimental results suggest that the use of bentonite and/or activated carbon samples as modifying agents of an alginate-carbofuran formulation could reduce the release rate of the carbofuran in comparison with the technical product and with alginate formulation without modifying agents. The greatest reduction in release rate corresponds to the formulations prepared with a higher percentage of activated carbon. The release of carbofuran, from the various alginate-based CRFs into water, may be due to diffusion where the sorption capacities of sorbent for carbofuran and formulations permeability are the most influential factors. Taking into account the variation shown for T_{50} values by the different systems prepared, this study might be useful for selecting the most appropriate formulation, depending on the environmental factor that affects carbofuran mobility. In addition, it has been shown that there is a good correlation between the T_{50} value and the content of activated carbon in dry granules (Q). So, from the Q values of granules, it could be possible to obtain a rough estimation of the release rate of carbofuran, and we may apply this to any system of similar structure to that used in our studies. Therefore, the use of formulations as those described in this paper could help to increase the efficiency of delivery of the bioactive material and also to prevent the environmental pollution by carbofuran.

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