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Controlled Release of Isoproturon, Imidacloprid, and Cyromazine from Alginate–Bentonite-Activated Carbon Formulations

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Different alginate-based systems of isoproturon, imidacloprid, and cyromazine have been investigated in order to obtain controlled release (CR) properties. The basic formulation [sodium alginate (1.50%), pesticide (0.30%), and water] was modified using different amounts of bentonite and activated carbon. The higher values of encapsulation efficiency corresponded to those formulations prepared with higher percentages of activated carbon, showing higher encapsulation efficiency values for isoproturon and imidacloprid than for cyromazine, which has a higher water solubility. The kinetic experiments of imidacloprid/isoproturon release in water have shown us that the release rate is higher in imidacloprid systems than in those prepared with isoproturon. Moreover, it can be deduced that the use of bentonite and/or activated carbon sorbents reduces the release rate of the isoproturon and imidacloprid in comparison with the technical product and with alginate formulation without modifying agents. The highest decrease in release rate corresponds to the formulations prepared with the highest percentage of activated carbon. The water uptake, permeability, and time taken for 50% of the active ingredient to be released into water, T_{50}, were calculated to compare the formulations. On the basis of a parameter of an empirical equation used to fit the pesticide release data, the release of isoproturon and imidacloprid from the various formulations into water is controlled by a diffusion mechanism. The sorption capacity of the sorbents and the permeability of the formulations were the most important factors modulating pesticide release. Finally, a linear correlation of the T_{50} values and the content of activated carbon in formulations were obtained.

KEYWORDS: Isoproturon; imidacloprid; cyromazine; controlled release; activated carbon; bentonite; alginate

INTRODUCTION

At present, the consumption of great quantities of pesticides for crop protection is an important challenge for the maintenance of the welfare state. The correct use of pesticides will contribute to the protection of natural resources, avoiding environmental pollution and harm on public health.

By using pesticides, we obtain an important increase in the performance of crops, avoiding, in this way, the breakthrough of vital natural areas for the conservation of many species. In addition, a drastic reduction on its application would bring about an increase in the costs of production and a decrease in the quality of the agricultural products in nonorganic farming. However, there is more and more evidence that shows the presence of pesticides in plants, uncultivated soils, the environment, and superficial or subterranean water, far from the places of application. All of them reveal a lack of enough methods to keep suitable control of the harmful effects on the environment caused by the pesticides (*1*−*4*).

Nevertheless, we have to assume that it is virtually impossible to develop a profitable agricultural production without using pesticides. Unlike the classical formulations, the controlled release formulations (CRFs) make a gradual and controlled release of the pesticides over time easy, which allows a lower concentration of the active ingredients in the environment and which, at the same time, is enough to fight against the pest. This fact also reduces losses by evaporation and filtration of the quantities of the active ingredient that does not reach its target. The use of these systems would diminish the intrinsic risks and those derived from the application of the farmer (*5*, *6*).

Isoproturon [3-(4-isopropylphenyl)-1,1-dimethylurea], imidacloprid [1-(6-chloro-3-pyridin-3-ylmethyl)-*N*-nitroimidazolidin-2-ylideamine], and cyromazine [*N*-cyclopropyl-1,3,5-triazine-2,4,6-triamine] are systemic pesticides that have been identified as potential leachers when using the groundwater ubiquity score (GUS) modeling technique (*7*). In relation to the previous idea, isoproturon, imidacloprid, and cyromazine have been found to leach (*8*−*10*).

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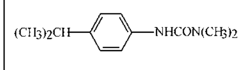
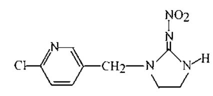
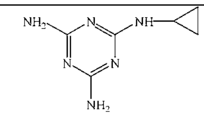
	Isoproturon	Imidacloprid	Cyromazine
			
Molecular formula	$C_{12}H_{18}N_2O$	$C_9H_{10}ClN_5O_2$	$C_6H_{10}N_6$
Molecular weight (g mol^{-1})	206.3	255.7	166.2
Melting point (ºC)	158	143	220
Vapour pressure (mPa)	$3.30 \cdot 10^{-3}$ (20 ºC)	$2.00 \cdot 10^{-4}$ (20 ºC)	$4.48 \cdot 10^{-4}$ (25 ºC)
Water solubility (mg L^{-1})	55 (20 ºC)	510 (20 ºC)	13000 (25 ºC)
Log K_{ow}	2.5	0.57	-0.061

Figure 1. Structure and physicochemical properties of isoproturon, imidacloprid, and cyromazine.

According to Wilkins (*11*), dispersion or dissolution of the active ingredient in a polymeric matrix is the most important technology to prepare CRFs of pesticides. Natural polymers like starch, lignin, alginate, and cellulose derivates have been used as matrix for CR pesticides (*12*−*15*) due to the possible degradation of the matrices (*16*). Pepperman et al. (*14*) and Fernández Pérez et al. (*17*) suggested that in alginate gel formulations, we should require the incorporation of sorbents within the gel to provide effective delay of release. Thus, the present study evaluates the potential use of a natural bentonite (sorbent with a low sorption capacity for nonionic pesticides), an activated carbon (sorbent with a high sorption capacity), and different mixtures of both sorbents as modifying agents in alginate-based CRFs of isoproturon, imidacloprid, and cyromazine.

With the use of bentonite and activated carbon as modifying agents, we intend to get a better encapsulation of isoproturon, imidacloprid, and cyromazine and to reach a higher variety of release profiles in pesticides. Bentonite is a layer silicate mineral containing montmorillonite as a major constituent. This material has been previously studied and characterized (*18*), and it was used as an inorganic model compound to study the interactions between the soil inorganic fraction and the pesticides (*19*). Commercially 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 (*20*, *21*).

The main objective of this work was to encapsulate isoproturon, imidacloprid, and cyromazine using a polymeric matrix of alginate. Moreover, the influence of incorporation of bentonite, activated carbon, and different mixtures of both sorbents into alginate-based formulations on the rate of pesticides release was evaluated. We also intend to obtain a deeper understanding of the release mechanism of the pesticides from the investigated formulations. In addition, the correlation between the characteristic release parameter (T_{50}) and the properties of granules was studied.

MATERIALS AND METHODS

Materials. The sorbent materials 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. (*18*), 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. The specific areas of bentonite and activated carbon were 70.26 and 727.27 $m^2\ g^{-1}$. This characteristic and the chemical properties of the bentonite and activated carbon samples were previously described by Fernández-Pérez et al. (*17*).

Technical grade isoproturon (98.0%), imidacloprid (99.0%), and cyromazine (99.0%) were kindly supplied by Rhône-Poulenc Agrochimie (Lyon, France), Bayer Hispania Industrial S.A. (Barcelona, Spain), and Industrias Afrasa S.A. (Valencia, Spain), respectively. The selected properties of isoproturon, imidacloprid, and cyromazine are shown in **Figure 1** (*22*). Solvents used in the mobile phase for high-performance liquid chromatography (HPLC) determinations were HPLC grade acetonitrile from Merck (Darmstadt, Germany), demineralized Milli-Q quality water from Millipore (Billerica, United States), and analytically pure KH_2PO_4 from Panreac S.A.. Chemical products used in the preparation and evaluation of CRFs were 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.

Preparation of CRFs. The prepared CRFs were based on the gelling properties of the alginate in the presence of divalent cations. It was made up of formulations in water containing different percentages of technical grade pesticide, sodium alginate (A), bentonite, and/or activated carbon (shown in **Table 1**). These mixtures were vigorously stirred for 1 h. The alginate mixtures (100 g) were dropwise added to a 300 mL gellant bath of 0.25 M $CaCl_2$ using the apparatus described by Connick (*23*). The resulting beads were kept in the 0.25 M $CaCl_2$ solution for a total of 20 min; then, they were filtered and dried first at room temperature and then in an oven (40 °C) to constant weight.

The resulting products are labeled in the text as IsA, IsAB, $IsABC_{10}$, $IsABC_{20}$, $IsABC_{30}$, $IsABC_{40}$, and $IsAC_{65}$ for CRFs containing isoproturon (Is); ImA, ImAB, $ImABC_{10}$, $ImABC_{20}$, $ImABC_{30}$, $ImABC_{40}$, and $ImAC_{65}$ for CRFs containing imidacloprid (Im); and CyA, CyAB, $CyABC_{10}$, $CyABC_{20}$, $CyABC_{30}$, $CyABC_{40}$, and $CyAC_{65}$ for CRFs containing cyromazine (Cy). The numbers 10, 20, 30, 40, and 65 are the percentages of activated carbon in dry granules.

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 Pesticides and Calcium in Granules. The concentration of pesticide 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 ultrasonic bath for 15 min. The resulting extract was filtered using nylon filters

Table 1. Percentage (by Weight) of Component of CRFs Containing Pesticides

formulation	technical pesticide (%)	Na–Alginate (%)	B (%)	C (%)	water (%)
pesticide–alginate (IsA, ImA, CyA)	0.30	1.50			98.20
pesticide–alginate–bentonite (IsAB, ImAB, CyAB)	1.22	1.40	5.02		92.36
pesticide–alginate–bentonite–10% of activated carbon in dry formulation ($IsABC_{10}$, $ImABC_{10}$, $CyABC_{10}$)	1.22	1.40	4.23	0.78	92.37
pesticide–alginate–bentonite–20% of activated carbon in dry formulation ($IsABC_{20}$, $ImABC_{20}$, $CyABC_{20}$)	1.22	1.40	3.46	1.55	92.37
pesticide–alginate–bentonite–30% of activated carbon in dry formulation ($IsABC_{30}$, $ImABC_{30}$, $CyABC_{30}$)	1.22	1.40	2.70	2.32	92.36
pesticide–alginate–bentonite–40% of activated carbon in dry formulation ($IsABC_{40}$, $ImABC_{40}$, $CyABC_{40}$)	1.22	1.40	2.00	3.08	92.30
pesticide–alginate–65% activated carbon ($IsAC_{65}$, $ImAC_{65}$, $CyAC_{65}$)	1.22	1.40		5.02	92.36

Table 2. Characteristics of Controlled Release Granules (Dry Products) Containing Isoproturon

formulations	isoproturon (%)	Ca^{2+} (%)	average weight (mg/granule)	average diameter (mm/granule)	yield[a] (%)	encapsulation efficiency[b] (%)
IsA	9.78 (0.12)[c]	9.45 (0.82)	1.59 (0.05)	0.83 (0.03)	2.45	85.64
IsAB	12.52 (0.15)	2.78 (0.36)	2.16 (0.08)	1.21 (0.06)	8.89	91.26
$IsABC_{10}$	13.47 (0.19)	3.12 (0.41)	2.17 (0.10)	1.30 (0.05)	8.99	99.23
$IsABC_{20}$	13.78 (0.27)	2.98 (0.42)	2.20 (0.06)	1.35 (0.04)	8.78	99.37
$IsABC_{30}$	14.07 (0.25)	3.40 (0.44)	2.23 (0.05)	1.51 (0.06)	8.59	99.43
$IsABC_{40}$	13.86 (0.15)	3.04 (0.33)	2.23 (0.04)	1.64 (0.03)	8.69	99.62
$IsAC_{65}$	14.09 (0.21)	3.27 (0.35)	2.29 (0.06)	1.85 (0.07)	8.65	99.91

[a] Yield = (weight of dry product/weight formulation processed) × 100. [b] Encapsulation efficiency = (amount of pesticide in dry product/amount of pesticide in formulation processed) × 100. [c] Values in parentheses represent the standard deviation.

(0.45 μm), and the pesticide concentration was determined by HPLC. The HPLC operating conditions were as follows: the separation, by isocratic elution, was performed on a 150 mm × 3.9 mm Nova-Pack LC-18 bonded-phase column from Waters for isoproturon and imidacloprid and on a 250 mm × 4.6 mm SUPELCOSIL LC-SCX bonded-phase column from Supelco Co. for cyromazine; sample volume, 20 μL for isoproturon and imidacloprid and 50 μL for cyromazine; flow rate, 1.0 mL min^{-1} for isoproturon and imidacloprid and 2.0 mL min^{-1} for cyromazine; and the mobile phase, an acetonitrile−water mixture 60:40 for isoproturon, 35:65 for imidacloprid, and an acetonitrile−aqueous solution of 15 mM KH_2PO_4 (pH 3.0) mixture 25:75 for cyromazine. Pesticides were analyzed at their wavelength of maximum absorption (239, 269, and 214 nm for isoproturon, imidacloprid, and cyromazine, respectively). 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 an 1100 B Perkin-Elmer spectrometer.

Water Uptake Tests. The water uptake was measured for granules using the method of Franson and Peppas (*24*). 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 (see Results and Discussion for intervals). The water excess 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 dried, first at room temperature and then in an oven (40 °C) to constant weight, so that the water uptake (g/g dry granule) could be calculated.

Pesticide Release Kinetics. An accurately weighed quantity of dry CR granules containing about 8.0 mg of pesticide 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 pesticides by HPLC using the methods described above (analysis of pesticides and calcium in granules), and 1 mL of fresh water was added to the flasks to maintain constant volume.

RESULTS AND DISCUSSION

Controlled-Release Formulations. Characteristics of alginate-based CR granules containing isoproturon and imidacloprid are shown in **Tables 2** and **3**, respectively. The granules were generally spherically shaped, and the technical grade isoproturon and imidacloprid were readily incorporated in the alginate matrix, obtaining granules of size between 0.83 and 1.96 mm. The addition of bentonite and activated carbon to the alginate formulation led to larger and heavier granules that were more spherical and dried with less aggregation. It is also observed that the pesticide content of the dried granules (ranged from 6.32% for ImA to 14.32% for $ImAC_{65}$) is adequate for a practical agricultural application where good coverage is needed (*25*, *26*). In all granules containing bentonite and/or activated carbon, the encapsulation efficiency was higher than 83.50%. The highest values are the formulations prepared with the highest percentages of activated carbon (99.91% for $IsAC_{65}$ and 99.65% for $ImAC_{65}$).

On the other hand, we notice that the encapsulation efficiency values for cyromazine formulations were low, ranging between 11.29% for CyA and 89.65% for $CyAC_{65}$ (**Table 4**). This could be due to the high water solubility of cyromazine, because the encapsulation process was made in aqueous solution. As well as in the isoproturon and imidacloprid formulations, the encapsulation efficiency increase in those formulations in which bentonite and/or activated carbon are present can be observed.

Table 3. Characteristics of Controlled Release Granules (Dry Products) Containing Imidacloprid

formulations	imidacloprid (%)	Ca^{2+} (%)	average weight (mg/granule)	average diameter (mm/granule)	yield[a] (%)	encapsulation efficiency[b] (%)
ImA	6.32 (0.10)[c]	11.98 (1.02)	0.84 (0.03)	0.92 (0.04)	2.24	50.51
ImAB	11.90 (0.18)	4.64 (0.43)	3.03 (0.09)	1.31 (0.06)	8.63	83.50
$ImABC_{10}$	12.51 (0.22)	4.09 (0.40)	3.01 (0.11)	1.30 (0.04)	8.65	89.44
$ImABC_{20}$	12.67 (0.27)	4.37 (0.47)	2.84 (0.07)	1.42 (0.06)	8.64	91.25
$ImABC_{30}$	12.57 (0.20)	5.13 (0.38)	2.63 (0.10)	1.50 (0.05)	8.57	89.77
$ImABC_{40}$	12.92 (0.15)	4.85 (0.31)	2.89 (0.08)	1.62 (0.03)	8.58	91.57
$ImAC_{65}$	14.32 (0.32)	4.24 (0.36)	2.99 (0.05)	1.96 (0.09)	8.42	99.65

[a] Yield = (weight of dry product/weight formulation processed) × 100. [b] Encapsulation efficiency = (amount of pesticide in dry product/amount of pesticide in formulation processed) × 100. [c] Values in parentheses represent the standard deviation.

Table 4. Characteristics of Controlled Release Granules (Dry Products) Containing Cyromazine

formulations	cyromazine (%)	Ca^{2+} (%)	average weight (mg/granule)	average diameter (mm/granule)	yield[a] (%)	encapsulation efficiency[b] (%)
CyA	1.52 (0.05)[c]	10.67 (1.14)	0.61 (0.02)	0.75 (0.04)	2.08	11.29
CyAB	3.72 (0.07)	4.46 (0.30)	2.30 (0.11)	1.25 (0.05)	8.09	24.67
$CyABC_{10}$	5.12 (0.22)	5.12 (0.41)	2.14 (0.08)	1.28 (0.04)	8.15	34.20
$CyABC_{20}$	6.06 (0.17)	4.10 (0.45)	2.49 (0.06)	1.35 (0.06)	8.16	40.51
$CyABC_{30}$	7.91 (0.26)	5.23 (0.37)	2.42 (0.09)	1.53 (0.04)	8.44	54.74
$CyABC_{40}$	9.38 (0.15)	4.93 (0.32)	2.34 (0.05)	1.66 (0.05)	8.73	67.09
$CyAC_{65}$	12.39 (0.34)	4.44 (0.35)	3.11 (0.07)	1.93 (0.07)	8.87	89.65

[a] Yield = (weight of dry product/weight formulation processed) × 100. [b] Encapsulation efficiency = (amount of pesticide in dry product/amount of pesticide in formulation processed) × 100. [c] Values in parentheses represent the standard deviation.

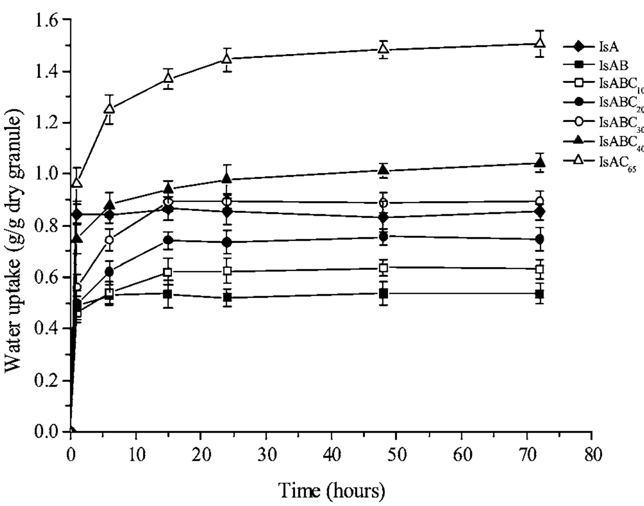


Figure 2. Water uptake of isoproturon granules over time (error bars represent the standard deviation of three replicates).

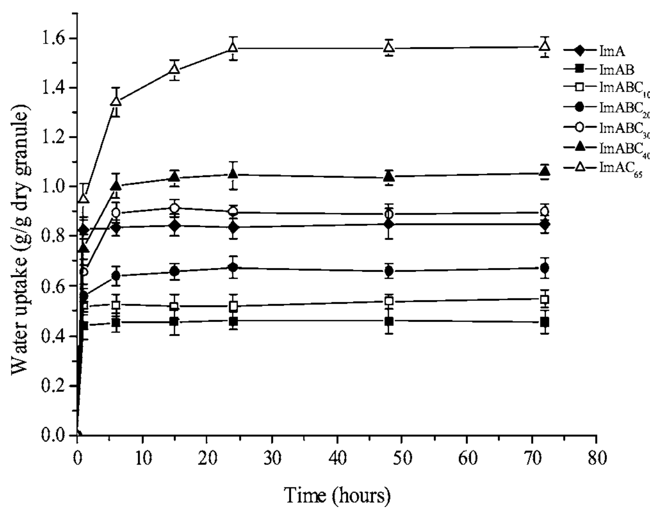


Figure 3. Water uptake of imidacloprid granules over time (error bars represent the standard deviation of three replicates).

According to these data, we realize that this method is suitable for cyromazine encapsulation, using the highest quantity of activated carbon.

Water Uptake. The water uptake of the granules containing isoproturon and imidacloprid vs time is shown in **Figures 2** and **3**, respectively. Water uptake curves were characterized by a fast initial uptake of water by means of the granules; an apparent equilibrium or a slow water uptake was observed later. In granules containing bentonite and/or activated carbon (IsAB, $IsABC_{10}$, $IsABC_{20}$, $IsABC_{30}$, $IsABC_{40}$, and $IsAC_{65}$; or ImAB, $ImABC_{10}$, $ImABC_{20}$, $ImABC_{30}$, $ImABC_{40}$, and $ImAC_{65}$), the highest values of water uptake corresponded to the formulations prepared with the highest percentage of activated carbon. The density of the activated carbon was lower than that of the bentonite (*17*). This fact and the highest percentage of activated carbon in granules may be responsible for the highest water uptake. The addition of activated carbon to the alginate formulation generates a greater percentage of microporosity producing 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 isoproturon and imidacloprid either with bentonite and/or with activated carbon could affect the diffusion through the granules and, hence, the release of the active ingredient. For granules without modifiers (IsA and ImA), it is necessary to consider that there are not additional bonds with other components of matrix on drying; thus, expansion by a swelling process is possible. Last, differences

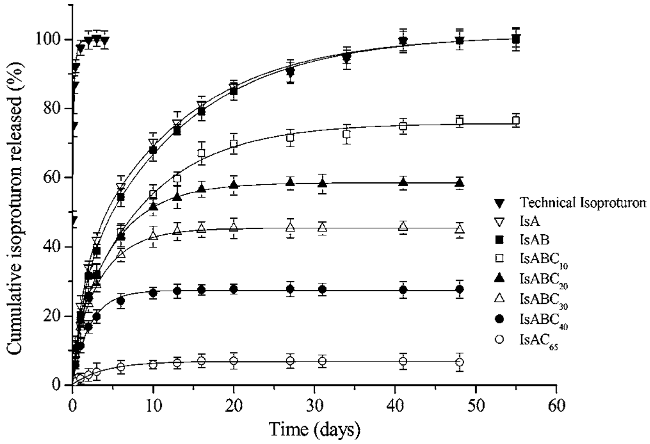


Figure 4. Cumulative release of isoproturon from granules into static water (error bars represent the standard deviation of three replicates).

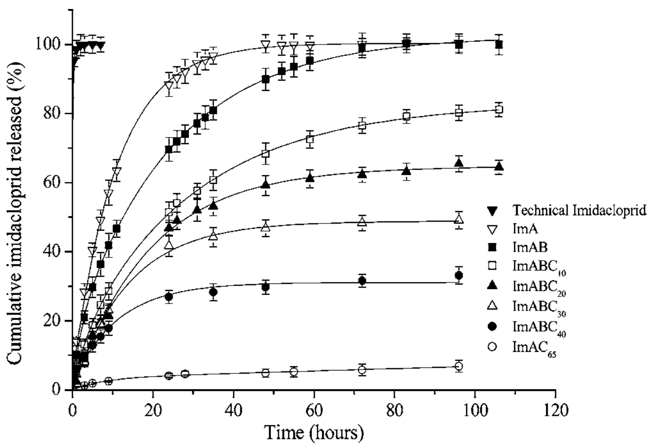


Figure 5. Cumulative release of imidacloprid from granules into static water (error bars represent the standard deviation of three replicates).

in the wetability and solubility of pesticides could also slightly affect the water uptake as reported by other authors (*27*).

Release Studies. In **Figures 4** and **5** are shown the cumulative release of isoproturon and imidacloprid from alginate-based CR granules and the solubility profile for technical grade pesticides. In **Figure 4**, 100% of technical grade isoproturon is dissolved in less than 3 days, although it takes at least 45 days to release the same percentage of active ingredient from the alginate-based CR formulation IsA. For the formulations containing bentonite and/or activated carbon as a modifying agent, 100% of isoproturon is released in 48 days for formulation IsAB. However, it takes the same time to release 6.62% of active ingredient from the alginate-based CR formulation $IsAC_{65}$. In **Figure 5**, it can be seen that 100% of technical grade imidacloprid is dissolved in less than 3 h, and it takes at least 48 h to release the same percentage of active ingredient from the alginate-based CR formulation ImA. For the formulations containing bentonite and/or activated carbon as modifying agents, 100% of imidacloprid is released in 83 h for formulation ImAB, and it takes the same time to release 2.30% of active ingredient from the alginate-based CR formulation $ImAC_{65}$.

For all formulations, a decline in the release of pesticide over time was observed. This result is probably due to an increase in the distance where 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 (*28*). The formulations of this research are described as systems containing finely divided solute particles, which are uniformly dispersed within the matrix phase. Higuchi (*29*) originally analyzed analogous systems, such as drugs dispersed in a stationary matrix, e.g., semisolid ointment. In these spherical monolith systems, Higuchi suggested the following equation, assuming Fickian diffusion ($y = kt^{1/2}$) (*29*, *30*):

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

product	$K_H \times 10^2$ (days)$^{-1/2}$	r	$P \times 10^4$ (mg days^{-1} mm^{-1})
IsA	6.58 ± 0.009[a]	0.999[b]	3.87 ± 0.003
IsAB	6.31 ± 0.010	0.999[b]	4.25 ± 0.007
$IsABC_{10}$	4.99 ± 0.007	0.999[b]	2.67 ± 0.008
$IsABC_{20}$	4.54 ± 0.013	0.998[b]	2.21 ± 0.013
$IsABC_{30}$	4.14 ± 0.019	0.999[b]	1.70 ± 0.011
$IsABC_{40}$	3.19 ± 0.015	0.997[b]	0.92 ± 0.005
$IsAC_{65}$	0.57 ± 0.08	0.997[b]	0.027 ± 0.002

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

Table 6. Constants from Fitting the Higuchi Equation to Release Data of Imidacloprid in Water and Matrix Permeability Parameter

product	$K_H \times 10^2$ (h)$^{-1/2}$	r	$P \times 10^4$ (mg h^{-1} mm^{-1})
ImA	7.03 ± 0.026[a]	0.999[b]	1.36 ± 0.007
ImAB	4.86 ± 0.011	0.999[b]	3.10 ± 0.015
$ImABC_{10}$	3.23 ± 0.006	0.998[b]	1.44 ± 0.006
$ImABC_{20}$	2.98 ± 0.017	0.993[b]	1.07 ± 0.012
$ImABC_{30}$	2.45 ± 0.022	0.989[b]	0.63 ± 0.011
$ImABC_{40}$	1.18 ± 0.015	0.986[b]	0.15 ± 0.007
$ImAC_{65}$	0.16 ± 0.007	0.985[b]	0.0026 ± 0.0003

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

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

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 nonlinear curve-fitting utility of SigmaPlot software (version 9.0, Systat Software, Inc.). These values are presented in **Tables 5** and **6** together with values of P for the formulations of isoproturon and imidacloprid, respectively.

In **Tables 5** and **6**, we can observe the different P values between isoproturon and imidacloprid systems. The average permeability of isoproturon systems is in the order of 10^{-5} mg/mm h, but those of imidacloprid are approximately 10 times more than the other ones, that is, the order of 10^{-4} mg/mm h, except for those systems prepared exclusively in activated carbon as the modifying agent where the used model may be not suitable, probably due to the low amount of released pesticide after finishing the experiments.

For all formulations containing bentonite and/or activated carbon as modifying agents, 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.

Table 7. Constants from Fitting the Empirical Equation $M_t/M_0 = Kt^n$ to Release Data of Isoproturon in Water

product	$K \times 10^2$ (days)$^{-n}$	n	r	T_{50} (days)
IsA	22.1 ± 0.007[a]	0.49 ± 0.008	0.991[b]	5.29
IsAB	20.1 ± 0.005	0.51 ± 0.010	0.993[b]	5.88
$IsABC_{10}$	16.7 ± 0.004	0.52 ± 0.011	0.993[b]	7.95
$IsABC_{20}$	17.7 ± 0.006	0.49 ± 0.015	0.995[b]	8.79
$IsABC_{30}$	15.7 ± 0.008	0.48 ± 0.017	0.989[b]	10.90
$IsABC_{40}$	10.6 ± 0.007	0.47 ± 0.013	0.973[b]	27.41
$IsAC_{65}$	1.83 ± 0.003	0.55 ± 0.019	0.985[b]	428.98

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

Table 8. Constants from Fitting the Empirical Equation $M_t/M_0 = Kt^n$ to Release Data of Imidacloprid in Water

product	$K \times 10^2$ (h)$^{-n}$	n	r	T_{50} (h)
ImA	16.6 ± 0.005[a]	0.54 ± 0.011	0.993[b]	7.58
ImAB	12.8 ± 0.003	0.52 ± 0.015	0.996[b]	13.57
$ImABC_{10}$	7.6 ± 0.005	0.58 ± 0.012	0.994[b]	25.66
$ImABC_{20}$	5.8 ± 0.006	0.63 ± 0.018	0.991[b]	30.69
$ImABC_{30}$	5.7 ± 0.004	0.60 ± 0.020	0.986[b]	36.97
$ImABC_{40}$	5.8 ± 0.009	0.49 ± 0.012	0.996[b]	79.16
$ImAC_{65}$	0.84 ± 0.005	0.47 ± 0.023	0.986[b]	6.29×10^3

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

To simplify the analysis of curves from three-dimensional devices, the release data were analyzed by applying the empirical equation proposed by Ritger and Peppas (*31*):

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

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 shows the transport mechanism.

The values of K and n obtained from 90% of maximum released pesticide, in each curve (**Figures 4** and **5**), were obtained using the nonlinear curve-fitting utility of SigmaPlot software. These values and the correlation coefficients are presented in **Tables 7** and **8** for the formulations of isoproturon and imidacloprid, respectively. According to correlation coefficients, we can deduce that the release profiles of isoproturon and imidacloprid formulations fit well to the empirical equation. The n values range from 0.47 for $ImAC_{65}$ and $IsABC_{40}$ formulations up to 0.63 for $ImABC_{20}$ formulations. If we compare the n values of isoproturon systems with those obtained for imidacloprid systems, we realize that they are similar. Values of n close to 0.43 are indicative of Fickian diffusion in spherical monolithic matrices (*31*). The fact is that values of n higher than 0.43 could be explained by the complexity of the studied heterogeneous system together with the capacity of the bentonite and activated carbon samples to interact with the active ingredient.

The K values range between 22.12×10^{-2} days^{-n} for IsA and 0.84×10^{-2} h^{-n} for $ImAC_{65}$. They are diminishing while the percentages of activated carbon are increasing. In general, the monolith systems in this study consist of a hydrophilic of alginate and calcium ions with the active ingredient dispersed in it, which makes up water quickly as is indicated in water uptake section. These systems are changed in some cases by the addition of bentonite and/or activated carbon. All of them make an alginate hydrogel with a continuous membrane around the pesticides and modifying agents. In this situation, the active ingredient dissolves from the crystal surface, spreads through the macromolecular network, and is released to the environment. Taking into account the molecular weights of isoproturon (206.3 g mol^{-1}) and imidacloprid (255.7 g mol^{-1}), it is likely that steric impediments are not produced by the alginate hydrogel. However, the crossing areas of alginate make the movement of the active ingredient difficult (*32*).

In fact, the presence of modifying agents such as bentonite and activated carbon increases the centers of interaction from the porosity of these components. All of them cause a decrease in diffusion of the active ingredient.

In addition to an increase in porosity, the presence of hydroxyl groups on the bentonite surface and in less quantity in the active carbon, which can interact with carboxylic groups of alginate to create a hydrogen bond, would give rise to systems with high crossing and, consequently, with less permeability, as we have seen in the water uptake section.

This behavior is shown again when evaluating the data referred to T_{50} parameter (the time taken for 50% of the pesticides to be released). The T_{50} values calculated from K and n constants are also presented in **Tables 7** and **8** for the formulations of isoproturon and imidacloprid, respectively. First, the values of the T_{50} parameter are observed to be higher in isoproturon systems than in those prepared with imidacloprid. This fact can be due to the smaller solubility of isoproturon (55 mg L^{-1}) than imidacloprid (510 mg L^{-1}).

The order of variation in this parameter for both groups of prepared systems is IsA < IsAB < $IsABC_{10}$ < $IsABC_{20}$ < $IsABC_{30}$ < $IsABC_{40}$ < $IsAC_{65}$ for the formulations containing isoproturon and ImA < ImAB < $ImABC_{10}$ < $ImABC_{20}$ < $ImABC_{30}$ < $ImABC_{40}$ < $ImAC_{65}$ for the formulations containing imidacloprid.

In each group, the lowest values of T_{50} are IsA and ImA granules, which mean that these CR preparations produce the fastest isoproturon and imidacloprid 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 produce a slower release rate as compared to the IsAB and ImAB formulations. 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 isoproturon and imidacloprid. 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 ingredient 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 to say, the sorption capacity of modifying agents and the matrix permeability (*30*).

In relation to the sorption capacity, the extent of interaction between the modifying agents and the isoproturon and imidacloprid will affect the release of pesticides from the alginate-based granules. This aspect could be quantified with sorption experiments of both pesticides with bentonite and activated carbon samples. A higher sorption capacity would result in a slower release of pesticide. Previous studies of the present authors—where batch sorption experiment were carried out with bentonite and activated carbonlike adsorbents, and isoproturon-, carbofuran-, and imidacloprid-like solutes—showed that the sorption capacities (K_f) of the activated carbon sample for these

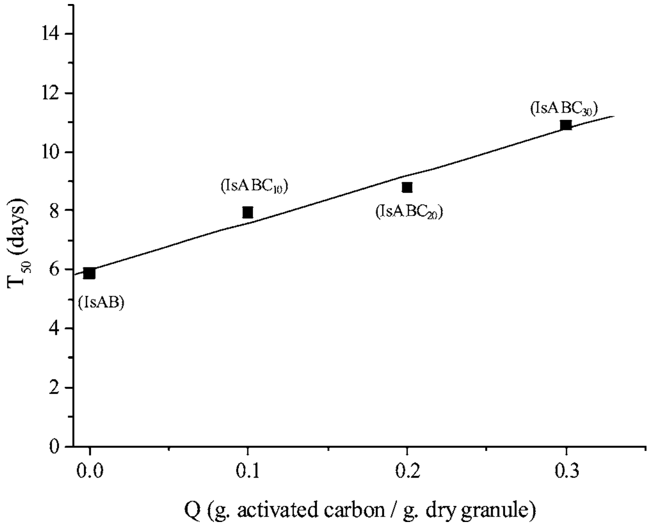


Figure 6. Correlation study with T_{50} and the content of activated carbon (Q) of isoproturon granules.

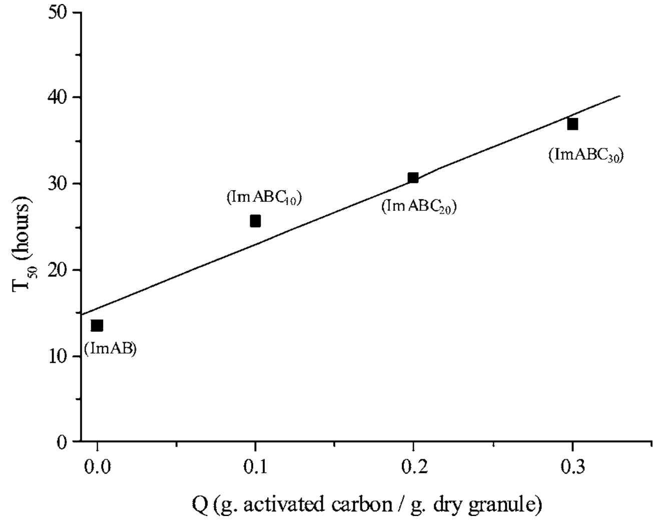


Figure 7. Correlation study with T_{50} and the content of activated carbon (Q) of imidacloprid granules.

pesticides were far higher than those obtained with the bentonite sample (*17, 33*). The results reveal that those granules containing bentonite and/or activated carbon as modifying agents (IsAB, $IsABC_{10}$, $IsABC_{20}$, $IsABC_{30}$, $IsABC_{40}$, and $IsAC_{65}$ and ImAB, $ImABC_{10}$, $ImABC_{20}$, $ImABC_{30}$, $ImABC_{40}$, and $ImAC_{65}$) produce a slower release as compared to IsA and ImA, without modifying agent. In addition, the incorporation of a higher percentage of activated carbon produces the slowest values of T_{50}. 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 isoproturon and imidacloprid tendency to leach.

In relation to the matrix permeability, a lower value of this parameter would result in a slower release of isoproturon and imidacloprid. The alginate-based CR formulation studied containing bentonite and/or activated carbon as modifying agents can be ranked according to the increase in P values as follows: $IsAC_{65} < IsABC_{40} < IsABC_{30} < IsABC_{20} < IsABC_{10} <$ IsAB for the formulations containing isoproturon and $ImAC_{65} < ImABC_{40} < ImABC_{30} < ImABC_{20} < ImABC_{10} <$ ImAB for the formulations containing imidacloprid. This variation order is the same as that obtained in the rate release of pesticides from granules.

There are various agronomic practices in which pesticides are used and in which it is necessary to control the rate release of pesticides to the environment. Thus, it is interesting to find a relationship between the main parameter in the release process (T_{50}) and some principal property of the granules that they let us predict the kinetics behavior of prepared systems. As it has been said above, it is likely that the content of activated carbon is the most influential factor that affects the release rate of isoproturon and imidacloprid. 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).

Figures 6 and **7** show the plots of the T_{50} values vs the Q values of the granules of isoproturon and imidacloprid, respectively. The analysis indicates that T_{50} values are well-correlated with the Q values for formulates containing a percentage of activated carbon range from 0 up to 30% (IsAB, $IsABC_{10}$, $IsABC_{20}$, and $IsABC_{30}$ and ImAB, $ImABC_{10}$, $ImABC_{20}$, and $ImABC_{30}$).

The higher Q values of the formulations, the higher interactions of isoproturon and imidacloprid with the activated carbon. This fact produces a higher T_{50} value, which means a slower release of pesticides. The equations of linear regression and correlation coefficients were acquired by applying the least-squares method to the data.

$$T_{50} = 15.90Q + 6.01 \tag{4}$$

where $r = 0.988$ and $p = 0.01$ and

$$T_{50} = 75.23Q + 15.44 \tag{5}$$

where $r = 0.980$ and $p = 0.02$.

From the linear correlations obtained, the release of isoproturon (*4*) and imidacloprid (*5*) from system of similar structure to those used in our experiments could be readily predicted from the Q values used in the ready formulations. Hence, we can design a right profile in release of active ingredient from granules in each agronomic practice.

In conclusion, controlled release systems of isoproturon, imidacloprid, and cyromazine have been obtained by gelling of sodium alginate with calcium ions and using different amounts of bentonite and activated carbon as modifying agents. As a result, isoproturon and imidacloprid formulations had good encapsulation efficiency: The higher values correspond to the formulations prepared with higher percentages of activated carbon. As the water solubility of cyromazine is high, we have come to the conclusion that only using the highest quantity of activated carbon is possible to encapsulate cyromazine. The kinetic experiments of release in water have shown us that (i) the release rates are higher in imidacloprid formulations than in those prepared with isoproturon, (ii) the use of bentonite and/or activated carbon samples as modifying agents of an alginate-isoproturon/imidacloprid formulation reduces the release rate of the isoproturon and imidacloprid in comparison with the technical product and with alginate formulation without modifying agents, and (iii) the highest decrease is in the release rate corresponding to the formulations prepared with the highest percentage of activated carbon. Moreover, the diffusion-caused release of isoproturon and imidacloprid from the various alginate-based CR formulations into water and in this diffusion the sorption capacity of modifying agents for pesticides and formulations permeability are the most influential factors. Finally, a linear correlation between the T_{50} value and the content of activated carbon in dry granules (Q) was obtained. Thus, from the *Q* values of granules, it is possible to obtain a rough estimation of the release rate of isoproturon and imidacloprid, and it can be applied to any system of similar structure to that used in our studies.

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