

Use of Activated Bentonites in Controlled-Release Formulations of Atrazine

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The herbicide atrazine (6-chloro-*N*²-ethyl-*N*⁴-isopropyl-1,3,5-triazine-2,4-diamine) was incorporated in alginate-based granules to obtain controlled-release (CR) properties. The basic formulation [sodium alginate (1.40%)–atrazine (0.60%)–water] was modified by the addition of sorbents. The effect on atrazine release rate caused by the incorporation of acid-treated bentonite (0.5 and 2.5 M H₂SO₄) in alginate formulation was studied by immersion of the granules in water under static conditions. 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 for the comparison of the preparations. *t*₅₀ values were longer for those formulations containing acid-treated bentonite (36.78 and 29.01 days for 0.5 and 2.5 M H₂SO₄ treatments, respectively) than for the preparation without bentonite (9.69 days). On the basis of a parameter of an empirical equation used to fit the herbicide release data, it appears that the release of atrazine from the various formulations into water is controlled by diffusion mechanism. The sorption capacity of the sorbents and the permeability of the formulations (ranging from 4.99 to 20.83 mg day⁻¹ mm⁻¹) were the most important factors affecting herbicide release.

KEYWORDS: Atrazine; controlled release; activated bentonite; sorption

INTRODUCTION

Public awareness of the health hazards of pesticides has increased as a consequence of the pollution of the water environment by these compounds. This fact has stimulated interest in developing new formulations to reduce the impact of pesticides in the environment. Controlled-release (CR) pesticide formulations have several advantages over standard formulations, including increased safety for the user and nontarget organisms, a reduction in the amount of pesticide applied, and reduced leaching potentials (1–4). Many different types of CR systems have been developed for use in agriculture (5–7) including those that use a natural polymer such as alginate as a matrix for controlled release of pesticides (8–11). Besides the benefits of delayed release profiles of the pesticide, alginate formulations do not disintegrate in soil as readily as other formulations of a related nature (12).

Atrazine is a generally applied herbicide (13) and has been identified as a potential leacher by using the groundwater ubiquity scores (GUS) modeling technique (14). Furthermore, atrazine has been widely detected in groundwater (15, 16). CR formulations of atrazine would potentially extend its commercial lifetime, reduce risks of leaching or runoff on application, and be safer for the user and nontarget organisms (17). Several

modifying agents have been used in CR systems to obtain different release profiles (9, 18) including those that used natural clays (11, 19, 20). Previous studies have shown that acid treatment given to the clays produced an increase in the specific surface area of the samples (21–23) and also improved their adsorptive characteristics (24, 25), so the present study evaluated the potential use of two acid-treated bentonite samples as modifying agents in alginate-based CR formulations of atrazine. The acid-treated bentonite samples were obtained from native bentonite clay from the region of Almería and were previously studied and characterized by the present authors (21).

The objective of the present work was to evaluate the effect of incorporation of acid-treated bentonite into alginate-based formulations on the rate of atrazine release. We intend also to obtain a deeper understanding of the release mechanism of the herbicide from the investigated formulations. Therefore, CR formulations were prepared by incorporating the herbicide–clay mixtures into alginate granules by using calcium chloride as gellant. The release rate of active ingredient from alginate-based CR granules was studied using a static immersion water test. The factors influencing the controlled release of atrazine were examined by studying the interactions between the active ingredients and the sorbents, in particular, the sorption processes of atrazine with acid-treated bentonite samples.

MATERIALS AND METHODS

Materials. A natural bentonite (98% montmorillonite, containing sodium as exchange ion), previously described by González-Pradas et

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Table 1. Characteristics of the Sorbents

sample	pH	surface area (m ² g ⁻¹)	cation exchange capacity (mequiv/100 g)	exchange acidity (mequiv/100 g)
B-0.5	2.78	183.0	76.9	67.4
B-2.5	3.31	484.8	54.4	50.4

Table 2. Percentage (by Weight) of Component and pH of Controlled-Release Formulations Containing Atrazine

	atrazine (%)	sodium alginate (%)	B (%)	B-0.5 (%)	B-2.5 (%)	water (%)	pH
AA _L	0.60	1.40				98.00	7.51 (0.13) ^a
AA _L B-0.5	1.20	1.40		5.00		92.40	3.98 (0.03)
AA _L B-2.5	1.20	1.40			5.00	92.40	4.13 (0.05)

^a Values in parentheses represent the standard deviation.

al. (26), was used for the preparation of acid-treated bentonite samples. Acid activation of the bentonite was carried out in a boiling solution of H₂SO₄ (concentrations = 0.5 and 2.5 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 (25). The two products so obtained are labeled in the text as B-0.5 and B-2.5.

Bentonite samples were analyzed by standard methods. Sample pH was determined in a 1:2.5 clay/water suspension using a glass electrode (27). Specific surface area was determined from N₂ 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 (28). Properties of the acid-treated bentonite samples are shown in **Table 1**.

Technical grade atrazine (98.0%) was kindly supplied by Ciba-Geigy, S.A. Solvents used in the mobile phase for high-performance liquid chromatography (HPLC) determinations were HPLC grade acetonitrile (Merk) and water of demineralized Milli-Q quality (Millipore Corp.). Chemical products used in the preparation and evaluation of CR formulations 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 (Barcelona, Spain).

Preparation of Controlled-Release Formulations. The CR formulations prepared were based on the gelling properties of the alginate in the presence of divalent cations. Formulations containing different percentages of technical grade atrazine (A), sodium alginate (A_L), and acid-treated bentonite samples (B-0.5 and B-2.5) were made up in water (as shown in **Table 2**) and vigorously stirred for 1 h.

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, 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 AA_L, AA_LB-0.5, and AA_LB-2.5.

Analysis of Herbicide and Calcium in Granules. The actual concentration of atrazine in the dry products was determined by dissolving 20 granules in a 0.03 M tripolyphosphate solution (20 mL) following an extraction into a water/methanol (80:20) mixture (300 mL) using an ultrasound bath for 15 min. The resulting extract was filtered using nylon filters (0.45 μm) and the herbicide 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-Pack LC-18 bonded-phase column (Waters, Millipore Corp.): sample volume, 20 μL; flow rate, 1.0 mL min⁻¹; mobile phase, acetonitrile/water mix (60:40). Atrazine was analyzed at 222 nm, its wavelength of maximum absorption. External standard calibration was used, and three replicates were carried out for each formulation.

Table 3. Characteristics of Controlled-Release Granules Containing Atrazine

	atrazine (%)	Ca ²⁺ (%)	av wt (mg/granule)	encap effic ^a (%)
AA _L	19.34 (0.22) ^b		0.93 (0.05)	90.91
AA _L B-0.5	12.33 (0.12)	10.85 (1.25)	2.62 (0.08)	96.32
AA _L B-2.5	13.01 (0.18)	10.54 (0.84)	2.92 (0.12)	97.30

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

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 thermostated bath at 25 ± 0.1 °C. Then, they were removed periodically (for intervals see Results and Discussion). 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 (grams per gram of dry granule) could be calculated.

Sorption Studies. The sorption experiments were carried out as follows: Aqueous calcium chloride solutions (0.02 M) containing initial atrazine concentrations (C₀) ranging between 2 and 24 mg L⁻¹ were prepared. Amounts of 0.5 g of each bentonite sample and atrazine 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 sorption equilibrium was reached. The time required for equilibrium to be reached between atrazine sorbed and atrazine in solution was 24 h. After shaking, the solutions were centrifuged and the concentration of atrazine in the supernatant was determined by HPLC using the method described above. The atrazine sorbed was calculated from the difference between initial and final solution concentrations. Blanks containing no atrazine and three replicates of each sorption point were used for each series of experiments.

Water Release Kinetics. An accurately weighed quantity of dry CR granules containing 20.0 mg of atrazine in each sample (three replicates) was immersed in water (50 mL), whereas 5.3 mg of technical grade atrazine (three replicates) was added to 500 mL of distilled water. 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 atrazine by HPLC as described above. For CR granules, all water was replaced with fresh to minimize saturation effects, whereas for the technical grade herbicide, unused sample portions were returned to the flasks.

The experiment was concluded once 90% of the active ingredient initially present in the granules was released. To establish the mass balance, the concentration of atrazine remaining in the granules was calculated. For that, granules were removed from each flask and the herbicide concentration was determined as above-described. The amounts of atrazine released plus atrazine remaining in the granules at the end of the experiment were in agreement with the total atrazine initially present in the granules. Total averaged recovery of atrazine from all the samples was 99.9 ± 0.2%.

RESULTS AND DISCUSSION

Controlled-Release Formulations. Characteristics of alginate-based CR granules containing atrazine are presented in **Table 3**. The granules were generally spherical in shape, and the technical grade atrazine was readily incorporated in the alginate matrix, obtaining granules of size between 0.3 and 0.91 mm. The herbicide content of the dried granules is adequate for a practical agricultural application where good coverage is needed. The addition of acid-treated bentonite samples to the

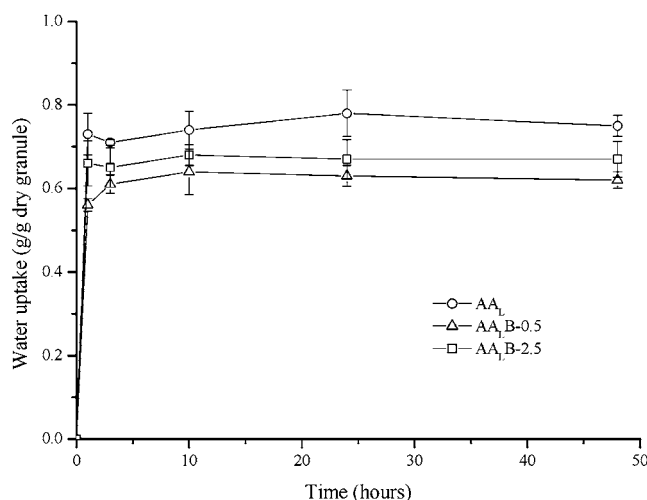


Figure 1. Water uptake of atrazine granules over time (error bars represent the standard deviation of three replicates).

alginate formulation led to larger and heavier granules that were more spherical and dried with less aggregation. In all cases, the encapsulation efficiency was >90.91%, the higher values corresponding to the formulations prepared with acid-treated bentonite samples.

Water Uptake. The water uptake of the granules versus 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 slow water uptake was observed. Water uptakes by granules containing acid-treated bentonite samples (AA₁B-0.5 and AA₁B-2.5) were less than that obtained for the alginate formulation prepared without bentonite (AA₁). Lack of structural expansion of the bentonite, together with the possible formation of bonds with the other components of the matrix on drying, may be responsible for the lower water uptake. This behavior was also observed and reported for other clays where swelling of extruded starch formulations of atrazine was reduced by the addition of increasing amounts of attapulgite, and no swelling was observed when the clay and herbicide were the only components extruded (19). Granules containing B-2.5 as modifying agent took up more water than the formulation containing B-0.5. This fact may be explained, according to a previous paper (21), by the gradual destruction of the bentonite periodic structure as the concentration of sulfuric acid used for the bentonite acid treatment increases (from 0.5 to 2.5 M), which occurs together with the formation of free silica, generating a higher percentage of microporosity and producing an increase in the specific surface area of the samples. The presence of a higher amount of SiO₂—that could be solvated by water—in B-2.5 could increase the amount of water uptake by AA₁B-2.5 formulations. The extent of swelling of the bentonite determines the volume occupied in the matrix and the area that can interact with the diffusing molecules of herbicide. Thus, water uptake and intensity of interactions of the herbicide with either B-0.5 or B-2.5 could affect the diffusion through the granules and, hence, the release of the active ingredient.

Sorption Studies. The sorption isotherms of atrazine on the natural untreated bentonite (B) and two acid-treated bentonite samples studied are shown in **Figure 2**. According to the initial portion of the curves, these isotherms may be classified as L type of the Giles classification (31), which suggests both that the samples have an average affinity for the herbicide atrazine and that there is no strong competition from the solvent for sorption sites.

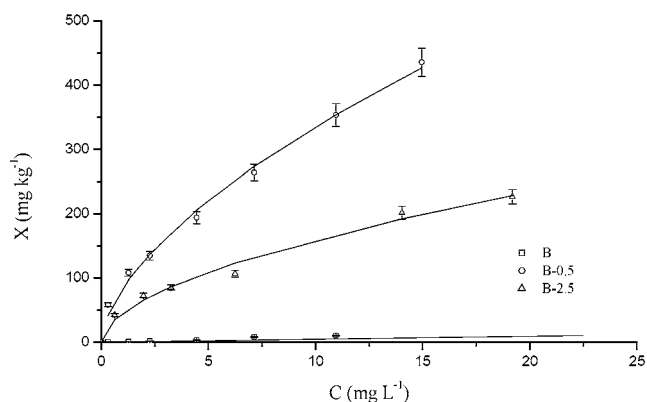


Figure 2. Sorption isotherms for atrazine on the B, B-0.5 and B-2.5 samples (error bars represent standard deviation of three replicates).

Table 4. Freundlich Coefficients, K_f and n_f , for the Sorption of Atrazine on the Bentonite Samples

sample	K_f (mg kg ⁻¹)	n_f	r^a
B	0.28 ± 0.11 ^b	1.15 ± 0.14 ^b	0.998*
B-0.5	80.86 ± 6.39	0.62 ± 0.03	0.996*
B-2.5	46.34 ± 4.53	0.54 ± 0.04	0.994*

^a An asterisk indicates significance at the 0.001 probability level. ^b These values represent the 95% confidence limits.

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 atrazine 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 herbicide. The constant K_f is the amount of herbicide 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 >0.99, the correlation being significant at $p = 0.001$.

As can be seen from **Table 4**, K_f values are 80.9 mg kg⁻¹ for B-0.5 and 46.3 mg kg⁻¹ for B-2.5, these values being much higher than that obtained for adsorption of atrazine on natural untreated bentonite (34). Increased adsorption of atrazine on bentonite samples is probably due to the decrease of the pH generated (35). The decrease of the pH leads to a greater protonation of atrazine, and then a greater sorption takes place by a cation exchange mechanism. This mechanism could operate complementarily to the sorption of nonprotonated species throughout relatively weak interactions such as van der Waals forces and hydrogen bonds (36). The lower pH generated and the higher cation exchange capacity of the B-0.5 sample compared with those observed for B-2.5 could lead to a higher sorption capacity of B-0.5 sample for atrazine.

Release Studies. The cumulative release of atrazine from alginate-based CR granules and the solubility profile for technical grade atrazine are shown in **Figure 3**. As can be seen, 89.78% of technical grade product is dissolved in <6 days, whereas it takes at least 108 days to release 93.43% of active ingredient from the alginate-based CR formulation AA₁B-0.5.

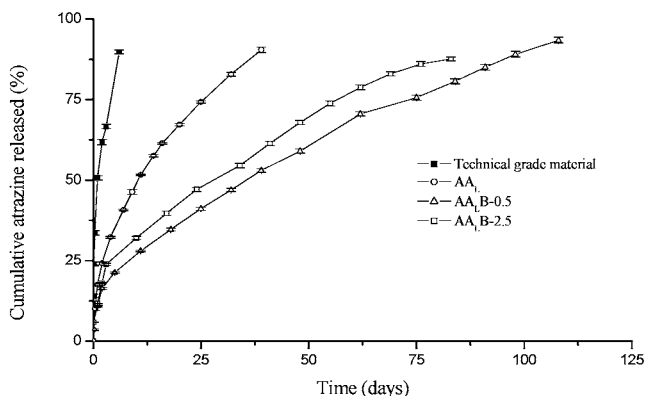


Figure 3. Cumulative release of atrazine from granules into static water (error bars represent the standard deviation of three replicates).

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

product	$K_H \times 10^2 \text{ (days)}^{-1/2}$	r^a	$P \times 10^5 \text{ (mg days}^{-1} \text{ mm}^{-1}\text{)}$
AA _L	4.35 ± 0.04^b	0.999*	20.83 ± 0.03
AA _L B-0.5	2.29 ± 0.03	0.992*	4.99 ± 0.05
AA _L B-2.5	2.65 ± 0.10	0.996*	7.00 ± 0.08

^a An asterisk indicates significance at the 0.001 probability level. ^b These values represent the standard error.

For all formulations, a decline in the release of herbicide 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 (37). 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, for example, semisolid ointment. The application of the model proposed by this author presumes that (1) a pseudo-steady-state exists, (2) the active ingredient particles are small compared to the average distance of diffusion, (3) the diffusion coefficient is constant, and (4) a perfect sink condition exists in the external medium. In these conditions, the following equation was derived for spherical monolith systems, assuming Fickian diffusion ($y = kt^{1/2}$) (38, 39):

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

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 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 . The higher value of permeability is clearly shown for AA_L granules, and lower values are shown for AA_LB-0.5 and AA_LB-2.5. Similar variation was observed for K_H values according to the likeness between the values of C_0 and r of the granules.

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

product	$K \text{ (days)}^{-n}$	n	r^a	$t_{50} \text{ (days)}$
AA _L	0.15 ± 0.002^b	0.53 ± 0.009	0.999*	9.69
AA _L B-0.5	0.11 ± 0.009	0.42 ± 0.026	0.997*	36.78
AA _L B-2.5	0.13 ± 0.008	0.40 ± 0.018	0.996*	29.01

^a An asterisk indicates significance at the 0.001 probability level. ^b These values represent the standard error.

To simplify the analysis curves from three-dimensional devices, the release data were analyzed by applying the empirical equation proposed by Ritger and Peppas (40):

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

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 that is indicative of the transport mechanism.

The values of K and n obtained from the initial 60% of released atrazine, 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 atrazine 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 0.40 for the AA_LB-2.5 formulation up to 0.53 for the AA_L formulation. Values of n close to 0.43 are indicative of Fickian diffusion in spherical monolithic matrices (40). The complexity of the heterogeneous system involved together with the capacity of the acid-treated bentonite 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 atrazine to be released) calculated from K and n constants ranged from 9.69 days for the AA_L CR formulation to 36.78 days for the AA_LB-0.5 CR formulation (**Table 6**). The release rate of atrazine from these granules is slower than that obtained by Carr et al. using different levels of clay in starch-encapsulated atrazine, where 50% atrazine was released from encapsulated products after 50 h (41). The alginate-based CR formulations can be ranked in order of increasing t_{50} values as follows:

$$AA_L < AA_L B-2.5 < AA_L B-0.5$$

The lowest value of t_{50} corresponds to AA_L granules, which means that this CR preparation produces the fastest atrazine release in water. The addition of acid-treated bentonite samples to the basic alginate formulation reduces the rate of release, the B-0.5 sample producing a slower release rate compared to the B-2.5 sample. For a soil system, the same trends in release rate of the herbicide 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 compared with the release of atrazine. 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, the sorption capacity of modifying agents and the matrix permeability (39).

In relation to the first factor, the sorption capacity, the extent of interaction between the modifying agents and atrazine, will affect the release of atrazine from the alginate-based granules. This aspect has been quantified with sorption experiments of atrazine with acid-treated bentonite samples. A higher sorption capacity would result in a slower release of herbicide. As related above, sorption experiments show that the sorption capacity (K_f) of the B-0.5 sample for atrazine ($K_f = 80.9 \text{ mg kg}^{-1}$) was higher than that obtained with the B-2.5 sample ($K_f = 46.3 \text{ mg kg}^{-1}$). The results obtained seem to be in agreement with the fact that granules containing acid-treated bentonite samples as modifying agents (AA_LB-0.5 and AA_LB-2.5) produce a slower release compared with that without modifying agent (AA_L). In addition, the incorporation of the B-0.5 sample produces the slowest value of t_{50} . Gerstl et al. studied the release of atrazine and alachlor into aqueous solution from controlled-release formulations (CRFs) prepared from alginate and pectin, with and without the addition of clay minerals (42). They reported that the addition of sodium montmorillonite to the CRFs was found to have a profound inhibitory effect on the release of alachlor. This was attributed to the sorption of the herbicide to the clay mineral. The t_{50} values for atrazine CRFs ranged from 290 h (atrazine/alginate/montmorillonite) to 300 h (atrazine/alginate-pectin/montmorillonite). These t_{50} values are lower than the values obtained for AA_LB-0.5 ($t_{50} = 36.78$ days) and AA_LB-2.5 ($t_{50} = 29.01$ days), probably due to the higher sorption capacity of activated bentonites (B-0.5 and B-2.5) for atrazine.

In relation to the second factor, a lower matrix permeability value would result in a slower release of atrazine. The alginate-based CR formulation studied can be ranked in order of increasing P values as follows:

$$\text{AA}_L\text{B-0.5} < \text{AA}_L\text{B-2.5} < \text{AA}_L$$

This variation in order is the same as that obtained when the rate release of granules was analyzed.

Conclusions. Experimental results suggest that the use of acid-treated bentonite samples as modifying agents of an alginate-atrazine formulation could reduce the release rate of the herbicide in comparison with the technical product and with alginate formulation without acid-treated bentonite. The release of atrazine from the various alginate-based CR formulations into water may be due to diffusion where the sorption capacity of sorbent for atrazine and formulation 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 affected atrazine mobility. Therefore, the use of formulations such as those described in this paper could help to prevent the environmental impact derived from the use of atrazine in the agricultural activity.

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