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Prevention of Herbicides Pollution Using Sorbents in Controlled Release Formulations

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1. Introduction

At present, the consume of great quantities of herbicides for crop protection is supposing an important challenge for the maintenance of the welfare state. The correct use of such substances will contribute to protect the natural resources avoiding environment pollution and harm on the public health.

In spite of the great effort made by the agrochemical industry in the last decades, developing new biodegradable herbicides, and producing new types of formulations such as concentrated in suspension, granules, soluble liquids, and so, there are still important problems derived from the immediate release of the active principles which compose them. Over 95% of sprayed conventional formulations of herbicides reach another destination than their target species, including nontarget species, air, water, bottom sediments, and food (Mogul et al., 1996). This situation leads to toxicity risks near the crops as a result of the high concentrations of active applied mass, as well as by the losses of active ingredients as a consequence of processes such as biodegradation, chemical degradation, photolysis, evaporation, surface runoff, and percolating groundwater, without considering the specific danger of these formulations to the applier by inhalation or absorption through skin.

The result of trying to compensate such losses is a tendency showing the use of excessive quantities of these dangerous chemical substances. This situation is an important economic loss and, at the same time, it is perilous for human health as well as for environment (Mogul et al., 1996).

2. Important

In the agrochemical industry the use of controlled release formulations (CRFs) could be a potential solution for low efficacy and environmental pollution derived from the use of conventional pesticide formulations (Scher, 1999). The aims of CRFs are to protect the supply of the agent, to allow the release of the agent to the target at a controlled rate, and to maintain its concentration in the system within the optimum limits, over a specified period of time, thereby providing great specificity and persistence (Flores Céspedes et al., 2007).

The parameters that affect the properties of CRFs depend on the nature and type of polymer used. Despite of several polymers employed in CRFs natural polymers such as starch, ethylcellulose, lignin, chitosan and alginate, are preferred to synthetic polymers because of

their non-toxic, low cost, free availability, and biodegradability characteristics (Fernández Pérez et al., 2004; 2010).

Alginate gel has been applied to produce an effective CR carrier of drugs (Liew et al, 2006) and pesticides (Fernández Pérez et al., 2000; 2004; 2005) because it forms strong gels in aqueous media and is bioerodible.

In this chapter, discussion is focused on the use of several sorbents as modifying agents in the preparation of alginate-based controlled release formulations of herbicides. The addition of sorbents such as natural and activated clays, humic acid, activated carbon or mineral carbon in CRFs shows that the encapsulation efficiency increases and a better control on release profiles of active ingredient is reached. Therefore, they reduce the environmental pollution by eliminating the need for widespread distribution of a large amount of herbicides at one time.

3. Information

3.1 Herbicides

Herbicides decrease growth, seed production and competitiveness of susceptible weeds, are an integral part of management systems for agricultural practices. Systemic widely soil-applied herbicides have been selected in this study. IUPAC name, applications and action mode are summarized in Table 1.

Herbicide	IUPAC name	Applications/action mode
Diuron	[3-(3,4-dichlorophenyl)-1,1-dimethylurea]	Widely soil-applied herbicide for general weed control
Atrazine	[2-chloro-4-(ethylamine)-6-(isopropylamine)-s-triazine]	Selective triazine herbicide used to control broadleaf and grassy weeds. It is also used as a non-selective herbicide on non-cropped industrial lands and on fallow lands.
Isoproturon	[3-[4-isopropylphenyl]- 1,1-dimethylurea]	Selective, systemic herbicide used in the control of annual grasses and broadleaved.
Chloridazon	[5-amino-4-chloro-2-phenyl-3(2H)-pyridazinone]	Selective herbicides, to be absorbed predominantly by the roots, with translocation to all plant parts. They are used for the control of annual broad-leaved weeds in field and vegetable crops.
Metribuzin	[4-amino-3-methylthio-6-ter-butyl-1,2,4-triazin-5(4H)-one]	

Table 1. Selected herbicides.

Herbicides applied in the field have several fates, including uptake by plants, degradation in plants or soil, off-target, movement, immobilization and unintended deposition in the environment. In a well-planed management system, herbicide should effectively control weeds with little or no adverse environmental effects. Nevertheless, high amounts of herbicides used in agronomic practices lead to the existence of polluted groundwater sources, mainly through leaching process. The most important elements that condition a herbicide to be susceptible to leach, being a potential pollutant in groundwater, are the properties of the herbicide, taking sorption and persistence in soil as the most relevance ones. Soil persistence of an herbicide is measured through half-life time in soils (DT_{50}, time

required for the herbicide to be degraded to a 50% of the initial amount of the herbicide in soil). Herbicides are ranked on the basis of DT_{50} as non-persistent when DT_{50} is under 30 days, slightly persistent when DT_{50} is between 30 and 100 days and persistent when DT_{50} is over 100 days. In this way, high half-life herbicides are mainly persistent and thus they possess great lixiviation potential to groundwaters. In addition, as previously mentioned, the sorption capacity of soil by a determined herbicide is an important factor that also affects potential to polluted groundwaters. The different models used to predict herbicide movement in soil take the constants describing the sorption process (K_d and K_f) as key input in the aforementioned models (Jury et al., 1987). Therefore a specific constant can be calculated for each herbicide, known as K_{oc}, which is a partition coefficient in relation to organic carbon in soil (O.C.) according to the equation.

$$K_{oc} = \frac{K_f}{O.C.} \times 100 \qquad (1)$$

Some physical-chemical properties of the herbicides selected in this study are shown in Table 2 (PPDB, 2009).

Herbicide	Molecular weight (g mol⁻¹)	Watersolubility (mg L⁻¹)	Log K_{ow}	K_{oc} (mL g⁻¹)	Soil DT_{50} (days)	Vapor pressure (mPa)
Diuron	233.1	36.4 (25 °C)	2.84	1067	75.5	$1.10 \cdot 10^{-3}$
Atrazine	215.7	33 (22 °C)	2.50	100	75	$3.85 \cdot 10^{-2}$
Isoproturon	206.3	65 (22 °C)	2.50	122	12	$3.15 \cdot 10^{-3}$
Chloridazon	221.6	340 (20 °C)	1.19	199	31	< 0.01
Metribuzin	214.3	1050 (20 °C)	1.60	38	11.5	0.06

Table 2. Physical-chemical properties of selected herbicides.

To evaluate leaching potential (LP) of a non-ionic herbicide, the K_{oc} and DT_{50} values can be used in the following equation 2 (Guftason, 1989).

$$LP = log(DT_{50} \ soil) \times (4 - log(K_{OC})) \qquad (2)$$

According to the values obtained through the application of this equation, herbicides can be classified as it follows: Non-leachers (LP < 1.8), transitional/intermediate leachers (1.8 < LP < 2.8) and leachers (LP > 2.8). LP parameters for diuron, isoproturon, chloridazon, metribuzin and atrazine have been obtained using the aforementioned equation. These values were 1.83, 2.07, 2.54, 2.57 and 3.75 for diuron, isoproturon, chloridazon, metribuzin and atrazine, respectively. It is clear that atrazine is a leacher due to its high LP value and diuron, isoproturon, chloridazon, metribuzin are right between transitional/intermediate leachers. Consequently diuron, isoproturon, chloridazon, metribuzin have been found to leach, and atrazine has been widely confirmed by the widespread detections in surface water and groundwater (Buchanan et al., 2009).

The risk of pollution resulting from rapid runoff and leaching of these relatively highly soluble herbicides can be minimized through their application in controlled release formulations (CRFs).

3.2 Alginate

Alginates constitute a family of linear binary copolymers, consisting of (1 / 4) linked β-D-mannuronic acid (M) and α-L-guluronic acid (G) residues (see Fig. 1a and b). Chemical composition and sequence may vary widely between algae species and even between different parts of the algae and the time of year when it is harvested. (Gombotz & Wee, 1998). Alginate has been determined to be a true block copolymer with no regular repeating unit; i.e. the alginate molecule consisted of M-blocks, G-blocks and stretches of blocks of a predominantly alternating structure.

The capability of this copolymer to form stable biodegradable gels in the presence of divalent cations has been known and studied extensively since the seventies. These gelation properties can be attributed to the simultaneous binding of the divalent cations such as Ca^{2+} to different chains of α-l-guluronate blocks (G-blocks) (Figure 2). As a result of their configuration, these chains form electronegative cavities, capable of holding the cations via ionic interactions, resulting in the cross-linking of the chains into a structure resembling an "egg box" (Papageorgiou et al., 2006).

Alginate has been used successfully for many years in the food and beverage industry as a thickening agent, a gelling agent and a colloidal stabilizer. Alginate also has several unique properties that have enabled it to be used as a matrix for the entrapment and/or delivery of a variety of products on many fields including agriculture, food, cosmetics, construction, pharmacology, analytics, biotechnology, and medicine (Liew et al., 2006).
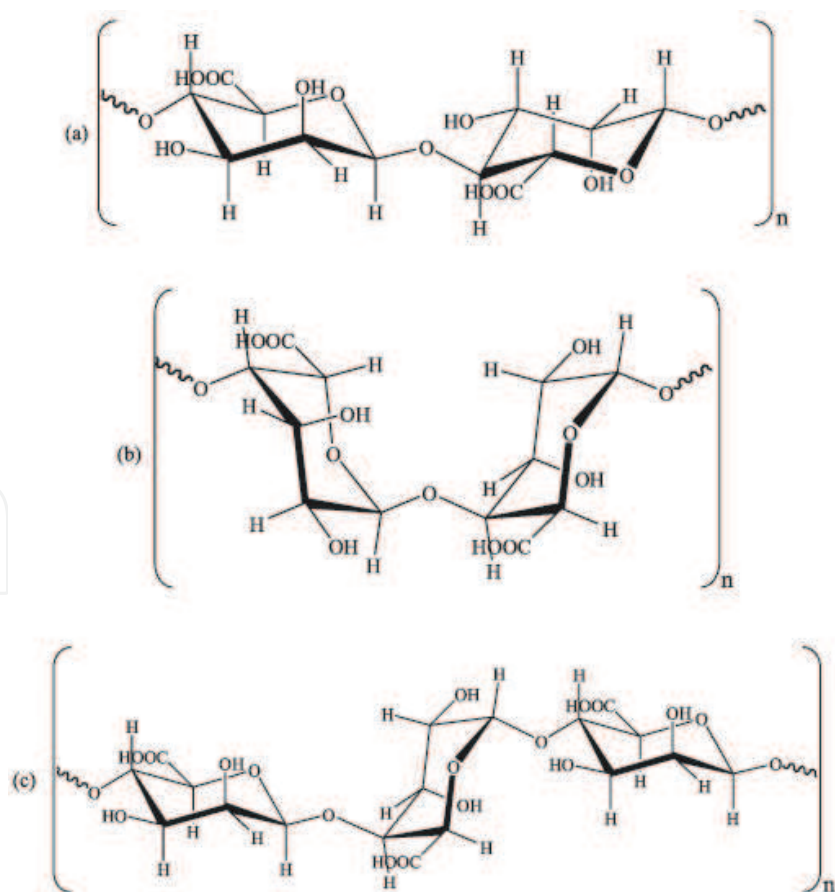

Fig. 1. The structure of the chemical units of alginate; mannuronic acid (a), guluronic acid (b) and mannuronic-guluronic chain (c).
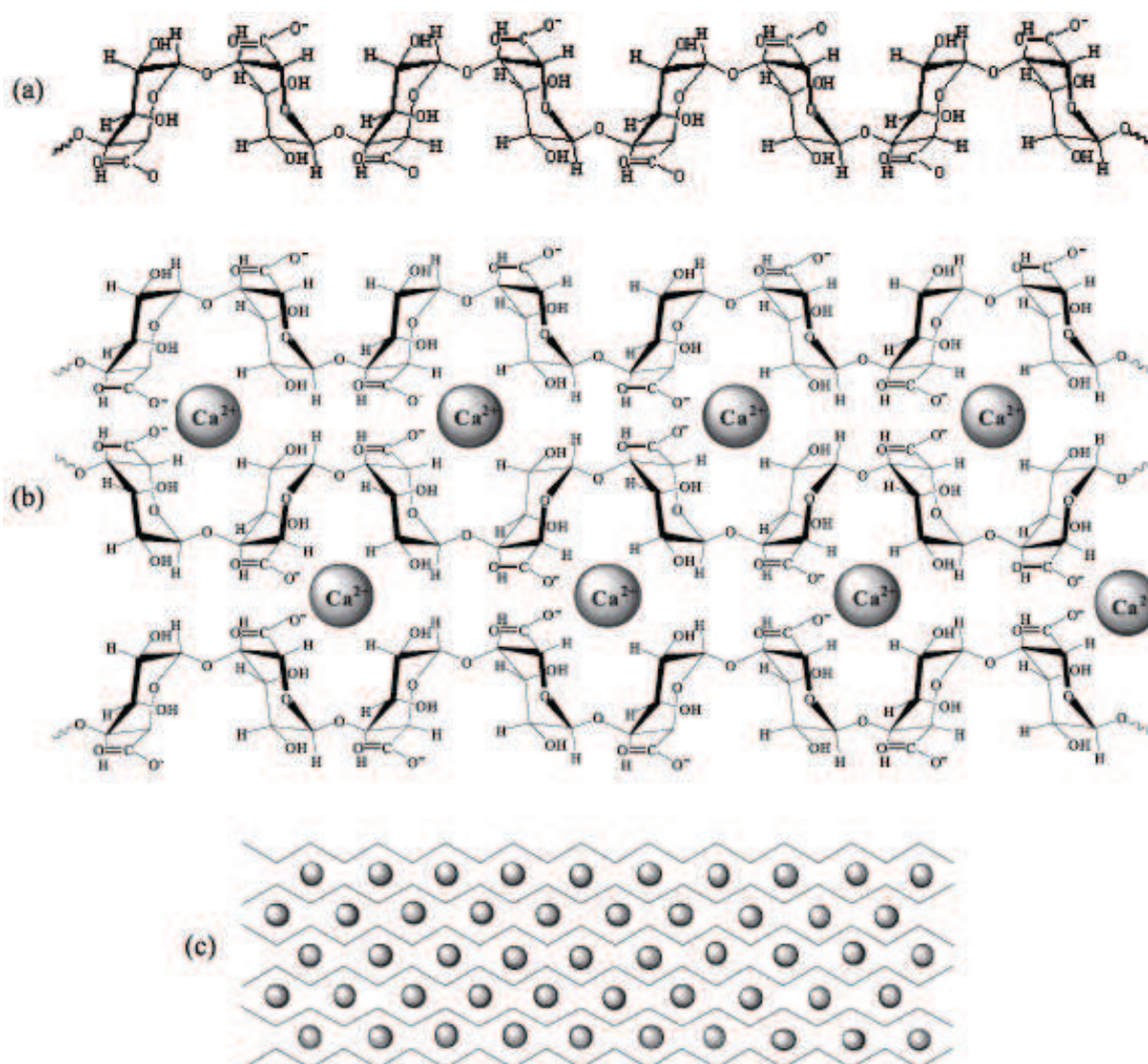
Fig. 2. Alginate gel formation, guluronic acid homopolymers in solution (a), binding between homopolymers chains by Ca^{2+} ions (b), gel formation by binging homopolymeric chains by Ca^{2+} ions (c).

3.3 Sorption and sorbents

Sorption is one of the main retention phenomena that determine the transport, transformation, and biological effects of herbicides in the environment. Besides, sorption is one of the methods which have been applied for removing organic and inorganic pollutants from waters using sorbents with highly developed surface properties. These types of sorbents can be also used as modifying agents in controlled release formulations to obtain different release profiles. The potential use of sorbents such as natural and acid-trated bentonite, a mineral carbon such as anthracite, and an activated carbon as modifying agents in alginate-based controlled release formulations of herbicides has been evaluated (Villafranca-Sánchez et al., 2000; Garrido-Herrera et al., 2006; Flores-Céspedes, et al., 2007).

Bentonites is a well-known silicate which include a significant group of natural materials mostly composed from fine-grained particles of minerals from the group dioctahedral smectite-montmorillonite. Viraraghavan and Kapoor (1994) noted that the abundance and

low cost of bentonite make it a strong candidate as a sorbent for the removal of heavy metals and organic contaminants from wastewaters. The composition of bentonite varies, though it consists mainly of montmorillonite. Montmorillonite clays have the smallest crystals, the largest surface area and the highest cation exchange capacity. Thus montmorillonite clays would be expected to have the highest sorptive capacity. Crystallochemical formula of bentonite:

$$[Si^{4+}_{7.36}Al^{3+}_{0.64}]_T [Al^{3+}_{3.18}Fe^{3+}_{0.32} Mg^{2+}_{0.687}]_O O_{20}(OH)_4 X^+_{0.76}$$
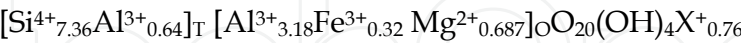
Previous studies have shown that acid treatments given to the clays produced an increase in the specific surface area of the samples (González-Pradas et al., 1991) and also improve their adsorptive characteristics (Jovanovic & Janackovic, 1991; González-Pradas et al., 1993).

Activated carbon in its broadest sense includes a wide range of processed amorphous carbon-based materials. It is not truly an amorphous material but has a microcrystalline structure. The activated carbons in general have a strongly developed internal surface and are usually characterized by a polydisperse porous structure consisting of pores of different sizes and shapes. These structural properties make activated carbons excellent adsorbents. The adsorption capacity of an activated carbon is determined by the physical or porous structure but strongly influenced by the chemical structure of the carbon surface. Carbon-oxygen surface groups are by far the most important surface groups that influence the surface characteristics such as the wettability, polarity, and acidity, and the physico-chemical properties such as catalytic, electrical, and chemical reactivity of these materials.

Anthracite is an intriguing feedstock for premium carbon materials; indeed, anthracite is essentially a carbon material. Most anthracites contain 92–98% carbon, virtually all of which is present as aromatic carbon in large polycyclic sheets. These sheets may contain 30 or more fused aromatic rings, resulting in extraordinary properties such as highly ordered carbon that also exhibits a high ultra-microporosity pore volume. The microporosity of anthracites makes them useful in, e.g., water filtration applications and sorption process.

	Surfacearea $(m^2 g^{-1})$	MicroporeVolume $(mL g^{-1})$	C.E.C meq/100g	pH
B	65.46	15.04	65.63	9.02
B$_{0.5}$	182.97	42.03	76.88	1.87
B$_{1.0}$	298.84	68.65	73.75	1.84
B$_{2.5}$	484.78	111.36	54.38	2.19
An	23.40	5.37		8.87
C	858.07	197.11		9.11

B: natural bentonite; **B$_{0.5}$**: bentonite treated with H_2SO_4 0.5 M; **B$_{1.0}$**: bentonite treated with H_2SO_4 1.0 M; **B$_{2.5}$**: bentonite treated with H_2SO_4 2.5 M; **An**: anthracite; **C**: activated carbon

Table 3. Physical-chemical characteristics of sorbents.

3.4 Controlled release formulations of herbicides
3.4.1 Preparation of controlled release formulations (CRFs)

Herbicides CRFs were prepared 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 herbicide, sodium alginate (A), bentonite (B) or acid-treated bentonite ($B_{0.5}$, $B_{1.0}$, $B_{2.5}$), anthracite (An) and activated carbon (C) (shown in Table 4).

Herbicide	Formulation	A.I. (%)	A (%)	B (%)	$B_{0.5}$ (%)	$B_{1.0}$ (%)	$B_{2.5}$ (%)	An (%)	C (%)
Atrazine	AA	0.60	1.40						
	AAB	1.20	1.40	5.00					
	$AAB_{0.5}$	1.20	1.40		5.00				
	$AAB_{2.5}$	1.20	1.40				5.00		
Diuron	DA	0.60	1.40						
	DAB	1.20	1.40	5.00					
	$DAB_{0.5}$	1.20	1.40		5.00				
	$DAB_{2.5}$	1.20	1.40				5.00		
Isoproturon	IA	0.67	1.87						
	IAB	1.19	1.87	3.28					
	$IAB_{0.5}$	1.19	1.87		3.28				
	$IAB_{1.0}$	1.19	1.87			3.28			
	$IAB_{2.5}$	1.19	1.87				3.28		
Chloridazon	ClA	0.28	1.47						
	ClAB	1.17	1.39	4.75					
	ClAAn	1.17	1.39					4.75	
	ClAC	1.17	1.39						4.75
	$ClABC_{20}$	1.17	1.39	3.29					1.46
Metribuzin	MA	0.28	1.47						
	MAB	1.17	1.39	4.75					
	MAAn	1.17	1.39					4.75	
	MAC	1.17	1.39						4.75
	$MABC_{20}$	1.17	1.39	3.29					1.46

Table 4. Percentage (by weight) of the components of CR formulations containing herbicides (water to 100%).

The alginate-sorbent mixtures were vigorously stirred and then were dropwise added to a gellant bath of 0.25 M $CaCl_2$ using the apparatus described by Connick (1982). The resulting beads were filtered and dried first at room temperature and then in an oven to constant weight.

Characteristics of dry granules such as active ingredient content, calcium content, granule size, average weight and encapsulation efficiency are shown in Table 5.

Herbicide	Formulation	Active ingredient (%)	Ca^{2+} (%)	Average weight (mg/granule)	Average diameter (mm/granule)	Encapsulation Efficiency[a] (%)
Atrazine	AA	19.34	-	0.93	0.78	90.91
	AAB	11.60	10.90	2.49	1.52	98.74
	AAB$_{0.5}$	12.33	10.85	2.62	1.62	96.32
	AAB$_{2.5}$	13.01	10.54	2.92	1.82	97.30
Diuron	DA	21.53	-	0.90	1.08	98.85
	DAB	12.75	8.30	2.66	1.38	98.56
	DAB$_{0.5}$	13.09	9.25	2.77	1.54	98.33
	DAB$_{2.5}$	13.57	13.36	2.77	1.80	98.56
Isoproturon	IA	15.85	10.10	1.49	1.22	98.46
	IAB	13.77	20.50	2.34	1.58	97.21
	IAB$_{0.5}$	13.80	23.10	2.48	1.60	91.92
	IAB$_{1.0}$	13.65	22.70	2.66	1.73	98.04
	IAB$_{2.5}$	14.06	25.00	2.68	1.79	99.27
Chloridazon	ClA	7.18	16.37	0.94	0.99	74.91
	ClAB	12.13	3.99	2.28	1.17	92.66
	ClAAn	13.17	4.77	2.54	1.25	92.44
	ClAC	12.72	5.32	3.02	1.73	99.67
	ClABC$_{20}$	11.93	5.76	2.57	1.30	93.61
Metribuzin	MA	4.00	16.84	0.72	0.95	38.12
	MAB	9.78	6.93	2.22	1.17	75.98
	MAAn	11.31	10.55	2.16	1.23	79.86
	MAC	11.84	6.88	2.69	1.66	90.24
	MABC$_{20}$	10.95	7.08	2.02	1.19	80.14

[a] Encapsulation efficiency= (amount of herbicide in dry product / amount of herbicide in formulation processed) x 100

Table 5. Characteristics of CR granules (dry products) containing atrazine, diuron, isoproturon, chloridazon and metribuzin.

3.4.2 Water uptake test

Water uptake behavior, including swelling ratio and water uptake kinetics, is a very important property for an alginate-herbicide delivery vehicle, because it has a great influence on controlled delivery behaviour. The swelling behavior of the CR granules was studied by using the method of Franson and Peppas (1983). As an example, the water uptake of the granules containing diuron and chloridazon vs. time is shown in Figure 3.

The presence of a higher amount of microporosity in granules increases the amount of water uptake in formulations containing sorbents as modifying agents (Fernández Pérez et al., 2005). The extent of swelling of the anthracite, bentonites and activated carbon 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 anthracite, bentonites and activated carbon could affect the diffusion through the granules, and hence, the release of the active ingredient. For granules without sorbents, it is necessary to consider that there are not additional bonds with other components of matrix on drying; thus expansion by swelling process is possible (Flores-Céspedes et al., 2007).
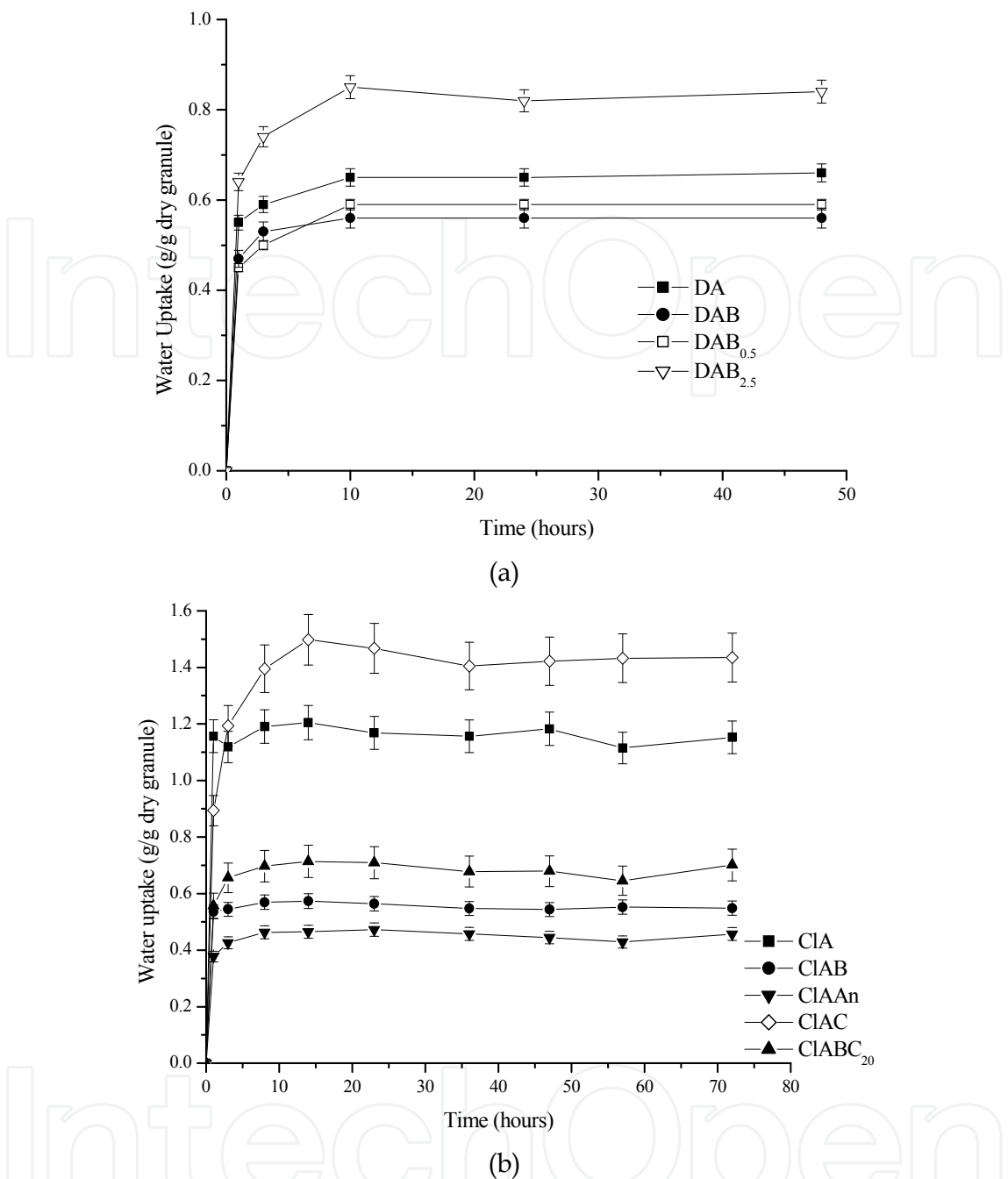
(a)

(b)

Fig. 3. Water uptake of diuron (a) and chloridazon (b) granules over time (error bars represent the standard deviation of three replicates).

3.4.3 Sorption studies

The effect of incorporation of different sorbents into alginate-based formulations on the rate of herbicide release can be evaluated through the study of the interactions between the active ingredients and the sorbents. Sorption isotherms of herbicides with natural bentonite, acid-treated bentonite, anthracite and activated carbon were compared using the K_f parameter of the Freundlich equation. The K_f and n values were calculated from the least-square method applied to the linear form of the Freundlich equation and their values are summarized in Table 6.

Herbicide	Sorbent	K_f (mg kg^{-1})	n	r
Atrazine	B	0.28	1.15	0.998
	$B_{0.5}$	80.86	0.62	0.996
	$B_{2.5}$	46.34	0.54	0.994
Diuron	B	2.58	0.69	0.970
	$B_{0.5}$	11.08	0.50	0.987
	$B_{2.5}$	13.00	0.74	0.991
Isoproturon	B	0.48	0.72	0.979
	$B_{0.5}$	8.53	0.75	0.987
	$B_{1.0}$	8.50	0.78	0.998
	$B_{2.5}$	13.43	0.79	0.999
Chloridazon	B	4.09	0.92	0.999
	An	$1.41 \cdot 10^3$	0.26	0.960
	C	$2.03 \cdot 10^5$	0.09	0.974
Metribuzin	B	0.53	1.17	0.983
	An	$0.55 \cdot 10^3$	0.20	0.996
	C	$1.16 \cdot 10^5$	0.14	0.964

Table 6. Freundlich coefficients, K_f and n_f, for the sorption of herbicides on the bentonite and acid-treated bentonites, anthracite and activated carbon samples.

Sorption capacities (K_f) of the acid-treated bentonite samples were higher than that obtained with natural bentonite for diuron, isoproturon and atrazine. Sulfuric acid treatments to the bentonite resulted in higher efficiencies of sorption due to the increase of the specific surface of the acid treated samples. A slightly increase of K_f values for acid-treated bentonites is observed for diuron and isoproturon as acid treatment increases. For atrazine, the lower pH generated and the higher cation exchange capacity of $B_{0.5}$ sample compared with these observed for $B_{2.5}$ lead to a higher sorption capacity for the first. The decrease of the pH leads to a greater protonation of atrazine and then a greater sorption takes place by a cation exchange mechanism.

Sorption of chloridazon and metribuzin on bentonite produce the lowest K_f values and the higher was obtained for the activated carbon, being intermediate the values obtained of K_f for the sorption of the herbicides on anthracite. The K_f values for sorption of chloridazon and metribuzin on activated carbon are approximately 10^2 times higher than those obtained for sorption on anthracite and approximately 10^5 times higher than those obtained for sorption of herbicides on bentonite. The highest porosity and surface area of the activated carbon compared with those obtained for the anthracite and bentonite samples could explain the higher sorption capacity of activated carbon for the herbicides. The higher value of K_f obtained for anthracite, with regarding to bentonite, seems to be related to the higher affinity of the surface of anthracite by herbicides (Andrésen et al., 2004).

3.4.4 Water release kinetics

Water release experiments, made as a static immersion water test, let to obtain a deeper understanding of the release mechanism of the herbicides from CRFs.

Figures 4, 5 and 6 showed the cumulative release of atrazine, chloridazon and metribuzin, respectively, from alginate-bentonite based CR granules and the solubility profile for technical grade product.
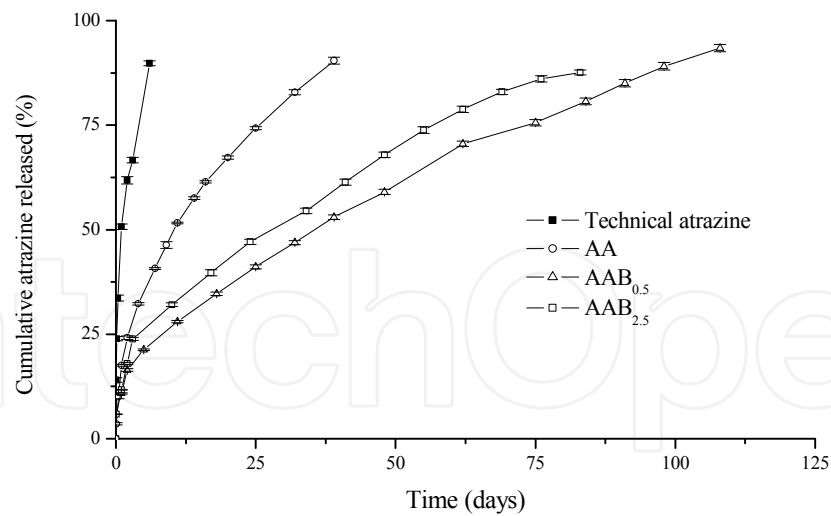
Fig. 4. Cumulative release of atrazine from alginate-bentonite CR granules into static water.
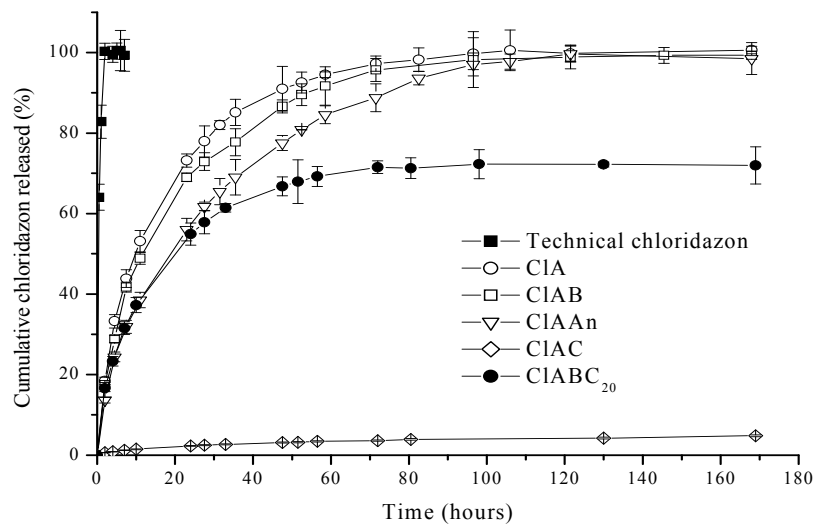

Fig. 5. Cumulative release of chloridazon from alginate CR granules into static water.
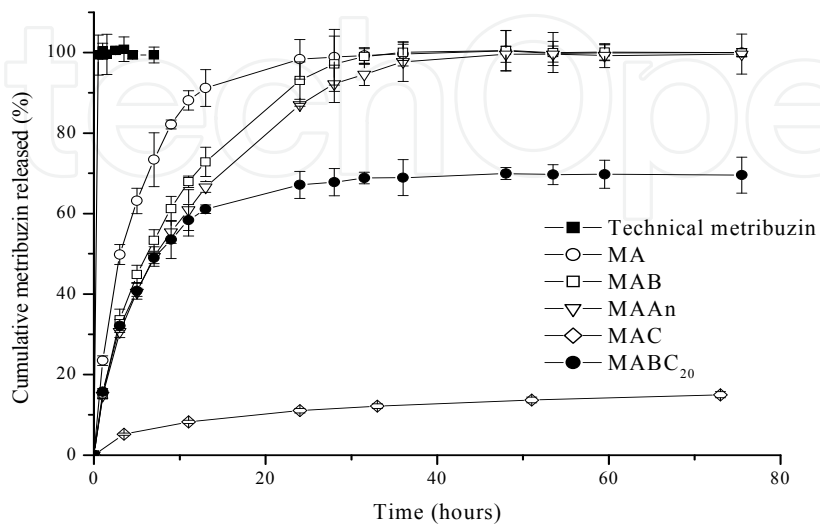

Fig. 6. Cumulative release of metribuzin from alginate CR granules in water.

The influence of the modifying agents such as natural and acid-treated bentonite, anthracite and activated carbon, appears clearly defined for all CR systems prepared. The presence of the sorbents produce a slower release rate in comparison to the CRFs prepared without these modifiers, being higher the decrease in the release rate of active ingredient for the sorbent with higher sorption capacity.

To evaluate the influence of the modifiers on the release rate of herbicides from CR granules, the release data must be analysed using diffusion-controlled models. The decline in the release of herbicide with time observed in Figures 4, 5 and 6 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. Alginate-sorbents formulations could be described as systems containing finely divided solute particles, which are uniformly dispersed within the matrix phase. Higuchi (1963) 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, (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 media. In these conditions, the following equation was derived for spherical monolith systems, assuming Fickian diffusion ($y = kt^{1/2}$) (Higuchi, 1963):

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

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). K_H values and correlation coefficients were obtained

Herbicide	Formulation	$K_H \times 10^2$ (h$^{-1/2}$)	r	$P \times 10^4$ (mg h^{-1}mm^{-1})
	ClA	4.90	0.999	0.65
	ClAB	4.37	0.999	1.50
Chloridazon	ClAAn	3.78	0.999	1.30
	ClAC	0.09	0.985	0.00061
	ClABC$_{20}$	2.92	0.996	0.66
	MA	10.00	0.999	1.33
	MAB	7.34	0.998	3.36
Metribuzin	MAAn	6.36	0.998	2.71
	MAC	0.36	0.986	0.0081
	MABC$_{20}$	5.20	0.998	1.57

Table 6. Constants from fitting Higuchi equation to the release data of chloridazon and metribuzin in water and matrix permeability parameter.

by applying the model proposed by Higuchi to release data. As examples, the values for the formulations containing chloridazon and metribuzin are presented in Table 6 together with values of matrix permeability.

The values of P for the granules that contain modifiers, in general, decrease as the herbicide sorption capacity of the modifiers increases. This variation order for P values is in agreement with those observed when the release rate was evaluated from the CR granules. This coincidence suggests that the factors which affect and control the permeability and the release of active ingredient from the different granules studied should be the same, and therefore produced by the presence of modifying agents as anthracite, bentonite, acid-treated bentonite and activated carbon.

Ritger and Peppas equation was used to obtain the time taken for 50% of the herbicides to be released (T_{50}). This equation is used to relate the amount of active ingredient released as an exponential function of the release time (Ritger and Peppas, 1987).

$$\frac{M_t}{M_0} = Kt^n \tag{4}$$

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.

The values of K and n and the correlations coefficients for atrazine, chloridazon and metribuzin are presented in Table 7. Values of n close to 0.43 are indicative of Fickian diffusion in spherical monolithic matrixes (Ritger and Peppas, 1987). Slightly different values than 0.43 of n could be explained by the complexity of the heterogeneous system involved together with the capacity of the sorbent to interact with the active ingredient. According to n values, the release of herbicide from the alginate-based CR formulations into water is due to diffusion where the sorption capacity of sorbent for herbicide and formulation permeability are the most influential factors.

T_{50} values, calculated from K and n constants, are presented in Table 7. The order of variation in T_{50} parameter for the different groups of prepared system is explained if we consider that the extent of the interactions between herbicides and modifying agents will affect the diffusing process and so on the release rate of herbicides from the alginate-based granules. This aspect has been quantified with sorption experiments of herbicides with bentonite, acid treated bentonite, anthracite and activated carbon samples. A higher sorption capacity result in a slower release of herbicide.

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 affect the herbicide mobility. This can be useful to prevent the polluting environmental risk derived from the use of herbicides mainly in soils with a low sorption capacity, where the herbicides shows a greater potential to cause groundwater pollution. In this sense, herbicides mobility from CRFs can be evaluates through leaching experiments in soil columns. Mobility of diuron, isoproturon and atrazine from an alginate-bentonite controlled release formulation in layered greenhouse soil (i.e., native soil, amended soil, peat, and sand) was researched. These studies indicate that the use of CR granules reduces the vertical mobility of herbicides into the soil layer columns and also diminish its presence in the leachate compared to the technical and commercial products (Fernández-Pérez et al., 1999; Villafranca-Sánchez et al., 2000).

Herbicide	Formulation	K (days)$^{-n}$	n	r	T_{50} (days)
Atrazine	AA	0.15	0.53	0.999*	9.69
	$AAB_{0.5}$	0.11	0.42	0.997*	36.78
	$AAB_{2.5}$	0.13	0.40	0.996*	29.01
		$K \times 10^2$ (h^{-n})	n	r	T_{50} (h)
Chloridazon	ClA	14.47	0.51	0.992	11.23
	ClAB	14.01	0.49	0.991	13.59
	ClAAn	10.75	0.51	0.996	19.81
	ClAC	0.50	0.46	0.987	$2 \cdot 10^4$
	$ClABC_{20}$	12.66	0.45	0.996	21.03
Metribuzin	MA	24.96	0.55	0.993	3.54
	MAB	16.65	0.58	0.992	6.71
	MAAn	15.91	0.56	0.996	7.77
	MAC	3.64	0.33	0.991	$2 \cdot 10^3$
	$MABC_{20}$	16.77	0.53	0.994	7.89

Table 7. Constants from fitting the empirical equation $M_t/M_o = Kt^n$ to the release data of herbicides in water.

4. Conclusions

Different sorbents have been applied as modifying agents to produce alginate-based CRFs of potential pollutant herbicides. The encapsulation efficiency increases and a better control on release profiles of active ingredient is reached with the use of these sorbents. The release of herbicides from the CRFs into water may be due to diffusion where the sorption capacities of sorbent for herbicide, water uptake and permeability of the formulations are the most influential factors. Concerning to the sorption capacities, the release is affected not only by the addition of natural bentonite and anthracite to the CRFs but also, and in a greater extent, by the addition of sorbents with higher sorption capacity such as acid-treated bentonites and activated carbon. The wide range of T_{50} values obtained was due to the different physical-chemical properties of the herbicides and also by the addition of sorbents. Taking into account the variation of T_{50} values, it is possible to select the most appropriate formulation, depending on the environmental factor that affected herbicide mobility. Therefore, the risk of pollution resulting from rapid runoff and leaching of relatively highly mobile herbicides can be minimized through their application in sorbents-alginate-based CRFs.

Significant potential exists to improve conventional methods of herbicide applications by the use of sorbent mixtures with different sorption capacity to modulate the release profiles of herbicides in alginate-based CRFs. Besides, low-cost lignin-sorbents mixtures coated with biodegradable polymers could be developed to obtain new CRFs of herbicides.

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Herbicides and Environment

Edited by Dr Andreas Kortekamp

Herbicides are much more than just weed killers. They may exhibit beneficial or adverse effects on other organisms. Given their toxicological, environmental but also agricultural relevance, herbicides are an interesting field of activity not only for scientists working in the field of agriculture. It seems that the investigation of herbicide-induced effects on weeds, crop plants, ecosystems, microorganisms, and higher organism requires a multidisciplinary approach. Some important aspects regarding the multisided impacts of herbicides on the living world are highlighted in this book. I am sure that the readers will find a lot of helpful information, even if they are only slightly interested in the topic.

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