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SHORT COMMUNICATION

New Trends for Controlled-Release of TBH Herbicide in the Field by Using a Biodegradable Polymer Fashion

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Abstract:

The herbicide Tebuthiuron (TBH) is widely used to weed control in sugar cane and cotton crops. However, TBH when applied to the soil is prone to the leaching process due to its high solubility, reaching soil layers below the required control zone. Here, we present a new insight for controlled-release of TBH herbicide by using a microparticulate system on the weed plants of difficult control. For this purpose, calcium alginate (Ca-ALG) microparticles containing the TBH herbicide were developed as a strategy to reduce the groundwater contamination, caused by the mobility of the herbicide element. The obtained results are innovative since demonstrates potential application in controlled-release as well as efficiency on the weed species control of Digitaria horizontalis (Willd) and Ipomoea grandifolia (Dammer) O'Donell weed species in pre-emergence.

Keywords: biodegradable polymer; field tests; microparticulate system; TBH weed control

1. Introduction

The sustained-release of biological compounds by using a microparticulate system is a common practice in the healthcare, personal grooming, food industry and in many applications [1, 2]. Recent works [3-6] demonstrated that these systems promote potential application in controlled release platforms in agricultural as well as for controlling of bioindicator plants and minimization of leaching processes. For weed control, herbicides are used worldwide, presenting mobility and varying degrees of persistence in the environment [7]. Therewithal, herbicides may be carcinogenic, toxic and mutagenic. According to AGROFIT [8], there are about 779 herbicides registered in Brazil in April 2020, among them Tebuthiuron (TBH) is widely used in the cultivation of sugar cane.

TBH (N- {5- (1,1-dimethylethyl)-1,3,4-thiadiazol-2-il}-n, n'-dimethylurea) is an inhibitor of Photosystem II exhibiting a long residual effect in the environment whose half-life is approximately 360 days, applied pre-emergence, in the cultivation of sugarcane and for use in the control of mono and eudicotyledonous species [9]. One way to mitigate the environment impacts caused by TBH herbicide in the agriculture and ensure effective weed control is the use of a powerful method to encapsulated the active ingredient, seeking to obtain a sustained-release system. Here, we present a new insight for controlled-release of TBH herbicide by using a microparticulate system (Ca-ALG) on the weed

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plants of difficult control. For this purpose, *Digitaria horizontalis* (Willd) and *Ipomoea grandifolia* (Dammer) O'Donell weed species were used. To the best of our knowledgment, this is first study concerning an effective controlled release system using the TBH herbicide encapsulated into a biodegradable polymer fashion with high prospects in agribusiness area for weed control species in pre-emergence.

2. Material and Methods

The Ca-ALG microparticles were prepared from the crosslinking of sodium alginate by Ca^{++} containing varied amounts of TBH supplied in $CaCl_2$ aqueous solution. All the necessary information about the microparticle's production process can be obtained at Dourado-Jr et al. [5] and Faria et al. [6,9]. The encapsulation efficiency (% EE) was evaluated by the difference of the amount of herbicide added in the Na-ALG + TBH solution and the unentrapped amount of TBH remaining in the supernatant after the removal of the formed microparticles, following the **Equation** 1.

$$\%EE = [\frac{TBH\ added - free\ unentrapped\ TBH}{TBH\ added}] x\ 100\% \quad (1)$$

The surface morphology of the Ca-ALG microparticles loaded THB herbicide was assessed by using scanning electron microscopy (SEM - JEOL-JSM7001F microscope equipped with EDX). In order to understand the controlled-release mechanisms of the TBH herbicide loaded in Ca-ALG microparticles, the results were fitted by using Korsmeyer-Peppas model (KP) for the 60% release of herbicide. The KP model [10] is a well-known model used to describe the release mechanism of an active ingredient and it follows the Equation 2:

$$\left[\frac{M_t}{M_{\propto}}\right] = At^n \quad (2)$$

Where, **Mt/M∞** represents the proportion of compound released in the time **t**, **K** is the kinetic constant, and ***n*** is the exponent which reflects the type of release mechanism.

The field tests were conducted in an experimental area of the Federal Institute of Education, Science and Technology of Triângulo Mineiro (IFTM), Campus Uberaba, latitude 19° 39' 19" S and longitude 47° 57' 27" W, Uberaba, Minas Gerais, Brazil. The soil used is characterized as dystrophic Red Latosol, with a medium texture, presenting an average of 220 g kg^{-1} of clay, 50 g kg^{-1} of silt, 730 g kg^{-1} of sand and 12 g dm^{-3} of organic matter. The climate of the region according to the classification of Köppen type is Aw (tropical, hot and humid summer, with cold dry winter) [11].

The Ca-ALG microparticles containing the THB herbicide were manually distributed in plastic vessels with a capacity of 1.5 L. The experimental design was completely randomized with 3 treatments and 4 repetitions. The treatments consisted of the herbicide absence (control), conventional application (1.2 L ha^{-1} of TBH) and Ca-ALG microparticles with 4 g L^{-1} of herbicide concentration. The conventionally applied herbicide was Combine 500 SC (500 g L^{-1} of TBH), sprayed on the top of vessels. At the time of TBH herbicide application, the weather conditions were favorable to the operation, with air temperature around 23.9 °C and air humidity of 78 % - collected dates at the IFTM meteorological station, approximately 300 m from the site.

Before sowing, the pots of all treatments were artificially irrigated during 14 days. Immediately, two weed species were sowed (*D. horizontalis* and *I. grandifolia*). These weeds were chosen because they showed high sensitivity to the herbicide of interest [9]. Ten seeds of each weed species were distributed homogeneously on the pots. The phytotoxicity evaluations were performed at 10, 20 and 30 days after sowing (DAS). For this purpose, the Latin American Weed Association (ALAM) [12] standard was used. To evaluate the dry mass of weeds, plants were collected at 30 DAS, packaged in paper bags, dehydrated in a forced circulation oven at 72°C until constant mass (measured performed in an analytical balance). Results were submitted to Shapiro-Wilk and Box-Cox tests to verify the normality and homogeneity of variance. Then analysis of variance (ANOVA) was carried out for dry mass results, and the means of the treatments were compared by the Tukey test ($p<0.05$). For phytotoxicity, the results were compared by Student's T test. The values were recorded as means ± standard deviations.

3. Results and Discussion

The %EE of the TBH herbicide on the Ca-ALG microparticles was 91%. This result is similar to those reported in the literature for formulations involving THB [9] and sulfentrazone herbicide [5] encapsulated on the Ca-ALG microparticles. The surface morphology of the TBH herbicide encapsulated on the Ca-ALG microparticles was assessed via SEM. **Figure 1 (a)** presents an overview of the Ca-ALG microparticles containing the TBH herbicide and **Figure 1 (b)** displays the presence of cracks on the surface. **Figure 1 (c)** shows the distribution of sodium chloride on the surface, including an intermittent aggregation. The chemical composition of the major elements was performed by using EDX in two different points (P_1 and P_2) as shown in **Figure 1 (d,e)**, confirming the presence of C, O, Na, Cl and Ca elements. The medium radius of dried Ca-ALG microparticles was (623 ± 24) μm (see **Figure 1 (f)**).

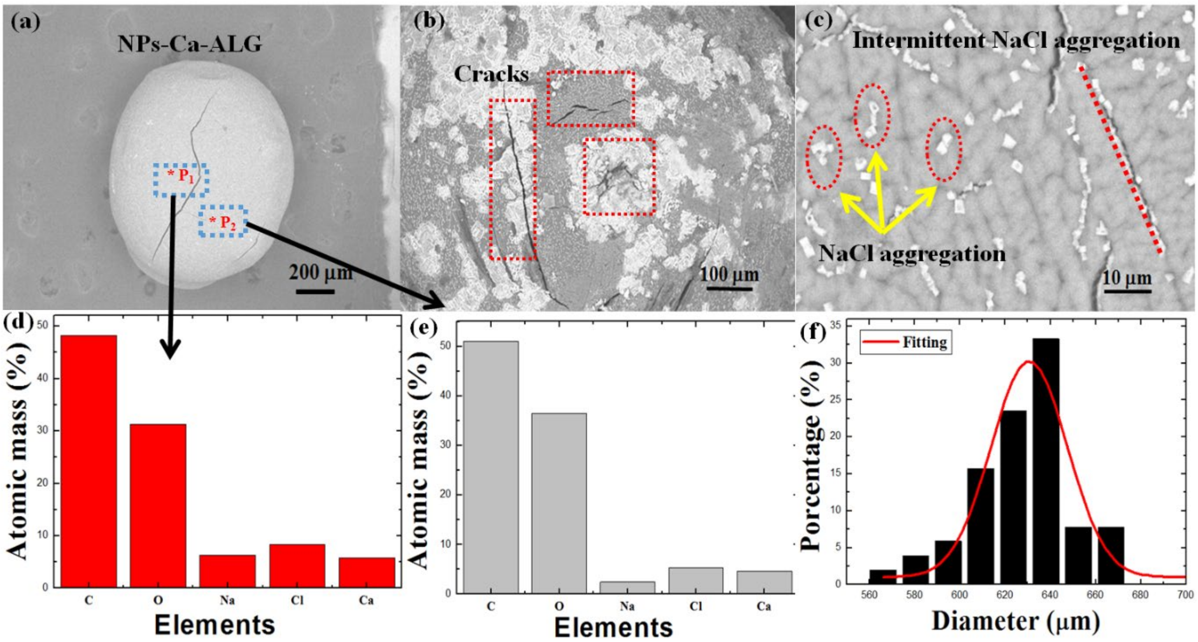

Figure 1. SEM micrographs of the Ca-ALG microparticles containing THB herbicide **(a)** overview of the microparticle, **(b)** cracks details, (**c)** distribution of sodium chloride on the surface, **(d, e)** chemical composition of the major elements in two different points (P_1 and P_2) and **(f)** polydispersity curve of dried Ca-ALG microparticles at 4 g L^{-1} herbicide concentration.

The cumulative release of TBH from the prepared beads (Ca-ALG) is shown in **Figure 2.** About of 50% of TBH herbicide was released during the first 150 min. The results demonstrated that 4 g L^{-1} herbicide concentration may be adjusted by using KP model, indicating **n** value closed to 0.51. As reported by Korsmeyer et al [10] and Siepmann & Peppas [13] values of $n \leq 0.43$ are an indicative of a release mechanism that follows the Fick's Law, $n > 0.85$ indicates that the mechanism is governed by relaxation processes of the polymeric matrix and an intermediate value suggests anomalous behaviour with non-Fickian release. Detailed informations regarding Fick's Laws can be obtained in the references [5,6], respectively.

Table 1 shows the average percentages of control for the weed species evaluated at different times. For *D. horizontalis,* conventional and 4 g L^{-1} treatment presented a 'regular' effect (41 to 60% of control) from 20 DAS, evolving to 'sufficient control' (61 a 70% of control) after 30 DAS. No difference was observed between treatments. Concerning to *I. grandifolia*, the 4 g L^{-1} treatment presented the highest percentage of phytointoxication of the plants after 20 and 30 DAS.

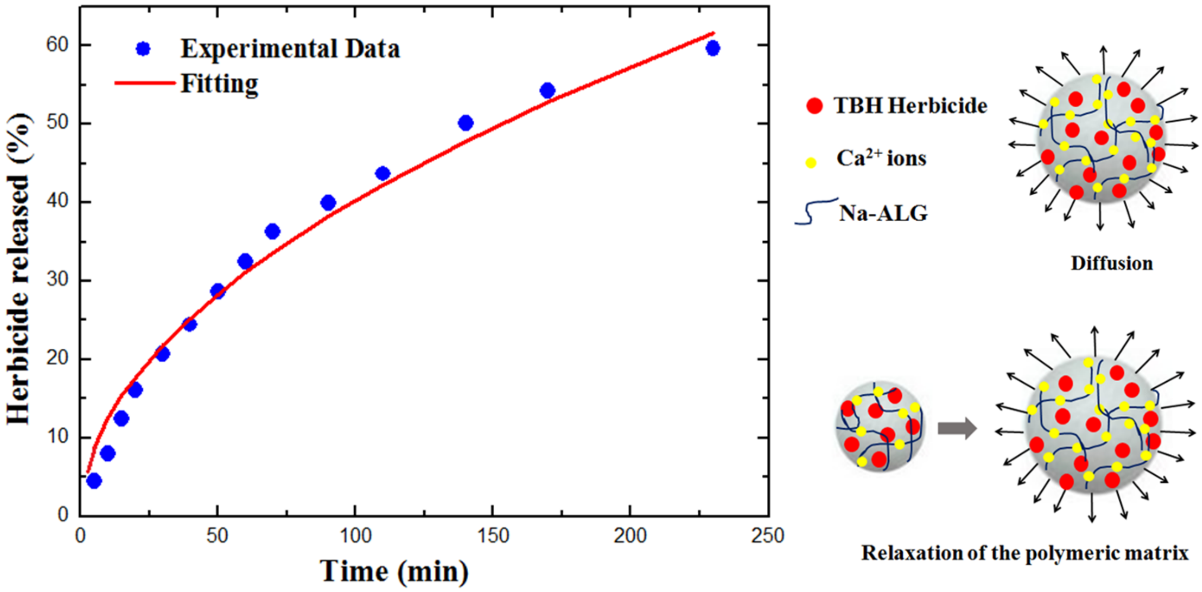

Figure 2. Results of *in vitro* release assays of TBH encapsulated on the Ca-ALG microparticles at room temperature.

Table 1. Percentage of phytotoxicity of *D. horizontalis* and *I. grandifolia* plants submitted to different treatments.

Treatment	***Digitaria horizontalis* (%)**			***Ipomoea grandifolia* (%)**		
	DAS			**DAS**		
	10	**20**	**30**	**10**	**20**	**30**
Control	-	-	-	-	-	-
Conventional	0.0 ^{a}	54.60 ^{a}	62.33 ^{a}	0.0 ^{a}	41.33 ^{b}	64.66 ^{b}
4 g L^{-1}	0.0 ^{a}	53.00 ^{a}	61.66 ^{a}	0.0 ^{a}	50.00 ^{a}	74.00 ^{a}

Means followed by the same letter in the column do not differ from each other by Student's T test ($p<0.05$).

For both weeds the 4 g L^{-1} treatment reduced the dry mass of the plants in comparison to control. Regarding *D. horizontalis* plants, the lower dry mass was presented by the conventional treatment, followed by the 4 g L^{-1} treatment (see **Table 2**). For *I. grandifolia* plants the lower dry mass was obtained by the 4 g L^{-1} treatment and the conventional treatment, which differed from the control treatment as presented in **Table 2**.

Figure 3 displays the symptoms caused by the TBH herbicide in *D. horizontalis* and *I. grandifolia* weed species. When the *D. horizontalis* and *I. grandifolia* species were submitted to the recommended doses of TBH herbicide, it was observed injury to the leaf that include chlorosis (**Figures 3 (a)** and **3 (b)**), of leaf tips and margins followed by necrosis beginning at leaf margins (**Figure 3 (e)**) and progressing toward the center (**Figure 3 (b)**).

Table 2. Dry mass of *D. horizontalis* and *I. grandifolia* at 30 DAS submitted to different treatments.

Treatment	**Dry mass (g)**	
	Digitaria horizontalis	***Ipomoea grandifolia***
Control	2.05 ± 0.04 ^{c}	3.27 ± 0.47 ^{b}
Conventional	0.55 ± 0.21 ^{a}	1.24 ± 0.88 ^{a}
4 g L^{-1}	1.41 ± 0.06 ^{b}	0.04 ± 0.03 ^{a}
F treatment	94.62^{**}	23.79^{**}
CV%	10.01	38.18
MSD	0.335	1.45

Means followed by the same letter in the column do not differ from each other by Tukey's test ($p<0.05$).
** Significant at 1% probability

The herbicide symptoms appear in lower leaves first progressing to the top of the plant (**Figures 3 (c) and 3 (d)**) and consist of initial water soaking followed by interveinal chlorosis (veins remain green) with necrosis of leaf tips and margins, like necrotic spots (**Figure 3 (f)**). The chlorosis occurs because the electron transport blocked and excess energy transferred to chlorophyll and carotenoids pigments, which are destroyed by photo-oxidation (role of carotenoids is to protect chlorophyll from photo-oxidation), because there is degradation of all pigments (see **Figure 3 (g)**). After, the necrosis occurs because the excess energy not "quenched" by the carotenoids generates triplet chlorophyll (Chl) produced by interaction between triplet chlorophyll and O_2 produces singlet oxygen (O_2) radicals, until the membrane lipids destroyed and leakage of cell contents (**Figures 3 (d)** and **3 (h)**) and finally, there are desiccation of plant tissue, then, the death of the plant occurs in some days (see **Figure 3 (g)**). These symptoms are in according with those reported by Ashton and Crafts [14].

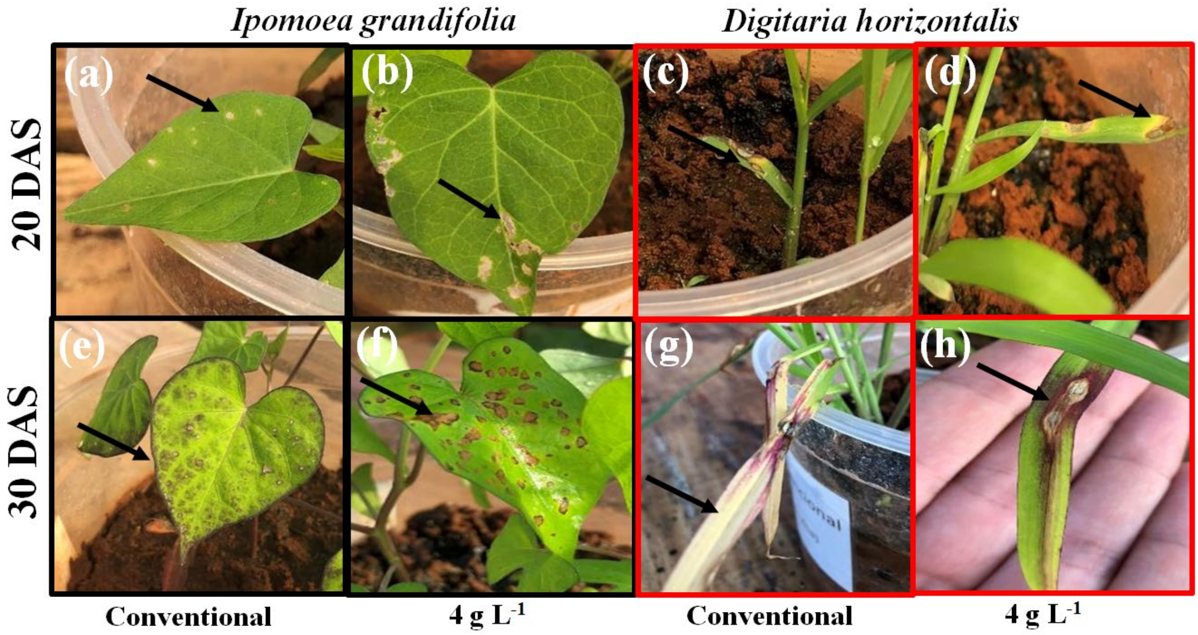

Figure 3. Symptoms caused by the TBH herbicide in *D. horizontalis* and *I. grandifolia* species.

4. Conclusions

This study shows that TBH herbicide encapsulated into a biodegradable polymer fashion is promising for control of *D. horizontalis* and *I. grandifolia* weed species with high prospects in agribusiness. In addition, the microparticulate system is optimal for use in formulating herbicidal slow release. Here, we presented a starting point for the development of robust systems with large-scale applications in field.

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