

A New Environmentally Safe Formulation and of Low Cost for Prolonged Release System of Atrazine and Diuron

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Abstract: Diuron and atrazine were incorporated in new formulations developed with the purpose to improve herbicides action through release systems, as well as to reduce the environmental toxicity. A low cost formulation (ALG/ESC) was obtained by combining sodium alginate (ALG) with fish scales of the Piau fish (ESC) from the *Leporinus elongatus* species. From the crosslinking of ALG/ESC with CaCl₂, the formulation ALG/ESC-CaCl₂ was obtained. For ALG/ESC-CaCl₂, the results are successful, showing a prolonged release of 3.5 and 4.5 days for atrazine and diuron, respectively. Based on parameters of an empirical equation used to fit the herbicide release data, it appears that the release systems of diuron and atrazine from ALG/ESC-CaCl₂ are by diffusion processes due to anomalous transport, which did not follow Fick's laws of diffusion.

Keywords: atrazine; diuron; fish scales; prolonged release; sodium alginate

1. INTRODUCTION

As known, the use of agrochemicals has great influence on quantity and quality of foods available for the growing world population. However, the undesirable effects arising from its conventional uses have led to the development of the controlled release systems that improve food productivity, minimizing the adverse impacts on the ecosystem. Advances in controlled release herbicide formulations over the last decades have shown the appreciation of its benefits [1-3]. The controlled release system of an herbicide reduces the required quantity of active substance and the cost of labor, increasing safety to the user and non-target organisms, thus it is of great environmental and economic interest [4].

Nowadays, biodegradable polymers are considered promising as formulation agents, since there is no risk of a heavy degradative load for the environment. Among them, polysaccharides such as chitosan and sodium alginate have achieved enormous attention because of their low cost and renewability [5, 6], furthermore polysaccharide formulations are not

toxic and can be used for safer control of weeds in agriculture.

The variety of molecules in agrochemicals confers varying degrees of environmental persistence and mobility, as well as different toxic, carcinogenic, mutagenic and teratogenic potentials [6]. Diuron (*N*-(3,4-dichlorophenyl)-*N,N*-dimethylurea), a substituted urea herbicide, has been widely used since the 1950s to control of both broadleaf and annual grassy weed and on non-crop areas such as roads, garden paths and railway lines and on many agricultural crops [7-9]. Diuron at high dietary levels (2500 ppm) induces rat urinary bladder hyperplasia after 20 weeks of exposure and neoplasia after 2 years [10]. Atrazine (6-chloro-*N*-ethyl-*N*-isopropyl-1,3,5-triazinediyl-2,4-diamine; (IUPAC) has become one of the most widely used as a selective pre-emergence and post-emergence herbicide for the control of weeds in a variety of agricultural crops [11]. The use of atrazine includes permanent control of its residues in water due to its biodegradation in nature within at least one year [3, 12]. Atrazine can cause cancer and do harm to reproductive system,

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endocrine system, central nervous system and the immune system of human [13].

In this work, formulation based on fish scales and sodium alginate is offered as potential carrier system for sustained release of atrazine and diuron. Fish scales of the Piau fish are mainly formed by hydroxyapatite and type I collagen [14]. Sodium alginate, a natural polysaccharide obtained from marine brown algae, is a weak polyelectrolyte composed of 1,4-linked β -D-mannuronic acid and α -L-guluronic acid residues [15]. Combining fish scales with polysaccharides it is possible to obtain formulations with good mechanical and chemical properties that can help to reduce environmental impacts due to their biodegradability. The new formulation with advantageous properties can be useful alternative in agricultural applications.

2. MATERIAL AND METHODS

Atrazine and diuron were obtained from Sigma-Aldrich in pure analytic quality. Sodium alginate (ALG) was purchased from Vetec. Sodium hydroxide and hydrochloric acid were obtained from Synth. The fish scales were acquired in a free market of Itabaiana city in the state of Sergipe -Brazil, in the months between February and March 2014. The fishes were from the San Francisco River and weighed around 2.0 kg. Deionized water used in all experiments was obtained from a Milli-Q system (Millipore).

Treatment and processing of the fish scales

Treatment and processing of the fish scales were performed as previously described [15]. After treatment, the fish scales were triturated in an industrial blender Skymesen model TA – 02, resulting in a mixture of powder and fibers. The powder was sieved using a 100 mesh sieve, resulting in a material hereafter called ESC.

Preparation of the spheres based on alginate/fish scale

The spheres obtained by combining sodium alginate and fish scale, were denominated ALG/ESC. In this stage, 2.0 g of ESC were added to 100 cm³ of an aqueous solution of hydrochloric acid 1.0 mol dm⁻³ and stirred for 48 h. After this time, an aqueous solution of sodium alginate 2% (w/v) was dripped yielding the ALG/ESC spheres that were washed and dried at 60 °C

for 4 h. The ALG/ESC spheres were stored in a desiccator.

Crosslinking of the ALG/ESC spheres with calcium chloride

About 2.0 g of fish scale powder were dissolved in 100 cm³ of an aqueous solution of hydrochloric acid at the concentration of 1.0 mol dm⁻³. Then the solution was neutralized with NaOH and it were added 4.0 g of CaCl₂, the resulting solution was kept under stirring for 48 h. After this period, an aqueous solution of sodium alginate 2% (w/v) was dripped under stirring. The spheres ALG/ESC crosslinked with CaCl₂, were denominated ALG/ESC-CaCl₂. The spheres ALG/ESC-CaCl₂ were washed, dried at 60 °C for 4 h and stored in a desiccator.

Characterization

The materials ALG, ESC, ALG/ESC and ALG/ESC-CaCl₂ were characterized by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis and X-ray diffraction (XRD). Scanning electron microscopy analysis (SEM) was used to characterize the ALG/ESC and ALG/ESC-CaCl₂ spheres. The surfaces of the ALG/ESC and ALG/ESC-CaCl₂ spheres were morphologically observed using scanning electronic microscope JEOL – JSM, model 6360 – LV, under vacuum, with a beam acceleration of 20 kV. The samples were metallized with gold. FTIR spectra were recorded as % transmittance using a Perkin Elmer 1600 series FTIR spectrophotometer and diffuse reflectance accessory at a resolution of 4 cm⁻¹. Thermogravimetric analysis was carried out with TGA – DTA SDT 2960 Thermogravimetric Analyzer, from TA Instruments, performed with 8–10 mg samples on a platinum pan under a nitrogen atmosphere at a heating rate of 20 °C/min from 25 to 800 °C. The X – ray diffractograms of the materials were obtained in a Shimadzu diffractogram except the diffractogram of alginate spheres, ALG, which was obtained in the X – ray diffractogram of Rigaku. Both equipment operated in a continuous scanning mode, with Cu-K α (1.5418 Å), generated at 40 kV with a 30 mA current. The scanning speed used was of 0.02°/second in 2 θ (10 to 50°). All diffractograms were obtained with the sample in powder state at environment temperature.

Herbicides entrapment

In this process, about 100.0 mg of ALG/ESC and ALG/ESC-CaCl₂ were immersed in 0.2 mL of alcoholic solutions of atrazine and diuron with the concentration of 5.10⁻³ mol.L⁻¹ for 24 h at room temperature. After this time, it was observed the complete solvent evaporation. The experiments were performed in triplicate.

Release experiments

The release experiments were carried out as follows: about 0.100 g of a specific material (ALG/ESC and ALG/ESC-CaCl₂) was placed in 10 mL of water in several amber flasks to prevent photodegradation of the herbicides. According procedure described in section 2.6, it was considered that 100% of each herbicide was impregnated. The amount of the herbicide released at each period of 12 h (initially, the amount of the herbicide released was evaluated at each period of 10 minutes) was evaluated by measuring the UV absorbance of the supernatant solution at wavelength 221 nm and 248 nm for atrazine and diuron, respectively. A Shimadzu mini 1240 UV-Visible spectrophotometer was used at room temperature. Thus, the release quantity (Q_{rel}) was determined. Each experiment was performed in triplicate. The average values were used for plotting.

3. RESULTS AND DISCUSSION

The functional abilities of both sodium alginate and Piau fish scales were combined and new formulations have been developed. Fish scales were dissolved in a very acid solution and because of the strong interaction of the cations Na⁺ present on sodium alginate with PO₄³⁻ ions of the fish scales, the spheres ALG/ESC were obtained. Ionic crosslinking of the ALG/ESC with Ca²⁺ ions facilitates strong adhesion with the phosphate ions [16], thus the spheres ALG/ESC-CaCl₂ were obtained. In this work, it is argued that although hydroxyapatite is not present in the new formulations, the phosphate groups from the inorganic phase were incorporated to the polymeric network of the polysaccharide, possibly as monocalcium phosphate monohydrate, Ca(H₂PO₄)₂.H₂O, once this is the stable form at pH from 0.0 to 2.0 [17].

Fourier Transform Infrared Spectroscopy Analysis

The FTIR spectra of ALG, ESC, ALG/ESC, and

ALG/ESC-CaCl₂ are shown in Fig.1. In all FTIR spectra is observed a broad and intense band between 3000 and 3500 cm⁻¹ attributed to O-H stretching vibrations [18-20]. In FTIR spectrum of ALG, the peak observed at 1096 cm⁻¹ is because of the stretching modes of the C—O bond [21, 22]. The bands at 1613 and 1415 cm⁻¹ are assigned to asymmetrical and symmetrical stretching modes of COO⁻ in alginate, respectively [18, 19, 21]. FTIR spectrum of ESC shows characteristics strong absorption bands at 565, 604 and 1031 cm⁻¹, corresponding to different vibrational modes of phosphate groups in the network of hydroxyapatite [01, 18, 19, 21]. The peaks at 875 and 1451 cm⁻¹ correspond to the carbonate absorption groups incorporated into the inorganic phase structure which must arise from carbon dioxide gas present in air [01, 18, 21, 23]. It is also possible to observe bands attributed to amides I, II and III of the type I collagen. The band corresponding to amide I is observed at 1657 cm⁻¹. The band at 1550 cm⁻¹ and 1243 cm⁻¹ are assigned to amide II and III, respectively [1, 23, 24].

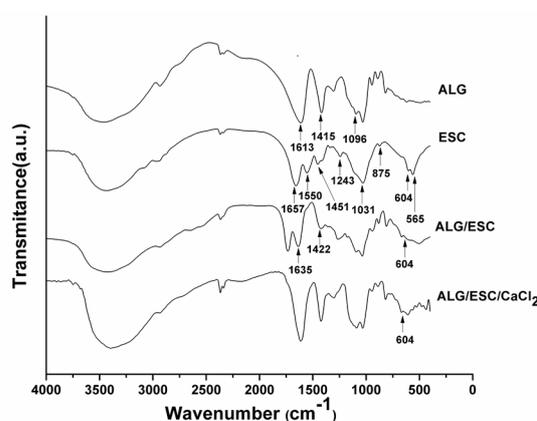


Figure 1. FTIR spectra of the materials ALG, ESC, ALG/ESC and ALG/ESC-CaCl₂.

The typical bands from ALG and ESC are also observed in ALG/ESC spectrum. The shifts of the peaks due to the asymmetric (1613 to 1635 cm⁻¹) and symmetric (1415 to 1422 cm⁻¹) stretching of the carboxylate group (COO⁻) for regions of higher wave numbers wavelengths, suggest a chemical interaction of Ca²⁺ of the mineral phase and the organic matrix with the carboxyl group in sodium alginate [18, 21]. As the ALG/ESC, the FTIR spectrum of ALG/ESC-CaCl₂ material has a band around 1098 cm⁻¹ which is attributed to C-O stretching. This band is considerably strengthened in the spectrum of ALG/ESC-CaCl₂ probable due to increased strain of the carboxyl group (C-O) as it stretches to accommodate the coordination

structure around the Ca^{2+} ions [25]. The band observed at 1413 cm^{-1} when compared to that of ALG is shifted to a higher wavenumber 1424 cm^{-1} . The bands at 1031 and 604 cm^{-1} assigned to different vibrational modes of phosphate groups are observed in the spectrum of ALG/ESC and ALG/ESC- CaCl_2 . The band at 604 cm^{-1} from phosphate groups, in ALG/ESC and ALG/ESC- CaCl_2 becomes wider and weaker, indicating decreased crystallinity by the effect of the alginate [21].

X-ray Diffraction Analysis

XRD patterns of ALG, ESC, ALG/ESC, and ALG/ESC- CaCl_2 are shown in Fig. 2.

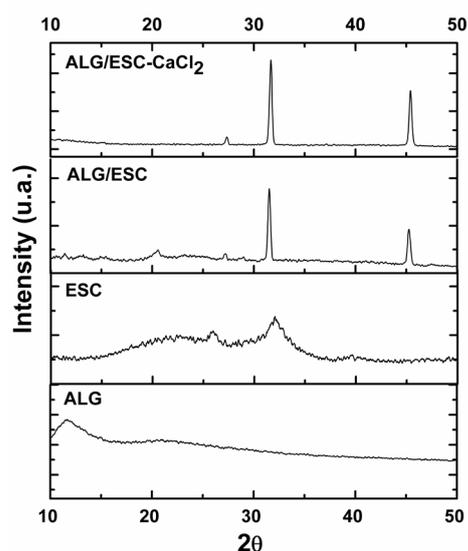


Figure 2. XRD patterns obtained at room temperature with powdered samples of ALG, ESC, ALG/ESC and ALG/ESC- CaCl_2 .

In the XRD pattern of ALG, there is a weak and broad diffraction peak at $2\theta = 11.67^\circ$ suggesting an amorphous structure of the sodium alginate [26, 27]. The XRD pattern of ESC shows wide reflections in $2\theta = 25.96^\circ$ and 32.04° . The peaks obtained were compared with the XRD patterns stored in the crystallographic database for crystalline compounds, ICDD. The reflections around 25.96° and 32.04° correspond to the crystalline phase of hydroxyapatite. The broad diffraction peaks observed indicates that the crystals are small and/or have low crystallinity or are structurally disordered. As indicated by the XRD patterns of ALG/ESC and ALG/ESC- CaCl_2 , there are new obvious peak reflections located at $2\theta = 45.26^\circ$, 31.52° and 27.24° typical of sodium chloride. Therefore, it is suggested that during the synthesis of the materials there is the formation of crystals of halite due to interaction of the chloride ions of the hydrochloric acid with the Na^+ ions of the sodium alginate. The crystals of NaCl formed remain trapped in the spheres, despite exhaustive washes of the materials with deionized water. The peak around 20.56° in the XRD pattern of ALG/ESC is possibly attributed to organic matter (type I collagen) present on the fish scales.

Scanning Electron Microscopy Analysis

The SEM images of ALG/ESC and ALG/ESC- CaCl_2 obtained with 1000X magnification are shown in Fig. 3.

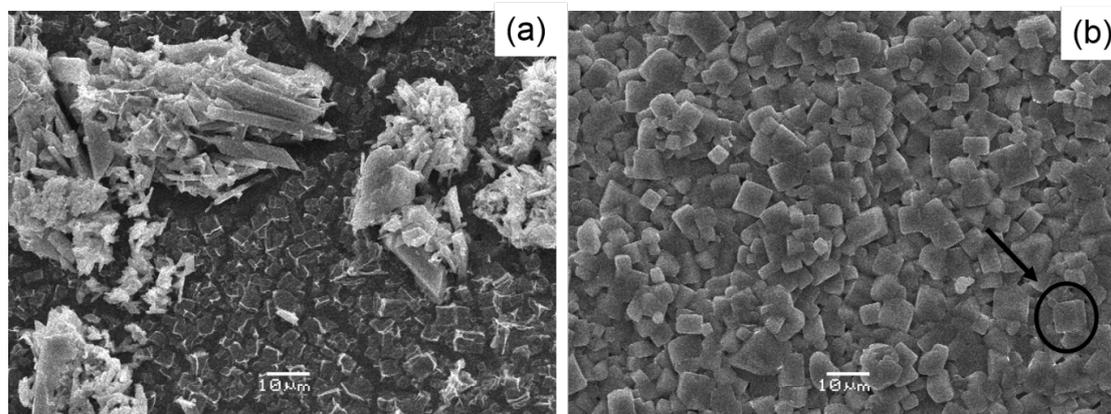


Figure 3. SEM micrographs (1000X magnification): (a) ALG/ESC and (b) ALG/ESC- CaCl_2 .

The micrograph of ALG/ESC (Fig. 3a) shows an assemblage of fine and irregular particles distributed

in an inhomogeneous surface. However, in case of ALG/ESC- CaCl_2 (Fig. 3b), cubic aggregates are

distributed homogeneously. From X-ray diffraction analysis, it was deduced that the particles are formed owing to aggregation of NaCl crystals.

Thermogravimetric analysis

The TG/DTG curves for ALG, ESC, ALG/ESC and ALG/ESC – CaCl₂ are shown in Fig.4.

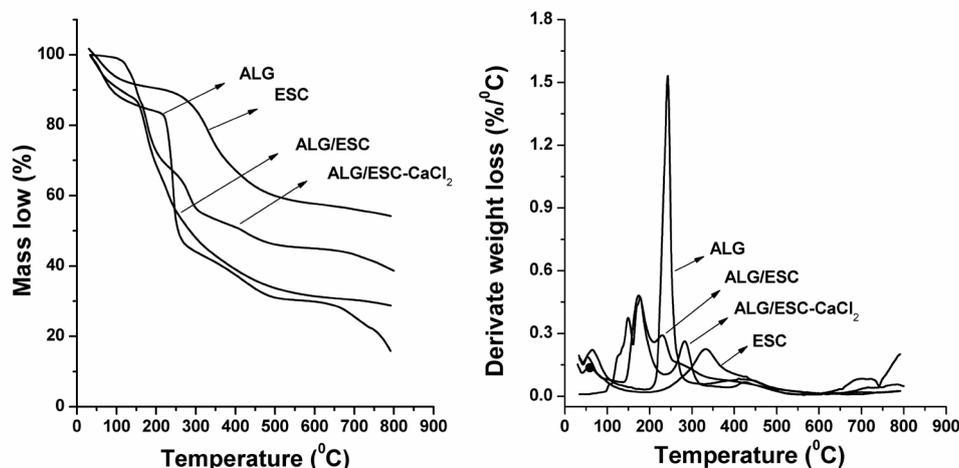


Figure 4. TGA and DTG curves of the materials ALG, ESC, ALG/ESC and ALG/ESC-CaCl₂.

In case of ALG, the temperature range between 40 and 160 °C with a mass loss of 6% with corresponds to the loss of different types of water molecules [28]. The second stage between 190 °C and 300 °C with a maximum at 243 °C and a mass loss of 65% is attributed to depolymerization that results in the evolution of CO, CO₂ and H₂O and the formation of polynuclear aromatic and graphitic carbon structures [29]. For ESC, the mass loss occurs in two stages: the first one between 30 and 200 °C, referring to 11% of water loss. The second stage with 33% of mass loss, from 200 to 590 °C (with a maximum at 330 °C) occurs due to the thermal degradation of the polymeric chains of collagen, possible dehydroxylation of the inorganic phase, and carbon material elimination [30]. Distinct degradation stages for ALG/ESC and ALG/ESC–CaCl₂ are observed. Their respective initial decomposition temperatures have been observed between 30 and 200 °C, with a maximum of 153 °C, and between 60 and 246 °C presenting a maximum at 177 °C. The final decomposition temperature for ALG/ESC was observed at 345 °C (maximum of 173°C), whereas the ALG/ESC–CaCl₂ is thermally more stable, with final decomposition temperature observed at approximately 550 °C with a maximum of 441 °C.

Release studies

Due to low solubility of the herbicides in water, it was used an ethanolic solution in the entrapment processes. As ethanol is a volatile solvent, it is assumed that all the herbicide was impregnated in ALG/ESC and ALG/ESC-CaCl₂. Thus, the initial quantity of herbicide impregnated in the materials was 1.10⁻⁵ mol.g⁻¹. The herbicide release quantities in function of time, Q_{rel(t)}, were calculated according to Eq. 1:

$$Q_{rel(t)} = \frac{C_{rel(t)} \times V}{m} \quad (1)$$

where C_{rel(t)} corresponds to the concentration of herbicide released (mol L⁻¹) at time t, V is the deionized water volume (L), and m is the mass in grams of the materials. For ALG/ESC, it was observed that the release times of both herbicides were of approximately one hour, thus this formulation is not appropriated for the prolonged release system. The release profiles for ALG/ESC-CaCl₂ are shown in Fig. 5.

Analysis of the release curves shows that diuron was released within 4.5 days and for atrazine, the release time was of 3.5 days. We observed that 60.1% of atrazine was released, whereas only 30.1% of diuron was released.

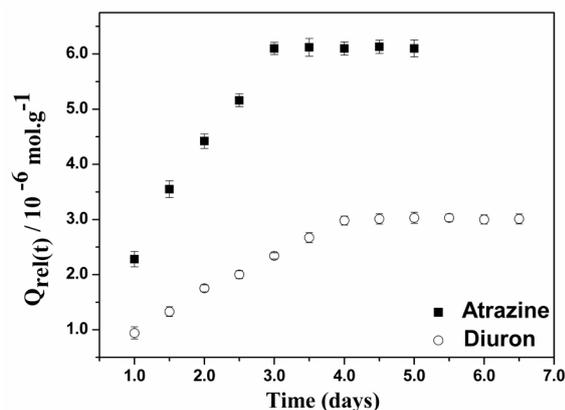


Figure 5. Profiles of release quantities of atrazine and diuron, impregnated in ALG/ESC-CaCl₂, in function of time at room temperature.

The release profiles were mathematically modeled in order to identify the type of mechanism involved. A very commonly used and easy to apply semi-empirical equation is the so-called power law, as introduced by Peppas and coworkers [31-33]. The model described by Peppas is able to predict release mechanisms based on processes governed by Fick's laws of diffusion, non-Fickian processes and Case II diffusion [34, 35]. Its linearized form is shown in the Eq. 2 [36]:

$$\ln \alpha = \ln k + n \ln t \quad (2)$$

where $\alpha = \frac{Q_{rel}(t)}{Q_{inf}(t)}$ ($Q_{inf}(t)$ is the quantity of herbicide release at infinite time), k is a constant that considers structural and geometrical aspects of the system, and the value of the exponent (n) indicates the release mechanism. A plot of $\ln \alpha$ versus $\ln t$ should result in a straight line whose slope and intercept give the n and k values, respectively. According Fig. 6, a straight line was not obtained throughout the full range times of the release processes.

The n values were 0.82 and 0.87 for diuron and atrazine, respectively. The values of k (min^{-1}) were 0.095 and 0.236 for diuron and atrazine, respectively. A value of $n = 0.5$ is expected for Fickian diffusion, values of $n = 1.0$ is expected for Case II diffusion,

while $0.5 < n < 1.0$ refers to non-Fickian diffusion [35-37]. The values of n obtained in this work, suggest that release processes of the atrazine and diuron impregnated in ALG/ESC-CaCl₂ are modeled by the Anomalous (non-Fickian) transport, which is controlled both by diffusion of herbicide and by the swelling of the material.

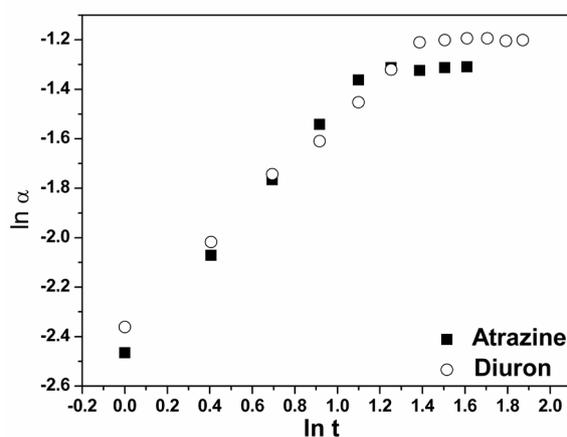


Figure 6. Plots of $\ln \alpha$ versus $\ln t$ for atrazine and diuron releases from ALG/ESC-CaCl₂ at room temperature.

The n and k values from the Peppas model were obtained for the linear range of applicability [36], as shown in Fig. 7.

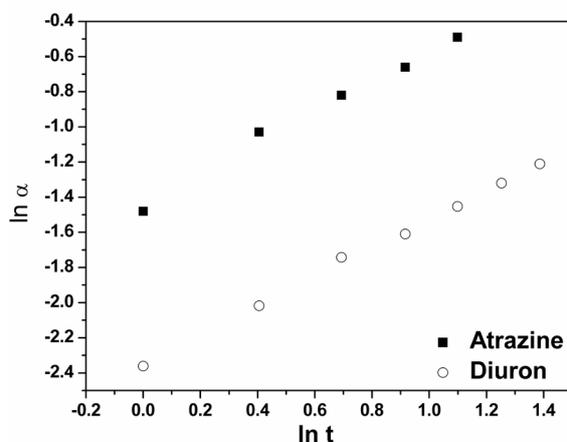


Figure 7. Plots of $\ln \alpha$ versus $\ln t$ for atrazine and diuron releases from ALG/ESC-CaCl₂ for the linear range of applicability.

4. CONCLUSION

From combination of sodium alginate with fish

scales (*Leporinus elongatus*) the formulations ALG/ESC and ALG/ESC-CaCl₂ were obtained. The release behaviors of atrazine and diuron impregnated in both formulations were investigated. The findings showed that ALG/ESC is not suitable to prolonged release of both herbicides, whereas ALG/ESC-CaCl₂ showed to be an efficient formulation with release times of 3.5 days for atrazine and 4.5 days for diuron. Mathematical modeling using the power law equation revealed that the release mechanism was by diffusion processes due to anomalous transport. We expect that the new formulation ALG/ESC-CaCl₂ may be a useful means of reducing harmful effects of herbicides, thus contributing to reduce adverse impacts on human health, as well as in the environment.

5. ACKNOWLEDGMENTS

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