Determination of The Release Rate Profiles of Aldicarb and Cadusafos as Alginate Controlled-Release Formulations Released in Water by Using Newly Modified Colorimetric Methods

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ABSTRACT

Cadusafos and aldicarb released from the alginate controlled release formulations and granule formulations in static water were determined using new colorimetric methods. These methods are sensitive and can be applied for the determination of levels as low as 0.02 ppm (20ppp) released in water. The active agents from commercial granule formulation of cadusafos (15G) and aldicarb (10G) were released faster into water than that from the corresponding alginate controlled release formulations (CR). After 21 days post- application, more than 58.72% of aldicarb was released from the granule formulation into water while for cadusafos granule formulation more than 91.56% of the cadusafos active ingredient was determined in solution. On the other hand, the C.R. formulations at the same period were released by not more than 3.98% and 13.33% of the originally applied amount of aldicarb and cadusafos, respectively. Aldicarb in calcium alginate beads was released in the following order FA_3>FA_6>FA_9. Also, cadusafos release rate was in the same trend (FC_3>FC_6>FC_9). The maximum release rate was achieved by the CR formulation of aldicard and cadusafos after 77days post- application and the range was 40.06% - 51.82% for aldicarb while for cadusafos was 50.64% - 65.85%. On the other hand, at the same time the concentrations of both active ingredient released from the commercial formulations was ranged between 0.28% - 0.34% of the original applied amount.

Key words: Alginate controlled release, aldicarb, cadusafos and colorimetric method.

INTRODUCTION

Cadusafos (*S,S*-di-*sec*-butyl *O*-ethyl phosphorodithioate), is a nematicide and it is introduced by the FMC Chemical Corporation and commonly marketed as Rugby®. It has been used for controlling a wide range of soil insect pests and nematodes (Bourdoxhe, 1990) particularly on tea (Yao and Yu, 1993), banana (Queneherve *et al.*, 1991), potato (Santo and Wilson, 1990), coffee (Vijayalakshmi *et al.*, 1991) and citrus (Zou *et al.*, 1992; McClure and Schmitt, 1996). It is classified by the World Health Organization (WHO, 1992-1993) as "highly hazardous" (class Ib). Also, it was considered the most harmful compound against earthworm among the other tested nematicides such as phenamiphos and oxamyl (Beltagy, 2000). Moreover, the residues of cadusafos were highly mobile in sandy soil and could be leached into ground-water, so cadusafos may be a potential for health hazard (Zheng *et al.*, 1994). Soltan (2002) reported that the amount of cadusafos hydrolyzed was temperature dependant, and the rapid hydrolysis was achieved at 40 ^{o} C with short half live ($t_{0.05}$= 3.31 days) Aldicarb (Temik)® is a carbamate insecticide, currently used in agriculture. Its sale and its use are strictly regulated. Also, aldicarb is classified by WHO (1990) as "extremely hazardous" (class 1a). In addition to problems associated with aldicarb contamination in drainage water, there also appeared to be a loss of nematode control because of chemical loss in the soil– surface soil (EL-gendi *et.al.,* 1978). Controlled-release formulations technology offers the potential to reduce the environmental loss of pesticides and increase their efficacy. Alginate gels are biodegradable and pesticides such as aldicarb and cadusafos can be easily incorporated into the matrix using an aqueous system at ambient temperature. For all the above mentioned reasons, alginate gels were selected as matrices for preparation of new controlled-release formulations of aldicarb and cadusafos nematicides. The objective of this research was to investigate the possible use of aldicarb and cadusafos in the form of alginate controlled released formulations. By such technique their release rate could be improved and its environmental loss could be reduced.

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MATERIALS AND METHODS

Spectrophotometric methods

a. Colorimetric determination of aldicarb

A new colorimetric method was developed in this study for determination of aldicarb residues. Stock standard solution of aldicarb (1000ppm) was prepared in acetone. Working standard solution was prepared by diluting the stock with methanol followed by distilled water (1mg/ml) for colorimetric method. One ml portion of working standard solution containing 0.1-1.0 mg aldicarb was pipette into a clean dry test tube. 0.1 ml of 30 N H_2SO_4 was added to the internal surface of each tube. Then, 0.2 ml of 5% $NaNO_2$ was added to each tube and the mixture was shaken well, followed by the addition of 0.2ml 0.5% sulfanilic acid. Finally, 0.8 ml 6N NaOH was added to each tube and kept at the room temperature for 5 min. with intermittent shaking until the color complex developed. The absorbance was measured at the wave length of 530 nm against blank.

b. Colorimetric determination of cadusafos

The method described by Soltan (2002) was used for the determination of cadusafos residues. Stock standard solution of cadusafos (100 mg/ 100 ml) was prepared in ethylacetate. Working standard solution was prepared by diluting the stock with methanol followed by distilled water (1mg/ml). One ml of working standard solution containing 0.1-1.0 mg cadusafos was transferred into clean dry test tubes. 0.5 ml of 15 N HNO_3 and 0.5 ml of 30 N H_2SO_4 was added to each tube. Tubes were kept on hot water bath (85^{o}C) with occasional shaking until the evolution of oxide of nitrogen has ceased (20 min.). Tubes were removed and they were left to stand for 10 min. at room temperature. 0.1 ml portion of 0.5% sulfanilic acid solution was pipette to each test tube and shaken well and 0.05 ml of 1% 4-amino antipyrine was added and kept for 2 min. with intermittent shaking until the color of the complex become yellow. Then, 4.5 ml of 6N sodium hydroxide were added and the tubes were left for another 5 min. in boiling water bath to develop a reddish color complex. Tubes were cooled in water to room temperature. The absorbance was measured at the wave length of 580 mm against blank. The standard extinction coefficient (K) obtained for the calibration curve between the optical densities estimated versus the working standard solution.

Preparation of controlled – release formulations of aldicarb and cadusafos

Different types of alginate controlled-release formulations (CRF.s) for each tested nematicide (aldicarb and/or cadusafos) were prepared in the present study. Among the coded CRF.s prepared, FA3, FA6 and FA9, for aldicarb and FC3, FC6 and FC9, for cadusafos were selected according to their appropriate release rate comparable to the other prepared formulations (Table 1).

Release-rate profiles of controlled-release formulations of aldicarb and cadusafos

Two separate experiments were carried out to study the release rate profiles of different formulations of aldicarb and cadusafos. Aldicarb contains alginate (FA3, FA6, and FA9) as well as cadusafos containing alginate (FC3, FC6, and FC9) versus the commercial formulation (15 G for aldicarb and 10 G for cadusafos) were studied in distilled water under static conditions. Aldicarb formulation contained 0.3 mg active ingredient and 0.5 mg (a.i.) for cadusafose replicated three times and added to 100 ml distilled water in brown glass

bottle with screw-cap. The samples were run in duplicate from each bottle at intervals of 2hrs, 24hrs, 3 days, 1 week, 2, 3, 4, 5, 6, 7, 8, 11 and 14 weeks after treatment and analyzed for the determination of concentrations of aldicarb and cadusafos. The bottles, for aldicarb and cadusafos, were shacked well and allowed to stand for 30 min. before each sampling. Aliquot of one ml samples were removed for determination of aldicarb and cadusafos by colorimetric method as described previously for each of aldicarb and cadusafos. Data were presented as percentage of the initial applied amount of aldicarb and cadusafos.

RESULTS AND DISCUSSION

1. Analytical methods of aldicarb

A new colorimetric method was developed during the course of this study. This method based upon the reaction of aldicarb with $NaNO_2$ in the present of H_2SO_4, and then the products of this reaction can react with a coupling reagent (sulfanilic acid) in the alkaline media to form a yellowish color compound with an absorption maximum at the wave length of 530 nm. Different methods are reported by many investigators and it can cited that Meaghor *et al.,* (1967) method is based on the determination of carboxyloxime group present in the molecule, that hydrolyzed to hydroxyl amine form. The later is converted to nitrous acid, and finally the nitrous acid reacts with sulfanilic acid followed by reacting with 1-naphthylamine to give a developed color. The optical density was measured at 530 nm. This method has many disadvantages such as the number of analysis procedure steps, and the number of reagents used and this method has a low detection limit (2ppm) than the method used in the present study (0.02ppm) in water. So, it could be concluded that this method is a highly sensitiveone and can be applied to determine the residue of levels as low as 0.02 ppm aldicarb in water. The relationship between the absorbance and concentrations measured between 0.1 to 1.0 ppm is illustrated in Fig. (1) and followed Beer's law. The extinction coefficient (k) value was 0.89024.

Table 1: Average weight, number of beads/g and percentage of active ingredient of different controlled release alginate formulations of aldicarb and cadusafos

Pesticide	Formulation code No.***	Average weight/bead (g)	Number of Beads/g	Active Ingredient %
	FA3*	0.989	1023	13.96
Aldicarb	FA6	3.355	298	17.24
	FA9	5.263	190	18.89
	FC3**	0.956	1046	6.008
Cadusafos	FC6	3.012	332	9.013
	FC9	3.937	254	10.36

*FA= Aldicarb controlled release formulations.
**FC=Cadusafos controlled release formulations
***All the controlled release formulations were developed by Prof. Dr. Hamdy R. Soltan (Unpublished data) and they have different code number

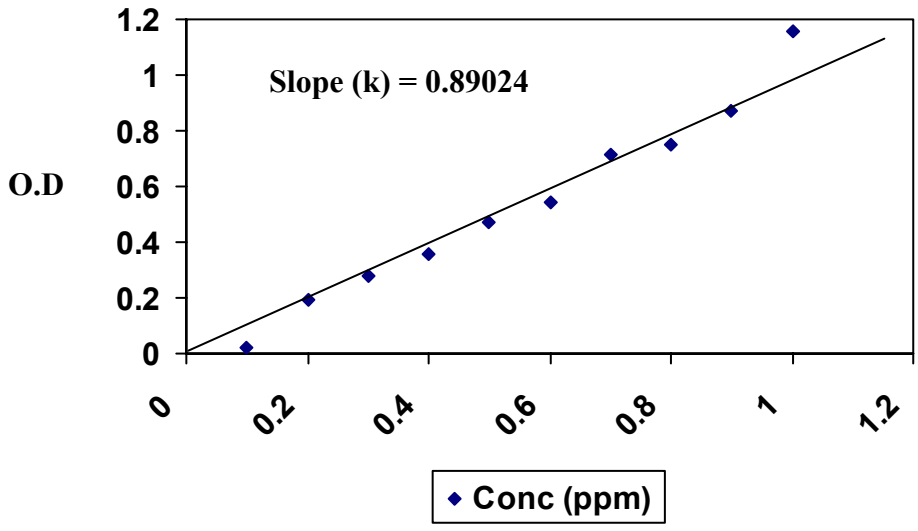

Fig. 1: Standard curve of aldicarb determined colorimetrically

2- Colorimetric method of cadusafos

Cadusafos residue level was measured colorimetrically according to the method that reported by Soltan (2002). This method is based on the oxidation of sulfur atom in cadusafose or its breakdown product by using concentrated HNO_3 and H_2SO_4. This oxidation product can react with sulfanilic acid and 4-amino antipyrine chromogenic reagents to form a colored compound in alkaline medium with maximum absorption at 580nm. The relationship between absorbance and concentration of cadusafos is linear and obeys Beer's law. *K* values were calculated at each concentration and illustrated in Fig. (2). Average of *K* values was used as an extinction coefficient (*K* value) for the determination the residue levels of cadusafos in water. In comparison of this method with other methods which are reported by many investigators, Cooper *et al.,* (1994) method was performed by GC/MS in fragmentmetric analysis mode, whereas, Soltan (2002) method was performed by GC/FID. Both methods have an advantage in minimum detectable quantity of cadusafos residue over the colorimetric method. It should be noted that the low detection limits for cadusafos using gas chromatography equipped with Flame Ionization Detector (F.I.D.) was 0.15 ng/ul and that equipped with mass spectrometry (M.S) was 0.02 ng/ul while, the detection limit by this colorimetric method was 20 ng/ul. Although, the colorimetric method was not as the gas-liquid chromatographic (G.L.C) method, this method was being simple, sensitive, rapid, and efficient with a satisfactory limit of detection for determining cadusafos residue in water and it does not involve elaborate liquid-liquid portioning or column clean up procedure, which is necessary in G.L.C. method.

3- Release rate profiles of aldicarb released from alginate formulation in water under static conditions

Fig. (3) illustrate the cumulative release of aldicarb from different types of formulations in water under static conditions. Migration of active agents from commercial granule formulations was faster than for calcium alginate beads. After 21 days of the initial treatment, more than 58% of aldicarb released from the commercial formulation in water, while the maximum released level from calcium alginate beads was not more than 3.98% at the same period. It appears that the release of aldicarb from the three-alginate formulations was more controlled than trhat released from the commercial formulation. However, calcium alginate beads had shown sufficient effects for slowing down the release rates of the active ingredients and a high release rate diminishes with time between 14 and 42 days whereas, aldicarb released from commercial formulation reached the maximum amount (94.25%) at 28 day. Kaolin is often added to pesticide formulations to increase the density of the granules or to decrease the price. Kaolin filled alginate granules gave slowed release of aldicarb than the alginate formulation (FA3) which did not contained kaolin. These results support the finding of many investigators (Marei *et al.*, 2000; Mousa, 1996; Schacht and Vandichel, 1988; Soltan, 1991 and 1996 and Vollner., *et al.*, 1988). Calcium gelled alginate granules released in the order FA3 >FA6>FA9. The percentages of aldicarb released from FA3, FA6 and FA9 reached the maximum of 51.82%, 46.84%, and 40.06%, respectively while the percentage released from the commercial formulation was determined to be 0.34% after 77 days, because the commercial formulations degraded earlier than CRFs as seen in Fig. 3.

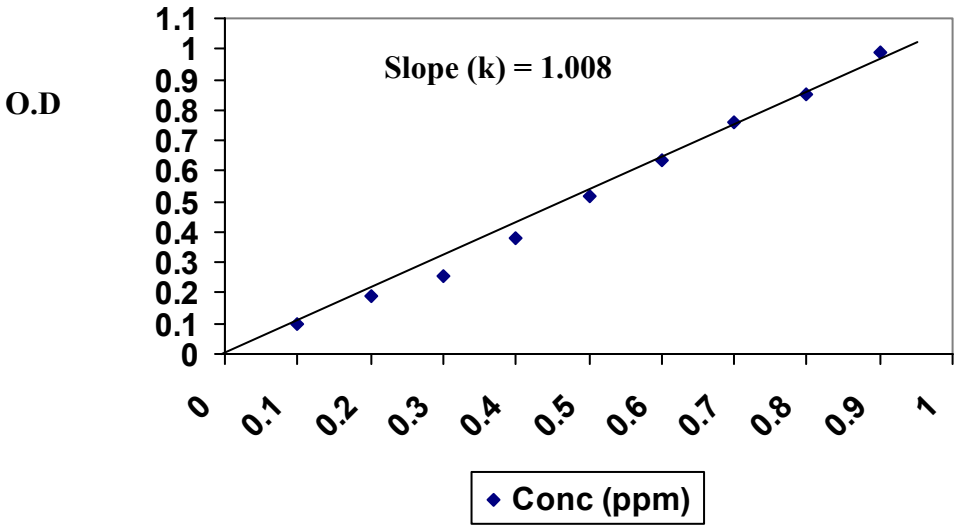

Fig. 2: Standard curve of cadusafos determined colorimetrically

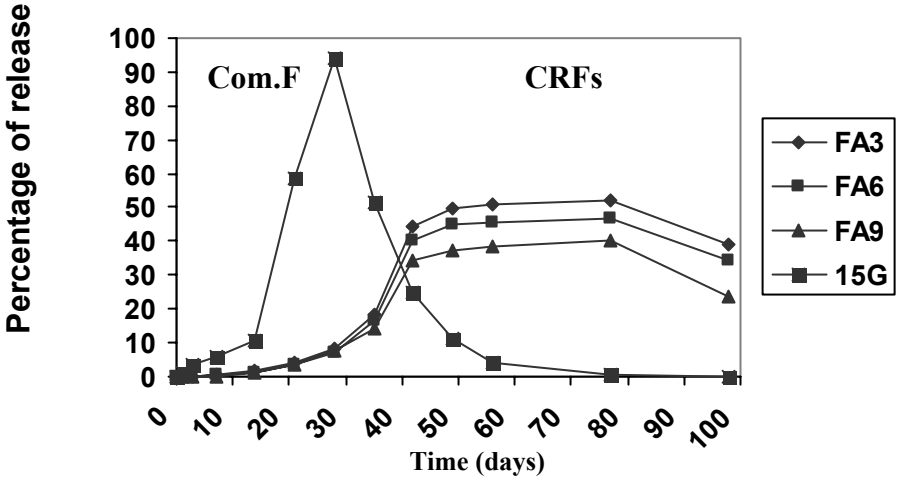

Fig. 3: Percentages of aldicarb released from different formulations in water in a closed bottle kept under static conditions.

*Com.F = Commercial Fornulation
**CRFs = Controlled Release Formulations

2- Release rate profiles of cadusafos released from alginate formulations in water under static conditions

Fig. (4) illustrate the release rate profiles of cadusafos from different types of formulations in water under static conditions. Migration of active agents from commercial granule formulation was faster than for calcium alginate beads. By 7 days, more than 17% of the cadusafose in the commercial formulation was released in solution, whereas the maximum released level from alginate beads was not more than 0.58%. It appears that the release of cadusafos from the three-alginate formulations was more controlled than from the commercial formulation. Cadusafos was rapidly released in the initial stages during the first 3 weeks and the concentration reached the maximum (91.56%) after 21 days following the addition of the granular commercial formulation. This concentration fastly decreased with the time. However, calcium alginate beads had shown sufficient effect for slowing down the release rates of the active ingredient and the high release rate diminishes with time between the 14 and 42 days.

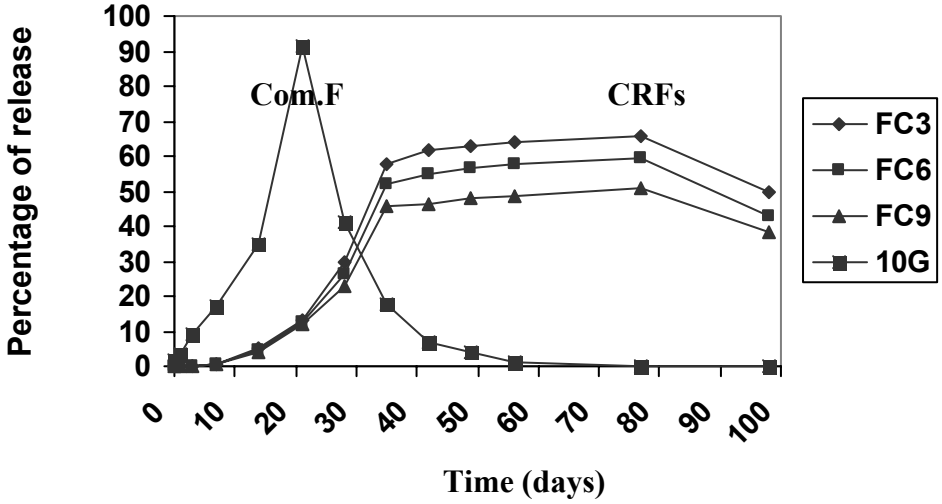

Fig 4: Percentages of cadusafos released from different formulations in water in a closed bottle kept under static conditions

Com.F = Commercial Fornulation
**CRFs = Controlled Release Formulations

It appears that the release of cadusafose from the alginate controlled release formulations were slower than the commercial formulation. Kaolin is often added to pesticide formulations to increase the density of the granules or to decrease the price of the product. Kaolin filled alginate granules gave slower release of cadusafos than the alginate formulation (FC_3) that did not contain Kaolin. These results support the finding of many investigators (Debongnie and Pussemier, 1991; Marei *et al*., 2000; Mousa, 1996; Soltan, 1991 and 1996 and Vollner *et al*., 1988). The calcium gelled alginate beads released as the following order FC_3>FC_6>FC_9. It could be concluded that FC_3, FC_6, and FC_9 formulations were released by 65.85%, 59.57%, and 50.64%, respectively after 77 days. Whereas, the commercial formulations was released by 0.28% after the same time, because most of the active ingredient of the commercial formulation was vanished after that long period (77 days).

It appears that the release rate of aldicarb and cadusafos from alginate controlled-release formulations were more controlled and persisted significantly longer than the granular commercial formulations under the experimental conditions. Moreover, the present investigation also indicated that controlling the rate of release of both pesticides resulted in reduction of rate of loss due the hydrolysis and evaporation from water.

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الملخص العربى

تقدير معدل تحرر مبيدى الاديكارب والكاديسافوس فى الماء الساكن والمنساب من تجهيزات الاليجنيت المحضرة فى تجهيزات متحكم فى تحرر المبيدان فيها وذلك بأستخدام طرق تقدير لونية جديدة معدلة

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تقدير معدل تحرر مبيدى الاديكارب والكاديسافوس فى الماء الساكن والمنساب من تجهيزات الاليجنيت المحضرة فى تجهيزات متحكم فى تحرر المبيدان والتجهيزات المحببة التجارية وذلك بأستخدام طرق تقدير لونية جديدة. هذه الطرق تتميز بحسّاسيتها المرتفعة والتى يُمْكِنُ من خلالها تُقدّر مستويات منخفضة من المبيدان تصل الى ٠٢, جزء فى المليون فى الماءِ (٢٠ جزء فى البليون). وأظهرت النتائج ان معدل انسياب المبيدان فى الماء من التجهيزات المحببة التجارية كان أسرع من المعدل المقدر من التجهيزات المحضرة فى صورة الاليجنيت المتحكم فى تحرر المبيد (CR). وقد وصلت تركيزات المبيدان المحرران من التجهيزات التجارية المحببة فى الماء الى أكثر مِنْ ٥٨.٧٢% من الكمية المطبقة لمبيد الاديكارب وأكثر مِنْ ٩١.٥٦% لمبيد الكاديسافوس بعد ٢١ يوم من التطبيق. على الجانب الاخر كانت تركيزات المبيدان المنسابان من التجهيزات المتحكم فى تحرر المبيدان فيها والمصنوعة من الاليجنيت فى نفس الفترة لاتتعدى ٣.٩٨% و١٣.٣٣% من الكميةِ الاصلية المطبقة لكلا من الاليكارب والكاديسافوس على التوالي. ويمكن ترتيب معدلات التحرر لمبيد الاديكارب من تجهيزات الكالسيوم أليجنيت للتجهيزات المتحكم فى تحرر المبيد فيها كالتالى $FA_3>FA_6>FA_9$ وأيضا كان نفس الاتجاة من التحرر لمبيد الكاديسافوس ($FC_3>FC_6>FC_9$) بناء على محتوى التجهيزات المحضرة على نسبة مادة الكاؤلين كمادة مالئة. تم تقدير أعلى تركيز لمبيدى الاديكارب و الكاديسافوس المتحرران من تجهيزات الالبجنيت بعد٧٧ يوم من تطبيقهما فى الماء وكان مدى التركيزات المسجلة لمبيد الاديكارب هوَ ٤٠.٠٦ %- ٥١.٨٢ % بينما كان مدى التركيزات المسجل لمبيد الكاديسافوس هو ٥٠.٦٤ % - ٦٥.٨٥ %. في نفس الوقت كانت تركيزات المبيدان المتحرران من التجهيزات التجارية المحببة قد وصلت الى مدى يترواح من ٠.٢٨% - ٠.٣٤% من الكميات الاصلية المطبقة.