Colorimetric Method for Determination of the Nematicide, Cadusafos in Aqueous Medium at Different Temperature and pH levels

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ABSTRACT

A colorimetric method has been developed to determinee residues of cadusafos in water. This method is based on the oxidation of sulphur atom in cadusafos or its breakdown product by using concentrated HNO_3 to the corresponding sulphone. Then the oxidation product can readily react with the p-aminobenzene sulfonic acid and 4-aminoantipyrine chromogenic reagents to form a colored compound in alkaline medium with maximum absorption at 580 nm. The relationship between absorbance and concentration of cadusafos is linear and obeys Beer's law in the range of 0.04-1.0 µg/6.65ml solution. The method is sensitive and can be applied to the determination of levels as low as 0.02 µg/ml cadusafos in water. The effect of pH and temperature on cadusafos stability in aqueous solution is also studied. The results indicated that the amount of cadusafos hydrolyzed was temperature dependent rather than pH dependent. The disappearance of cadusafos appeared to follow first order kinetics with different rates. The highest hydrolysis rate was found at 40°C followed by 20°C and the lowest was at 5°C ($k = 0.19$-0.20 day^{-1}, 0.15-0.16 day^{-1} and 0.095 - 0.1 day^{-1}, respectively). Rapid hydrolysis rate was obtained at pH 5 and 40°C with short half life ($t_{0.5} = 3.31$ days) whereas the rate of hydrolysis was slower at pH 6.5 and 5°C ($t_{0.5} = 7.27$ days).

INTRODUCTION

Cadusafos (O-ethyl-S,S,-bis [1-methylpropyl] phosphorodithioate), is a new nematicide and insecticide introduced to market under the trade name It is introduced by the FMC Chemical Corporation and commonly marketed as Rugby. It has been used for control 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 couled be leached into ground-water, so may be a potential for health hazard (Zheng *et al*, 1994).

A part of water surveillance and monitoring programs, there is a need to determine the insecticides such as cadusafos in water. At the present time, the literture on cadusafos is very sparing, but some articles describing analytical methods have been published. Cooper *et al* (1994) studied the determination of four organophosphorus nematicide residues including cadusafos in banana-field soils by gas-liquid chromatography/mass spectrometry. Nevertheless, publication about cadusafos presistence in water is not found. So, the objective of the present study was to develop a simple, rapid, and efficient colorimetric method for the analysis of cadusafos in water. The effect of different temperatures and pH levels on cadusafos stability in aqueous medium was also studied.

MATERIALS AND METHODS

Apparatus

(a) Spectrophotometer- Bausch and Lomb spectronic 20.

(b) Gas chromatography - Hewlett-Packard model 5890 series II equipped with flame ionization detector and fitted 30m × 0.32mm id. capillary column, coated with 5% methyl silicon was used. The inlet and detector temperatures were 220 and 250°C, respectively. The column oven temperature was 200°C. Nitrogen was used as a carrier gas with a flow rate of 3ml/min. The detector gases were air with a flow rate of 400 psi expressed as pressure and hydrogen with flow rate of 30 psi.

Reagents

(a) Cadusafos standard:- Analytical grade, 98.1% purity, was supplied by FMC Corporation, Agricultural Chemical Group, Richmond, California.

(b)Sulfanilic acid: - 0.5g sulfanilic (p-aminobenzene sulfonic acid) was dissolved in 75ml distilled water and add 25 ml glacial acetic acid.

(c) 4- aminoantipyrine: - 1g of 4-aminoantipyrine was dissolved in 100 ml distilled water.

(d) Sulfuric acid (30N).

(e) Nitric acid (15N).

Preparation of cadusafos standard solution:

Stock standard solution of cadusafos (100 mg /100 ml) was prepared in ethyl acetate. Working standard solution was prepared by diluting the stock with methanol followed by distilled water (1μg/ml) for colorimetric method. Another stock solution was prepared as 100 mg /L in ethyl acetate for gas chromatographic method.

Preparation of standard curve

(a) 1ml of working standard solution containing 0.02- 1.0 ug cadusafos was transferred into clean dry test tubes. 0.5 ml 15 N HNO_3 and 0.5 ml 30 N

H_2SO_4 are added to each tube. Tubes were kept on hot-water bath (85 °C) with occasional shaking until the evolution of oxide of nitrogen has ceased (20 min). Tubes were removed and let stand 10 min at room temperature. 0.1 ml portions of 0.5% sulfanilic acid solution was pipetted to each test tube and shaken well. 0.05 ml 1% 4-aminoantipyrine was added and kept for 2 minutes with intermittent shaking until the color of the complex became yellow. Then 4.5 ml 6N sodium hydroxide were added and the tubes were left for another 5 minutes in boiling water bath to develop a color complex. Tubes were cooled in water to room temperature. The absorbance was measured at 580 nm against blank.

(b) Another cadusafos standard solution ranged from 0.15 to 1µg per ml ethyl acetate was prepared for gas chromatographic determination.

Persistence of cadusafos in water at various temperatures and pH levels

Solutions of different pH values were prepared as follows: pH 5; 0.01 M calcium hydroxide was adjusted to pH 5 with hydrochloric acid. pH 6.5; filtered distilled water was adjusted to pH 6.5 with hydrochloric acid. pH 8; 0.025 M sodium carbonate solution was adjusted to pH 8 with sodium hydroxide. A volume of 99.5 ml water samples was placed in a brown bottle and sealed with rubber cap (for treatment each). Each treatment was replicated three times. The solutions were autoclaved for one hour and incubated at appropriate constant temperature (5, 20 and 40 °C) prior to the addition of cadusafos. Half ml of cadusafos solution (2000ug/ml acetone) was added to each bottle to get a final concentration of 10 1µg /ml. The solutions were thoroughly mixed by hand and placed in an incubator at the tested temperatures. Water samples were collected at different time intervals after application, i.e., 2hr. and 1, 2, 3, 9, 15, and 21 days for colorimetric analysis. 0.1 ml from each replicate was transferred into test tube and diluted to 1ml with distilled water, and then analysis was proceeded as described above without extraction and clean-up.

Reaction Rate Constant

The decrease in concentration was described by the first order rate equation:

$dc/dt = -kc$ where "k "is the first order rate constant and "t" is the time in days. Assuming first order kinetics, a reaction rate (k = slope x 2.303) and half life can be calculated according to the equation of the first order reaction: $t_{0.5} = 0.659/k$.

RESULTS AND DISCUSSION

The proposed method based on the oxidation of sulphur atom in the cadusfos or in its degradation products by using concentrated HNO_3 in the presence of concentrated H_2SO_4 to the corresponding sulphone (Vogel, 1979 and Vogel, 1991). This oxidation process was accompanied with evolution reddish-brown fumes of nitrogen dioxide and the latter being largely produced by combination of nitric oxide with the oxygen of the air. The oxidation product of cadusafos or its breakdown moiety can be readily reacted with the p-aminobenzene sulfonic acid and 4-aminoantipyrine chromogenic reagents. The color of this complex was developed under alkaline condition. Thus, the concentration of cadusafos can be calculated by measuring the absorbance at 580 nm.

Optimization of reaction conditions:

To obtain optimum conditions for oxidation of cadusafos or its breakdown product by the acid mixture, the effect of reaction temperature, absorbance maxima and reaction time on stability and development of the color were investigated.

Absorbance was recorded in wavelengths ranged from 450 to 600nm. Maximum absorption occurred at 580nm. The color reaction was performed with different concentrations of nitric acid and sulfuric acid. Absorbance increased gradually with increasing the concentration of the acid mixture and reached to the maximum when the concentration of nitric acid was 15N and the concentration of sulfuric acid was 30 N. Oxidation was done at 25, 50, 70, 85 or 100°C. For 85°C, maximum absorbance was recorded after 20 minutes of oxidation. The stability of the colored complex developed with 1µg cadusafos was studied by recording absorbance at 580 nm for 2h. Absorbance increased with increasing time from 5 to 40minutes. The relationship between the concentration and the color intensity obeyed Beer's law in the range of 0.04 - 1.0 ug per 6.615 ml solutions as shown in Fig.1. It should be noted that the low detection limits for cadusafos using gas chromatography equipped with flame ionization detector was 0.15 ng. (Fig.2), while the detection limit by the colorimetric method was 20 ng (Fig.1).

Although the colorimetric method was not as the gas-liquid chromatographic (GLC) 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 partitioning or column clean up procedure, which is necessary in the GLC method.

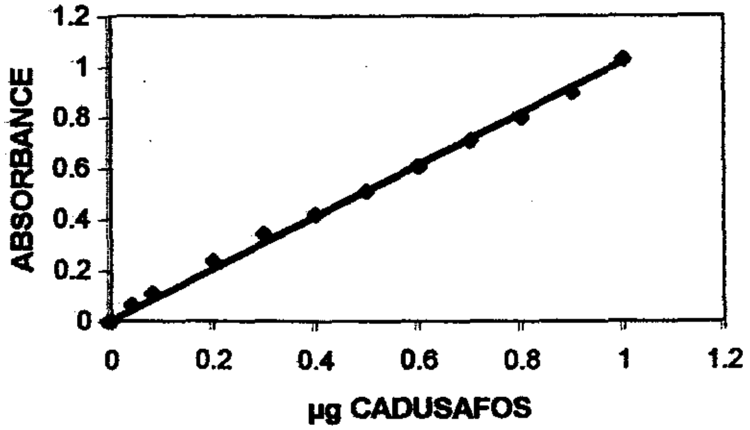

Fig.(1):Standard curve of cadusafos by colorimetric method.

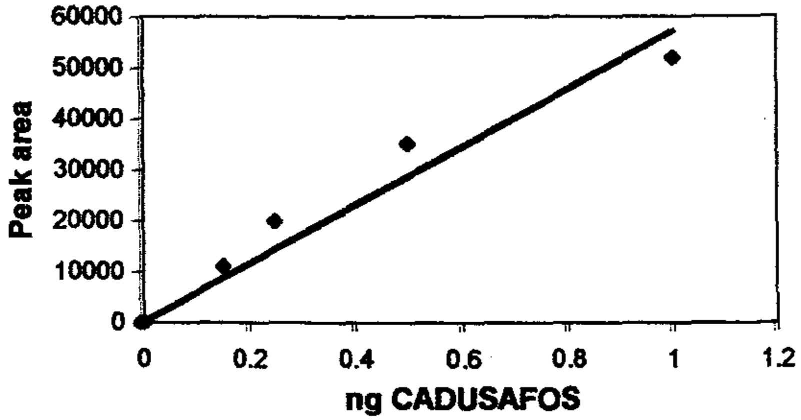

Fig. (2): Standard curve of cadusafos using GLC-FID.

Persistence of cadusafos in water at various temperatures and pH levels

The present satisfactory rapid colorimetric procedure has been applied to study the hydrolysis reaction rate of cadusafos under sterile condition at pH 5, 6.5 and 8 as well as different temperatures of 5, 20 and 40°C.

The data presented in Fig. (3,4 and 5) indicated that the effect of the tested temperature and different pH values on the persistence of cadusafos in water after different time intervals, i.e., 2 hr. and 1,2,3,9,15and 21 days, plays an important role in this respect. The disappearance of cadusafos appeared to follow first order kinetics with different rates. The half life ($t_{0.5}$) values of cadusafos in aqueous medium indicated that the disappearance rate of cadusafos was temperature dependent rather than pH dependent (Table 1). These results indicated that the cadusafos was unstable and break- down rapidly at 40°C. The highest degradation rates were found at pH 5 and/or 8 and 40°C with a short half life values (k= 0.209-0.206 day^{-1} and $t_{0.5}$ = 3.31-3.36 days). The other rates were less than those of pH 5 and/or 8 and 40°C. The hydrolysis rates for cadusafos at low temperature (5°C) and low pH levels (pH 6.5 and 5), were less than 0.1 day^{-1} and half-life values weremore than 7 days. These results are comparable with those found by El-Shoura *et al*, (1983) who reported that the highest hydrolysis rate of carbofuran was found at 40°C and the slower hydrolysis rate was at 5°C. Also, Meikel and Yyoungson (1970) cited that the temperature and pH significantly affect chloropyrifos half-life in water.

From the pervious results it can be concluded that, under comparable temperature and pH conditions, cadusafos breakdown rates can be fairly describeed by first order kinetics. However, the hydrolytic breaakdown of cadusafos was much slower at 5°C than in case of 20 and 40°C under the tested pH levels. The hydrolysis study discussed in here can be used to estimate the maximum time required for decomposition of cadusafos residues in water.

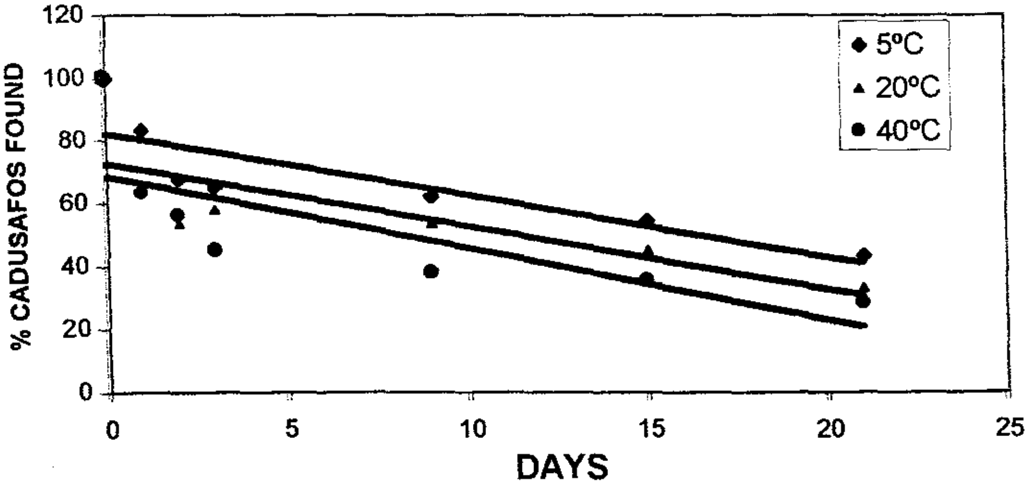

Fig. (3): Percentages of cadusafos found in aqueous solutions at pH 5 and temperature; 5, 20 or 40°C.

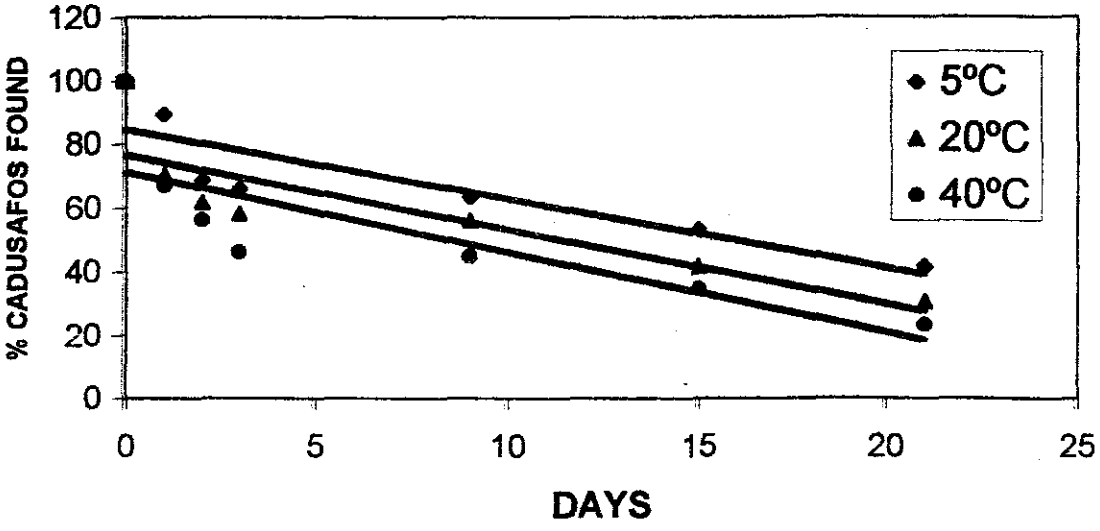

Fig. (4): Percentages of cadusafos found in aqueous solutions at pH 6.5 and temperature; 5, 20 or 40°C.

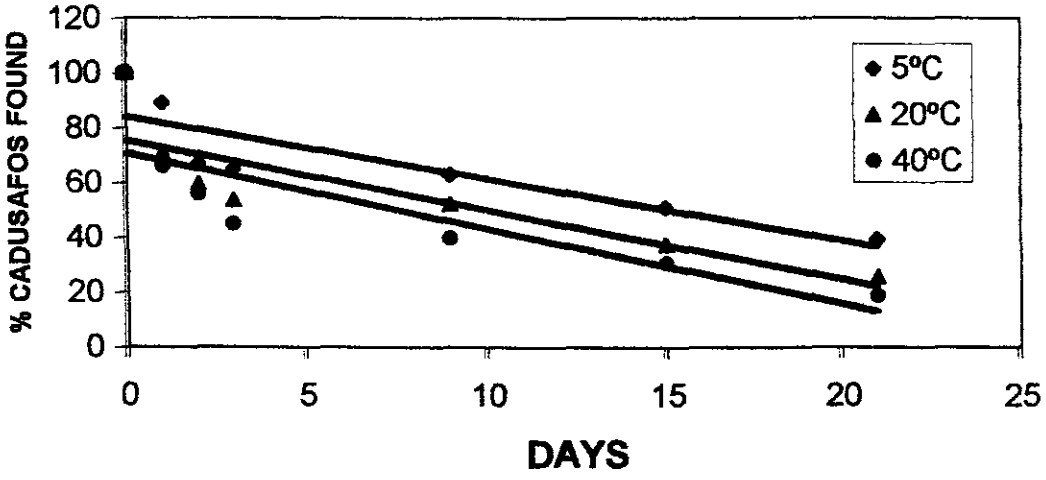

Fig. (5): Percentages of cadusafos found in aqueous solutions at pH 8 and temperature; 5, 20 or 40°C.

Table 1. Half-life values and rate of hydrolysis constant of cadusafos in Sterile water.

Physicochemical Parameters	pH5			pH6.5			pH8		
	5°C	20°C	40°C	5°C	20°C	40°C	5°C	20°C	40°
Rate of hydrolysis (days^{-1})	0.0957	0.0952	0.10	0.168	0.158	0.168	0.209	0.196	0.2
Half life ($t_{0.5}$) day	7.23	7.27	6.92	4.12	4.37	4.11	3.31	3.52	3.3

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الملخص العربي

طريقة لونية لتقدير المبيد النيماتودى كاديسفوس فى البيئة المائية على درجات حرارة مختلفة و مستويات مختلفة من الاس الايدروجينى

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تم استنباط طريقة لونية لتقدير المبيد النيماتودى كاديسفوس تعتمد على أكسدة ذرة الكبريت آلى السلفون المقـابل بواسطة حامض النتريك . ثم تفاعل ناتج الأكسدة (المركب الأصلي أو ناتج تحطمه) مع جوهر بارا امينو بنزين حامض السليفونيك و ٤- امينو انتبيرين فى وجود حامض الكبريتيك . يتكون معقد ملون يقاس عند طول موجة ٥٨٠ نانوميتر عند إضافة القاعدة . و كانت العلاقة ما بين التركيز المستخدم و الطاقة الضوئية الممتصة علاقة خطية في مدى التركيزات ٠,٠٤ - ١ ميكروجرام / ٦,٦٥ ميلليتر محلول . و هذه الطريقة تعتبر بسيطة و حساسة و تصل حدود التقدير فيها إلى ٠,٠٢ جزء في المليون . و قد تم تقدير ثبات مبيد الكاديسفوس في الماء على ثلاث درجات حرارة مختلفة و هي ٥ و ٢٠ و ٤٠ درجة

إلى أن معدل التحلل المائي لهذا المبيد تتوقف بالدرجة الأولى على درجات الحرارة أكثر من الآس الأيدروجين . أن مقدار التحلل المائي يتبع معادلة التفاعل من المرتبة الأولى . و كان أعلى مقدار لتحطم المبيد في البيئة المائية التي على درجة حرارة ٤٠ درجة مئوية يليها التحطم على درجة حرارة ٢٠ درجة مئوية و أقلهم التحطم على درجة حرارة ٥ درجات مئوية (قيم ثابت معدل التحلل المائي كالتالي : ٠,١٩ – ٠,٢ و ٠,١٥ – ٠,١٦ و ٠,٠٩٥ – ٠,١ يوم – ١ على التوالي) . و كان معدل التحطم الأسرع للمبيد على قيمة آس أيون أيدروجين يساوى ٥ و درجة حرارة ٤٠ درجة مئوية مسجلا أقل فترة نصف عمر للمبيد و هي ٣,٣١ يوم بينما كان معدل التحطم الأبطأ على قيمة آس أيون أيدروجين يساوى ٦,٥ و درجة حرارة ٥ درجة مئوية مسجلا أكبر فترة لنصف عمر المبيد و هي ٧,٢٧ يوم .