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ORIGINAL RESEARCH PAPER

DETERMINATION OF KINETICS OF DEGRADATION AND MOBILITY OF DITHIOCARBAMATES FUNGICIDES IN WATER AND IN MOROCCAN SOIL

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Abstract: Contribution analysis of dithiocarbamates pesticides used on tomatoes treatment has been reported. The study is focused on analysis and determination of some dithiocarbamates like, Maneb, Mancozeb, Zineb and Propineb, in order to achieve accurate impact of theses pesticides on water and soil. Analysis method is based on decomposition of dithiocarbamate by heating under acidic attack to give carbon disulfide complexed with copper acetate solution in presence of diethanolamine. Complex formed is dosed spectrophotometrically at 435 nm. Degradation kinetic of dithiocarbamate in aqueous media have been realized and proved that dithiocarbamate are degraded by simple air exposition. In the other hand, *pH* affects also dithiocarbamate degradation by increasing hydroxyl ions to participate for dithiocarbamate instability. Dithiocarbamate mobility on Moroccan soils samples have been realised and don't have the same degradation mode.

Keywords: *dithiocarbamate, fungicides, kinetic, degradation, mobility, water, soil.*

Résumé: Actuellement, le problème de résidus des pesticides dans l'environnement et dans les denrées alimentaires se pose avec une grande acuité et fait l'objet de nombreuses recherches.
Nous avons alors porté notre contribution à l'analyse des dithiocarbamates utilisés dans le traitement des tomates. Nous nous sommes alors focalisés notre étude essentiellement sur l'analyse et la détermination de quelques dithiocarbamates à savoir (Manèbe, Mancozèbe, Zinèbe, et le Propinèbe) dans le but de réaliser une étude d'impact de ces fongicides sur l'environnement.
L'analyse des dithiocarbamates repose sur une détermination indirect qui se base sur leur dégradation en milieu acide dans le but de produire le disulfure de carbone qui formera un complexe de coloration jaune dosé à une longueur d'onde fixe.
Par la suite, nous avons réalisé une étude concernant la cinétique de dégradation des dithiocarbamates en solution aqueuse. Nous avons réalisé aussi une étude concernant la dégradation des dithiocarbamates en fonction du *pH*.
L'étude de la mobilité des dithiocarbamates a été aussi réalisée sur différents types de sols de la région de Souss-Massa.

Mots clés: *dithiocarbamate, fongicides, cinétique, dégradation, mobilité, eau, sol.*

INTRODUCTION

Dithiocarbamates (DTCs) are important organosulfur compounds, which act as inhibitors of metal dependant and sulfhydryl enzymes and have serious consequences on biological systems. They have been studied extensively over last decades in a response to their growing applications in any new area of chemistry, industry or biology. They have various applications in agriculture as fungicides, as well as, in the rubber industry as vulcanization accelerators and antioxidants [1]. In this way, DTCs are the main group of fungicides used to control approximately 400 pathogens of more than 70 crops and are registered in all the EU member states and many other countries [2, 3].
Dithiocarbamates are one of the most commonly used pesticides around the world, including Morroco. These compounds are also the most frequently detected pesticides in monitoring programs worldwide [4].
There is much interest in the potential environmental impact of DTCs usage in agriculture and their effect on human health. Generally, the DTCs are not considered to be highly toxic. However, toxicity is increased with the presence of a heavy metal ion in the molecule. Short-term exposure to DTCs can cause eye, respiratory and skin irritation whilst long-term exposures may cause dermatitis and skin sensitization. Moreover, their metabolites, ethylenethiourea (ETU, imidazolidine-2-thione) or propylenethiourea (PTU, 4-methylimidazolidine-2-thione) affect the thyroid, and furthermore, neurotoxic effects have been observed, as well. Also, these compounds are suspected to be carcinogenic, mutagenic and teratogenic. The formation of these

compounds begins during storage of pesticide formulation [5, 6]. The ethylene-bis-dithiocarbamate (EBDC, Mancozeb) was considered to be a multipotent carcinogenic agent in along-term rat study [7]. Ethylenethiourea (ETU), formed by the degradation and metabolism of EBDCs present in foods, inhibits thyroid peroxidase and thus induces thyroid cancer in laboratory animals [8]. Figure 1 presents the chemical structures of the main DTCs studied.
The aim of this work is the realization of a degradation kinetic study of DTCs in aqueous media caused by simple air exposition. On the other hand, we have observed the effect of *pH* on DTCs degradation. Dithiocarbamate's mobility on Moroccan soil samples has been also studied.

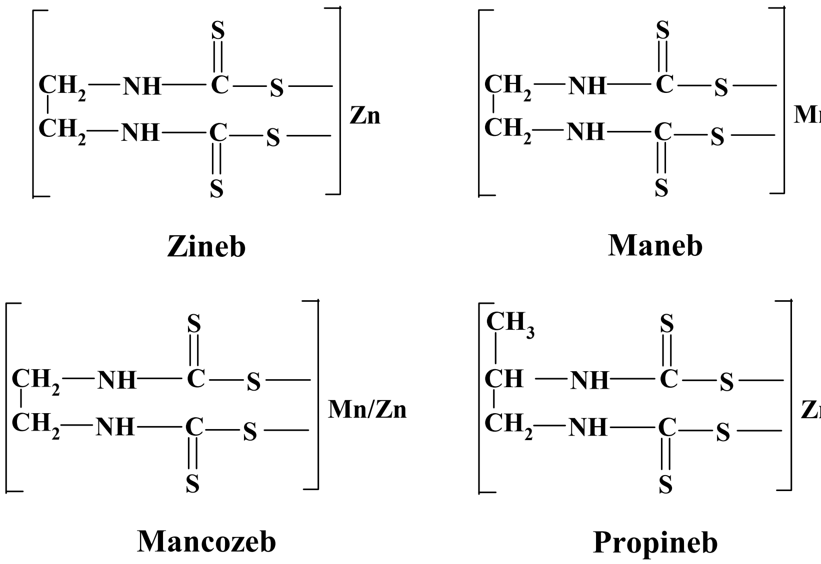

***Figure 1**. Chemical structures of the main DTCs studied*

EXPERIMENTAL SECTION

Method of dosage

DTCs residues were assessed on the basis of the method described by Keppel *et al.* [9]. DTCs residues are decomposed by refluxing the sample with boiling dilute sulfhydric acid. The decomposition of dithiocarbamates was carried out at high or low temperature. The CS_2 evolved is carried by gas stream through a first trap to remove H_2S and other volatile interferences. It then reacts, in a second trap, with color reagent to form yellow complex. The yellow complex is the cupric salt of *N,N*-bis(2-hydroxyethyl)dithiocarbamic acid, which optical density (OD) was measured spectrophotometrically at 435 nm. Figure 2 represents the formation of cupric complex in the second trap.
The yellow coloration obtained is measured at 435 nm with a sensitivity limit of 10 mg of CS_2 corresponding to about 20 µg of DTC. Usually the DTC are not present in open water at low concentrations located below the threshold of sensitivity of the dosage.

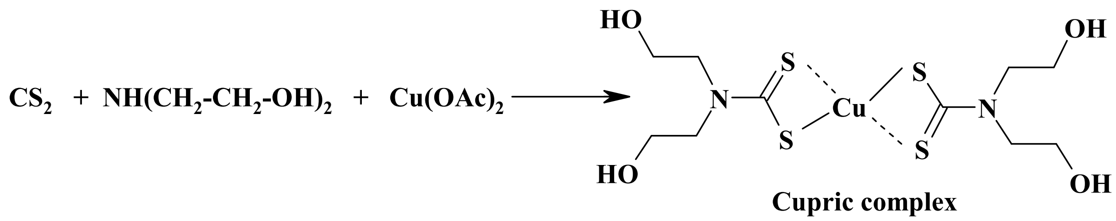

Figure 2. *Reaction for cupric complex formation*

Materials & Apparatus

All solutions were prepared from analytical reagent grade chemicals in 18 MΩ water obtained from Elgast UHQ II System (Elga, Antony, France).
Sodium hydroxide and sulfuric acid were purchased from Merck (Darmastadt, Germany). Copper acetate, diethanolamine and carbon disulfide were purchased from Fluka (St Quentin Fallavier, France). Absolute ethanol and toluene were purchased from Prolabo (Paris, France). Maneb, Zineb, Propineb and Mancozeb were purchased from Agrimatco (Casablanca, Maroc).
A JASCO model 7800 UV/VIS spectrophotometer equipped with deuterium lamp in the UV region and tungsten iodine lamp in the visible region was used. The *pH* values were measured with a Beckman *pH*-meter (Model Φ 10, Gagny, France).
The apparatus for the production of CS_2 formed after hydrolysis and formation of the CS_2 cupric complex used in the Cullen and Keppel method has been utilized by laboratories over the years with no significant changes from its original design [10 – 12]. The objective of this work was to propose a new CS_2 reaction system, less fragile than the traditional design, with the potential of decreasing analysis times and increasing sample throughput while maintaining good analytical performance and low cost.

Procedure

100 mL solution of dithiocarbamate and 20 mL of H_2SO_4 2N solution with few grains of pumice are introduced into a 250 mL flask connected to refrigerant and the two traps. The first bubbler contains 10 mL of NaOH (10%) and 5 mL of toluene. The second bubbler contains 12.5 mL of solution of copper acetate. Then the content of the flask was heating to boiling (80 – 90 °C) under a slight vacuum for 30 min. When the yellow color of the contents of the second bubbler appears, it is introduced into a 25 mL flask. Then it is rinsed with absolute ethanol and made up to 25 mL. The mixture is stirred and then the yellow colored complex is measured after 15 min at 435 nm against a control sample (blank) prepared with a solution of copper acetate half diluted with absolute ethanol.

RESULTS AND DISCUSSION

Calibration curve

In order to realize a quantitative analysis of DTCs fungicides for evaluating the kinetics studies of degradation and mobility, it was necessary to raise a calibration curve. This latter is presented as a variation of optical density (OD) according the amount of CS_2. In this case, we have prepared an original solution of 1 g of CS_2 in 100 mL of ethanol, then, we diluted it to a hundred, twice. For the measurement of optical density OD, prelevement of quantities of CS_2 in order: 10, 25, 50, 75, 100, 150 and 200 µg corresponding of a prelevement of the samples assays of: 0.1, 0.25, 0.5, 0.75, 1.0, 1.5 and 2.0 mL respectively of the original solution completed with 12.5 mL of solution of cupric acetate and gauged with ethanol to 25 mL. The calibration curve representing the variation of OD according to the amount of CS_2 was obtained with a satisfactory linearity, as shown in Figure 3.

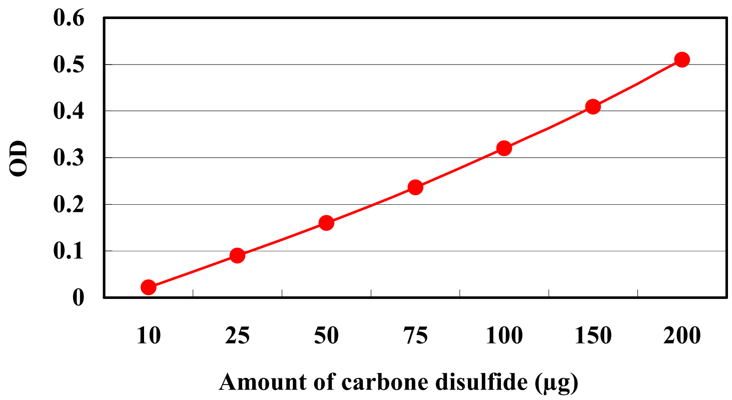

***Figure 3**. Calibration curve for carbon disulfide*

Kinetic degradation study of DTCs in aqueous media

The kinetics of degradation of dithiocarbamates in aqueous solution is achieved by preparing solutions of various DTCs (Maneb, Zineb, Mancozeb and Propineb). The following analyses of these DTCs are always achieved by decomposition to CS_2. Figure 4 shows the kinetics degradation of DTCs. Percentages of presence of DTCs after 8 days were between 25 and 35%.

In the light of these results, it appears that the quantity of each DTC decreases with time increasing. This decrease may be due to exposure of these dithiocarbamates to air (light rays). Table 1 summarizes the half life $t_{1/2}$ (h) and the rate constant k (s^{-1}) of degradation of each DTC.

***Table 1.** Kinetic parameters of degradation of DTCs*

	Mancozeb	Maneb	Zineb	Propineb
$t_{1/2}$ (h)	72	48	55	59
k (s^{-1})	6.55×10^{-06}	9.82×10^{-06}	8.57×10^{-06}	7.991×10^{-06}

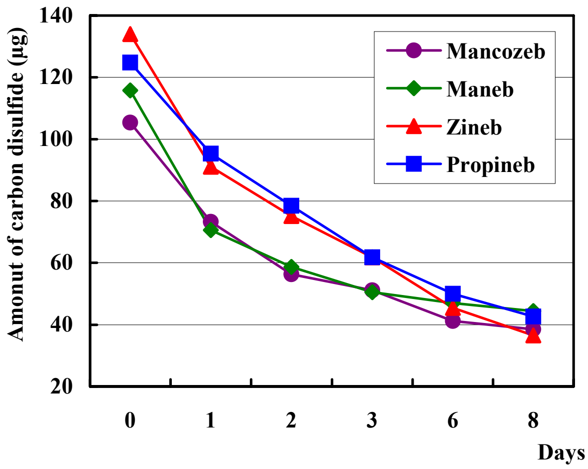

Figure 4. *Kinetics of degradation of DTCs in water*

Through the values of half-life period, we have classified these DTCs by increasing persistence with the following order:

Maneb < Zineb < Propineb < Mancozeb

The degradation of these DTCs occurred by a first order kinetics.

Effect of *pH* on kinetics of degradation of DTCs in aqueous media

The study concerning on the effect of *pH* on the kinetics of degradation of DTCs is achieved by preparing a solution from 0.01 g of the corresponding DTC (in 500 mL of distilled water). On the resulting solution stirred for 15 minutes and filtered, the *pH* is adjusted to 2, 3, 4, 5 and 6 respectively, by adding a 2N solution of H_2SO_4. The solutions thus prepared are left outdoors. Figure 5 shows the degradation profiles of DTCs (Maneb, Zineb and Mancozeb) in relation to *pH*.
An increase of *pH* of the medium causes a decrease in the amount of DTC. Indeed, an increase of *pH* causes a decrease in the concentration of protons and an increase in the concentration of OH^- ions. We therefore deduce that DTCs are unstable in alkaline environments. Thus, the basic conditions promote further degradation of DTCs studied. In passing from *pH* 2 to 5, the Maneb undergoes slight degradation. By moving to a *pH* 6 (slightly neutral), it undergoes a sharp deterioration. This confirms once again the instability of Maneb in alkaline conditions. Similarly, Mancozeb and Zineb suffer a drastic degradation by passing an alkaline medium.

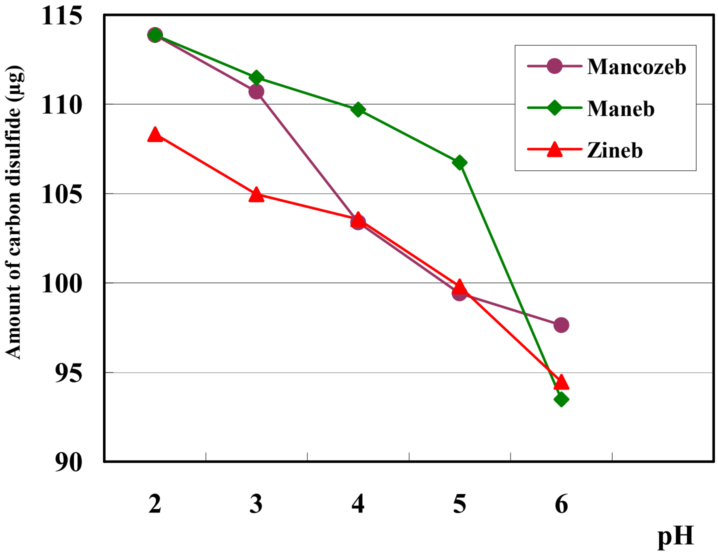

Figure 5. *Effect of pH on the degradation of DTCs*

Mobility study of DTCs on Moroccan soil

The latest step concerning our analysis is the determination of mobility of DTCs on soil. Soil samples collected from the region Chtouka Ait Baha were analyzed at the Agronomic and Veterinarian Institute "Hassan II", Agadir horticultural complex to determine their physical-chemical properties. The results of these tests are grouped in Table 2.

Table 2. *Soil characteristics studied*

Characteristic*	Profiles (cm)		
	0 – 10	10 – 20	20 – 30
C.S. (%)	25.10	26.20	26.20
F. S. (%)	6.92	65.90	65.20
T. S. (%)	92.01	91.83	91.43
c.s. (%)	5.57	4.04	5.50
f.s. (%)	0.55	1.47	1.51
t.s. (%)	6.10	5.52	6.99
Clay (%)	2.43	2.70	1.75
O.M. (%)	3.4	2.8	1.9
pH	7.00	6.72	6.69

** C.S. - Coarse sand; F.S. - Fine sand; T.S. -Total Sand; t.s. - Total silt; c.s. - Coarse silt; f.s. - Fine silt; O.M. - Organic matter*

From these granulometric analyses, we can note that the soil used throughout our experiments has a homogeneous profile in the range of 0 – 30 cm, while having a sandy texture. The chemical analysis showed that soil *pH* is near neutrality and the percentages of organic matter are high enough.

In order to perform the study of DTCs mobility (Mancozeb, Zineb, Maneb and Propineb), we have used PVC columns with an internal diameter of about 5 to 10 cm and height of 55 cm cut into five parts.
We chose these parameters for conditions related to reality [13-16]. In order to get an idea on the dose applied to the soil columns that we have prepared, we are inspired of the doses applied per hectare given in Table 3 [17]. Filling in a pile was necessary for effective preparation columns. The application of the dose of DTC is achieved by spraying the first day. The processing will be made then the second day. Control of monitoring the mobility of each pesticide is performed on each profile column.

***Table 3**. Dose treatment*

Dithiocarbamate	Mancozeb	Maneb	Propineb	Zineb
Dose treatment for a one ha (g)	2000	2000	2500	3000
Dose treatment for a one hL (g)	200	200	250	300
Dose treatment for 10 mL columns (g)	0.019625	0.019625	0.019625	0.02355

The examination of the results from Figure 6 shows that the mobility of DTCs is not homogeneous. DTCs in this study can be divided into 3 basic categories of mobility based on their movement in soil columns: low, moderate and high.

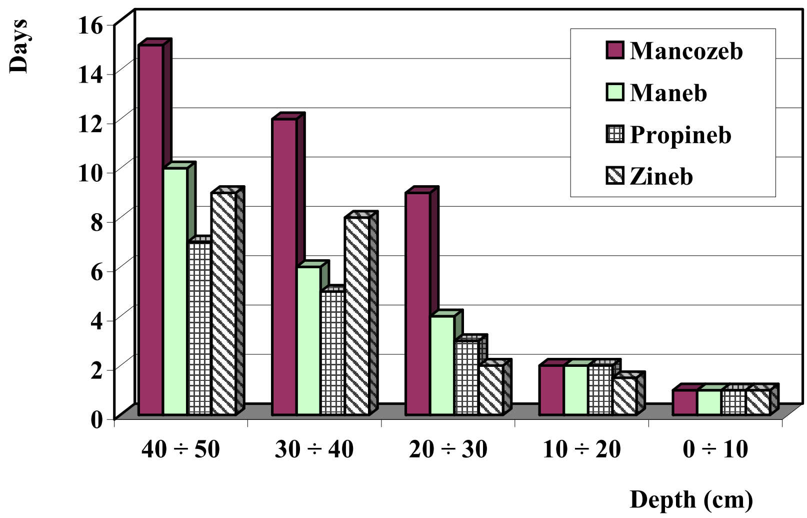

***Figure 6.** Kinetic mobility of DTCs according to the depth*

Mancozeb had the lower mobility and shifted from 0 to 50 cm in the soil for 15 days. The DTCs moderately mobile were Maneb and Zineb, they moved to a depth of 50 cm in 9 to 10 days. Propineb was the most mobile in this study; it has moved from 0 to 50 cm for 7 days. A ranking after reaching the increasing mobility profile 40 – 50 cm:

$$\text{Mancozeb} < \text{Maneb} \approx \text{Zineb} < \text{Propineb}$$

CONCLUSION

In this work, we tried to bring our contribution to the analysis and determination of DTCs. Initially, we carried out the kinetics of degradation of DTCs (Maneb, Zineb, Mancozeb and Propineb) in aqueous solution. The results obtained show that these DTCs are decomposed by simple exposure to air. In a second step, we realized a study of the influence of *pH* on degradation of DTCs. The results show that increasing *pH* increases the hydroxide ions involved in the instability of DTCs studied. Finally, a study has shown that the mobility of DTCs does not occur in a uniform way. Thus, the Propineb is more mobile, while Mancozeb is the least mobile.

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