

Study the Effect of UV-Light on the Degradation of Thiobencarb Technical Ismail, I. I.

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ABSTRACT

The photodegradation of thiobencarb technical by UVC ($\lambda=254$) was studied to investigate the degradation of thiobencarb after exposure to UVC light for 144 hours, in addition to identification of some by-products by GC/MS. The obtained results showed that, the rate of degradation of thiobencarb was fairly fast so the loss percentage was increased to reach 71.57% after 144 hours and the half-life ($t_{0.5}$) was 4.95 hours. Analysis of samples after exposure to UVC light using GC/MS identified three by-products: thiobencarb sulfoxide, S-4-chlorobenzyl acetyl (ethyl)thiocarbamate and S-benzyl diethylthiocarbamate.

Keywords: Thiobencarb; UVC Photodegradation; By-products.

INTRODUCTION

Thiobencarb (S- [(4-chlorophenyl)methyl] diethylcarbamothioate) is a kind of herbicide called thiocarbamate that has been generally used in rice lands (Pentyala and Chetty, 1993). Thiobencarb is a systematic & selective herbicide, absorbed by coleoptile, mesocotyl, roots and leaves, pre-emergence herbicide that acts by stopping new growth of emerging saplings (U.S EPA, 1997). The main tricky with treatment of carbamates is their tenacity in the environs that might last for many years for certain compounds. Due to their great solubility in aquatic, their remains can mix in aqueous milieu by filtering and overflow from soil into sediment and superficial water (Wu *et al.*, 2010). Thiobencarb degraded by photodegradation after revealed to both sunlight and ultraviolet light of short wavelength (254 nm). It was broke down quicker however by ultraviolet light than by sunlight. Thiobencarb was decayed into some metabolites when exposed to sunlight containing thiobencarb sulfoxide and desethyl benthioencarb (Cheng 1976). The effectiveness of different kinds of rays, short wavelength ultraviolet UVC ($\lambda = 254$ nm) and long wavelength ultraviolet UVA ($\lambda = 365$ nm), was contrasted. UVC photodecomposition given that the top elimination with a whole breakdown for a certain fungicides. Adding of hydrogen peroxide below UVC light permitted a development of the reaction kinetics, particularly for the utmost intractable fungicides, getting in wholly examples eliminations greater than 82% in less than 6 min. (Celeiro *et al.*, 2017). Thiobencarb would be positively decomposed in the Visible light photo catalyst BiVO₄ hydrogen peroxide method. At the ideal effective factors, its breakdown effectiveness might influence 97% in five hours (Lai *et al.*, 2014). The rate of thiobencarb photolysis by MoS₂ Photo catalytic agent was established to rise with raising the pH to 6–9 significance with growing the catalytic agent concentration to the decay rate touch 95% in half day, moreover they proposed that dealkylation, hydroxylation, and C-S link splitting are three probable conversions in thiobencarb breakdown (Huang *et al.*, 2018).

The important target of this study to discuss the photodegradation of thiobencarb after exposure to UVC light, and also matching of some by-products by GC/MS. The chemical structure of thiobencarb is shown in Fig. 1.

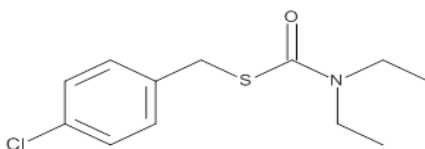


Fig. 1. Chemical structure of thiobencarb

MATERIALS AND METHODS

Thiobencarb technical 96% produced by Kumiai chemical industry company Japan and it was obtained from Kafir El Zayat for pesticides and chemicals company Egypt.

Procedure

A stock solution (500 $\mu\text{g ml}^{-1}$) of thiobencarb technical was prepared in methanol. One milliliter methanol containing 500 $\mu\text{g ml}^{-1}$ thiobencarb. 1 ml from stock solution was put in petri dishes and it were left to dry at room temperature then petri dishes was exposed to a short wave length of an ultra violet lamp (254 nm) for 0, 1, 2, 4, 6, 12, 24, 48, 72, 144 hours. All exposed tested thiobencarb were transferred quantitatively with methanol and the content of the residue of thiobencarb was determined by GC.

Measurements

1. Gas Chromatography Determination

This procedure according to CIPAC 338/TC/(M)- (1988). Agilent 7890B gas chromatograph with autosampler 7693 equipped with Flame Ionization Detector (FID) at 250 oC, capillary column HP-50+ (30 m x 0.25 mm I.D., 0.25 μm film thickness). Nitrogen was used as a carrier gas with constant flow 4 ml/min. The oven temperature program was held at 200 oC for 1 min, then ramp 20 oC /min to 280 oC. Injector temperature was 250 oC with splitless mode. The injection volume was 1 μl . under these conditions the typical retention time of thiobencarb was 3.525 min. A good linearity was obtained in the range 5-500 ng μl^{-1} of active ingredient with correlation coefficient of 0.99975 as shown in Fig. 2.

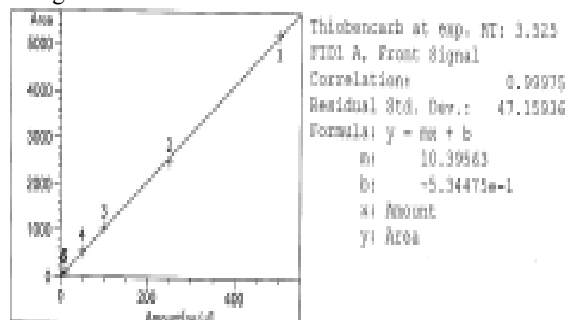


Fig. 2. Standard calibration curve of thiobencarb using GC

2. Gas chromatography-mass spectrometry analysis (GC/MS)

The GC/MS analysis was performed with an Agilent 7890B gas chromatograph equipped with 5977 A MSD Agilent mass spectrometric detector, with a direct capillary interface and fused silica capillary column HP-5MS(30 m x 0.25 mm x 0.25 μm film thickness). Helium was used as

carrier gas at approximately 1.0 ml/min pulsed split mode, split ratio (10:1). The solvent delay was 4 min, and the injection volume was 1 µl. The GC temperature program was held at 50 oC for 0.5 min, then ramp 10 oC /min to 190 oC for 1 min. followed by ramp 10 oC /min to 300 and held for 2 min oC (total run time 29.5 min, the injector temperature was set at 280 oC. EI mass spectra were identified using Wiley mass spectral data base Library.

3. Kinetic study

The half-life time ($t_{0.5}$) of thiobencarb was calculated according to (Moye *et al.*, 1987) and (Anderson and Scott, 1991).

$$t_{0.5} = \ln 2 / K$$

$$K = (1/t_x) \ln (a/b_x)$$

Where,

$t_{0.5}$ = the time required to reach 50% of the initial concentration.

K = rate of degradation

a = initial concentration

t_x = time in hours

b_x = concentration at x time

RESULTS AND DISCUSSION

1. The photodegradation of thiobencarb after exposure to UVC light

Table 1 and Fig. 3 demonstrated the effect of exposure to UVC light on the degradation of thiobencarb technical and indicates that, the loss percentages of thiobencarb increased by extend the duration of the period of exposure, and it were 41.26, 42.88, 44.94, 53.68, 58.04, 59.07, 62.24, 67.10, and 71.57% after 1, 2, 4, 6, 12, 24, 48, 72, and 144 hours, respectively of exposure to UVC light and the half-life ($t_{0.5}$) was 4.95 hours. The previous results clearly indicated that the rate of degradation of thiobencarb was fairly fast and influenced by several factors including chemical structure and the period of exposure.

Table 1. Effect of exposure to UVC light on the degradation of thiobencarb technical.

| Exposure time (h) | µg | % Loss |
|-------------------|--------|--------|
| 0 | 500 | 0 |
| 1 | 293.68 | 41.26 |
| 2 | 285.61 | 42.88 |
| 4 | 275.30 | 44.94 |
| 6 | 231.61 | 53.68 |
| 12 | 209.80 | 58.04 |
| 24 | 204.64 | 59.07 |
| 48 | 188.82 | 62.24 |
| 72 | 164.51 | 67.10 |
| 144 | 142.14 | 71.57 |
| $t_{0.5}$ (h) | | 4.95 |

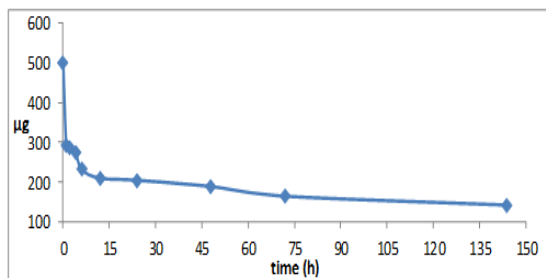


Fig. 3. Effect of exposure to UVC light on the degradation of thiobencarb technical

Our findings are in harmony with (Cheng 1976) reported that thiobencarb was broke down quicker however by ultraviolet light than by sunlight, also the

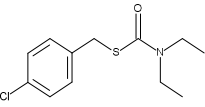
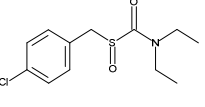
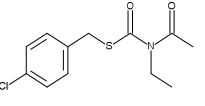
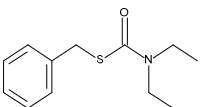
obtained results were agreement with (Lai *et al.*, 2014) and (Huang *et al.*, 2018).

2. Matching of the by-products of thiobencarb by GC/MS

The samples of thiobencarb were analyzed after exposure to UVC light for 144 hours using GC/MS to identify the degradation products, and found that the characteristic ions at m/z 257, 272, 271 and 223 were molecular ions of thiobencarb, thiobencarb sulfoxide, S-4-chlorobenzyl acetyl (ethyl)thiocarbamate and S-benzyl diethylthiocarbamate, however Table (2) indicated that, Matching of the by-products of thiobencarb by GC/MS.

Thiobencarb was decayed into some by-products when exposed to UVC light containing thiobencarb sulfoxide, where Cleavage of the S-C bond to form a 4-chlorobenzyl radical that is further oxidised, oxidation at sulfur to give the thiobencarb sulfoxide and this is agreement with (Cheng 1976) and (Ruzo and Casida 1985).

Table 2. Matching of the by-products of thiobencarb by GC/MS

| Structure | RT (min) | Characteristic ions (m/z) |
|--|----------|---|
|  | 23.016 | [M] ⁺ =257,125,100,72 thiobencarb |
|  | 22.243 | [M] ⁺ =271[M ⁺ -3], 242, 172,157,125,90,73 thiobencarb sulfoxide |
|  | 23.913 | [M] ⁺ =271,156,146,125, 89,72 S-4-chlorobenzyl acetyl (ethyl)thiocarbamate |
|  | 4.819 | [M] ⁺ =223,194,165,123, 91,77 S-benzyl diethylthiocarbamate |

It is very clear that the hydroxyl radical has electrophilic properties so carbon hydrogen links close to nitrogen are answerable for a pronounced stereo electronic effect that yields great amounts of hydrogen atom abstraction. Consequently, the α -hydrogen atoms in the N-ethyl group of thiobencarb compound were the greatest vulnerable to radical attack. Hydroxyl radicals produced radicals of central carbon depend on the hydrogen atom elimination from the N-ethyl group, or they re-joined with the lone-pair electron on the N atom to produce cationic radicals, where then transformed into carbon-centered radicals (Lee and Choi 2004). The carbon-centered radical produced when adding of oxygen creating the peroxy radical broke down to S-4-chlorobenzyl acetyl (ethyl)thiocarbamate, and also agreement with (Lai *et al.*, 2012 and Lai *et al.*, 2014).

There is another possible degradation pathway of thiobencarb which formed by loss chlorine atom and give S-benzyl diethylthiocarbamate. The possible degradation pathways of thiobencarb were showed in Fig. 4.

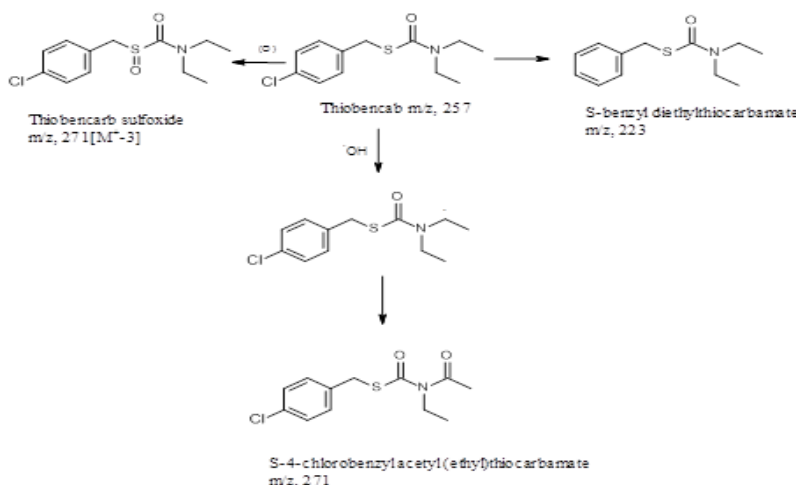


Fig. 4. The possible degradation pathways of thiobencarb

CONCLUSION

Thiobencarb was affected by exposure to UVC light and the rate of degradation increased by the long period of exposure. The photodegradation of thiobencarb UVC light can produce some intermediates through many pathways like oxidation and N-dealkylation by hydroxyl radical.

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دراسة تأثير الأشعة فوق البنفسجية فوق البنفسجية على انهيار خام الثيوبنكارب اسماعيل ابراهيم اسماعيل المعمل المركزي للمبيدات - مركز البحوث الزراعية - الدقى - جيزه - مصر

تمت دراسة التحلل الضوئي لمبيد ثيوبنكارب خام بواسطة الأشعة فوق البنفسجية ($\lambda=254$) وذلك لبحث انهيار الثيوبنكارب بعد التعرض للأشعة فوق البنفسجية لمدة 144 ساعة، بالإضافة الى التعرف على بعض نواتج التكسير باستخدام جهاز GC/MS. أظهرت النتائج التي تم الحصول عليها ان معدل انهيار الثيوبنكارب كان سريعاً الى حد ما حيث زادت نسبة الفقد حتى وصلت الى 71,57% بعد 144 ساعة وفترة نصف العمر ($t_{0.5}$) كانت 4,95 ساعة. وعند تحليل العينات بعد تعرضها للأشعة فوق البنفسجية باستخدام جهاز GC/MS تم التعرف على ثلاثة نواتج تكسير وهم S-4-chlorobenzyl acetyl (ethyl)thiocarbamate و S-benzyl diethylthiocarbamate.