Degradation Kinetics and Half-Lives of Fenitrothion and Thiobencarb in The New Reclaimed Calcareous Soil of Egypt Using GC-MS

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ABSTRACT: The degradation process of pesticides is one of the mechanisms for losing such chemical from the soil after application. The persistence, degradation kinetics and half-lives of fenitrothion (insecticide) and thiobencarb (herbicide) in the new reclaimed calcareous soil in Egypt were studied under laboratory conditions. The recovery percentages of fenitrothion and thiobencarb were 89.67 and 88.34%, respectively. The results of degradation kinetics showed that residues of fenitrothion and thiobencarb were rapidly decreased during the first five days after treatment. Residues of fenitrothion and thiobencarb remained on the second day were 72.45% and 57.63%, while on the fifth day were 37.72 and 47.18%, respectively. Both tested pesticides disappeared very rapidly from the soil following a bi-phasic pattern. According to the graphical and integral methods, the fit model to describe the degradation kinetic of fenitrothion and thiobencarb is the first order model. The rate constant \( k \) values for degradation of the two pesticides were 0.036 and 0.068 for fenitrothion and thiobencarb, respectively. The estimated values of half-life were 19.36 days for fenitrothion and 10.24 days for thiobencarb. In general, thiobencarb degraded in sandy clay loam soil about twice faster than fenitrothion.

Keywords: Fenitrothion; insecticide; thiobencarb; herbicide; degradation; kinetics; half-life.

INTRODUCTION: The presence of pesticides in water, soil, and air has raised concern for environmental protection. To compensate for transport and degradation losses and to ensure adequate pest control for a suitable period, pesticides are applied at concentrations greatly exceeding those required for control of the target organisms, thus increasing the contamination. Only a part of the applied amount of a pesticide is bioactive, the rest is distributed in the environment (Kovacević et al., 2011). The biological availability (the resultant impact on non-target organisms), behaviour, persistence, and eventual decomposition of soil-adsorbed insecticides are, to a large extent, influenced by their adsorption-desorption phenomena, mobility, leaching and diffusion in the soil matrix (Bailey and White, 1970; Sundaram et al., 1997).

Among all pollutants, pesticides are the most dangerous contaminant for human being and biological diversity because of their negative impacts (Ayranci and Hoda 2005). It was reported that the agrochemicals used on rice are the third consumed in the world with an approximate 9% of the global market share and demand for these pesticides will continue to grow. Substantial quantities of pesticides used in rice crop and their projected increase raise major concern about their impact on the environment and human health (Anyushева et al., 2016). Pesticides are used to increase and control the crop yield by farmers for many years. Although much benefit is obtained from their uses, they have some undesirable side effects such as toxicity, carcinogenicity and mutagenicity (Becker and Wilson 1980; Kouras et al., 1998).

Among newly developed pesticides, organophosphate and carbamate group of pesticides are most commonly used due to their good selectivity and inexpensive cost (Armaghan and Amini 2008). However, these pesticides are reported as highly toxic and carcinogenic for human being by WHO (2004). Organophosphate pesticides (OPs) were discovered as toxic nerve agents. They kill insects by disrupting their brains and nervous systems. Unfortunately, it was discovered in 1932 that OPs can cause neurotoxic effects in humans such as cholinergic syndrome, intermediate syndrome, and organophosphate-induced delayed polyneuropathy (Jokanovic and Kosanovic, 2010; U.S.EPA, 1999). Fenitrothion can extensively be detected in the environment (Wang et al., 2012; Oiwa et al., 2020). Moreover, the kinetic analysis indicated that degradation of fenitrothion followed a first order reaction irrespective of the soil and water regime (Adhya et al., 1987). Another toxic pesticide group, carbamate group pesticides, thiobencarb which belong to the carbamothioates group, is extensively used in the paddy fields. Thiobencarb is relatively immobile and accumulates in the upper layers of the soil. Laboratory and greenhouse studies have shown that about 93% (in unsaturated flow) to 70% (in saturated flow) of thiobencarb remains in the...
upper one cm soil layer after leaching, indicating strong adsorption of thiobencarb (Braverman et al., 1990; Doran et al., 2008). Adsorption on soil particles can prevent the dissipation of herbicides in aquatic media and prolong their half-lives. Half-life is a significant indicator of herbicide dissipation in the natural environments. This parameter is frequently used to manage herbicide application and irrigation programs. Different half-lives have been reported for thiobencarb in paddy fields water, ranging from 5 to 9 days in California (Ross and Sava, 1986; Mabury et al., 1996); 12 days in Spain (Redondo et al., 1994) and 16 to 21 days in Australia (Quayle et al., 2006). Studies have shown that half-life is significantly increased in the adjacent of soil particles. In flooded soils, half-life of thiobencarb has been determined to be 100 to 200 d in Australia, 100 d in Japan, and 200 d in the US (Quayle et al., 2006). In non-flooded conditions, its half-life has been ranged from 10 to 77 d (Kawamoto and Urano, 1990; Sudo et al., 2002; Quayle et al., 2006). These relatively large differences in half-life show the effects of environmental conditions.

The longer is the persistence of herbicide the higher is the controlling effect on weeds. Moreover, the herbicide residue may have environmental risk, and may influence rotational crops (Mahmoudi et al., 2011). Among others, adsorption on soil particles and chemical and biological degradation are two major factors that affect the activity and persistence of herbicides in water, soil, and other natural ecosystems. In degradation process, herbicide is however broken down through biological, chemical, and photochemical reactions (Kodaka et al., 2003). Soil pH, temperature, moisture, and organic matter content are the major factors that influence chemical and microbial degradation (Mabury et al., 1996).

The objectives of this work were to assess the persistence, degradation kinetics and the half-lives of fenitrothion and thiobencarb under laboratory conditions in the new reclaimed soil (calcareous soil) located in from Elmahda region, Elamria, Alexandria Governorate, Egypt.

MATERIALS AND METHODS

Tested pesticides

Fenitrothion (Insecticide), O, O-Dimethyl O-4-nitro-m-tolyl phosphorothioate. The chemical structure is shown in Figure (1). Solubility in water 0.038 g/L, Hexane 24 g/L, P value: 0.57. Technical 97.0% a.i. Production Company: Shandong Chuangying Chemical Co., China. It is used for controlling chewing and sucking insects on rice, orchard fruits, vegetables, cereals, cotton, and forest. Also fly, mosquito, and cockroach control in public health programs.

Thiobencarb (Herbicide), S-4-Chlorobenzyl diethyl thiocarbamate. Chemical structure is shown in Figure (1). Solubility in water 0.030 g/L, Hexane: 500 g/L, P value: 1.70 X 104. Technical 97.0 % a.i. Production Company: Shandong SanYoung Industry Co., Ltd, China. It is a pre-emergence and early post-emergence herbicide for weed control in rice paddy fields and other situations.

Tested soil

The kind of soil used in the current experiment was calcareous from the new Egyptian reclaimed. The soil samples were collected from the surface layer (0-20 cm) from different locations in Elmahda region, Elamria, Alexandria Governorate. The soil samples had no history of pesticide applications. The physical and chemical properties were determined at the Department of Soil and Water Sciences, Faculty of Agriculture, University of Alexandria and the data are presented in Tables 1 & 2. Soil was air-dried, ground and passed through a 2-mm sieve prior to use. The soil texture was determined by the hydrometer method (Gee and Bauder, 1986). Soil pH was determined using 0.01 M calcium chloride (CaCl2) in a 1:2 w/w soil: solution slurry. The OM content was determined by dichromate oxidation according to the Walkley-Black method (Nelson et al., 1996).
Table (1): Physical properties of the tested soil

<table>
<thead>
<tr>
<th>Particle size distribution (%)</th>
<th>Texture class</th>
<th>WHC (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silt</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sand</td>
<td>Sandy clay loam</td>
<td>38</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>67</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table (2): Chemical properties of the tested soil

<table>
<thead>
<tr>
<th>EC (m mohs/cm) at 25˚C</th>
<th>pH</th>
<th>OM (%)</th>
<th>Total carbonate (%)</th>
<th>Total soluble cations (meq/L)</th>
<th>Total soluble anions (meq/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.03</td>
<td>8.15</td>
<td>1.54</td>
<td>44.64</td>
<td>60.30</td>
<td>50.30</td>
</tr>
</tbody>
</table>

Chemicals and Instrumentation

Anhydrous sodium sulfate (Na2SO4), sodium hydroxide (NaOH), commercial solvents including acetonitrile and acetone were purchased from Algomhoria Chemical Co., Alexandria, Egypt. Solvents HPLC-grade methanol, dichloromethane, n-hexane and acetonitrile were purchased from Sigma Aldrich Co. (Spruce Street, Louis., MO, USA).

GC-MS a thermo Scientific gas chromatograph GC Trace 1300 coupled with an EI Mass spectrometer ISQ 7000 model (Thermo Scientific USA) equipped with Thermo TR-50 MS capillary column (30 m in length × 250 μm in diameter × 0.25 μm in thickness of film).

Sonicator, Mod: LBS 2 4, 5Lt; Cod: 616.1020.05; Ser.N°: B133276; Year: 2013.

Rotary evaporator bibby scientific limited stone. Staffordshire. St15 0SA. UK.

Centrifuge, Model 90-1 UK.

Water distillatory, DESA 0035, Eu.

Digital balance, ViBRA AJ-320E, 0.01-150 g. Japan.

Pesticide determination and recovery by GC-MS

GC standard solution

To prepare stock solutions of individually tested pesticides, the standards of fenitrothion and thiobencarb were dissolved in methanol-HPLC (1000 mg/L), considering standard purity, by accurately weighing individual analytical standards into volumetric flasks, dissolving and diluting them to volume with methanol and stored at 4°C in the dark. The working standard solution was freshly prepared by appropriately diluting multiple stock solutions with dichloromethane-HPLC. The standard solution (100 μg/mL) was determined immediately before the samples.

Degradation study

Soil treatment

The degradation of fenitrothion and thiobencarb in clay soil was monitored under laboratory conditions. A weight of 150 g soil was placed in 500-mL glass bottle and treated with each tested pesticide (75 μg a.i. /g soil). Three replicates were made for each treatment. The tested pesticides were dissolved in an amount of distilled water equals to 60 % of water holding capacity (WHC) of the tested soil. The solution was added to the soil to reach an adequate concentration of 75 μg/g. All bottles were incubated at 25 ºC for up to 84 days. Through the incubation period, the appropriate amount of water was added to replace lost soil moisture (Fouad, 2017; Badawy et al., 2017).
Extraction and determination of tested pesticides
The soil was sampled at different times (0, 2, 5, 13, 20, 27, 48, 55 and 84 day). The tested pesticides were extracted from air dried soil samples by dichloromethane-HPLC with sonication. The extraction and clean-up of pesticide residues from soil samples were processed according to the procedure described in Figure (2). The residues were analyzed by GC-MS (Redondo et al., 1994).

Assessment of half-life values
Dissipation kinetics of fenitrothion and thiobencarb were investigated, different kinetic models were tested to select the fit model with the data. The degradation rate was obtained from the straight line plot of the 1st-order kinetic model, \(\ln[C_t] = \ln[C_0] - k_t \times t\). The half life values of tested pesticides were assessed by the following equations (Moye et al., 1987; Badawy et al., 2017; Yuan et al., 2020).

\[ t_{1/2} = \frac{0.6932}{k} \]

Where, \(k\) is the dissipation rate, \(t_{1/2}\) (Half-life) is a time it takes for an amount of a compound to be reduced by half through degradation (Badawy et al., 2017; Fardillah et al., 2020).

Recovery of tested pesticides by GC-MS
To confirm the efficiency of the extraction method and chromatographic analysis for the determination of tested pesticides in soil, recovery experiments were carried out. The soil samples were spiked with a concentration of 75 \(\mu\)g/g soil fenitrothion and thiobencarb individually. The recovery percentage was calculated according to the following equation;

\[ \text{Recovery} \% = \frac{(\mu\text{g pesticide determined/g soil})}{(\mu\text{g pesticide add/g soil})} \times 100 \]

Table (3): Recovery percentages of fenitrothion and thiobencarb in soil determined by GC-MS

<table>
<thead>
<tr>
<th>Pesticides</th>
<th>Fenitrothion</th>
<th>Thiobencarb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recovery %</td>
<td>89.67</td>
<td>88.34</td>
</tr>
</tbody>
</table>

Persistence of tested pesticides in soil
The persistence of fenitrothion and thiobencarb was investigated in calcareous (sandy clay loam) soil under laboratory conditions. The soil was treated with a concentration of 75 \(\mu\)g/g soil of fenitrothion and thiobencarb individually. Then the treated soil was incubated at 25 °C and sampled at different times (0, 2, 5, 13, 20, 27, 48, 55 and 84 day). After that, the soil samples were extracted, cleaned up and analyzed by GC-MS. The results in Table (4) summarized the residues of fenitrothion and thiobencarb in soil during 84 days after treatment. Initial residues of fenitrothion and thiobencarb were 67.26 and 66.26 \(\mu\)g/g soil, while after 48 days, the residues dropped to 8.87 \(\mu\)g/g soil (13.19% of the initial residues remaining) and 4.52 \(\mu\)g/g soil (6.82% of the initial residues remaining). It was observed that the residue of thiobencarb was detected while that of fenitrothion was non-detected at 55th day, however the two pesticide residues were non-detectable at 84th day. It was seen that the residues of the fenitrothion and thiobencarb
rapidly decreased during the first five days after treatment. Fenitrothion remained at 2\(^{nd}\) day was 72.45% and at 5\(^{th}\) day was 37.72. Also, the remain thiobencarb was 57.63% and 47.18% at 2\(^{nd}\) and 5\(^{th}\) day, respectively. The disappearance curves of fenitrothion and thiobencarb are shown in Figure (3). Within 84 days of incubation, residues of fenitrothion and thiobencarb were monitored in soil samples. The two tested pesticides disappeared very rapidly from the soil following a bi-phasic pattern. Just two weeks after treatment the maximum concentrations of fenitrothion and thiobencarb were reduced to about one third and one fourth. This sharp drop was followed by a period of a slow incremental decrease for five weeks.

**Table (4): Residue (μg/g soil) and remaining (%) of fenitrothion and thiobencarb in sandy clay loam soil determined by GC-MS**

<table>
<thead>
<tr>
<th>Time (day)</th>
<th>Fenitrothion</th>
<th></th>
<th>Thiobencarb</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Residue (µg/g soil)</td>
<td>Remaining (%)</td>
<td>Residue (µg/g soil)</td>
<td>Remaining (%)</td>
</tr>
<tr>
<td>0</td>
<td>67.26</td>
<td>100.00</td>
<td>66.26</td>
<td>100.00</td>
</tr>
<tr>
<td>2</td>
<td>48.72</td>
<td>72.45</td>
<td>38.19</td>
<td>57.63</td>
</tr>
<tr>
<td>5</td>
<td>25.37</td>
<td>37.72</td>
<td>31.26</td>
<td>47.18</td>
</tr>
<tr>
<td>13</td>
<td>20.29</td>
<td>30.16</td>
<td>17.86</td>
<td>26.96</td>
</tr>
<tr>
<td>20</td>
<td>19.28</td>
<td>28.67</td>
<td>15.08</td>
<td>22.77</td>
</tr>
<tr>
<td>27</td>
<td>18.30</td>
<td>27.21</td>
<td>5.94</td>
<td>8.96</td>
</tr>
<tr>
<td>48</td>
<td>8.87</td>
<td>13.19</td>
<td>4.52</td>
<td>6.82</td>
</tr>
<tr>
<td>55</td>
<td>ND</td>
<td>-</td>
<td>0.66</td>
<td>0.99</td>
</tr>
<tr>
<td>84</td>
<td>ND</td>
<td>-</td>
<td>ND</td>
<td>-</td>
</tr>
</tbody>
</table>

ND: None-detectable, -: no data

**Fig. (4): Disappearance curves of fenitrothion and thiobencarb in soil**

Degradation kinetics of tested pesticides in soil
To evaluate the decline of fenitrothion and thiobencarb residues in the studied soils, residue data should be subjected to statistical analysis to determine the statistical parameters that describe these processes, as proposed by Likas and Tsiropoulos (2007). Two methods were used to determine the best kinetic model for the degradation data, graphical and integral methods. A linear regression can be obtained after an appropriate transformation of the residue using different formal models described in Table (5). To select the best fit model, the values of determination coefficient R\(^2\) were calculated for each model. As is well known, R\(^2\) ≤ 1, and the larger this coefficient, the better the decline curve fits the data. If R\(^2\) becomes negative or zero for any model, then the fit is automatically rejected.
Besides, according to the integral method, the correlation is confirmed when SD of calculated K values is a low value. The SD of the K values were calculated as K 100%, to compare among them. It can be seen from Figure (4) and Table (5) the 1st order model give the highest R² value (0.91) and the lowest SD of K values (63.47) for thiobencarb. This model gives R² for fenitrothion (0.82) which is lower than R² (0.86) obtained by 3rd order model, although the 1st order model gives a lower SD of K values (60.92) compared to that obtained by 3rd order model (62.44). Therefore, the fit model to describe the degradation kinetic of fenitrothion and thiobencarb is the 1st order model. Various studies have been carried out fitting decline curves in a first-order model for many pesticides (Adhya et al., 1987). However, that interpretation is not always applicable, because the residues frequently diminish quicker at first and much more slowly at a later stage in comparison with the 1st-order model (Aguiler-del et al., 1999; Martinez-Galera et al., 2003). Also, it was demonstrated that the degradation of fenitrothion in five different soils followed a first order reaction (Adhya et al., 1987).

Therefore, the degradation kinetics of fenitrothion and thiobencarb were estimated by first-order exponential decay model $C_t = C_0 e^{-kt}$, where $C_t$ is the concentration of pesticide remaining in the soil after time $t$, $C_0$ is the initial concentration and k is the first-order kinetic constant (Fouad, 2017; Badawy et al., 2017). It can be seen from Figure (4) the straight line plot of the 1st-order kinetic model, $\ln[C_t] = \ln[C_0] - Kt$. The rate constant (k) values for degradation of the two pesticides were 0.036 and 0.068 for fenitrothion and thiobencarb, respectively. The results of linear equation, the rate constant (k) and half-life ($t_{1/2}$) of fenitrothion and thiobencarb in soil are shown in Figure (4) and Table (6). The half-live ($t_{1/2}$) has been calculated (Table 6) from the 1st-order model using equation ($t_{1/2} = \frac{0.6932}{k}$). It can be seen the estimated values of half-life were 19.36 days for fenitrothion and 10.24 days for thiobencarb. Clearly, the herbicide thiobencarb degraded in sandy clay loam soil faster than fenitrothion. These values are in agreement with the half-life fenitrothion values in the literature, which from 10.5, 10.9 and 20 days in three soils different organic matter (Adhya et al., 1987). Fenitrothion is not persistent because of its rapid degradation by physical, chemical or biological means (Roy et al., 1996). Fenitrothion degraded in upland and submerged soils with a half-life of fewer than 7 days and was of shorter persistence as compared with its half-life of 12-28 days under upland conditions and less than 14 days under submerged conditions found by Takimoto et al. (1976). Generally, the degradation process of the pesticides is favoured by the presence of oxygen and by aerobic microorganisms (Khan, 2016). Also, the half-life of thiobencarb is in agreement with previous studies which found that the half-life was 12 days in soil (Redondo et al., 1994). However other studies indicated that the half-life of thiobencarb ranged from 14 to 21 days (Wauchope et al., 1992). The dissipation of the pesticide residues in soil depending on the environmental conditions, type of application, dosage, temperature, pH, and the interval between applications (Khay et al., 2008; Scholz-Starke et al., 2017). It is very important to indicate that the degradation of pesticides under different conditions was recently studied for fenitrothion by Oiwa et al. (2020) and Meng et al. (2019) also, for thiobencarb by Wang et al. (2021) and Guarda et al. (2020).
In conclusion, the recovery percentages of fenitrothion and thiobencarb in calcierous (sandy clay loam soil) were very closed. The degradation kinetics showed that the residues of the fenitrothion and thiobencarb rapidly decreased during the first five days after treatment. Residues remained at 2nd day was 72.45% and 57.63%, at 5th day was 37.72 and 47.18% for fenitrothion and thiobencarb, respectively. Both tested pesticides disappeared very rapidly from the soil following a bi-phasic pattern. Just two weeks after treatment the maximum concentrations of fenitrothion and thiobencarb were reduced to about one third and one fourth, respectively. This sharp drop was followed by a period of a slow incremental decrease for five weeks. According to the graphical and integral methods, the fit model to describe the degradation kinetic of fenitrothion and thiobencarb is the 1st order model. The straight line plot of the 1st-order kinetic model was \( \ln[C_t] = \ln[C_o] - kt \). The rate constant (k) values for degradation of the two pesticides were 0.036 and 0.068 for fenitrothion and thiobencarb, respectively. The estimated values of half-life were 19.36 days for fenitrothion and 10.24 days for thiobencarb. Clearly, the herbicide thiobencarb degraded in sandy clay loam soil about twice faster than fenitrothion.
Fig. (4): Plots of different orders rate for degradation of fenitrothion and thiobencarb in soil.

Fenitrothion ● Thiobencarb ○

Table (6): Degradation kinetics of fenitrothion and thiobencarb in soil fitted in first-order kinetic model

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Linear equation</th>
<th>k</th>
<th>t_{1/2} (day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fenitrothion</td>
<td>y = -0.036x + 3.786</td>
<td>0.036</td>
<td>19.36</td>
</tr>
<tr>
<td>Thiobencarb</td>
<td>y = -0.068x + 3.906</td>
<td>0.068</td>
<td>10.24</td>
</tr>
</tbody>
</table>

REFERENCES


Sudo, M., T. Kunimatsu and T. Okubo (2002). Concentration and loading of pesticide residues
in Lake Biwa basin (Japan). Water Res. 36, 315–329.


