Current Chemistry Letters 12 (2023) 383–396

Contents lists available atGrowingScience

Current Chemistry Letters

homepage: www.GrowingScience.com

Experimental modeling design to study the effect of different soil treatments on the dissipation of metribuzin herbicide with effect on dehydrogenase activity

Mohamed Riad Fouad[a*], **Mohamed E. I. Badawy**[a], **Ahmed F. El-Aswad**[a] and **Maher I. Aly**[a]

[a]*Department of Pesticide Chemistry and Technology, Faculty of Agriculture, Alexandria University, Aflaton St., 21545, El-Shatby, Alexandria, Egypt*

C H R O N I C L E

Article history:
Received July 12, 2022
Received in revised form
August 2, 2022
Accepted November 30, 2022
Available online
December 1, 2022

Keywords:
Minitab software
Metribuzin
HPLC
Dissipation
Soil
Half-life
Dehydrogenase

A B S T R A C T

The dissipation and side-effect of metribuzin (MBZ) were studied with various factors; two soil types (clay loam and sandy loam), soil amendment (wheat straw and without amendment), two temperature levels (25 and 50°C), sterilization (sterilized and unsterilized soil) and time of incubation (15 and 30 days) and designed by Windows version of MINITAB software package to reduce the time and the cost as well as increased the precision. Determination of MBZ by HPLC with recoveries ranged from 50.85 to 108.09%. The MBZ residues were detected in all samples up to 60 days of storage, respectively with decline in their concentrations with the time of incubation. The clay loam soil showed higher dissipation than the sandy loam soil. The different factors in the present study confirmed that the wheat straw amendment, non-sterilization and incubation at 50°C caused higher dissipation of MBZ than without wheat straw, sterilization and incubation at 25°C. The dissipation was described mathematically by a first order equation with t0.5 was ranged from 9.62 to 16.82 days in clay loam soil and from 10.01 to 16.04 days in sandy loam soil. The side-effect of MBZ was tested on soil dehydrogenase activity that can be considered as an indicator of the biological activity and microbial degradation. The result proved that the enzyme activity was significantly decreased in all treatments compared with the controls at 1 and 3 days of incubation then it was gradually increased at 7, 10, 15 and 30 days of incubation. Treatments of wheat straw, non-sterilized and incubated at 25°C or 50°C showed the lowest enzyme inhibition among all treatments.

1. Introduction

Various studies on metribuzin (MBZ) have been investigated by using the electro analytical method,[1] chromatographic methods such as HPLC,[2] GC,[3, 4] micellar electro kinetic chromatography,[5] capillary zone electrophoresis and molecularly imprinted polymer.[6] The extraction method using methanol and then a SPE showing recoveries ranging from 86.7% to 104.2% while using methanol-water (75:25), recover was about 75% and represents a valuable alternative to HPLC with the detection limit in soil of 1250 µg/ kg.[5, 7]

Microbiological activity apparently is important in the degradation of MBZ in soil,[8] with most degradation in the soil occurring as a result of aerobic microbial activity which is influenced by temperature and organic substrate in the soil. It was found that degradation is slower in subsurface horizons and attribute this to inherently lower microbial activity. An order of degradation rate of MBZ > alachlor > atrazine was observed.[9] MBZ degradation followed first-order kinetics and pseudo-first order kinetics.[8, 10] MBZ $t_{0.5}$ is from 16 to 50 day,[11] 22 day under optimum conditions at 20ºC,[12] approximately 22 day over treatments and seasons,[13] in ranged 5.3 d to 12.5 day dependent on the field rainfall or irrigation and 17 to 28 day under greenhouse conditions,[14] approximately 3 months under field conditions,[15] about 30 to 60 days during the

---

* Corresponding author.
E-mail address mohammed.riad@alexu.edu.eg (M.R. Foaud)

doi: 10.5267/j.ccl.2022.12.001

growing season at normal use rates.[16] It was measured average MBZ concentrations in the top ten centimeters of soil 300 days after application.

MBZ is mainly microbially degraded, thus those environmental factors favoring microbial activity will also favor MBZ degradation.[12] Moreover, MBZ was degraded more rapidly in nonautoclaved field soil and in soil enriched with glucose than in soil that had been air dry for 1 year or had been autoclaved.[8] Management of plant residues left after harvest can affect persistence of herbicides in soil. Crop residue accumulation on or near the soil surface may provide both a physical and chemical barrier for movement of soil applied herbicide. The physical barrier is derived from the surface mat which blocks access to soil pores, whereas the chemical barrier occurs when herbicides are sorbet to surfaces of decomposed plant residues. These processes can affect the chemical degradation of herbicides.[17] Depending on the solubility of an applied herbicide and its ability to desorb from plant residue, water from rainfall may eventually wash much of it off the plant residue into soil pores. Once in the soil, the herbicide is again subject to leaching, sorption, and degradation. Herbicide which remains sorbet to plant residue may not be released into the soil until the plant residue completely decomposes.[18] Field results indicated faster degradation of MBZ with increasing temperature. The degradation was more rapid at 30ºC than at 20ºC. Laboratory studies indicated that MBZ degradation at temperatures below 5 ºC was found to be so slow that we would not expect the soil microorganisms to be able to exploit this increased availability of MBZ.[12]

Comparative studies show that the atrazine treatments induced significant changes in the microbial population. Although the total numbers of bacteria and fungi were not altered. The significantly minimum DHA was observed under post-emergence application of MBZ 250 g a.i. ha^{-1}, whereas, pre-emergence application of pendimethalin 1000 g a.i. ha^{-1} resulted in significantly higher DHA of experimental field.[19] DHase was the least tolerant to the effect of the herbicide MBZ, whereas alkaline phosphatase was the most tolerant one.[20]

The fate of the pesticides in the soil environment in respect of pest control efficacy; non-target organism exposure and offsite mobility has become a matter of environmental concern potentially because of the adverse effects of pesticides on soil microorganisms.[21, 22, 23] Considerable interest of the effect of pesticides on non-target organisms has been recently developed. The side effect of pesticides on soil microflora could be investigated by studies of microbial respiration and soil enzymes. Several measurements have emerged as important parameters of the general biological activity in soils, especially respiration rates. Several pesticides had no effect while other inhibited CO_2 evolution from soil.[24]

An ideal pesticide should be toxic only to the target organism, biodegradable and undesirable residues should not affect non-target surfaces. Therefore, studies were undertaken to further characterize the relationship among pesticide concentration in soil, dehydrogenase activity (as an indicator of microbial activity), and degradation rate.[25]

2. Materials and Methods

2.1. Soil and chemicals

Two types of the common Egyptian soils clay loam and sandy loam from Agricultural Research Station, Abis and sandy loam soil from Bangar Elsokar region were tested in the present study. Physicochemical properties of the tested soils including soil texture, organic matter, pH, EC, water holding capacity, total carbonate percentage and soluble cations and anions concentration were measured (**Table 1**).[26- 28] Technical grade metribuzin (MBZ), (4-amino-6-terbutyl-3-methylsulfanyl-1,2,4-triazin-5-one), was obtained from DuPont Corp., Wilmington, DE ((≥ 98% purity). Triphenyltetrazolium chloride (TTC), triphenylformazan (TPF), water (HPLC grade), methanol (HPLC grade), acetonitrile (HPLC grade) and PTFE syringe filter (0.2 µm) were purchased from Sigma Aldrich Co. (Spruce Street, Louis., MO, USA). Anhydrous magnesium sulfate, sodium chloride, sodium acetate and activated charcoal were purchased from El-Nasr Pharmaceutical Chemicals Co. (El Gomhoriya St., Abu Zaabal Area 491, Qalyub, Egypt).[29]

Table 1. Physicalchemical properties of the tested soils.

Code	**Particle Size (%)**			**Texture class**	**pH**	**EC (ds/m)**	**Total soluble cations (meq/L)**	**Total soluble anions (meq/L)**	**Total carbonate (%)**
	Clay	**Silt**	**Sand**						
A	43	18	39	Clay loam	8.25	1.32	18.17	13.30	7.87
B	14	11	75	Sandy loam	8.20	2.33	33.50	23.30	40.09

2.2. Apparatus and instrumentation

UV-Vis Spectrophotometer, Ultra Microplate Reader, Orbital shaker, Centrifuge, water bath, Water Distillation, Incubator, and Digital balance. The instrument used for the quantification of MBZ was an Agilent 1260 HPLC Infinity system equipped with an Agilent variable wavelength ultraviolet detector. The system consisted of a quaternary gradient solvent pump to control the flow rate of the mobile phase and an auto-sampler for automatic injection, a vacuum degasser.

2.3. Experimental design

Utilizing Minitab software, the experiment was designed using the response surface methodology to optimize the dissipation of MBZ in various soil treatments. The experimental ranges for the parameters included soil type (A & B), soil amendment (wheat straw), temperature (25 & 50°C), sterilization (sterilized soil & non-sterilized soil) and time of incubation (15 & 30 days). The trials were modelled by the program, which also improved precision while cutting down on time and expense. A two-level full generate factorial design was used to conduct 12 trials for each insecticide (**Table 2**).

Table 2. Experimental design of metribuzin dissipation in soil using Minitab software.

Treatment	Soil type	Amendment	Temperature	Sterilization	Incubation time (day)
1	Soil B	Without	25ºC	Sterilized	10
2	Soil B	Wheat straw	25ºC	Non-sterilized	30
3	Soil A	Without	25ºC	Non-sterilized	10
4	Soil B	Without	50ºC	Non-sterilized	30
5	Soil B	Without	50ºC	Sterilized	30
6	Soil A	Wheat straw	50ºC	Sterilized	30
7	Soil A	Without	50ºC	Non-sterilized	10
8	Soil A	Wheat straw	25ºC	Non-sterilized	30
9	Soil B	Wheat straw	50ºC	Sterilized	10
10	Soil B	Without	25ºC	Sterilized	10
11	Soil A	Wheat straw	50ºC	Non-sterilized	10
12	Soil A	Wheat straw	25ºC	Sterilized	30

2.4. Standard stock solution preparation

Following the dissolution of 10000 µg of the substance into a volumetric flask, the volume was increased to 10 mL with acetonitrile to create a standard stock solution of MBZ (1000 µg/mL). Working solution of 50 mg/L was diluted to reach the required final concentration.

2.5. Soil treatment

A weight of 300 g of each soil type was placed in a 1000-mL glass bottle and treated with MBZ (50 µg a.i./g soil). Three replicates were made for each treatment. The stock of the pesticide was mixed with distilled water equal to 60 % of water holding capacity of the soil. All bottles were incubated throughout the experimental period according to experimental Minitab design.[2]

2.6. Determination of metribuzin in soils

Wavelength of maximum absorbance and HPLC-standard calibration curve

The standard solutions of MBZ were scanned in the range of 200-400 nm by UV-Visible spectrophotometer (Thermo Corporation, Nicolet, evolution 100, Germany).

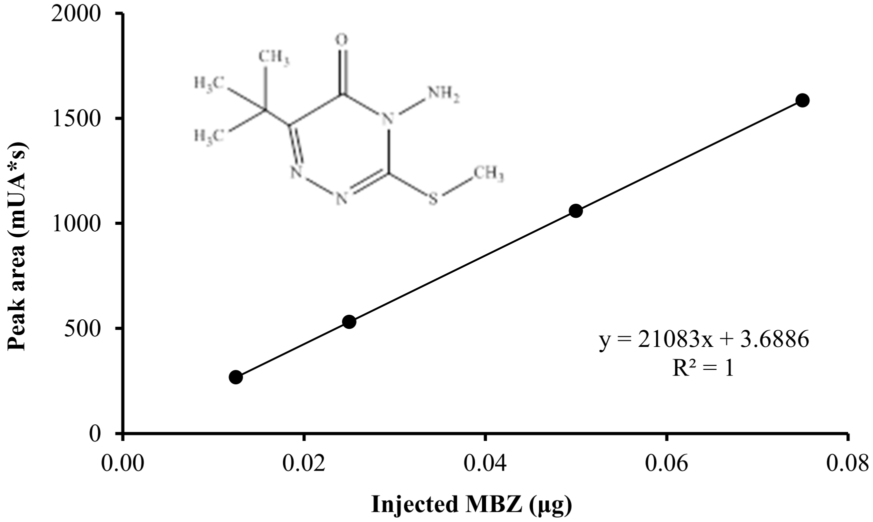

Fig. 1. Calibration curve of metribuzin using Agilent 1260 HPLC-VWD

MBZ showed maximum absorbance at 290 nm. This wavelength was selected for determination by HPLC. For preparation of stock solution for HPLC, standard of MBZ was dissolved in methanol (100 mg/L), by accurately weighing individual analytical standards into volumetric flasks, dissolving and diluting them to volume with methanol (**Fig. 1**).

Extraction and clean up

A weight of 20 g of soil sample was taken at different times of (0, 3, 7, 10, 15, 30 and 60 day), grind with a mixture of salt (composed of 0.5 g of anhydrous magnesium sulfate, 0.1 g sodium chloride, 0.15 g of sodium acetate) for about 5 minutes. 40-mL of solvent mixture of methanol-water (80:20) was added. Transferred solution to 50 mL centrifuge tubes. The tube was closed and stirred vigorously by hand for 1 min and centrifuged for 5 min at 3000 rpm and then filtered through Whatman filter paper No. 1. The organic layer was transferred to a 30-mL centrifugation tube containing 0.15 g of $MgSO_4$ and 0.05 g activated charcoal to remove undesired co-extractives. The tube was closed, shaken vigorously by hand for 30 s, and centrifuged for 5 min at 3500 rpm.

Determination by HPLC

The quantification of MBZ was determined by an Agilent 1260 HPLC Infinity system. Five microliter of each sample extract was injected onto the HPLC column using the autosampler apparatus with a 100 µL sample loop. Separation was performed on the ZORBAX Eclips Plus C_{18} column. The mobile phase composition was methanol and water (80:20) with a flow rate of 1 mL/min. Data was managed using HP Chemstation software.

Recovery assay

Soil samples were homogenized with solutions of MBZ (5, 10, and 50 µg/g soil). The samples were processed according to the above procedure. At each fortification level, three replicates were analyzed. Results of MBZ were corrected according to the recovery rate.

2.7. Dissipation kinetics and modeling studies

For dissipation kinetics study, the soil samples were collected at different time intervals and were analyzed by HPLC. The calculation for dissipation kinetics of MBZ in the soil was done by plotting the residue concentration against time. Half-life of MBZ was fitted by first-order kinetics equation, $\ln C_t = \ln C_0 - kt$. The tests were modelled using the Minitab software, which also improved precision while cutting down on time and expense. In order to ensure a good model, the quality of the fit of model equation was expressed by r^2, the coefficient of determination.[30]

2.8. Side effect of metribuzin on dehydrogenase activity in soils

The DHase activity in soil was determined colorimetrically according to the reduction of 2,3,5-triphenyltetrazolium chloride (TTC, colorless) to triphenylformazan (TPF, red color) and measured using ELISA reader at 490 nm. At each time, 5 g of the treated soil sample were inserted into a test tube (10 mL capacity) and addition of 1 mL of TTC (1%) and 2 mL of distilled water. The tubes were tightly covered with parafilm paper and then incubated in the dark at 37°C for a day. The absorbance of TPF was determined colorimetrically at 490 nm by ELISA reader. DHase activity was expressed based on the dry weight of soil in micromoles of TPF per gram of soil per day.

2.9. Statistical analysis

Experimental data are presented as mean ± standard error and the statistical analysis was performed by Minitab software. One -way analysis of variance (ANOVA) was used to analyze the data of dissipation and enzymatic activity and means property values were separated ($p \leq 0.05$) with Student-Newman-Keuls (SNK) test.

3. Results

3.1. Conditions and determination parameters by HPLC

The development and validation method for determination of MBZ was performed on Agilent 1260 HPLC Infinity system equipped with an Agilent variable wavelength ultraviolet detector. Data were managed using a HPLC Chemstation software and the method conditions and determination parameters are presented in **Table 3**.

Table 3. Method conditions and determination parameters used for determination of metribuzin residues by HPLC.

Flow rate (mL/min)	Column temperature (°C)	Elution system	Ret-time ± SD (min)	LOD (µg injected)	LOQ (µg injected)
1	40	Isocratic	3.98±0.001	0.0012	0.003

(LOD = 3 SD/Slope), (LOQ = 10 SD/Slope)

3.2. Recovery of metribuzin in soils

The results of recoveries of MBZ in soil clay loam and sandy loam are shown in **Table 4**. The recovery percentages were 108.9±5.03, 98.26±4.33 and 70.64±0.34 µg/g clay loam soil, 90.07±2.94, 86.86±14.90 and 50.85±2.79 µg/g sandy loam soil, respectively. Regarding the existence of interfering elements removed with the target insecticides, the recovery can sometimes be greater than 100%. Found that recovery decreased with increase of concentration. In addition, clay loam soil indicated higher recoveries than sandy loam soil. This may refer to the high organic matter in clay loam soil compared with the sandy loam soil.

Table 4. Recovery percentages of metribuzin in soils by HPLC

Pesticide	Soil Type	Recovery (%) ± SE			
		5 ug/g soil	10 ug/g soil	50 ug/g soil	Mean ± SE
MBZ	Clay loam	108.9^{a} ±5.03	98.26^{b} ±4.33	70.64^{b} ±0.34	92.60±3.23
	Sandy loam	90.07^{b} ±2.94	86.86^{c} ±14.90	50.85^{d} ±2.79	74.59±6.88

Values are mean of three replicates and given as mean ± standard error. Different letters (a-d) in columns indicate the range from higher to lower rank as significant differences according to the SNK test ($P \leq 0.05$).

3.2. Dissipation of metribuzin in soils

The effectiveness of the soil type and selected factors in measuring trace levels of MBZ was monitored and studied under laboratory conditions. The residues of MBZ (µg/g) in different soil treatments at different time intervals during the storage at 25 or 50°C are shown in Fig. 2. The herbicide residues were detected in all samples up to 60 days of storage with decline in their concentrations with the time of storage. However, the residues were still detected at day 60 (LOD = 0.0012 µg) of the dose applied. The residues of MBZ in treatment T_5 of soil clay loam, (wheat straw, non-sterilized and incubated at 50°C) rapidly decreased during the experiment (from 118.99 µg/g soil at zero time to 5.39 µg/g soil at 60 day). However, treatment T_{11} of soil sandy loam, (wheat straw, sterilized and incubated at 25°C) slightly decreased during the storage period (from 116.80 µg/g soil at zero time to 7.27 µg/g soil at 60 day). The average levels of MBZ residues found approximately 60 days after treatment were 5.39 and 15.72 µg/g soil in soil clay loam and sandy loam, respectively. It can be noted that the soil clay loam showed higher MBZ dissipation than the soil sandy loam. This may refer to the soil clay loam was richer in organic matter than soil sandy loam. The dissipation rates of MBZ residues in soil clay loam and sandy loam at different time intervals by HPLC are presented in **Table 5**. Generally, MBZ dissipates rapidly after application with all soil treatments in both soil clay loam and sandy loam. The percentage of MBZ dissipation after three days of treatment ranged from 15.89 to 37.41% in soil clay loam and from 7.12 to 18.77% in soil sandy loam. However, the percentage of dissipation after 60 days of treatment ranged from 91.68 to 95.47% in soil clay loam and from 86.54 to 93.78% in soil sandy loam. It can be noted that the treatments T_3 of soil clay loam that (without wheat straw, incubated at 50°C and non-sterilized) and T_5 (wheat straw, incubated at 50°C and non-sterilized) led to dissipate the MBZ rapidly than the other treatments (95.24 and 95.47% at day 60, respectively). However, the soil without wheat straw, incubated at 25°C and non-sterilized (T_1) and that wheat straw, inculcated at 25°C and sterilized (T_6) did not dissipate MBZ rapidly (91.68 and 95.47%, respectively at day 60). It can be noted that the soil sandy loam that without wheat straw, inculcated at 50°C and non-sterilized (T_9), without wheat straw, inculcated at 50°C and sterilized (T_{10}) and that of wheat straw, inculcated at 50°C and sterilized (T_{11}) led to dissipation the MBZ rapidly than the other treatments (93.06, 93.12 and 93.78 at day 60, respectively). However, soil without wheat straw, inculcated at 25°C and sterilized (T_7) and that of wheat straw, inoculated at 25°C and sterilized (T_{12}) showed lower dissipation (86.54 and 91.42 during 60 days of incubation) compared to the other treatments.

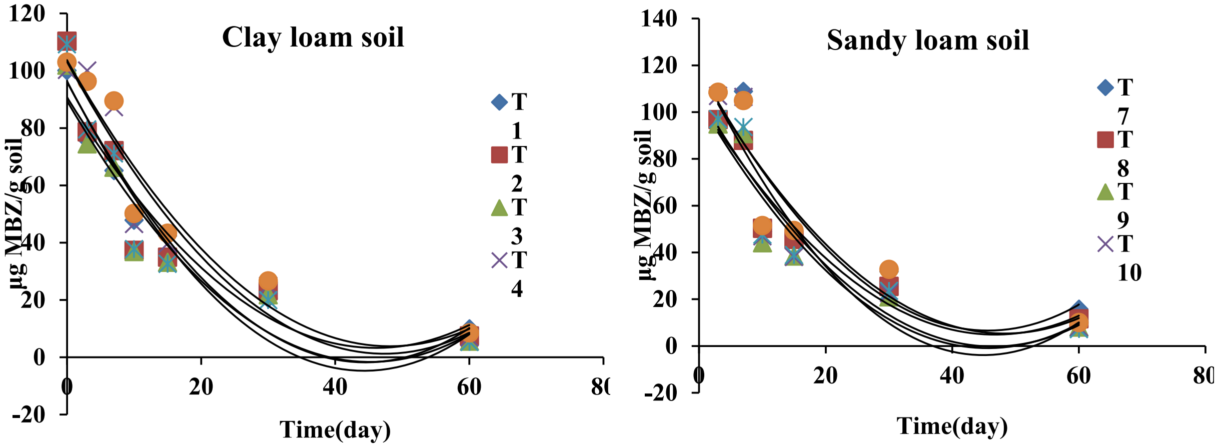

Fig. 2. Dissipation curves of metribuzin in soil clay loam and sandy loam with or without wheat straw at deferent conditions

Table 5. Dissipation percentages of metribuzin in soils at different time intervals by HPLC

Treatments	**Dissipation (%) at time (day)**						
	0	**3**	**7**	**10**	**15**	**30**	**60**
T_1	15.89^a ± 0.01	36.15^b ± 0.00	45.23^a ± 0.02	59.80^b ± 0.00	64.36^d ± 0.00	82.64^b ± 0.00	91.68^d ± 0.02
T_2	7.27^e ± 0.00	33.88^c ± 0.00	39.39^b ± 0.01	68.62^a ± 0.00	73.60^a ± 0.01	82.48^b ± 0.00	94.74^b ± 0.00
T_3	14.30^b ± 0.00	37.41^a ± 0.00	44.26^a ± 0.00	68.96^a ± 0.01	72.13^b ± 0.00	81.64^c ± 0.00	95.24^a ± 0.00
T_4	15.69^a ± 0.02	15.89^e 0.00	26.67^c ± 0.00	60.88^b ± 0.01	66.63^c ± 0.01	79.02^d ±0.03	94.17^b ± 0.00
T_5	8.21^d ± 0.00	33.16^c ± 0.00	40.18^b ± 0.00	68.28^a ± 0.00	72.58^a ± 0.00	83.24^a ± 0.01	95.47^a ± 0.00
T_6	13.44^c ± 0.00	19.04^d ± 0.01	24.79^d ± 0.01	57.78^d ± 0.02	63.57^d ± 0.00	77.56^e ± 0.00	92.83^c ± 0.03
T_7	0.91^e ± 0.00	7.48^c ± 0.00	6.74^e ± 0.02	58.08^d ± 0.00	59.71^c ± 0.00	72.78^f ± 0.02	86.54^f ± 0.01
T_8	2.49^b ± 0.01	17.07^b ± 0.00	24.72^a ± 0.01	56.88^e ± 0.01	60.97^b ± 0.00	78.17^d ± 0.01	90.04^d ± 0.00
T_9	1.45^c ± 0.00	18.77^a ± 0.02	22.24^b ± 0.03	62.20^a ± 0.00	67.07^a ± 0.00	81.96^a ± 0.00	93.06^b ± 0.00
T_{10}	2.55^a ± 0.00	8.43^c ± 0.03	8.88^d ± 0.00	59.80^b ± 0.02	67.40^a ± 0.01	80.65^b ± 0.01	93.12^b ± 0.00
T_{11}	1.55^c ± 0.01	16.93^b ± 0.00	19.78^c ± 0.00	59.25^c ± 0.00	66.67^a ± 0.00	79.81^c ± 0.00	93.78^a ± 0.00
T_{12}	1.10^d ± 0.00	7.12^d ± 0.01	10.17^d ± 0.00	55.90^f ± 0.01	57.70^d ± 0.02	71.93^e ± 0.00	91.42^c ± 0.00

Values are mean of three replicates and given as mean ± standard error. Different letters (a-f) in columns indicate the range from higher to lower rank as significant differences according to the SNK test ($P \leq 0.05$).

The dissipation was described mathematically by a first order equation. The results of Equation order (n); constant (K) and half-life ($t_{0.5}$) of MBZ in soil clay loam and sandy loam are shown in **Table 6**. The equation order (n) found to be one as obtained is theoretical and curve. For soil clay loam, the constant K was ranged from 0.055 to 0.075 for calculated values and from 0.041 to 0.052 for that obtained from the curve. T_2, T_3 and T_5 showed the highest K value (0.072, 0.071 and 0.075, respectively) however; T_1; T_4 and T_6 showed the lowest value (0.055, 0.058 and 0.056, respectively). The data of $t_{0.5}$ that calculated from equation ($t_{0.5} = 0.6932/K$) showed that T_1 and T_6 were the highest values (12.60 and 12.48 day, respectively). However, T_2, T_3 and T_5 were the lowest ($t_{0.5}$ = 9.62, 9.82 and 9.23 day, respectively). Treatment T_4 showed moderate value of $t_{0.5}$ (11.88 day). For soil sandy loam, the constant K was ranged from 0.057 to 0.069 for calculated values and from 0.047 to 0.058 for that obtained from the curve. T_9, T_{10} and T_{11} showed the highest K value (ranging from 0.067 to 0.069) however, T_7; T_8 and T_{12} showed the lowest value (ranged from 0.057 to 0.058). The data of $t_{0.5}$ calculated from equation ($t_{0.5} = 0.6932/K$) showed that T_7 and T_{12} were the highest values (12.05 and 12.17 day, respectively). However, T_{11}, T_{10} and T_9 were the lowest ($t_{0.5}$ = 10.29, 10.24 and 10.01 day, respectively). Treatments of T_8 showed moderate value of $t_{0.5}$ (11.92 day).

Table 6. Equation order (n); constant (K) and half-life ($t_{0.5}$) of metribuzin in clay loam and sandy loam without and with wheat straw at different conditions.

Soil type	**Treatment**	**N**		**K**		**$t_{0.5}$**	
		Calculated	**Curve**	**Calculated**	**Curve**	**Calculated**	**Curve**
Clay loam	**T_1**	1	1	0.055	0.041	12.60	16.82
	T_2	1	1	0.072	0.050	9.62	14.00
	T_3	1	1	0.071	0.045	9.82	15.54
	T_4	1	1	0.058	0.046	11.88	15.23
	T_5	1	1	0.075	0.052	9.23	13.43
	T_6	1	1	0.056	0.043	12.48	16.04
Sandy loam	**T_7**	1	1	0.058	0.052	12.05	13.28
	T_8	1	1	0.058	0.051	11.92	13.67
	T_9	1	1	0.069	0.057	10.01	12.26
	T_{10}	1	1	0.068	0.058	10.24	11.91
	T_{11}	1	1	0.067	0.054	10.29	12.81
	T_{12}	1	1	0.057	0.047	12.17	14.68

Equation order (n) was calculated from $n = 1 + [(\log t1/t_2)/(\log a_2/a_1)]$. K was calculated from $K = [2.303/t_2\text{-}t_1] \log [C_1/C_2]$. $t_{0.5}$ was calculated from $t_{0.5}=(0.6932/K)$

3.3. Modeling of metribuzin in soils

The results of the models obtained from Minitab software using create factorial design for MBZ in soil clay loam and sandy loam at different time intervals are shown in **Table 7**. Twenty-one models were generated with high correlation coefficient (r^2 from 0.45-0.99) and low *s* value (2.67-23.42). The most fit model for prediction of dissipation study was model 6 (r^2 = 0.99 and s = 5.65). The standardized effects of the independent variables and their interactions on the dependent variable (dissipation of pesticide in the soil) were investigated by preparing a Pareto chart (**Fig. 3**). The variables and interactions which can be considered as especially important for the treatments are the incubation time which has the highest effect on the dissipation and was statistically significant. The length of each bar in the chart indicates the standardized effects of the factor on the response. The fact that the bar for A (soil type), B (soil amendment), C (time of incubated) and D (sterilization) factors remained inside the reference line (2.45 at α = 0.05) in **Fig. 4**, and the smaller coefficients for these terms compared to other terms in Equation (6), indicated that these terms contributed the least in prediction of the dissipation (%) efficiency. The negative coefficient for the model components (soil amendment, -1.97) indicated an unfavorable or antagonistic effect on the MBZ dissipation efficiency, while the positive coefficients for the model components (soil type, temperature, sterilization and time of incubation, 0.97, 0.17, 0.20 and 1.45, respectively) showed a favorable or synergistic effect on the MBZ dissipation efficiency.

Table 7. Proposed models obtained from Minitab software using create factorial design for metribuzin in soil clay loam and sandy loam at different time intervals.

Number	Time (day)	Model MBZ of dissipation in soil	S	r^2
1	0 and 3	Dissipation (%) = 7.92 + 3.30 Soil Type - 0.90 soil Amendment - 1.12 Temperature + 2.56 Sterilization + 3.33 Time of incubation	7.72	0.64
2	0 and 7	Dissipation (%) = 7.67 + 2.96 Soil Type - 2.19 soil Amendment - 0.53 Temperature + 3.69 Sterilization + 2.298 Time of incubation	8.04	0.76
3	0 and 10	Dissipation (%) = 6.69 + 1.71 Soil Type - 1.38 soil Amendment - 0.04 Temperature + 0.41 Sterilization + 5.467 Time of incubation	6.63	0.97
4	0 and 15	Dissipation (%) = 6.44 + 1.30 Soil Type - 1.43 soil Amendment + 0.15 Temperature - 0.08 Sterilization + 4.010 Time of incubation	6.44	0.98
5	0 and 30	Dissipation (%) = 6.16 + 0.96 Soil Type - 1.94 soil Amendment + 0.27 Temperature - 0.34 Sterilization + 2.478 Time of incubation	5.76	0.99
6	0 and 60	Dissipation (%) = 6.35 + 0.97 Soil Type - 1.97 soil Amendment + 0.17 Temperature + 0.20 Sterilization + 1.4521 Time of incubation	5.65	0.99
7	3 and 7	Dissipation (%) = 19.7 + 5.04 Soil Type - 5.97 soil Amendment - 1.07 Temperature + 2.20 Sterilization + 0.80 Time of incubation	10.78	0.53
8	3 and 10	Dissipation (%) = 3.22 + 3.75 Soil Type - 5.18 soil Amendment - 0.55 Temperature - 1.11 Sterilization + 5.97 Time of incubation	10.31	0.88
9	3 and 15	Dissipation (%) = 8.48 + 2.65 Soil Type - 6.00 soil Amendment - 0.04 Temperature - 1.94 Sterilization + 3.975 Time of incubation	10.29	0.90
10	3 and 30	Dissipation (%) = 14.33 + 3.06 Soil Type - 5.14 soil Amendment - 0.59 Temperature - 1.75 Sterilization + 2.203 Time of incubation	10.38	0.94
11	3 and 60	Dissipation (%) = 12.57 + 3.04 Soil Type - 5.75 soil Amendment - 0.37 Temperature - 1.30 Sterilization + 2.750 Time of incubation	9.60	0.96
12	7 and 10	Dissipation (%) = -62.6 + 4.59 Soil Type - 6.45 soil Amendment - 0.52 Temperature - 0.74 Sterilization + 12.58 Time of incubation	12.46	0.81
13	7 and 15	Dissipation (%) = -12.6 + 4.20 Soil Type - 6.51 soil Amendment - 0.35 Temperature - 1.22 Sterilization + 5.41 Time of incubation	12.51	0.84
14	7 and 30	Dissipation (%) = 45.4 + 2.74 Soil Type - 0.28 soil Amendment - 4.73 Temperature + 5.25 Sterilization + 1.033 Time of incubation	23.42	0.50
15	7 and 60	Dissipation (%) = 15.88 + 3.87 Soil Type - 7.05 soil Amendment - 0.32 Temperature - 0.94 Sterilization + 1.325 Time of incubation	11.91	0.94
16	10 and 15	Dissipation (%) = 48.09 + 0.89 Soil Type - 1.16 soil Amendment - 0.20 Temperature - 2.02 Sterilization + 1.263 Time of incubation	4.91	0.45
17	10 and 30	Dissipation (%) = 50.19 + 0.55 Soil Type - 1.65 soil Amendment - 0.09 Temperature - 2.27 Sterilization + 1.024 Time of incubation	3.82	0.92
18	10 and 60	Dissipation (%) = 53.97 + 0.56 Soil Type - 1.70 soil Amendment - 0.17 Temperature - 1.74 Sterilization + 0.6658 Time of incubation	4.12	0.97
19	15 and 30	Dissipation (%) = 46.96+ 1.353 Soil Type 2.420 soil Amendment - 0.514 Temperature - 2.548 Sterilization+ 1.139°Time of incubation	3.11	0.93
20	15 and 60	Dissipation (%) = 54.27 + 1.36 Soil Type - 2.46 soil Amendment - 0.60 Temperature - 2.02 Sterilization + 0.6642 Time of incubation	3.49	0.97
21	30 and 60	Dissipation (%) = 61.53 + 1.804 Soil Type 2.199 soil Amendment - 0.089 Temperature 0.884 Sterilization+ 0.5383 Time of incubation	2.67	0.94

The results of dissipation (%) of MBZ using model 6 versus observed dissipation values in soil clay loam and sandy loam at different time intervals are shown in **Table 8**. That dissipation (%) at time 0, 3, 7, 10, 15, 30 and 60 days using HPLC and calculated by previous model showed good fitness at 0, 3, 7 and 60 days. However, there is a little variation between practically and calculated values at 10, 15 and 30 days. From $t_{0.5}$ values obtained by model 22, as it can be noted this is high fitness between calculated and theoretical values by this model. The theoretical half-life of MBZ obtained in model 22 in T_1 to T_6 ranged from 13.89 to 15.76 days for soil clay loam and T_7 to T_{12} ranged from 12.50 to 15.20 days for soil sandy loam.

Model 22. Half-life predicted for MBZ in soil A and B with or without wheat straw at deferent condition.

$$t_{0.5} = 14.143 + 0.089 \text{ Soil type} - 0.444 \text{ Soil Amendment} + 0.145 \text{ Temperature} + 0.935 \text{ Sterilization}$$

$$r^2 = 0.99 \qquad\qquad s = 4.24$$

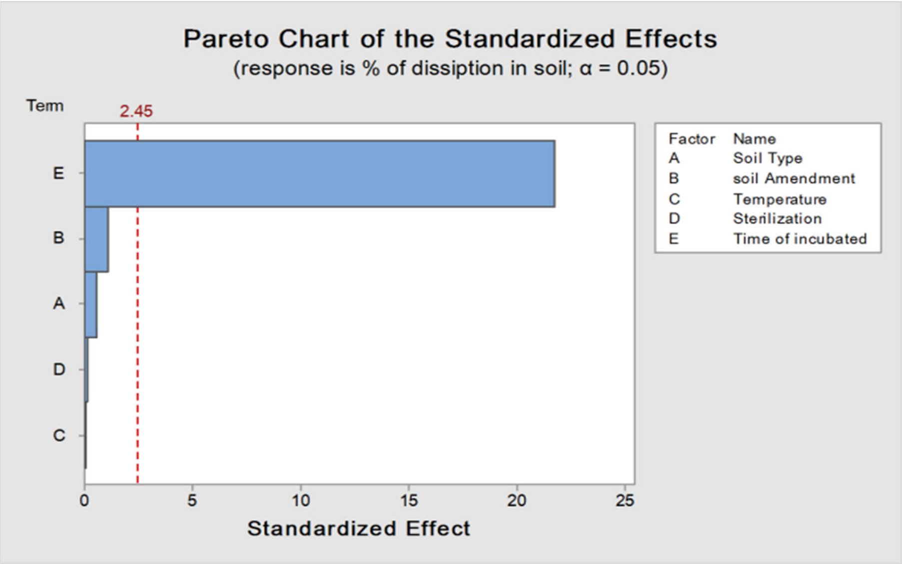

Fig. 4. Pareto chart of the standardized effects of metribuzin in soil A and B with or without wheat straw at deferent conditions

Table 8. Predicted dissipation (%) of metribuzin using model 6.versus practical dissipation values in soils at different time intervals.

Treatment	**Dissipation (%) at time**													
	0		3		7		10		15		30		60	
	Theoretical	**Piratical**	**Theoretical**	**Piratical**	**Theoretical**	**Piratical**	**Theoretical**	**Piratical**	**Theoretical**	**Piratical**	**Theoretical**	**Piratical**	**Theoretical**	**Piratical**
T_1	9.6	15.8	14.0	36.1	19.8	45.2	24.1	59.7	31.4	64.3	53.2	82.6	96.7	91.6
T_2	5.3	7.2	9.7	33.8	15.5	39.3	19.9	68.6	27.1	73.6	48.9	82.4	92.5	94.7
T_3	6.9	14.2	11.3	37.4	17.1	44.2	21.5	68.9	28.7	72.1	50.5	81.6	93.1	94.2
T_4	7.7	15.6	12.0	15.8	17.8	26.6	22.2	60.8	29.5	66.6	51.2	79.0	94.8	94.1
T_5	9.2	8.2	13.6	33.1	19.4	40.1	23.7	68.2	31.0	72.5	52.8	83.2	96.3	95.4
T_6	5.3	13.4	9.7	19.0	15.5	24.7	19.9	57.7	27.1	63.5	48.9	77.5	92.5	92.8
T_7	3.3	0.9	7.7	7.4	13.5	6.7	17.9	58.0	25.1	59.7	46.9	72.7	90.5	86.5
T_8	7.3	2.4	11.7	17.0	17.5	24.7	21.9	56.8	29.1	60.9	50.9	78.1	94.5	90.0
T_9	5.3	1.4	9.6	18.7	15.4	22.2	19.8	62.2	27.1	67.0	48.8	81.9	92.4	93.0
T_{10}	3.0	2.5	7.3	8.4	13.2	8.8	17.5	59.8	24.8	67.3	46.6	80.6	90.1	93.1
T_{11}	8.9	1.5	13.2	16.9	19.0	19.7	23.4	59.2	30.7	66.6	52.4	79.8	96.0	93.7
T_{12}	3.7	1.1	8.1	7.1	13.9	10.1	18.3	55.8	25.5	57.6	47.3	71.9	90.9	91.4

Dissipation (%) = 6.35 + 0.97 Soil Type - 1.97 soil Amendment + 0.17 Temperature + 0.20 Sterilization + 1.4521 Time of incubation

3.4. Effect of metribuzin on soil dehydrogenase activity

The results of dehydrogenase activity in soil clay loam and sandy loam treated with MBZ at different conditions are shown in **Table 9**, respectively. Generally, the enzyme activity (μmol TPF/g soil/24 h) was significantly decreased in all treatments compared with the controls at all-time intervals. The result proved that the enzyme activity was significantly decreased at 1, 3 and 7 days of incubation then it was gradually increased at 10, 15 and 30 days of incubation. This finding may be due to the increase of pesticide dissipation.

In soil clay loam, the enzyme activity significantly increased from 0.166-0.533 µmol TPF/g soil/24 h for control sterilized however, the enzyme of control non-sterilized increased from (0.306 to 0.901 µmol TPF/g soil/24 h). It can be noted that the treatment T_1 (without wheat straw, non-sterilized and incubated at 25°C), T_3 (without wheat straw, non-sterilized and incubated at 50°C), T_4 (wheat straw, non-sterilized and incubated at 25°C) and T_5 (wheat straw, non-sterilized and incubated at 50°C) that were non-sterilized showed the highest activity in the dehydrogenase compared to the sterilized treatments (T_2 and T_6) through 30 days of the experiments. This result may be due to the presence of microorganisms in non-sterilized soils. T_2 (wheat straw, sterilized and incubated at 50°C) more than inhibit dehydrogenase followed by T_6 which was (wheat straw, sterilized and incubated at 25°C). However, treatments of T_4 and T_5 showed the lowest enzyme inhibition within all treatments (0.167-0.529 and 0.151-431 µmol TPF/g soil/24 h, respectively)

In soil sandy loam, the enzyme activity significantly increased from 0.169 to 0.509 µmol TPF/g soil/24 h for control sterilized however, the activity in non-sterilized control was ranged from (0.266 to 0.817 µmol TPF/g soil/24 h). T_8 (wheat straw, non-sterilized and incubated at 25°C) and T_9 (without wheat straw, non-sterilized and incubated at 50°C) that were non-sterilized showed the highest activity in the dehydrogenase compared to the sterilized treatments (T_7, T_{10}, T_{11} and T_{12}). T_7 (without wheat straw, sterilized and incubated at 25°C), T_{10} (without wheat straw, sterilized and incubated at 50°C), T_{11} (wheat straw, sterilized and incubated at 50°C) and T_{12} (wheat straw, sterilized and incubated at 25°C) were the highest treatments in of inhibition dehydrogenase. However, treatments of T_8 and T_9 showed the lowest enzyme inhibition (0.164-0.393 and 0.125-0.376 µmol TPF/g soil/24 h, respectively).

Table 9. Side effect of metribuzin on dehydrogenase in soils

Treatments	Activity (µmol TPF/g soil/24 h) ± SE at time (day)					
	1	3	7	10	15	30
Control sterile	0.166^{b} ± 0.003	0.165^{b} ± 0.003	0.227^{b} ± 0.007	0.347^{d} ± 0.013	0.347^{d} ± 0.026	0.533^{b} ± 0.019
Control non-sterile	0.306^{a} ± 0.026	0.323^{a} ± 0.017	0.398^{a} ± 0.013	0.479^{a} ± 0.000	0.586^{a} ± 0.054	0.901^{a} ± 0.027
T_1	0.071^{d} ± 0.012	0.067^{e} ± 0.003	0.080^{e} ± 0.011	0.187^{e} ± 0.013	0.213^{e} ± 0.000	0.272^{d} ± 0.031
T_2	0.004^{e} ± 0.000	0.002^{f} ± 0.000	0.007^{g} ± 0.000	0.047^{g} ± 0.006	0.055^{g} ± 0.002	0.140^{f} ± 0.019
T_3	0.067^{d} ± 0.011	0.062^{e} ± 0.004	0.075^{f} ± 0.016	0.144^{f} ± 0.019	0.189^{f} ± 0.024	0.237^{e} ± 0.034
T_4	0.167^{b} ± 0.010	0.162^{c} ± 0.015	0.219^{c} ± 0.015	0.390^{b} ± 0.046	0.476^{b} ± 0.083	0.529^{b} ± 0.002
T_5	0.151^{c} ± 0.033	0.156^{d} ± 0.012	0.184^{d} ± 0.005	0.355^{c} ± 0.053	0.396^{c} ± 0.076	0.431^{c} ± 0.051
T_6	0.004^{e} ± 0.000	0.002^{f} ± 0.000	0.007^{g} ± 0.000	0.047^{g} ± 0.003	0.058^{g} ± 0.003	0.146^{f} ± 0.021
Control sterile	0.169^{b} ± 0.007	0.140^{b} ± 0.017	0.218^{b} ± 0.008	0.323^{c} ± 0.004	0.355^{d} ± 0.034	0.509^{b} ± 0.021
Control non-sterile	0.266^{a} ± 0.017	0.305^{a} ± 0.025	0.376^{a} ± 0.004	0.458^{a} ± 0.017	0.523^{a} ± 0.003	0.817^{a} ± 0.018
T_7	0.006^{d} ± 0.000	0.005^{e} ± 0.000	0.043^{f} ± 0.007	0.050^{f} ± 0.002	0.061^{g} ± 0.004	0.070^{f} ± 0.002
T_8	0.164^{b} ± 0.002	0.090^{c} ± 0.001	0.162^{c} ± 0.022	0.334^{b} ± 0.021	0.392^{b} ± 0.041	0.393^{c} ± 0.038
T_9	0.125^{c} ± 0.001	0.069^{d} ± 0.001	0.157^{d} ± 0.020	0.315^{d} ± 0.040	0.381^{c} ± 0.052	0.376^{d} ± 0.041
T_{10}	0.004^{d} ± 0.002	0.002^{f} ± 0.000	0.039^{f} ± 0.002	0.041^{g} ± 0.000	0.051^{h} ± 0.002	0.051^{g} ± 0.002
T_{11}	0.006^{d} ± 0.000	0.004^{e} ± 0.001	0.044^{f} ± 0.004	0.055^{f} ± 0.005	0.071^{f} ± 0.002	0.082^{e} ± 0.002
T_{12}	0.007^{d} ± 0.001	0.006^{e} ± 0.002	0.051^{e} ± 0.002	0.062^{e} ± 0.002	0.082^{e} ± 0.002	0.089^{e} ± 0.002

Values are mean of three replicates and given as mean ± standard error. Different letters (a-g) in columns indicate the range from higher to lower rank as significant differences according to the SNK test ($P \leq 0.05$).

4. Discussions

4.1. Recovery of metribuzin in soils

Papadakis and Mourkidou studied the recovery of MBZ and major conversion products in soils by microwave-assisted water extraction followed by liquid chromatographic analysis of extracts and they found that the recovery was ranged from 80.30 to 103.20% at concentration of 5 to 10 mg/kg. [31]P´erez and others studied the recovery of MBZ from soil and they found that the recovery were 78.30, 87.10 and 91.30% at concentration 0.15, 0.25 and 0.35 mg/kg respectively.[5] Janaki et al studied the recovery of MBZ in soil by QuEChERS method and they found that the recoveries were 86.70 to 104.20%.[32] Li Xie and co-author studied the simultaneous analysis of herbicide MBZ and its transformation products in tomato using QuEChERS-based gas chromatography coupled to a triple quadrupole mass analyzer the found that recovery was ranged from 72.35 to 95.86% at concentration ranged from 0.05-1.00 mg/kg.[33]

4.2. Dissipation of metribuzin in soils

Our results are in agreements with Savage who studied MBZ persistence in soil and he found that the degradation was followed the first-order kinetics with half-life values ranged from 17 to 28 days in six soils under greenhouse condition.[8] Gallaher and Mueller studied the effect of crop presence on persistence of atrazine, MBZ, and clomazone in surface soil and they found that the half-life was averaged over treatments and seasons and were approximately 27, 22, and 55 day.[13] López-Piñeiro et al studied the MBZ dissipation curves in soils and found that it was fitted to the first-order kinetics.[34] The factor of soil type in the present study confirmed that the soil clay loam showed higher dissipation of MBZ soil sandy loam. The result is in agreement with other previous studies which proved that the clay loam soil containing pesticides showed higher dissipation than that of sandy loam soil.[11, 35] The factor of temperature in the present study confirmed that the soil that incubated at high temperature (50°C) showed higher dissipation than that incubated at 25°C. This result is in agreement with other previous studies which proved that the soil including pesticides showed high dissipation rat when it incubated at high temperature compared to that incubated at low temperature.[37, 38, 39] Sterilized soil is often used, for example in degradation studies of pesticides, sorption experiments, microbiological tests and plant test systems, to distinguish between microbial processes and abiotic reactions.[40] The most commonly used technique for sterilization is autoclaving of the soil. Another technique is irradiation with high-level gamma radiation (γ-radiation).[41] One major drawback of sterilization procedures is the possible alteration of the structure of soil components, for example the organic matter. Rice and co-authors evaluated the influence of concentration, soil moisture, soil depth, and sterilization on the persistence and degradation of metolachlor in soil.[40] A significant reduction in the quantity of extractable metolachlor degradates and unextractable soilbound residues in sterile soil revealed the significance of biodegradation to the dissipation of metolachlor in soil. Our results comparing the sterilized and non-sterilized soils confirm the findings of Bouchard et al., as well as Beestman and Deming, who have shown that the degradation of MBZ, metolachlor, and fluometuron herbicides was greatly reduced in autoclaved soils.[42,] In addition, Rice et al., found that degradation of metolachlor in non-sterilized soil was higher than that of sterilized.[40] Overall, the increased dissipation of MBZ in the non-autoclaved soils supports the observations that biodegradation is very important to the dissipation of such herbicide in soil. Soil containing organic amendments, and their hydrosoluble fraction, play an important factor on pesticide dissipation, affecting their adsorption and transport processes through various chemical interactions.[34, 43, 44, 45, 46, 47] Although in most cases, addition of organic amendments increases sorption, leaching of the pesticides can be either reduced or promoted. On the contrary, organic matter content might enhance the retardation of organic pollutants through different coating processes such as cumulative sorption or cosorption.[48] Because of that, their effect on pesticide behavior must be assessed in order to optimize their use. In the present study, the addition of wheat strew as soil amendment showed increase in the dissipation of MBZ compared to the other soil treatment without wheat strew. García-Jaramillo et al., studied the effect of soil amendment with different organic residues from olive oil production on the dissipation of bentazone and tricyclazole pesticides used in rice crops and the found that the organic matter induced the dissipation of these pesticides and changed the physicochemical properties of the tested soil surface.[47] Cabrera et al, studied the influence of biochar amendments on the dissipation of aminocyclopyrachlor, bentazone and pyraclostrobin pesticides in an agricultural soil and they found that pyraclostrobin was highly sorbed to soil, and the addition of biochars to soil did not further increase its sorption. On the other hand, biochars with high surface areas and low organic contents can increase the sorption of highly mobile pesticides in soil.[49] López-Cabeza and others studied the dissipation of the enantiomers of the herbicide imazaquin, *S*-imazaquin and *R*-imazaquin, in two soils under different application regimes with addition of two olive-mill wastes, biochar and organoclay.[35] They reported that the addition of these amendments did not enhance the negligible sorption of imazaquin enantiomers by the soils, but accelerated their dissipation.

4.3. Modeling of metribuzin in soils

Standardized Pareto charts for the main effects. The effect of a factor in a factorial design is defined as the difference between the mean value of all measurements at the maximum and the mean value at the minimum of the factor. The Pareto chart shows a graphical representation of effects; the most significant factors are grouped at the top. Factor bars which graphically surpass the significance line exert a statistically significant influence on the result. Pareto charts of some pesticides.[50]

The results are in agreements with Shah et al., who studied the extractive spectrophotometric method for determination of MBZ herbicide and application of factorial design in optimization of various factors.[51] Ara et al., studied the spectrophotometric determination of MBZ herbicide with *p*-dimethylamino-benzaldehyde using factorial designs for optimization of experimental variables.[6] Torres et al. studied the experimental design approach to the optimization of ultrasonic degradation of alachlor and enhancement of treated water biodegradability. The reduced model has been obtained by taking into account the variables (power and alachlor concentration) and the interaction between them since these are the most significant in this chemical process V_0 (mg L^{-1} min^{-1}) = 0.041002 + 4.3357 X 10^{-4} [Alachlor] + 6.29601 X 10^{-3} [Power] + 1.80232 X 10^{-4} [Alachlor] [Power].[52]

4.4. Effect of metribuzin on soil dehydrogenase activity

The enzymes play an important role in the life process of microorganisms in the soil. Although a few enzymes can only function within a viable cell eg dehydrogenase.[53] Studies of enzyme activities in soil are important as they indicate the potential of the soil to support biochemical processes Soil dehydrogenase activity is often used as a measure of any disruption caused by pesticides, trace elements or management.[54] The effect of some herbicides (atrazine, butylate, ethalfluralin, imazethapyr, linuron, metolachlor, metribuzin and trifluralin) on was studied activities of microorganisms and enzymes in soil found that laboratory tests were conducted with eight herbicides applied to a loamy sand at rate of 10 μg/g to determine if these materials caused any serious effects on microbial and enzymatic activities related to soil fertility. Some herbicides showed an effect on bacteria and fungi for the first week of incubation, but, subsequently, the populations returned to levels similar to those obtained in the controls. After several herbicide treatments there appeared to cause a slight depression of nitrification. Sulfur oxidation was better than that obtained with untreated soil in all treatments. Oxygen consumption was increased significantly after 96 h incubation with atrazine. The soil dehydrogenase and amylase activities were inhibited by ethalfluralin treatment respectively for 1 week and 1 day, and p-nitrophenol liberation was inhibited for 2 h by all herbicide treatments. Results indicated that the herbicidal treatments at the level tested were not drastic enough to be considered deleterious to soil microbial and enzymatic activities which are important to soil fertility.[55] Järvan and co-other found that the soil microbial communities and dehydrogenase activity depending on farming systems.[56] Sahoo and other studied the effect of pretilachlor on soil enzyme activities in tropical rice Soil. twenty days after herbicide application, the dehydrogenase activity was inhibited up to 27 %, 28 % and 40 % of initial values of 600, 1200, 6000 g a.i. ha^{-1}, respectively.[57] There is no doubt that there are many organic and inorganic compounds with good biological and pharmacological activities and all these findings presented in this paper confirm the importance of these compounds in different fields.[58-75]

5. Conclusion

The results of recoveries of MBZ in soil clay loam and sandy loam ranged from 50.85 to 108.90 % at concentrations of 5 to 50 μg/g**.** The residues were still detected at day 60 (LOD = 0.0012 μg) of the dose applied. The residues of MBZ in treatment T_5 of soil clay loam, (wheat straw, non-sterilized and incubated at 50°C) rapidly decreased during the experiment (from 118.99 μg/g soil at zero time to 5.39 μg/g soil at 60 day). However, treatment T_{11} of soil sandy loam, (wheat straw, sterilized and incubated at 25°C) slightly decreased during the storage period (from 116.80 μg/g soil at zero time to 7.27 μg/g soil at 60 day). The dissipation was described mathematically by a first order equation. The constant K was ranged from 0.055 to 0.075 for calculated values and from 0.041 to 0.058 for that obtained from the curve. The data of $t_{0.5}$ that calculated from equation ($t_{0.5}$ = 0.6932/K) showed that T_1 and T_6 were the highest values (12.60 and 12.48 day, respectively). However, T_2, T_3 and T_5 was the lowest ($t_{0.5}$ = 9.62, 9.82 and 9.23 day, respectively). Treatment T_4 showed moderate value of $t_{0.5}$ (11.88 day). T_7 and T_{12} were the highest values (12.05 and 12.17 day, respectively). However, T_{11}, T_{10} and T_9 were the lowest ($t_{0.5}$ = 10.29, 10.24 and 10.01 day, respectively). Treatments of T_8 showed moderate value of $t_{0.5}$ (11.92 day). The results of the models obtained from Minitab software using create factorial design for MBZ in soil clay loam and sandy loam at different time intervals are Twenty-one models were generated with high correlation coefficient (r^2 from 0.45-0.99) and low s value (2.67-23.42). The most fit model for prediction of dissipation study was model 6 (r^2 = 0.99 and s = 5.65). That dissipation (%) at time 0, 3, 7, 10, 15, 30 and 60 days using HPLC and calculated by previous model showed good fitness at 0, 3, 7 and 60 days. However, there is a little variation between practically and calculated values at 10, 15 and 30 days. The theoretical half-life of MBZ obtained in model 22 in T_1 to T_6 ranged from 13.89 to 15.76 days for soil clay loam and T_7 to T_{12} ranged from 12.50 to 15.20 days for soil sandy loam. The result proved that the enzyme activity was significantly decreased at 1, 3 and 7 days of incubation then it was gradually increased at 10, 15 and 30 days of incubation. This finding may be due to the increase of pesticide dissipation.

References

1. Skopalová J., Lemr K., Kotouček M., Čáp L., and Barták P. (**2001**) Electrochemical behavior and voltammetric determination of the herbicide metribuzin at mercury electrodes. *Fresenius J. Anal. Chem*., 370 (7) 963-969.
2. Badawy M. E., El-Aswad A. F., Aly M. I., and Fouad M. R. (**2017**) Effect of different soil treatments on dissipation of chlorantraniliprole and dehydrogenase activity using experimental modeling design. *Int. J. Adv. Res. Chem. Sci*., 4 (12) 7-23.
3. Fouad M. R., Abou-Elnasr H., Aly M. I., and El-Aswad A. F. (**2021**) Degradation Kinetics and Half-Lives of Fenitrothion and Thiobencarb in The New Reclaimed Calcareous Soil of Egypt Using GC-MS. *Journal of the Advances in Agricultural Researches*, 26 (1) 9-19.
4. Aly M. I., Fouad M. R., Abou-Elnasr H. S., and El-Aswad A. F. (**2021**) Comparison of Dissipation Kinetics and Residual Behaviour for Fenitrothion Insecticide and Thiobencarb Herbicide in Clay Soil. *Alex. J. Agric. Sci*., 66 (1) 1-11.

5. Huertas-Pérez J.F., del Olmo Iruela M., García-Campaña A.M., González-Casado A., and Sánchez-Navarro A. (**2006**) Determination of the herbicide metribuzin and its major conversion products in soil by micellar electrokinetic chromatography. *J. Chromatogr. A*, 1102, 280-286.
6. Ara B., Shah J., Jan M.R., and Muhammad M. (**2016**) Spectrophotometric determination of metribuzin herbicide with p-dimethylamino-benzaldehyde using factorial designs for optimization of experimental variables. *J. Saudi Chem. Soc.*, 20, S566-S572.
7. Henriksen T., Svensmark B., and Juhler R.K. (**2002**) Analysis of metribuzin and transformation products in soil by pressurized liquid extraction and liquid chromatographic–tandem mass spectrometry. *J. Chromatogr. A*, 957 (1) 79-87.
8. Savage K. (**1977**) Metribuzin persistence in soil. *Weed Sci.,* 55-59.
9. Walker A., Moon Y. H., and Welch S. J. (**1992**) Influence of temperature, soil moisture and soil characteristics on the persistence of alachlor. *Pestic. Sci.,* 35 (2) 109-116.
10. Moorman T., and Harper S. (**1989**) Transformation and mineralization of metribuzin in surface and subsurface horizons of a Mississippi Delta soil. *J. Environ. Qual*., 18 (3) 302-306.
11. Khoury R., Geahchan A., Coste C., Cooper J.F., and Bobe A., (**2003**) Retention and degradation of metribuzin in sandy loam and clay soils of Lebanon. *Weed Res.,* 43 (4) 252-259.
12. Stenrød M., Perceval J., Benoit P., Almvik M., Bolli R. I., Eklo O. M., Sveistrup T. E., and Kværner J., (**2008**) Cold climatic conditions: Effects on bioavailability and leaching of the mobile pesticide metribuzin in a silt loam soil in Norway. *Cold Reg. Sci. Technol.,* 53 (1) 4-15.
13. Gallaher K., and Mueller T. C. (**1996**) Effect of crop presence on persistence of atrazine, metribuzin, and clomazone in surface soil. *Weed Sci.,* 44 (3) 698-703.
14. Banks P. A., and Robinson E. L. (**1982**) The influence of straw mulch on the soil reception and persistence of metribuzin. *Weed Sci.,* 3 (2) 164-168.
15. Sharom M. S., and Stephenson G. (**1976**) Behavior and fate of metribuzin in eight Ontario soils. *Weed Sci.,* 24 (2) 153-160.
16. Milburn P., O'Neill H. Gartley C., Pollock T., Richards J., and Bailey H. (**1991**) Leaching of dinoseb and metribuzin from potato fields in New Brunswick. *Can. Agric. Eng.*, 33 (2) 197-204.
17. Fouad M. R., and El-Aswad A. F., (**2018**) Competitive and non-competitive adsorption of atrazine and diuron on alluvial soil. *Alex. Sci. Exch. J.*, 39 (July-September) 527-533.
18. Locke M. A., and Harper S. S. (**1991**) Metribuzin degradation in soil: I—effects of soybean residue amendment, metribuzin level, and soil depth. *Pest. Manag. Sci.,* 31 (2) 221-237.
19. Dewangan M., Singh A., and Chowdhury T. (**2016**) Influence of Herbicides on Phytotoxicity and Soil Dehydrogenase Enzyme Activity in Chickpea (Cicer arietinum L.). *Int. j. bio-resour. stress* manag., 7 (4) 533-538.
20. Singh R. (**2012**) Soil Enzyme Activities of Wheat Soil in Response to Metribuzin and Fertilizers in Aligarh Soil. *Int. J. Sci. Res.,* 3 (6) 1705-1709.
21. Fouad M. R. (**2021**) Study on toxicity effect of bispyribac-sodium herbicide on earthworms by filter paper and soil mixing method. *International Journal of Agriculture and Environmental Research*. 7 (4) 755-766.
22. Fouad M. R., Shamsan A. Q. S., and Abdel-Raheem Sh. A. A. (**2023**) Toxicity of atrazine and metribuzin herbicides on earthworms (*Aporrectodea caliginosa*) by filter paper contact and soil mixing techniques. *Curr. Chem. Lett.*, 12 (1) 185-192.
23. Cardaropoli G., Araujo M., and Lindhe, J. (**2003**) Dynamics of bone tissue formation in tooth extraction sites. *J. Clin. Periodontol.,* 30 (9) 809-818.
24. Greaves M., and Malkomes H. (**1980**) Effects on soil microflora. Interactions between herbicides and the soil.
25. Felsot A. S., and Dzantor E. K. (**1995**) Effect of alachlor concentration and an organic amendment on soil dehydrogenase activity and pesticide degradation rate. *Environ. Toxicol. Chem.,* 14 (1) 23-28.
26. El-Aswad A. F., Aly M. I., Fouad M. R., and Badawy M. E., (**2019**) Adsorption and thermodynamic parameters of chlorantraniliprole and dinotefuran on clay loam soil with difference in particle size and pH. *J. Environ. Sci. Health B,* 54 (6) 475-488.
27. Fouad M. R. (**2022**) Validation of adsorption-desorption kinetic models for fipronil and thiamethoxam agrichemicals on three soils in Egypt. *Egypt. J. Chem.*, Accepted Manuscript (DOI: 10.21608/EJCHEM.2022.143450.6289).
28. Fouad M. R. (**2023**) Physical characteristics and Freundlich model of adsorption and desorption isotherm for fipronil in six types of Egyptian soil. *Curr. Chem. Lett.*, 12 (1) 207-216.
29. Fouad M. R. (**2022**) Spectrophotometric detection and quantification limits of fipronil and neonicotinoids in acetonitrile. *International Journal of Food Science, Nutrition Health and Family Studies,* 3 (1) 106-123.
30. Fouad M. R., El-Aswad A. F., Badawy M. E. I., and Aly M. I. (**2019**) Adsorption isotherms modeling of herbicides bispyribac-sodium and metribuzin on two common Egyptian soil types. *Journal of Agricultural, Environmental and Veterinary Sciences*, 3 (2) 69-91.
31. Papadakis E. N., and Papadopoulou-Mourkidou E. (**2002**) Determination of metribuzin and major conversion products in soils by microwave-assisted water extraction followed by liquid chromatographic analysis of extracts. *J. Chromatogr. A*, 962 (1-2) 9-20.
32. Janaki P., Sundaram K. M., Chinnusamy C., and Sakthivel N. (**2015**) Determination of residues of metribuzin in soil and sugarcane by QuEChERS. *Asian J. Chem.,* 27 (10) 3692.

33. Xie Y. L., Zhao Z. D., Zhang X. L., Tang L. l., Zhang Y., and Zhang C. H. (**2017**) Simultaneous analysis of herbicide metribuzin and its transformation products in tomato using QuEChERS-based gas chromatography coupled to a triple quadrupole mass analyzer. *Microchem. J.,* 133, 468-473.
34. López-Piñeiro A., Peña D., Albarrán A., Becerra D., and Sánchez-Llerena, J., (**2013**) Sorption, leaching and persistence of metribuzin in Mediterranean soils amended with olive mill waste of different degrees of organic matter maturity. *J. Environ. Manage.,* 122, 76-84.
35. López-Cabeza R., Gámiz B., Cornejo J., and Celis, R., (**2017**) Behavior of the enantiomers of the herbicide imazaquin in agricultural soils under different application regimes. *Geoderma,* 293, 64-72.
36. Singh N., and Singh S. (**2015**) Adsorption and Leaching Behaviour of Bispyribac-Sodium in Soils. *Bull. Environ. Contam. Toxicol*., 94 (1) 125-128.
37. Abate G., and Masini J. C. (**2005**) Sorption of atrazine, propazine, deethylatrazine, deisopropylatrazine and hydroxyatrazine onto organovermiculite. *J. Braz. Chem. Soc.,* 16, 936-943.
38. Castillo M. d. P., and Torstensson L. (**2007**) Effect of biobed composition, moisture, and temperature on the degradation of pesticides. *J. Agric. Food Chem.,* 55 (14) 5725-5733.
39. Fouad, M. R. (2022). Effect of temperature and soil type on the adsorption and desorption isotherms of thiamethoxam using the Freundlich equation. *Egypt. J. Chem.,* (DOI: 10.21608/ejchem.2022.164539.7015).
40. Rice P. J., Anderson T. A., and Coats J. R. (**2002**) Degradation and persistence of metolachlor in soil: Effects of concentration, soil moisture, soil depth, and sterilization. *Environ. Toxicol. Chem.,* 21 (12) 2640-2648.
41. Berns A., Philipp H., Narres H.D., Burauel P., Vereecken H., and Tappe W. (**2008**) Effect of gamma-sterilization and autoclaving on soil organic matter structure as studied by solid state NMR, UV and fluorescence spectroscopy. *Eur. J. Soil Sci.,* 59 (3) 540-550.
42. Bouchard D. C., and Lavy, T. L., Marx D. B. (**1982**) Fate of metribuzin, metolachlor, and fluometuron in soil. *Weed Sci.,* 30 (6) 629-632.
43. Fernandes M. C., Cox L., Hermosín M. C., and Cornejo J. (**2003**) Adsorption–desorption of metalaxyl as affecting dissipation and leaching in soils: role of mineral and organic components. *Pest. Manag. Sci.,* 59 (5) 545-552.
44. Briceño G., Palma G., and Durán N. (**2007**) Influence of organic amendment on the biodegradation and movement of pesticides. *Crit. Rev. Environ. Sci. Technol.,* 37 (3) 233-271.
45. Cox L., Velarde P., Cabrera A., Hermosín M., and Cornejo J. (**2007**) Dissolved organic carbon interactions with sorption and leaching of diuron in organic-amended soils. *Eur. J. Soil Sci.,* 59 (58) 714-721.
46. Thevenot M., Dousset S., Hertkorn N., Schmitt-Kopplin P., and Andreux F. (**2009**) Interactions of diuron with dissolved organic matter from organic amendments. *Sci. Total Environ.,* 407 (14) 4297-4302.
47. García-Jaramillo M., Cox L., Cornejo J., and Hermosín M. (**2014**) Effect of soil organic amendments on the behavior of bentazone and tricyclazole. *Sci. Total Environ.,* 466, 906-913.
48. Haham H., Oren A., and Chefetz B. (**2012**) Insight into the role of dissolved organic matter in sorption of sulfapyridine by semiarid soils. *Environ. Sci. Technol.,* 46 (21) 11870-11877.
49. Cabrera A., Cox L., Spokas K., Hermosín M., Cornejo J., and Koskinen W. (**2014**) Influence of biochar amendments on the sorption–desorption of aminocyclopyrachlor, bentazone and pyraclostrobin pesticides to an agricultural soil. *Sci. Total Environ.,* 470, 438-443.
50. Carro N., García I., Ignacio M., and Mouteira A., (**2006**) Microwave-assisted solvent extraction and gas chromatography ion trap mass spectrometry procedure for the determination of persistent organochlorine pesticides (POPs) in marine sediment. *Anal. Bioanal. Chem.,* 385 (5) 901-909.
51. Shah J., Jan M. R., Ara B., and Mohammad M. (**2009**) Extractive spectrophotometric method for determination of metribuzin herbicide and application of factorial design in optimization of various factors. *J. Hazard. Mater.,* 164 (2-3) 918-922.
52. Torres R. A., Mosteo R., Pétrier C., and Pulgarin C. (**2009**) Experimental design approach to the optimization of ultrasonic degradation of alachlor and enhancement of treated water biodegradability. *Ultrason. Sonochem.,* 16 (3) 425-430.
53. Dick R. P. (**1994**) Soil enzyme activities as indicators of soil quality. *Defining soil quality for a sustainable environment,* 35, 107-124.
54. Brzezińska M., Stępniewska Z., and Stępniewski, W. (**1998**) Soil oxygen status and dehydrogenase activity. *Soil Biol. Biochem.,* 30 (13) 1783-1790.
55. Tu C. (**1992**) Effect of some herbicides on activities of microorganisms and enzymes in soil. *J. Environ. Sci. Health B,* 27 (6) 695-709.
56. Järvan M., Edesi L., Adamson A., and Võsa T. (**2014**) Soil microbial communities and dehydrogenase activity depending on farming systems. *Plant Soil Environ.,* 60 (10) 459-463.
57. Sahoo S., Adak T., Bagchi T.B., Kumar U., Munda S., Saha S., Berliner J., Jena M., and Mishra B. (**2017**) Effect of pretilachlor on soil enzyme activities in tropical rice soil. *Bull. Environ. Contam. Toxicol*., 98 (3) 439-445.
58. Ahmed A. A., Mohamed S. K., and Abdel-Raheem Sh. A. A. (**2022**) Assessment of the technological quality characters and chemical composition for some Egyptian Faba bean germplasm. *Curr. Chem. Lett.*, 11 (4) 359-370.
59. Mohamed S. K., Mague J. T., Akkurt M., Alfayomy A. M., Abou Seri S. M., Abdel-Raheem Sh. A. A., and Abdul-Malik M. A. (**2022**) Crystal structure and Hirshfeld surface analysis of ethyl (3*E*)-5-(4-chlorophenyl)-3-{[(4-chlorophenyl)formamido]imino}-7-methyl-2*H*,3*H*,5*H*-[1,3]thiazolo[3,2-a]pyrimidine-6-carboxylate. *Acta Cryst.*, 78 (8) 846-850.

60. Kaid M., Ali A. E., Shamsan A. Q. S., Salem W. M., Younes S. M., Abdel-Raheem Sh. A. A., and Abdul-Malik M. A. (**2022**) Efficiency of maturation oxidation ponds as a post-treatment technique of wastewater. *Curr. Chem. Lett.*, 11 (4) 415-422.
61. Elhady O. M., Mansour E. S., Elwassimy M. M., Zawam S. A., Drar A. M., and Abdel-Raheem Sh. A. A. (**2022**) Selective synthesis, characterization, and toxicological activity screening of some furan compounds as pesticidal agents. *Curr. Chem. Lett.*, 11 (3) 285-290.
62. Abd-Ella A. A., Metwally S. A., Abdul-Malik M. A., El-Ossaily Y. A., Abd Elrazek F. M., Aref S. A., Naffea Y. A., and Abdel-Raheem Sh. A. A. (**2022**) A review on recent advances for the synthesis of bioactive pyrazolinone and pyrazolidinedione derivatives. *Curr. Chem. Lett.*, 11 (2) 157-172.
63. Tolba M. S., Sayed M., Kamal El-Dean A. M., Hassanien R., Abdel-Raheem Sh. A. A., and Ahmed M. (**2021**) Design, synthesis and antimicrobial screening of some new thienopyrimidines. *Org. Commun.*, 14 (4) 334-345.
64. Abdel-Raheem Sh. A. A., Kamal El-Dean A. M., Abdul-Malik M. A., Hassanien R., El-Sayed M. E. A., Abd-Ella A. A., Zawam S. A., and Tolba M. S. (**2022**) Synthesis of new distyrylpyridine analogues bearing amide substructure as effective insecticidal agents. *Curr. Chem. Lett.*, 11 (1) 23-28.
65. Abdelhamid A. A., Elsaghier A. M. M., Aref S. A., Gad M. A., Ahmed N. A., and Abdel-Raheem Sh. A. A. (**2021**) Preparation and biological activity evaluation of some benzoylthiourea and benzoylurea compounds. *Curr. Chem. Lett.*, 10 (4) 371-376.
66. Tolba M. S., Abdul-Malik M. A., Kamal El-Dean A. M., Geies A. A., Radwan Sh. M., Zaki R. M., Sayed M., Mohamed S. K., and Abdel-Raheem Sh. A. A. (**2022**) An overview on synthesis and reactions of coumarin based compounds. *Curr. Chem. Lett.*, 11 (1) 29-42.
67. Abdel-Raheem Sh. A. A., Kamal El-Dean A. M., Abdul-Malik M. A., Abd-Ella A. A., Al-Taifi E. A., Hassanien R., El-Sayed M. E. A., Mohamed S. K., Zawam S. A., and Bakhite E. A. (**2021**) A concise review on some synthetic routes and applications of pyridine scaffold compounds. *Curr. Chem. Lett.*, 10 (4) 337-362.
68. Abdelhafeez I. A., El-Tohamy S. A., Abdul-Malik M. A., Abdel-Raheem Sh. A. A., and El-Dars F. M. S. (**2022**) A review on green remediation techniques for hydrocarbons and heavy metals contaminated soil. *Curr. Chem. Lett.*, 11 (1) 43-62.
69. Abdel-Raheem Sh. A. A., Kamal El-Dean A. M., Abd ul-Malik M. A., Marae I. S., Bakhite E. A., Hassanien R., El-Sayed M. E. A., Zaki R. M., Tolba M. S., Sayed A. S. A., and Abd-Ella A. A. (**2022**) Facile synthesis and pesticidal activity of substituted heterocyclic pyridine compounds. *Rev. Roum. Chem.*, 67 (4-5) 305-309.
70. Tolba M. S., Kamal El-Dean A. M., Ahmed M., Hassanien R., Sayed M., Zaki R. M., Mohamed S. K., Zawam S. A., and Abdel-Raheem Sh. A. A. (**2022**) Synthesis, reactions, and applications of pyrimidine derivatives. *Curr. Chem. Lett.*, 11 (1) 121-138.
71. Abdel-Raheem Sh. A. A., Kamal El-Dean A. M., Zaki R. M., Hassanien R., El-Sayed M. E. A., Sayed M., and Abd-Ella A. A. (**2021**) Synthesis and toxicological studies on distyryl-substituted heterocyclic insecticides. *Eur. Chem. Bull.*, 10 (4) 225-229.
72. Abdel-Raheem Sh. A. A., Kamal El-Dean A. M., Hassanien R., El-Sayed M. E. A., Sayed M., and Abd-Ella A. A. (**2021**) Synthesis and spectral characterization of selective pyridine compounds as bioactive agents. *Curr. Chem. Lett.*, 10 (3) 255-260.
73. Shamsan A. Q. S., Fouad M. R., Yacoob W. A. R. M., Abdul-Malik M. A., and Abdel-Raheem Sh. A. A. (**2023**) Performance of a variety of treatment processes to purify wastewater in the food industry. *Curr. Chem. Lett.*, Accepted Manuscript (DOI: 10.5267/j.ccl.2022.11.003).
74. El-Aswad A. F., Fouad M. R., Badawy M. E., and Aly M. I. (**2022**) Effect of Calcium Carbonate Content on Potential Pesticide Adsorption and Desorption in Calcareous Soil. *Commun. Soil Sci. Plant Anal.*, Accepted Manuscript (DOI: 10.1080/00103624.2022.2146131).
75. Fouad M. R., El-Aswad A. F., and Aly M. I. (**2022**) Acute toxicity, biochemical and histological of fenitrothion and thiobencarb on fish Nile tilapia (Oreochromis niloticus). *Nusantara bioscie.*, 14 (2) 217-226.