Sorption characteristics and thermodynamic parameters of bispyribac-sodium and metribuzin on alluvial soil with difference in particle size and pH value

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

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

CHRONICLE	ABSTRACT
	The behavior of bispyribac-sodium and metribuzin herbicides was investigated into alluvial soil. Effect of pH, temperature, and particle size of soil on the sorption process was studied. Sorption isotherms by bulk soil and its sand, silt, clay and humic acid (HA) fractions were quantified using the batch equilibration technique. The results showed that sorption of herbicides tested was significantly affected by temperature and was a spontaneous interfacial process into soil. Freundlich equation accurately predicted the sorption behavior of two herbicides. Thermodynamic parameters summarized that the negative values of the standard free energy changes ($\Delta G°$) were obtained therefore, the adsorption of tested pesticides in soil was spontaneous and small negative values indicate the sorption is physical in nature involving weak forces of attraction. The negative $\Delta H°$ value, indicating metribuzin and bispyribac-sodium interactions are exothermic processes and products are energetically stable with a high binding of compound to soil sites. There was an increase in the entropy of tested pesticides-soil systems as shown by positive values of $\Delta S°$. The highest adsorption in soil was at pH 5 for bispyribac-sodium and at pH 7 for metribuzin. The sorption of metribuzin and bispyribac-sodium were significantly greater on HA fraction followed by clay fraction than the bulk soil. The KF and Kd values increase with decreasing particle size particularly in the case of adsorption of metribuzin.

1. Introduction

Behavior of pesticides in soil greatly depends on adsorption-desorption phenomena.[1-3] Binding, sequestration of a solute into certain elements of the soil organic matter (OM), or entrapment of the solute in micro-porous structures or the soil OM matrix are the typical ways that sorption-desorption hysteresis is characterized.[4] Adsorption-desorption phenomena can influence translocation, persistence and bioavailability. Adsorption was controlled by Van der Waal's forces and π-π interactions. Higher OM content soils had more strong desorption hysteresis than lower OM content soils.[5] A crucial mechanism determining the fate of organic contaminants in all compartments of environment is adsorption.[6] The eventual fate of these chemicals in the soil environment is influenced by various processes such as transport, leaching, degradation, volatilization, bioaccumulation, and bioavailability that are affected by pesticide adsorption.[7-12] Sorption of pesticides can be physical or chemical. Physical sorption is the result of Van der Waal's forces interacting between neutral molecules and the surface of soil colloids. Chemical sorption is the result of coulombic forces interacting between oppositely charged adsorbent and adsorbates. Depending on the physico-chemical characteristics of the molecules and the soils involved, the sorption of pesticides happens with a limited degree of reversibility.[11,13,14] As long as the total organic carbon (OC) content is greater than 0.1%, natural OM serves as the main sorbent of hydrophobic organic pollutants in soils and sediments.[15] The chemical composition of the soil or sedimentary OM and its concentration are the two key determinants of organic pollutant sorption.[4,16] The following formulae can be used to determine the adsorption partition

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

coefficient (Kd) based on the organic content of the soil and either the solubility or the octanol-water distribution coefficient.[17]

$$\log K_{oc} = 3.64 - (0.557 \times \log Soul) \text{ and/or } \log K_{oc} = 1.00 (\log K_{ow}) - 0.21$$
$$K_d = (K_{oc} \times OC\%) / 100.$$

where, K_{oc} = OC distribution coefficient; $Solu$ = solubility, in milligrams per liter and K_{ow} = octanol-water distribution coefficient.

The temperature is one of the primary environmental elements that affect the adsorption of organic molecules in soil. It is often assumed that adsorption is an exothermic process, whereby rising temperatures result in slower adsorption and faster desorption rates. However, due to the complexity of the soil environment, thermodynamic investigations have revealed a very varied relationship to temperature.[18] When the free energy of the sorptive exchange is negative, a chemical will sorb on a solid sorbent.[19] $\Delta G = \Delta H - T \Delta S$, where ΔG is change of Gibbs free energy (kJ mol^{-1}), ΔH is change in enthalpy (kJ mol^{-1}) and ΔS is change in entropy (kJ mol-1 K^{-1}).[1,11] Solubility and adsorption coefficients for organic substances are inversely correlated.[20] The rate of pesticide degradation, the water-air partition coefficient, and the water-soil partition coefficient are all influenced by the soil temperature.[21] Adsorption of anionic molecules by soil is largely dependent on soil components with pH dependent charges, i.e., primarily the clay kaolinite and minerals such as gibbsite, goethite, and hematite. These minerals contain hydroxides and oxyhydroxides of aluminum or iron that have no permanent charge. The pH value at which these minerals or compounds are neutral is termed the zero point of charge (ZPC) and it varies with specific minerals. The ZPC of kaolinite is 6.7; thus, kaolinite develops a net positive charge when the pH < 6.7. The ZPC of iron oxide, iron oxyhydroxide, and aluminum oxyhydroxide is 8.5, 9.0, and 10.4, respectively. These minerals and compounds are adsorptive to anions provided the pH is below the ZPC. It was reported that decreasing soil pH resulted in increased anion adsorption in soils that were rich in goethite and gibbsite. Thus, in agricultural soils, the adsorption of both cations and anions can occur. However, adsorption of anions in particular can be pH dependent.[22] The adsorption of acidic and basic herbicides was adversely affected by the pH of the soil.[23] Given the variation in soil properties, exact pH dependency for any given soil-herbicide interaction will vary.[22]

Particle size is an important factor in adsorption. The impacts of sediments' physical and chemical characteristics on sorption and transport can be coupled via particle size.[24] The majority of soils' mineral fraction is made up of clays. They are good cation adsorbents with significant reactive surface areas for ion exchange or electrostatic attraction because of their tiny particle sizes, lamellar architectures, and negatively charged surfaces.[25] Zeolites and activated carbon adsorption rates are inversely related to particle size. Adsorption of tetrachlorobenzene and pentachlorobenzene increase with decreasing sediment particle-size.[24] The rate constant *(k)* of paraquat herbicides adsorption by the clay adsorbent decreased with increasing particle size.[25]

2. Materials and Methods

2.1. Tested herbicides

Bispyribac-sodium; Sodium 2,6-bis[(4,6-dimethoxypyrimidin-2-yl)oxy] benzoate, technical 95 % a.i., and solubility in water 7330 mg L^{-1}. *Metribuzin;* 4-amino-6-terbutyl-3-methylsulfanyl-1,2,4-triazin-5-one, technical 98 % a.i., and solubility in water 1200 mg L^{-1}. The chemical structure of these pesticides is shown in **Fig. 1**.
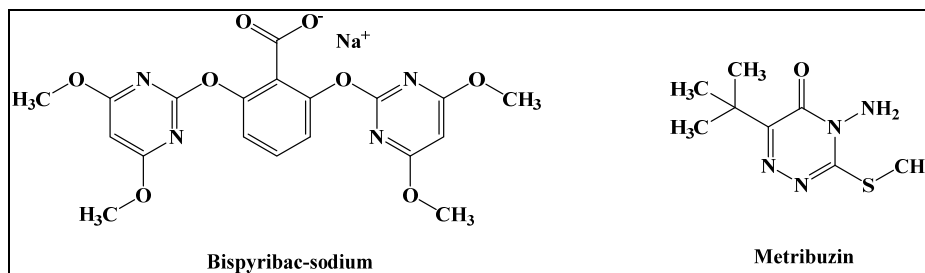

Fig. 1. Chemical structure of bispyribac-sodium and metribuzin.

2.2. Tested soil

Alluvial soil from Alexandria Governorate, Egypt, was tested in the present study. Soil analysis showed that texture is clay loam (42% clay, 18% silt, 40% sand), WHC (water holding capacity) 46 mL, EC 1.32 m mohs cm^{-1}, pH 8.25, organic matter 3.31%, total carbonate 7.87%, soluble cations concentration 18.7 meq L[-1], and soluble cations concentration 13.3 meq L[-1].[11,12,14]

2.3. Soil component fractionation

2.3.1. Extraction of humic acid fraction

The humic acid fraction (HA) was extracted from soil with sodium hydroxide (0.5 M) as described before.[1] At a ratio of 1:10 (w/v), 700 mL of NaOH and 70 g of air-dried soil were added to a 1-L volumetric flask. Flask was shaken for 1 day

at 150 rpm on a rotary shaker. The slurry was centrifuged at 10,000 rpm for 10 minutes to separate the supernatant that contained both HA and fulvic acid (FA) after being allowed to settle for one day in the dark. To separate HA and FA, the supernatant was acidified to pH 1 and let to stand for a day. The HA was separated from FA by centrifugation for 35 min at 11,000 rpm. HA was purified by placing it in a dialysis membrane and then placed in distilled water to get rid of salts and impurities. The substance was dried at a maximum temperature of 35°C until a constant weight was attained, and the resulting dark brown granules were pulverized, sieved, and kept in storage until needed.[1]

2.3.2. Extraction of sand, silt and clay fractions

The sand, silt and clay fractions of soil were separated using a wet sedimentation technique. A soil sample that had been air dried was treated with 30 % H_2O_2 to get rid of soil OM and HCl (6N) to get rid of calcium carbonate. The treated sample was suspended and dispersed with shaking overnight in D.W. (1:5 w:v) containing 25 mL of 0.1 M sodium hexametaphosphate solution after heating for approximately 30 min at 80°C. The soil suspension was left to settle for 8 hours. The supernatant fraction, containing the < 2-μm clay particles, was decanted and exposed to washing several times by distilled water to remove any chloride. The remaining soil suspension was redistributed and allowed to settle for an additional 8 hours to separate the sand fraction from the silt. The various fractions of the slurry were air dried, pulverised, sieved, and placed in storage pending use.[1]

2.4. Adsorption isotherm of tested herbicides

An adsorption isotherm by soil was quantified using batch equilibration technique.[9,10] Bulk soil (1:5), sand, silt and clay fraction (1:10), and HA fraction (1:20) sorbent mass to pesticide solution ratio were all used in the experiments. Initial pesticide concentrations of in 5-50 mg L^{-1} range were prepared in 0.01 M $CaCl_2$. The herbicide solutions were equilibrated with soil in 25-mL centrifuge tubes and shaken mechanically at 160 rpm for 24 hours to achieve equilibrium and centrifuged at 5000 rpm for 16 min. The herbicide concentration in supernatants was determined by spectrophotometer at proper λ_{max} (bispyribac-sodium-246 nm, metribuzin-293 nm).[1,2]

2.5. Desorption of tested herbicides

For all concentrations, desorption experiments were conducted immediately after adsorption experiments. 5 mL of fresh 0.01 M $CaCl_2$ background solution was added to each tube after the sorption experiment using the decant refill procedure for the desorption equilibrium stage (24 hr). To create a new desorption equilibrium, tubes were mechanically shaken at 160 revolutions per minute. The liquid phase that contained the desorbed herbicides was analyzed following centrifugation.[10]

2.6. Effect of temperature

Using the batch tests mentioned above, the adsorption enthalpy of the tested herbicides on soil was calculated. There were two different temperatures used for the adsorption process: 25 and 50 °C. Thermodynamic parameters are calculated from the variation of the thermodynamic equilibrium constant (K_o), standard free energy change ($\Delta G°$), standard enthalpy changes ($\Delta H°$) and standard entropy changes ($\Delta S°$) with changes in temperature.[1,11]

2.7. Effect of pH

The pH values of $CaCl_2$ solution (0.01M) were adjusted of 5, 7 and 9 with help of HCl (2N) and NaOH (2N). The tested herbicides were added to the $CaCl_2$ solutions modified pH values to obtain known pesticide concentrations.[1]

2.8. Effect particle size

Effect of adsorbent particle size on adsorption isotherms of tested herbicide was carried out using HA, clay, silt and sand fractions isolated from tested soil which differs in particle size and surface area.[1]

2.9. Calculation amount of herbicide
The amount of herbicide sorbed, C_s, by solid phase after equilibrium was calculated,

$$C_s = (C_i - C_e) \times \frac{V}{M_s}$$

where C_s is amount of herbicide (μg g^{-1}), C_i is initial concentration of herbicide (μg mL^{-1}), C_e is equilibrium concentration of herbicide (μg mL^{-1}), V is volume of added solution (mL) and M_s is weight of the adsorbent sample (g).[1,9-11]

2.10. Freundlich model

The following can be used to represent the Freundlich equation's empirical formula;

$$\log q_e = \frac{1}{n} \log C_e + \log K_F$$

where q_e is amount of herbicide (μg g^{-1}), 1/n is Freundlich adsorption exponent, and K_F is Freundlich adsorption coefficient (mL g^{-1}).[11]

2.11. Statistical analysis

The SPSS program was used to conduct the statistical analysis on the experimental results, which are reported as mean ± standard error.

3. Results

3.1. Effect of temperature on tested herbicides sorption in soil

The sorption of tested herbicides bispyribac-sodium and metribuzin in alluvial soil at 25 and 50˚C was studied. **Fig. 2** indicated that the significant greater amounts of bispyribac-sodium and metribuzin were adsorbed and desorbed at 25˚C than at 50˚C in soil. Adsorption percentage of soil was decreased from 74 to 62% of bispyribac-sodium and from 41 to 30% of metribuzin at 25 and 50˚C, respectively. The reduction of the adsorption corresponds of a weakening of attractive forces between pesticides molecules and soil matrix. The values of Freundlich adsorption coefficient (K_F), Freundlich adsorption exponent (1/n) and correlation coefficient (R^2) to adsorption of bispyribac-sodium and metribuzin into alluvial soil are presented in Table (1). The correlation coefficient ($R^2 = 0.91 – 0.98$), indicating that Freundlich equation was best fist of tested herbicides adsorption. The K_F values of bispyribac-sodium in soil at 25 and 50˚C were almost the same while, the Kd values were 17.3 and 9.9 indicate that bispyribac-sodium was strongly bound at 25˚C more than at 50˚C into soil. In contrast, value of K_F to metribuzin was 0.39 at 25˚C while 0.14 at 50˚C. According to the 1/n values, particularly at 25˚C it is suggested that the adsorption of bispyribac-sodium in soil is linear. The 1/n value of bispyribac-sodium in soil at 50˚C was 0.9.

Table 1. Adsorption characteristics and Freundlich parameters of bispyribac-sodium and metribuzin onto alluvial soil and its constituents

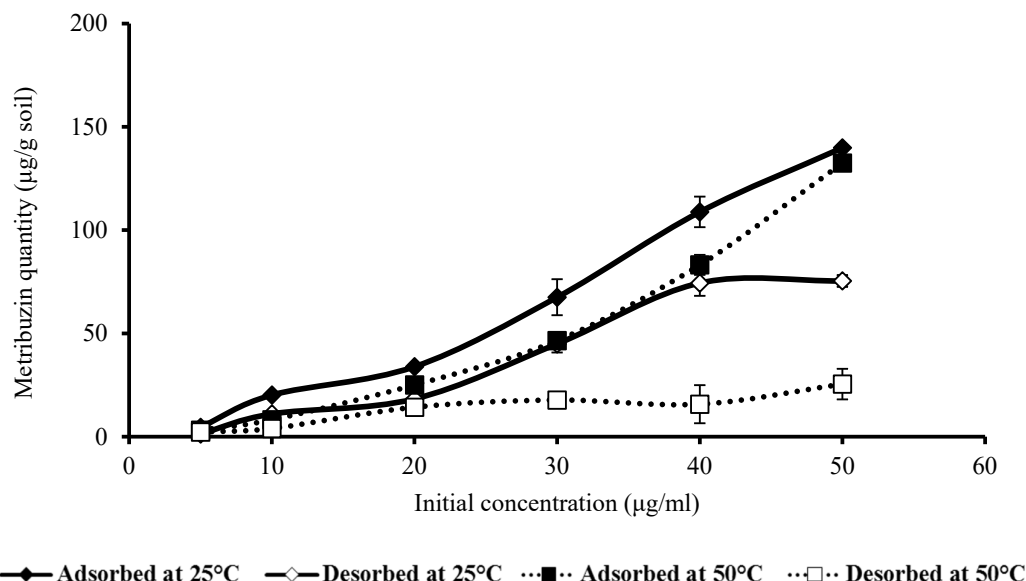| Pesticide	Bispyribac-sodium				Metribuzin			
Adsorbents	K_F	1/n	R^2	Kd	K_F	1/n	R^2	Kd
Bulk soil at 25 ºC	11.2	1.3	0.91	17.3	0.39	1.888	0.94	4.0
Bulk soil at 50 ºC	11.7	0.9	0.98	9.9	0.14	1.993	0.98	2.4
HA fraction	25.2	1.3	0.99	47.2	27.8	1.325	0.88	58.9
Clay fraction	0.7	2.0	0.73	9.6	11.8	1.023	0.92	12.7
Silt fraction	22.2	0.6	0.66	11.2	7.0	1.102	0.95	8.6
Sand fraction	0.2	2.3	0.88	1.0	5.7	1.172	0.95	8.6
Bulk soil at pH 5	7.1	1.1	0.97	8.2	11.7	0.747	0.94	7.4
Bulk soil at pH 7	6.9	1.0	0.99	6.1	10.2	0.877	0.76	8.9
Bulk soil at pH 9	11.8	0.8	0.99	7.3	18.12	0.475	0.85	9.1
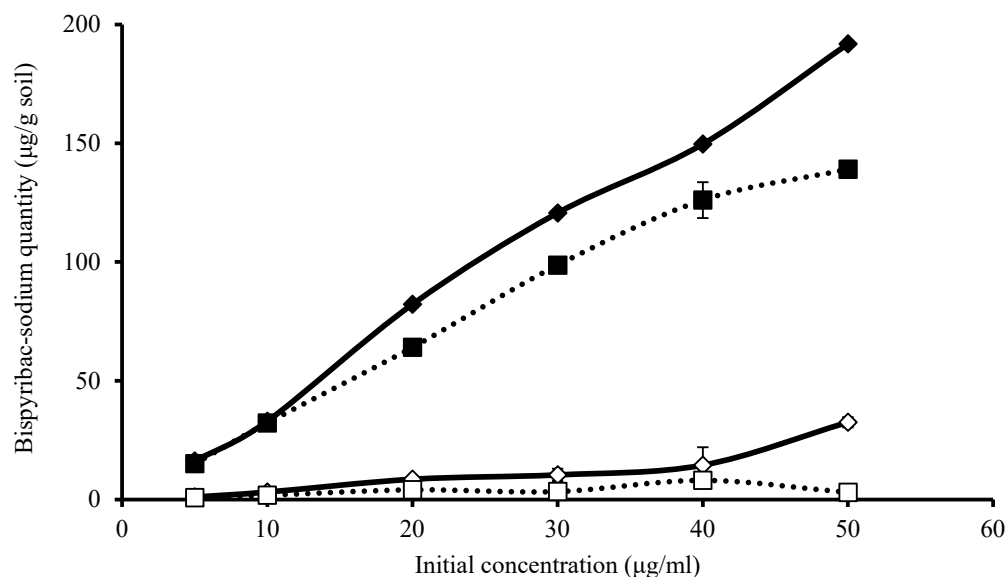
**Fig. 2.** Adsorption and desorption isotherms of bispyribac-sodium and metribuzin in soil at 25 and 50°C.

The thermodynamic constant (Ko), standard free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy change ($\Delta S°$) of tested herbicides in soil are presented in Table (2). The values of the standard free energy change ($\Delta G°$) of the bispyribac-sodium adsorption reaction at 25 and 50°C were -22.88 and -24.76 kJ/mol, respectively, indicating a physical and spontaneous adsorption process. Standard enthalpy change ($\Delta H°$) was negative into soil; the bispyribac-sodium-soil interaction is exothermic. The standard free energy change ($\Delta G°$) of the metribuzin adsorption was negative under 25 and 50°C. Therefore, the adsorption of metribuzin in alluvial soil is spontaneous process. Furthermore, between 25 to 50 °C, metribuzin's ability to bind to soil molecules declines. It might be as a result of the lesser attractive forces at higher temperatures. A negative heat of adsorption ($\Delta H°$) thus describes the interaction. The results of metribuzin interaction with soil are exothermic and energetically stable with a high binding of the herbicide to the soil sites, as shown by the negative values of the standard enthalpy change ($\Delta H°$). The metribuzin-soil system's entropy increased, as seen by the positive values of $\Delta S°$.

Table 2. Thermodynamic parameters of tested pesticides adsorption in alluvial soil.

| Thermodynamic parameters	Bispyribac-sodium		Metribuzin	
	25°C	50°C	25°C	50°C
K_o (mmol /g)	10230.0	10112.0	7874.4	6455.2
$\Delta G°$ (J/mol)	-22875.7	-24763.6	-22227.3	-23558.3
$\Delta H°$ (J/mol)	-371.4		-6361.5	
ΔS (J/K)	75.6		53.3	

3.2. Effect of pH variation on tested herbicides adsorption

The pH variation test was carried out same way as standard adsorption experiments, but prior to test pH of $CaCl_2$ solution (0.01M) was adjusted of 5, 7 or 9 with 0.1M HCl and NaOH. All adsorption data of the tested pesticides with variation of pH fitted well to the Freundlich equation. The adsorption parameters are summarized in **Table (1)**. They demonstrate that the tested pesticides' intrinsic physicochemical properties determine how much the Freundlich isotherm exponent 1/n deviates from 1 in each case. The low values of 1/n are associated with high organic matter content in clay loam soil particularly in the case of metribuzin. The sorption coefficient (Kd), which is determined by dividing the amount sorbed by the corresponding equilibrium concentration, may serve as an indicator of the pH effect. For instance, the average values for the sorption coefficient. When comparing the adsorption behaviour of various tested pesticides based on their Kd values and the average of the adsorption, it was found that there was a direct correlation between Kd and the percentage of adsorption for tested pesticides at pH values of 5, 7, and 9. The sorption of in soil at pH 5 was statistically higher than that at pH 7 and pH 9 (Figure 3). Consequently **Table 1** revealed that the Freundlich coefficient values of bispyribac-sodium were lowest at pH 7. Regarding to the herbicide metribuzin at pH 5 and pH 9, the sorption of metribuzin was lower than that at pH 7. The average values of the metribuzin adsorption percentages were 51.6, 55.4 and 47.7 % in soil at pH 5, 7 and 9, respectively. The KF and Kd values were higher at pH 9.
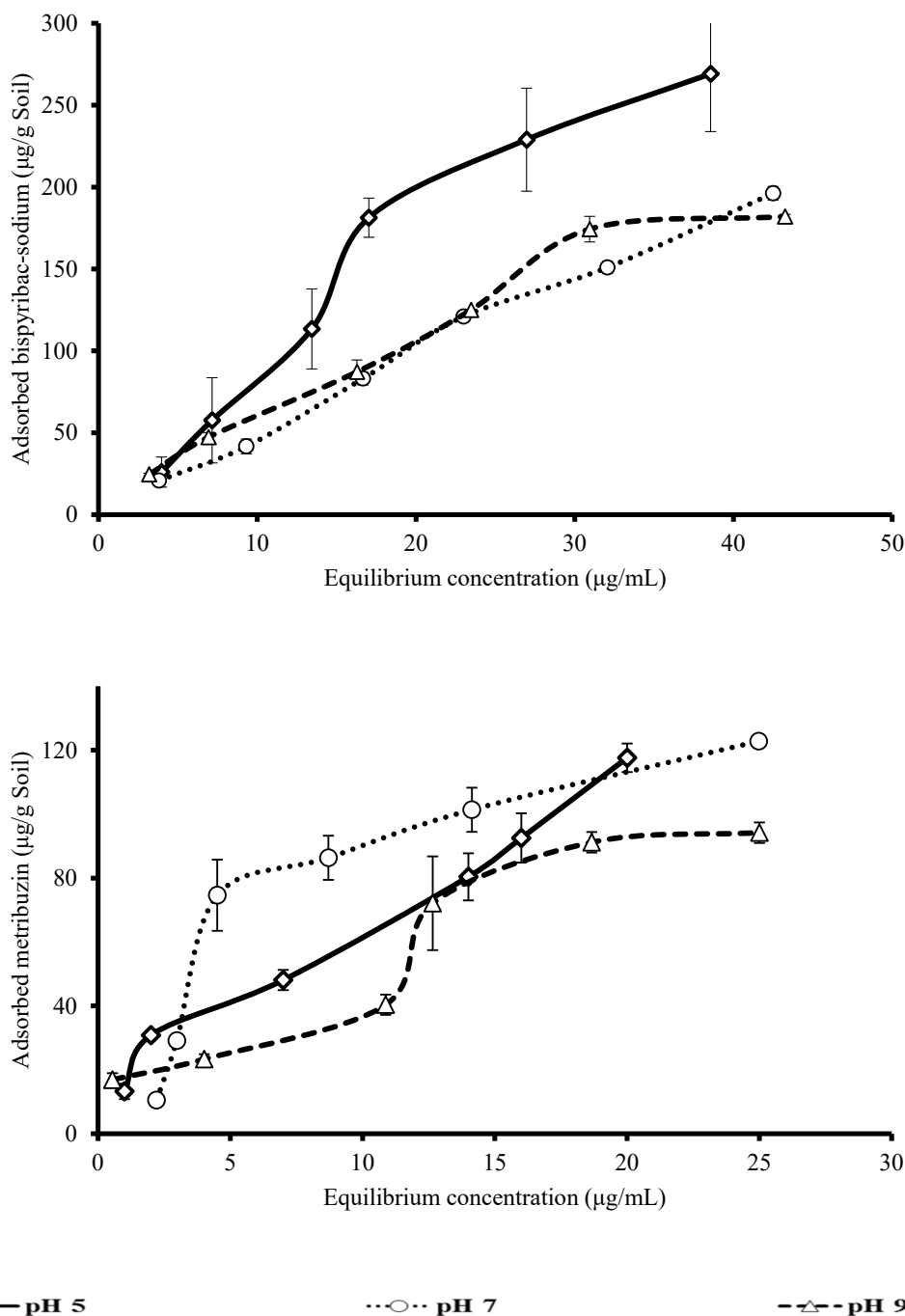
Fig. 3. Adsorption of bispyribac-sodium and metribuzin in soil at different pH values (Error bars represent one standard error of the mean).

3.3 Adsorption of tested herbicides on bulk soil and its constituent fractions

The efficiency of different sorbents (soil, sand, silt, clay and HA) of herbicides adsorption was described and compared. **Fig. (4)** indicated that the adsorption of bispyribac-sodium and metribuzin were significantly greater on clay and HA fractions than silt, sand and the bulk soils. Also, the tested herbicides adsorption was greater on HA fraction compared to clay fraction. The obtained results were confirmed by calculated the adsorption mean. The average of the adsorption were 98.9, 33.0, 94.0, 121.5 and 619.2 µg bispyribac-sodium/g sorbent and 62.5, 115.6, 112.6, 133.3 and 638.4 µg metribuzin/g sorbent for bulk soil, sand, silt, clay and HA fractions, respectively. That bispyribac-sodium sorption on clay fraction was more higher than that onto sand fraction while, sorption on silt fraction was higher than that of sand fraction while, lower than that on clay fraction at high equilibrium concentrations. About herbicide metribuzin, significant differences were recorded between adsorption of metribuzin onto HA, clay, silt and sand.
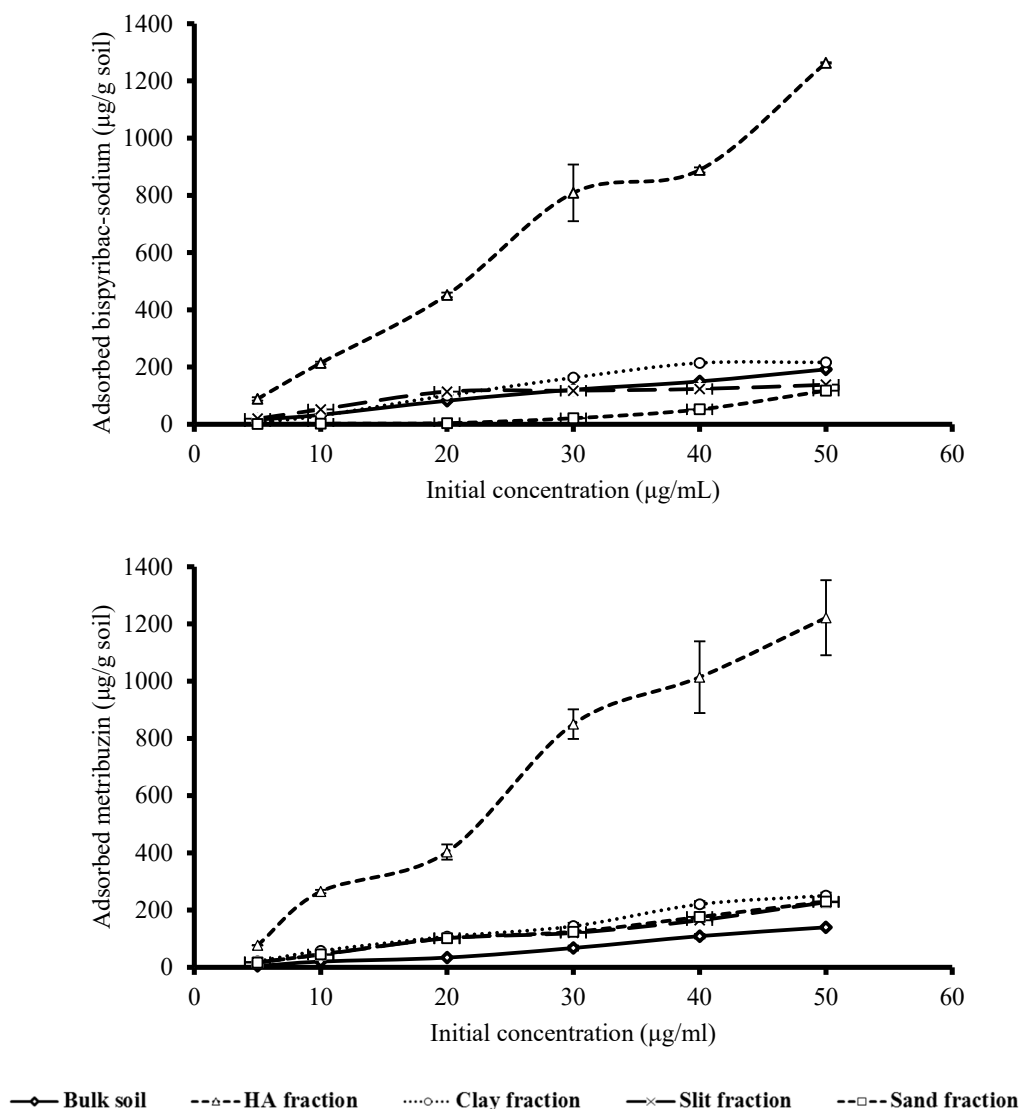
Fig. 4. Adsorption of bispyribac-sodium and metribuzin (±SE) on soil and its constituents.

Freundlich parameters of bispyribac-sodium and metribuzin adsorption on bulk soil and their constituents sand, silt, clay and HA fractions are presented in Table 1. Values of 1/n for all adsorbents were more than 1 except for the adsorption of bispyribac-sodium on silt (1/n = 0.6), indicating the adsorption of tested pesticides in soil and their constituents HA, clay, silt and sand is S-type. The S-shaped isotherms show that the more pesticide that has already been adsorbed on the clay, silt, and sand fractions, the simpler it is for new molecules to become stuck, most likely due to hydrophobic pesticide-pesticide interaction. Only in some cases such as adsorption of bispyribac-sodium on silt fraction, the slope (1/n) values were less than unity suggesting nonlinear adsorption. It demonstrated L-type isotherms, which are marked by a decrease in adsorption at greater aqueous concentrations of chemicals; as a result, the sorption of these compounds in these situations was concentration-dependent. The presence of this sort of adsorption isotherms, which account for the high affinity of the sorbent for the solute at low concentrations, is caused by the sorbed molecules being in a flat position and not being subject to significant competition from the water molecule. However, sorption diminishes as concentration rises because sorption sites become limited. Other meaning, less pesticide was adsorbed with increasing the pesticide concentration. The adsorption of bispyribac-sodium on the bulk soil, clay fraction and HA fraction increases with increasing the initial concentration of the herbicide. The KF values and Kd values indicated that the sorption capacity of bispyribac-sodium was more on HA fraction followed by bulk soil than that on clay fraction of soil. The KF values increase with decreasing particle size particularly in case for adsorption of metribuzin on HA, clay, silt and sand fractions. The higher KF of clay (11.8 mL/μg metribuzin) than silt (7.0 mL/μg) indicated that metribuzin were more easily adsorbed on clay fraction.

As a result, it is anticipated that soil and sediments with higher levels of OM and clay will be better at sequestering pollutants than soils with lower levels of both. Compared its own fractions for adsorption of bispyribac-sodium and metribuzin, the mass unit of bulk soil adsorbed approximately 10 % for metribuzin and 16 % for bispyribac-sodium of the

same of HA and 50 and 80 % for metribuzin and bispyribac-sodium, respectively of that of clay fraction. Following a suggested model to estimate the contribution of OM and clay, it can be separately and simply calculated according to the following equation;

$$C_{S\ soil} = f_{OM}\ C_{S\ OM} + f_{clay}\ C_{S\ clay} + f_{silt}\ C_{S\ silt} + f_{sand}\ C_{S\ sand}$$

where C_S soil is total amount of herbicide that could be adsorbed on all fractions of soil, f_{OM} = 0.0331g OM/g soil, f_{clay} = 0.42 g clay/g soil, f_{silt} = 0.18 g silt/g soil and f_{sand} = 40 g sand/g soil. The measured levels of tested pesticides adsorbed on alluvial soil are shown in Table 3 together with the fractions of sand, silt, clay, and HA. Based on these actual amounts adsorbed on sand ($C_{S\ sand}$), silt ($C_{S\ silt}$), clay ($C_{S\ clay}$) and OM ($C_{S\ OM}$) fractions multiplied by their practically determined fraction in soil, their specific contribution was estimated, assuming the independency and full accessibility of their sites for herbicides binding. Using fraction contribution and its assumptions; 0.0331 g fraction of OM per mass unit of bulk soil could have contributed 20.5 and 14.6 µg, 0.42 g fraction of clay per mass unit of soil could have adsorbed 50.0 and 39.2 µg, 0.18 g fraction of silt per mass unit of soil could have adsorbed 19.9 and 14.1 µg, and the 0.40 g fraction of silt per mass unit of soil could have adsorbed 9.6 and 32.1 µg of bispyribac-sodium and metribuzin, respectively.

Table 3. Actual amounts of herbicides adsorbed onto soil and its constituent fractions and their specific contribution to soil adsorption.

	Actual adsorption amounts (µg/g)					Calculate potential contribution					Contribution (%)				Actual adsorption on bulk soil
Co (µg/mL)	Cs HA	Cs clay	Cs silt	Cs sand	Cs soil	HA contr.	Clay contr.	Silt contr.	Sand contr.	Total Cs soil	HA	Clay	Silt	Sand	
							Bispyribac-sodium								
5	88.7	5.4	19.5	0.9	16.2	2.9	2.3	3.5	0.3	9.1	32.4	24.9	38.8	3.8	179.2
10	214.3	30.4	51.8	2.3	32.9	7.1	12.7	9.3	0.9	30.1	23.6	42.4	31.0	3.1	109.5
20	452.0	100.4	114.0	4.0	82.2	15.0	42.2	20.5	1.6	79.2	18.9	53.2	25.9	2.0	103.8
30	808.9	162.8	117.3	21.3	120.7	26.8	68.4	21.1	8.5	124.8	21.5	54.8	16.9	6.8	96.7
40	888.7	213.9	123.4	52.1	149.6	29.4	89.8	22.2	20.9	162.3	18.1	55.3	13.7	12.8	92.2
50	1263.0	216.4	138.3	117.6	191.8	41.8	90.9	24.9	47.0	204.6	20.4	44.4	12.2	23.0	93.8
Mean	725.4	144.8	109.0	39.5	115.5	24.0	60.8	19.6	15.8	120.2	20.5	50.0	19.9	9.6	99.2
							Metribuzin								
5	77.0	20.5	18.1	16.5	4.6	2.6	8.6	3.3	6.6	21.0	12.2	41.0	15.5	31.4	21.8
10	264.8	57.7	44.1	45.2	20.1	8.8	24.2	7.9	18.1	59.0	14.8	41.0	13.5	30.7	34.1
20	402.9	107.1	101.0	101.9	33.9	13.3	45.0	18.2	40.8	117.3	11.4	38.4	15.5	34.8	28.9
30	849.9	143.9	120.5	124.0	67.5	28.1	60.4	21.7	49.6	159.8	17.6	37.8	13.6	31.0	42.2
40	1014.2	220.2	164.4	176.4	108.8	33.6	92.5	29.6	70.5	226.2	14.8	40.9	13.1	31.2	48.1
50	1221.6	250.5	227.8	229.8	139.9	40.4	105.2	41.0	91.9	278.6	14.5	37.8	14.7	33.0	50.2
Mean	750.7	155.9	131.6	135.5	74.0	24.8	65.5	23.7	54.2	168.2	14.6	39.2	14.1	32.1	40.7

4. Discussion

Temperature is an important parameter that can influence rates and equilibria of different environmental processes.[1,11] It has been discovered that a rise in temperature reduces the solubility and vapour pressure of herbicides, which in turn reduces their ability to bind to soil. Within a number of herbicide families, especially s-triazines, the amount of adsorption and solubility are inversely correlated.[26] Adsorption generally increases in temperature lowers adsorption.[1] Freundlich equation was best fist to tested herbicides sorption as reported in other previous studies.[27] According to the reported data before,[16] when the correlation coefficient (R^2) is very close to 1, the Freundlich isotherm equation accurately captures the experimental data. The Kd values were reduced with temperature increases of metribuzin. Everyone agrees that the size of the Kd values often indicates the affinities of the compound to the adsorbent matrix.[28] The results showed that Kd value to two herbicides was high of the adsorption at 25°C compared to that at 50°C. According to the 1/n values, adsorption of bispyribac-sodium in soil is linear,[29] stated that the pesticide adsorption is non-linear when the 1/n value is less than 1 and the fraction of pesticide adsorbed decreased with increasing equilibrium concentration. The S shape of the isotherm for metribuzin at both temperatures (1/n > 1), suggests that the adsorption of metribuzin increases with increasing initial concentration within tested range. Adsorption pattern represents the S-type where sorption becomes easier as concentration in liquid phase increases.[30] The relation between 1/n value and organic matter content for different pesticides was observed by Weber Jr et al..[31]

The variation of the thermodynamic equilibrium constant Ko with temperature variations is used to derive thermodynamic parameters. The Ko values were calculated according to.[32,11] The Van't Hoff isochore equation was used to determine the standard enthalpy changes (ΔH°). Also, standard entropy changes (ΔS°) are obtained according to Biggar and Cheung.[32] The standard free energy change (ΔG°) of bispyribac-sodium was negative indicating a physical and spontaneous adsorption process. The positive values of ΔS° indicate that the system's entropy is increasing. As a result, the system as a whole experiences an increase in entropy, rather than a reduction in randomness brought on by the immobilisation of

herbicide molecules. The sorption process can also be influenced by two different types of driving forces: entropy-related forces, which include changes in the randomness or disorder of the sediment/water system, and enthalpy-related forces, which affect the relative affinities of a chemical to the sorbent versus the affinity of the chemical to the solvent. The standard free energy change (ΔG°) of the metribuzin adsorption was negative. Therefore, the adsorption of metribuzin is spontaneous process. The negative values of ΔG° related with adsorption process which were expected for many herbicides because of reported persistence and resistance for degradation of herbicides into soil. Dao and Lavy found that the adsorption of metribuzin in different soil is spontaneous and endothermic process.[33]

When pH was close to their pKa (1.7-2.6), where half of the s-triazine is present in the cationic form and the other half remains in the non-ionic form, the maximal adsorption of s-trizine herbicide happened normally.[34] Triazines are weakly basic herbicides, therefore they may have some pH-dependent processes like hydrogen bonds and van der Waals interactions. The sorption of weakly acidic pesticides is affected by soil pH, according to numerous laboratory investigations.[35]

It is well known that the organic matter in soils acts as a key site for the binding of pesticides and as the main factor affecting the retention of non-ionic pesticides in soils.[36] Humic compounds, which are mostly made up of HA and FA, make up the majority of the soil's organic matter. Humic compounds have aliphatic moieties and the aromaticity of HA ranges from 20 to 70%. These acids have a variety of inherent chemical characteristics that greatly improve how they interact with organic insecticides.[36] Clay minerals can be divided into two categories: clays that swell and clays that don't swell.[37] Since organic chemicals can attach to clay minerals in both categories, the kind of clay will undoubtedly affect pesticide retention. Significant differences were recorded adsorption of HA, clay, silt and sand. It was clearly indicated that at lower concentration of herbicides; atrazine and metribuzin, particle size had no effect of herbicides adsorption. However, the effect of particle size is very obvious at greater concentrations. Atrazine showed higher sorption at increasing herbicide concentrations in the 150 - 250 μm fractions, but metribuzin showed maximum adsorption in the < 150 μm fraction. Adsorption of tested pesticides in soil and their constituents HA, clay, silt and sand is S-type according to classification by.[38] The S-shaped isotherm for adsorption to α–alumina has been found for adsorption of benzoic acid and adsorption of 2,4-D onto ferrihydrite.[39,40] The Kd values increase with decreasing particle size for adsorption of tested herbicides on HA, clay, silt and sand fractions. The distribution coefficient (Kd) represents adsorption at equilibrium concentrations a higher than KF. Different pesticides' adsorption behaviours can be compared based on their Kd values, which clearly shows an inverse relationship between Kd and adsorbent particle size. This work confirms that organic and inorganic compounds are very important substances due to their different uses as reported before.[41-73]

5. Conclusion

The aim of the present work was to understand the behaviour of two herbicides; bispyripac-sodium and metribuzin in clay loam soil. Consequently, the study included the experimental and modeling of sorption-desorption isotherm, the effect of, pH, temperature, and particle size. The alluvial soil was collected from Alexandria Governorate, Egypt. The soil component clay, silt, sand and humic acid were fractionated. Adsorption isotherms by soil and its clay and HA fractions were quantified using the batch equilibration technique. Experiments were carried out in duplicate with a sorbent mass to pesticide solution ratio of 1:5 for the bulk soil and a 1:20 ratio for both clay and HA fractions. Desorption experiments were conducted immediately after the sorption experiments for all concentrations using parallel system. The amount of the tested herbicides adsorbed by the soil was significantly influenced by the temperature. Freundlich parameters and distribution coefficient illustrated that the increasing temperature reduces the adsorption capacity. As the temperature was increased 25 to 50ºC, the average of the adsorption was decreased from 74 to 62% for bispyribac-sodium, and from 41 to 30% for metribuzin in soil, respectively. The adsorption of tested heribicdes in alluvial soil was spontaneous and the small negative values indicate the adsorption is physical in nature. A direct relationship of Kd and percentage of the adsorption was recorded for pesticides in soil types at different pH values 5, 7 and 9. The sorption of herbicides was significantly greater on humic acid fraction followed by clay fraction followed by silt fraction followed by sand fraction compared than the bulk soil.

References

1. 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.
2. 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 – AJSRP*, 3 (2) 69-91.
3. 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.
4. Chefetz B., Bilkis Y. I., and Polubesova T. (**2004**) Sorption–desorption behavior of triazine and phenylurea herbicides in Kishon river sediments. *Water Res.*, 38 (20) 4383-4394.

5. Olu-Owolabi B. I., Diagboya P. N., and Adebowale K. O. (**2015**) Sorption and desorption of fluorene on five tropical soils from different climes. *Geoderma*, 239 179-185.

6. 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 (IJAER)*. 7 (4) 755-766.

7. 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 7-23.

8. 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.

9. 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).

10. 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.,* Accepted Manuscript (DOI: 10.21608/ejchem.2022.164539.7015).

11. 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.

12. Fouad, M. (**2023**) Effect of peat, compost, and charcoal on transport of fipronil in clay loam soil and sandy clay loam soil. *Curr. Chem. Lett.*, 12 (2) 281-288.

13. Boivin A., Cherrier R., and Schiavon M. (**2005**) A comparison of ive pesticides adsorption and desorption processes in thirteen contrasting field soils. *Chemosphere*, 61 (5) 668-676.

14. El-Aswad A. F., Fouad M. R., Badawy M. E., and Aly M. I. (**2022**) Effect of Calcium Carbonate Content on PotentialPesticide Adsorption and Desorption in Calcareous Soil. *Commun. Soil Sci. Plant Anal.*, Accepted Manuscript (DOI:10.1080/00103624.2022.2146131).

15. Piatt J. J., Backhus D. A., Capel P. D., and Eisenreich S. J. (**1996**) Temperature-dependent sorption of naphthalene, phenanthrene, and pyrene to low organic carbon aquifer sediments. *Environ. Sci. Technol.*, 30 (3) 751-760.

16. 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.

17. Carsel R. F. (**1984**) *Users manual for the pesticide root zone model (PRZM), release 1*. Environmental Research Laboratory, Office of Research and Development, US Environmental Protection Agency..

18. Harper S. S. (**1994**) Sorption-desorption and herbicide behavior in soil. *Rev. Weed Sci.*, 6 207-225.

19. Von Oepen B., Kördel W., and Klein W. (**1991**) Sorption of nonpolar and polar compounds to soils: processes, measurements and experience with the applicability of the modified OECD-Guideline 106. *Chemosphere*, 22 (3-4) 285-304.

20. Chiou C. T., Peters L. J., and Freed V. H. (**1979**) A physical concept of soil-water equilibria for nonionic organic compounds. *Science*, 206 (4420) 831-832.

21. Paraiba L. C., and Spadotto C. A. (**2002**) Soil temperature effect in calculating attenuation and retardation factors. *Chemosphere*, 48 (9) 905-912.

22. Grey T. L., Walker R. H., Wehtje G. R., and Hancock H. G. (**1997**) Sulfentrazone adsorption and mobility as affected by soil and pH. *Weed Sci.*, 45 (5) 733-738.

23. Chirukuri R., and Atmakuru R. (**2015**) Sorption characteristics and persistence of herbicide bispyribac sodium in different global soils. *Chemosphere*, 138 932-939.

24. Barber II L. B., Thurman E. M., and Runnells D. D. (**1992**) Geochemical heterogeneity in a sand and gravel aquifer: Effect of sediment mineralogy and particle size on the sorption of chlorobenzenes. *J. Contam. Hydrol.*, 9 (1-2) 35-54.

25. Tsai W. T., Lai C. W., and Hsien K. J. (**2003**) The effects of pH and salinity on kinetics of paraquat sorption onto activated clay. *Colloids Surf. A Physicochem. Eng. Asp.*, 224 (1-3) 99-105.

26. Bailey G. W., and White J. L. (**1970**) Factors influencing the adsorption, desorption, and movement of pesticides in soil. *Single Pesticide Volume: The Triazine Herbicides*, 29-92.

27. Singh N., and Singh S. B. (**2015**) Adsorption and leaching behaviour of bispyribac-sodium in soils. *Bull. Environ. Contam. Toxicol.*, 94 (1) 125-128.

28. Cleveland C. B. (**1996**) Mobility assessment of agrichemicals: current laboratory methodology and suggestions for future directions. *Weed Technol.*, 10 (1) 157-168.

29. Sonon L. S., and Schwab A. P. (**1995**) Adsorption characteristics of atrazine and alachlor in Kansas soils. *Weed Sci.*, 43 (3) 461-466.

30. Delle Site A. (**2001**) Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants. A review. *J. Phys. Chem. Ref. Data*, 30 (1) 187-439.

31. Weber Jr W. J., McGinley P. M., and Katz L. E. (**1992**) A distributed reactivity model for sorption by soils and sediments. 1. Conceptual basis and equilibrium assessments. *Environ. Sci. Technol.*, 26 (10) 1955-1962.

32. Biggar J. W., and Cheung M. W. (**1973**) Adsorption of picloram (4-amino-3, 5, 6-trichloropicolinic acid) on panoche, ephrata, and palouse soils: a thermodynamic approach to the adsorption mechanism. *Soil Sci. Soc. Am. J.*, 37 (6) 863-868.

33. Dao T. H., and Lavy T. L. (**1978**) Atrazine adsorption on soil as influenced by temperature, moisture content and electrolyte concentration. *Weed Sci.*, 26 (3) 303-308.

34. Gao J. P., Maguhn J., Spitzauer P., and Kettrup A. (**1998**) Sorption of pesticides in the sediment of the Teufelsweiher pond (Southern Germany). I: Equilibrium assessments, effect of organic carbon content and pH. *Water Res.*, 32 (5) 1662-1672.

35. Carrizosa M. J., Koskinen W. C., Hermosin M. C., and Cornejo J. (**2001**) Dicamba adsorption–desorption on organoclays. *Appl. Clay Sci.*, 18 (5-6) 223-231.

36. Barraclough D., Kearney T., and Croxford A. (**2005**) Bound residues: environmental solution or future problem?. *Environ. Pollut.*, 133 (1) 85-90.

37. Pu X., and Cutright T. J. (**2006**) Sorption–desorption behavior of PCP on soil organic matter and clay minerals. *Chemosphere*, 64 (6) 972-983.

38. Giles C. H., MacEwan T. H., Nakhwa S. N., and Smith D. (**1960**) A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. *J. Chem. Soc.*, 111 3973-3993.

39. Madsen L., and Blokhus A. M. (**1994**) Adsorption of Benzoic Acid on α-Alumina and γ-Boehmite. *J. Colloid Interface Sci.*, 166 (1) 259-262.

40. Celis R., and Koskinen W. C. (**1999**) Characterization of pesticide desorption from soil by the isotopic exchange technique. *Soil Sci. Soc. Am. J.*, 63 (6) 1659-1666.

41. 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., and Abd-Ella A. A. (**2022**) Facile synthesis and pesticidal activity of substituted heterocyclic pyridine compounds. *Rev. Roum. Chem.*, 67 (4-5) 305-309.

42. 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.

43. 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.

44. 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.

45. 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.

46. Kamal El-Dean A. M., Abd-Ella A. A., Hassanien R., El-Sayed M. E. A., Zaki R. M., and Abdel-Raheem Sh. A. A. (**2019**) Chemical design and toxicity evaluation of new pyrimidothienotetrahydroisoquinolines as potential insecticidal agents. *Toxicol. Rep.*, 6 (2019) 100-104.

47. Abdel-Raheem Sh. A. A., Kamal El-Dean A. M., Hassanien R., El-Sayed M. E. A., and Abd-Ella A. A. (**2021**) Synthesis and characterization of some distyryl-derivatives for agricultural uses. *Eur. Chem. Bull.*, 10 (1) 35-38.

48. 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.

49. 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.

50. 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.

51. 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.

52. 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.

53. 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.

54. 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.

55. 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.

56. Abd-Ella A. A., Metwally S. A., Abdul-Malik M. A., El-Ossaily Y. A., AbdElrazek 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.

57. Gad M. A., Aref S. A., Abdelhamid A. A., Elwassimy M. M., and Abdel-Raheem Sh. A. A. (**2021**) Biologically active organic compounds as insect growth regulators (IGRs): introduction, mode of action, and some synthetic methods. *Curr. Chem. Lett.*, 10 (4) 393-412.

58. Tolba M. S., Sayed M., Abdel-Raheem Sh. A. A., Gaber T. A., Kamal El-Dean A. M., and Ahmed M. (**2021**) Synthesis and spectral characterization of some new thiazolopyrimidine derivatives. *Curr. Chem. Lett.*, 10 (4) 471-478.

59. 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.

60. 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.

61. 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.*, 12 (2) 431–438.

62. El-Aal M. A., and Seto T. (**2021**) Spark discharge deposition of au/cu nanoparticles for surface-enhanced Raman scattering. *Surf. Interface Anal.*, 53 (9) 824-828.

63. Goda M. N., Said A. E. A. A., and Abd El-Aal M. (**2020**) The catalytic performance of ultrasonically prepared $Cu_xCo_{3-x}O_4$ catalysts towards CO oxidation at relatively low temperature. *Mol. Catal.*, 494 111121.

64. Abd El-Aal M., Mogharbel R. T., Ibrahim A., Almutlaq N., Zoromba M. S., Al-Hossainy A. F., and Ibrahim S. M. (**2021**) Synthesis, characterization, and photosensitizer applications for dye-based on ZrO_2-acriflavine nanocomposite thin film $[ZrO_2+ ACF]^C$. *J. Mol. Struct.*, 1250 131827.

65. Elhady O., Mansour E., Elwassimy M., Zawam S., and Drar A. (**2022**) Synthesis and characterization of some new tebufenozide analogues and study their toxicological effect against Spodoptera littoralis (Boisd.). *Curr. Chem. Lett.*, 11 (1) 63-68.

66. Kulawik-Pióro A., and Tal-Figiel B. (**2017**) Influence of preparation method on size distribution of the dispersed phase of primary emulsions. *Chem. Eng. Technol.*, 40 (2) 412-420.

67. Kulawik-Pióro A., Klimaszewska E., Ogorzałek M., Ruman J., and Rożnawska K. (**2020**) Effectiveness of protective preparations: Impact of vegetable oil additives to recipes. *Eur. J. Lipid Sci. Technol.*, 122 (12) 2000130.

68. Kulawik-Pióro A., and Miastkowska M. (**2021**) Polymeric gels and their application in the treatment of psoriasis vulgaris: a review. *Int. J. Mol. Sci.*, 22 (10) 5124.

69. Miastkowska M., Kulawik-Pióro A., and Szczurek M. (**2020**) Nanoemulsion gel formulation optimization for burn wounds: Analysis of rheological and sensory properties. *Processes*, 8 (11) 1416.

70. Kulawik-Pióro A., Ptaszek A., and Kruk J. (**2019**) Effective tool for assessment of the quality of barrier creams-relationships between rheological, textural and sensory properties. *Regul. Toxicol. Pharmacol.*, 103 113-123.

71. Kulawik-Pióro A., Drabczyk A. K., Kruk J., Wróblewska M., Winnicka K., and Tchórzewska J. (**2021**) Thiolated Silicone Oils as New Components of Protective Creams in the Prevention of Skin Diseases. *Materials*, 14 (16) 4723.

72. Kulawik-Pióro A., and Goździcka W. J. (**2022**) Plant and herbal extracts as ingredients of topical agents in the prevention and treatment radiodermatitis: a systematic literature review. *Cosmetics*, 9 (3) 63.

73. Kulawik-Pióro A., Kurpiewska J., and Kułaszka A. (**2018**) Rheological and sensory properties of hydrophilic skin protection gels based on polyacrylates. *Int. J. Occup. Saf. Ergon.*, 24 (1) 129-134.