Effect of pH variation and temperature on pesticides sorption characteristics in calcareous soil

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CHRONICLE	ABSTRACT
	The effect of pH value at three levels (5, 7, and 9) and temperature at two levels (25 and 50ºC) on the sorption properties of chlorantraniliprole-CAP, dinotefuran-DNF, bispyribac-sodium-BPS, and metribuzin-MBZ were studied in calcareous soil. The sorption of CAP at pH 5 (38.2%) was significantly higher than that at pH 7 (32.4%) and 9 (28.4%), whereas the sorption of DNF at pH 5 was lower than that at pH 7. The adsorption of BPS at pH 9 was statistically significantly higher than that at pH 5 and pH 7. Regarding the herbicide MBZ adsorption percentages were 47.0, 61.1 and 57.1 % at pH 5, 7 and 9. The number of tested pesticides adsorbed by the soil was significantly influenced by the temperature. The adsorbed amount of CAP was decreased from 37% to 33% as the temperature was increased from 25˚C to 50 ˚C, while no significant differences of adsorbed DNF. Data showed that the adsorption of BPS and MBZ statistically decreases with temperature. The data from the adsorption behaviour of CAP, DNF, BPS, and MBZ in tested soil at different temperatures correspond well with the Freundlich isotherm. The negative ΔG˚ indicated that the adsorption of CAP, DNF, BPS, and MBZ were spontaneous at different temperatures. There was an increase in the entropy of the pesticide-soil systems as shown by the positive values of ΔS˚.

1. Introduction

Sorption is a major process controlling the fate of organic pollutants in all compartments of the environment. Pesticides sorption affects other processes like transport, leaching, degradation, volatilization, bioaccumulation, bioavailability which influence the final fate of these compounds in the soil environment.[1,2,3] Sorption influences pesticides leaching in the subsurface and has to be account when predicting pesticides transport.[1,3] Kinetic studies have pointed out that several interactions between sorption and degradation and that sorption also controls the persistence and irreversible bonding of pesticides.[4,5,6] Sorption has major effects on the physical accessibility of microorganisms to the pollutant and plays a significant role in the pollutant's mobility.[7,8]

Acidic herbicides exist as either anions or neutral molecules depending upon whether the soil solution pH is below or above the pKa. Theoretically, anionic, and neutral forms will be present in equal amounts when the pH is equal to the pKa. For imazaquin, chlorimuron, and bentazon as soil pH was elevated, soil adsorption decreased, and mobility increased. Adsorption of imazaquin (quinolinecarboxylic acid) and imazethapyr (pyridinecarboxylic acid) to soil increased as soil

pH decreased from 8.0 to 3.0 in laboratory studies. Significantly more imazethapyr than imazaquin was adsorbed at soil pH levels 3.0 and 5.5, while the greatest difference in adsorption behaviour between the two herbicides was observed at a soil pH of 5.5. In addition, the greater adsorption and lesser desorption of imazaquin were observed at low soil pH.[9] Also, laboratory and field studies of imazaquin adsorption indicated that the adsorption increased as pH decreased from about 4.5 to 7. Imazaquin persistence increased as soil pH decreased, over a pH range from 4.5 to 6.5. Increased persistence with decreasing pH was attributed in part to increased adsorption and decreased availability for microbial degradation. Soil pH, through its effect on the degree of ionization of the functional groups or variable charges on soil clays determines the extent of imazaquin adsorption to soil. Increase in adsorption at low pH has been attributed to protonation of both ionizable groups on the imazaquin molecule. Protonation of the carboxyl group results in a loss of negative charge, which would reduce-the repulsion of molecules from negatively charged soil surfaces and promote hydrogen bonding. Protonation of the basic quinoline group causes the molecule to acquire a positive charge, and ionic attraction between the herbicide molecule and soil surfaces would result in increased adsorption. Over a pH range of 4 to 6 or above, the degree of ionization of the carboxyl group should have a greater effect on adsorption than ionization of the quinoline group, which would be fully ionized above a pH of 4. The effective acidity at colloid surfaces can be 2 to 3 pH units lower than the soil solution, and protonation of the quinoline group could occur at soil pH levels above.[10]

One of the main environmental factors that influence adsorption of organic compounds in soil is the temperature.[7,11] It is often assumed that adsorption is an exothermic process, whereby an increase in temperature leads to decreased adsorption and increased desorption rates.[12,13] However, thermodynamic studies have shown a highly variable relationship to temperature due to the complexicity of the soil environment.[7,13] Temperature play crucial role in determining the extent of pesticide that gets adsorbed on the soil. Sorption of a chemical on a solid sorbent occurs when the free energy of the sorptive exchange is negative.[7, 14]

The soil temperature affects the pesticide degradation rate, water-air partition coefficient and water-soil partition coefficient. These three parameters contribute to determine the pesticide behaviour in the environment. The Arrhenius equation, van't Hoff equation and Clausius-Clapeyron equation are used for estimating the soil temperature effect on the pesticide degradation rate, water-air partition coefficient and soil-water partition coefficient, respectively. These dependence relationships, between results of calculating factors and the soil temperature at different depths, can aid to understand the potential pesticide groundwater contamination on different weather conditions.[14,15] Standard thermodynamic parameters, Gibb's free energy (ΔG^o), change in enthalpy (ΔH^o) and change in entropy (ΔS^o) and equilibrium constant, K_o, have revealed spontaneous and exothermic nature of adsorption process. The gained results indicate the phenomena of physical adsorption.[7, 14, 16]

2. Materials and methods

2.1. Tested pesticides

Chlorantraniliprole (CAP)

IUPAC name: 3-Bromo-N-[4-chloro-2-methyl-6-(methylcarbamoyl) phenyl]-1-(3-chloro-2-pyridine-2-yl)-1H-pyrazole-5-carboxamide. Chemical class: Anthranilic diamide. Chemical structure: Figure 1. Product: Technical 95.3% a.i. Pesticide type: Insecticide. Formulations: Coragen 20% SC, Rynaxypyr 20% SC. Uses: in fruit, vegetables, cotton, grapes, potatoes, rice and landscaped areas. It is used against moths, beetles, caterpillars, etc.

Dinotefuran (DNF)

IUPAC name: (RS)-1-methyl-2-nitro-3-(tetrahydro-3-furylmethyl) guanidine. Chemical class: Neo-nicotinoid. Chemical structure: Figure 1. Product: Technical 90.0% a.i. Pesticide type: Insecticide. Formulations: 20% Starkle SG. Uses: in fruit, vegetables, paddy rice and turf. It can be applied to foliage, soil, nursery boxes and to paddy water by spray, drench, broadcast and 'pricking-in-hole' treatment. It is used against sucking insects such as whiteflies, plant bugs and leafhoppers.

Bispyribac-sodium (BPS)

IUPAC name: Sodium 2,6-bis[(4,6-dimethoxypyrimidin-2-yl)oxy] benzoate. Chemical class: Pyrimidinyloxybenzoic acid. Chemical structure: Figure 1. Product: Technical 95% a.i. Pesticide type: Herbicide. Uses: Control of grasses, sedges and broad-leaved weeds, especially *Echinochloa spp.*, in direct-seeded rice and weeds in non-crop situations.

Metribuzin (MBZ)

IUPAC name: 4-amino-6-terbutyl-3-methylsulfanyl-1,2,4-triazin-5-one. Chemical class: Triazinone. Chemical structure: Figure 1. Product: Technical 97.0% a.i. Pesticide type: selective systemic herbicide. Formulations: Sencor 70% WP. Uses: for pre and post-emergence control of many grasses and broad-leaved weeds in soya beans, potatoes, tomatoes, sugar cane, and cereals.
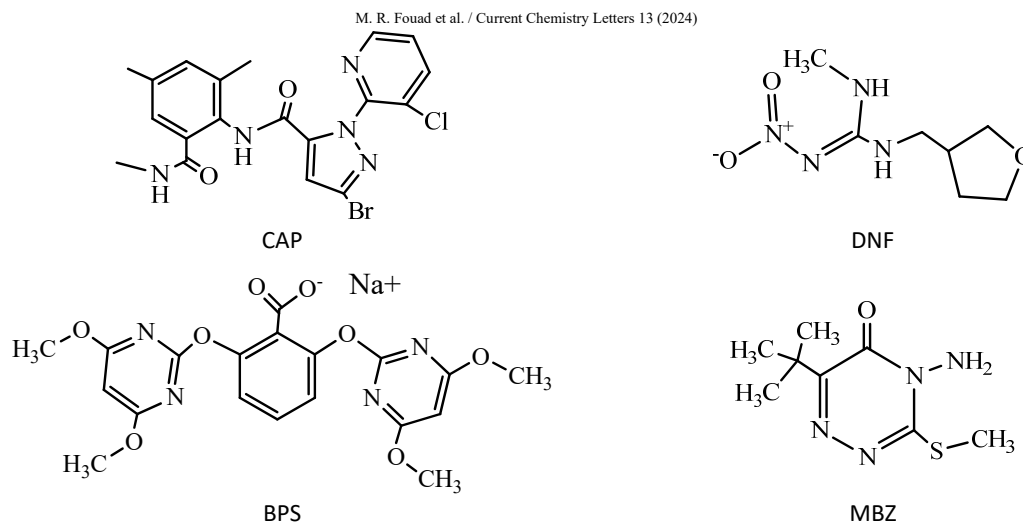
Fig. 1. Chemical structures of tested pesticides.

2.2. Tested soil

The samples were collected from the top layers of the soil profiles from different locations from Bangar Elsokar region, Alexandria, Egypt. The physical and chemical properties of tested soil were presented in **Table 1**.

Table 1. Physiochemical properties of the tested soil.

Soil type	Texture class	Organic matter (%)	pH	EC	Total carbonate (%)	Cations conc. (meq/L)	Anions conc. (meq/L)
Calcareous	Sandy loam	1.3	8.2	2.3	40.1	33.5	23.3

2.3. Determination of pesticides

Each pesticide standard solution (0.1-100 mg/mL) were prepared by the stepwise dilution of the pesticide stock solution (0.5 g/L). The tested pesticide concentrations in different experiments were analyzed by a UV-Vis Spectrophotometer (Thermo Corporation, Nicolet, evolution 100).

2.4. Sorption isotherm of tested pesticides

A sorption isotherm by soil was quantified using the batch equilibration technique. Experiments were carried out in duplicate with a sorbent mass to pesticide solution ratio of 1:5 for soil. Initial pesticide concentrations of in 1 to 50 μg/mL range were prepared in 0.01 M $CaCl_2$. The pesticide solutions were equilibrated with soil in 25-mL polypropylene centrifuge tubes. The tubes were shaken mechanically at 175 rpm at room temperature for 24 hours to achieve equilibrium and centrifuged at 4000 rpm for 12 min. The pesticide concentration in supernatants was determined by spectrophotometer at the proper λ_{max}. The pH values of 0.01 M $CaCl_2$ solutions were adjusted to 5, 7 and 9 with the help of 2N HCl or 2N NaOH, in the case of studying the effect of pH variation. The sorption process was also carried out at different temperatures (25 and 50 °C).[7,14,16]

2.5. Statistical analysis

Experimental data are presented as mean ± standard error and the statistical analysis was performed by the SPSS program (ver. 21.0, USA).[3,17]

3. Results

3.1 Effect of pH variation on tested pesticide sorption characteristics

The pH variation test was carried out the same way as the standard sorption experiments, but prior to the test the pH of the 0.01M $CaCl_2$ solution was adjusted to 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 sorption parameters are summarized in **Table 2**. They confirm that the extent to which the Freundlich isotherm exponent 1/n for the tested pesticides differs from 1 is dependent on their intrinsic physicochemical characteristics. The pH effect may be indicated by the sorption coefficient (Kd) calculated from dividing the amount sorbed by the corresponding equilibrium concentration. For instance, the sorption coefficient as the average values. Comparison of the adsorption behavior of different tested pesticides based on their Kd values and the

average of the adsorption, indicated that a direct relationship of Kd and percentage of the adsorption was recorded for all tested pesticides; CAP, DNF, BPS and MBZ in calcareous soil at different pH values 5, 7 and 9.

The sorption of CAP in the calcareous soil at the lowest pH (pH 5) was significantly higher than that at pH 7 and 9 particularly at the lower equilibrium concentrations, up to 25 μg/mL (Table 3 and Fig. 2). Regarding the average of the adsorption, the adsorption percentage of CAP were 38.2, 32.4 and 28.4 %, respectively. These results indicated that pH 5 slightly increased the average of the adsorption percentage compared to the adsorption at pH 7. Compared to the adsorption percentage CAP at pH 7, the pH 9 decreased. Whereas the sorption of DNF at pH 9 was lower than that at pH 5 and from equilibrium concentration of 8 μg/mL and pH 7 form equilibrium concentration of 2 μg/mL. The adsorption of DNF at pH 5 was lower than that at pH 7. Also, the adsorption precentages and Kd values of DNF confirmed this result. The adsorption of BPS at pH 9 was statistically significantly higher than that at pH 5 and pH 7. The average of the adsorption percentages, distribution coefficient values and Freundlich coefficient values of BPS were lowest at pH 7. Regarding the herbicide MBZ at pH 5 and pH 9, the sorption of MBZ was lower than that at pH 7 up to equilibrium concentration of 10 μg/mL, then the relation was inversed where, the adsorption of MBZ at pH 7 was the lowest one. The average values of the MBZ adsorption percentages were 47.0, 61.1 and 57.1 % at pH 5, 7 and 9, respectively. The K_F and Kd values were higher at pH 7 (**Table 2**).

Table 2. Freundlich and physical parameters of tested pesticides sorption in calcareous soil at different pH values

Pesticides	CAP			DNF			BPS			MBZ		
Parameter	pH 5	pH 7	pH 9	pH 5	pH 7	pH 9	pH 5	pH 7	pH 9	pH 5	pH 7	pH 9
Adsorption (%)	38.2	32.4	28.4	66.5	82.4	72.0	74.9	72.1	82.0	47.0	61.1	57.1
Kd	21.2	8.5	6.6	11.9	40.6	20.6	14.0	11.8	27.4	4.8	8.6	7.1
K_F	25.176	7.823	1.882	6.7781	17.94	34.92	25.915	21.585	41.607	0.4768	16.624	1.0214
1/n	0.494	1.046	1.735	1.2862	1.9191	0.4578	0.5762	0.6316	0.4698	1.9335	0.623	1.8251
R^2	0.985	0.959	0.942	0.8996	0.9247	0.9042	0.9588	0.9702	0.976	0.9946	0.8236	0.905

Table 3. Adsorption of tested pesticides (μg/g soil ± SE) in calcareous soil at different pH values

| Initial conc. (μg/mL)	CAP			DNF			BPS			MBZ		
	pH 5	pH 7	pH 9	pH 5	pH 7	pH 9	pH 5	pH 7	pH 9	pH 5	pH 7	pH 9
5	11.492 ±4.847	8.196 ±1.083	4.314 ±4.172	16.126 ±0.485	20.238 ±0.000	22.403 ±0.099	21.998 ±1.286	20.833 ±1.633	24.342 ±2.560	5.874 ±0.791	16.393 ±2.172	9.973 ±0.037
10	22.191 ±4.946	14.998 ±3.980	9.556 ±4.125	31.740 ±7.192	38.080 ±0.000	44.103 ±2.691	43.008 ±12.014	41.928 ±0.738	44.721 ±0.909	18.007 ±0.418	35.786 ±0.732	16.337 ±0.168
20	38.925 ±1.967	27.972 ±0.424	29.928 ±1.525	59.897 ±5.240	82.685 ±0.650	76.511 ±1.596	69.101 ±20.789	73.137 ±3.201	76.489 ±2.822	46.800 ±2.431	79.252 ±3.620	56.252 ±2.018
30	54.040 ±5.029	48.650 ±3.802	52.742 7.011	93.951 ±4.612	130.362 ±0.562	78.082 ±0.074	111.583 ±3.545	91.465 ±0.438	119.966 ±0.343	82.292 ±16.740	87.899 ±9.338	104.041 ±27.943
40	68.712 ±3.385	75.598 ±5.963	67.665 ±5.757	150.307 ±2.727	162.749 ±0.091	122.380 ±0.293	123.443 ±9.152	142.192 ±9.152	156.464 ±11.257	117.547 ±19.523	93.213 ±9.091	152.239 ±9.075
50	74.226 ±0.457	84.180 ±4.744	88.105 ±5.905	184.033 ±1.866	215.414 ±0.964	161.266 ±0.646	174.913 ±23.563	149.890 ±23.563	176.156 ±7.651	155.022 ±16.518	112.822 ±9.431	170.962 ±12.487
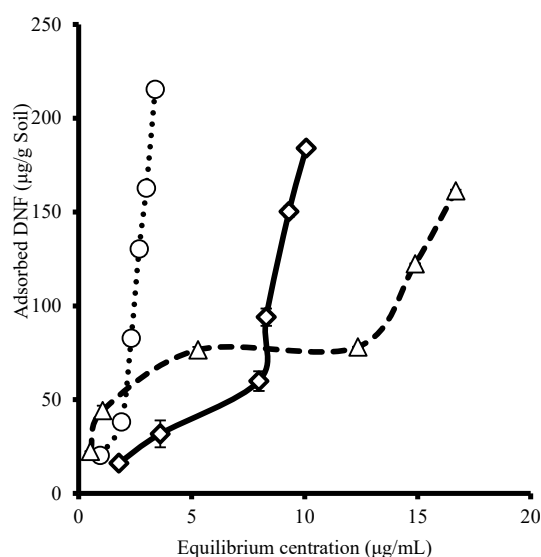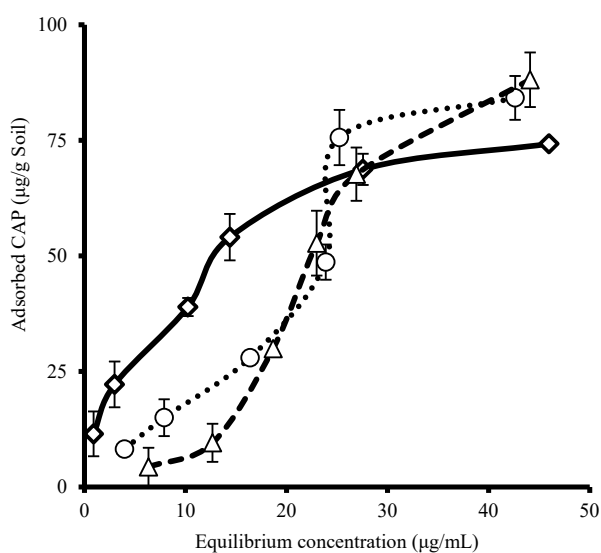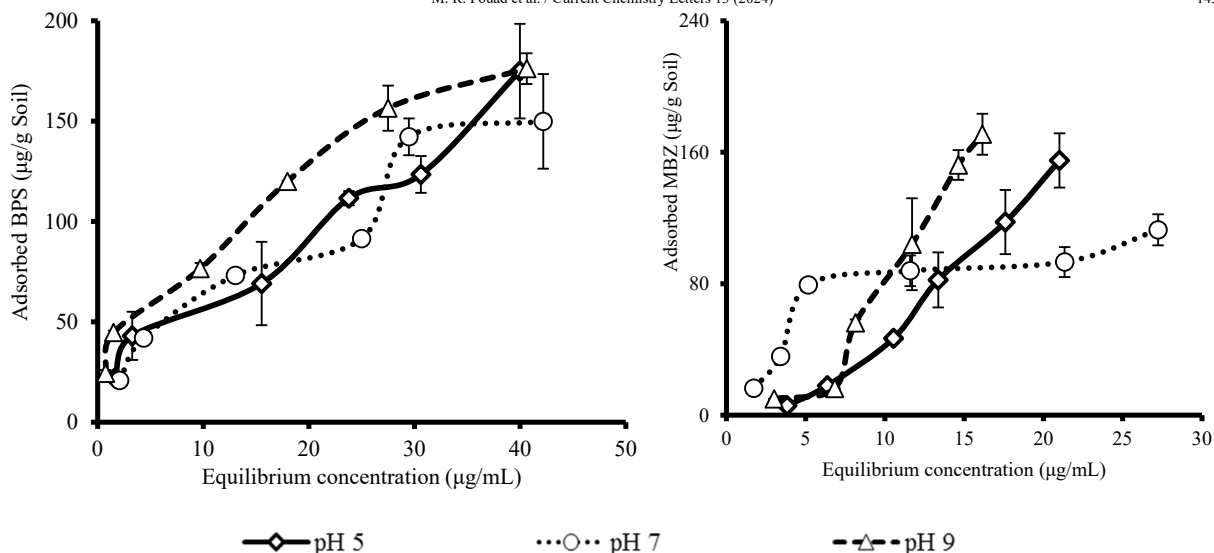
Fig. 2. Adsorption of tested pesticides (µg/g ±SE) in calcareous soil at different pH values

3.2 Effect of the temperature on pesticide sorption in soil

The adsorption of tested pesticides CAP, DNF, BPS and MBZ in calcareous soil at 25 and 50°C was studied (Table 4 and Fig. 3). The amount of CAP adsorbed by the soil was significantly influenced by the temperature particularly with the concentrations of 20 µg/mL and above. The adsorbed amount of CAP was decreased from 37% to 33% as the temperature was increased from 25°C to 50 °C. While no significant differences of adsorbed DNF were detected between 25°C and 50°C except at the concentration of 30 µg/mL. The adsorption percentage of DNF was decreased from 96 to 90% at 25 and 50°C, respectively. Data showed that the adsorption of BPS statistically decreases with temperature. The average of the adsorption was decreased from 65 to 60% at 25 and 50°C, respectively. Temperature increase from 25 to 50°C was found to reduce the adsorption of MBZ in soil. The average of the adsorption percentage was decreased from 30 and 18%.

The values of Freundlich adsorption coefficient (K_F), the Freundlich adsorption exponent ($1/n$) and correlation coefficient (R^2) for adsorption of CAP, DNF, BPS, and MBZ are presented in Table (5). The data from the adsorption behaviour of CAP, DNF, BPS, and MBZ in calcareous soil at different temperatures corresponded will with the Freundlich isotherm. The value of K_F for CAP was 0.011 at 25°C while 1.885 at 50°C. Whereas the $1/n$ values were more than unity (> 1.0), indicating relative increased adsorption of CAP with increasing initial concentration. The Kd values at 25 and 50°C were 3.65, and 2.66 for adsorption of CAP, respectively. These values indicate that CAP was strongly bound at 25°C. The value of Freundlich adsorption coefficient K_F is higher at 25 °C (125.78) than that at 50°C (41.288), indicate that the soil has a higher adsorption capacity for DNF at 25°C than at 50°C. In addition, the distribution coefficient, Kd, were 119.23 and 37.06 at 25 and 50°C, respectively. The Kd values of BPS in soil were 9.19 and 8.32 indicate that BPS was strongly bound at 25°C more than at 50°C. According to the $1/n$ values, particularly at 25°C it is suggested that the adsorption of BPS in soil is linear.

Table 4. Adsorption of tested pesticides (µg/g ± SE) in calcareous soil at 25 and 50°C

| Initial conc. (µg/mL)	CAP		DNF		BPS		MBZ	
	25ºC	50ºC	25ºC	50ºC	25ºC	50ºC	25ºC	50ºC
5	2.089 ±0.276	4.363 ±1.069	23.377 ±0.001	23.724 ±2.298	16.015 ±0.989	15.561 ±1.839	6.882 ±0.912	2.942 ±0.023
10	2.391 ±0.634	21.681 ±1.064	47.078 ±0.001	42.835 ±0.731	33.335 ±0.587	29.067 ±0.928	15.741 ±0.322	4.536 ±0.052
20	42.830 ±0.649	38.835 ±4.417	96.429 ±0.757	88.014 ±3.023	65.222 ±2.854	61.182 ±2.658	36.568 ±1.670	15.328 ±0.605
30	72.013 ±5.628	48.127 ±1.624	144.535 ±0.595	117.018 ±0.854	99.005 ±0.474	91.617 ±9.983	43.041 ±4.572	30.271 ±2.243
40	110.468 ±8.716	60.072 ±5.245	193.398 ±0.108	187.253 ±0.535	131.253 ±8.397	121.664 ±10.699	77.265 ±7.535	42.147 ±2.865
50	151.256 ±8.524	87.263 ±7.126	241.883 ±1.083	242.535 ±3.010	160.073 ±8.334	147.152 ±7.762	123.099 ±10.290	72.175 ±2.231
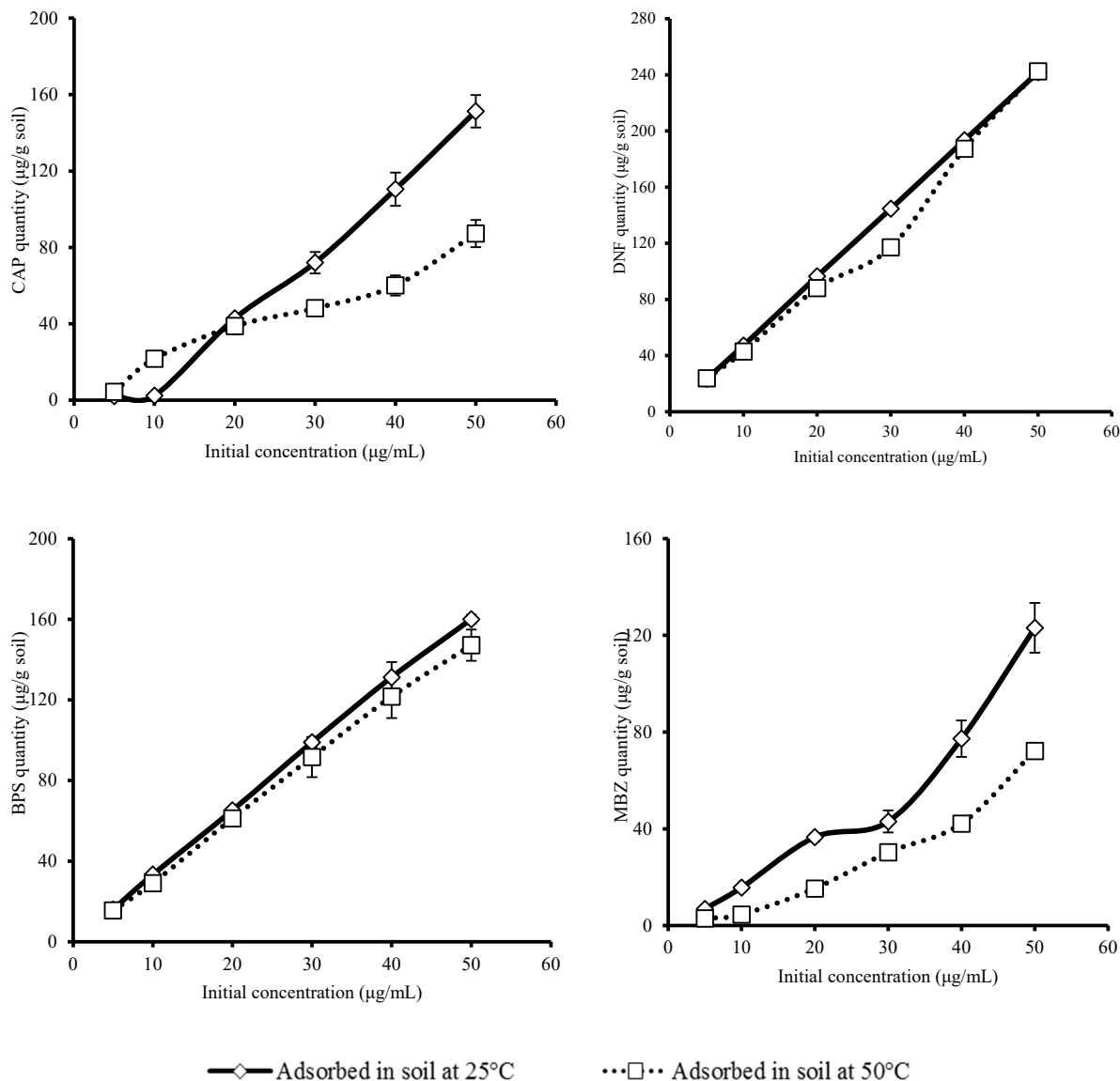
Fig. 3. Adsorption of tested pesticides (μg/g ± SE) in calcareous soil at 25 and 50°C

Table 5. Freundlich parameters of tested pesticides adsorption in calcareous soil at 25 and 50°C

Parameters	K_F		1/n		R^2		Kd	
Pesticides	50°C	50°C	25°C	50°C	25°C	50°C	25°C	50°C
CAP	0.011	1.8845	3.0983	1.105	0.8243	0.8226	3.646	2.664
DNF	125.78	41.288	1.4892	0.8249	0.9766	0.8937	119.230	37.059
BPS	8.2244	7.7772	1.056	1.0334	0.9973	0.9971	9.191	8.317
MBZ	1.2988	0.2313	1.2768	1.5369	0.9272	0.9579	2.798	1.136

The thermodynamic parameters summarized in Table (6). The negative ΔG° indicated that the adsorption of CAP was spontaneous at different temperatures. The standard enthalpy change ΔH° values were positive (1.879 kJ/mol), indicating the endothermic nature of the reaction. There was an increase in the entropy of the CAP-soil systems as shown by the positive values of ΔS°. The values of the standard free energy changes (ΔG°) were negative values of DNF. This indicates that the adsorption of DNF is spontaneous with a high affinity. It also suggests a high persistence and resistance to degradation of DNF. Whereas the ΔH° value was negative and the standard entropy change (ΔS°) was positive value. The values of the standard free energy change (ΔG°) of the BPS adsorption reaction at 25 and 50°C were -22.66 and -24.64 kJ/mol, indicating a physical and spontaneous sorption process. The standard free energy change (ΔG°) of the MBZ adsorption was negative under 25 and 50°C. The negative values of the standard enthalpy change (ΔH°) show that MBZ

interaction with soil is exothermic and the products are energetically stable with a high binding of the herbicide to the soil sites. There was an increase in the entropy of the MBZ-soil system as shown by the positive values of $\Delta S°$.

Table 6. Thermodynamic parameters of tested pesticides adsorption in calcareous soil at 25°C and 50°C

Thermodynamic parameters	CAP		DNF		BPS		MBZ	
	25°C	50°C	25°C	50°C	25°C	50°C	25°C	50°C
K_o (mmol /g)	7476	7928	13721	10054	9389	9657	7174	3973
$\Delta G°$ (J/mol)	-22098	-24110	-23603	-24748	-22663	-24640	-21996	-22254
$\Delta H°$ (J/mol)	1879.2		-9953.8		900.3		-18918.0	
ΔS (J/mol/K)°	80.5		45.8		79.1		10.3	

4. Discussion

It has been shown that the effect of pH on pesticide sorption differ from soil to soil and from compound to other. Sorption study with 11 pesticides in 13 types of soil showed that the soil characteristics including pH influenced the adsorption coefficient.[18] The sorption reactions of ionic organic compounds onto natural particles are affected by the physicochemical characteristics in the adsorption system such as pH.[19,20] At applicable environmental pH ranges pesticides with a very low or very high pKa will be present primarily as one type of species; their sorption behavior is unlikely to be dependent on soil pH as the pH value at which they would dissociate would not occur in the environment.[21] Our results indicated that the influence of the adsorption process in soil for MBZ (pKa = 1) and DNF (pKa = 12.6) was lower compared to that for BPS (pKa = 3.1) and CAP (pKa = 10.9). The sorption bahaviour of ionisable pesticides is strongly dependent on the soil pH. There are three main types of sorption behaviour that have been observed to occur as a function of soil pH. With increasing soil pH, sorption most often either; decrease (it is usually only observed for weak basic compounds) or increases (it occurs for weak bases that are adsorbed as neutral molecules or by molecules that form complexes with cations).[12] A change in pH may change the charge properties of ionizable pesticides resulting in a substantial change in their sorption in soils. With a pKa value, the ionizable pesticide is present in solution primarily in the molecular form at pH 5 < pKa value and as an anionic species at pH 5 > pKa value. The molecular form of the pesticide clued be more effectively sorbed than its anionic species.[22] The non-ionic pesticides probably interact with the non-ionic parts of the soil organic matter surfaces (hydrophobic bonding), which are probably not much influenced by the pH of the soil.[23] In addition, an increasing pH may enhance release of native organic matter from the soil into solution and therefore result in decreased pesticide adsorption.[24] Adsorption of anionic molecules by soil is largely dependent on soil components with pH dependent charges. The acidic pesticides exist as either anions or neutral molecules depending upon whether the soil solution pH is below or above the pKa. Theoretically, anionic and neutral forms will be present in equal amounts when the pH is equal to the pKa.[25] The organic matter, and to a lesser extent clay, have pH-dependent charges.[26] Organic matter contains carboxylic acid and phenolic groups that have pH-dependent ionization with pKa values of approximately 5.2.[27] Soil pH also affects pesticides ionization. At pH values greater than their pKa values, acidic pesticides exist predominantly in the anionic form and are repelled by negatively charged soil colloids.[7] Because the effective acidity at the soil colloid surface is believed to be several units lower than in bulk solution an increase in pesticide molecules present in the nonionic or may not initially occur when the solution pH is equal to the pKa of the pesticide, but rather at a solution pH one to two unit above the pKa and lower.[9,] As soil pH increases, increasing concentrations of weak acidic herbicides should be available for root uptake which concentration increased phytotoxicity to sensitive plants.[9]

The adsorption data of insecticides; CAP and DNF and herbicides; BPS and MBZ in calcareous soil at 25 and 50 C° are in close agreement with the Freundlich model. The adsorption isotherms and quantities, Freundlich parameters and distribution coefficient illustrated that the increasing temperature reduces the adsorption of tested pesticides in calcareous soil. In addition, the $\Delta G°$ values of the adsorption process were negative at 25 and 50°, indicating the spontaneity of the process. The standard enthalpy change was indicated to the adsorption of CAP is endothermic process while, the adsorption of MBZ is exothermic reaction. Also, low values of $\Delta H°$ pointed toward physical adsorption mechanism. This observation confirms the results of the adsorption experiments at different temperatures and agrees with results reported by Memon et al, for the adsorption of methyl.[28,29,30,31]

5. Conclusion

A direct relationship of Kd and percentage of the adsorption was recorded for all tested pesticides; CAP, DNF, BPS and MBZ in tested soil at different pH values 5, 7 and 9. The affecting of the adsorption process by the pH variation depends on the pesticide type. The pH 9 decreased the adsorption of CAP and DNF compared to pH 5 and 7. In contrast, the pH 9 increased the adsorption of BPS and MBZ. The highest adsorption was at pH 5 for CAP, at pH 7 for DNF and at pH 9 for BPS and MBZ. The influence of the adsorption process for MBZ (pKa = 1) and DNF (pKa = 12.6) was lower compared to that for BPS (pKa = 3.1) and CAP (pKa = 10.9). The number of tested pesticides adsorbed by the soil was significantly influenced by the temperature. Freundlich parameters and distribution coefficient illustrated that the increasing temperature reduces the adsorption capacity and affinity of the tested pesticides. The S shape of the isotherm at both temperatures (1/n > 1), suggests that the adsorption of DNF and MBZ increases with increasing the initial concentration within the tested range. As the temperature was increased 25 to 50°C, the average adsorption was decreased from 37% to 33% for CAP; from

96 to 90% for DNF; from 65 to 60% for BPS and from 31 to 18% for MBZ. The thermodynamic parameters summarized that the negative values of the standard free energy changes ($\Delta G°$) were obtained therefore, the adsorption of all tested pesticides in calcareous soil was spontaneous and the small negative values indicate the adsorption is physical in nature involving weak forces of attraction. There was an increase in the entropy of the tested pesticides-soil systems as shown by the positive values of $\Delta S°$.

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