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# Adsorption and Desorption Characteristics of Bispyribac-Sodium Pesticide in Eight Soil in South of Iraq

Layla Balasem Almalike, Anis A. Al-Najar, Zaki N. Kadhim

**Abstract-** Kinetic batch experiments were used to study the adsorption-desorption behavior of bispyribac-sodium (Herbicide, pyrimidinyl oxybenzoic acid) in soils from different locations in south of Iraq, Nasiriya, Amara, and mostly Basrah soils to study their physico-chemical properties which are regarded as responsible for adsorption-desorption properties, such as moisture content, loss on ignition, pH, organic matter contents, particle size distribution, analysis and exchangeable cations and anions. The kinetic study of adsorption processes were performed with four different initial concentrations of each pesticide, 3, 5, 10, and 15 µg ml$^{-1}$ ( ratio1:10 ). The kinetic experiments were carried out after equilibration for 0.5, 1, 2, 3, 4, 6, 24, 48, and 72 hours for each pesticide. Desorption was evaluated using the samples in the tubes after the adsorption tests. The quantification of the linear adsorption coefficient ($K_d$) for soils plays a vital role to predict fate and transport of pesticides in the soil-water environment. The equations for kinetic studies of the investigated adsorption processes were first order rate law, Elovich equation, and power function equation. The isothermal models Linear, Freundlich, and Langmuir were applied to describe the adsorption-desorption affinities to the soils. Standard thermodynamic parameters, Gibb's free energy ($\Delta G^0$), change in enthalpy ($\Delta H^0$) and change in entropy ($\Delta S^0$) and equilibrium constant, $K_0$, have revealed spontaneous and exothermic nature of adsorption process. The gained results indicate the phenomena of physical adsorption. The effect of organic matter and clay content on the adsorption of bispyribac-sodium in soil samples was studied. Also the adsorption effect caused by surfactants like cationic PAM, anionic PAA, and nonionic PVA on the solid liquid interface was investigated. Batch adsorption technique was employed for the metal ions adsorption in soils. The amount of metal ions adsorbed increased with time. Copper ion has more adsorption rates than nickel and iron ions.

**Index Terms**— batch experiments, bispyribac-sodium, adsorption-desorption process, $K_d$, $\Delta G^0$, $\Delta H^0$,$\Delta S^0$, equilibrium constant, surfactant.

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## INTRODUCTION

The term soil structure defines the size, shape, and arrangement of the primary soil particles and the aggregates they form[1] . The properties of soil result from the net effect of the interactions of materials[2]. Soils are rarely composed of a single size class of particles; they are mixtures of different size classes. However, one or two size classes usually dominate the physical behavior of the soil[3]. There are two types of particles, primary and secondary particles. Individual discrete particles are called primary particles and their aggregates are known as secondary particles. Primary particles with the maximum "effective diameter" of 2 mm are classified into three categories-sand, silt, and clay[3].

Adsorption is the primary process of how the soil retains a pesticide[4]. Adsorption is due to the attraction or repulsion between a solid surface and, in this case, a vapor or solution. This attraction or repulsion is the resultant of the interaction between the fields of force emanating from the surface of the adsorbent and the molecules or ions of the adsorbate[5]. The adsorbing species, usually an organic compound, is called the adsorbate, and the solid, usually soil, to which the adsorbate is attracted, is known as the adsorbent. This attraction results from some form of bonding between the chemical and adsorption receptor sites on the solid[6]. Adsorption of pesticides to soil components has been extensively studied by the classical batch equilibration method[7]. Batch equilibration was used also to measure adsorption behavior of colloid materials[8]. This method involves addition of a range of solute concentrations to a known amount of soil at a constant temperature, and agitating the mixture until equilibrium conditions are achieved. Then, the equilibrium concentration in the liquid phase($C_e$) is measured, and the equilibrium concentration of the solute in the solid phase($C_s$) is usually calculated by mass balance considerations. The plot of $C_s$ versus $C_e$, the so called adsorption isotherm[9]. Pesticides constitute a heterogeneous category of chemicals specifically designed for the control of pests, weeds or plant diseases[10]. These pesticides are mobile in the environment and this movement is beneficial if the pesticides are used for few decades. Concerns have been raised over the impact of agricultural use of pesticides on the environment due to their extensive use throughout the world[11]. Bispyribac-sodium ISO is the common name for sodium 2,6-bis(4,6-dimethoxypyrimidin-2-yloxy)benzoic acid (IUPAC) is a selective herbicide of the group of pyrimidine-benzoates. Its structure is shown in Figure ( 1 )[12]. Due to the fact that is the bispyribac-sodium, a vari

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- *Layla Balasem Almalike, Southern Technical University Technical Eng.*
- *College/Brash, Petrochemical Engineering Dept., Layla_almalike@yahoo.com*
- *Anis A.Al-Najar & Zaki N. Kadhim, University of Basrah, College of Science, chemistry Dept.*

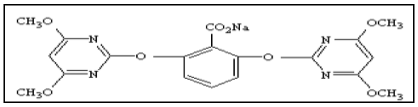


Figure1: Structural formula of Bispyribac-sodium

ant of bispyribac, is used in the formulated product. Bispyribac-sodium, is a class of pyrimidinyloxybenzoic acid herbicides. The only other compound in this class is pyriminobac. Its mode of action is by branched chain amino acid synthesis inhibition. In sensitive plants, bispyribac-sodium is adsorbed through the feat surface and runs throughout the location of the plant. In rice plants, bispyribc-sodium is rapidly metabolized to non-herbicidal products. Bispyribac sodium is broken down by microbes and has a half-life 42-115 days[13].

## 2. Material and methods

All chemicals and solvents used in these experiments were very pure and purchased from Aldrich, Germany. Stock solutions of Bispyribac sodium were equally mixed and diluted with methanol to make spiking mixture and working standard solutions. Standard solutions were stored at 4 °C in the dark[14]. Appropriate volumes of the standard stock solution were diluted by water to obtain the desired concentrations 3, 5, 10, and 15µg ml$^{-1}$. Pesticide experiment for calibration and a control in two replicates concentrations were done with methanol: water solution( 70:30% ). The absorbance's were measured at 246 nm against blank solution. A linear relationship was obtained between the absorbance and the concentration of bispyribac sodium within the range (2-15 ppm).

### 2.1. Soil Analysis

Eight fresh soil samples were selected from the top layer (0-15cm depth), are which supposed to have the highest organic content. After the removal of stones and debris, the soil was air-dried under shade, ground, sieved through 2 mm mesh screen and stored in closed black glass container. These soils were used for adsorption-desorption studies[2]. Several tests have been conducted in Table 2.

### 2.2. Organic Carbon content

One gram of air-dried soil was added to 500 ml ( 1 N ) potassium dichromate solution followed by introducing 20 ml of concentrated sulfuric acid added to the suspension, then allowed to stand for 30 minutes after which the organic carbon is oxidized by the dichromate $Cr_2O_7^{2-}$ , which is reduced to chromic, $Cr^{3+}$ . Then addition of 200 ml de-ionized water and 10 ml concentrated orthophosphoric acid was done. After cooling the mixture, 10-15 drops of diphenyl amine indicator was added, then the used amount of dichromate was determined by titration with 0.5 M ferrous ammonium sulfate solution with continuous stirring with the aid of Teflon-coated magnetic stirring bar, until the color changed from violet-blue to green at which the ferrous ion $Fe^{2+}$ is oxidized to ferric ion Fe3+.

To find the exact end point, the color of the sample was compared with that of the blank solution. The same procedure was followed with two blanks ( with all reagents but without soil ). The percentage of the organic matter in soil was calculated from the following equations[15].

$$M=10/V_{blank} \ldots\ldots (1)$$

$$\%\text{Oxidizeable organic carbon(TOC)(w/w)}=\{[V_{blank}-V_{sample}]x10^{-3}xM\}\ \text{Wt of soil X 100} \ldots\ldots (2)$$

$$\%\ \text{Total organic carbon (w/w)}=1.334*\%\text{oxiaizable organic carbon} \ldots\ldots (3)$$

Where : M = Molarity of ferrous ammonium sulfate solution ( Approx. 0.5 M ). Vblank = Volume of ferrous ammonium sulfate solution required to titrate the blank (ml), Vsample = Volume of ferrous ammonium sulfate solution required to titrate the sample (ml)

Wt = Weight of air-dry soil ( g ), 3 = is the equivalent weight of carbon. The factor 1.334 is used to calculate the TOC which is approximate; they may vary with soil depth as well as the types of soils[15].

### 2.3. Organic matter content

Estimation of organic matter from Loss on ignition(LOI) is done by regression analysis. Eighty soils were selected. The resulting equation is used to convert % LOI values into % organic matter. The equation is[16]:

$$\%\ \text{Organic Matter} = \%\ \text{LOI X } 0.956 \ldots\ldots (4)$$

### 2.4. Cation exchange capacity

Many minerals in soil are negatively charged and as a consequence, then can attract and retain cations. Since Cation Exchange Capacity ( CEC ) is a reversible process, it can be held in the soil and not lost through leaching, and can subsequently be released for crop uptake. Certain organic compounds also contribute to CEC. Additionally, CEC is influenced by soil pH. A certain portion of the total negative charge is permanent, while a variable portion is pH-dependent. The most involved saturation of the soil with an index cation $NH^{4+}$ removal by washing of excess cation, and subsequent replacement of the adsorbed index cation by another cation $Na^+$ and the measurement of the index cation can be detected in the final extract[17].

Higher cation exchange capacity values reflect the dominance of 2:1 clay minerals, while lower values reflect the presence of 1:1 clay minerals, so the basic exchangeable cations, $Na^+$ commonly occur in soil are determined as follow: 5 g of soil was placed in a 50 ml conical flask followed by the addition of 25 ml of ammonium acetate ( $NH_4C_2H_3O_2$ ) with continuous shaking for 10 minutes, then centrifuged until the supernatant liquid was clear. The supernatant was decanted into a 100 ml volumetric flask. Three additional extractions were made in the same manner. The combined extracts diluted to 100 ml with $NH_4C_2H_3O_2$. The solutions was then mixed and analyzed by using flame photometer for the determination of cations $Na^+$ as CEC and as $Na^+$ alone exchanged in the solution[18]. The results of the analysis were summarized in equation 5:-

$$CEC(meq/100g) = \left(\frac{meq}{L}\right) Na^+ \cdot \frac{A}{Wt} \cdot \frac{100}{1000} \ldots\ldots (5)$$

Where: A = Total volume of the extract ( ml ), Wt = Weight of the air-dry soil ( g ).

Table 1: Soil pH, texture, moisture, Organic carbon and Organic matter for soil before pollution.

| Soil Properties | $S_1$ | $S_2$ | $S_3$ | $S_4$ | $S_5$ | $S_6$ | $S_7$ | $S_8$ |
|---|---|---|---|---|---|---|---|---|
| pH value | 7.67 | 8.34 | 7.84 | 8.19 | 8.21 | 7.82 | 8.03 | 7.83 |
| Clay (%) | 43.01 | 43.01 | 51.87 | 53.56 | 25.25 | 22.45 | 22.79 | 49.41 |
| Silt (%) | 52.49 | 52.49 | 52.49 | 45.30 | 22.10 | 25.67 | 74.31 | 34.08 |
| Moisture content | 1.95 | 2.10 | 1.49 | 5.90 | 3.66 | 1.43 | 1.49 | 5.90 |
| Organic Carbon % | 0.13 | 0.38 | 0.19 | 1.02 | 0.32 | 1.98 | 0.19 | 1.02 |
| Organic matter % | 6.697 | 9.321 | 4.863 | 2.373 | 0.434 | 4.525 | 4.863 | 2.373 |
| CEC(meq100g$^{-1}$ ) | 43.13 | 8.94 | 1.98 | 5.40 | 0.118 | 10.87 | 7.02 | 10.83 |

### 2.5.Adsorption study

#### 2.5.1. Kinetic study

The adsorption kinetic study was carried out in batch mode using 10 ml centrifuge tubes with Teflon screw caps with (1 g) of solid: solution mass ratio of (1:10) and 1 ml of 3, 5, 10, and15 $\mu g\ ml^{-1}$ of technical bispyribac sodium solution. The studies were first conducted in duplicate for all soils, without any herbicide, on an orbital shaker for a period of 24 h at room temperature (25 ± 10C). Then to each test tube the appropriate concentration of herbicide was added. After equilibration for 0.5, 1, 2, 3, 6, 24, 48, and 72 h, the suspension was then centrifuged for 30 minutes at 3500 rpm, and 1 ml aliquot of each clear supernatant solution was removed and analyzed on UV-Visible spectrophotometer [19].

#### 2.5.2. Desorption

After completion of the adsorption study process, the entire reaction mixture was centrifuged and the supernatant in the conical flask was decanted carefully and analyzed for the residual bispyribac-sodium concentration. The same amount of decanted supernatant was replaced with different eluents. deionized water and methanol. The flasks were then kept in an orbital shaker at 3500 rpm for a period of 24 h at $25^0$C. Soils were left for 0.5, 1, 2, 3, 6, 24, 48, and 72 h to attain the desorption equilibria. After 24 h, 1 mL of sample was withdrawn from each flask and analyzed for bispyribac-sodium concentration using UV-visible spectrophotometer [20].

#### 2.5.3. Effect of pH on adsorption isotherm

One gram of air-dried soil was mixed with 10 ml of buffer solution with pH values of 3, 7, and 9 for each of bispyribac-sodium. The exact amount of pesticide volume was adjusted to reach 10 $\mu gl^{-1}$ concentrations in 15 ml Stopper centrifuge tube for each soil adsorption experiments was used, with shaking. The suspensions were centrifuged for 20 min. The amount of pesticide in supernatant was determined by UV. The corresponding pH of the supernatant was then measured. Thus variations in pesticide adsorption with pH were studied by modifying the soil suspension pH[21].

#### 2.5.4. Effect of temperature

The experiments were carried out in the dark with an initial concentration of 3, 5, 10, 15 $\mu gl^{-1}$ for bispyribac-sodium. The duplicates sample of air-dry soil were equilibrated with a minimum volume of de-ionized water for 24 h before the day of the experiment. Afterwards a certain volume and concentration were adjusted as motioned before adsorption kinetic of the stock solution for each of the studied pesticide. So each test tube was placed in a thermostated shaker at 15, 25, and $350\pm1^0$C. The suspension was then centrifuged after different intervals of time, for 20 min at 3500 rpm, and then 1 ml of the clear supernatant was removed and analyzed by UV [22].

#### 2.5.5. Pesticide surfactant suspension

The amount of each studied pesticide adsorbed in the presence of cataionic, anionic and nonionic surfactants was determined by using the batch equilibration technique. The selected surfactants comprised cationic polyacrylamide ( PAM ), the anionic polyacrylic acid ( PAA), and nonionic polyvinyl alcohol ( PVA ) surfactants. Four concentrations of each pesticides 3, 5, 10, and 15 $\mu gl^{-1}$ were used. A 24 h batch equilibrium experiment was conducted to compare and contrast differences in adsorptive properties of bispyribac-sodium.

A surfactant concentration of 3, 5, 10, and 15 $\mu gl^{-1}$ were used and air-dried soils were weighed into 10 ml stoppered centrifuge tubes, the soils were then treated with the same ratio as mentioned before the solutions of surfactants were equilibrated by shaking for 24 h for pesticides in mechanical shaker thermostated at $25^0$C the time had previously been confirmed to be sufficient for equilibrium to be reached. Following equilibration, the suspensions were centrifuged for 30 min at 3500 rpm. To determine the pesticide concentration at equilibrium, a 1 ml aliquot of clear supernatant solution was removed and analyzed by UV. All measurements were carried out in duplicate. The same experiments done before for bispyribac-sodium were carried out. [23].

#### 2.5.6. Effect of metal ions

The ionic strength of the soil solution has been observed to influence the sorption behaviour of ionisable compounds; variations in ionic strength appear to have a limited effect on the sorption behaviour of neutral compounds. In the present study, different salt solutions, including $CaCl_2$, $FeSO_4$, $NiCl_2$, have been used to assess the effect of electrolyte composition on pesticide sorption behaviour. These variations can strongly affect the sorption behaviour of ionic molecules. A negative relationship between ionic strength and sorption has also been observed[24]. The same experiments done before for bispyribac-sodium were carried out. [25].

### 3. Results and Discussion

#### 3.1. The effect of time on concentration of bispyribac-sodium

Figure 2 represents the concentration of control solution during the course of the batch experiments for Bispyribac-sodium. It is evident that there was no significant losses of pesticide from the solution during the experiment by the equipment that used[26].

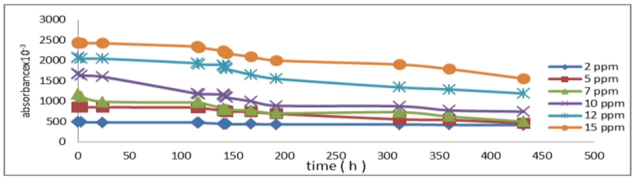
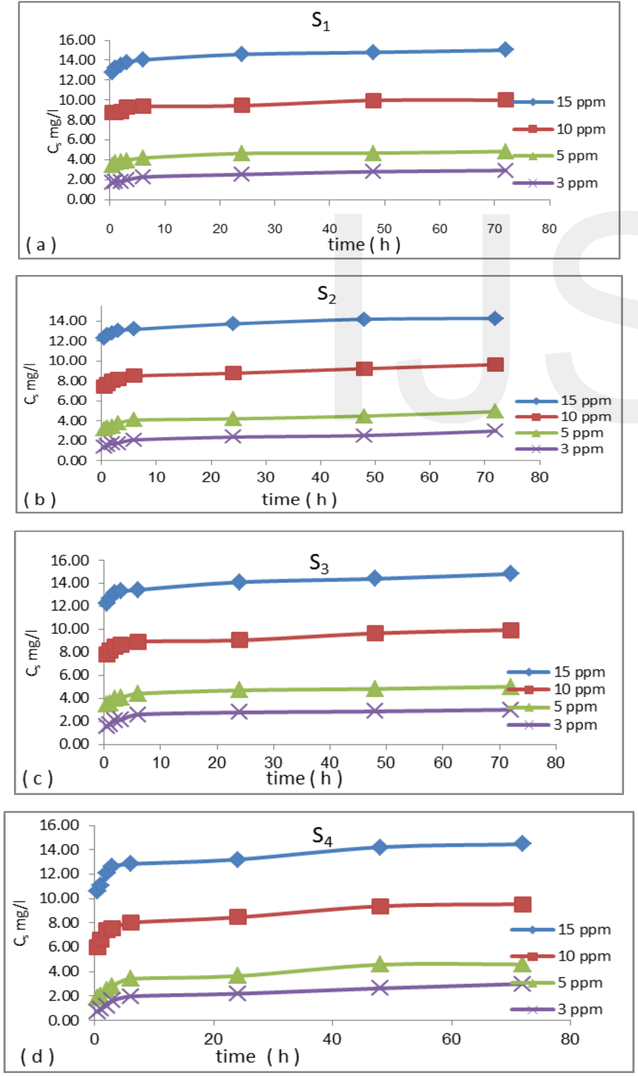


Figure 2: Variation of absorbance with time for Bispyribac-sodium.

#### 3.2. The effect of concentration of bispyribac-sodium on adsorption of soils

Equilibrium was defined as the bound concentration which varied by less than 5% between two consecutive time measurements. Equilibrium for soil system depends on the temperature of the solution and not on the pressure of the air or the composition of the system which was fixed for any given temperature in which a solid is in equilibrium with its solution. The mentioned figure 3 showed an extremely rapid rate of the pesticide being removed from solution within the first few hours of the 24 h sorption experiments. Whilst, a second phase of slow sorption appeared to occur over the remaining 48h of the experiment, the duration of which presides any definite conclusions on long term sorption phenomena.

Adsorption was increased with concentration, the initial step is characterized as rapid and low energy while the second step is slow and high energy accompanied by slow diffusion to sites within the soil matrix. This second step probably has a physical origin and corresponds to diffusion through natural organic matter and intraparticle nonporous of the soil[26]. The rapid phase is most likely the result of adsorption on surface sites of organic matter, clay colloids, and soil organic matter colloid complexes. The rapid phase of sorption was regarded to be reversible, resulting in sorption and desorption partitioning coefficients that are practically equal. The more gradual phase of sorption probably results in diffusion of pesticides into three-dimensional soil structures[27]. This suggests that the 24h "equilibrium" distribution coefficients may be adequate to characterize the sorption of these chemicals in the field. So sorption coefficients which were derived by using batch techniques that give the reproducible results are unaffected by losses arising from the sorption to the experimental apparatus[28].



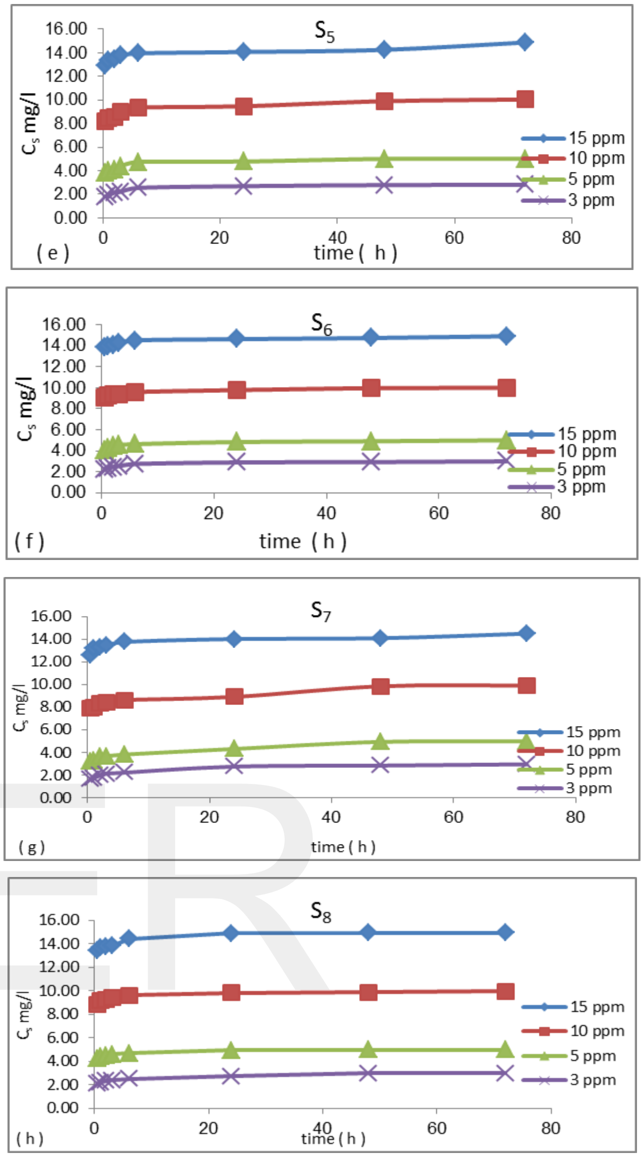


Figure 3: Variation of concentration with time for adsorption of Bispyribic-sodium on selected soil samples (a) $S_1$, (b)$S_2$, (c)$S_3$, (d) $S_4$, (e)$S_5$, (f)$S_6$, (g)$S_7$, and (h)$S_8$.

### 3.3. **Kinetic study of adsorption on soils**

Kinetics of pesticide-soil interactions have been described by a variety of empirical mechanistic models, these include simple one-site linear or nonlinear kinetic models, two-site, sorption models, and several others. The array of kinetics equations used to describe kinetics of soil-pesticide interactions include zero-, first-, and second order[29]. Sorption rate constants were estimated by using the first order rate expression for the pesticide[30], which can be formulated as :-

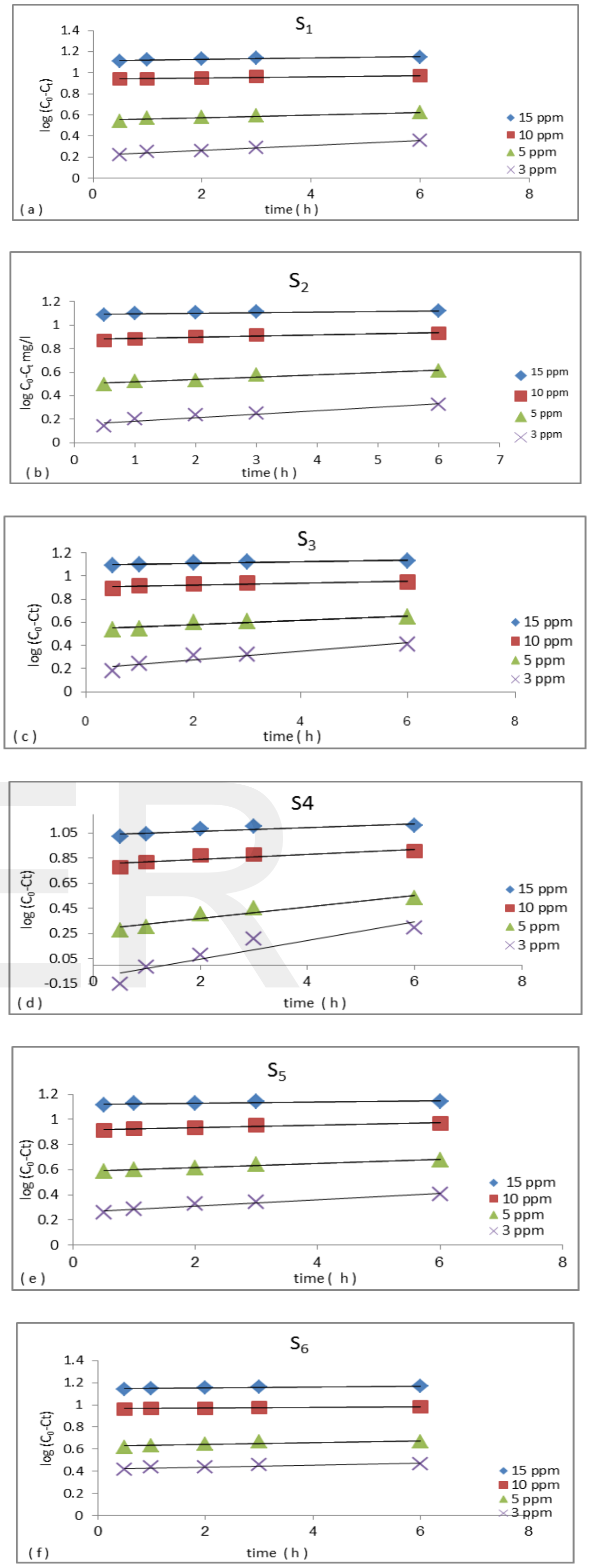
$$C_t = C_0 e^{-K0t} \quad \ldots\ldots (6)$$

$$K_0 = \left(\frac{2.303}{t}\right) \log \left[\frac{C_0}{C_0 - C_t}\right] \quad \ldots\ldots (7)$$

Where $K_0$ is the rate constant ($h^{-1}$), t the time (h), $C_0$ the concentration of pesticide added (μg $ml^{-1}$) and $C_t$ the amount adsorbed ($\mu g\ ml^{-1}$) at time t. In all cases, first order equation provided satisfactory fit for the data by linear plots of $\log C_0-C_t$ against t[31]. The calculated values of $k_0$ were summarized in Table 2. Figure 4 illustrates the final results which supports that the adsorption of the studied pesticides followed first order kinetics; such results are in accordance with those obtained for other system. The calculated $K_0$ values were oscillated from 0.22 to 1.39. This can be attributed to the value of octanol water partition coefficient $\log K_{ow}$ 0.0932 for Bispyribac-sodium. The Standard error ( S.E ) values were from 0.0001 to 0.079. The values of the rate constants follow the trend: $S_6 > S_8 > S_1 > S_5 > S_3 > S_2 > S_7 > S_4$ were in the order. The adsorption rate constant and amount adsorbed are not constant but rather increased to some extent with an increase in the organic matter content of soil indicating that the adsorption occurred via organic matter and also it depends on the chemistry of the organic matter.

Table 2: Adsorption rate constants calculated for bispyribac-sodium on the selected soil samples.

| Soils | ppm | K(calc $h^{-1}$) | S.E | $R^2$ |
|---|---|---|---|---|
| $S_1$ | 3 | 0.46 | 0.023 | 0.984 |
| | 5 | 0.68 | 0.014 | 0.871 |
| | 10 | 1.12 | 0.006 | 0.837 |
| | 15 | 1.23 | 0.007 | 0.815 |
| $S_2$ | 3 | 0.39 | 0.030 | 0.910 |
| | 5 | 0.58 | 0.020 | 0.733 |
| | 10 | 0.76 | 0.010 | 0.885 |
| | 15 | 0.93 | 0.005 | 0.759 |
| $S_3$ | 3 | 0.48 | 0.039 | 0.900 |
| | 5 | 0.69 | 0.020 | 0.873 |
| | 10 | 0.88 | 0.010 | 0.814 |
| | 15 | 0.95 | 0.008 | 0.702 |
| $S_4$ | 3 | 0.22 | 0.079 | 0.649 |
| | 5 | 0.30 | 0.047 | 0.915 |
| | 10 | 0.56 | 0.023 | 0.745 |
| | 15 | 0.72 | 0.016 | 0.735 |
| $S_5$ | 3 | 0.56 | 0.025 | 0.943 |
| | 5 | 0.86 | 0.016 | 0.972 |
| | 10 | 0.97 | 0.010 | 0.910 |
| | 15 | 1.10 | 0.006 | 0.968 |
| $S_6$ | 3 | 0.81 | 0.009 | 0.968 |
| | 5 | 0.99 | 0.010 | 0.712 |
| | 10 | 1.32 | 0.004 | 0.937 |
| | 15 | 1.39 | 0.005 | 0.969 |
| $S_7$ | 3 | 0.07 | 0.033 | 0.879 |
| | 5 | 0.60 | 0.015 | 0.798 |
| | 10 | 0.85 | 0.009 | 0.815 |
| | 15 | 1.03 | 0.006 | 0.778 |
| $S_8$ | 3 | 0.31 | 0.007 | 0.986 |
| | 5 | 1.11 | 0.0001 | 0.910 |
| | 10 | 1.26 | 0.0002 | 0.822 |
| | 15 | 1.25 | 0.006 | 0.795 |



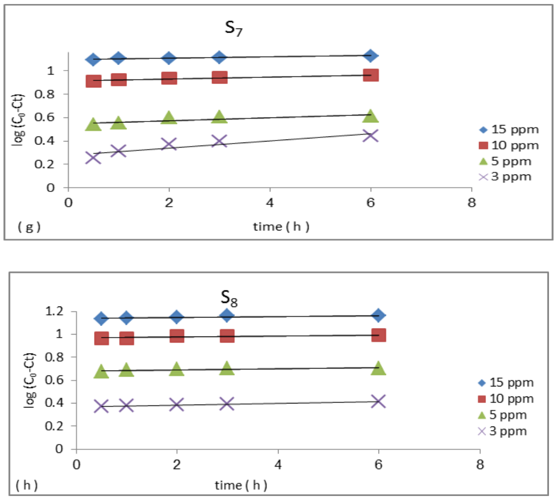


Figure 4: Application of 1st order rate law for Bispyribac-sodium on the selected soil samples (a) $S_1$, (b) $S_2$, (c) $S_3$, (d) $S_4$, (e) $S_5$, (f)$S_6$, (g)$S_7$, and (h) $S_8$.

### 3.4. Desorption Kinetics

Desorption of pesticides was studied in the eight selected soil samples initially treated with different concentrations ( 3, 5, 10, 15 ) µg ml$^{-1}$. The amount of pesticides that remained on soils at each desorption stage was calculated as the difference between the initial amount adsorbed ( the amount of pesticides sorbed at equilibrium concentration corresponding to the initial concentration ) and the amount desorbed ( after each removing ), all determinations were carried out in duplicate.

### 3.5. Adsorption isotherm

Adsorption values over the range of concentrations 3, 5, 10, and 15 µg l$^{-1}$ used in this research, were utilized to fit linear form of both Freundlich and Langmuir models[32]. Adsorption data are usually expressed in terms of a constant value such as the Freundlich adsorption constant ($K_f$ ), Langmuir adsorption coefficient ( $K_l$), Linearity factor ( n ), maximum concentration adsorbed( $C_m$ ) and regression factor ( $R^2$ ). This constant area is characteristic of the particular soil-pesticide combination and is related to the free energy changes of adsorption, and obtained by using their appropriate equations[33] and the results were summarized in Table 3.

The most simple and widely used model of the equilibrium adsorption isotherms is that given by a linear relationship, by which it is assumed that the amount of the solute adsorbed by the soil matrix and the concentration $C_s$ of the solute in the soil solution is given by the relationship:-

$$K_d = C_s/C_e \quad \ldots\ldots (8)$$

Where the distribution coefficient "$K_d$", is a measure of the retention of the solute by the soil matrix, $C_s$ is the concentration of adsorbed pesticide and $C_e$ the pesticide concentration, in the supernatant solution at equilibrium. The $K_d$ values for Bispyribac-sodium were ranged from 9.032 to 16.950 ml g$^{-1}$.

The adsorption isotherms are well fitted to the Freundlich model: it can be expressed as:-

$$C_s = K_f\, C_e^n \quad \ldots\ldots (9)$$

where: $C_s$ is the amount of adsorbed pesticide per unit mass of soil, $C_e$ is the equilibrium pesticide concentration in solution, $K_f$ is Freundlich sorption coefficient, n is empirical constant[34]. Adsorption isotherm parameters were calculated by using the linearized form of Freundlich equation ( 10 ) :-

$$\log C_s = \log K_f + n \log C_e \quad \ldots\ldots (10)$$

Values of $K_f$ calculated from the linearized form of equation (10 ) by plotting of log$C_s$ versus log $C_e$[35], were also summarized in table 3. which oscillated between 8.892-54.916 ml g-1. Values of Kf were in the following order $S_8 > S_3 > S_4 = S_6 > S_2 = S_5 > S_1 > S_7$.

Data from the batch adsorption on the selected soil samples will conform to Langmuir equation.

$$C_s = C_m ( K_l C_e /1+K_l C_e ) \quad \ldots\ldots (10)$$

Where $C_s$ and $C_e$ are defined before, Cm is the maximum amount of pesticide adsorbed( adsorption maxima µg g$^{-1}$), and it reflects the adsorption capacity and $K_l$ is Langmuir adsorption coefficient, ( binding energy coefficient )( ml g$^{-1}$ ). The linear form of Langmuir equation is:-

$$C_e/C_s = 1/( C_m \; K_l ) + C_e /C_m \quad \ldots\ldots (11)$$

Values of $K_l$ were obtained by plotting $C_e/C_s$ versus $C_e$, and data are tabled in table 3 such values of adsorption capacity $K_l$ ranged from 0.407-1.317 mlg$^{-1}$ because they can vary among soils due to the quantities and composition of soil components[35]. Values of Kl for adsorption of bispyribac-sodium were in the order $S_8 > S_3 > S_6 > S_2 > S_4 > S_5 > S_7 > S_1$. The maximum amount of pesticides adsorption ( Cm µg g$^{-1}$ ) ranged from 6.456-31.15.

Table 3: Adsorption isotherm parameters for the linear, Freundlich and Langmuir models for bispyribac-sodium.

| Adsorption model | parameter | Soils | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $S_1$ | $S_2$ | $S_3$ | $S_4$ | $S_5$ | $S_6$ | $S_7$ | $S_8$ |
| Distr. coffi. | $K_d$(calc.) | 8. | 12.741 | 14.085 | 9.247 | 13.273 | 9.358 | 7.077 | 16.54 |
| | S.E | 0.971 | 2.616 | 0.916 | 2.592 | 2.561 | 2.658 | 2.536 | 2.624 |
| | $R^2$ | 0.98 | 0.92 | 0.94 | 1.00 | 0.99 | 0.94 | 0.99 | 0.95 |
| Freundlich | $K_f$(mlg$^{-1}$) | 15.388 | 21.071 | 27.327 | 24.603 | 21.071 | 24.603 | 8.802 | 54.91 |
| | S.E | 0.156 | 0.166 | 0.156 | 0.163 | 0.166 | 0.163 | 0.158 | 0.160 |
| | n | 1.05 | 2.55 | 1.09 | 2.10 | 2.55 | 2.10 | 0.90 | 2.02 |
| | $R^2$ | 0.99 | 0.96 | 0.96 | 0.98 | 0.96 | 0.98 | 0.85 | 0.93 |
| Langmuir | $K_l$(mlg$^-$1) | 0.407 | 0.887 | 1.144 | 0.757 | 0.572 | 1.041 | 0.492 | 1.317 |
| | S.E | 0.003 | 0.026 | 0.003 | 0.018 | 0.007 | 0.005 | 0.017 | 0.012 |
| | $C_m$ | 31.153 | 6.456 | 14.283 | 10.010 | 20.040 | 6.685 | 8.518 | 6.935 |
| | $R^2$ | 0.93 | 0.84 | 1.000 | 0.97 | 0.91 | 0.960 | 0.94 | 0.82 |

### 3.6. Effect of soil characteristics on adsorption coefficients

#### 3.6.1. Effect of organic matter in soil

Organic carbon is a major adsorbent for pesticide, and can be described by the organic carbon normalized partition coefficient $K_{oc}$ ( mlg$^{-1}$):-

$$K_{oc}= (K_d \times 100)/OC \quad \ldots\ldots (12)$$

while they define new coefficients according to the formula:

$K_{OM}=(K_d \times 100)/OM$ ……..…………………………..……………. (13)

Where OC and OM are the organic carbon and organic matter contents[36]. The relationship between the soil OC and adsorption coefficients ($K_f$ and $K_l$) for bispyribic-sodium were shown in figures 5 and 6: A significant increase in adsorption coefficient was observed with the increasing OC in soil[37].

The values KOC on selected soil samples were in the following order $S_8 > S_2 > S_7 > S_1 > S_3 > S_5 > S_4 > S_6$. Thus the results showed that none of these sequences were completely fitted with the sequence of the soil organic contents in Table 4.

Table 4: organic carbon normalized adsorption coefficient $K_{oc}$ for bispyribac-sodium.

| parameter | Soils | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $S_1$ | $S_2$ | $S_3$ | $S_4$ | $S_5$ | $S_6$ | $S_7$ | $S_8$ |
| $K_{OM}$ | 300.48 | 137.59 | 266.79 | 853.55 | 3917.58 | 161.30 | 140.63 | 282.18 |
| $K_{OC}$ | 1.97 | 7.04 | 1.50 | 1.28 | 1.36 | 0.39 | 5.469 | 241.65 |

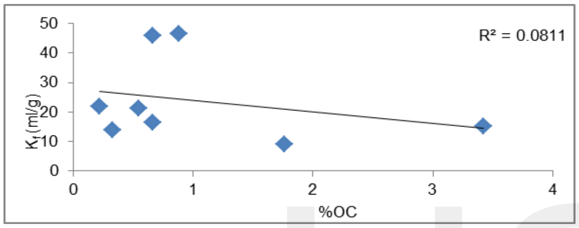


Figure 5: Relation between the soil organic carbon and adsorption coefficients ( $K_f$ ) for bispyribic-sodium in the selected soil samples.

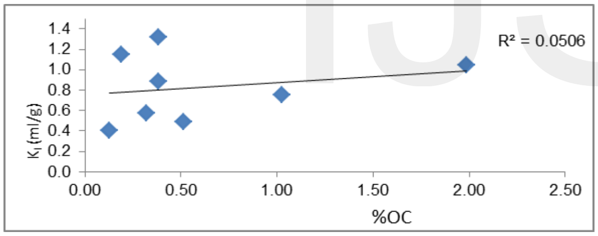


Figure 6: Relation between the soil organic carbon and adsorption coefficients ( $K_l$ ) for bispyribic-sodium in the selected soil samples.

### 3.6.2. Effect of soil clay

The clay contents for soils were in order $S_4 > S_3 > S_8 > S_2 > S_1 > S_5 > S_7 > S_6$. Adsorption coefficient of the pesticide in the selected soils was related to clay content of each sample as presented in Table 2. and Figures 7 and 8. The $K_f$ values for the numbered $S_1$-$S_8$ are 15.388, 21.071, 27.327, 24.603, 21.071, 24.603, 8.802, and 54.916 $mlg^{-1}$ respectively, while the $K_l$ values 0.407, 0.887, 1.144, 0.757, 0.572, 1.041, 0.492, and 1.317 $mlg^{-1}$ respectively. The clay contents for soils were in order $S_4 > S_3 > S_8 > S_2 > S_1 > S_5 > S_7 > S_6$. Adsorption coefficient of the pesticide in the selected soils was related to clay content of each sample as presented in Table 2. and Figures 7 and 8. The $K_f$ values for the numbered $S_1$-$S_8$ are 15.388, 21.071, 27.327, 24.603, 21.071, 24.603, 8.802, and 54.916 $mlg_{-1}$ respectively, while the $K_l$ values 0.407, 0.887, 1.144, 0.757, 0.572, 1.041, 0.492, and 1.317 ml $g^{-1}$ respectively.

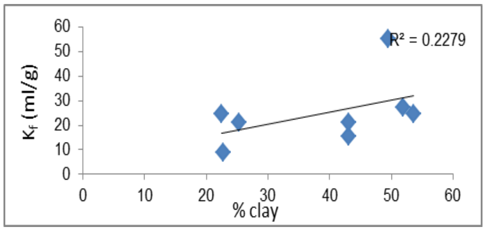


Figure 7: Relation between the soil clay content and adsorption coefficients ( $K_f$ ) of bispyribic-sodium in the selected soil samples.

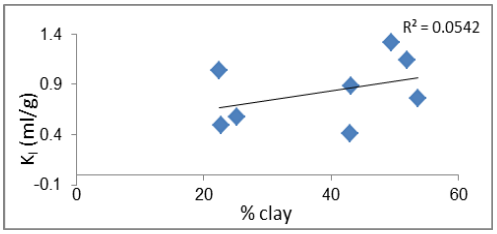


Figure 8: Relation between the soil clay content and adsorption co-efficients ( $K_l$ ) of bispyribic- sodium in the selected soil samples.

### 3.6.3 Effect of Soil CEC

These results were in agreement with the quantity of exchangeable cations in the selected soil samples. In Table 2, $S_1$ has the highest quantity of exchangeable cations (43.137 meq $100g^{-1}$ ). The lowest values of CEC is on $S_5$ ( 0.118 meq $100g^{-1}$ ). Values of CEC on soil samples were in the order: $S_1 > S_6 > S_8 > S_2 > S_7 > S_4 > S_3 > S_5$. It is clear that the negative surface charge ( CEC ) attenuates the ability of the organic anions to interact with the positively charged sites on the same surface[38]. The relation between the CEC of soil and adsorption coefficient of the studied pesticides were shown in Figure 8 and 9.

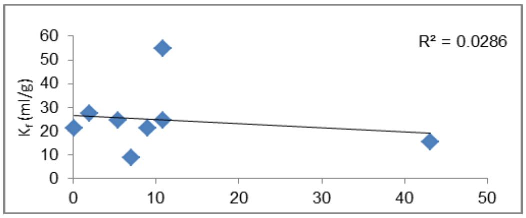


Figure 8: Relation of the soil cation exchangeable capacity and adsorption coefficients ( $K_f$ ) bispyribic-sodium in the selected soil samples.

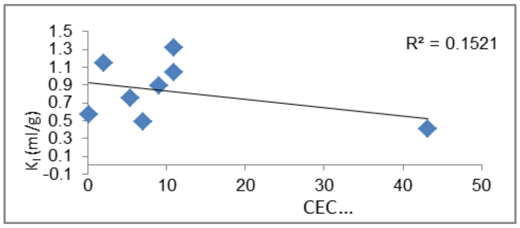


Figure 9: Relation of the soil cation exchangeable capacity and ad-sorption coefficients ( $K_l$ ) of bispyribic- sodium in the selected soil samples.

### 3.6.4. Effect of soil pH

The $K_d$ values of the studied pesticide were plotted against pH of the soils in Figure 10 the from which it is obvious that there are a positive exponential trends between $K_d$ and pH for the soils adsorption for.

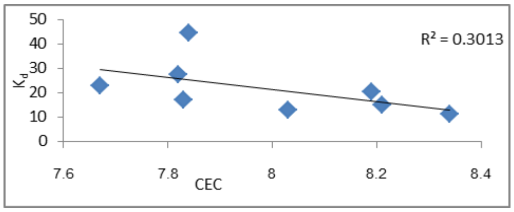


Figure 10: Variation of $K_d$ with natural soil pH of bispyribic-sodium.

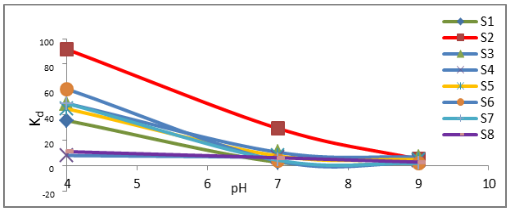


Figure 11: variation of $K_d$ with experimentally modified pH for bispyribac sodium, with the experimental pH for selected soils.

Table 5: Exponential correlation between $K_d$ and experimental modified pH for adsorption of bispyribac-sodium on the selected soil samples, n ( exponential linearity ) and $R^2$ ( correlation coefficient ).

| Parameter | Soils | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $S_1$ | $S_2$ | $S_3$ | $S_4$ | $S_5$ | $S_6$ | $S_7$ | $S_8$ |
| n | -7.018 | -17.588 | -8.801 | -0.803 | -8.343 | -12.198 | -9.853 | -1.647 |
| $R^2$ | 0.854 | 0.983 | 0.897 | 0.930 | 0.887 | 0.858 | 0.930 | 1.000 |

## 4. Thermodynamic studies of adsorption

The knowledge of kinetic and thermodynamic is essential to understand the basic reactions in soils, but unfortunately such investigations of clay and soils are limited. This is particularly true for soils that contain complex mixtures of clay minerals, non-crystalline components, oxides, hydroxides and organic matter[40]. So adsorption experiments were conducted at 288.15, 298.15, and 308.15 K to study the thermodynamic parameter, associated with the adsorption of the studied pesticides on the selected soil samples.

As well known, the equilibrium constants $K_0$ is the leading factor for calculating the essential thermodynamic parameters for physic-chemical equilibrium associated with the adsorption processes. These can be calculated from the variation of $K_0$, with change in temperature, $K_0$ during any adsorption reaction can be defined as:

$K_0 = a_s/a_e = (\gamma_s\ C_s)/(\gamma_e\ C_e)$ ………………………….………….. (15)

Where as : activity of the adsorbed solute, ae : activity of the solute in the equilibrium solution, $C_s$ is the amount of pesticides adsorbed per milliliter of the solvent in contact with soils, $C_e$ ($\mu g\ ml^{-1}$) is the pesticide concentration in equilibrium suspension, $\gamma_s$ and $\gamma e$ are the activity coefficients of the adsorbed solute and solute in equilibrium suspension respectively and assumed to be unity at infinite dilution. Equation ( 15 ) may then be formulated.

$C_s \to 0 \qquad C_s/C_e = (a_s/a_e)\ K_0$ ……..…….……………..………. (16)

$\ln K_0 = \ln(C_s/C_e)$ ……………..…………………………………………. (17)

The values of $K_0$ were obtained by plotting ln $(C_s/C_e)$ vs. $C_s$ and then extrapolating $C_s$ to zero.[41].

The results of equilibrium constants obtained at 288.15, 298.15, and 308.15 K for soils are summarized in Table 6. It is obvious that the trend of thermodynamic equilibrium constant $K_0$ is decreasing with increase in temperature for all soil pesticides interaction this is in accordance with the literature [42]. However, the highest value was for $S_6$ soil followed by $S_3 > S_5 = S_8 > S_4 > S_1 > S_7 > S_2$ soils. Values of $\ln k_0$ were in the range 0.5-3.5.

Assuming that the activity coefficients are unity in each phase due to the multicomponent nature of the solution and hydrophobic interaction between pesticide and soil organic matter, the standard free energy for the transfer of pesticide molecules between the solid and aqueous phases was estimated using

$\Delta G^0 = -RT \ln K_0$ ……………………..…………………………. (18)

Where R is the universal gas constant ($J.\ mol^{-1}.K^{-1}$) and T (K) is temperature[43]. The values of $\Delta G^0$ for adsorption at 288.15, 298.15, and 309.15 K were summarized in Tables 7. The $\Delta G^0$ values were in the range -8.381 to -1.280 ($kJ\ mol^{-1}$) which indicate a spontaneous process.

Table 7: Equilibrium constants and standard free energy change at three different temperatures for adsorption of bispyribac-sodium on the selected soil samples.

| | parameter | Soils | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $S_1$ | $S_2$ | $S_3$ | $S_4$ | $S_5$ | $S_6$ | $S_7$ | $S_8$ |
| $T_1$k | $\ln K_0$ | 1.8 | 1.35 | 3.1 | 2 | 2.5 | 3.5 | 1.6 | 2.5 |
| | $\Delta G^0 (kJ.\ mol^{-1})$ | -4.31 | -3.23 | -7.42 | -4.78 | -5.98 | -8.38 | -3.83 | -5.98 |
| $T_2$K | $\ln K_0$ | 1.6 | 1.2 | 2.4 | 1.9 | 2 | 2.6 | 1 | 2.3 |
| | $\Delta G^0 (kJ.\ mol^{-1})$ | -3.96 | -2.97 | -5.94 | -4.70 | -4.95 | -6.44 | -2.47 | -5.69 |
| $T_3$K | $\ln K_0$ | 1.3 | 1.1 | 1.9 | 1.82 | 1.4 | 2 | 0.5 | 2.2 |
| | $\Delta G^0 (kJ.\ mol^{-1})$ | -3.32 | -2.81 | -4.86 | -4.66 | -3.58 | -5.12 | -1.28 | -5.63 |

The standard enthalpy change of adsorption ($\Delta H^o$) represents the difference in binding energies between the solvent and the soil with the pesticides, they explain the binding strength of pesticides to the soil[44]. By non-calorimetric method for the measurement of reaction enthalpies, values of $\Delta H^0$ also determined graphically from the following equation 19[45].

$\ln K_0 = (-\Delta H^0)/RT + (\Delta S^0)/R$ ………………………………… (19)

The enthalpy of adsorption in the range 288.15-308.15 K was calculated from the slope of the plot of $\ln k_0$ against 1/T while intercept equals $\Delta S^0/R$ ( Figure 12 ). It is evident that a straight line obtained in each soil and the results for both $\Delta H^0$ and $\Delta S^0$ were summarized in table 8. The negative values of ΔH0 indicated the exothermic behavior reactions. Also, the negative values of $\Delta S^0$ confirming the uniform and stability of molecules during the adsorption processes.

The most probable nature of the adsorption was physical type, and a hydrogen bond formation was suggested[44]. The values of $R^2$ were in the range 0.97-0.99 which supported the linear nature of the plot.

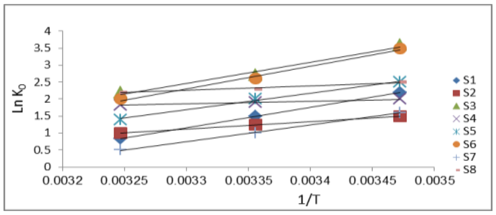


Figure 12: Variation of $\ln K_0$ with 1/T for adsorption of bispyribac-sodium.

Table 8: Standard enthalpy change and standard entropy change ( determined graphically ) for adsorption of bispyribac-sodium.

| parameters | Soil | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $S_1$ | $S_2$ | $S_3$ | $S_4$ | $S_5$ | $S_6$ | $S_7$ | $S_8$ |
| $\Delta H^0$ (kJ.mol$^{-1}$) | -18.44 | -9.22 | -44.25 | -6.63 | -40.56 | -55.31 | -40.56 | -11.06 |
| $\Delta S^0$ (J.mol$^{-1}$K$^{-1}$) | -48.73 | -20.90 | -128.31 | -6.46 | -119.67 | -163.64 | -18.70 | -17.88 |
| $R^2$ | 0.98 | 0.99 | 0.99 | 1.00 | 0.99 | 0.99 | 0.97 | 0.97 |

## 4.1. Isosteric enthalpy of Adsorption

The isosteric enthalpy of adsorption is the standard enthalpy of adsorption at a fixed surface coverage[26]. Values of isosteric heat of the adsorption as a function of the amount of the chemical adsorbed was calculated by the expression[46]:

$$\ln\frac{(K_0)_{T_2}}{(K_0)_{T_1}} = \frac{\Delta H^0}{R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (20)$$

The values of isosteric enthalpy of adsorption were listed in Table 9 followed the range -73.22-38.27 kJmol$^{-1}$ for bispyribac-sodium.

Table 9 : Isosteric heat change of adsorption of bispyribac-sodium on the selected soil samples.

| $\Delta H^0$ (kJmol$^{-1}$) | Soils | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $S_1$ | $S_2$ | $S_3$ | $S_4$ | $S_5$ | $S_6$ | $S_7$ | S8 |
| $T_1$:$T_2$ | -63.43 | -63.43 | -55.24 | -67.79 | -57.08 | -53.01 | -44.60 | -65.65 |
| $T_2$:$T_3$ | -62.20 | -70.17 | -60.60 | -73.32 | -53.58 | -58.88 | -38.27 | -73.22 |

## 4.2. Organic matter normalized free energy change of adsorption

Organic matter was the most important factor that governed the adsorption of pesticides on soils. The organic matter normalized free energy changes ( $\Delta G^0_{OM}$ ) of adsorption of bispyribac-sodium were calculated by using the following equation[47].

$$\Delta G^0_{OM} = -RT \ln K_{OM} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (21)$$

The values of $\Delta G^0_{OM}$ which summarized in Table 10 were in the range -10.44 to-24.32 kJ mol$^{-1}$. The negative values of $\Delta G^0_{OM}$ revealed that the adsorption of the three pesticides in the eight soil samples are spontaneous process and the adsorption has physical nature[48]. The values of $\Delta G^0_{OM}$ for adsorption under the effect of temperatures were in the order $T_1 > T_2 > T_3$ for the studied pesticides. This indicates that as the temperature increases the adsorption coefficients decrease for the studied pesticide.

Table 10: Organic matter normalized free energy change of adsorption of bispyribac-sodium on the selected soil samples.

| ΔG0OM (kJ mol-1) | Soils | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | S1 | $S_2$ | $S_3$ | $S_4$ | $S_5$ | $S_6$ | $S_7$ | $S_8$ |
| T1 | -20.31 | -13.71 | -19.02 | -18.07 | -24.32 | -18.18 | -15.49 | -17.58 |
| T2 | -14.14 | -12.20 | -13.84 | -16.72 | -20.50 | -12.59 | -12.25 | -13.98 |
| T3 | -11.65 | -10.44 | -12.12 | -12.82 | -18.34 | -12.28 | -11.42 | -12.86 |

## 4.3. Temperature dependency of adsorption coefficients

Temperature is a factor which has an influencing power in any adsorption processes. Data obtained from the experiments are clearly indicated that adsorption decreased with increase in temperature. The observed decrease in the adsorption capacity with increase of temperature (Figure 13) indicates that indicates that low temperature favors the adsorption process onto soil[49].

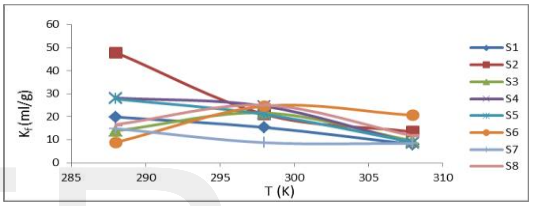


Figure 13: Variation of adsorption coefficient with temperature for bispyribac-sodium on the eight selected soil samples.

## 4.4. Effect of Surfactant on adsorption

Surfactant adsorption is a consideration in any application where surfactant come in contact with a surface or interface. Adsorption of surfactants may lead to positive effects, as in surface wettability alteration, or be detrimental, as in the loss of surfactants from solution, while many physical and compositional properties influence surfactant adsorption. Surfactant adsorption may occur due to electrostatic interaction, van der Waals interaction, hydrogen bonding, and/or solvation and desolvation of adsorbate and adsorbent species[50].

To investigate the effect of different types of surfactants on adsorption behavior of pesticides, the Freundlich adsorption equation in the presence of surfactant is used as follows[51].

$$\log C_s = \log K_s + n_s \log C_e \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (22)$$

Where $K_s$ and $n_s$ $n_s$ are the Freundlich affinity and nonlinearity coefficients respectively.

Values of adsorption coefficient Ks of bispyribac-sodium in the presence of the three surfactants Polyacrylamide PAM ( cationic surfactant ), of Polyacrylicacid PAA ( anionic surfactant ), and Polyvinylalcohol PVA ( non-ionic surfactant ) were summarized in table11. The results of PAM follow the range 11.984-18.365 ml g-1, $R^2$ values ranged 0.853-0.999, and n values ranged 0.583-1.575. The results of the present study showed that $K_s$ values increase slightly with respect to those obtained in surfactant-free system[52].

With the addition of PAA( anionic surfactant ), the $K_s$ values determined and tabulated in Table 11. The $K_s$ values were in the range 1.287-8.892 ml $g^{-1}$, while $R^2$ values ranged 0.508-0.995, and n values ranged 0.208-4.329.

The $K_s$ values for adsorption in the presence of non-ionic surfactant PVA in pesticide soil-water systems have been calculated in order to find its effect on the adsorption behavior of bispyribac-sodium. The measured values of $K_s$ which were summarized in Table 11, followed the range 2.168-22.522 ml $g^{-1}$, $R^2$ values ranged 0.942-0.999, and n values ranged 0.943-4.493.

Table 11: Freundlich adsorption coefficient for the adsorption of Bispyribac-sodium in the presence of PAM, PVA, and PAA on the selected soil samples.

| Soils | $K_s$ without surfactant | PAM | | | PVA | | | PAA | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $K_s$ | $R^2$ | n | $K_s$ | $R^2$ | n | $K_s$ | $R^2$ | n |
| $S_1$ | 15.488 | 12.445 | 0.987 | 1.322 | 12.511 | 0.969 | 1.563 | 6.596 | 0.946 | 1.197 |
| $S_2$ | 20.893 | 18.365 | 0.980 | 1.025 | 22.522 | 0.999 | 0.996 | 8.892 | 0.930 | 0.862 |
| $S_3$ | 21.677 | 12.841 | 0.853 | 0.952 | 10.887 | 0.943 | 0.943 | 2.076 | 0.508 | 0.208 |
| $S_4$ | 24.547 | 16.850 | 0.979 | 0.997 | 3.543 | 0.942 | 3.815 | 5.195 | 0.930 | 1.453 |
| $S_5$ | 20.893 | 14.625 | 0.959 | 0.583 | 10.118 | 0.982 | 1.383 | 4.386 | 0.995 | 4.329 |
| $S_6$ | 24.547 | 17.458 | 0.947 | 1.334 | 2.168 | 0.975 | 4.493 | 1.287 | 0.889 | 3.585 |
| $S_7$ | 8.710 | 12.706 | 0.999 | 0.770 | 8.630 | 0.998 | 1.326 | 5.756 | 0.982 | 1.882 |
| $S_8$ | 54.954 | 11.984 | 0.998 | 1.575 | 7.872 | 0.998 | 1.642 | 1.388 | 0.992 | 4.174 |

### 4.6. Effect of metal ions

Values of Langmuir adsorption isotherm $K_l$, the regression factor and Cm for adsorption of pesticide on the selected soil samples in the presence of concentration ratio ( 1:1 ) $Cu^{+2}$, $Ni^{+2}$, and $Fe^{+2}$ were summarized in table 12. By comparison with data in table 3, it will be concluded that the values of $K_l$ for adsorption of pesticide in the selected soil samples in the presence of the metal ions were generally higher than in metal ion free solution.

Values of Langmuir isotherm $K_l$ in presence of $Cu^{+2}$, ranged from 0.788-1.718 ml.$g^{-1}$, $C_m$ values ranged from 0.995-18.553 µg $g^{-1}$, and with coefficients of determination $R^2$ ranging from 0.836-1.000 and values $K_l$ presence of $Ni^{+2}$, ranged from 0.425-1.520 ml.$g^{-1}$, $C_m$ values ranged from 2.023-16.000 µg $g^{-1}$, and with coefficients of determination $R^2$ ranging from 0.857-0.998 while values of $K_l$ presence of $Fe^{+2}$, ranged from 0.342-0.946 ml $g^{-1}$, $C_m$ values ranged from 1.424-17.762 µg $g^{-1}$, and with coefficients of determination $R^2$ ranging from 0.852-0.999.

Table 12: Adsorption isotherm constants Kl, Cm and regression factor R2 for pesticide in the presence of metal ions on the selected soil sample

| metals | parameter | Soils | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $S_1$ | $S_2$ | $S_3$ | $S_4$ | $S_5$ | $S_6$ | $S_7$ | $S_8$ |
| $Cu^{+2}$ | $K_l$ | 0.788 | 1.004 | 1.164 | 1.718 | 0.795 | 1.276 | 0.848 | 1.563 |
| | $C_m$ | 0.995 | 18.553 | 4.212 | 2.137 | 7.968 | 17.452 | 10.121 | 5.447 |
| | $R^2$ | 0.953 | 0.836 | 0.888 | 1.000 | 0.886 | 0.998 | 0.995 | 0.983 |
| $Ni^{+2}$ | $K_l$ | 0.792 | 0.681 | 0.506 | 0.593 | 0.772 | 0.615 | 0.425 | 1.520 |
| | $C_m$ | 2.080 | 2.959 | 3.245 | 2.023 | 6.456 | 5.549 | 16.000 | 2.658 |
| | $R^2$ | 0.998 | 0.989 | 0.891 | 0.973 | 0.857 | 0.989 | 0.971 | 0.997 |
| $Fe^{+2}$ | $K_l$ | 0.713 | 0.946 | 0.482 | 0.497 | 0.698 | 0.501 | 0.342 | 0.832 |
| | $C_m$ | 7.364 | 1.424 | 1.999 | 1.968 | 3.149 | 4.131 | 17.762 | 2.639 |
| | $R^2$ | 0.965 | 0.999 | 0.859 | 0.944 | 0.852 | 0.876 | 0.990 | 0.974 |

## CONCLUSIONS

The batch kinetics experiments were used to investigate the behavior ofbispyribac-sodium in eight agricultural soil samples. Generally, adsorption increased with concentration, the initial step was characterized as rapid and low energy while the second step was slow and high energy accompanied by slow diffusion to sites within the soil matrix. The magnitude of all $K_d$, $K_f$ and $K_l$ values were indicated as moderate to low adsorption for all pesticides. Freundlich model more accurately predicted the behavior of pesticides desorption. Decrease of adsorption with increasing pH. The higher negative value of $\Delta G^0$, the slower was the rate of adsorption. The values of $\Delta G^0$ increased with rise in temperature. The trend of adsorption of pesticides in the presence of surfactants enhancement was as follows PAM > PVA > PAA. While The trend of adsorption process with ions is in the order: $Cu^{2+} > Ni^{2+} > Fe^{2+}$.

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