



Kinetics and Thermodynamics of β - 1 Endosulfan Pesticide Adsorption in Jordan Valley Soils

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Abstract- Knowledge of the β - endosulfan adsorption characteristics of soil is necessary for predicting its mobility and fate in soil environments. To examine the characteristics of β - endosulfan retention, sorption batch experiments were performed on three Xeropsamments soils having different properties. The sorption data were applied to various kinetics models. The results reveal that the tested models fitted the adsorption data in the order: first-order~modified Freundlich > parabolic diffusion > Elovich. The energy of activation (E_a) and enthalpy ($\Delta H^\#$), entropy ($\Delta S^\#$), and free energy of activation ($\Delta G^\#$) related to β - endosulfan sorption were calculated using the Arrhenius equation. The activation energy (E_a) values ($18.57 - 38.18 \text{ kJ mol}^{-1}$) and the positive $\Delta H^\#$ values characterize β -endosulfan adsorption process onto the sorbents studied as physisorption with an endothermic nature. The negative values of $\Delta S^\#$ ($-23 - -17 \text{ J mol}^{-1}$) obtained in this study suggest that the β -endosulfan sorption process involves an associative mechanism.

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I. INTRODUCTION

The increasing use of pesticides in the modern agricultural practices leads to several environmental problems in soil and water. Transport of pesticides sorbed onto soil particles can represent a significant pathway from the original land application to receiving water bodies (Sen and Khilar 2006). Identifying and understanding the mechanisms controlling the fate of pesticides in the soil environment are vital for both maintaining environmental quality and optimizing sustainable agriculture practices (Soulas and Lagacherie 2001). Endosulfan (6,7,8,9,10-hexachloro-1,5,5a,6,9,9 a-hexahydro-6, 9-methano-2,3,4-enzodioxathiepin-3-oxide) is a broad spectrum contact insecticide and acaricide that is used throughout the world on a wide variety of fruits, vegetables, cereals, and cotton, and ornamental plants in commercial agricultural settings. Endosulfan is classified in the U.S. Environmental Protection Agency toxicity category I. Technical grade endosulfan is composed of two stereo chemical isomers: " α -endosulfan and β -endosulfan, in concentrations of approximately 70% and 30%, respectively (Herrmann 2002). The α -isomer is more

volatile and dissipative, while the β -isomer is generally more adsorptive and persistent (Rice et al.1997). The moderately adsorptive and persistency properties of β - isomer enable it to stay in the environment for an extended period (US EPA2007). Endosulfan has been detected in the atmosphere, soils, sediments, estuaries, surface, ground and rain waters, and food stuffs (Spark and Swift 2002). Once endosulfan is applied to crops, it can either persist in soil as a sorbed phase or be removed through several physical, chemical, and biological processes (Siddique et al. 2003). Because elevated endosulfan concentrations could result in both acute and chronic risks of concern for terrestrial and aquatic organisms, knowledge of the endosulfan adsorption characteristics of soil is necessary for predicting their mobility and fate in soil environments. Extensive use of endosulfan more than a decade to control insects in Jordan Valley, east of west bank is of great concern regarding the potential transport in the environment. The use of uncontrolled and large amount of endosulfan may deteriorate the soil and groundwater quality. The fate of endosulfan as an insecticide has not been examined yet thoroughly in Palestine and specifically in the Jordan Valley which is considered the main vegetable production area in the country. The main objective of this study was to determine sorption kinetics and thermodynamics from batch experiments for β -endosulfan and to ascertain sorption characteristics in representative soils of Jordan valley. Such information is necessary for understanding the mechanisms involved in the adsorption of endosulfan and the prediction of its movement in Jordan valley soils in order to establish risk assessment and remediation strategies for endosulfan contaminated soils (Kumar and Philip 2006; Krishna and Philip2008).

II. MATERIALS AND METHODS

a) Study area

Soil samples were taken from three locations intensely cultivated with vegetable and extended from northern part to southern part of the Jordan valley. These locations represent Jordan valley soils and included Bardaleh in northern part of Jordan Valley, Al-Zubeidate in middle part of Jordan valley, and Al-Nwueimeh in southern part of Jordan Valley. The study

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area has 5654 ha of irrigable land and is located between 31° 46' – 32° 24' North latitudes and 35° 27' – 35° 34' East longitudes. The Jordan valley has semi-arid climate with almost no precipitation between April and September. The long-term mean annual precipitation is about 166 mm, the mean annual atmospheric temperature is about 29.6 °C and the evaporation is 1500 mm. The soils of the Jordan valley are mainly sandy loamy, slightly alkaline (pH 7.2– 7.8) and classified as Xeropsamments according to the USDA system. The farmers in these locations usually apply large quantities of endosulfan (Thionex® 35) for insect and pests control. The study area contains more than 125 wells, distributed from northern part of Jordan valley to southern part of Jordan valley mostly used for irrigation only 12 wells are used for drinking.

b) Soil samples

Three different soils were chosen to represent the most common types in Jordan valley, Bardaleh in northern part of Jordan valley, Al-Zubeidate in middle of Jordan Valley and Al-Nwueimeh in southern part of Jordan valley. 101 Three surface samples (0 – 30 cm) were collected from each location, air-dried, ground, sieved (< 2 mm). and preserved in air tight polyethylene bags before use. Selected physical and chemical properties of these samples were determined (Table 1).

c) Adsorption kinetic study

Kinetic retention using the batch method was used to quantify adsorption isotherms for β -endosulfan by the three studied soils at three different temperatures 298, 308 and 318K. Triplicate 2-g samples of each soil were placed in Teflon centrifuge tubes and mixed with 40-mL solution of 15 and 30 110 mg L⁻¹ initial β -endosulfan concentrations. The mixtures were

e) Kinetics Modeling

Four kinetic models were applied to the sorption data:

First-order rate [Elkhatib et al.2013]

Elovich (Elkhatib et al.1992)

Parabolic Diffusion (Elkhatib and Hern 1988)

Power Function (Elkhatib and Hern 1988)

Where

q or q_t = β -endosulfan adsorbed (mg kg⁻¹) at time t , q_o = β -endosulfan adsorbed (mg kg⁻¹) at equilibrium, k_a = apparent sorption rate coefficient, α = the initial adsorption rate (mg g⁻¹ min⁻¹), β = a constant related to the extent of surface coverage (mg g⁻¹), a = a constant; k_d = apparent diffusion rate coefficient, q = adsorbed β -endosulfan (mg kg⁻¹), C_o = initial β -endosulfan concentration (mg l⁻¹), t = reaction time (min), k_a = sorption rate coefficient (min⁻¹), and $1/m$ = constant.

f) Statistical analysis

The linear least-squares optimization program provided by SAS PROC LIN (SAS Institute 2000) was utilized to obtain best-fit parameters which provide the best description of the adsorption data.

continuously shaken on a temperature-controlled shaker at 120 rpm and then centrifuged at 5,000×g for 10 min prior to sampling. After 0.5, 1, 2, 4, 8 and 24 h hours of reaction time, a 5-mL aliquot was taken, extracted with n-hexane solution and filtered through anhydrous sodium sulphate to remove moisture content and analyzed using HPLC, model (Perkin Elmer, USA). Amounts of endosulfan sorbed by the soil matrix were determined by the difference between the concentrations of the supernatant and that of the initial solutions.

d) Analysis of β -endosulfan

The extracted samples were analyzed using high-performance liquid chromatography model (Perkin Elmer Series 200). Analyses were performed in isocratic system using a 325 reverse phase C18 column (25 cm x 4.6 mm id). For separation of endosulfan, a 70:30 mixture of methanol and water was passed through the column at a flow rate of 0.7 ml/min and the wavelength of the UV/visible detector was fixed at 214 nm (Siddique et al., 2003). Column temperature was ambient and injection was made with a 50- μ l SGE syringe and a manual loop injector (20- μ l). Sample filtration was carried out 125 with solvent compatible Gellman syringe filter of 0.20- μ m GHP membrane. The eluent was degassed by purging with helium. Laboratory and instrumental blanks were frequently analyzed to ensure the absence of contaminants, or interference arising from samples or laboratory handling. Recoveries, calculated from spiked matrixes, were greater than 90%.Detection limits (LOD), ranged between 0.08 and 0.33 ng mL⁻¹ in agreement with values reported in the literature (Keith et al., 1983).

$$\ln(q_o - q) = a - k_a t \quad (1)$$

$$q t = (1/\beta) \ln(\alpha \beta) + (1/\beta) \ln t \quad (2)$$

$$q = a + k_d t^{1/2} \quad (3)$$

$$q = k_a C_o t^{1/m} \quad (4)$$

III. RESULTS AND DISCUSSION

a) β -endosulfan Sorption vs. time

Sorption of β -endosulfan on the three studied soils versus time at two initial concentrations and a

temperature of 298K are illustrated in Fig.1. In the three studied soils the sorption of β -endosulfan kinetics exhibited an immediate rapid sorption by which about 73% -92% of initially β -endosulfan sorbed in the first hour followed by a slow sorption at 298K. The initial sorption rate for β -endosulfan was high as a large number of adsorption sites were available at the onset of the process. Adsorption slowed down in later stages because after some time the remaining vacant surface sites may be difficult to occupy due to the repulsive forces between β -endosulfan molecules on the solid and liquid phase (Anirudhan and Ramachandran 2007). When initial β -endosulfan concentrations were changed (15 and 30 mg/L) at temperature 298K; the amount sorbed per unit mass showed an increase with rise in initial β -endosulfan concentrations (Fig.1). This is due to the increase in the mass driving force which allows more β -endosulfan molecules to pass from the solution to the adsorbent surface. At low initial β -endosulfan concentration, the ratio of β - endosulfan in solution to the available sorption sites is small and consequently the sorption is dependent of the initial concentration, but as the concentration of the β -endosulfan increase, the competition for sorption sites becomes fierce (Sarvanane et al. 2002). Similar results were reported by Ismail et al. (2002) when studying adsorption of β -endosulfan on soils, they found that sorption of β -endosulfan increased with increasing solution concentrations.

b) Kinetics Modeling

The kinetics of β -endosulfan sorption on the three studied soils were analyzed using various kinetic models; first-order, Elovich, intraparticle diffusion model, and, modified Freundlich. The conformity between experimental data and the model predicted values was expressed by the coefficient of determination (R^2) values and the standard error of estimate (SE). Based on R^2 and SE values (Table2), the modified Freundlich and the first-order models best described β -endosulfan sorption on the three studied soils. The parabolic diffusion law described the adsorption data of β -endosulfan satisfactorily as the R^2 values were quite high and SE values were low (Table 2). The empirical Elovich model did not describe the β -endosulfan reaction as the R^2 values were lower and SE values were quite high for this model (Table 2). The order of application of various kinetic models to describe β -endosulfan adsorption data was first-order~modified freundlich>parabolic diffusion>Elovich Sorption processes in soil systems are complex and often involving some changes taking place during it, e.g. (1) An increase in vacant site numbers as sorption progress act. (2) Changes in solution conditions such as ionic strength. Therefore, careful selection of appropriate rate models capable of describing the inherently complex and system-specific dynamics of sorption processes is necessary for

accurate fate and transport modelling (Elkhatib et al.1992; Xie et al. 2011;193 Saha et al. 2013).

c) Effect of initial concentrations and temperatures on β -endosulfan sorption

First-order equation was among the best kinetic equations studied 195 to describe the rate of β -endosulfan sorption as evidenced by the overall high values of R^2 and low SE values (Table 2). Therefore, the first order rate equation was employed (Table3 and Fig.2) to analyze the sorption rate of β -endosulfan onto the soils studied. To ascertain that a reaction is a first order, a change in only one parameter (e.g., initial concentration) should generate parallel kinetic plots resulting from similar apparent rate coefficients. Fig.3 shows the first order kinetic plots for β -endosulfan sorption at initial concentrations of 15 and 30 mg L⁻¹ on Al-Zubeidate soils at 298K. The slopes (apparent rate coefficients) correspond well and are nearly equal confirming that the reactions are first order. For example, at 15 and 30 mg β -endosulfan L⁻¹ concentrations, β -endosulfan sorption on Al-Zubeidate soil at 298 K resulted in apparent rate coefficients of 0.0032 and 0.0035 respectively (Table 3).

Effect of temperature on β -endosulfan sorption was studied in all the three soils in the range of 298–318K at 15 and 30 mg L⁻¹ initial β -endosulfan concentrations. The β -endosulfan sorption rate on the studied soils, from greatest to least, at all three temperatures was as follows: Al-Zubeidate, Al-Nwueimeh and Bardaleh soils (Table 3). As the temperature of the reaction increased from 298 to 318K, with all other reaction conditions remaining constant, the β -endosulfan sorption increased on all soil sorbents. Elshafei et al. (2009) observed that the adsorption rate of cadusafos on soil at 298, 308 and 318K increased with increasing temperature. This work shows that at a low temperature (298K), β -endosulfan sorption is relatively slow, compared with sorption observed at 318K in the laboratory. The enhanced adsorption with temperature may be attributed to either increase in the number of active binding sites available for adsorption on the adsorbent surface or due to the decrease in the boundary layer thickness surrounding the adsorbent, and thereby decreased 219 boundary layer mass transfer resistance owing to the decrease in the viscosity of the solution. Often soil temperatures can rise above 318K in arid soils, indicating that sorption rates in the field can be even faster than reported here and thus allow higher soil surface loading levels.

d) Activation Energy and Thermodynamic Parameters of β -endosulfan adsorption

By applying first order kinetic model and plotting $\ln k_a$ vs. $1/T$ for each soil concentration studied (Fig.4), where "T" is the temperature in Kelvin and " k_a " is the apparent sorption rate coefficient, the following linear relationship is obtained:

$$\ln k_a = (-E_a/RT) + \ln A$$

Where

R= gas constant (8.314 kJ/mol),

A= universal frequency factor.

It can be seen that the slope is given by $-E_a/R$ and the intercept by $\ln A$. Therefore, the thermodynamic parameters can be obtained using the following equations:

$$\Delta H^\# = E_a - RT$$

$$(\Delta S^\#/R) = \ln A - 1/n \text{ (BTe/h)}$$

$$\Delta G^\# = \Delta H^\# - T\Delta S^\#$$

Where

$\Delta H^\#$ = enthalpy of activation

$\Delta S^\#$ 238 = entropy of activation

$\Delta G^\#$ = free energy of activation

B = Boltzman's constant

h = Planck's constant

e = electronic charge

The values of E_a for β -endosulfan sorption on the studied soils followed the range 21.25 to 22.47, 18.57 to 20.67 and 38.07 to 38.18 kJ mol⁻¹ for Al-Nnuweimeh, Al-Zubeidate and Bardaleh soils, respectively (Table 4). The energy of activation measures the magnitude of the forces to be overcome during the process of sorption reactions and may give an idea about the type of sorption. The activation energy for physical adsorption is usually less than 42 kJ mol⁻¹, and higher values represent chemical reaction process as chemical adsorption is specific and involves forces much stronger than in physical adsorption (Elkhatib et al. 1993; Sparks 2003). In the present study, the values of activation energy confirm that the nature of β -endosulfan sorption onto studied soil is physical adsorption. The finding is in accordance with the observations of previous studies by Gulen et al. (2005). They found that, the value of activation energy (E_a) for azinphosmethyl sorption onto pyrolyzed Horse shoe sea crab shell was about 1.52 kJ mol⁻¹, this value is within the range of physical adsorption.

In order to get an insight whether the sorption process follows an activated complex, it is necessary to consider the thermodynamic activation parameters of the process. Values of enthalpy of activation ($\Delta H^\#$), entropy of activation ($\Delta S^\#$), and 258 free energy of activation ($\Delta G^\#$) were computed and presented in Table 4. The values of enthalpy of activation ($\Delta H^\#$) followed the range 18.77-19.99, 16.10-18.19 and 35. 60- 36.82 KJ mol⁻¹, for Al- Nuweimeh, Al-Zubeidate and Bardaleh soils, respectively. Data in Table 4 showed that enthalpy of activation values decrease with increasing initial concentration signifying less energy requirements for the reaction system as a result of increasing initial β -endosulfan concentration in to the studied soils. The positive values of $\Delta H^\#$ imply that the β -endosulfan adsorption process is endothermic and the magnitude of $\Delta H^\#$ may indicate the type of binding mechanism

involved, i.e., physical and/or chemical sorption. The heat evolved during physical adsorption is in the range 2.1-< 40 kJ mol⁻¹, while the heats of chemisorptions is about 40 kJ mol⁻¹, a value that has been recognized in the literature as the transition boundary between both types of sorption processes (Liu and Liu, 2008). The calculated values of $\Delta H^\#$ for β -endosulfan sorption were lower than 40 kJ mol⁻¹, indicative of physical adsorption mechanism. This observation agrees with results reported by Memon et al. (2007) for the adsorption of methyl parathion onto chestnut shells. The values of ΔG were in the range 87.59 to 87.79, 86.99 to 87.22, and 89.34 to 89.61 kJ mol⁻¹, for Al- Nnuweimeh, Al-Zubeidate and Bardaleh soils, respectively (Table 4). The positive values of ($\Delta G^\#$) indicate that sorption reactions require some energy from an external source to convert reactants into products and the nonspontaneous nature of β -endosulfan sorption onto the studied soil. The values of $\Delta S^\#$ were in the range -23.08 to -22.74, -23.77 to -23.15 and -18.02 to -17.88 J mol⁻¹ K⁻¹, for Al- Nuweimeh, Al-Zubeidate and Bardaleh soils, respectively (Table 4). The negative $\Delta S^\#$ values (i.e., entropy decreases as a result of sorption) suggests the stability of sorption process with no structural change at solid-liquid interface. This occurs as a result of redistribution of energy between the sorbate and the sorbent. Before sorption occurs, the β -endosulfan molecules near the surface of the sorbent will be less ordered than in the subsequent sorbed state. As a result, the distribution of rotational and translational energy among a small number of molecules will decrease with increasing sorption by producing a negative value of $S^\#$. Additionally, the magnitude and sign of $\Delta S^\#$ gives an indication whether the sorption reaction is an associative or dissociative mechanism.

Entropy values ≥ 10 J mol⁻¹ generally imply a dissociative mechanism (Atwood, 1997). Therefore, the negative values of $\Delta S^\#$ (-23- -17 J mol⁻¹) obtained in this study suggest that the β -endosulfan sorption process involves an associative mechanism. Similar results were reported by Yedla and Dikshit (2001) for endosulfan sorption onto wood charcoal.

IV. CONCLUSION

The results of the present study showed that The Al-Zubadate soil had the highest affinity for β -endosulfan sorption while the Bardaleh soil exhibited the lest affinity; β -endosulfan sorption on Al-Nuweimeh soil was intermediate between that observed for Al-Zubadate and Bardaleh soils. Adsorption rate constant of β -endosulfan were highest for Al-Zubadate soil whereas, it was the least for Bardaleh soil, these suggest that the β -endosulfan have affinity to calcium carbonate and organic matter. Adsorption of β -endosulfan in all soils followed Freundlich isotherm model and it is inferred that the sorption was monolayer.

The influence of temperature on β -endosulfan sorption onto the soils were observed that an increase in the temperature for 298K to 318K led to an increase in percentage sorption for all studied soils the increase in sorption could be due to changes in pore size or an increase in kinetic energy of the sorption with increase in temperature suggests endothermic nature. The activation energy (E_a) for sorption of β -endosulfan onto studied soils was determined using the Arrhenius equation, the values of activation energy for β -endosulfan sorption less than 42 kJ mol⁻¹. Since E_a values < 42 KJ mol⁻¹ indicates that diffusion controlled process, it is concluded that β -endosulfan adsorption for the studied soils is a diffusion controlled reaction. The positive values of ($\Delta H^\#$) suggest that the sorption reactions are energy consuming process. The enthalpy ($\Delta H^\#$) of sorption reaction were positive suggest that sorption process were endothermic reaction. The small negative values for ($\Delta S^\#$) suggesting that β -endosulfan sorption for the studied soils is associative mechanism. The positive values of ($\Delta G^\#$) which are an indication of a nonspontaneous sorption process that is, due to the endothermic character. The magnitude of ($\Delta G^\#$) increased with the rise in temperature.

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Table 1: Selected physical and chemical characteristics of the three different soils used for the present study

Characteristics	Al-Nwueimeh soil	Al-Zubeidate soil	Bardaleh soil
pH #	7.76±0.2	7.28±0.007	7.64±0.05
EC [#] (dsm ⁻¹)	2.25±0.02	21.41±0.01	3.49±0.007
Total carbonate [#] (%)	39.14±0.3	35.74 ±0.4	12.43±0.3
Sand (%)	75.55± 1.2	71.27 ± 1.3	69.61±0.98
Silt (%)	10.4 ±1.5	11.38 ± 1.2	18.34±0.86
Clay (%)	14.05± 1.9	17.35±1.5	12.05±1.3
Texture [§]	sandy loam	sandy loam	sandy loam
Organic matter [¥] (%)	1.37±0.04	3.25±0.06	1.04±0.04
CEC ^{§§} cmol(+).kg ⁻¹	13.755 ±0.4	35.815±0.3	14.651±0.2

Soil: water ratio 1:2 ## Nelson,1982 § Day, 1965 § Rhoades ,1982 ¥ Nelson and Sommers,1982

Table 2: Range and mean values of coefficient of determination (R^2) and standard error of estimates (SE) for different kinetics models fitted to the β -endosulfan sorption on the three studied soils

Model	R^2		SE	
	Range	Mean	Range	Mean
Kinetics Models				
Modified Freundlich	0.962-986	0.978	0.035-0.093	0.065
First order	0.922***-988	0.948	0.001-0.13	0.075
Elovich	0.882**-984	0.937	0.33-0.79	0.498
Parabolic Diffusion	0.939-987	0.971	0.11-0.65	0.313

, * significant at $p < 0.01$ and $p < 0.001$ respectively

Table 3: Calculated first order equation parameters β -endosulfan sorption for the three studied soils under isothermal conditions

Initial Conc. (mg L ⁻¹)	Al-Nuweimeh soil		Al-Zubeidate soil		Bardaleh soil	
	ka min ⁻¹ x 10 ³	a μg g ⁻¹	ka min ⁻¹ x 10 ³	a μg g ⁻¹	ka min ⁻¹ x 10 ³	a μg g ⁻¹
298K						
15	2.61	2.28	3.22	2.11	1.21	2.47
30	2.82	2.47	3.54	2.33	1.31	2.59
308K						
15	3.42	1.28	4.43	1.07	2.22	1.12
30	3.71	2.41	4.71	2.25	2.64	2.59
318K						
15	4.63	1.26	5.4	1.35	3.24	1.17
30	4.81	2.40	5.6	2.18	3.43	2.56

Table 4: Thermodynamic parameters of β -endosulfan sorption on the three studied soils at two β -endosulfan initial concentrations

Initial Conc. mg L ⁻¹	Ea kJ mol ⁻¹	$\Delta G^\#$ (kJ mol ⁻¹)	$\Delta S^\#$ J mol ⁻¹	$\Delta H^\#$ (kJ mol ⁻¹)
Al-Nuweimeh soil				
15	22.47±0.04	87.79±0.002	-22.74±3.88	19.99±0.001
30	21.25±0.04	87.59±0.42	-23.08±0.69	18.77±0.21
Al-Zubadate soil				
15	20.67±0.002	87.22±0.004	-23.15±7.14	18.19±0.002
30	18.57±0.002	86.99±0.004	-23.77±7.71	16.10±.002
Bardaleh soil				
15	38.18±0.004	89.61±0.008	-17.88±0.014	36.28±0.004
30	38.07±0.001	89.34±0.0002	-18.02±0.38	35.60±0.0001

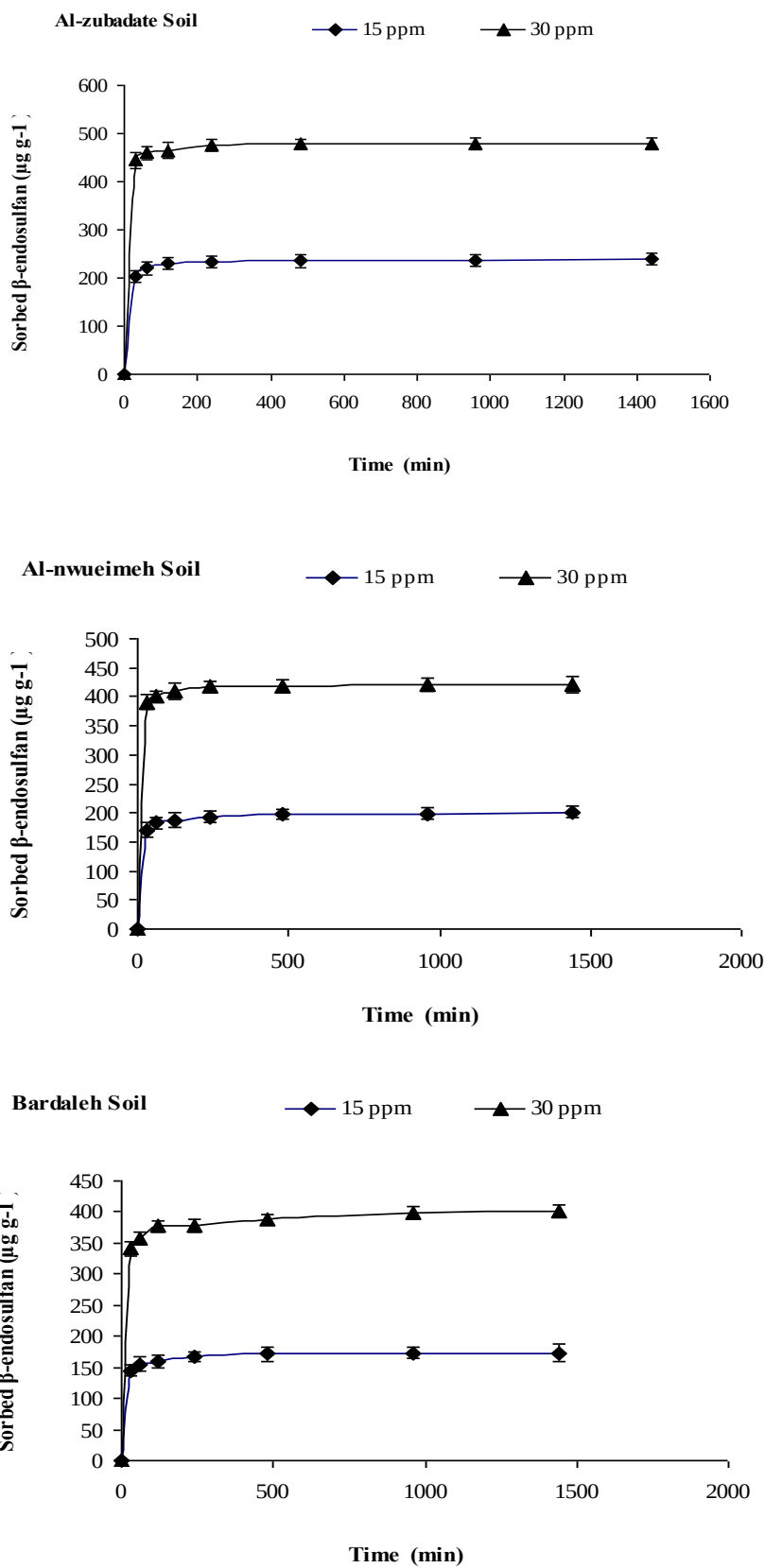


Fig. 1: Macroscopic sorption of β -endosulfan sorbed on three studied soils at 298K 546 and two different initial β -endosulfan concentrations vs. time

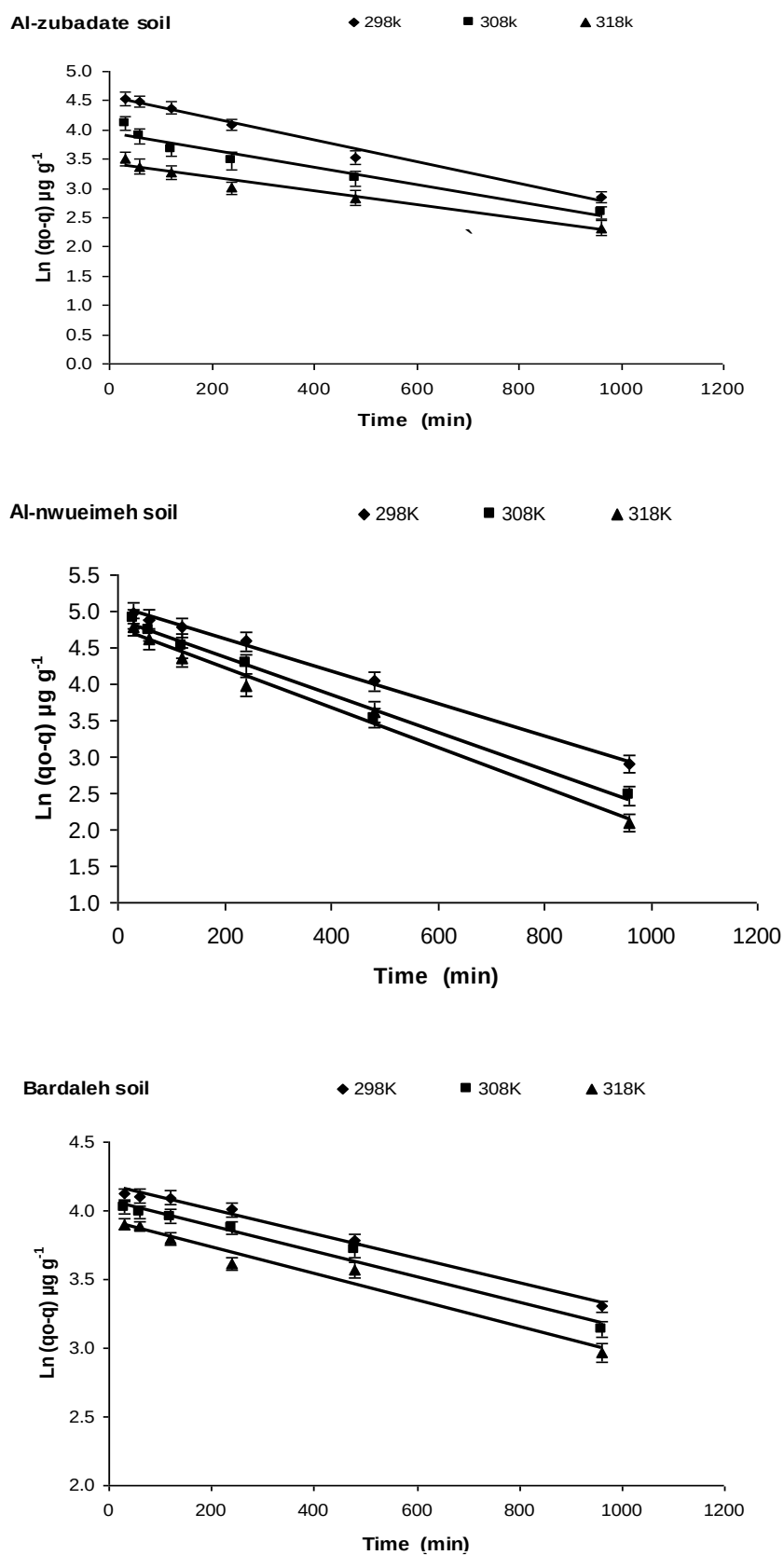


Fig. 2: First order equation plots of β -endosulfan sorption on the three studied soils at 3 temperatures and 30 mg ml^{-1} initial β -endosulfan concentration

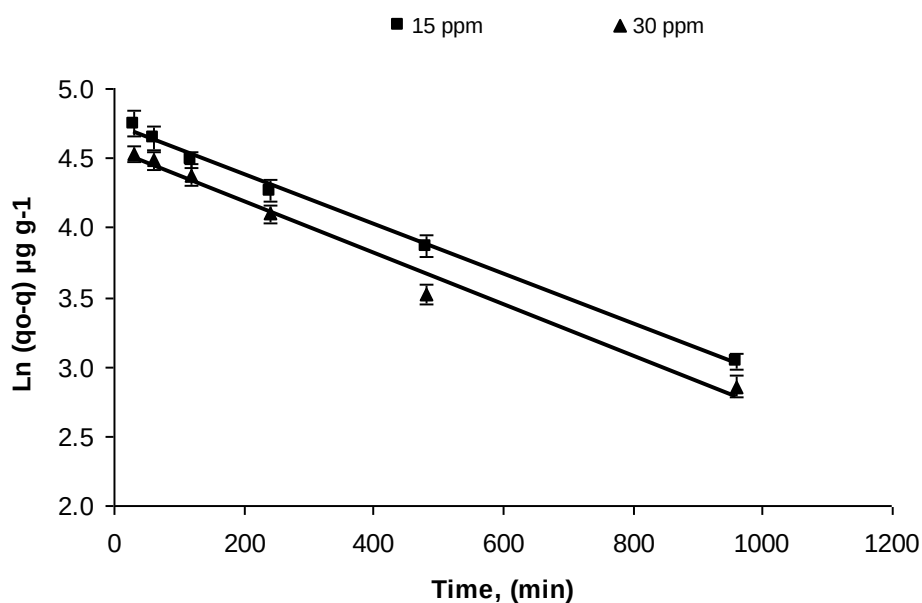


Fig. 3: Parallel relationship of the first order kinetic model with Al-Zubeidat soils at 298K and changing initial concentration while all other reaction parameters remained constant

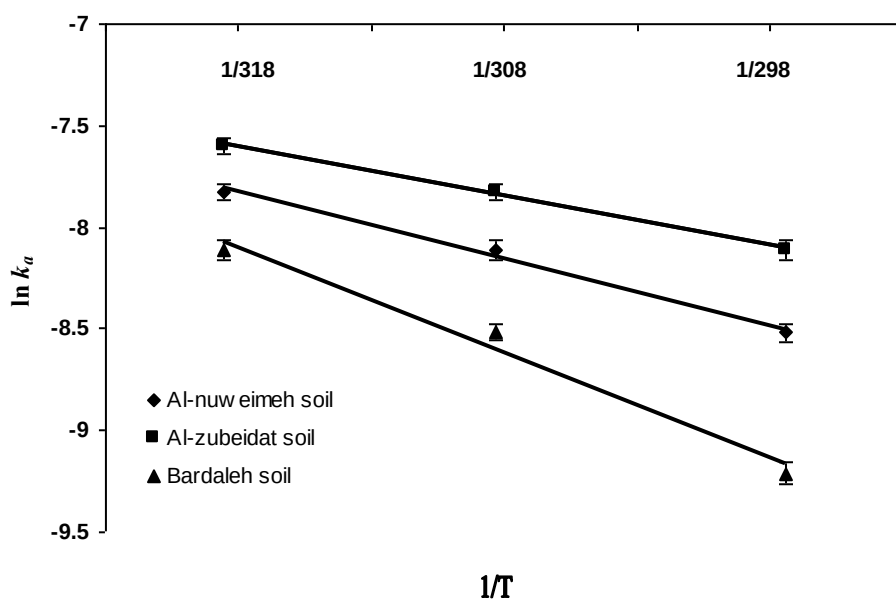


Fig. 4: Arrhenius plots of β -endosulfan sorption for three studied soils in Jordan Valley at three different temperatures