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THERMODYNAMIC APPROACH TO STUDY PHOSPHATE SORPTION FOR CALCAREOUS SOILS IN SULAIMANI AND HALABJA GOVERNORATES, KURDISTAN REGION-IRAQ

A Thesis

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In

Soil and Water Sciences

Soil Chemistry

By

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SUMMARY

This thesis presents the results of an investigation of P sorption characteristics of soils from nine representative locations within the agricultural area of Sulaimani and Halabja Governorates. Various models are used to describe adsorption processes in the soils. The isotherms equations are Langmuir, Freundlich and Temkin equations. The P sorption maximum (b), bonding energy constant (K_L), maximum P buffering capacity (MPBC), dimensionless equilibrium parameter (R_L), adsorption capacity (K_f), strength of adsorption (n), standard thermodynamic equilibrium constant (K_d), heat of sorption constant (B), equilibrium binding constant of Temkin isotherm (A_T), constant of Temkin isotherm related to heat of sorption (b_t), free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy changes ($\Delta S°$) for the sorption of P are correlated with physicochemical properties of the selected soils for better understanding of P dynamics.

This research was conducted for the purpose of measuring the adsorption of phosphorus in different some calcareous and non-calcareous soils to evaluate the use of isotherm equations in nine agricultural locations depending on the variation in their soil physicochemical properties. The soil samples were collected from two different depths (0 to 30 and 30 to 60 cm). Phosphorus sorption characteristics were determined by the using of the batch equilibrium technique at three different temperatures (278, 298 and 318 ^{o}K).

The main results could be summarized as follows:

1-The value of maximum adsorption (b) for Langmuir model at the surface layer was ranged from 2.50 mg kg^{-1} to 16666.60 mg kg^{-1}. While, for subsurface layer it was ranged from 99.01 mg kg^{-1} soil to 111111.10 mg kg^{-1}soil.

2-The value of bonding energy (K_L) for Langmuir model at the surface layer was ranged from 0.01 L mg^{-1} to 6.30 L mg^{-1}, while for subsurface layer it was ranged from 0.003 L mg^{-1} to 9.43 L mg^{-1}.

3- The Maximum Buffering Capacity of soil (MBC) at surface layer ranged from 0.02 mg kg^{-1}soil to 19666.59 mg kg^{-1}soil, while at subsurface layer was ranged from 20.00 mg kg^{-1}soil to 333667.00 mg kg^{-1}soil.

4- The Langmuir separation factor (R_L) which is a dimensionless constant. The values of R_L at surface layer ranged from 0.04 to 0.19, while at subsurface layer it ranged from 0.01 to 0.42. The

different values of R_L at the two layers and three different temperatures were greater than zero but less than one ($0<R_L<1$) this indicating that the sorption process of P is favorable at both depths for all studied locations.

5- The value of strength of adsorption (n) for the Freundlich model at the surface layer was ranged from 0.329 to 1.842 while for the subsurface layer ranged from 0.779 to 15.38.

6- The value of adsorption capacity (K_f) for Freundlich model at the surface layers of studied soils ranged from 0.951 mg kg^{-1} to 46.85 mg kg^{-1}, moreover at the subsurface layer, it ranged from 7.74 mg kg^{-1} to 122.50 mg kg^{-1}.

7- (A_T) which was the equilibrium binding constant of Temkin model at the surface layer was ranged from 0.0000013 to 1.0000051, however, at the subsurface layer, it ranged from 1.00000003 to 1.00009.

8- b_t (which was related to the heat of sorption) for Temkin models at the surface layer ranged from 1431.10 to 1303985.20, while for the subsurface layer it ranged from 5034.60 to 688214.40.

9- Heat of sorption constant (B) for Temkin model at surface layer it ranged from 0.0019 J mol^{-1} to 0.0136 J mol^{-1}, but at the subsurface layer, it ranged from 0.0036 J mol^{-1} to 0.4921 J mol^{-1}.

10- Langmuir model proved better over both Freundlich and Temkin models for P sorption-based on the average coefficient of determination (R^2) and standard error of estimate (SE) values, that at all three different temperatures which were used in this study, at both layers for all the soils under investigation

11- From the relationships between soil physicochemical properties and isothermal equations parameters in studied soils it is found that the heat of sorption (b_t) (J mol^{-1}) from a Temkin isotherm equation was positively correlated with active calcium carbonate content ($r = 0.727$. $p = 0.026$), sand content ($r = 0.724$. $p= 0.027$) and also strength of adsorption (n) from Freundlich isotherm equation was correlated with silt content ($r = 0.736$. $p = 0.023$).

12- From the relationships between soil physicochemical properties and amount of adsorbed P (Q_e) on soil surface particles it found that the amount of Q_e not correlated with most of the physicochemical properties of the soil except it correlated with organic matter content significantly ($r =0.756^*$) from the applying Langmuir equation, and it had a high and significant correlation with active $CaCO_3$ equivalent and silt content from the applying of Freundlich equation ($r=0.840^{**}$) and ($r= 0.858^{**}$) respectively.

13- ΔG° which is an important parameter in adsorption thermodynamics, according to that, it can be said that a non-spontaneous adsorption has occurred in the studied area and this because of the positive values of ΔG° which are ranged from 22.82 kJ mol^{-1} to 36.28 kJ mol^{-1} at surface layer but for subsurface layer it ranged from 10.05 kJ mol^{-1} to 97.09 kJ mol^{-1}.

14- The strength of binding P to the soil is explained by ΔH°, and the enthalpy changes of adsorption is a measure of the heat of adsorption, and it ranged from 24.20 kJ mol^{-1} to 34.30 kJ mol^{-1} for the surface layer, however at the subsurface layer it ranged from 13.25 kJ mol^{-1} to 111.89 kJ mol^{-1}.

15- The nine studied locations found to have an endothermic reactions and this is due to the positive value of ΔS°. The values of ΔS° was ranged from -6.24 J $mol^{-1}K^{-1}$ to 4.38 J $mol^{-1}K^{-1}$ at the surface layer, but for the subsurface soil it ranged from -8.01 J $mol^{-1}K^{-1}$ to 53.25 J $mol^{-1}K^{-1}$. The positive values of ΔS° are an indication of increasing in randomness in the processes of adsorbing P.

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List of Abbreviations

A.$CaCO_3$ active calcium carbonate.

A_T equilibrium binding constant of Temkin isotherm.

B heat of sorption constant.

b maximum adsorption

b_t constant of Temkin isotherm related to the heat of sorption.

C_o initial concentration

C_e equilibrium concentration

C_f final concentration of P

C clay

cm centimeter

g gram

GPS global positioning system

J Joule

K Kelvin

K_d standard thermodynamic equilibrium constant

K_f Freundlich adsorption capacity

kg kilogram

kJ kilojoule

K_L bonding energy constant

L Liter

L loam

MBC maximum buffering capacity

MPBC maximum P buffering capacity

n strength of adsorption

O.M. organic matter

P Phosphor

Q_e amount of adsorbed adsorbent.

R Gas constant (8.314J mol^{-1} k^{-1}).

R_L separation factor, dimensionless constant.

Rpm round per minutes

SE standard error

SC Silty clay

SCL silty clau loam

T absolute temperature (measured in Kelvin).

T.$CaCO_3$ Total calcium carbonate.

V Volume

W Weight

ΔG° Gibbs free energy

ΔH° enthalpy

ΔS° entropy

CHAPTER ONE

INTRODUCTION

Soil and its content are essential factors that control the yield of agricultural production. As with the other living being, plants require food for their growth and reproduction. The challenge for agriculture in the coming decades will be to fulfill the world's growing demand for food in a supportable way (Tamungang *et al.*, 2016). What made this task to be more difficult is mismanagement of fertilizer which led to declining fertility and plant's nutrient deficiency. Amongst the three elements (Nitrogen, Phosphorus, and Potassium) which are the constituent of N-P-K fertilizer, P is considered as an essential one, and at most times P found to be unavailable to plants.

Since Phosphorus is one of the essential elements for plant growth, knowledge on the behavior of phosphorus is fundamental to understand the plant nutrition and the soil biochemical cycle (Afsar *et al.*, 2012). Phosphorus is an important component of cell membranes. Also, it's responsible for plant genetic material, energy storage and transforming system for a chemical reaction in a plant cell. The early growth of the plant is dependent on P because it is essential for the division and expansion of the cells (Tamungang *et al.*, 2016). As the importance of P in the soil for plants has been mentioned, the efficiency of phosphate fertilization is becoming more important for an economically and environmentally maintainable agricultural system (Afsar *et al.*, 2012).

One of the factors that have effects on the availability of P is $CaCO_3$. Mostly soil of Kurdistan is considered as calcareous because of the presence of high amount of both total and active $CaCO_3$. As mentioned by (Naeem *et al.*, 2013), when P fertilizer is added to soil it reacts with the constituent of the soil and decreases the availability of phosphorus. In soil that contains large amounts of calcium carbonate, when P fertilizer is added it often participates as dicalcium phosphate or octacalcium phosphate. Moreover, the concentration of the P highly determines whether adsorption or precipitations will occur. In which at low P concentration active $CaCO_3$ might results in P adsorption, whereas at high concentration of P, precipitation might be predominant (Naeem *et al.*, 2013). The surface area of carbonate has an influence on the reactivity of $CaCO_3$, and the dynamics of P is accomplished by calcite, which strongly graps P and therefore keeps low P concentration in the soil solution. Along with $CaCO_3$, physical and chemical properties have to influence the amount of adsorption. Amongst them soil texture which showed great relations.

The sorption isotherm can be used to determine the amount of P which must be added to the soil to increase the P concentration in the soil solution. In many areas of the world level of phosphorus cause serious environmental and agricultural problem, thus to decrease such problems studying adsorption process is important (Zhao *et al.*, 2017). Adsorption defined as equilibrium relationship between both of adsorbed and dissolved P in a constant temperature (Tamungang *et al.*, 2016). The measureable explanation of P sorption by the soil has been made by Langmuir, Freundlich and Temkin equations. The main reasons for using these equations are: to realize the processes involved and to summarize several results by few parameters (Afsar *et al.*, 2012).

In view of above facts and since there is a few study on phosphor adsorption in Kurdistan Region, thus this study was selected for investigating the following points:

1. Determining the ability of representative calcareous soils to adsorb Phosphate and to compare sorption isotherm between the soils.
2. Using Langmuir, Freundlich and Temkin isotherm equations to describe the P adsorption.
3. To summarize many parameters for the isotherms mentioned above equations.
4. Estimating the correlation between P adsorption and some physiochemical properties of studied soils.
5. Finding out the amount of fertilizer needs to be added to soil to avoid excesses and reduce water pollution by fertilizers.

CHAPTER TWO

LITERATURE REVIEW

2.1 Phosphorus In Soil

One of the key components of any sustainable cropping system is Phosphorus. Phosphorus is classified as a macronutrient because plant requires P in a large amount. Phosphorus is considered as an essential nutrient for plant nutrition in which its deficiency limits its growth. The importance of phosphorus comes after Nitrogen, and it limits agricultural production in most regions of the world. One of the techniques that are used for predicting P requirements by crops in different soil system is phosphorus adsorption isotherm because it successfully uses the relationship between adsorbed P (capacity factor) and soil solution (intensity factor) (Mnthambala *et al.*, 2015). Phosphate is found in soil in different forms; solution P, active P and fixed P. The solution P usually will be in the form of orthophosphate in which plant only take up P in that form, while active P is the solid phase forms of it in which it easily released to soil. Moreover, the fixed P contains more inorganic Phosphate component in which it’s very insoluble. Because of the importance of P to plants and crop production, so phosphorus fertilization management is very important especially in the soil of Kurdistan in which many researchers found its problem in soil and its reaction with $CaCO_{3.}$ (Mam Rasul and Saeed, 2014).

2.2 Fate of Phosphorus Added to Soil

The phosphor is added to soil either by fertilizer or by manure form in which they are quite soluble and available. When manure and phosphate fertilizer is added to the soil, during that contact with the soil, different reactions will occur in which it makes the phosphate less available and less soluble (Busman *et al.*, 2002). Many researchers also reviewed the state of P in the soil among them was Mnthambala *et al*. (2015) stated that; when the phosphorus fertilizer in it's both forms liquid, and solid are applied to the soil, some of the orthophosphate ions in forms of H_2PO_4 and HPO_4 will react with soil component and convert the state of P to less soluble. Soil conditions have a great influence on such reactions, and they are dependent on pH, clay content, type of mineral that already present in the soil and also the amount of $CaCO_3$. The added phosphate will gradually migrate away from the fertilizer particle and will start reacting with mineral found in the soil. Generally, phosphate reacts with minerals in the soil by adsorbing to the soil or by combining with the elements in the soil such as iron (Fe), magnesium (Mg), calcium (Ca) and aluminum (Al). Gradually these reactions make the available P to be unavailable or fixed P, and by passing the time, it results in a decrease of P in the soil. (Busman *et al.*, 2002) also, this state of P in soil has been argued by mangy researchers including [Parfitt, 1978; Sample *et al.*,1980; Matar *et al.*, 1992].

2.3 Phosphorus in Calcareous Soil

Most of the soil of Kurdistan region is considered as a sever calcareous soil and this is because of the high amount of $CaCO_3$ that presents in it. For that reason, the availability of phosphate is very low in calcareous soil because adsorption or precipitation reactions will occur between P and the soil constituent (Mam Rasul and Saeed, 2014). To attain economic, agricultural yields in those soils, adding lime and P fertilizer is essential because such addition brings severe changes in the ionic equilibria and this will influence the rates of ion supply to plant root and will have effects on plant growth (Anghinoni *et al.*, 1996). Thus far, several studies illustrated the mechanism of phosphorus adsorption to $CaCO_3$ [Bilgili *et al.*, 1998; Mehmood *et al.*, 2010; Mam Rasul and Saeed, 2014, and Millero, 2001]. They suggested that calcite initially uptake phosphate by chemisorption, followed by a slow conversion of amorphous calcium phosphate to crystalline apatite. Moreover, the surface of calcite is highly dynamic, even when it's exposed to air, and it has the ability to unite adsorbed material into the near-surface bulk. This nature of calcite surface can progressively create new sorption sites that may have important significant in the behavior of adsorbed P in soils with a high amount of carbonate (Bilgili *et al.*, 1998). Samadi (2006) demonstrated that phosphorus adsorption in calcareous soils was normally correlated to the amount of $CaCO_3$ in the soil, both active and total $CaCO_3$ content have an effect on adsorption of P.

2.4 Phosphorus sorption

The ability of the soil varies greatly in supplying the adequate amount of available P which is required by the plant. Plants requirement of P for optimal growth is also varied (Afsar *et al*, 2012). To increase the amount of available P in the soil for plant growth, better management of phosphate fertilizer is required. This management can be achieved by studying the behavior of P sorption-adsorption in the soil because it reflects the partitioning of P between soil solution and soil solid phase (Afsar *et al*, 2012). The principle process which involved in the release and retention of P is sorption and desorption reactions (Afsar and Osman, 2012).

Calcareous soils make up some of the most productive agricultural lands in Kurdistan region of Iraq. Due to their minimal occurrence, little research has been done on these soils. Understanding phosphorus (P) chemistry is necessary for environmentally sound management of these soils. In this study, P sorption phenomenon was investigated using several thermodynamic isotherms like Langmuir, Freundlich and Temkin equations. The information on chemical forms and sorption are of particular interest since it reveals not only the availability of P but also the likely the retention mechanisms when additional P is applied to soils (Hongthanat, 2010).

Phosphorus (P) is an essential element for plant and animal growth; however, improper management of P can adversely affect the environment. Phosphorus loading of surface water is a major water quality issue in Kurdistan region of Iraq. When P is added to soils, a reaction called P sorption occurs. Phosphorus sorption refers to the fast surface reaction and slow reaction of P on a solid phase (soil minerals and organic compounds). Sorption of P initially proceeds by a rapid exothermic ligand exchange reaction that takes place with the reactive surface groups. After a hydroxyl (OH^-) or H_2O molecule is released from the surface, a phosphate surface complex is formed (Frossard *et al*., 1995). After the fast reaction, a slow reaction occurs by ion exchange with exchangeable cations or cations in crystal lattices. Phosphorus sorption in this context also includes “adsorption” and “retention”. “The two main types of adsorption are; physisorption and chemisorption. Physiosorption is a nonspecific adsorption which occurs as a result of long-range weak Van der Waals forces between adsorbate and adsorbent. This adsorption is reversible, and the amount of material adsorbed may correspond to several monolayers. The energy released when a particle is physisorbed is of the same magnitude as the enthalpy of condensation. The enthalpy of physisorption is monitoring the rise in temperature of samples of known heat capacity. Chemisorption is a specific adsorption and limited to monolayers coverage of the substrate. Here, a covalent bond is formed between the adsorbate and adsorbent. The enthalpy of chemisorption is within the range of 200 kJ mol^{-1} (Atkins,1999). The sorption process is controlled by the concentration of P in solution (intensity) and the ability of solid phase to replenish P into solution (capacity). When inorganic P is added to soil, sorption reactions proceed until a new equilibrium is reached.

One way to determine P sorption capacity of soil is to develop a P sorption isotherm, because the P sorption isotherm technique is a time-consuming and laborious batch-type experiment, easily measures soil properties (Hongthanat, 2010).

Sorption isotherms of phosphate have been widely used to describe the status of P, and also it's used to find the fertilizer requirements of soils (Anghinoni *et al.*, 1996). Various models are used to describe adsorption processes in the soils, and the models have effectively described the nutrient uptake by plants under the changing soil and plant parameters. The isotherms equations are Langmuir, Freundlich and Temkin equations.

2.4.1 Langmuir Isotherm Equation

The Langmuir isotherm (Langmuir, 1916) has been widely applied in adsorption studies. It assumes a monolayer adsorption in which adsorbates are adsorbed to a finite number of definite localized sites that are identical and equivalent with no lateral interaction (Foo and Hameed, 2010).

Langmuir equation has been used to explain the adsorption since 1957 (Del-Bubba *et al.*, 2003). The Langmuir equation allows the estimation of an adsorption maximum and bonding energy constant (Olsen and Watanabe, 1957). Langmuir equation implies that adsorption occures in a monolayer on the soil surface. The adsorption maximum derived from Langmuir equation is a useful parameter for estimating P adsorption capacity and comparing different soils (Borling, 2003). Then, the Langmuir equation has often used to describe ion adsorption on soil materials (Brown *et al.*, 2005). It is now widely recognized that Langmuir is probably the best known applied sorption isotherm because it has made a good agreement with a variety of experimental data (HO *et al.*, 2002).

"Langmuir represents the equilibrium distribution of metal ions between the solid and liquid phase" (Dada *et al.*, 2012).

The non-linear expression of Langmuir isotherm model can be illustrated as follow:

$$Q_e = \frac{bK_LC_e}{1 + K_LC_e} \qquad (2.1)$$

In the linear form, the equation (2.1) can be written as:

$$\frac{1}{Q_e} = \frac{1}{b} + \frac{1}{bK_L C_e} \qquad (2.2)$$

Hussain, *et al* (2006) argued that the Langmuir parameters (b) maximum adsorption and (K_L) bonding energy constant are dependent on soil chemical and physical properties. According to (Naeem *et al.*, 2013) which stated that more value of (b) will increase the P adsorption capacity of the soil and the amount of $CaCO_3$ has great influence on the value of parameters. A similar argument has been stated by Hussain *et al.* (2003); Hussain *et al.* (2006); Mehmood *et al.* (2010) and Rehyanitabar *et al*. (2010). While Samadi (2006) stated that both total and active $CaCO_3$ is less important for the values of parameters in P adsorption. R_L which is the equilibrium parameter and a dimensional constant referred to as separation factor or equilibrium parameter. Much of the literature on Langmuir study claimed that the value of R_L is an indication of natures of the adsorption and it would be either favorable, unfavorable, linear and irreversible.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L). This parameter is defined by Tan (2008) and Surchi (2011)

$$R_L = \frac{1}{(1 + K_L)C_e} \qquad (2.3)$$

If $R_L>1$ unfavorable adsorption $R_L=1$ linear adsorption, $0<R_L<1$ favorable adsorption and $R_L= 0$ irreversible adsorption.

2.4.2 Freundlich Isotherm Equation

Freundlich isotherm was developed to study the adsorption of a material onto animal charcoal (Freundlich, 1906). It is, however, presently applied in heterogeneous systems especially for organic compounds or highly interactive species on activated carbon and molecular sieves. It is an empirical model which applies to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface (Foo and Hammed, 2010).

In 1906, Freundlich offered the earliest recognized equation for adsorption isotherm (Freundlich, 1906). It is the first adsorption equation in the collect work on soil P. Kipling (1965) presented a justification for its application to adsorption from dilute solution. The Freundlich equation is an experiential approach and resembles an adsorption model in which the affinity term declines exponentially as the quantity of adsorption upsurges. This is an empirical model, which can be applied to non-ideal adsorption on diferent surfaces along with multilayer adsorption. This is often appraised for missing a basis of fundamental thermodynamic since it does not decrease to Henry's law at low concentrations (Ho *et al*., 2002).

The Freundlich isotherm has been resulting by supposing an exponentially declining adsorption site energy distribution (Zeldowitsch, 1934). According to the Polyzopoulos *et al*. (1985), the Freundlich equation is characterized by the effortlessness of form, based on more genuine supposition. Now, it is capable of rigorous derivation for both adsorptions of gas molecules and exchange of ions with soil colloids (Sposito, 1980). Therefore, it can be used in preference to the others, since its parameters, like those of the Langmuir equation, allow comparison among soils.

The equation is expressed as:

$$Q_e = K_f\, C_e^{1/n} \qquad (2.4)$$

The equation can be expressed in its linear form as:

$$logQ_e = logK_f + \frac{1}{n} logC_e \qquad (2.5)$$

Much of the published studies described the Freundlich equation parameters, (n) which is the strength of adsorption and (K_f) which is the Freundlich adsorption capacity, in their relation with the soil chemical and physical properties. Puttamat and Pavarajam (2016) demonstrated the influence of temperature on the value of parameters, as the temperature is increased n and K_f value will also increase. Moreover, Dada *et al* (2012) claimed that value of n is an indication of the type of sorption process. However, Ali *et al.* (2013) found that the value of K_f and the capability of the soil for adsorbing P can be estimated.

Freundlich proportionality constant (K_f) can be calculated by taking antilog of the value of Y-intercept, when data is to be plotted according to Freundlich model. Assimakopoulos *et al*. (1986) stated that K_f of the Freundlich model represents the quantity of adsorbed P required to maintain P concentration in the solution. Consequently, soils with already a large portion of their occupied adsorption sites would retain less P from the soil solution in order to maintain its concentration at 1 unit. Freundlich K_f value is the ratio of the amount of P in the solid phase to the amount of P solution. According to Shayan and Davey (1978), it is capability factor indicating that a soil having a higher K_f value has more adsorption capacity than a soil has less K_f value. George *et al*. (2005) stated that the benefit of the Freundlich isotherm is that it is a diverse binding model that can provide accommodation and quantify the heterogeneity and it is extensively valid in determining the heterogeneity. The Freundlich equation is often measured to be purely empirical in nature but broadly has been used to designate the adsorption of phosphorus by the soil (Thakur *et al*., 2004). Some of investigators stated that the Freundlich adsorption isotherm describes adsorption data in a better way than by the Langmuir equation (Sidhu *et al*., 2004).

2.4.3 Temkin Isotherm Equation

The origin of the Temkin isotherm equation theorized that lowering in the heat of sorption is linear rather than logarithmic (Hoet *et al*. 2001). Similarly, Puttamat and Pavarajam (2016) stated that heat of adsorption (a function of temperature) of all molecules in the layer would be decreased linearly rather than in a logarithmic manner with the coverage.

Temkin isotherm contains a factor that takes into account the adsorbent-adsorbate interactions (Tempkin and Pyzhev,1940). The model is given as follow:

$$Q_e = BlnA_T + BlnC_e \qquad (2.6)$$

$$B = \frac{RT}{b_t} \qquad (2.7)$$

2.5 Thermodynamic Study of Phosphate Adsorption

The thermodynamics of metal ion sorption has been investigated extensively. There are two common types: endothermal and exothermal sorption processes. If the sorption increases with increasing temperature, it means that the sorption is an endothermal process. Whereas the sorption decreases with increasing temperature, indicates the exothermal sorption process. Zhoa *et al.* (2011) reported that the thermodynamic parameters such as free energy (ΔG°), enthalpy (ΔH°) and entropy changes (ΔS°) for the sorption of P were computed to predict the nature of sorption process by carrying out the adsorption experiments at three different temperatures (278^oK, 298^oK, and 318^oK). The value of enthalpy (ΔH^o) and entropy (ΔS^o) can be estimated from the slope and intercept of ln K_d vs. 1/T plots according to Van’t Hoff equation:

$$lnK_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \qquad (2.8)$$

Gibbs free energy (ΔG°), a force that determines the spontaneity of adsorption reactions was obtained using the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\, \Delta S^\circ \qquad (2.9)$$

The models and equations are mentioned in details from the materials and methods chapter.

CHAPTER THREE

MATERIAL AND METHODS

3.1 Area of Study

This study was conducted for the purpose of measuring the adsorption of phosphorus in different soils and to evaluate the use of isotherm equations in selected soils. Samples for this study were located in Kurdistan Region of Iraq. Soil samples were collected from nine different agricultural locations. The locations were: Bazyan, Halabja, Saidsadiq, Dukan, Chwarta, Kanipanka, Bakrajo, Khurmal, Girdjan. Soil samples were taken at two different depths; (0-30 and 30-60) cm. The global positioning system GPS for the selected locations are present in the table (3.1) and the locations are pointed out on the map of figure (3.1).

Table 3.1 Positions of studied locations by GPS.

Locations	N	E	Elevation (m)
Bazyan	35° 38′518″	045° 0.2 ′ 233″	869
Halabja	35° 16 ′ 34″	045° 56 ′ 415″	497
Saidsadiq	35° 20 ′ 430″	045° 56 ′ 249″	507
Dukan	35° 50 ′ 762″	045° 03 ′ 881″	719
Chwarta	35° 43 ′ 897″	045° 29 ′ 662″	941
Kanipanka	35° 22 ′ 887″	045° 43 ′ 083″	559
Bakrajo	35° 32 ′ 569″	045° 21 ′ 122″	737
Khurmal	35° 18 ′ 125″	045° 59 ′ 689″	534
Girdjan	36° 12 ′ 900″	044° 97 ′ 161″	537

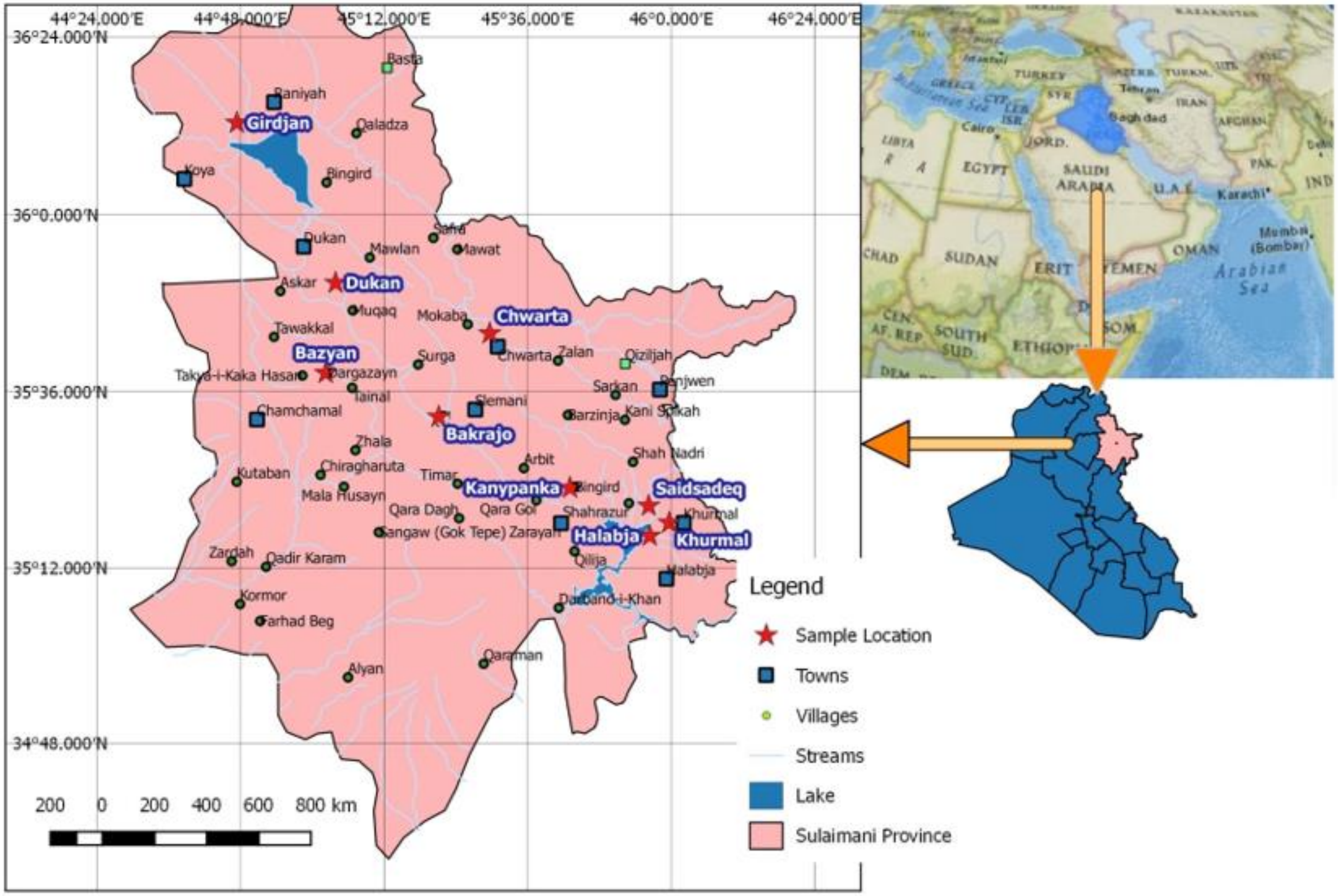

Figure 3.1A map representing the nine studied locations in Kurdistan region of Iraq

3.2 Laboratory Analyses:

3.2.1 Samples preparations

The soil samples which were collected from nine different areas were taken from two different depths (0 to 30 and 30 to 60) cm. The soil samples were brought to the laboratory and air dried, ground with a mortar and passed through 2mm sieve to separate the fragments (<2mm).

3.2.2 Physical Analyses:

3.2.2.1. Soil particle size distribution

Soil particle size distribution was determined according to the international pipette method as described by Gee and Bauder (1986).

3.2.3 Chemical Analyses

The following chemical analyses were conducted according to the following procedures:

3.2.3.1 Electrical Conductivity (EC_e)

The electrical conductivity (EC_e) was measured for the soil saturation extract with EC-meter (WTW).

3.2.3.2 Soil Reaction (pH)

The pH of the soil saturation extract was measured with a pH-meter, model (inolab WTW).

3.2.3.3 Soil Organic Matter

Organic matter content was measured by using wet digestion according to the Walkley and Black method as described by Jakson (1958).

3.2.3.4 Total calcium carbonate ($CaCO_3$) equivalent

The total calcium carbonate equivalent was determined with 1 *M* HCl and the excess of HCl, was titrated with 1 *M* NaOH by using phenolphthalein indicator as described by Richards (1954).

3.2.3.5 Active calcium carbonate equivalent

The active calcium carbonate equivalent was determined titremetrically using (Droulinean) procedure in which; 0.5 g of soil samples were shaken with 0.2 *M* ammonium oxalate solution to precipitate calcium oxalate and the excess of ammonium oxalate, was determined by titration with potassium permanganate according to Kozhekov and Yakovleva (1977).

3.2.3.6 Available Phosphorous:

It was determined according to (Olsen and Sommeres method, 1982) method as described by Rowell (1996).

3.3 Phosphorus sorption study

Phosphorus sorption characteristics were determined by batch equilibrium methods in which soil samples for both depths were agitated with P solution of known concentration (Gaeta and Nair, 2009). Soil samples collected from nine locations (Bazyan, Halabja, Saidsadiq, Dukan, Chwarta, Bakrajo, Kanipanka, Khurmal, Girdjan) that were previously used for soil physicochemical analyses were used in P-sorption study. All samples were chosen depending on amount of available P in the and they all were at a temperature between 20-25^{o}C crushed and sieved through a 2mm sieve.

Phosphorus as KH_2PO_4 was dissolved in 0.1 *M* solution of calcium chloride in distilled water. The $CaCl_2$ solution is used as the aqueous solvent phase to improve centrifugation and minimize cation exchange (Fuhrman *et. al.*2005).

According to the methods of Fernandes and Coutinho (1994) to study the sorption of P by soils, five grams air-dried samples of each soil were placed in 100 ml plastic bottle to leave free space for 50 ml of 0.01*M* $CaCl_2$. Fifty milliliters of a solution containing 0, 5, 10, 15, 20, 30, 40, 50 and 60 mg L^{-1} of P prepared from (KH_2PO_4) were added to these bottles. Three to four drops oftoluene was added to inhibit microbial activity. The bottles were capped tightly and incubated for 24 hours at three different temperatures (278K, 298K and 318K). After equilibration time, the suspension was centrifuged for 10 minutes at 3500 rpm after that the suspension was filtered through Whatman filter paper No.42 and the concentration of P in the clear extract was determined according to Olsen and Summers 1982 method. The amount of adsorbed P by each soil in mg kg^{-1} was calculated using the formula reported by Vanderborght and Van Grieken (1977):

$$\frac{(C_o - C_f) x\ V}{weight\ of\ soil\ (kg)} \qquad (3.11)$$

Where

C_o = initial concentration of P (mg L^{-1})

C_f = final concentration of P (mg L^{-1})

V= volume of solution (L)

The P sorption data of the soils were fitted to linearized forms of Langmuir, Freundlich and Temkin equation because linear regression is convenient and best of the data-fitting process as described in detail from the literature and review chapter.

3.3.1 Langmuir equation

The linear form of Langmuir adsorption isotherm was used to evaluate adsorption parameters.

$$Q_e = \frac{bK_L C_e}{1 + K_L C_e} \qquad (3.12)$$

$$\frac{1}{Q_e} = \frac{1}{b} + \frac{1}{bK_L C_e} \qquad (3.13)$$

Where

Q_e = amount of adsorbed P (mg kg^{-1}).

C_e = P concentration in equilibrium soil solution.

b = maximum adsorption (mg P kg^{-1} soil).

K_L = factor of bonding energy constant (L mg^{-1}).

The data plotted as ($1/Q_e$ vs. $1/C_e$) and the plot gives a straight line of the equation with an intercept 1/b and slope1/bK_L.

The Langmuir constants were used to calculate maximum P buffering capacity (MPBC) which is the product of P sorption capacity and phosphate affinity constant. Maximum buffering capacity (MBC) measures the ability of soil to supply P in the soil solution when it tends to be depleted; it was calculated as a product of b x K_L according to Karimian and Moafpourian (1999) and Reyhanitabar *et al*. (2007).

$$MBC = b \times K_L \qquad (3.14)$$

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L) were calculated from the following equation:

$$R_L = \frac{1}{(1+K_L)\, C_e} \qquad (3.15)$$

3.3.2 Freundlich equation

The Freundlich isotherm was chosen to estimate the adsorption intensity of the adsorbent towards the adsorbate. It is represented by the equation (Mckay *et. al*.1982).

$$Q_e = K_f\, {C_e}^{1/n} \qquad (3.16)$$

Q_e = the amount of P adsorbed on a unit mass of solid phase (mg kg^{-1}).
C_e = equilibrium concentration of P in solutions (mg L $^{-1}$).
K_f = Freundlich adsorption capacity (mg kg^{-1}).
n = strength of adsorption

By fitting log C_e against log Q_e the values of constants were calculated and from the linear form of the equation slope is 1/n and the intercept is log K_f :

$$log Q_e = log K_f + \frac{1}{n} log C_e \qquad (3.17)$$

3.3.3 Temkin equation

This isotherm contains a factor that is explicitly taking into the account of adsorbent-adsorbate interactions (Dada *et al*., 2012). Heat of sorption constant (B value is determined from Q_e

equation, and the experimental data were carried out by plotting Q_e against $\ln C_e$. The constants were determined from the slope (B) and intercept ($B\ln A_T$). The Temkin equation is as following:

$$Q_e = B\ln A_T + B\ln \qquad (3.18)$$

$$B = \frac{RT}{b_t} \qquad (3.19)$$

Where

B = heat of sorption constant (J mol^{-1}).
A_T = equilibrium binding constant of Temkin isotherm (L kg^{-1}).
b_t = constant of Temkin isotherm (J mol^{-1}) related to the heat of sorption.
R = Gas constant (8.314 J mol^{-1} k^{-1}).
T = absolute temperature.

3.4 Thermodynamic parameters calculation

What stands out in the study of thermodynamic of phosphate adsorption is whether the reaction is exothermic or endothermic. Values of ΔH° and ΔS° are carried out from the linear form of the Van’t Hoff equation:

$$\ln K_d = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \qquad (3.20)$$

The relation between lnKd and 1/T is called the Van 't Hoff plot and is widely used to estimate the enthalpy and entropy of a chemical reaction. From this plot, $-\Delta H/R$ is the slope, and $\Delta S/R$ is the intercept of the linear fit.

The Van 't Hoff plot can be used to assess a reaction when the temperature changes.[Kim, 2012; Hino *et al*, 2010]. Knowing the slope and intercept from the Van't Hoff plot, the enthalpy and entropy of a reaction can be easily obtained using:

ΔH= -R * slope and ΔS= R * intercept. From the value of ΔH the type of reactions can be indicated, if the value of ΔH, for an endothermic reaction, $\Delta H > 0$ and R is the gas constant. While from an exothermic reaction, $\Delta H < 0$ and R is the gas constant. Thus, for an exothermic reaction, the Van 't Hoff plot should always have a positive slope. The distribution coiffetent Kd (was calculated from the concentration of P and suspention (C_o) and that of P in the supernanat (C_e) after centrifugation according to the equation (3.21) (Seker *et al*., 2008).

$$K_d = \left(\frac{C_o - C_e}{C_e}\right) x \frac{V}{W} \qquad (3.21)$$

Where

K_d = the standard thermodynamic equilibrium constant (L g^{-1}) defined by Q_e / C_e.

Q_e = the amount of P adsorbed on a unit mass of solid phase (mg kg^{-1}).

C_o = initial concentration of P (mg L^{-1})

C_e = equilibrium concentration of P in solutions (mg L^{-1}).

V = Volume of $CaCl_2$ which added to the soil samples.

W = Wight of the soil samples.

The free energy (ΔG°) of phosphate adsorption in the soil can be calculated as follow:

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ \qquad (3.22)$$

Where:

ΔG^o = Gibbs free energy change (kJ mol^{-1})

ΔH_f^o = Enthalpy change (kJ mol^{-1})

ΔS° = Entropy change (J mol^{-1} K^{-1}).

From defined the value of ΔG, which also tells us about the spontaneity of the reaction, becomes:

$\Delta G < 0$ favorable reaction (Spontaneous).

$\Delta G = 0$ Neither the forward nor the reverse reaction prevails (Equilibrium)

$\Delta G > 0$ unfavorable reaction (Nonspontaneous)

3.5 Statistical Analyses

Statistical data analyses like pair-wise comparison (Duncan's multiple range test) was performed by XLSTAT version 7.5. Computer programs were used to estimate relationships between phosphate sorption and different soil physicochemical properties (Addinsoft, 2007). Correlation coefficients were calculated between phosphate sorption parameters for Langmuir, Freundlich and Temkin isotherm equations. Suitability of various adsorption equations was studied by calculating the R^2 values of the respective equations. Regression curves were drawn by the Microsoft Office Excel program.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

Soils used in this study were differed widely in their ability of P adsorption. The adsorption phenomenon was investigated for nine locations from Sulaimani and Halabja Governorates of Kurdistan Region of Iraq, the soils of most of locations are calcareous, except the soil of both Halbja and Khurmal locations, with a pH ranged from 7.31 to 8.18, EC_e 0.15 to 0.52 dS m^{-1}, organic matter content 2 to 44.2 g kg^{-1} soil, total $CaCO_3$ content 70 to 350 g kg^{-1} soil and active $CaCO_3$ content ranged from 18.00 to 80.00 g kg^{-1} soil and the available P was ranged from 2.78 to 22.64 mg/L and different textures of the soils Table 4.1. The locations were selected depending on the variation in available P content.

Table 4.1 Some chemical and physical analyses of all the soil samples at two depths.

Location	Depth cm	pH	Ec dS m^{-1}	Available P mg L^{-1}	O.M.	Calcium Carbonate equivalent		PSD gm kg^{-1}			Texture Class
						Total	Active	Sand	Silt	Caly	
					g kg^{-1}						
Bazyan	0-30	7.74	0.39	2.79	23.8	175	38	52	534	414	SC
	30-60	7.75	0.40	2.79	23.8	180	45	34	489	477	SC
Halabja	0-30	7.31	0.51	11.51	36	100	78	269.3	483.4	247.3	L
	30-60	7.31	0.52	11.51	32	120	80	254.9	508.4	23.67	SL
Said Sadiq	0-30	7.79	0.15	16.32	22.4	325	68	273.7	413.8	312.5	CL
	30-60	7.81	0.15	16.32	2	350	75	210.4	359.2	430.4	C
Dukan	0-30	7.69	0.37	10.63	24	300	78	33	489.5	477.5	SC
	30-60	7.71	0.40	10.63	24	330	80	36.9	480.4	482.8	SC
Chwarta	0-30	8.18	0.25	2.78	9.5	200	32	32.8	502.3	464.9	SC
	30-60	8.18	0.33	2.78	9.5	320	50	42	476.8	481.2	SC
Kany Panka	0-30	7.39	0.26	5.26	17.6	250	28	40.5	495.2	464.3	SC
	30-60	7.40	0.29	5.26	15.1	280	50	238.8	376.2	385	CL
Bakrajo	0-30	7.60	0.33	10.16	23	180	30	71.9	596.9	331.2	SCL
	30-60	7.62	0.37	10.16	23	260	45	75.6	518.3	406.1	SC
Khurmal	0-30	7.88	0.43	22.64	44.2	70	38	75.7	533.2	391.1	SCL
	30-60	7.89	0.45	22.64	40	100	70	56.1	536.7	407.2	SC
Girdjan	0-30	7.99	0.38	6.14	38	250	18	210.4	359.2	430.4	C
	30-60	7.99	0.39	6.14	32	290	30	143.2	462.6	394.2	SCL

*The depth of 0 to 30 cm = surface layer.

*The depth of 30 to 60 cm = sub surface layer.

4.1 Sorption Isotherms

The P sorption data was adequately plotted according to the Langmuir, Freundlich and Temkin isotherms for all studied soils and the results are shown in Table 4.2.

Table 4.2 Values of each Isotherms equation's constant and their parameters in all soils samples.

Locations	Depths Cm	Temp. K°	Langmuir					Freundlich				Timken			
			B mg kg^{-1}	K_L L mg^{-1}	MBC mg kg^{-1}	R_L	R^2	1/n	n	K_f mg kg^{-1}	R^2	A_T	b_T J mol^{-1}	B J mol^{-1}	R^2
Bazyan	0-30	278	121.90	0.22	26.82	0.04	0.5812	0.6315	1.583	20.37	0.6758	1.0000048	260797.05	0.0095	0.6181
		298	10000	0.02	20.00	0.13	0.972	1.0364	0.964	26.68	0.9231	0.0000013	516160.8	0.0048	0.7612
		318	96.15	0.01	0.96	o.2	0.939	2.1841	0.457	6.15	0.8992	1.0000008	1303985.2	0.0019	0.6847
	30-60	278	99.01	0.52	51.49	0.04	0.1806	0.5799	1.724	27.37	0.4753	1.0000037	313616.7	0.0079	0.5568
		298	1250	0.04	50.00	0.42	0.7059	0.4696	2.129	61.50	0.3204	1.0000005	406159.3	0.0061	0.3074
		318	666.60	0.04	26.66	0.16	0.8947	0.9592	1.042	44.22	0.8695	1.0000005	505626.9	0.0049	0.8373
Halabja	0-30	278	250	0.06	15.00	0.07	0.8161	0.6315	1.538	20.37	0.8002	1.000003	495514.4	0.005	0.6189
		298	625	0.02	12.50	0.11	0.6267	1.31	0.763	9.43	0.6277	1.0000015	991028.8	0.0025	0.4731
		318	1111.10	0.03	33.33	0.14	0.9372	1.1056	0.904	26.23	0.9444	1.000001	589898.1	0.0042	0.7569
	30-60	278	156.20	0.21	32.80	0.06	0.6474	0.5799	1.724	27.37	0.7443	1.000003	406159.3	0.0061	0.604
		298	2000	0.01	20.00	0.12	0.854	0.7761	1.288	44.26	0.8478	1.0000006	353938.8	0.007	0.8814
		318	625	0.06	37.50	0.13	0.9267	0.9531	1.049	33.49	0.92	1.000001	467466.4	0.0053	0.824
Said-sadeq	0-30	278	144.90	0.28	40.57	0.06	0.584	0.5799	1.724	27.73	0.6528	1.000002	467466.4	0.0053	0.5057
		298	16666.60	1.004	19666.59	0.06	0.8535	1.3331	0.750	12.26	0.8129	1.000001	799216.7	0.0031	0.6127
		318	2.500	0.01	0.03	0.14	0.9095	1.181	0.846	9.48	0.8926	1.000001	619393	0.004	0.7427
	30-60	278	144.90	0.28	40.57	0.06	0.584	0.5799	1.724	27.73	0.6528	1.000002	467466.4	0.0053	0.5057
		298	3333	0.01	33.33	0.2	0.753	0.8769	1.140	60.15	0.9033	1.0000009	450467.6	0.0055	0.9066
		318	1000	0.04	40.00	0.11	0.9589	0.9028	1.107	28.87	o.944	1.000002	412928.6	0.006	0.833

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Locations	Depths Cm	Temp. K°	Langmuir					Freundlich				Timken			
			B mg kg^{-1}	K$_L$ L mg^{-1}	MBC mg kg^{-1}	R$_L$	R²	1/n	n	K$_f$ mg kg^{-1}	R²	AT	b$_T$ J mol^{-1}	B J mol^{-1}	R²
Dukan	0-30	278	10.54	0.05	0.53	0.06	0.9436	3.035	0.329	30.86	0.9431	1.0000027	750779.3	0.0033	0.7537
		298	666	0.05	33.30	0.11	0.9585	0.7696	1.299	42.35	0.9054	1.0000006	330342.9	0.0075	0.9098
		318	138.80	0.09	12.49	0.15	0.9813	1.7592	0.568	0.951	0.9689	1.000001	884847.1	0.0028	0.7791
	30-60	278	243.90	0.18	43.90	0.07	0.9417	0.6067	1.648	7.74	0.8892	1.0000022	320142.9	0.0089	0.6766
		298	10000	0.003	30.00	0.13	0.9812	0.7247	1.379	54.75	0.8753	1.0000001	321762	0.0077	0.8793
		318	1111.10	0.03	33.33	0.14	0.8997	0.8935	1.119	39.56	0.8981	1.0000008	434661.7	0.0057	0.8481
Chwarta	0-30	278	588.20	0.04	23.53	0.1	0.9714	0.9246	1.081	23.63	0.943	1.0000019	412928.6	0.006	0.8076
		298	312.50	0.06	18.75	0.07	0.8939	0.9193	1.087	15.71	0.9646	1.0000003	317637.4	0.0078	0.8813
		318	238.90	0.04	9.56	0.11	0.9825	1.4142	0.707	8.984	0.9187	1.000001	619393	0.004	0.8297
	30-60	278	5000	3.90	19500.	0.01	0.9564	0.7809	1.281	27.73	0.9142	1.000001	272260.6	0.0091	0.9487
		298	769.20	0.04	30.77	0.14	0.8827	0.0657	15.38	122.5	0.3107	1.0000013	635274.8	0.0039	0.7229
		318	555.50	0.04	22.22	0.18	0.8445	1.106	0.904	27.62	0.9157	1.000001	576179.5	0.0043	0.7962
Bakrajo	0-30	278	100	0.22	22.00	0.05	0.2313	0.9301	1.075	10.41	0.6192	1.000003	406159.3	0.0061	0.622
		298	10000	0.01	100.00	0.08	0.9904	0.955	1.047	15.13	0.9574	1.000003	334807.2	0.0074	0.8703
		318	370.30	0.06	22.22	0.17	0.9338	1.3316	0.571	22.31	0.9235	1.0000009	669614.1	0.0037	0.8759
	30-60	278	333.30	0.08	26.66	0.08	0.8914	0.8258	1.211	24.53	0.8158	1.000002	467466.4	0.0053	0.6111
		298	416.60	0.08	33.33	0.23	0.9889	1.2822	0.779	40.51	0.9782	1.00000003	669614.1	0.0037	0.9063
		318	25000	1.07	33500.	0.05	0.9447	1.0618	0.941	25.39	0.8957	1.000002	257142.9	0.0047	0.798

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Locations	Depths Cm	Temp. K°	Langmuir					Freundlich				Timken			
			B mg kg^{-1}	K_L L mg^{-1}	MBC mg kg^{-1}	R_L	R^2	1/n	n	K_f mg kg^{-1}	R^2	AT	b_T J mol^{-1}	B J mol^{-1}	R^2
Kanypanka	0-30	278	1111.10	6.30	6999.93	0.06	0.8097	1.3696	0.730	7.343	0.8659	0.012	1431.1	0.0051	0.7274
		298	400	0.08	32	0.07	0.795	0.5427	1.842	46.85	0.8038	1.0000002	206464.3	0.012	0.8475
		318	136.90	0.11	15.059	0.19	0.7046	1.5257	0.655	20.97	0.898	1.0000007	750779.3	0.0033	0.9444
	30-60	278	161.20	0.21	33.852	0.05	0.9075	0.5396	1.853	32.39	0.9679	1.000002	168542.3	0.0147	0.8515
		298	11111.10	3.003	333667	0.05	0.9677	0.9654	1.035	39.39	0.8861	1.0000008	505626.9	0.0049	0.8084
		318	588.20	0.09	52.938	0.15	0.9698	0.9484	1.054	39.06	0.9455	1.00009	5034.6	0.4921	0.8539
Khurmal	0-30	278	144.90	0.32	46.368	0.06	0.4726	0.74	1.351	24.29	0.6895	1.0000029	369786.8	0.0067	0.6344
		298	188.60	0.19	35.834	0.06	0.7553	0.5719	1.748	32.97	0.7259	1.000003	302142.9	0.0082	0.5745
		318	909.10	0.03	27.273	0.14	0.936	1.0715	0.933	27.12	0.947	1.000001	563084.5	0.044	0.7654
	30-60	278	126.50	0.28	35.42	0.05	0.4654	0.7921	1.262	17.78	0.7133	1.000003	393265.3	0.0063	0.6049
		298	769.20	0.04	30.768	0.14	0.8718	1.1639	0.859	22.03	0.8653	1.0000013	688214.4	0.0036	0.6698
		318	1250	0.02	25	0.11	0.9653	1.2701	0.787	22.18	0.9406	1.000001	688214.4	0.0036	0.7671
Girdjan	0-30	278	45.66	0.04	1.8264	0.05	0.8722	1.5296	0.653	8.087	0.9078	1.0000051	313616.7	0.0079	0.9539
		298	344.80	0.14	48.272	0.07	0.9206	1.2242	0.816	19.37	0.827	1.000002	182174.4	0.0136	0.8358
		318	344.80	0.07	24.136	0.1	0.733	0.9546	1.047	22.37	0.7408	1.000001	516160.8	0.0048	0.6485
	30-60	278	172.40	0.16	27.584	0.06	0.8421	0.7361	1.358	20.70	0.8344	1.0000034	393265.3	0.0063	0.5913
		298	277.70	0.12	33.324	0.07	0.7191	0.9533	1.048	23.22	0.8386	1.000002	476456.1	0.0052	0.7422
		318	2500	9.43	23575	0.01	9.8972	0.9501	1.052	26.92	0.9537	1.000002	412928.6	0.006	0.8916

4.1.1 Langmuir adsorption Isotherm

The Langmuir equation describes a formation of a monolayer of adsorbate on the adsorbent surface which prevents further adsorption (Dada *et al.*, 2012). Depending on Langmuir equations adsorption data were plotted as ($1/C_e$ vs. $1/Q_e$) which are shown in Figures 4.1 to 4.6. The unit of Langmuir adsorption maximum (b) is mg kg^{-1} soil. The maximum adsorption (b) can be used to estimate the amount of fertilizer to be added to an unfertilized soil (Rehman *et al* 2004). Maximum adsorption and P adsorption energy varied with soil. According to Woodruff and Kamprath (1965), a higher equilibrium solution concentration is required for soils with a low adsorption capacity for maximum growth. And the soils with higher b value required less P saturation than those with lower b value. Kuo *et al*. (1988) reported that the Langmuir equation underestimates the adsorption capacity of soil.

Values of maximum adsorption (b) for the two different layers of each location at three different temperatures (278, 298, 318K) are shown in the Table (4.2). Starting from values of maximum adsorption b, at the depth of 0 to 30 cm the minimum value of b, was 2.50 mg kg^{-1} soil at 318K in Saidsadiq location also, the maximum value of b was 16666.60 mg kg^{-1} soil at 298K at Saidsadiq location, and at the 30 to 60 cm the minimum value of b was 99.01 mg kg^{-1} soil at 278K in Bazyan location, while the maximum value of b was 111111.10 mg kg^{-1} soil at 298K in Kanipanka Location. As the adsorption process is exothermic, a variation of temperature can cause variation in the process performance, thus one of the basic requirements for a good production of adsorption isotherm is temperature (Pila *et al.* 2015). The data in the Table 4.2 suggests that, for the two layers, the highest values of maximum adsorption (b) were at 298 K. These results are in agreement with those obtained by Pila *et al*. (2015), in which they stated that the proper temperature for good adsorption performance is 298 K further confirmation of the results are illustrated in Table 4.2.

The affinity coefficient (K_L) indicated comparatively how easily the added P is adsorbed on or release from the adsorbed surface (Rehman *et.al*, 2005). According to Mehadi and Taylor (1988), smaller the K_L values indicated that more amount of adsorbed P would be converted to non-exchangeable from either by the formation of crystalline P or by occultation through P ions. According to Del-Bubba *et al*. (2003), K_L is a measure of the affinity of the adsorbate for the adsorbent. The minimum value of bonding energy (K_L) for the surface layer (0 to 30) cm was 0.01 L mg^{-1} at 318 K in Saidsadiq location, and the maximum value of K_L was 6.30 L mg^{-1} at 278 K in Kanipanka location. While at the depth of 30 to 60 cm the minimum value of K_L was

0.003 L mg^{-1} at 298 K in Dukan location and the maximum value of K_L was 9.43 L mg^{-1} at 318 K in Girdjan Location. These results are in agreement with the results of Mam Rasul and Saeed (2014) in which they stated that high values of K_L give an indication of a strong attraction between sorbed P and soil surface which is sorbent surface in the study of phosphorus sorption in some great soil groups of Iraqi Kurdistan Region.

Soil P sorption capacity is related to the maximum buffering capacity (MBC) (Uzoho *et al*., 2014). Maximum Buffering Capacity (MBC) referred to the resistance to changes in soil solution ion concentration or the labile P pool in the solid phase (Litaor *et al*., 2005). The Maximum Buffering Capacity of the studied soil (MBC) at the surface soil had a minimum value which is 0.02 mg kg^{-1}soil at 318 K in Saidsadiq location while the maximum value of MBC was 19666.59 mg kg^{-1}soil at 298 K in Saidsadiq location, moreover at the subsurface soil the minimum value of MBC was 20.00 mg kg^{-1}soil at 298K in the soils of Halabja location but the maximum value of MBC was 333667 mg kg^{-1}soil at 298 K in Kanipanka location. Afsar and Hossain (2012) proposed that value of MBC of P is affected by soil conservation measure, application of manure rather than solution phosphate concentration.

The last parameter to be discussed is the Langmuir isotherm separation factor (R_L) which is a dimensionless constant. For the depth of 0 to 30 cm soil values of R_L were ranged from 0.04 to 0.19 at and it also ranged from 0.01 to 0.42 at the 30 to 60 cm layer of the soil. The different values of R_L at the two layers and three different temperatures were greater than zero but less than one ($0<R_L<1$), this indicating that the sorption process of P is favorable at both depths for all studied locations.

Knowledge of the relationship between soil capacity and soil's chemical and physical properties is necessary to understand the sorption behavior in different soils, moreover to know their effects on the Langmuir, Freundlich and Temkin parameters. It is evident that soil has different capacity on each side for adsorbing P, Table 4.2 showed that Kanipanka was found to have the highest value of maximum adsorption b among all the soils. The value of b was 111111.10 mg kg^{-1} soil at 298 K for depth of 30 to 60 cm. Many previous studies stated that one of the most important factors which effects on the amount of adsorption are organic matter (Uddin *et al*, 2017 and Mozard *et al.* ,2010) There is a negative relation between adsorption and organic matter, as organic matter decreased adsorption will increase, and vice versa one of the possible reasons is that organic matter reduce the positive charges on soil particles and this decline the attraction of P to surface of the soil (Hadgu *et al.*, 2014). Data in the Table 4.1 and 4.2 clarify this estimation, when the amount of organic matter was lowest for the soil of Kanipanka (15.10 g kg^{-1}), maximum adsorption was highest also for Kanipanka among all the studied soils which was 111111.10 mg kg^{-1} soil. The significant correlation between maximal P adsorption and clay content, and the total amount of phosphorus adsorbed into the soil can be attributed to the presence of sportive sites. This could be related to the relatively large number of positive charges that can react and strongly bind the negatively charged phosphate ions in the solution (Hadgu *et a.l*, 2014). (Bilgili *et al.*, 2008) also stated the negative correlation between organic matter and value of maximum adsorption in the soil. The Dukan location had the lowest value of b (2.50 mg kg^{-1} soil) among all the soils at 0 to 30 cm at 278 K. This low value of maximum adsorption might be related to the clay content at that depth. Soil clay content had a significant relation with P adsorption. The high amount of clay content increases the soil's capacity of P adsorption in the soil. Numerous studies stated that alumino-silicate clay minerals have great influence on P sorption by soils. Commonly, those clay minerals that hold greater anion exchange capacity (due to the positive surface charge) have a greater affinity for phosphate ions. The silicate clays, 1:1 type's clays have greater phosphate retention than 2:1 type clays. Soils that have a great amount of Kaolinite group minerals will maintain larger quantities of added phosphate rather than those containing the 2:1 type clay minerals (Samadi, 2006).

As previously mentioned, Anderson and Wu (2001) in their study stated that high K_L value is a sign of high clay content in the soil and also it gives a hint on the strength of bonding to clay minerals in the soil. This finding can also be seen in this study, the highest value of K_L was found at Girdjan location from the depth of 30 to 60 cm at 318K which was (9.43 L mg^{-1} P) at the same time the highest clay content was also found at the same location. The surface of the clay content in the soil hold negative charges and they encourage more P adsorption in the soil also made a strong bond between them (Samadi, 2006). The lowest K_L value again was found at Dukan location. Some authors have considered the effects of pH on P sorption and on parameters of the equations. Sato (2003) in the study of phosphorus sorption and desorption in a Brazilian ultisol: found that increasing in pH value will reduce the K_L value and thus the affinity of P to the sorbed surface will reduce. Calculated data in table (4.1, 4.2) match with those obtained by Sato (2003), as the pH of the surface layer (0 to 30 cm), was high (7.71) value of K_L reduced to (0.003 L mg^{-1} P) at the same layer for Dukan location.

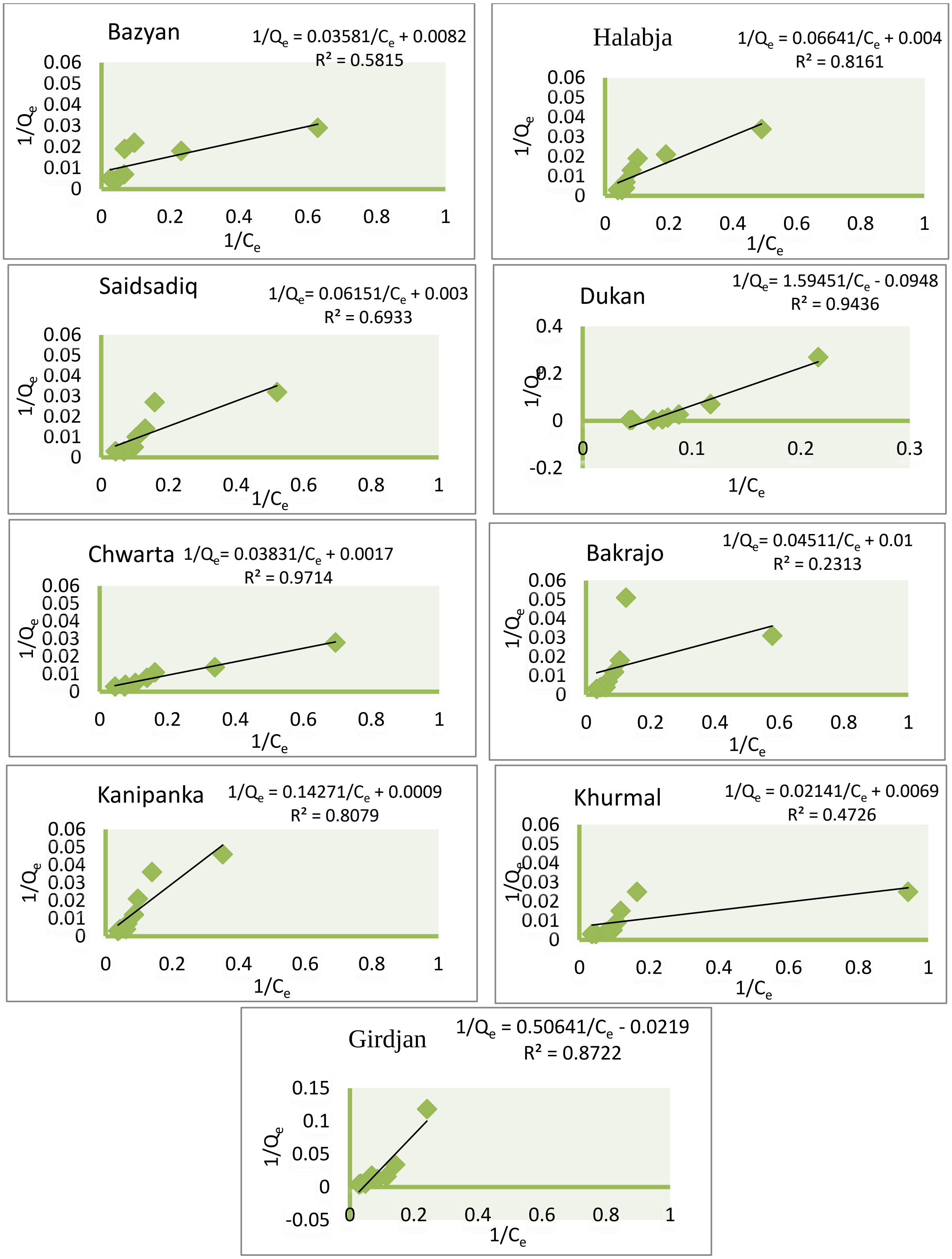


Figure 4.1 Pathway reaction according to linearized Langmuir sorption isotherm plot for P at a depth of 0 to 30 cm at 278 K° for all the soil under investigation.

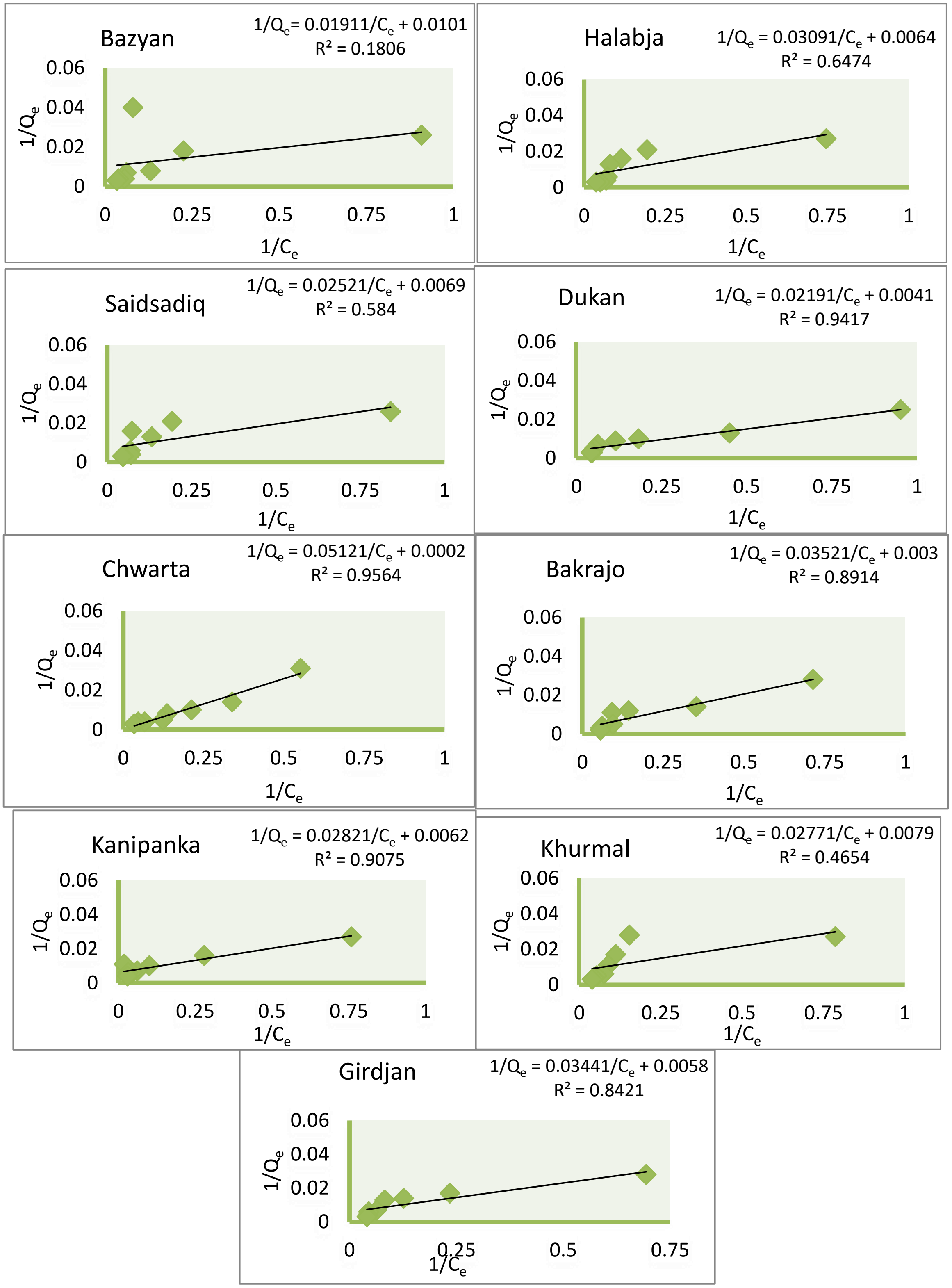
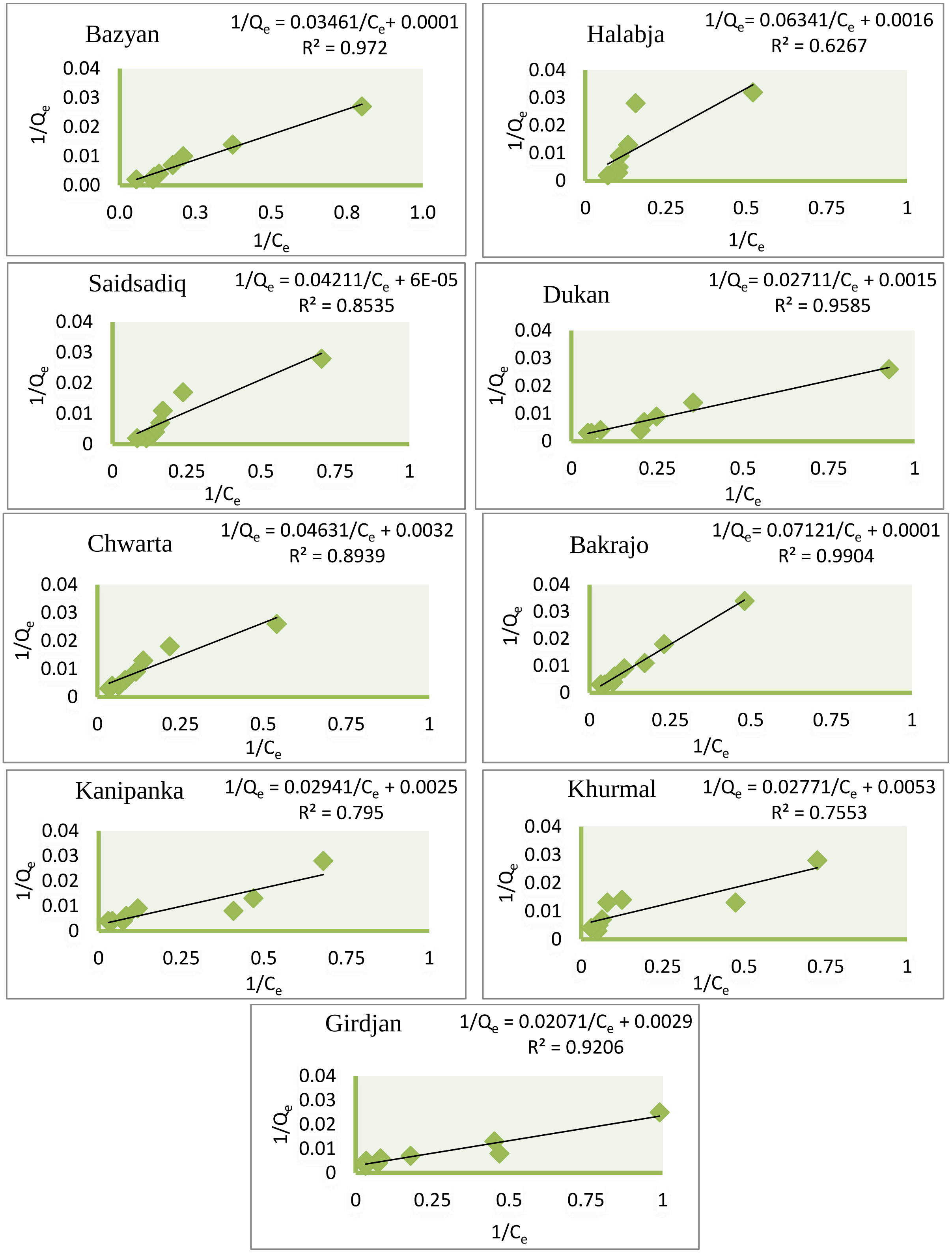


Figure 4.2 Pathway reaction according to linearized Langmuir sorption isotherm plot for P at a depth of 30 to 60 cm at 278 K for all the soil under investigation.



Bazyan

Halabja

Saidsadiq

Dukan

Chwarta

Bakrajo

Kanipanka

Khurmal

Girdjan

Figure 4.3 Pathway reaction according to linearized Langmuir sorption isotherm plot for P at a depth of 0 to 30 cm at 298 K for all the soils under investigation.

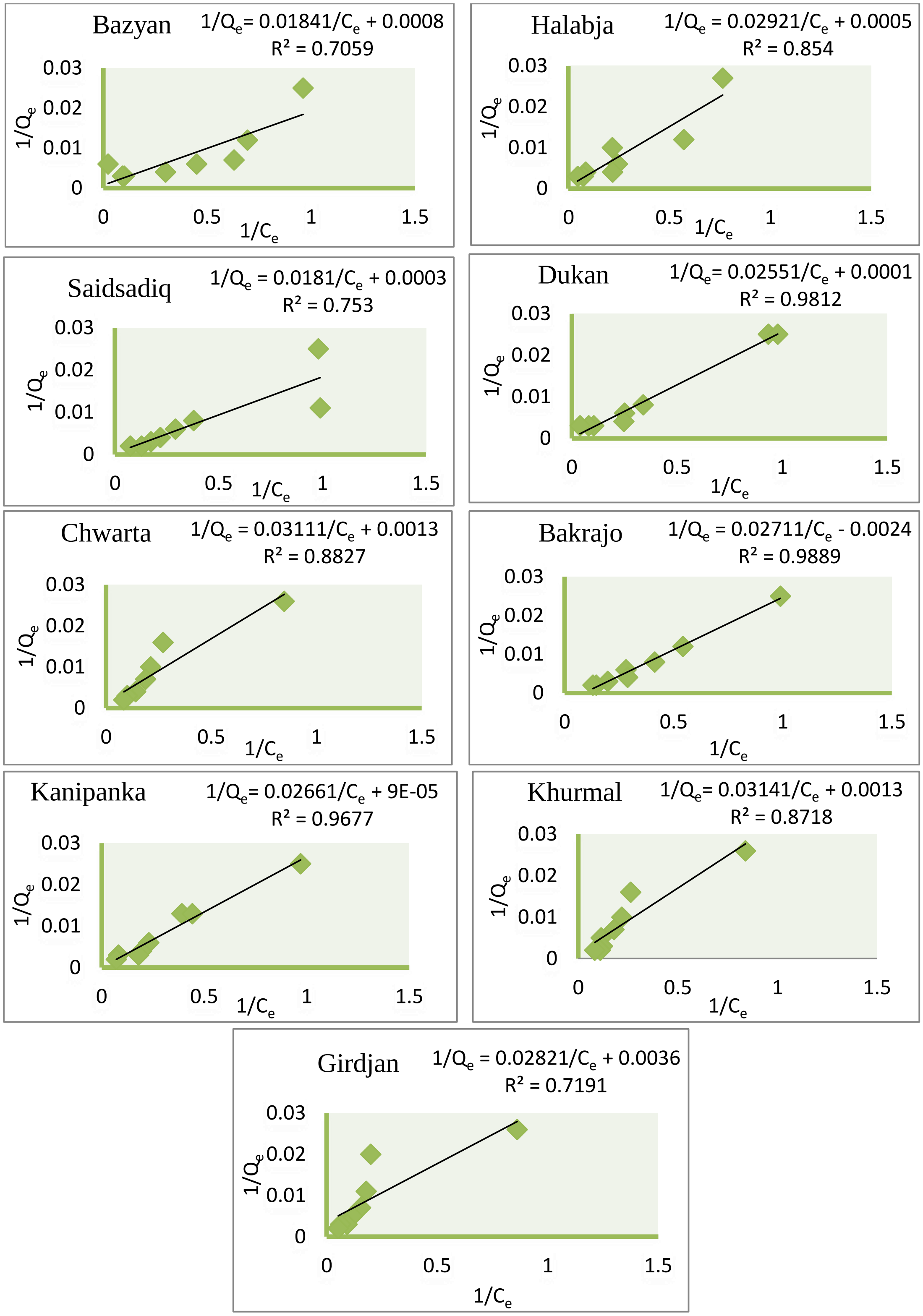


Figure 4.4 Pathway reaction according to linearized Langmuir sorption isotherm plot for P at a depth of 30 to 60 cm at 298 K for all the soils under investigation.

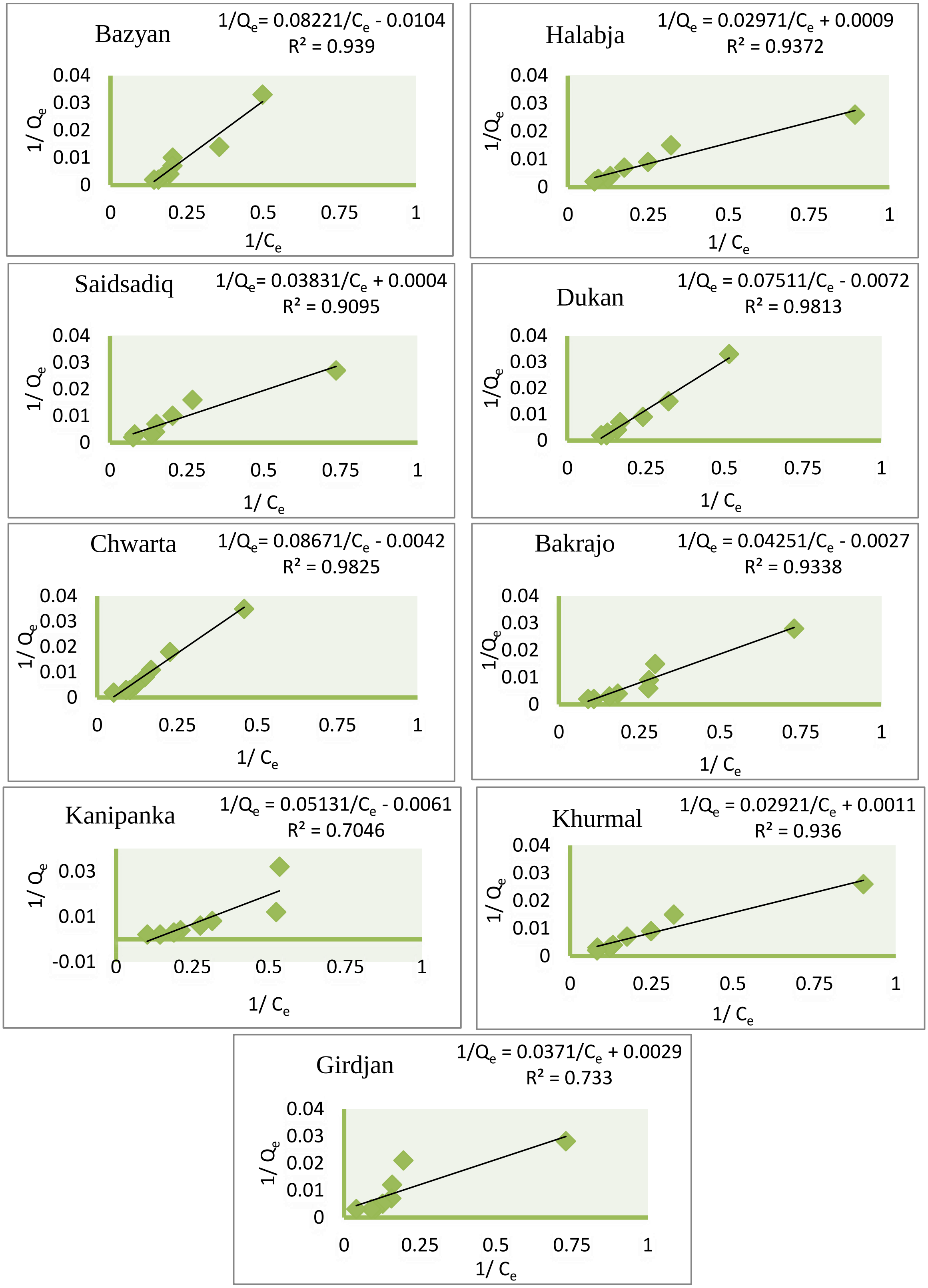
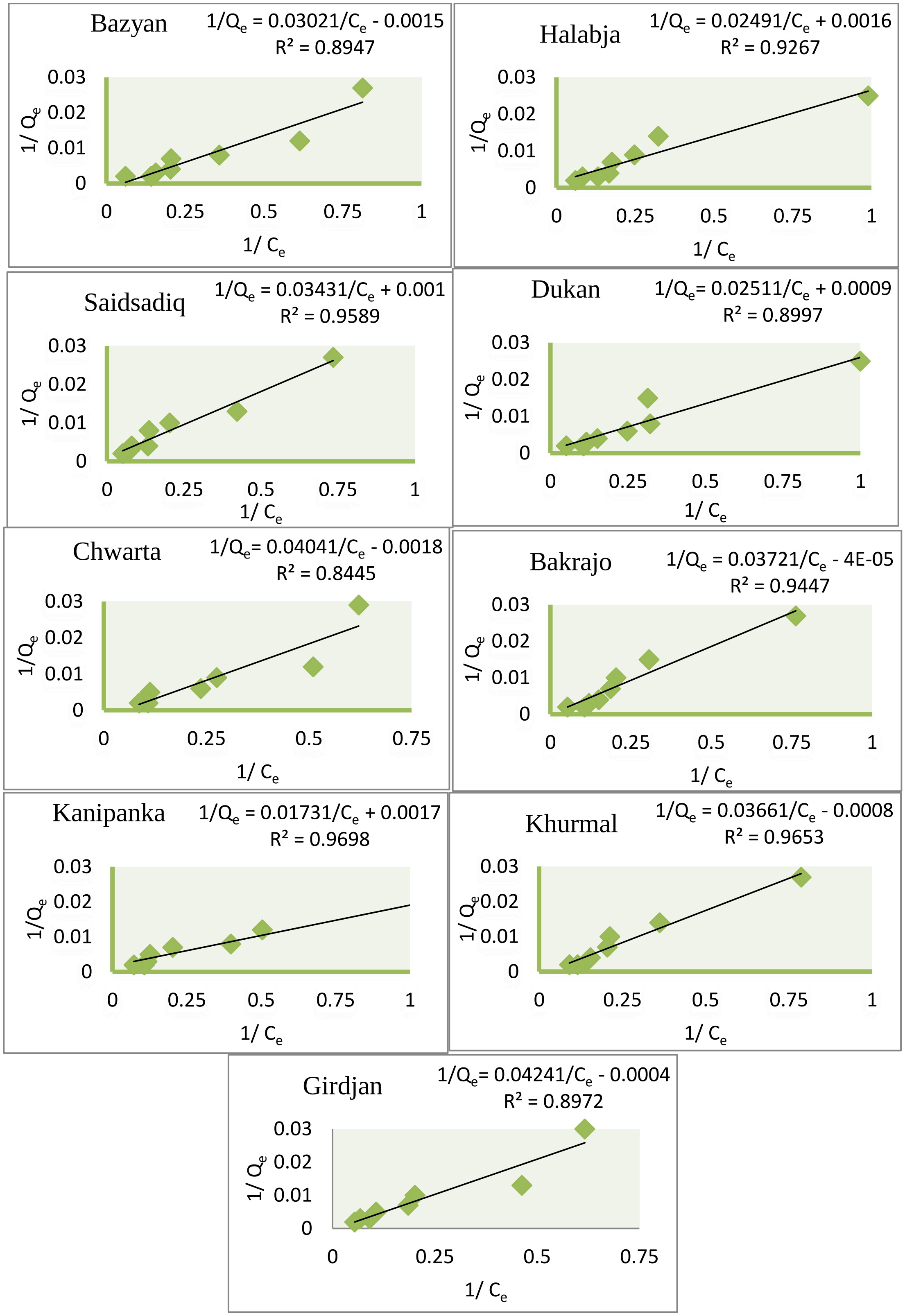


Figure 4.5 Pathway reaction according to linearized Langmuir sorption isotherm plot for P at a depth of 0 to 30 cm at 318 K for all the soils under investigation.



Figures 4.6 Pathway reaction according to linearized Langmuir sorption isotherm plot for P at 318 K at a depth of 30 to 60 cm for all the soils under investigation.

4.1.2 Freundlich equation

Freundlich adsorption isotherm is mostly used to describe the adsorption characteristics of the homogeneous surface (Dada *et al.*, 2012). In Freundlich isotherm equation the data were plotted by (log Q_e vs. log C_e) and Figures (4.7 to 4.12) shows the plotted data. The same procedure was carried out for Freundlich isotherm was done according to Langmuir. As expected, the results were different for each area under investigation and at each depth. If we follow the same sequence with surface soil being the first we look at, the minimum value of n was 0.329 at 278 K in Dukan location, while the maximum value of n was 1.84 at 298 K in Kanipanka area, but for the subsurface soil the minimum value of n was 0.779 at 298 K in Bakrajo location, while the maximum value of n was 15.38 at 298 K in Chwarta location. A value of n which represents the strength of adsorption in adsorption process is positively correlated with pH of the soil (Ayaz *et al.*, 2010). This can be seen clearly from the data in the Table 4.1, 4.2, high value of pH resulted in producing a high value of n.

The constant K_f is an indication of adsorption capacity, and adsorption capacity for all the studied soils ranged from 0.95 mg kg^{-1} at 318 K in Dukan location to 46.85 mg kg^{-1} at 298K in Kanipanka location and ranged from 7.74 mg kg^{-1}at 278 K° in Dukan location to 122.50 mg kg^{-1} at 298 K in Chwarta location for surface and subsurface soil respectively. Mam Rasul and Saeed (2014) in their study on phosphorus sorption in some great soil groups of Iraqi Kurdistan Region stated that the constant K_f is an indication of the amount of adsorption capacity. The low value of K_f indicates low adsorption capacity and vice versa. As the value of K_f was different among the soils and this is because soil properties had great effects on the value of K_f. Variation in K_f value is dependent on the variation of soil properties like $CaCO_3$, clay content and organic matter (Hussain *et al*, 2003). Thus far, previous studies have revealed a significant correlation between soil clay content and value of, Freundlich adsorption capacity (K_f) will increase as the amount of clay increase (Samadi, 2006). In the soil of Kanipanka role of clay content was clearly realized, when the amount of clay was high (464.30 g kg^{-1}) values of K_f was also high (46.85, mg kg^{-1}). Also up to now some of the studies found the effect of $CaCO_3$ on Freundlich adsorption capacity among them was the study on phosphorus adsorption parameters in relation to soil characteristics by Mehmood *et al.* (2010), in their studies they stated that as the amount of $CaCO_3$ increase value of K_f increase as well. Similar results have been found in this study, value of K_f increases with increasing amount of $CaCO_3$ in the soil, Table 4.1, 4.2.

Freundlich adsorption capacity (K_f) was found to be the highest at Chwarta location among all the soils, in which it was 122.50 mg kg $^{-1}$ at 298 K at a depth of 30 to 60 cm. Possible explanations for these results are due to the negative correlation between the value of K_f and the amount of organic matter in the soil (Mehmood *et al.*, 2010). When the amount of organic matter was lowest among all the soils (9.5 to 8.5 g kg^{-1}) value of K_f was found to be the highest (122.50 mg kg^{-1}). These results were vice versa for Dukan location which had the lowest value of K_f and high value of organic matter. At a depth of 0 to 30 cm, the lowest value of K_f was 0.95 mg kg^{-1} at 318 K, along with the value of organic matter was high at the same depth which was 24 g kg^{-1}. A recent study by Pattamat and Pavarajarn (2016) claims that temperature has an effect on the value of K_f and as the temperature became higher the adsorption rises more slowly, and higher concentration is requiring in order saturating the surface. Similarly, in this study it is found that the lowest value of K_f has found at highest temperature which was 0.95 mg kg^{-1} at 318 K.

To date, most researchers are agreed on the effect of physicochemical soil properties on sorption processes [Tamungang *et al.*, 2016; Samadi 2006; Mehmood *et al*, 2010]. Likewise, Table 4.1, 4.2 showed that agreement. As the pH of soil in considered as one of the major variables that affected on the adsorption of P, thus Dukan location had the lowest value of n among all the soils in which it was 0.32 at 278K for a depth of 0 to 30 cm, this low value might refer to the value of pH in which it was 7.69. Furthermore, Chwarta location found to have the highest value of n at a depth of 30 to 60 cm at 298K. The value of n was increased with increasing the value of soils pH, in which it was 8.18 and the value of n also had the highest value which was 15.38 at 298K at 0 to 30 cm of Chwarta location. These results are in a harmonic with other research which found the significant correlation between the value of strength of adsorption and soil pH [Pattamat and Pavarajarn 2016; Mehmood *et al.*, 2010 and Samadi 2006].

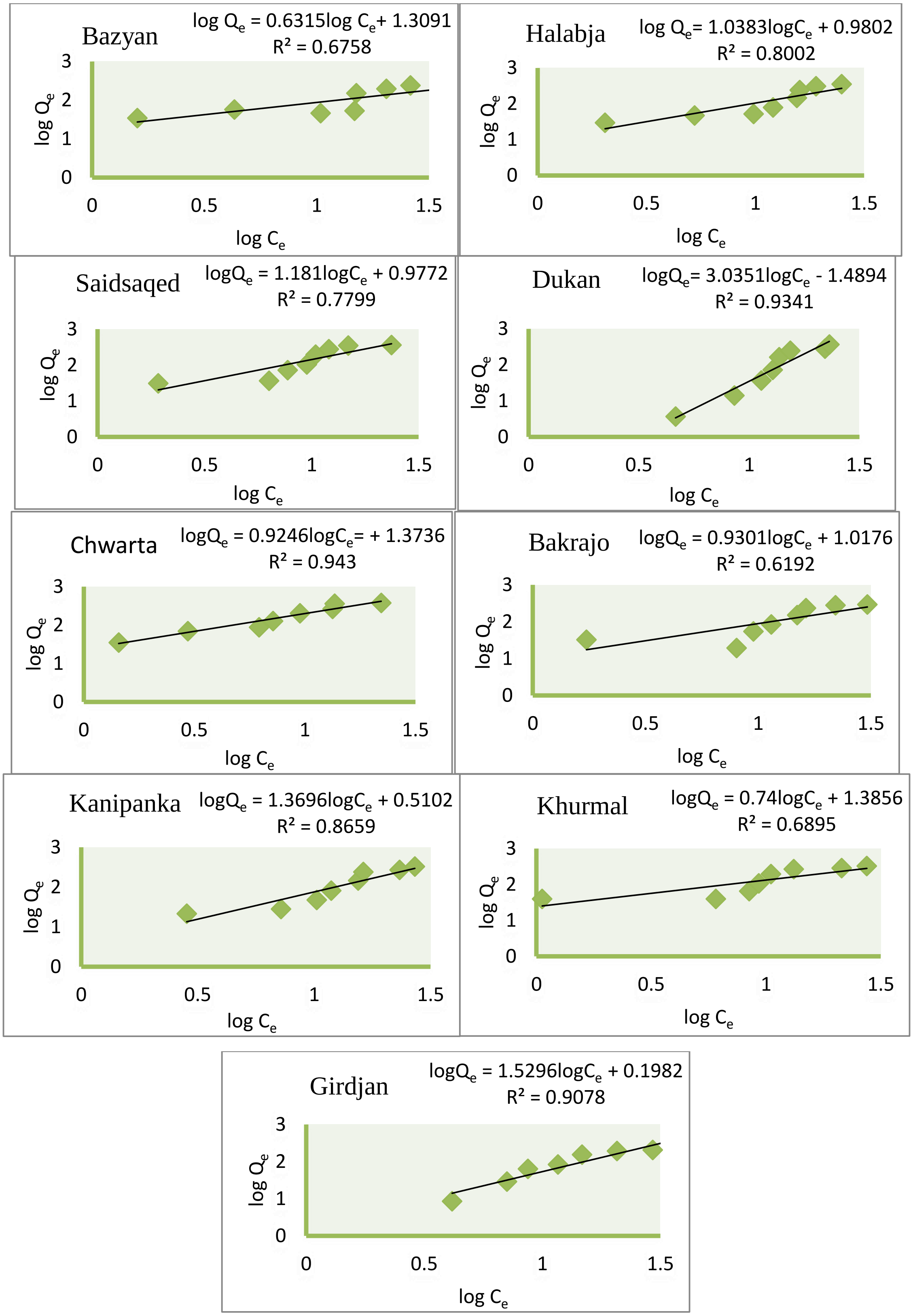


Figure 4.7 Pathway reaction according to linearized Freundlich sorption isotherm plot for P at a depth of 0 to 30 cm at 278 K for all the soils under investigation.

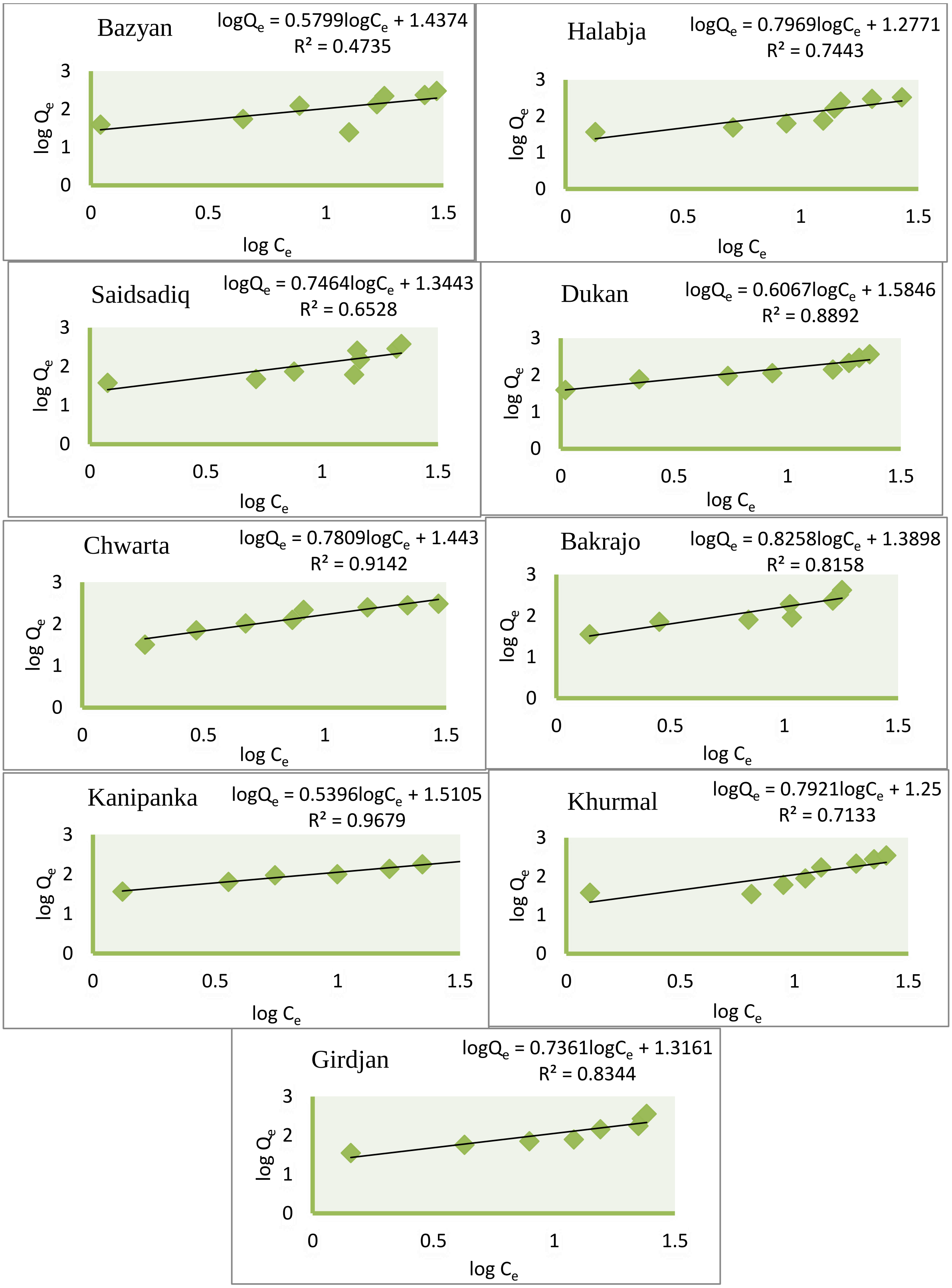


Figure 4.8 Pathway reaction according to linearized Freundlich sorption isotherm plot for P at a depth of 30 to 60 cm at 298 K for all the soils under investigation.

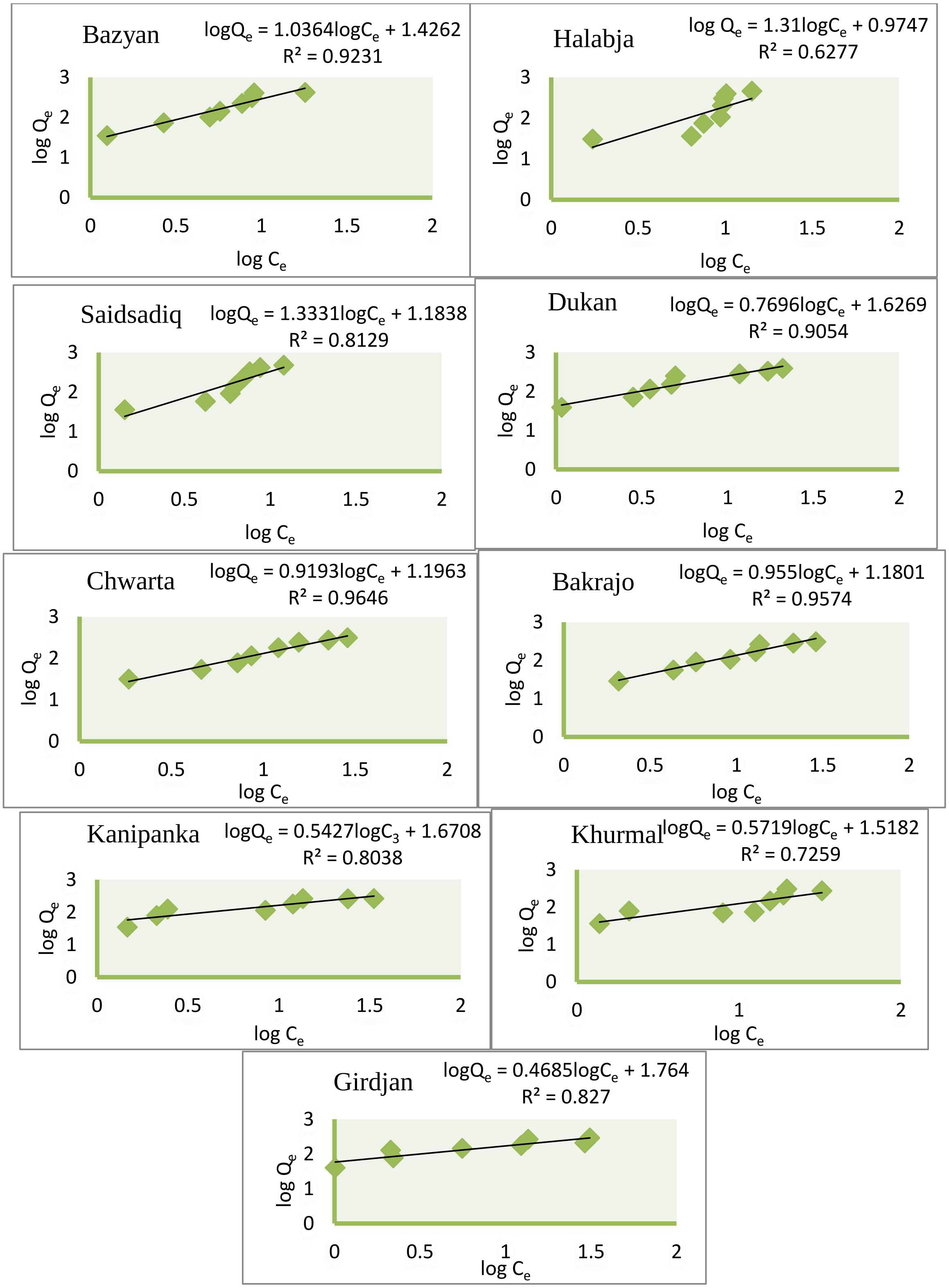


Figure 4.9 Pathway reaction according to linearized Freundlich sorption isotherm plot for P at a depth of 0 to 30 cm at 278 K for all the soils under investigations.

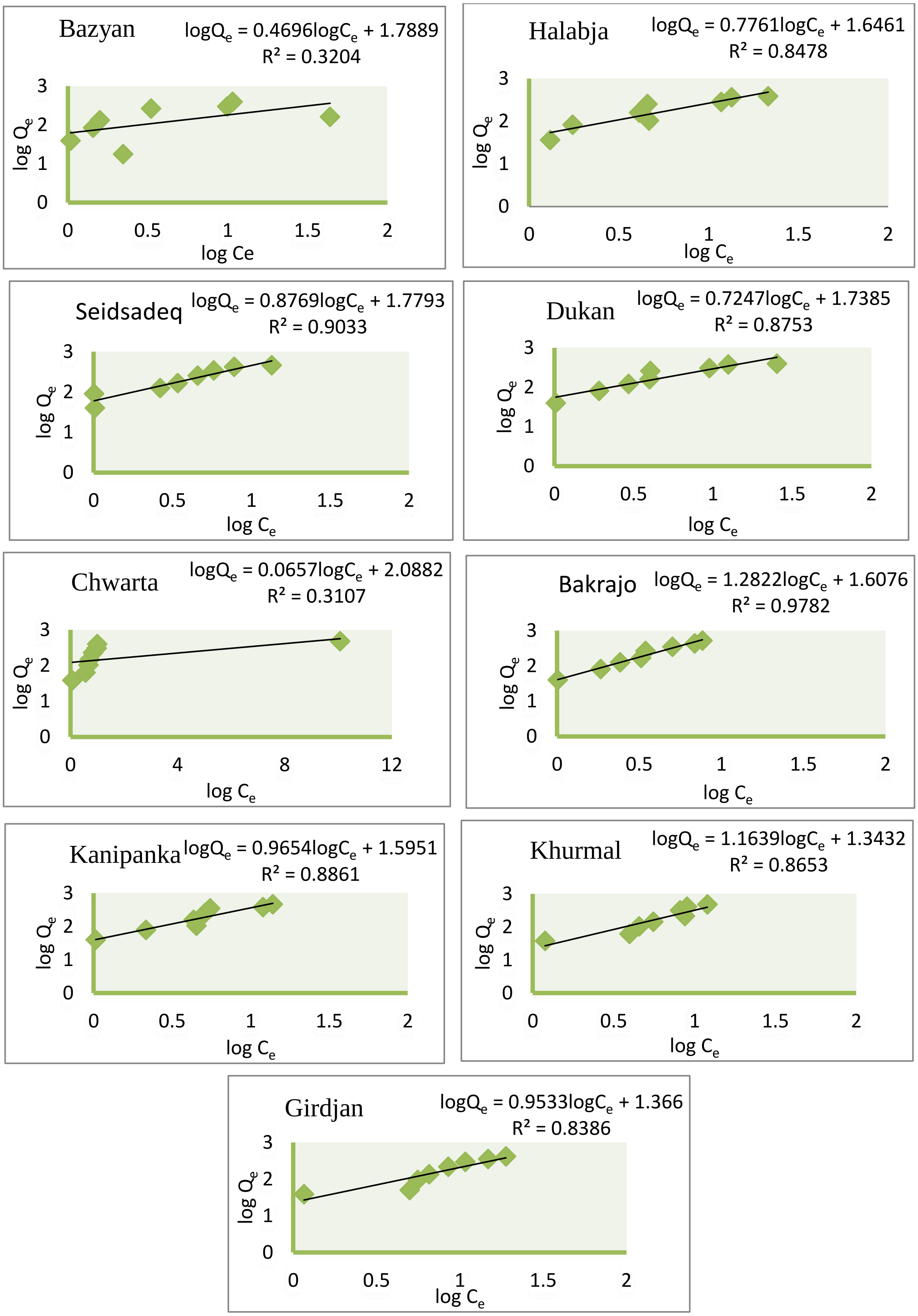


Figure 4.10 Pathway reaction according to linearized Freundlich sorption isotherm plot for Pat a depth of 30 to 60 cm at 298 K for all the soils under investigation.

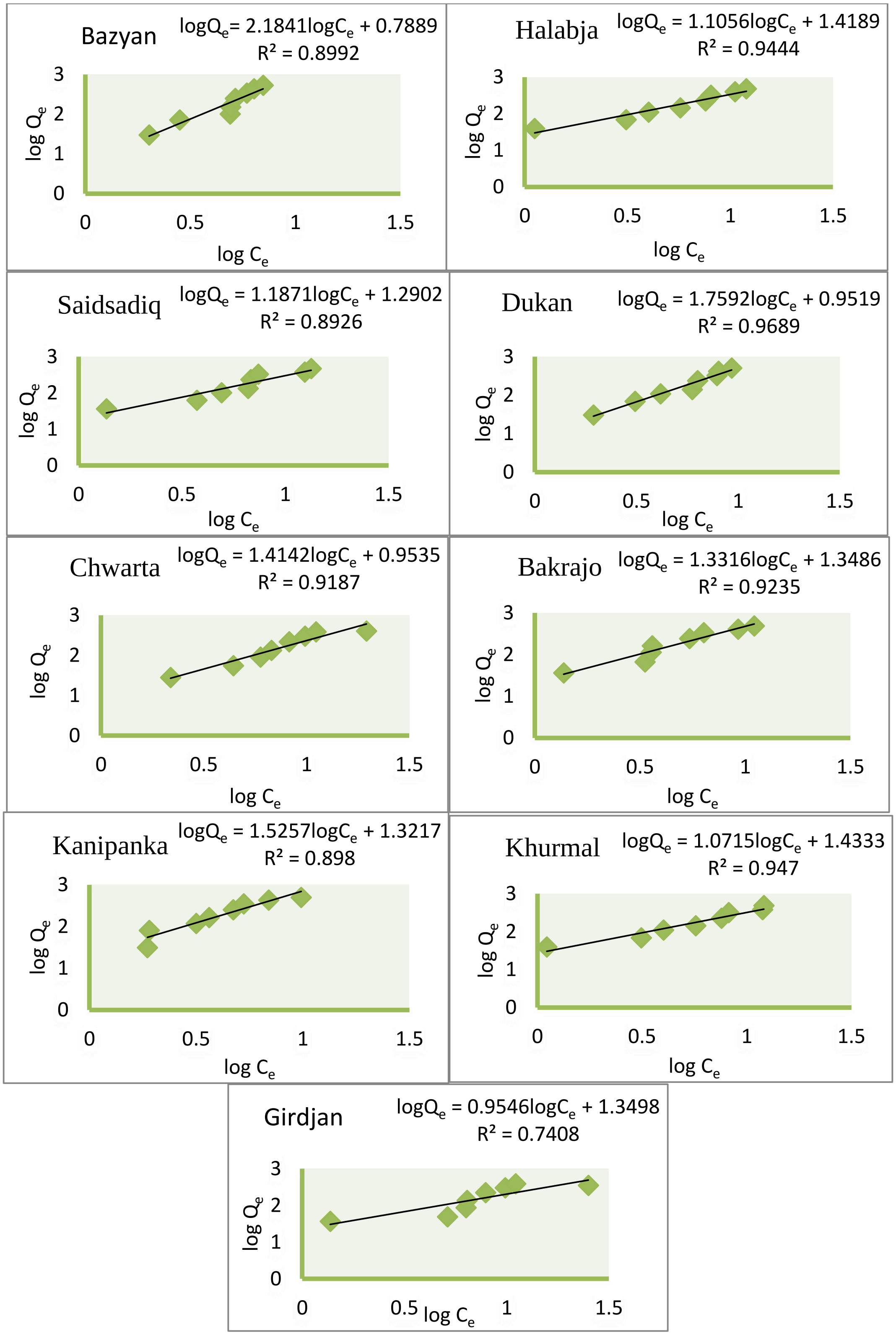
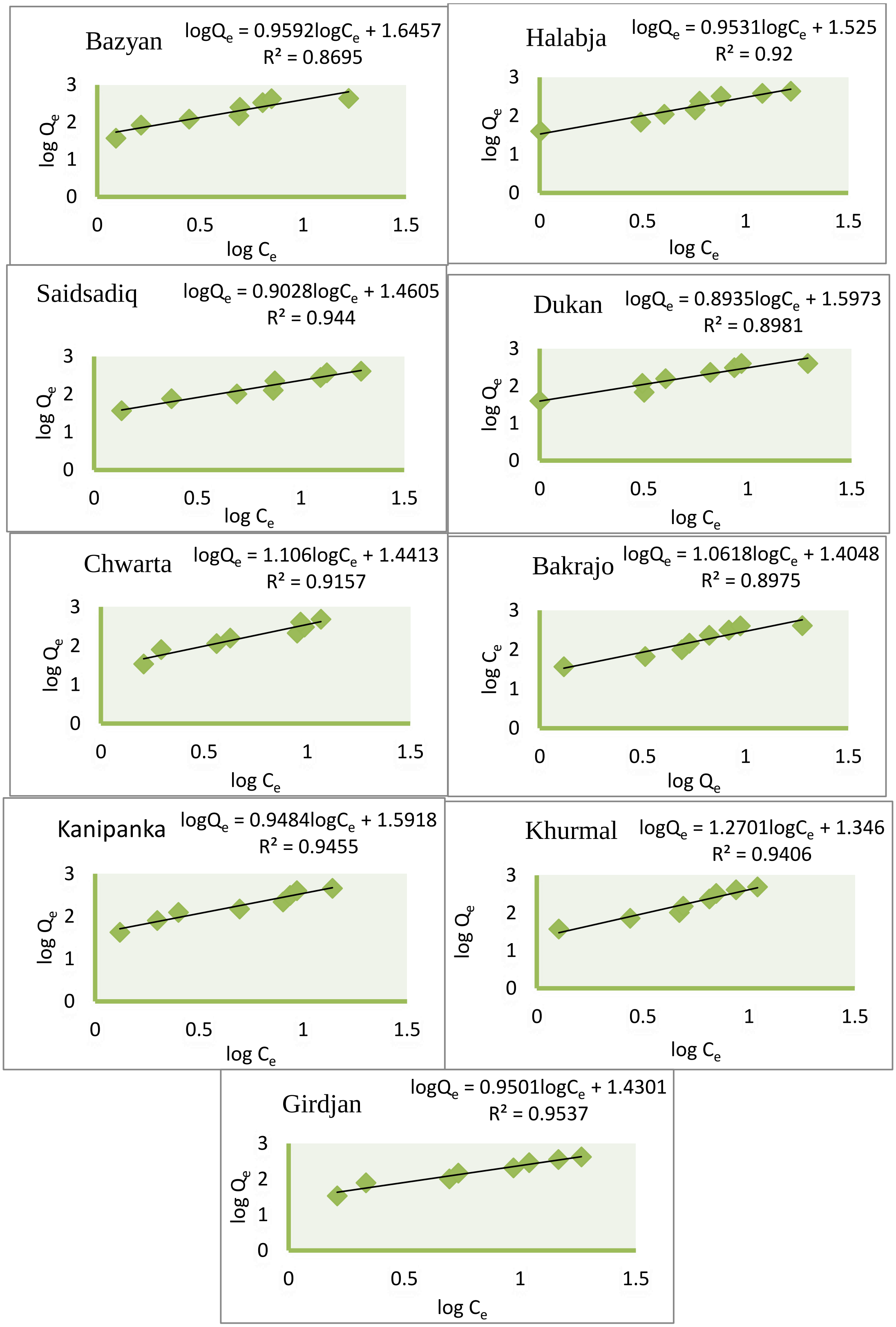


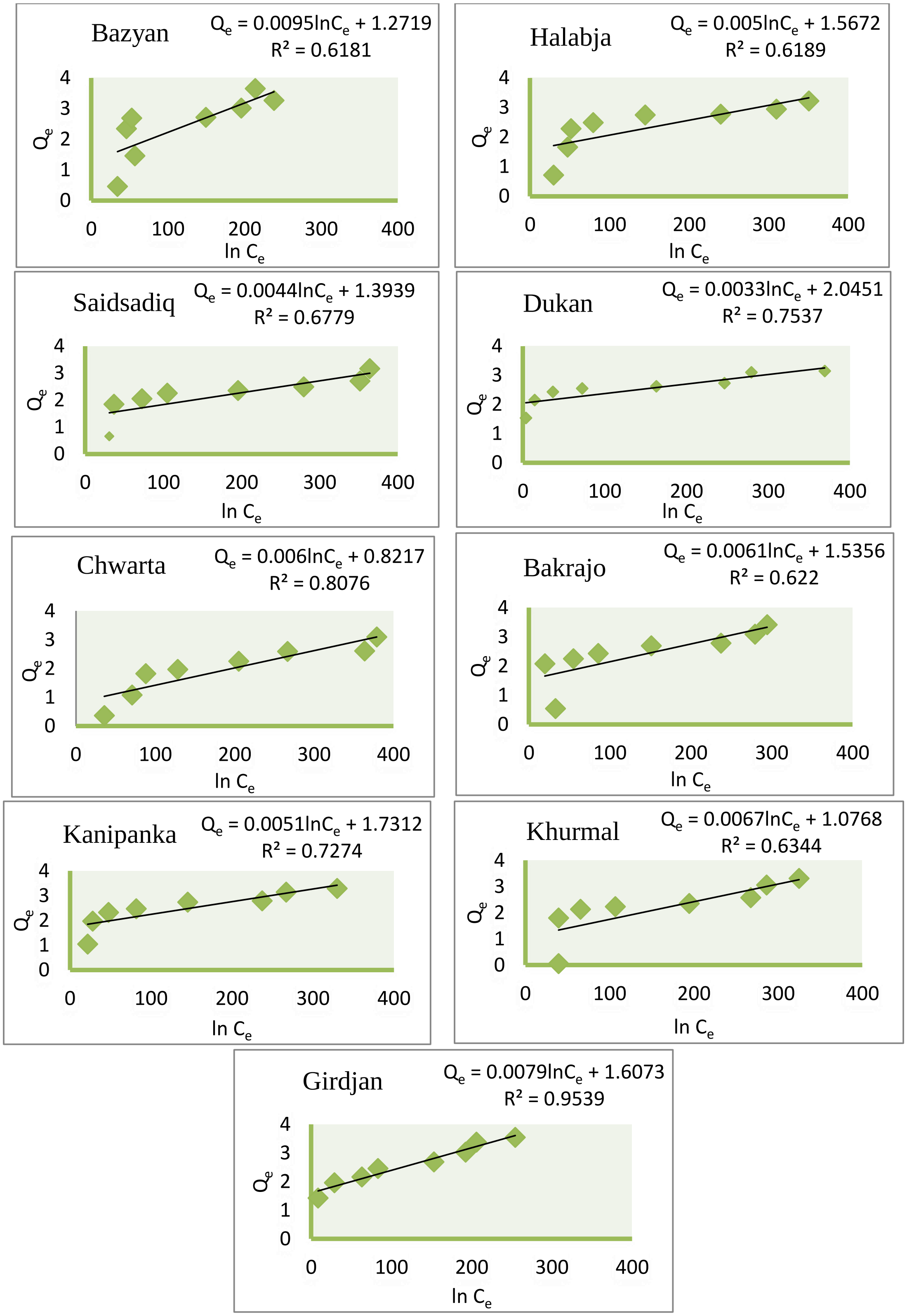
Figure 4.11 Pathway reaction according to linearized Freundlich sorption isotherm plot for P at 318 K at a depth of 0 to 30 cm for all the soils under investigation.



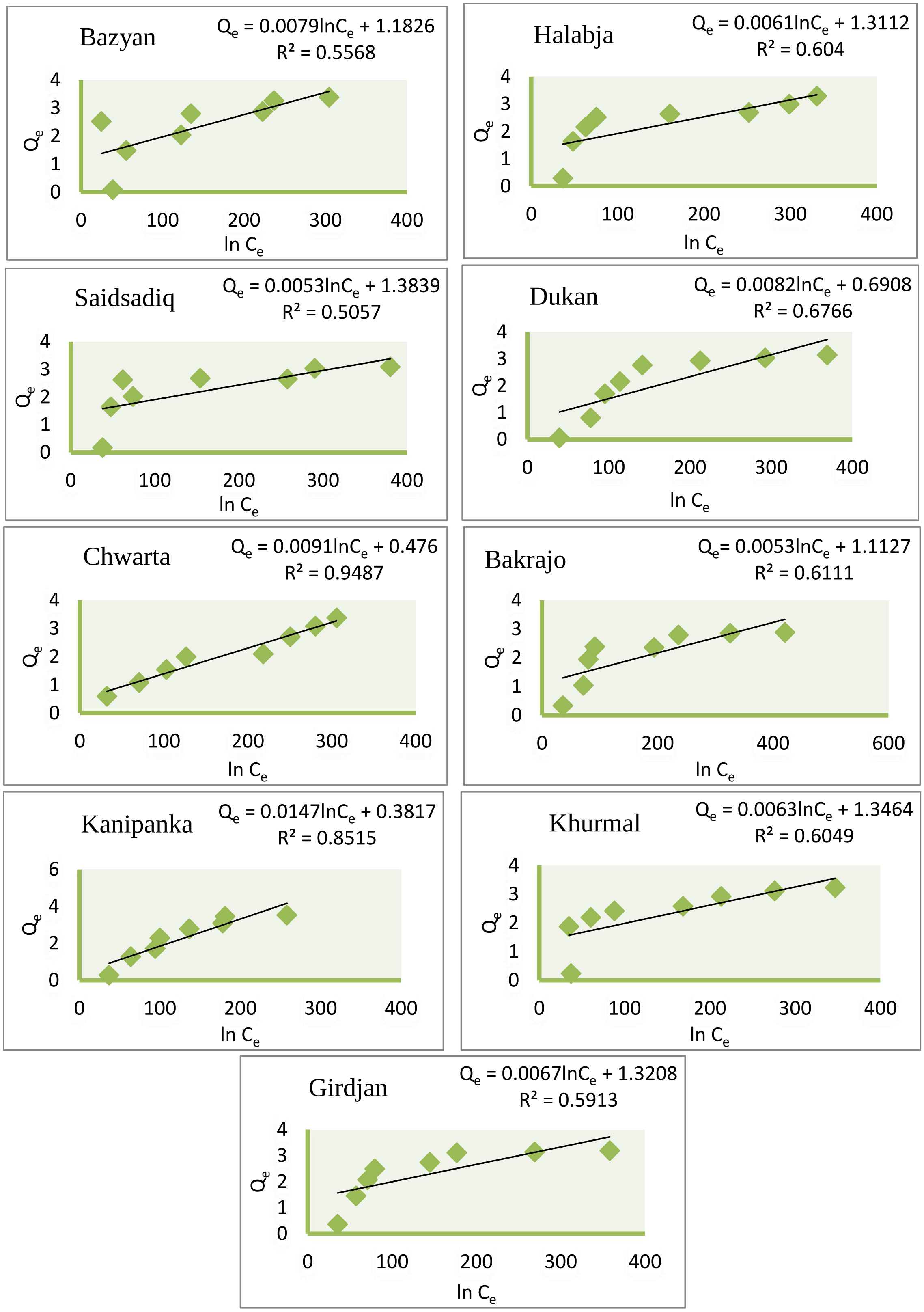
Figures 4.12 Pathway reaction according to linearized Freundlich sorption isotherm plot for P at 318 K at a depth of 30 to 60 cm for all the soils under investigation.

4.1.3 Temkin equation

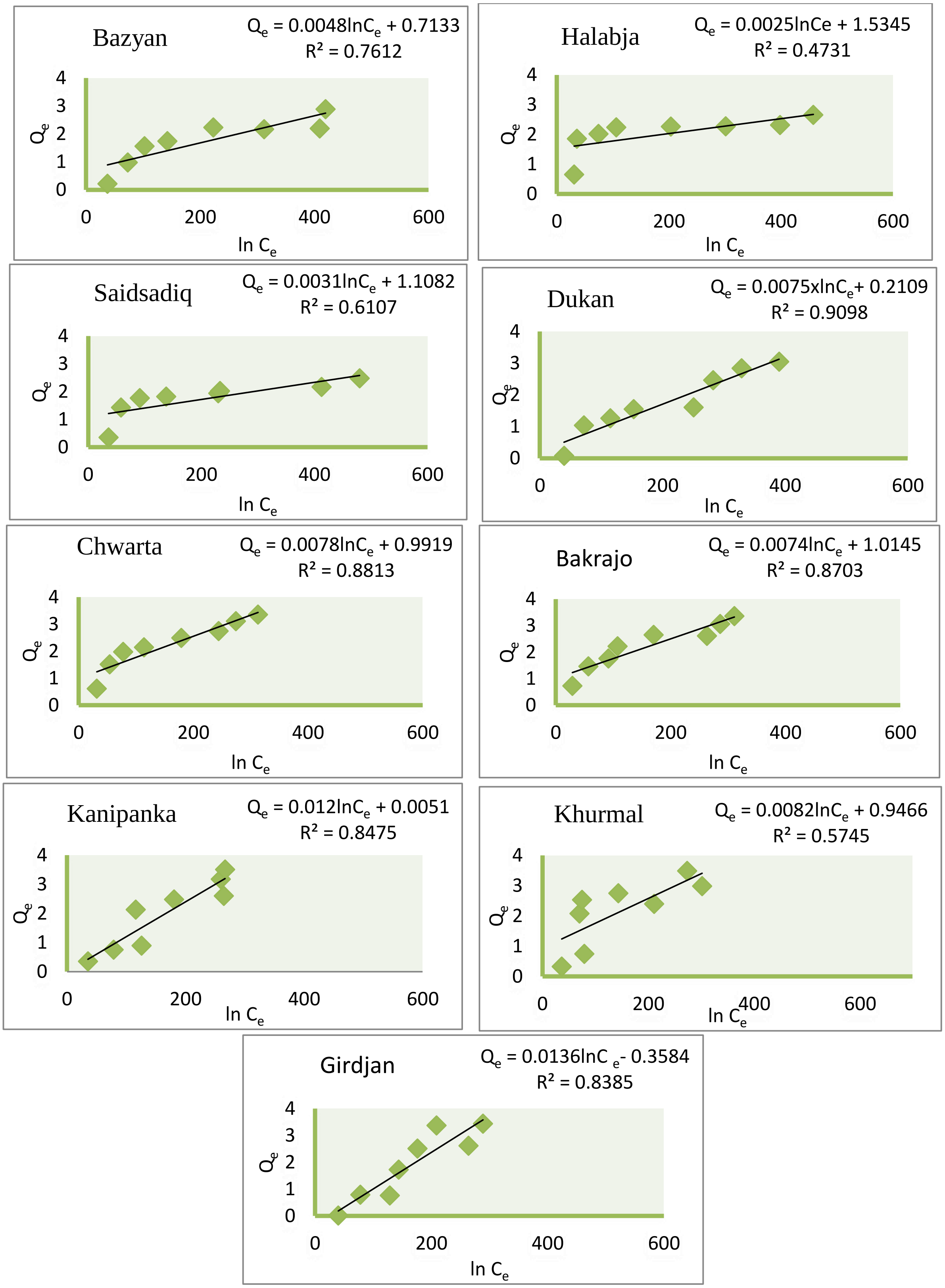
Temkin isotherm was used in this study to obtain the results that will be discussed in the following paragraphs. Since nine different regions each at two different depths were originally chosen to be studied, Temkin isotherm was also used for the same regions and for the same purpose. To give a brief description of the Temkin isotherm, it contains a factor that is explicitly taking into the account of adsorbent-adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes the heat of adsorption (a function of temperature) of all molecules in the layer would decrease linearly rather than in a logarithmic manner with the coverage. The data were plotted by (Q_e vs. ln C_e) and figures (4.13 to 4.18) show the plotted data. To move on to effects obtained through this theory, the results listed in the Table 4.2 can be looked at. The lowest value of A_T was 0.0000013 at 298K, and the highest value of A_T was 1.0000051 at 278K at depth (0 to 30) cm for Bazyan and Girdjan locations, respectively. Moreover, the subsurface soil had the lowest value of A_T which was 1.00000003 at 298 K for the soil of Bakrajo location, but the highest value of A_T was 1.00009 at 318 K for the soil of Kanipanka. The next parameter of Temkin isotherm is b_t which was related to the heat of sorption. The minimum value of b_t was 1431.10 at 278 K in Kanipanka location while the maximum value of b_t was 1303985.20 at 318 K in Bazyan location for the surface soil. While at the subsurface soil 30 to 60 cm the lowest value of b_t was 5034.60 at 318 K° in Kanipanka location and the highest value of b_t was 688214.40 at 318K in Khurmal location. The last parameter of Temkin equation is heat of sorption constant (B). At the surface soil the lowest value of B was 0.0019 J mol^{-1} at 318 K from Bazyan location, and the highest value of B was 0.0136J mol^{-1} at 298 K from Girdjan location. From the subsurface soil, the lowest value of B was 0.0036 J mol^{-1} at 298K from Khurmal location, but the highest value of B was 0.4921J mol^{-1} at 318 K from Kanipanka location.



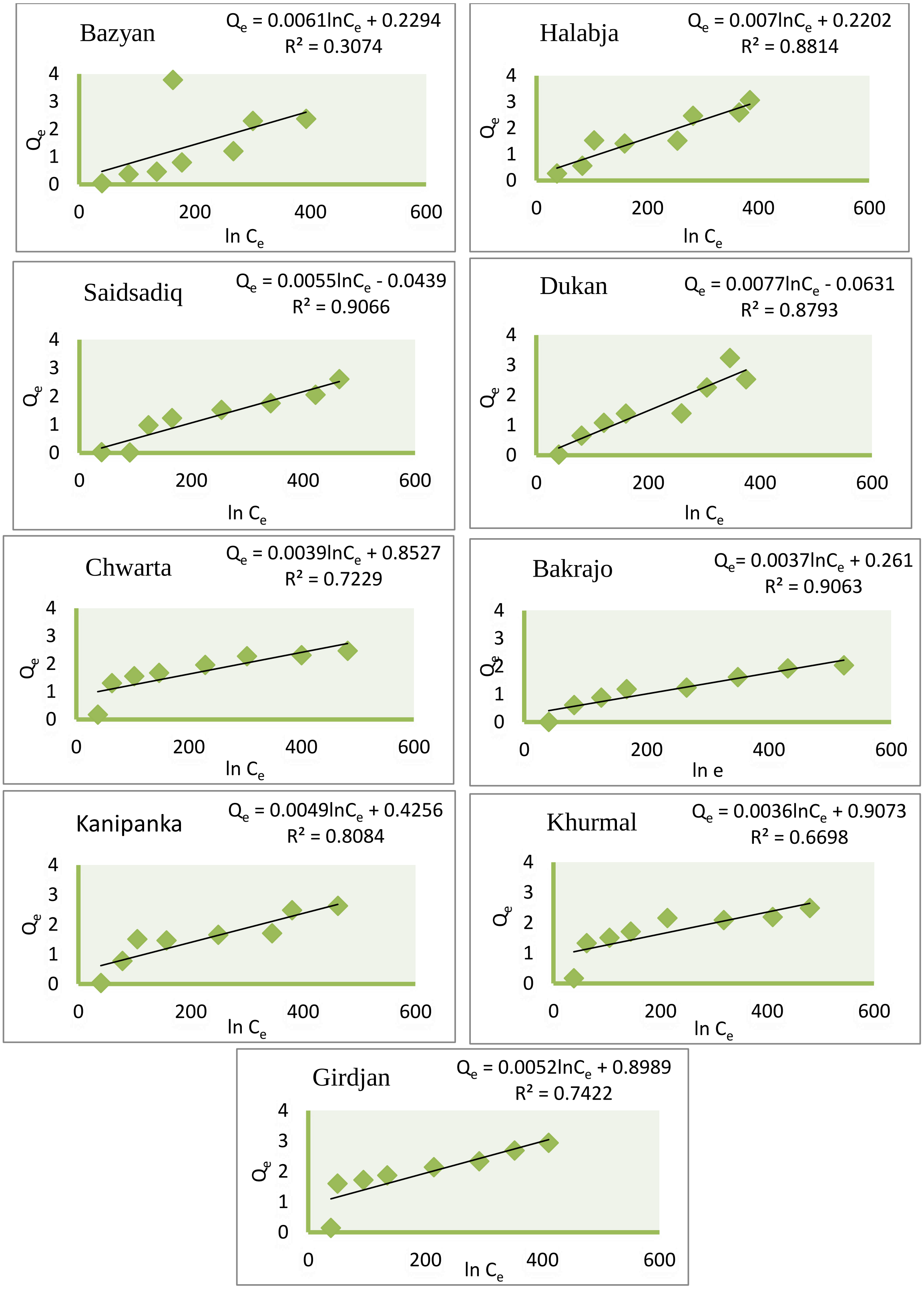
Figures 4.13 Pathway reaction according to linearized Temkin sorption isotherm plot for P at 278 K at a depth of 0 to 30 cm for all the investigated soils.



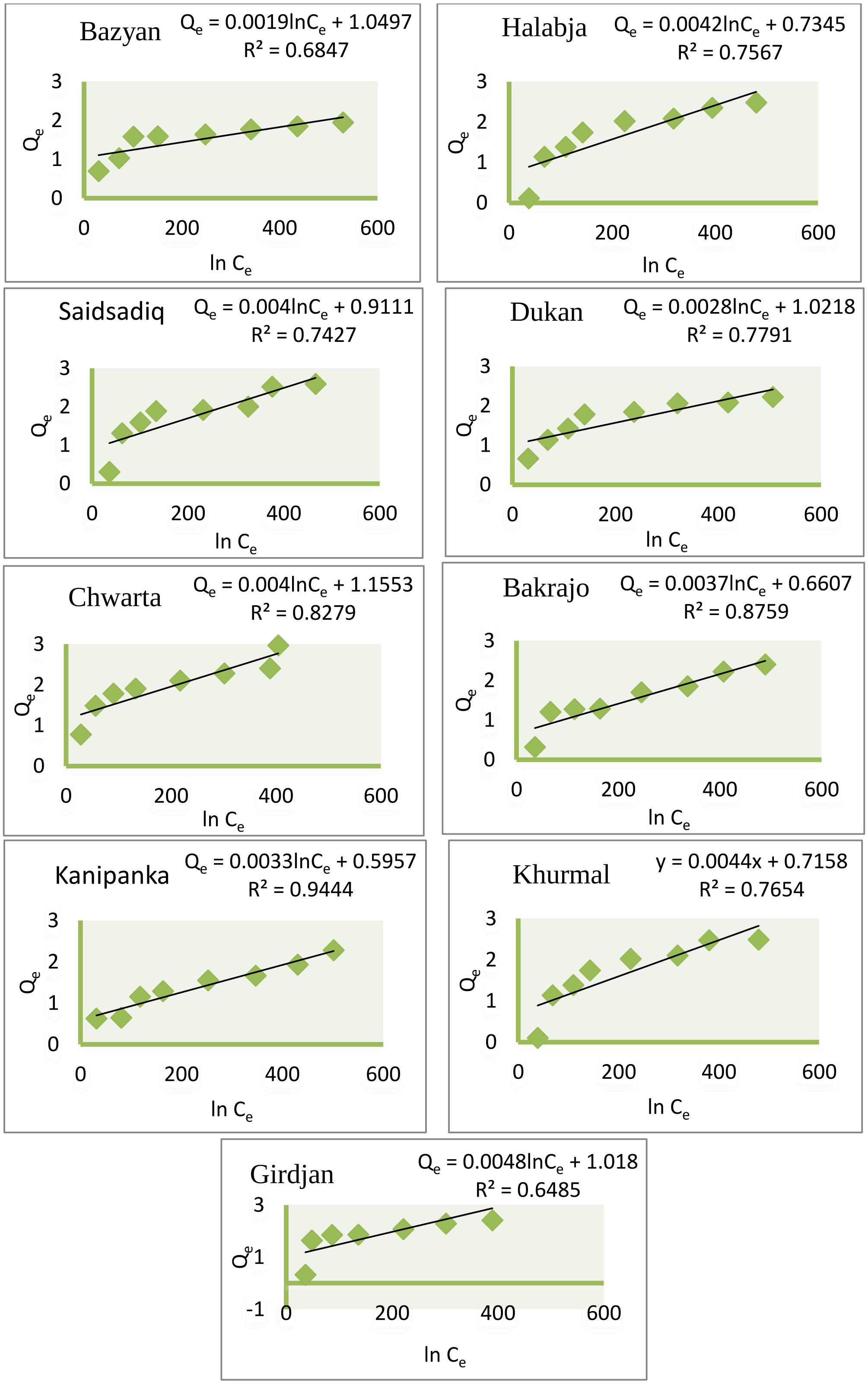
Figures 4.14 Pathway reaction according to linearized Temkin sorption isotherm plot for P at 278 K at a depth of 30 to 60 cm for all the investigated soils.



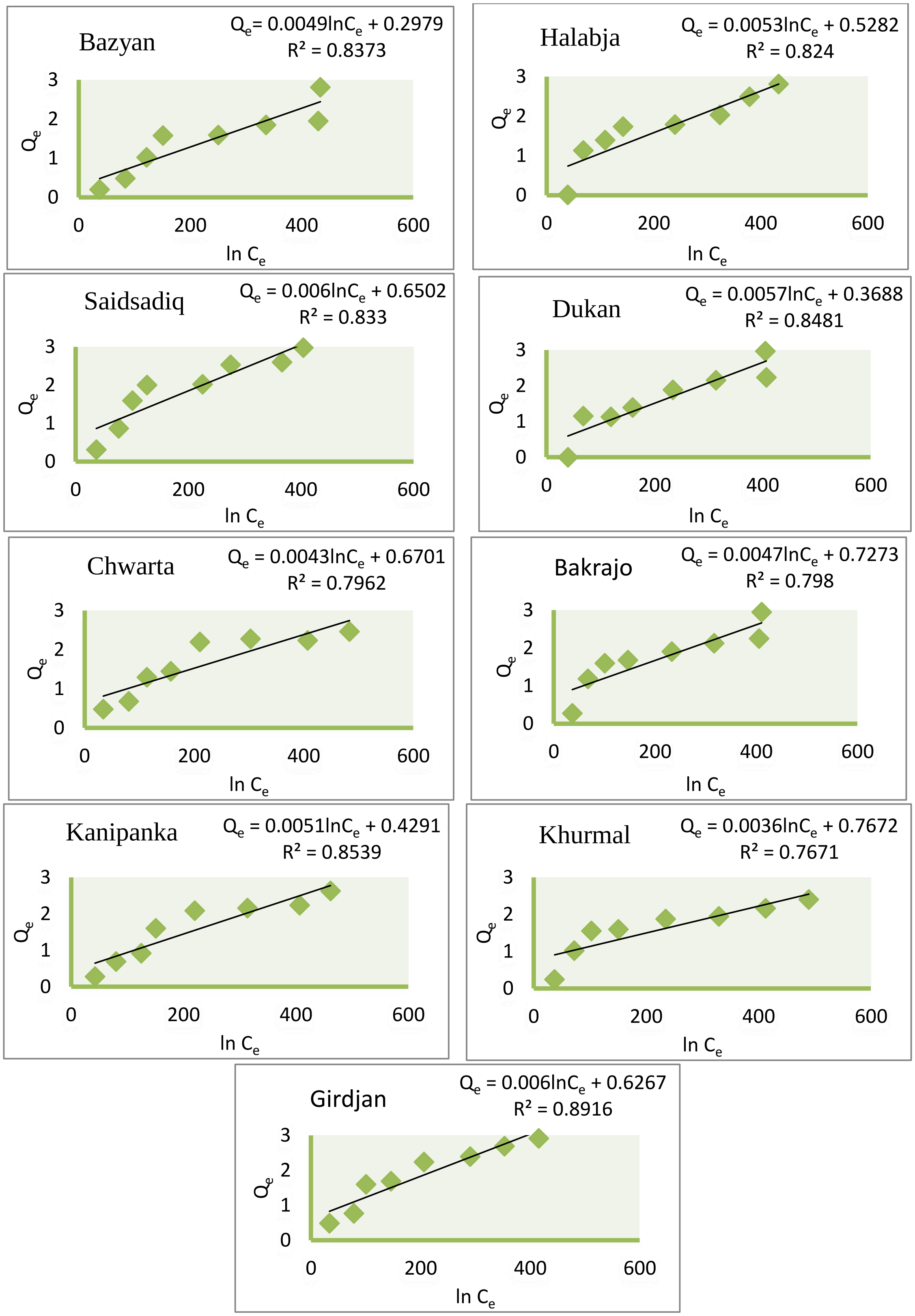
Figures 4.15 Pathway reaction according to inearized Temkin sorption isotherm plot for P at 298 K at a depth of 0 to 30 cm for all the investigated soils.



Figures 4.16 Pathway reaction according to inearized Temkin sorption isotherm plot for P at 298 K at a depth of 30 to 60 cm for all the investigated soils.



Figures 4.17 Pathway reaction according to linearized Temkin sorption isotherm plot for P at 318 K at a depth of 0 to 30 cm for all the investigated soils.

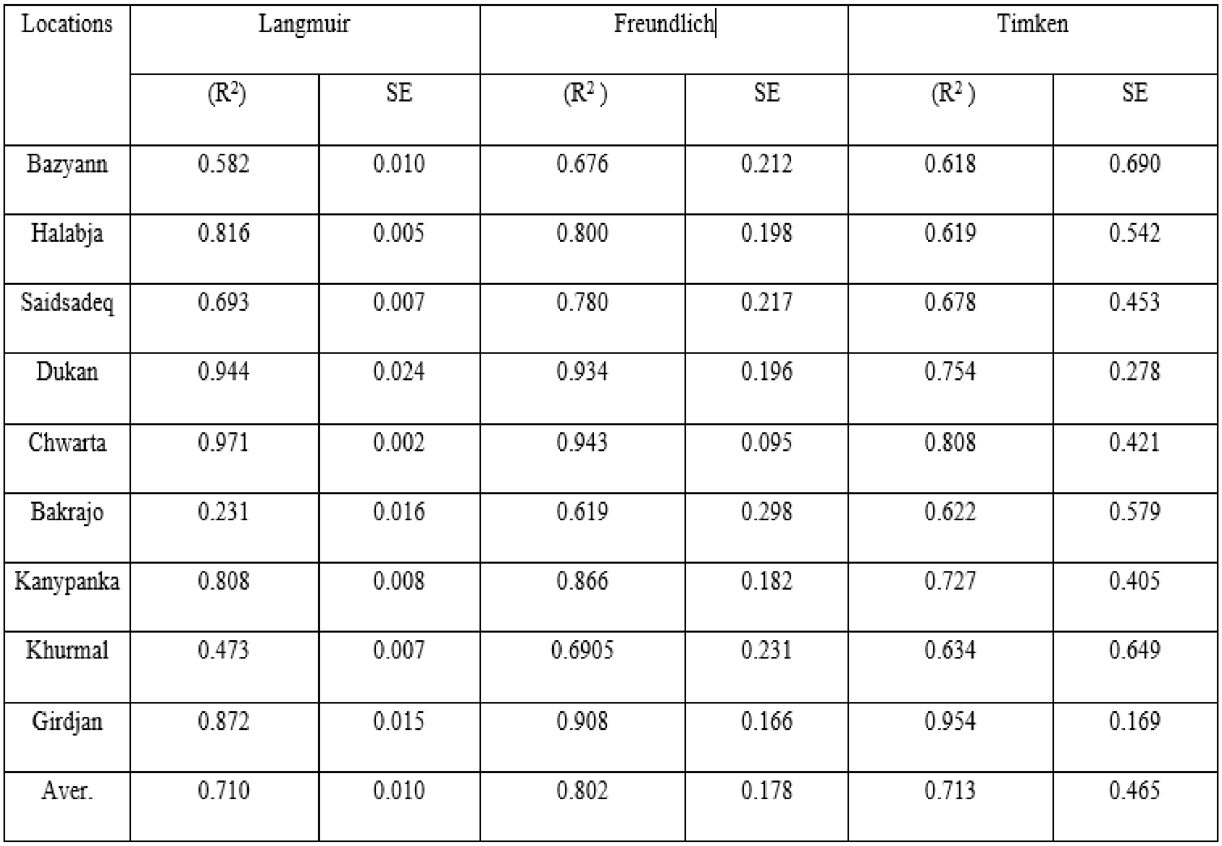


Figures 4.18 Pathway reaction according to linearized Temkin sorption isotherm plot for P at 318 K at a depth of 30 to 60 cm for all the investigated soils.

4.2 Comparison of the models

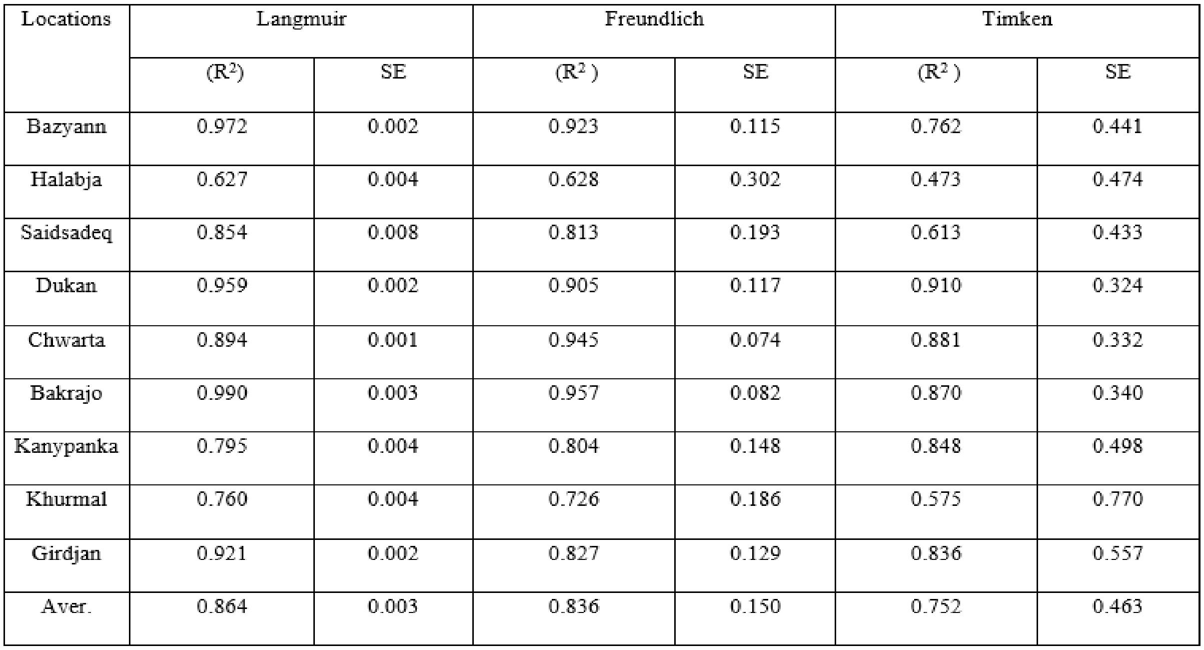
Generally, the choice among models is often based on the goodness of fit (Polyzopulos *et al*., 1985). To choice the best-fit equation depending on the highest value of the coefficient of determination (R^2) and the lowest value of the standard error of estimate (SE) (Sparks, 1992). It is clear from the Tables (4.3,4.4 and 4.5), that at all three different temperatures that are used in this study, Langmuir model proved better over both Freundlich and Temkin models for the P adsorption based on average coefficient of determination (R^2) and standard error values in all the soils under investigation, These results in agreement with the results of Polyzopulos *et al*. (1985) and Del Bubba *et al*. (2003), they reported that the better results of the Langmuir model than the Freundlich model during the P adsorption studies.

Table 4.3 Coefficient of determination (R^2) and standard error (SE) for Langmuir, Freundlich and Temkin isorherm equations for studied soils at 278K.



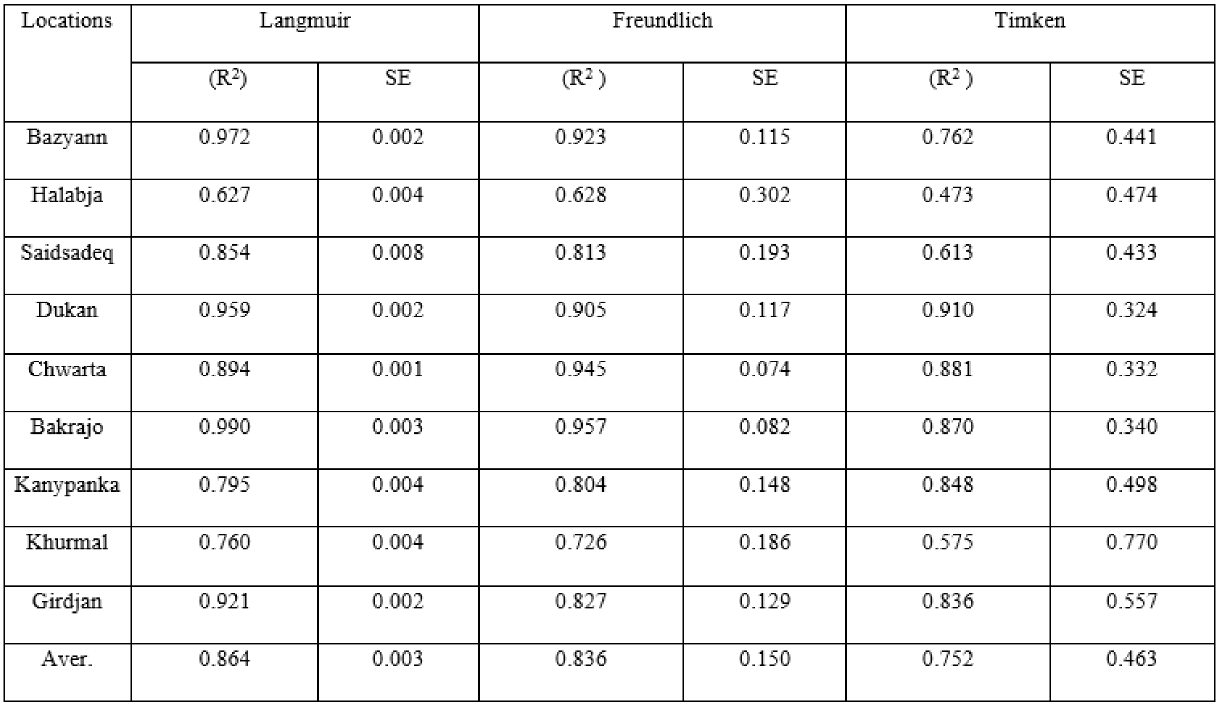
Locations	Langmuir		Freundlich		Timken	
	(R^2)	SE	(R^2)	SE	(R^2)	SE
Bazyann	0.582	0.010	0.676	0.212	0.618	0.690
Halabja	0.816	0.005	0.800	0.198	0.619	0.542
Saidsadeq	0.693	0.007	0.780	0.217	0.678	0.453
Dukan	0.944	0.024	0.934	0.196	0.754	0.278
Chwarta	0.971	0.002	0.943	0.095	0.808	0.421
Bakrajo	0.231	0.016	0.619	0.298	0.622	0.579
Kanypanka	0.808	0.008	0.866	0.182	0.727	0.405
Khurmal	0.473	0.007	0.6905	0.231	0.634	0.649
Girdjan	0.872	0.015	0.908	0.166	0.954	0.169
Aver.	0.710	0.010	0.802	0.178	0.713	0.465

Table 4.4 Coefficient of determination (R^2) and standard error (SE) for Langmuir, Freundlich and Temkin isorherm equations for studied soils at 298K.



Locations	Langmuir		Freundlich		Timken	
	(R^2)	SE	(R^2)	SE	(R^2)	SE
Bazyann	0.972	0.002	0.923	0.115	0.762	0.441
Halabja	0.627	0.004	0.628	0.302	0.473	0.474
Saidsadeq	0.854	0.008	0.813	0.193	0.613	0.433
Dukan	0.959	0.002	0.905	0.117	0.910	0.324
Chwarta	0.894	0.001	0.945	0.074	0.881	0.332
Bakrajo	0.990	0.003	0.957	0.082	0.870	0.340
Kanypanka	0.795	0.004	0.804	0.148	0.848	0.498
Khurmal	0.760	0.004	0.726	0.186	0.575	0.770
Girdjan	0.921	0.002	0.827	0.129	0.836	0.557
Aver.	0.864	0.003	0.836	0.150	0.752	0.463

Table 4.5 Coefficient of determination (R^2) and standard error (SE) for Langmuir, Freundlich and Temkin isorherm equations for studied soils at 318K.



Locations	Langmuir		Freundlich		Timken	
	(R^2)	SE	(R^2)	SE	(R^2)	SE
Bazyann	0.972	0.002	0.923	0.115	0.762	0.441
Halabja	0.627	0.004	0.628	0.302	0.473	0.474
Saidsadeq	0.854	0.008	0.813	0.193	0.613	0.433
Dukan	0.959	0.002	0.905	0.117	0.910	0.324
Chwarta	0.894	0.001	0.945	0.074	0.881	0.332
Bakrajo	0.990	0.003	0.957	0.082	0.870	0.340
Kanypanka	0.795	0.004	0.804	0.148	0.848	0.498
Khurmal	0.760	0.004	0.726	0.186	0.575	0.770
Girdjan	0.921	0.002	0.827	0.129	0.836	0.557
Aver.	0.864	0.003	0.836	0.150	0.752	0.463

4.3 Relationships between soil physicochemical properties and isothermal equations parameters

The relationships between soil physicochemical properties and isothermal equations parameters in studied soils are summarized in Table 4.6. the results show that the heat of sorption (bt) (J mol^{-1}) from a Temkin isotherm equation was positively correlated with active calcium carbonate content (r = 0.727. p = 0.026), sand content (r = 0.724. p = 0.027) and also strength of adsorption (n) from Freundlich isotherm equation was correlated with silt content (r = 0.736. p = 0.023) Figuer.4.20. This relationship suggests that the heat of sorption (bt) (J mol^{-1}) increased with the amount of active calcium carbonate and the strength of adsorption (n) increased with the amount of silt content.

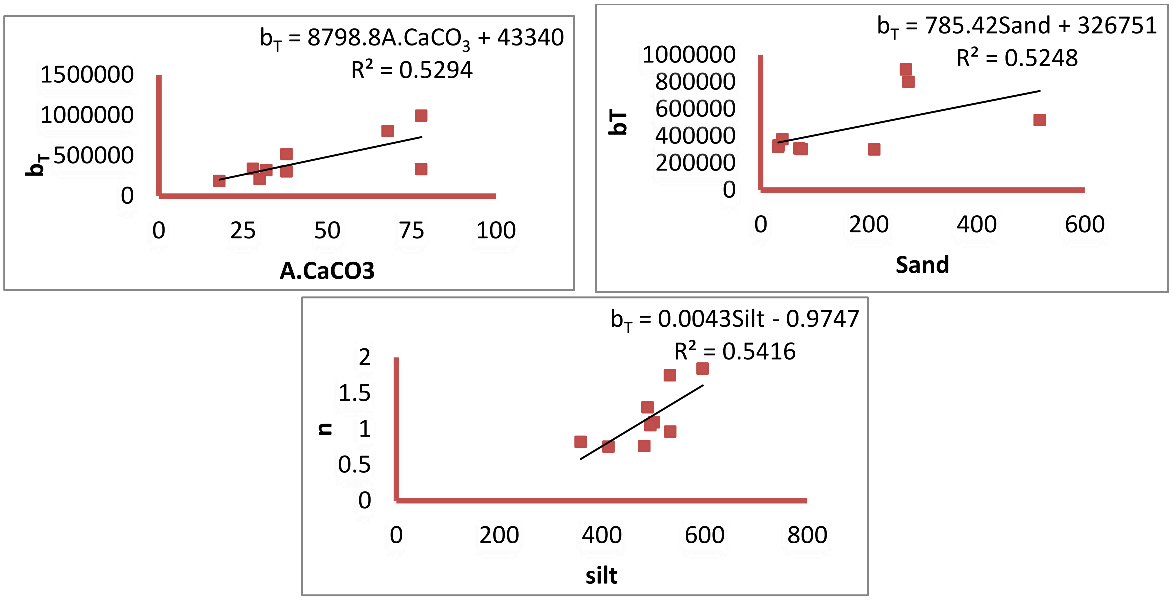
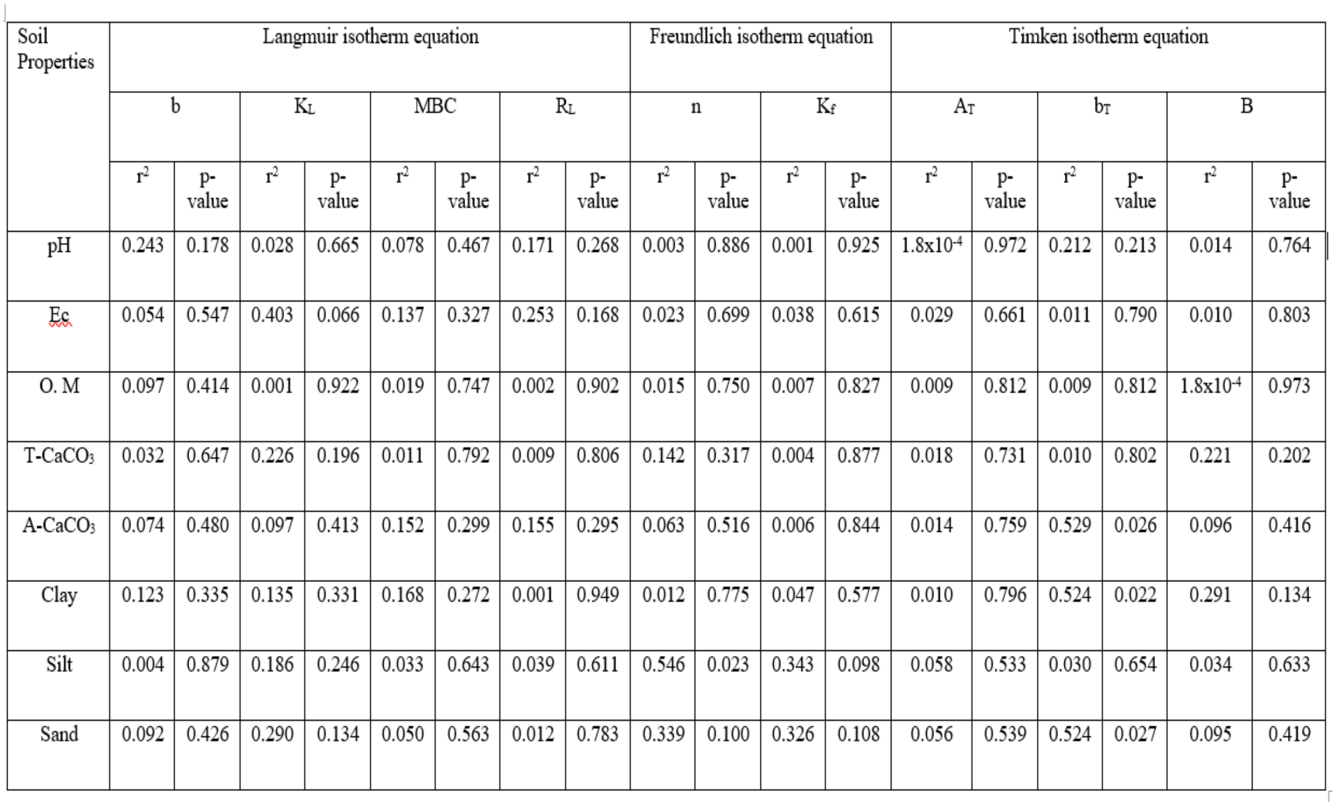


Figure 4.19 Shows relationship between soil physicochemical properties and parameters of the equations.

Table 4.6 Relationship between soil physiochemical properties and isothermal equation parameters used in this study.



Soil Properties	Langmuir isotherm equation								Freundlich isotherm equation				Timken isotherm equation					
	b		K_L		MBC		R_L		n		K_f		A_T		b_T		B	
	r^2	p-value	r^2	p-value	r^2	p-value	r^2	p-value	r^2	p-value	r^2	p-value	r^2	p-value	r^2	p-value	r^2	p-value
pH	0.243	0.178	0.028	0.665	0.078	0.467	0.171	0.268	0.003	0.886	0.001	0.925	1.8×10^{-4}	0.972	0.212	0.213	0.014	0.764
Ec	0.054	0.547	0.403	0.066	0.137	0.327	0.253	0.168	0.023	0.699	0.038	0.615	0.029	0.661	0.011	0.790	0.010	0.803
O. M	0.097	0.414	0.001	0.922	0.019	0.747	0.002	0.902	0.015	0.750	0.007	0.827	0.009	0.812	0.009	0.812	1.8×10^{-4}	0.973
T-$CaCO_3$	0.032	0.647	0.226	0.196	0.011	0.792	0.009	0.806	0.142	0.317	0.004	0.877	0.018	0.731	0.010	0.802	0.221	0.202
A-$CaCO_3$	0.074	0.480	0.097	0.413	0.152	0.299	0.155	0.295	0.063	0.516	0.006	0.844	0.014	0.759	0.529	0.026	0.096	0.416
Clay	0.123	0.335	0.135	0.331	0.168	0.272	0.001	0.949	0.012	0.775	0.047	0.577	0.010	0.796	0.524	0.022	0.291	0.134
Silt	0.004	0.879	0.186	0.246	0.033	0.643	0.039	0.611	0.546	0.023	0.343	0.098	0.058	0.533	0.030	0.654	0.034	0.633
Sand	0.092	0.426	0.290	0.134	0.050	0.563	0.012	0.783	0.339	0.100	0.326	0.108	0.056	0.539	0.524	0.027	0.095	0.419

4.4 Relationships between the adsorbed of P (Q_e) and some physicochemical properties of the soils under the investigation

The relationships between the amount of adsorbed P on the surface of soil particles (Q_e) and some physicochemical properties of the soils under this investigation are shown in Figures 4.20, 4.21 and 4.22 and Table 4.7 using the polynomial adsorption model, Langmuir, Freundlich and Temkin isotherms equation depending on the correlation coefficient (r) values it is found that the amount of sorbed P on the surface of soil particles did not significantly correlated with the soil physicochemical properties from all the tested models except the amount of the organic matter content that correlated significantly ($r = 0.756^{*}$) from the Langmuir equation and high significantly correlated with active $CaCO_3$ equivalent and silt content from the Freundlich equation ($r = 0.840^{**}$ and ($r = 0.858^{**}$), respectively.

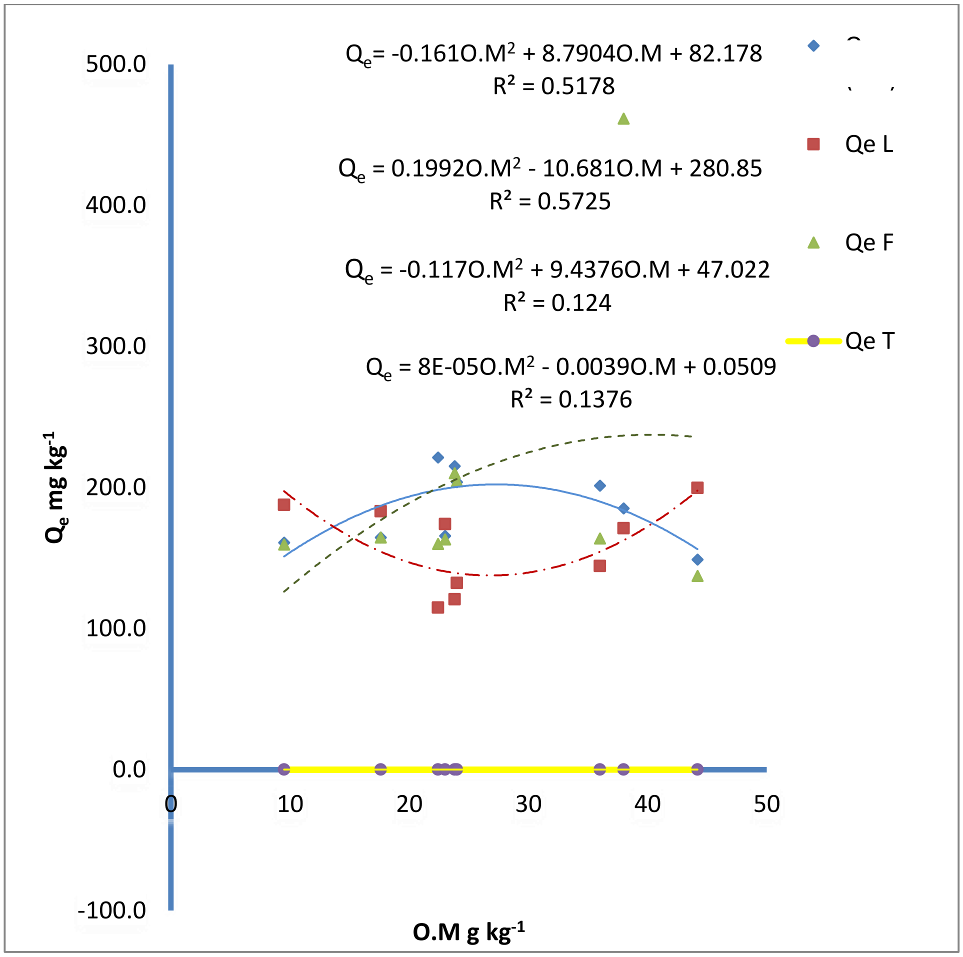


Figure 4.20 Relationship between the amount of adsorbed P (Q_e) and organic matter content

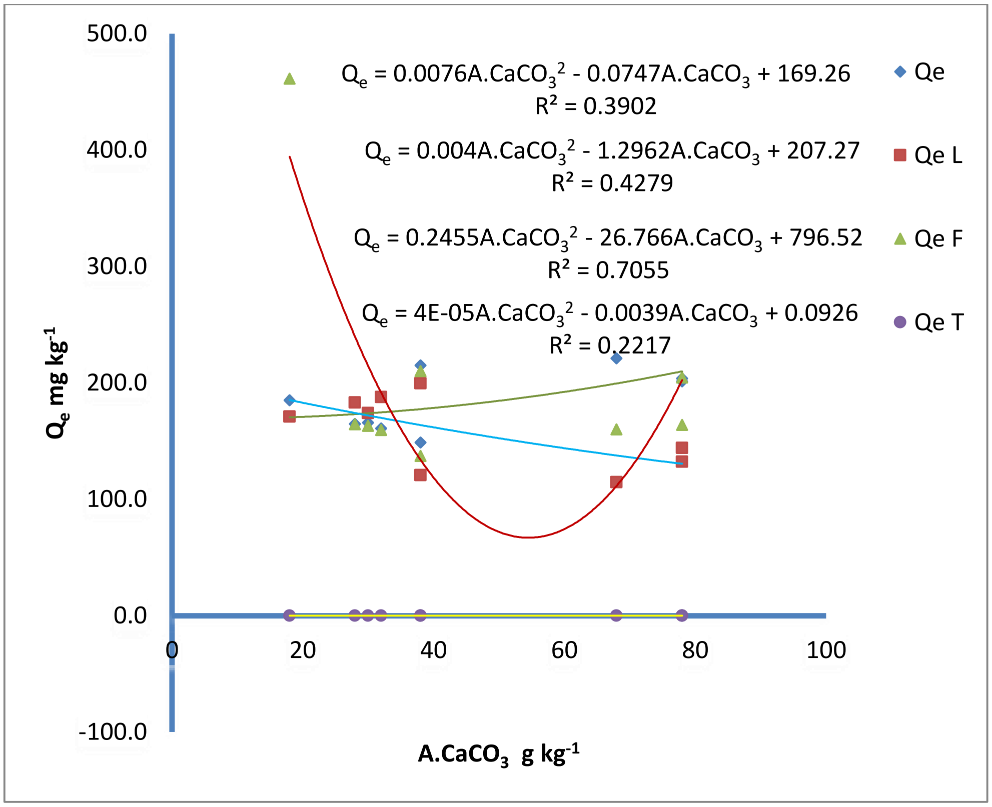


Figure 4.21 Relationship between amount of adsorbed P (Q_e) and active $CaCO_3$ equivalent content

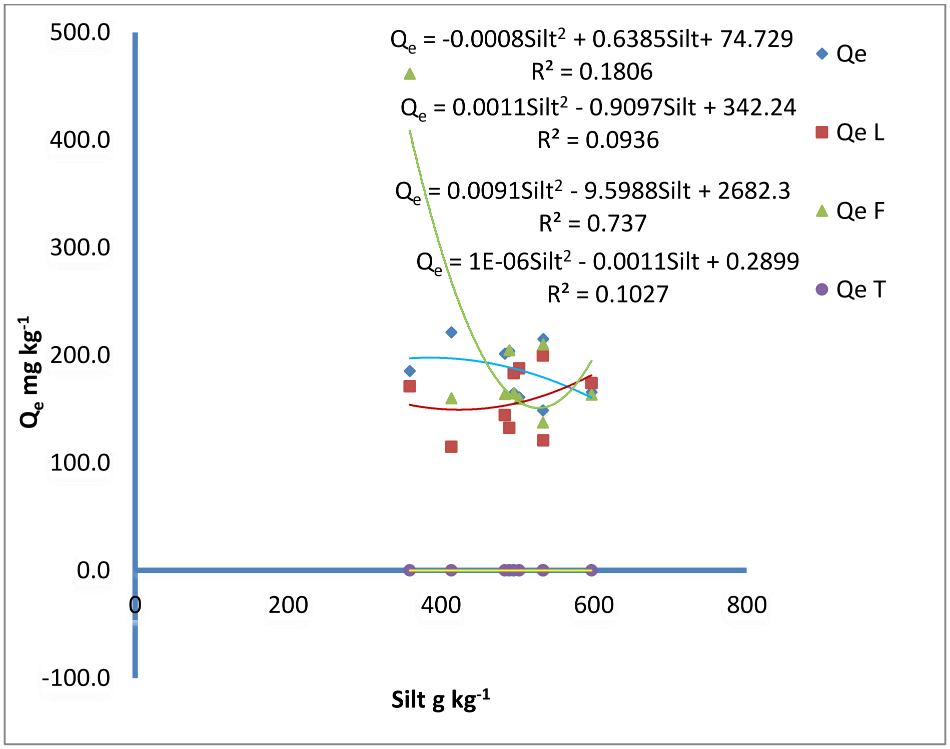
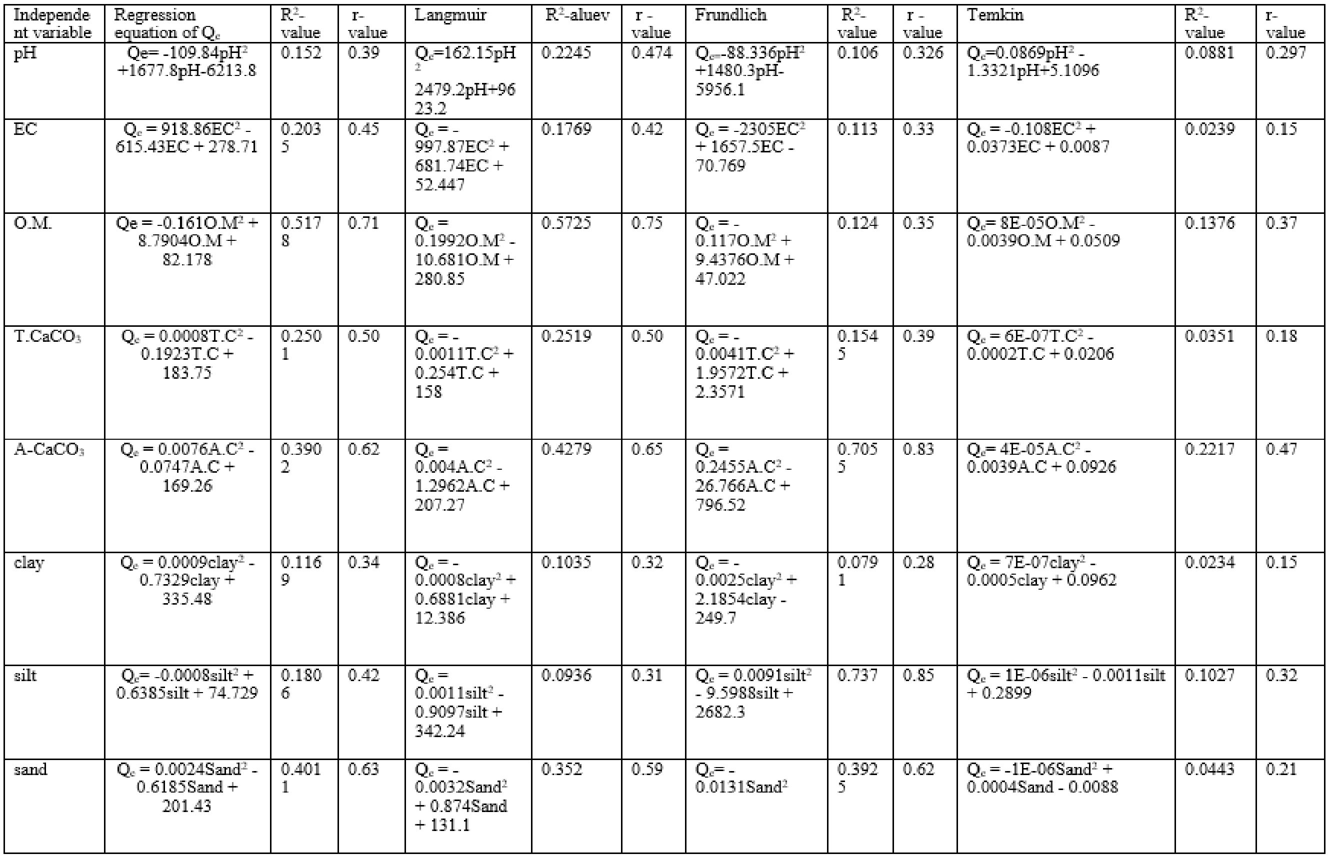


Figure 4.22 Relationship between amount of adsorbed P (Q_e) and silt content

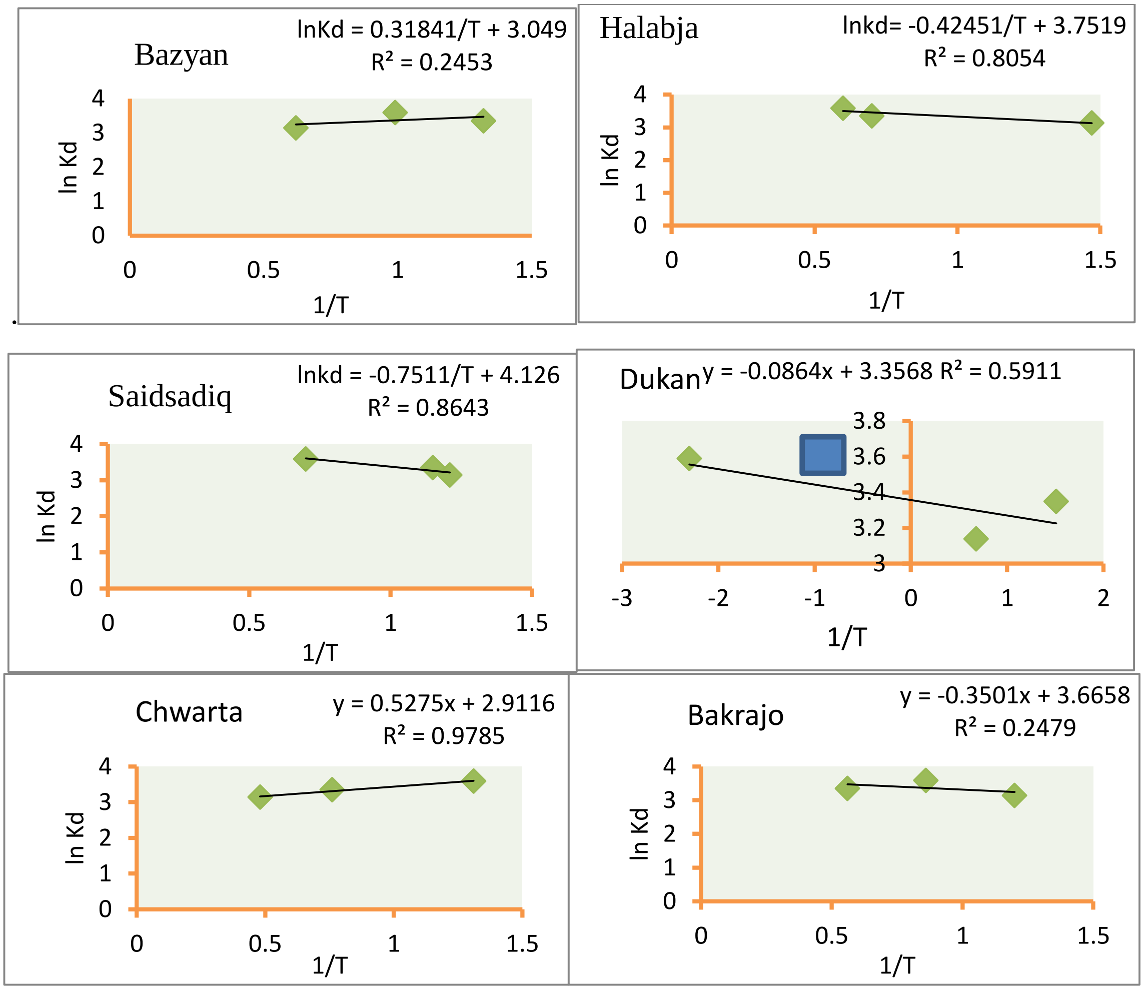
Table 4.7 Adsorption regression equation for adsorption of P (Qe) to some soil properties.



Independent variable	Regression equation of Q_e	R^2-value	r-value	Langmuir	R^2-aluev	r -value	Frundlich	R^2-value	r -value	Temkin	R^2-value	r-value
pH	$Qe= -109.84pH^2 +1677.8pH-6213.8$	0.152	0.39	$Q_e=162.15pH^2$ $2479.2pH+9623.2$	0.2245	0.474	$Q_e=-88.336pH^2 +1480.3pH-5956.1$	0.106	0.326	$Q_e=0.0869pH^2 - 1.3321pH+5.1096$	0.0881	0.297
EC	$Q_e = 918.86EC^2 - 615.43EC + 278.71$	0.2035	0.45	$Q_e = -997.87EC^2 + 681.74EC + 52.447$	0.1769	0.42	$Q_e = -2305EC^2 + 1657.5EC - 70.769$	0.113	0.33	$Q_e = -0.108EC^2 + 0.0373EC + 0.0087$	0.0239	0.15
O.M.	$Qe = -0.161O.M^2 + 8.7904O.M + 82.178$	0.5178	0.71	$Q_e = 0.1992O.M^2 - 10.681O.M + 280.85$	0.5725	0.75	$Q_e = -0.117O.M^2 + 9.4376O.M + 47.022$	0.124	0.35	$Q_e= 8E-05O.M^2 - 0.0039O.M + 0.0509$	0.1376	0.37
T.$CaCO_3$	$Q_e = 0.0008T.C^2 - 0.1923T.C + 183.75$	0.2501	0.50	$Q_e = -0.0011T.C^2 + 0.254T.C + 158$	0.2519	0.50	$Q_e = -0.0041T.C^2 + 1.9572T.C + 2.3571$	0.1545	0.39	$Q_e = 6E-07T.C^2 - 0.0002T.C + 0.0206$	0.0351	0.18
A-$CaCO_3$	$Q_e = 0.0076A.C^2 - 0.0747A.C + 169.26$	0.3902	0.62	$Q_e = 0.004A.C^2 - 1.2962A.C + 207.27$	0.4279	0.65	$Q_e = 0.2455A.C^2 - 26.766A.C + 796.52$	0.7055	0.83	$Q_e= 4E-05A.C^2 - 0.0039A.C + 0.0926$	0.2217	0.47
clay	$Q_e = 0.0009clay^2 - 0.7329clay + 335.48$	0.1169	0.34	$Q_e = -0.0008clay^2 + 0.6881clay + 12.386$	0.1035	0.32	$Q_e = -0.0025clay^2 + 2.1854clay - 249.7$	0.0791	0.28	$Q_e = 7E-07clay^2 - 0.0005clay + 0.0962$	0.0234	0.15
silt	$Q_e= -0.0008silt^2 + 0.6385silt + 74.729$	0.1806	0.42	$Q_e = 0.0011silt^2 - 0.9097silt + 342.24$	0.0936	0.31	$Q_e = 0.0091silt^2 - 9.5988silt + 2682.3$	0.737	0.85	$Q_e = 1E-06silt^2 - 0.0011silt + 0.2899$	0.1027	0.32
sand	$Q_e = 0.0024Sand^2 - 0.6185Sand + 201.43$	0.4011	0.63	$Q_e = -0.0032Sand^2 + 0.874Sand + 131.1$	0.352	0.59	$Q_e= -0.0131Sand^2$	0.3925	0.62	$Q_e = -1E-06Sand^2 + 0.0004Sand - 0.0088$	0.0443	0.21

4.5 Thermodynamics study

The thermodynamics parameters also change during the process of adsorption; thus these parameters were calculated in this study. The parameters were free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°). The calculated data are presented in Table 4.8 also values of ΔH° and ΔS° which were determined from the slope and intercept of linear form of the Van 't Hoff equation, plotting ln K_d vs.1/T, are shown in Figures 4.23 and 4.24. The standard free energy (ΔG°) of the adsorption process of P is the measure of how much concentration of ion in the solution must lessen before the state of equilibrium is gain. The strength of binding P with the soil is described by values of (ΔH°), Moreover the order and disorder which is produced in a system during a reaction are measured by the changes in entropy (ΔS°).



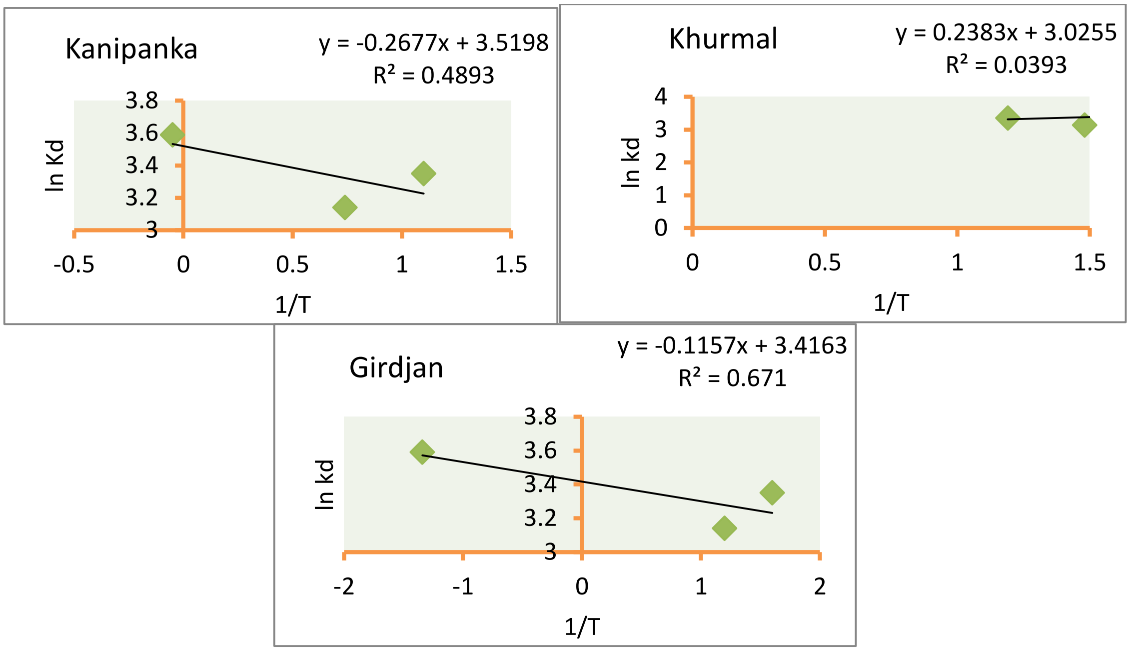
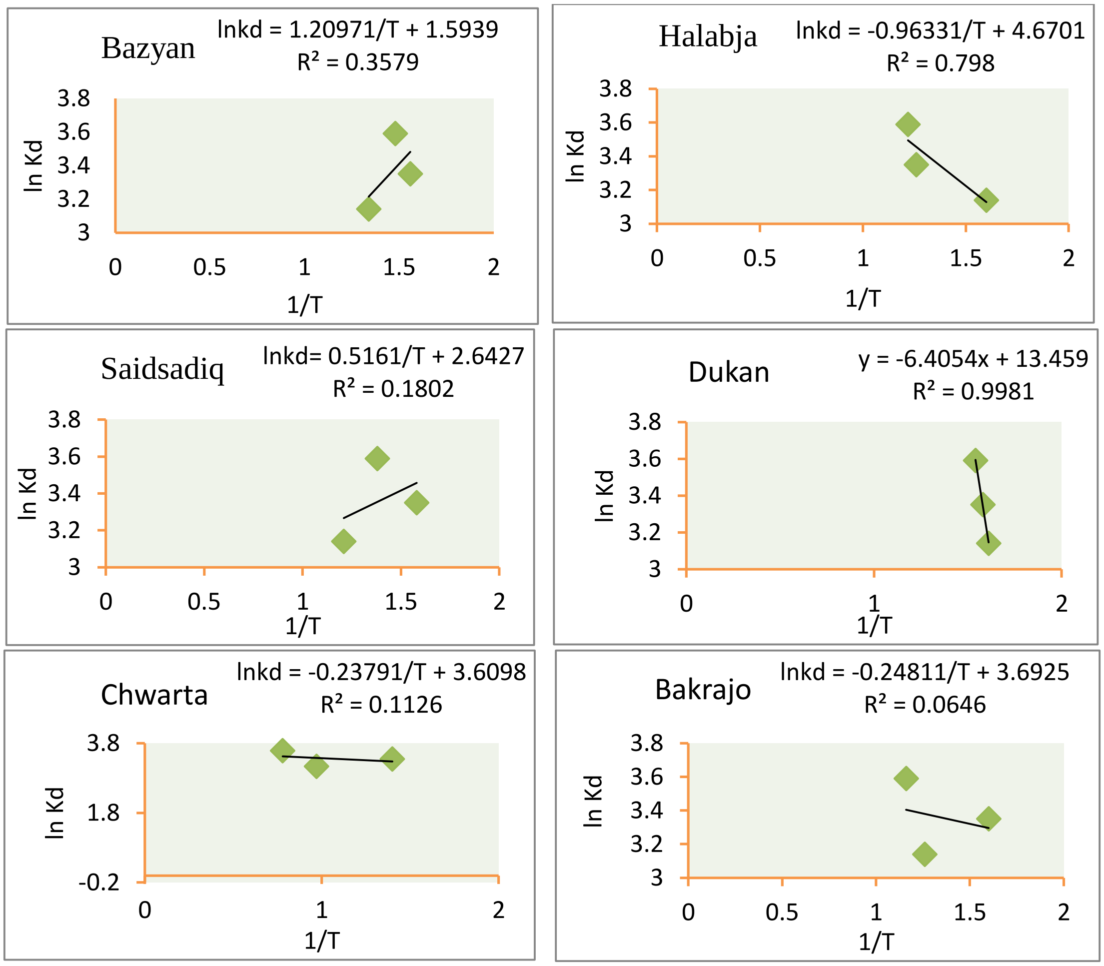


Figure 4.23 Effect of temperature on the distribution coefficient of P for the surface soil samples in this study at different initial concentration.



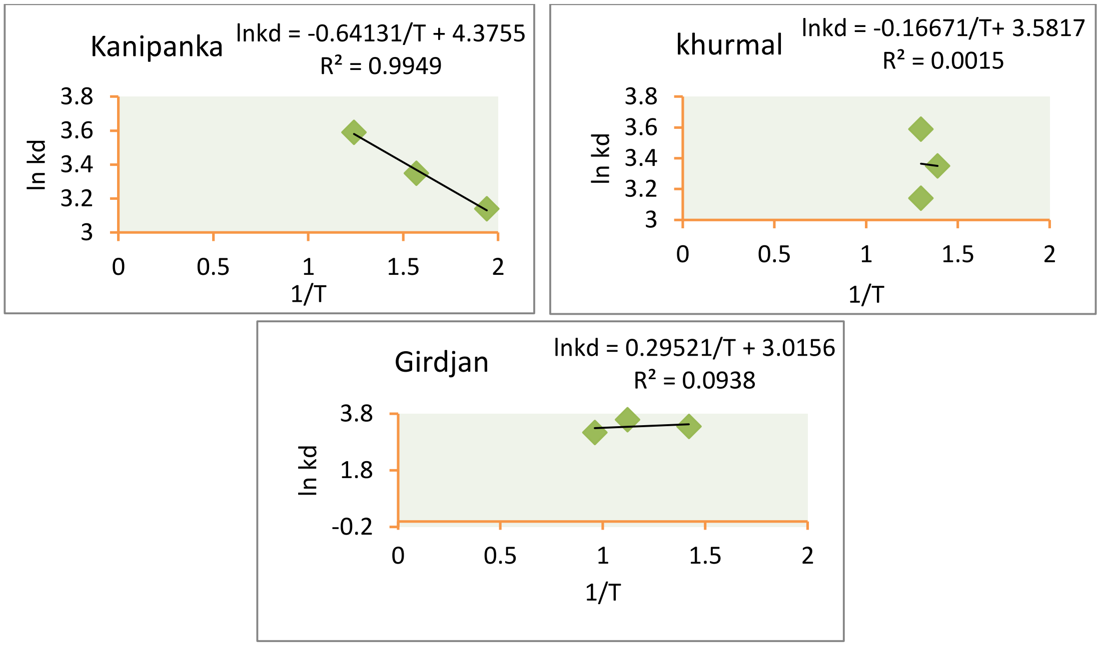


Figure 4.24 Effect of temperature on the distribution coefficient of P for the subsurface soil samples in this study at different initial concentration.

Table 4.8 Thermodynamic parameters for P adsorption for the soil samples under investigations.

Locations	Depth (cm)	ΔG° (kJ mol^{-1})			ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1}K^{-1})
		278 K°	298 K°	318 K°		
Bazyan	0-30	24.61	24.55	24.50	25.34	2.64
	30-60	10.46	10.26	10.05	13.25	10.05
Halabja	0-30	32.17	32.24	32.31	31.19	-3.52
	30-60	41.05	41.21	41.37	38.82	-8.01
Saidsadiq	0-30	36.03	36.16	36.28	34.30	-6.24
	30-60	20.78	20.69	20.61	21.97	4.29
Dukan	0-30	28.11	28.12	28.14	27.91	-0.71
	30-60	97.09	96.02	94.96	111.89	53.25
Chwarta	0-30	22.99	22.90	22.82	24.21	4.38
	30-60	30.56	30.60	30.64	30.01	-1.99
Bakrajo	0-30	31.28	31.34	31.40	30.47	-2.91
	30-60	31.26	31.30	31.35	30.69	-2.06
Kanipanka	0-30	29.88	29.92	29.97	29.26	-2.22
	30-60	34.89	34.78	34.68	36.37	5.33
Khurmal	0-30	30.15	30.18	30.21	29.77	-1.38
	30-60	24.60	24.56	24.52	25.15	1.98
Girdjan	0-30	28.43	28.43	28.43	28.40	-.096
	30-60	24.39	24.34	24.29	25.07	2.45

ΔG° is an important parameter in adsorption thermodynamics, hence, it can be said that a non-spontaneous adsorption has occurred in the studied area and this because of the positive values of ΔG° which is ranged from 22.82kJ mol $^{-1}$ at 318K in the Chwarta location to 36.28kJ mol $^{-1}$ at 318 K for the Saidsadiq location from the surface soil, while it ranged from 10.05kJ mol $^{-1}$ at 318 K for the Bazyan location to 97.09 kJ mol $^{-1}$ at 278 K for the Dukan location. One of the factors that effects on adsorption parameters is temperature. Thus adjustment of temperature during the adsorption process may be required. As generally observed from the data in the Table 4.8, that increasing the temperature from 278 K to 318 K leads to decreasing the values of free energy.

This possibly might be due to the endothermic effects of surrounding during the adsorption process of phosphorus (Aljeboree and Alshirifi, 2012).

The strength of binding P to the soil is explained by ∆H° and the enthalpy changes of adsorption which is a measure of the heat of adsorption and it ranged from 24.21 kJ mol $^{-1}$ for Chwarta location to 34.30 kJ mol $^{-1}$ for Saidsadiq location from the surface soil, while in subsurface soils were ranged from 13.25 kJ mol^{-1} for Bazyan location to 111.89 kJ mol $^{-1}$ for Dukan location. The nine studied locations found to have an endothermic reactions and this is due to the positive value of ∆H°. The results are in agreement with the finding of Solomon *et al.* (2013) and Dandanmozd and Hosseinpur (2016).

The values of ∆S°, for the surface and sub surface soils it was ranged from -6.24 J mol $^{-1}$ for Saidsadiq location to 4.38 J mol $^{-1}$ for Chwarta location from the surface soil locations while, it ranged from -8.01 J mol $^{-1}$ for Halabja location to 53.25 J mol $^{-1}$ for Dukan location. The positive values indicate increasing in randomness in the processes of adsorbing P. Also this positive value suggests the presence of randomness and it decreases within the adsorption process of phosphate, these results are in a harmonic with the results of Yuan *et al*. (2015). As well as, the negative values were analyzed as a result of water molecules replacement in the process of adsorbing P in the soil (Hamdy and El.Gendy, 2012).

In Conclusion, as noticed from the data in the Table 4.8 Dukan location found to have the largest value of ∆G° and possible suggestion for that might be referring to high amount of silt and clay at that soils the same suggestion was reported by Kumar *et al.* (2013). Changes in the values of ∆G° are probably due to the changes in values of soil pH and organic matter content in all the depths this suggestion was reported by Uzoho and Igbojionu, (2014). For all the soils values of ∆H° was positive which means that adsorption of P was endothermic. Values of ∆S° were both negative and positive during the adsorption process of P. In agricultural soils the high value of positive ∆S° implies a decrease in capacity of the process of sorption and this is due to an increase in randomness (Kumar *et al*. 2013).

4.5.1 Relationships between soil physicochemical properties and thermodynamics parameters used in this study

The relationships between soil physicochemical properties for the soils of the areas under investigation and thermodynamics parameters used in this study are summarized in Table 4.9. it is found that the thermodynamics parameters did not significantly correlated with soil physicochemical properties for all the soils under the investigation

Table 4.9 Relationships between soil physicochemical properties and thermodynamics parameters used in this study.

Soil properties	ΔG°		ΔH°		ΔS°	
	R^2	p-value	R^2	p-value	R^2	p-value
pH	0.265	0.156	0.0.247	0.173	0.318	0.114
EC	0.032	0.643	0.036	0.626	0.022	0.702
O.M.	0.106	0.393	0.106	0.396	0.104	0.396
T-$CaCO_3$	0.035	0.631	0.031	0.650	0.048	0.0.573
A-$CaCO_3$	0.168	0.273	0.168	0.274	0.164	0.280
Clay	0.379	0.078	0.382	0.076	0.361	0.087
Silt	0.082	0.454	0.0 86	0.445	0.075	0.477
Sand	7.1×10^{-5}	0.983	1.9×10^{-4}	0.978	5.1×10^{-5}	0.985

4.6 Conclusions and Recommendations

4.6.1 Conclusion

1-The study of phosphorus sorption in nine soils of Kurdistan Region of Iraq showed that the Langmuir and Freundlich sorption models can be used to describe P sorption satisfactorily on soil colloids. Among the soil properties organic matter content, active $CaCO_3$ was significantly influenced P sorption capacity of soils and were strongly correlated with the amount of P sorption (Q_e) on soil colloids.

2-The results of the study depicted that both Langmuir and Freundlich adsorption models are robust in predicting P adsorption in the soils of the Kurdistan Region of Iraq. The results of this study also revealed the differences in P adsorption among the soils studied.

3-Sound knowledge about P sorption properties in different soils is necessary for sustained use of soil for crop production. Results of this study revealed differences in P adsorption and identified soil organic matter and active $CaCO_3$equivalent as main predictors of P activity in the study areas.

4.6.2 Recommendations

1- The results of this study showed that both Langmuir and Freundlich adsorption models are the best in predicting P adsorption than Temkin model in the calcareous soils, for that we are recommending not using Temkin model in the study of P sorption in calcareous soil in the future.

2- Knowing the relationship between parameters and soil physiochemical properties is a good indication for predicting fertilizer recommendations.

3- Depending on the obtained results from this study we suggest using the higher concentration of added P for the using of batch equilibrium technique than the P concentrations used in this study

4- We also recommend using the adsorption phenomenon of phosphate in the studying of the ground water pollution by phosphorus mineral fertilizers.

5- Comparison between the behaviors of different calcareous soils by applying phosphorus sorption isotherms for phosphorus uptake by plants, because results from this study revealed that the calcareous soils varied noticeably in their phosphate retention capacities.

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