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Thermodynamic and Kinetic study of Selenium in some soil from southern Iraq.

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I. Abstract

Two laboratory experiments were counducted in eight soils from different locations in Southern Iraq to study the adsorption thermodynamics using the terms of the standard free energy change (ΔGº), enthalpy change (ΔHº), and entropy change (ΔSº) at temperatures (15, 25, 35, 45) ºC, in addition to studying the kinetics of the selenium element in soils with time through the kinetic equations (Elovich, Fraction power, Zero order, First order, Pseudo First order, Second order, Pseudo Second order, Intraparticle diffusion). The results showed that the values of the standard enthalpy change (ΔHº) were positive values ranging from (2.13-9.00) KJ mol^{-1}, which indicates that the adsorption of selenium is of the endothermic type, while the values of the standard entropy (ΔSº) ranged from (0.0258-0.047) KJ mol^{-1} K^{-} which indicates the randomness of the reaction in the system. While the values of the standard free energy change (ΔGº) for selenium adsorption on the studied soils colloids were negative values indicating that the reaction was spontaneous and ranged from (-4.633--6.076) KJ mol^{-1} k^{-1}. The kinetic model (Fractional Power) showed the best description of selenium adsorption data with time for the soils of (soil 1,2,3,5 and 8) through the highest regression R^2 and the lowest MPSD value. while the kinetic model (Zero order) gave the best description of the selenium adsorption reaction with time for the (soil 4, 6). As for the Maysan soil (soil 7), the pseudo-first order kinetic model equation succeeded in describing the selenium adsorption data with time.

***Keyword:* *Selenium-Kinetic models – thermodynamic parameters – dynamic equilibrium constant*.**

II. Introduction

Berzelius (1818) discovered the element selenium while studying the method of preparing sulfuric acid from sulfur-bearing rocks. Selenium is a crystalline metalloid with properties similar to sulfur. Its atomic number is 79 and is located in Group 6 of the periodic table (Winkel *et al.*, 2015). Selenium has a relatively narrow safety range compared to other trace elements, making it difficult to address selenium deficiency or toxicity. The range between toxic and beneficial amounts for human consumption is very small, estimated at between 30 µg Se day^{-1}, which is considered insufficient, and 1-900 µg Se day^{-1}, which is potentially harmful (Rayman, 2020). The recommended dose by the World Health Organization is 55 µg Se day^{-1} for adults (Wesselink *et al.*, 2019). Lara *et al.* noted that adding adequate amounts of selenium benefits plant growth by enhancing antioxidants, metabolism, and detoxifying heavy metals. However, the importance of selenium remains controversial despite the beneficial effects of low doses on plants. Plants play an indispensable role in the accumulation of selenium in nutrients, and plant selenium uptake depends on the availability of the element in the soil. Yang (2022) stated that selenium plays an important role in regulating the functions of the soil, plant, and human ecosystems, and that the chemical behavior of selenium and its effects on the soil-plant system have become a focus of interest in recent decades.

Chawla *et al.* (2020) indicated that selenium content in most soils is low, within the range of 0.01–2.00 mg Se kg^{-1} soil, with a global average of 0.4 mg Se kg^{-1} soil, and is considered heterogeneous based on geographic distribution. Galic *et al.* (2023) found low selenium concentrations in soil samples from cold, humid regions, which they attributed primarily to climatic variations, particularly evaporation and transpiration rates, which play a crucial role in soil leaching. Liu *et al.* (2021) demonstrated that selenium distribution in soils is influenced by a variety of factors, including topography, parent material, and climate, which in turn contribute to the development of soil physical and chemical properties. The availability of selenium in soil varies greatly depending on soil properties.

Thermodynamics is a fundamental branch of physics that studies energy, its transfer, and transformations in various systems. This theory has played a pivotal role in developing our understanding of physical and chemical processes (Dehli *et al.*, 2023). The concept of kinetics is used by those interested in the subject of nutrient interaction to understand the continuous interaction of ions in the soil solution over time, to determine the amplitude of these ion interactions, and the fate of these interactions (Das *et al.* 2013). Emphasis has been placed on the use of this concept because the soil-plant system is a kinetic system, especially in relation to nutrients. The interest in studying the kinetics of adsorption of various elements on mineral surfaces is important for understanding adsorption kinetics. Many studies have been conducted on the kinetics of selenite in soil and pure phases, while only a few studies have been conducted on selenate, despite it being the most mobile. This may be due to selenate being reduced to other forms in the soil, or its mobility being very high, and thus migrates quickly into groundwater (Loffredo *et al.*, 2011). The research aims to study the thermodynamics of selenium adsorption and the kinetics of selenium reaction and to show the adsorption rate using different kinetic equations to understand the mechanism of selenium behavior in some soils of southern Iraq.

III. Materials and Methods

Eight composite soil samples (0-30 cm) were collected from arable lands in southern Iraq. Some of physical and chemical properties of these soils were estimated (Table 2), as reported in (Jackson 1958 ; Black *et al.* 1965 ; Page *et al.* 1982).

Table 1: physicochemical properties of study soils.

Soil No.	Se (µg 100g^{1-})	EC dS m^{-1}	pH	CaCO$_3$	O.M	Clay	Silt	Sand	Textuer
				gm kg soil^{-1}					
1	0.0964	2.09	7.60	360.0	7.5	417	387	196	Clay loam
2	0.0649	3.72	8.02	440.0	6.7	390	500	110	Silt Clay
3	0.1019	11.30	7.60	30.0	6.0	122	252	625	Sandy Loam
4	0.0912	3.84	7.80	76.25	6.5	78	241	681	Sandy Loam

5	0.0685	4.75	7.66	330.0	7.4	263	574	163	Silt Loam
6	0.0600	4.33	7.61	210.0	7.1	240	410	359	Loam
7	0.0574	5.91	7.61	320.0	5.9	290	570	140	Silty Clay Loam
8	0.0964	5.60	7.55	235.0	6.7	252	352	396	Loam

2-1.Thermodynamic experiment

2.5 g of the study soil was taken and placed in plastic containers. 25 ml of a selenium solution with a concentration of 600 µg Se ml^{-1} was added to the container. The samples were shaken at different temperatures (15, 25, 35, and 45) °C for one hour, and then the samples were filtered through filter paper. The selenium concentration in all solutions was determined using Inductively Coupled Plasma (ICP) emission spectrometry. The adsorbed selenium was calculated from the difference between the selenium concentration in the initial solutions and the equilibrium concentration.

Thermodynamic parameter calculations:

A-ΔH^{o}: The change in standard enthalpy, calculated from the slope value of the relationship between the reciprocal of temperature 1\T and the logarithm of the dynamic equilibrium constant (Log Kd), derived from the following equation:

LogKd=$\frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT}$, Kd was calculated from the equation: $K_d = \frac{(Co-Ce)}{Ce} * \frac{V}{m}$

Co: Initial concentration µg ml^{-1} , Ce: Concentration in the equilibrium solution concentration µg Se ml^{-1} V: Volume (ml) , m: Weight (g)

B- ΔS°: The change in standard entropy, calculated from the intercept value

C- ΔG°: The change in standard free energy, calculated from the following equation:

$\Delta G^{\circ}=\Delta H^{\circ}-T\Delta S^{\circ}$

T: Absolute temperature in Kelvin

2-2.Kinetics Experiment

The experiment was carried out as in the previous experiment (same soil weight, solution volume, and selenium concentration). Samples were shaken at different intervals (5, 10, 20, 40, 80, 160, 320) minutes. The adsorbed amount of the element was calculated: $x = \frac{(C_o - C_e)v}{m}$

where: X: adsorbed amount µg Se g^{-1}

used diferent kinetic models describe the reaction of selenium overtime (Table 2)

Table 2: Kinetic models used in the study

Kinetic	Equations	Expression	Plot	Parameter

Elovich	$q_t = \beta\ln(\beta\alpha t)$	$q_t = \beta\ln(\beta\alpha) + \beta\ln t$	$q_t \text{ Vs . } \ln t$	β=slope α=(slope)$^{-1}$exp(intercept/slope)
Fractional power	$q_t = kt^v$	$\ln qt = \ln k + v\ln t$	$\ln q_t \text{Vs.} \ln t$	K=exp(intercept) v=slope
Zero order	$q_t = q_e - k_0 t$	$q_t = q_e - k_0 t$	$q_t \text{Vs.} t$	q_e=intercept K_0=-(slope)
First order	$q_t = q_e - \exp(k_1 t)$	$\ln qe - k_t t = \ln q_t$	$\ln q_t \text{Vs.} t$	q_e=exp(intercept) K_1=-(slope)
Pseudo-first order	$q_t = q_e[1 - \exp(-k_{1p}t)]$	$\ln(q_e - q_t) = \ln q_e - k_1 p_t$	$\ln(q_e - q_t) \text{ Vs.} t$	q_e=exp(intercept) K_{1p}=-(slope)
Second order	$q_t = \frac{q_e}{1 + q_e k_2 t}$	$\frac{1}{q_t} = \frac{1}{q_e} + k_2 t$	$\frac{1}{q_t} \text{Vs.} t$	q_e=(intercept)$^{-1}$ K_2=slope
Pseudo-second order	$q_t = \frac{k_{2p} q_t^2 t}{1 + q_e k_{2p} t}$	$\text{Type(I)}(\frac{t}{q_t}) = \frac{1}{k_{2p} q_e^2} + t/q_e$	$\frac{t}{q_t} \text{Vs.} t$	q_e=slope^{-1} q_{2p}=(slope^2)/intercept
		$\text{Type(II)}(\frac{1}{q_t}) = \left(\frac{1}{k_{2p} q_e^2}\right)\left(\frac{1}{t}\right) + (\frac{1}{q_e})$	$\frac{1}{q_t} \text{Vs.} \frac{1}{t}$	q_e=intercept^{-1} K_{2p}=(intercept^2)/slope
		$\text{Tyep(III)} q_t = q_e - (\frac{1}{k_{2p} q_e}) q_t/t$	$q_t \text{Vs.} \frac{q_t}{t}$	q_e=intercept K_{2p}=-1/(slope*intercept)
		$\text{Tyep(IV)} \left(\frac{q_t}{t}\right) = k_{2p} q_e^2 - k_{2p} q_e q_t$	$\frac{q_t}{t} \text{Vs.} q_t$	q_e=-intercept/slope K_{2p}=(slope^2)/intercept
Intraparticle diffusion	$q_t = k_p t^{0.5}$	$q_t = k_p t^{0.5}$	$q_t \text{ vs } t^{0.5}$	K_I=slope

q_t: adsorbed amount µg g^{-1} , q_m: adsorption capacity µg g^{-1} , t: time min^{-1} , α: kinetic model constant Elovich µg g^{-1} min^{-1} , β: kinetic Elovich model constant gm $µg^{-1}$, K: kinetic fractional power model constant µg g^{-1} min^{-1} , v: kinetic fractional power model constant , k_0: kinetic zero order model constant µg g^{-1} min^{-1} , k_1: kinetic first order model constant min^{-1} , k_2: kinetic second order model constant g $µg^{-1}$ min^{-1} , k_{1p}: kinetic pseudo-first order model constant min^{-1} , k_{2p}: kinetic pseudo-second order model constant g $µg^{-1}$ min^{-1} , k_p: kinetic constant of the intraparticle diffusion model, g $µg^{-1}$ $min^{-0.5}$

The constants of these equations were calculated, and the regression coefficient (R^2), was used to identify the best equations for representing the experimental values by achieving the maximum value of the coefficient of determination. The results were also subjected to statistical models that represent a measure for calculating the percentage standard deviation (Marquardt's Percent Standard Deviation MPSD).

It is derived from the following equation:

$$\mathrm{MPSD} = 100 * \sqrt{\frac{1}{n-p}\sum_{n-p}^{n}\left(\frac{q_e\mathrm{exp} - q_e\mathrm{cal}}{q_e\mathrm{exp}}\right)^2}$$

Where: $q_e$exp= experimental adsorption, $q_e$cal= calculated adsorption , n = number of observations

IV. Results and Discussion

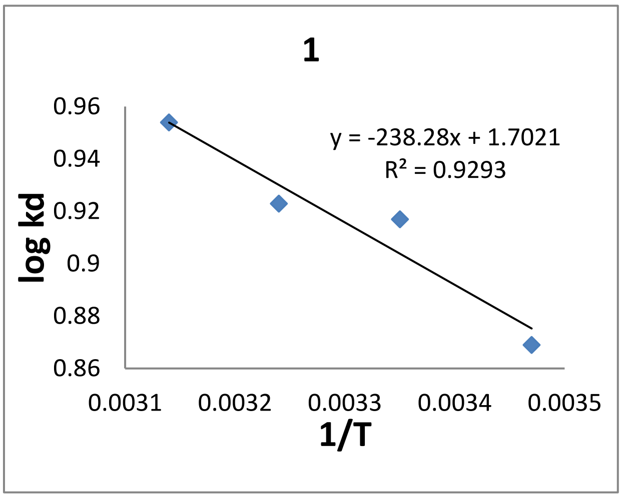
1-3.Thermodynamic experiment

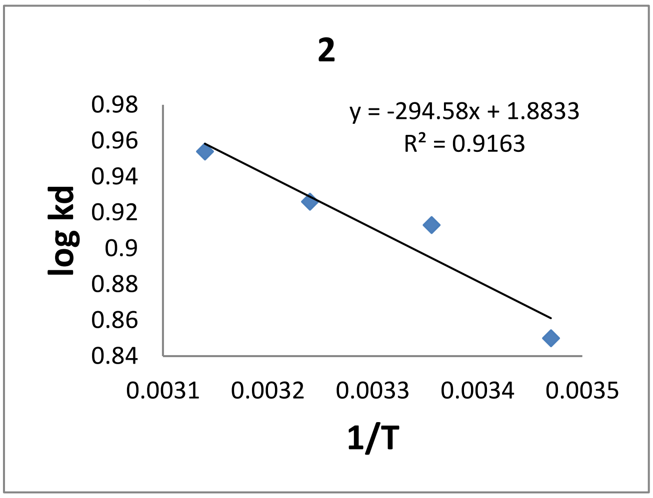
Studying the effect of temperature on the adsorption process is extremely important, as temperature affects the efficiency of binding or retention, and the adsorption rate of materials often varies with temperature. Increasing temperature increases the kinetic energy of the material's molecules, thus increasing the spaces between the molecules. Nouri *et al.* (2007) confirmed that temperature is directly related to the kinetic energy of ions, and that increasing temperature leads to increased diffusion due to decreased viscosity in the solution. Changes in temperature affect the adsorption capacity of certain elements on the adsorbent surface (Ozdemir and Esin 2021). The results (Table 3) showed that there was an increase in the percentage of selenium ions removed from the solution by the soil with increasing temperature. The amount of selenium retained by soils varied due to the difference in the physicochemical properties of soils, such as soil texture, clay and calcium carbonate content, cation exchange capacity, organic matter content, etc. However, no clear effect of any single property on selenium ion Selenate retention was observed. Rather, it is believed that the overall effect of each soil is the interaction of several properties and their reflection on the total amount that binds the element. Ren *et al.* (2020) stated that a change in temperature leads to a change in everything related to movement and equilibrium, expressed by an increase in kinetic energy that facilitates the access of ions to active sites and an increase in the surface activity of the adsorbent, which leads to an increase in active sites.

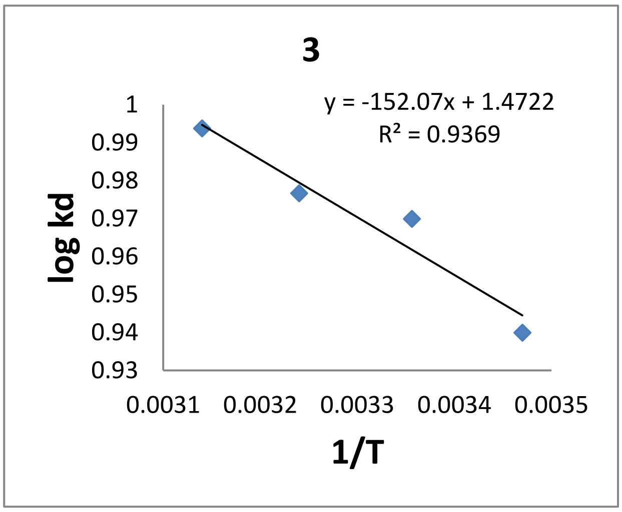
Table 3 : Percentage of selenium removed by different temperatures in the study soils

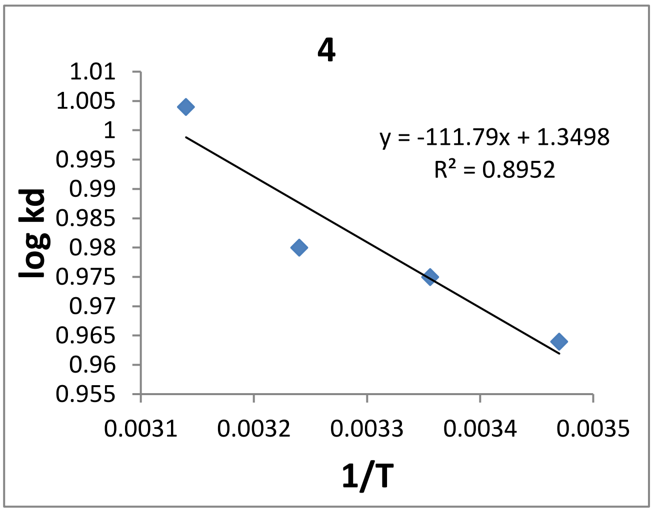
Soil NO.	temperature (°C)			
	15	25	35	45
1	42.66	45.21	45.61	47.36
2	41.44	45.01	45.78	47.36
3	46.91	48.40	48.66	49.65
4	40.18	45.23	47.05	48.26
5	41.84	45.89	46.86	47.51
6	40.27	46.14	46.64	49.66
7	40.97	46.66	46.87	48.01

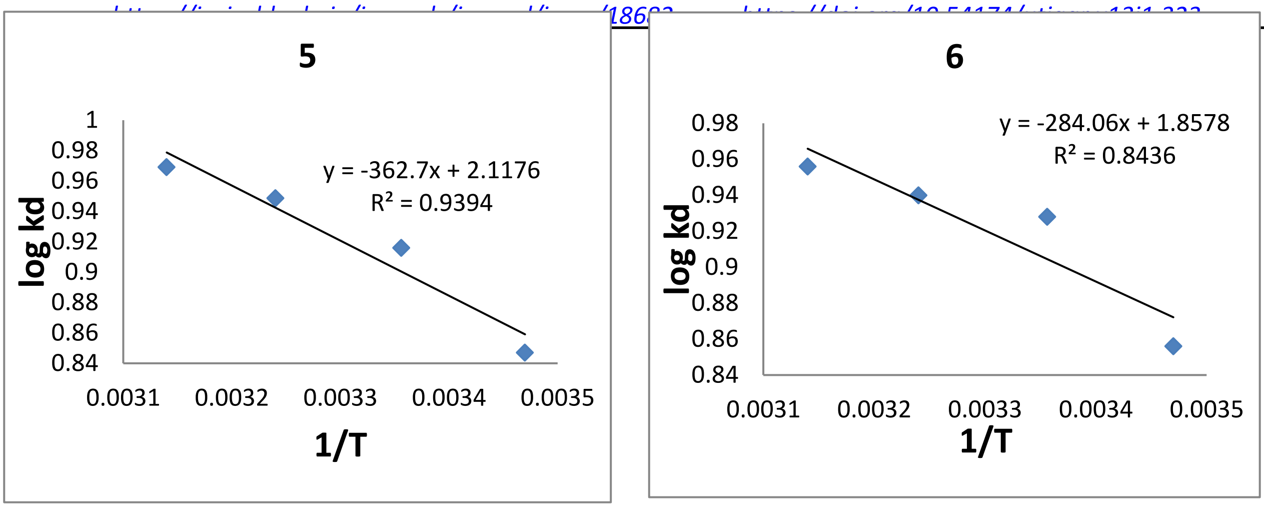
To demonstrate the effect of temperature and calculate thermodynamic parameters, the relationship between the distribution coefficient (Kd) and temperature (1/T) was applied. The results indicated an increase in the distribution coefficient (the increase in the amount of selenium ions adsorbed or retained with increasing temperature), (Fig 1) which may indicate an increase in the strength of the interaction between the elemental ion in solution and the

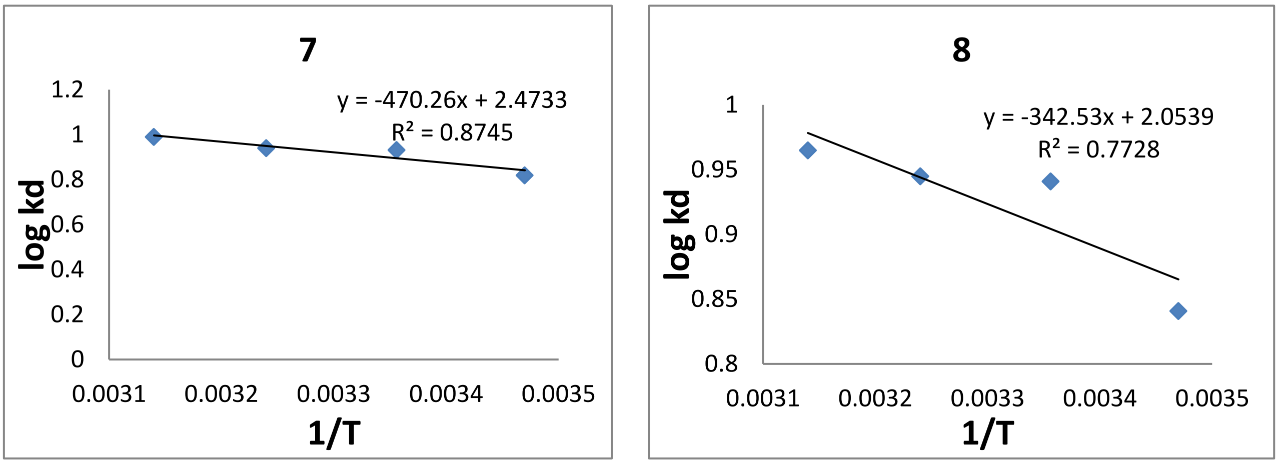












surfaces of soil colloids. The results also revealed a highly correlated linear relationship (regression coefficient R^2) ranging from0.7728 to 0.9394, supporting the accuracy of the thermodynamic concepts (change in standard free energy ΔGº, change in standard enthalpy ΔHº, and change in standard entropy ΔSº) in explaining the thermodynamic behavior of selenium ions with soil colloids. ΔHº was calculated from the slope value, while ΔSº was calculated from the intercept value of the relationship between Log Kd and 1/T. The results indicated that the reaction mechanism may not change with the change in temperature, but the amount of the retained selenium ion is affected by the change in energy supply (Dadanmozed and Hosseinpur 2010)

Figure 1: Linear relationship between Log Kd and 1/T for selenium adsorption on the study soil surfaces .

The results (Table 4) indicated that the enthalpy change values (ΔHº) for the study soils were positive, ranging between (2.13 - 9.00) KJ mol^{-1}, indicating that the reaction is endothermic and favorite (Mohammad Ali, 2023)). This indicates that the selenium ion binding increases quantitatively with increasing temperature, which supports the previous statement. Although there is no reliable measure to use to determine the ΔHº values in distinguishing the behavior of a reaction, whether it is physical or chemical, some researchers have indicated that the ΔHº range, which between 8.4 and 12.6 KJ mol^{-1}, represents ion exchange reactions (Horsfall and Spiff ,2005). Uniu and Ersoz (2006) stated that the heat of reaction, 5-100 Kcal, (20.9-418.4) KJ mol^{-1}, represents the heat of chemical reactions. The results of the current study, which examined ΔH° values, revealed that the interaction is physical (physisorption), meaning that van der Waals forces or weak electrical forces control the binding of selenium ions to the surfaces of soil colloids, interstitial pores, or spaces between these particles. This means there are no strong chemical bonds between selenium and the surface of the particles.

The values of entropy change (ΔS°) ranged between 0.0258 and 0.047 KJ mol^{-1} k^{-1} (Table 4). Positive entropy values indicate randomness among the selenium ions in the solution and their interaction with the surfaces of the soil particles. Increasing values of ΔS° indicate increased ion mobility across the various soil components and within the pore spaces between these components, indicating a favorable interaction (Hassan, 2020). The standard free energy change values ΔG° showed negative values ranging from (-4.63--5.30) KJ mol^{-1} at 15 °C (288 K), (-5.56--5.10) KJ mol^{-1} at 25 °C (298 K), (-5.42--5.81) KJ mol^{-1} at 35 °C (308 K), and (-5.75--6.075) KJ mol^{-1} at 45 °C (318 K). A negative value indicates that the reaction is spontaneous in nature, meaning that the reaction occurs easily and quickly or of the favored type, and the reaction becomes more spontaneous with increasing temperature because the values of ΔG° become more negative with increasing temperature. Okoye and Obi (2012) reported that the standard free energy change values (ΔG°) as high as (-20 KJ mol^{-1}) include electrostatic interaction between adsorption sites and element ions (physical), while the values of ΔG° that are greater than (-40 KJ mol^{-1}) include charge sharing and transfer from the adsorption surface to element ions to form chemical covalent bonds. Since the standard values of ΔG° in the study of the interaction of selenium with soil colloids do not exceed (-6.0 KJ mol^{-1}) in most of them, this indicates that the interaction is of the physical type and that it is the common mechanical type in the adsorption process of selenium

Table 5: Thermodynamic parameters of selenium adsorption on the surfaces of the study soils under different temperatures.

Soil NO.	(KJ ΔH° mol^{-1})	(KJΔS° mol^{-1})	(KJ mol^{-1})ΔG°			
			288K	298K	308K	318K
1	4.561	0.032	-4.777	-5.101	-5.426	-5.759
2	5.638	0.036	-4.743	-5.104	-5.464	-5.824
3	2.911	0.028	-5.204	-5.486	-5.768	-6.049
4	2.139	0.0258	-5.301	-5.559	-5.817	-6.076
5	6.942	0.0400	-4.731	-5.136	-5.541	-5.947
6	5.437	0.035	-4.804	-5.159	-5.515	-5.871
7	9.001	0.047	-4.633	-5.106	-5.579	-6.053

8	6.556	0.039	-4.766	-5.159	-5.552	-5.945

2-3.Kinetics experiment

Table 5 shows the effect of shaking duration on the amount of selenium (SeO_4^{-2}) retained in the soils under study. The results indicate an increase in the adsorbed amount with increasing time in all the soils of the study. The soils differed in the adsorbed amount during the time. This amount ranged between (1735.91-2146.60) µg Se gm^{-1} soil in the soil (no.1), (1879.14-2293.70) µg Se gm^{-1} soil (no.2), (1955.49-2299.76) µg se gm^{-1} soil in the (no.3), (1833.30-2002.35) µg se gm^{-1} soil in (no.4) , (2008.5-2233.56) µg se gm^{-1} soil (no.5), and (2021.73-2203.59) µg se gm^{-1} soil (no.6) and (1595.50-1895.27) µg se gm^{-1} soil in (no.7) and (1722.60-2113.98) µg se gm^{-1} soil in (no.8). The lowest adsorption value was recorded in (soil no.7) at 5 minutes which was 1595.50 µg se gm^{-1} soil while the highest adsorption value was in (soil no.3) at 320 minutes 2299.76 µg se gm^{-1} soil. This is due to the difference in the physicochemical properties of the study soil in terms of availability of adsorption sites, method of binding or retention, nature of the surface, size and number of pores, presence of charged surfaces, etc. It is also noted that the variation in the adsorbed amount between soils is not large, which indicates that many soil properties are somewhat similar. In addition, other different properties may affect the amount of selenium retained, either negatively or positively, such that they overlap with each other, reducing the general variation in the behavior of these soils towards adsorption. Also, the selenium forms available in the solution are in the form of SeO_4^{-2}, and most of the soil colloids and the pH of the solution contribute to the dominance of the negative charge compared to the positive charge. The general characteristic of the association between selenium ions and the solid surface is the physical type, as previously mentioned. It is also clear that the adsorbed quantities in the study soils during the time are not gradual, meaning that rapid adsorption occurs at a certain time, followed by slow adsorption at a later time, and so on with the continuation of the shaking time, which gives the impression that there is a difference in the multiplicity of adsorption sites and a difference in their nature and energies in terms of distribution, size, or charge. This is due to the influence of the physicochemical properties of the soils under study, to some extent, such as the content of clay, calcium carbonate, organic matter, the nature of the soil solution, salinity, concentration of different ions, etc. This is clearly evident when calculating the percentage of the adsorbed quantity of selenium on colloids and between soil particles, as it is clear from Table 6 that the percentage values at their highest value for all soils do not exceed 39% of the added quantity. This may be attributed to the speed of movement of selenium in the form of SeO_4^{-2} in the solution and the migration of these ions towards groundwater (washed), which reduces the importance of their retention on Different soil colloids and between them (Zafeiriou *et al.* 2022 a, b). Zafeiriou *et al.* (2023) also indicated that the selenium form (SeO_4^{-2}) forms weak outer-sphere complexes with soil colloids. This leads to weak (poor) adsorption by the soil, which contributes significantly to the movement of selenium into groundwater. This type of association is weak (non-specific) adsorption and is common in rapid reactions, as direct binding to the surface does not occur, but rather a water membrane separates the two connection. Sharma (2010) also confirmed that selenate (SeO_4^{-2}) is weakly held by soil particles and is readily available for plant uptake, unlike selenite (SeO_3^{-2}), which is strongly adsorbed to the soil exchange site .

Table 5: Adsorbed amount (µg gm^{-1}) of selenium element with time on the surfaces of the study soils

Time (min)	Soil No.							
	1	2	3	4	5	6	7	8
5	1735.91	1879.14	1955.49	1833.3	2008.57	2021.73	1595.80	1722.60
10	1780.60	1956.59	2104.72	1858.00	2053.31	2037.98	1635.10	1724.20
20	1795.58	1977.62	2118.19	1844.30	2061.04	2043.05	1641.00	1783.50
40	1823.70	1990.16	2147.86	1858.30	2124.86	2074.51	1676.60	1798.34
80	2055.51	2153.20	2182.46	1873.90	2138.88	2079.24	1809.10	1960.32
160	2085.09	2277.50	2207.63	1965.70	2216.16	2195.56	1868.30	2010.00
320	2146.60	2293.70	2299.76	2002.35	2233.56	2203.59	1895.27	2113.98

Table 6: Percentage of removed selenium with different time

Soil NO.	time (min)						
	5	10	20	40	80	160	320

1	28.931	29.676	29.926	30.395	34.258	34.752	35.776
2	31.319	32.609	32.960	33.169	35.886	37.958	38.229
3	32.592	35.078	35.303	35.798	36.374	36.794	38.329
4	30.555	30.738	30.966	30.972	31.231	32.762	33.372
5	33.476	34.222	34.350	35.414	35.648	36.936	37.226
6	33.695	33.966	34.051	34.575	34.654	36.593	36.726
7	26.596	27.252	27.350	27.943	30.152	31.138	31.588
8	28.710	28.736	29.725	29.972	32.672	33.500	35.233

In order to study the behavior of selenium adsorption on soil colloids and to demonstrate the rate of the amount of adsorbed material over time, thus contributing to the interpretation the nature of the connection, selenium adsorption data over time were subjected to several kinetic equations, including the Elovich equation, fractional power, zero order, first order, pseudo-first order, second order, pseudo-second order (I, II, III, IV), and the intrapartilcle diffusion equation. The results showed that these experimental mathematical models differed in their description of selenium adsorption data depending on the soil. The accuracy of these equations describing selenium adsorption values on soil colloids was tested using the regression coefficient (R^2) and the percentage standard deviation (MPSD). The Fraction power equation gave the best description of selenium adsorption on the soils no. (1,2,5 and 8) recording the highest R^2 values and the lowest MPSD values (0.9047,2.025), (0.9173,1.680), (0.971,0.500) and (0.9308,1.345) respectively (Table 7). In addition to soil no.(3), although the Elovich equation is superior in the values of R^2 and MPSD (0.8970,1.211), the values of the constants of this equation are unrealistic and do not describe the case of the adsorption rate in an applied manner (Table 7). In addition, the values of R^2 and MPSD of the Fraction Power equation are very close to the above values (0.8884,1.233) and have constants that can accurately and realistically describe the reaction state. Therefore, this equation can also be successful in describing the kinetic reaction of no. (3) soil. The success of the Fraction Power kinetic model indicates that the adsorption surface is energetically heterogeneous (strong or weak), that the adsorption rate varies with time depending on the availability of adsorption sites and their occupancy rate, and that there is more than one mechanism controlling the reaction (diffusion in the pores + surface interaction). The interaction is often of a physical nature (such as Van der Walls forces, etc.). While the zero-order kinetic model successfully described the selenium adsorption reaction over time in the soils no. (4 and 6), recording R^2 and MPSD values of (0.9284,0.664) and (0.8485,0.987), respectively, compared to the other kinetic equations, this zero-order kinetic model means that the reaction rate does not depend on the reactant concentration, meaning that adsorption increases in a straight line with time regardless of the reactant concentration. It is noted that the zero-order kinetic model successfully described the data for two soils with very different properties, indicating that in heavy-textured soils (soil no. 6), there are factors (other than the element concentration in the solution) that can affect the reaction, including the extent of saturation of sites, limited surface area, and limited mass transport (diffusion limitation). In contrast, in light soils (soil no. 4), there is no intense or real competition for sites (meaning that the surface is not fully occupied by binding and there is no intense competition). Adsorption is limited in principle and the interaction is weak (physical), leading to a clear appearance of concentration. In other words, the presence of these overlaps in properties and their reflection in the effect on the adsorption process is what prevented the differences in data values, which made them subject to the same kinetic model. When studying the kinetics of selenium adsorption on (soil no.7) sites, the results showed the superiority of the pseudo-first order equation in describing the reaction rate with values of R^2 and MPSD (0.9771,1.076), respectively. The concept of this kinetic model indicates that the adsorption rate is directly proportional to the difference between the element concentration at equilibrium and the element concentration at time, meaning that adsorption increases when the solution is rich in the element and then gradually decreases with time. The forces controlling the interaction are physical forces with weak bonding to the surface, in addition to the fact that the surface is heterogeneous (gradient in adsorption energy), as adsorption occurs quickly on easily accessible sites without obstruction in the internal structure of the surfaces of soil colloids, and the concentration of the element in the solution is the determining factor for the adsorption rate, not the type or number of sites (Wang and Guo, 2020). The difference in kinetic models in describing the soils under study can be attributed to the fact that these kinetic models are experimental mathematical equations with different hypotheses imposed on the adsorption process and are not subject to purely physical laws, they are not mechanical models.

Table 7: the regression coefficient (R^2), percentage standard deviation MPSD, and constants for the kinetic adsorption models of selenium according to the different study soils.

Soil NO.	Model	R^2	MPSD	Constants
1	Elovich	0.9008	2.133	β = 108.25 µg g^{-1} , α = 11390.08
	Fraction Power	0.9047	2.025	K= 1554.18 µg g^{-1} min^{-1} , v=0.0561
	Zero Order	0.763	3.061	= 1745.6 µg g^{-1},, K= -1.2522 µg g^{-1} min^{-1}q_e
	First Order	0.7512	3.010	= 1799.03 µg g^{-1},, K= -0.0007 µg g^{-1} min^{-1}q_e
	Pseudo-first order	0.9489	60.274	= 407.97 µg g^{-1},, K= 0.0093 µg g^{-1} min^{-1}q_e
	Second order	0.7395	7.398	= 1666.6 µg g^{-1},, K= -3*10^{-7} µg g^{-1} min^{-1}q_e
	Pseudo-second order I	0.9996	11.927	= 2000 µg g^{-1},, K= 0.00014 µg g^{-1} min^{-1}q_e
	Pseudo-second order II	0.59	4.193	= 2000 µg g^{-1},, K= 0.00050 µg g^{-1} min^{-1}q_e
	Pseudo-second order III	0.5654	4.379	= 2022.1 µg g^{-1},, K=0.000477 µg g^{-1} min^{-1}q_e

	Pseudo-second order IV	0.5654	79.189	= 2102.5 µg g^{-1},, K=0.000259 µg g^{-1} min^{-1}q_e
	Intraparticle diffusion	0.8902	60.987	K=28.474 µg g^{-1} min$^{-0.5}$
2	Elovich	0.9105	1.751	β = 105.37 µg g^{-1} , α =84959.04
	Fraction Power	0.9173	1.680	K= 1718.14 µg g^{-1} min^{-1} , v=0.0505
	Zero Order	0.7461	2.630	= 1645.6 µg g^{-1},, K= -0.9477µg g^{-1} min^{-1}q_e
	First Order	0.7379	2.745	= 1959.22 µg g^{-1},, K= -0.0006 µg g^{-1} min^{-1}q_e
	Pseudo-first order	0.9575	60.266	= 412.65 µg g^{-1},, K= 0.0136 µg g^{-1} min^{-1}q_e
	Second order	0.7287	3.829	= 2000.0 µg g^{-1},, K= -3*10^{-7} µg g^{-1} min^{-1}q_e
	Pseudo-second order I	0.9996	10.068	= 2500 µg g^{-1},, K= 0.00011 µg g^{-1} min^{-1}q_e
	Pseudo-second order II	0.6434	10.452	= 2000 µg g^{-1},, K=0.00063 µg g^{-1} min^{-1}q_e
	Pseudo-second order III	0.6115	3.642	= 2181.1 µg g^{-1},, K=0.000476 µg g^{-1} min^{-1}q_e
	Pseudo-second order IV	0.6115	79.172	= 2248.1 µg g^{-1},, K=0.000283 µg g^{-1} min^{-1}q_e
	Intraparticle diffusion	0.8848	61.161	K=27.926 µg g^{-1} min$^{-0.5}$
3	Elovich	0.897	1.211	β = 67.13 µg g^{-1} , α = 28086307356
	Fraction Power	0.8884	1.233	K= 1907.59 µg g^{-1} min^{-1} , v=0.0315
	Zero Order	0.6905	2.107	= 2038.9 µg g^{-1},, K= -0.6035µg g^{-1} min^{-1}q_e
	First Order	0.663	2.227	= 2074.76 µg g^{-1},, K= -0.0004 µg g^{-1} min^{-1}q_e
	Pseudo-first order	0.9366	2.949	= 274.32 µg g^{-1},, K= 0.0078 µg g^{-1} min^{-1}q_e
	Second order	0.6352	3.251	= 2000.0 µg g^{-1},, K=-2*10^{-7} µg g^{-1} min^{-1}q_e
	Pseudo-second order I	0.9996	7.768	= 2500 µg g^{-1},, K= 0.00015 µg g^{-1} min^{-1}q_e
	Pseudo-second order II	0.8758	7.035	= 2500 µg g^{-1},, K=0.00053 µg g^{-1} min^{-1}q_e
	Pseudo-second order III	0.8468	4.277	=2115.4 µg g^{-1},, K=0.000681 µg g^{-1} min^{-1}q_e
	Pseudo-second order IV	0.8468	78.263	= 2239.9 µg g^{-1},, K=0.000545 µg g^{-1} min^{-1}q_e
	Intraparticle diffusion	0.8058	60.659	K=16.830 µg g^{-1} min$^{-0.5}$
4	Elovich	0.8075	1.119	β = 39.46 µg g^{-1} , α = 4.09 *10^{17}

	Fraction Power	0.8126	1.098	K= 1751.28 µg g^{-1} min^{-1} , v=0.0206
	Zero Order	0.9284	0.664	= 2060.5 µg g^{-1},, K= -0.6507µg g^{-1} min^{-1}q_e
	First Order	0.9259	0.729	= 1841.25 µg g^{-1},, K= -0.0003 µg g^{-1} min^{-1}q_e
	Pseudo-first order	0.9753	3.432	= 209.12 µg g^{-1},, K= 0.0099 µg g^{-1} min^{-1}q_e
	Second order	0.9233	6.306	= 2000.0 µg g^{-1},, K= -1*10^{-7} µg g^{-1} min^{-1}q_e
	Pseudo-second order I	0.9997	8.980	= 2000 µg g^{-1},, K= 0.00021 µg g^{-1} min^{-1}q_e
	Pseudo-second order II	0.4193	8.180	= 2000 µg g^{-1},, K=0.00125 µg g^{-1} min^{-1}q_e
	Pseudo-second order III	0.4067	2.980	= 1924.3 µg g^{-1},, K=0.001627 µg g^{-1} min^{-1}q_e
	Pseudo-second order IV	0.4067	79.253	= 1973.1 µg g^{-1},, K=0.000645 µg g^{-1} min^{-1}q_e
	Intraparticle diffusion	0.9377	60.196	K=11.251 µg g^{-1} min$^{-0.5}$
5	Elovich	0.9692	1.089	β = 38.52 µg g^{-1} , α = 3.75*10^{20}
	Fraction Power	0.971	0.500	K= 1922.92 µg g^{-1} min^{-1} , v=0.0262
	Zero Order	0.9226	1.38	= 1840.7 µg g^{-1},, K= -0.5524 µg g^{-1} min^{-1}q_e
	First Order	0.77	1.384	= 2060.29 µg g^{-1},, K= -0.0003 µg g^{-1} min^{-1}q_e
	Pseudo-first order	0.9757	0.639	= 210.73 µg g^{-1},, K= 0.0110 µg g^{-1} min^{-1}q_e
	Second order	0.7602	3.405	= 2000.0 µg g^{-1},, K= -1*10^{-7} µg g^{-1} min^{-1}q_e
	Pseudo-second order I	0.9999	8.666	= 2500 µg g^{-1},, K= 0.00020 µg g^{-1} min^{-}q_e
	Pseudo-second order II	0.7231	5.461	= 2000 µg g^{-1},, K=0.00125 µg g^{-1} min^{-1}q_e
	Pseudo-second order III	0.7052	1.565	= 2176.7 µg g^{-1},, K=0.000931 µg g^{-1} min^{-1}q_e
	Pseudo-second order IV	0.9198	79.129	= 2179.9 µg g^{-1},, K=0.000775 µg g^{-1} min^{-1}q_e
	Intraparticle diffusion	0.7602	60.587	K=14.324 µg g^{-1} min$^{-0.5}$
6	Elovich	0.8481	1.023	β = 46.21 µg g^{-1} , α = 2.56*10^{16}
	Fraction Power	0.8535	1.041	K= 1930.24 µg g^{-1} min^{-1} , v=0.0219
	Zero Order	0.8485	0.987	= 2075.4 µg g^{-1},, K= -0.7687 µg g^{-1} min^{-1}q_e
	First Order	0.8467	0.996	= 2039.17 µg g^{-1},, K= -0.0003 µg g^{-1} min^{-1}q_e

	Pseudo-first order	0.951	2.137	= 221.36 µg g^{-1},, K= 0.0352 µg g^{-1} min^{-1}q$_e$
	Second order	0.8448	2.400	= 2000.0 µg g^{-1},, K= -1*10^{-7} µg g^{-1} min^{-1}q$_e$
	Pseudo-second order I	0.9996	11.418	= 2000 µg g^{-1},, K= 0.00028 µg g^{-1} min^{-1}q$_e$
	Pseudo-second order II	0.5497	4.635	= 2000 µg g^{-1},, K=0.00125 µg g^{-1} min^{-1}q$_e$
	Pseudo-second order III	0.472	8.729	= 2134.9 µg g^{-1},, K=0.001313 µg g^{-1} min^{-1}q$_e$
	Pseudo-second order IV	0.472	79.258	= 2181.0 µg g^{-1},, K=0.000607 µg g^{-1} min^{-1}q$_e$
	Intraparticle diffusion	0.9159	60.401	K=12.708 µg g^{-1} min$^{-0.5}$
7	Elovich	0.9276	1.444	β = 78.98 µg g^{-1} , α = 1050809.04
	Fraction Power	0.9314	1.366	K= 1461.76 µg g^{-1} min^{-1} , v=0.0453
	Zero Order	0.838	2.358	= 1959.5 µg g^{-1},, K= -1.2783 µg g^{-1} min^{-1}q$_e$
	First Order	0.773	2.471	= 1645.34 µg g^{-1},, K= -0.0005 µg g^{-1} min^{-1}q$_e$
	Pseudo-first order	0.9771	1.0767	= 300.36 µg g^{-1},, K= 0.0112 µg g^{-1} min^{-1}q$_e$
	Second order	0.7624	8.667	= 1666.6 µg g^{-1},, K=-3*10^{-7} µg g^{-1} min^{-1}q$_e$
	Pseudo-second order I	0.9998	8.609	= 2000 µg g^{-1},, K=0.00016 µg g^{-1} min^{-1}q$_e$
	Pseudo-second order II	0.6126	6.923	= 1666 µg g^{-1},, K=0.00090 µg g^{-1} min^{-1}q$_e$
	Pseudo-second order III	0.5903	3.358	= 1808.1 µg g^{-1},, K=0.000668 µg g^{-1} min^{-1}q$_e$
	Pseudo-second order IV	0.5903	79.106	= 1861.1 µg g^{-1},, K=0.000383 µg g^{-1} min^{-1}q$_e$
	Intraparticle diffusion	0.9151	60.891	K=20.725 µg g^{-1} min$^{-0.5}$
8	Elovich	0.9244	1.715	β = 99.06 µg g^{-1} , α = 41206.94
	Fraction Power	0.9308	1.345	K= 1540.09 µg g^{-1} min^{-1} , v=0.0523
	Zero Order	0.8666	2.137	= 1799.6 µg g^{-1},, K= -1.3007 µg g^{-1} min^{-1}q$_e$
	First Order	0.8505	2.317	= 1760.58 µg g^{-1},, K= -0.0007 µg g^{-1} min^{-1}q$_e$
	Pseudo-first order	0.9459	3.010	= 439.26 µg g^{-1},, K= 0.0078 µg g^{-1} min^{-1}q$_e$
	Second order	0.834	5.592	= 1666.6 µg g^{-1},, K= -3*10^{-7} µg g^{-1} min^{-1}q$_e$
	Pseudo-second order I	0.9993	13.416	= 2000 µg g^{-1},, K= 0.00011 µg g^{-1} min^{-1}q$_e$

	Pseudo-second order II	0.5575	16.214	= 2000 µg g^{-1},, K=0.00063 µg g^{-1} min^{-1}q_e
	Pseudo-second order III	0.5416	4.214	= 1965.2 µg g^{-1},, K=0.00055 µg g^{-1} min^{-1}q_e
	Pseudo-second order IV	0.5416	79.066	= 2043.1 µg g^{-1},, K=0.000281 µg g^{-1} min^{-1}q_e
	Intraparticle diffusion	0.959	60.545	K=26.698 µg g^{-1} min$^{-0.5}$

Conclusions

The results showed that selenium adsorption on the study soils was endothermic, spontaneous, random, and physically bound, and of the preferred type. The kinetic models differed in their description of the adsorption rate depending on the study soils. The fractional power kinetic model provided the best description for five soil sites, while the zero-order kinetic model successfully described two other soil sites, and the pseudo-first-order model successfully described one soil site. Therefore, it is recommended to use the fractional power equation to study the selenium release rate for most of the study soils.

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