Article

a special issue for the scientific conference held by the Department of Chemistry- College of Education for Girls/University of Kufa and in cooperation with Hilla University College, under the title
(**5'th Postgraduate Students Annual Conference**) **(PSAC2024)**,
which held for Wednesday, **24/4/2024.**

A practical and theoretical study of the pesticide thiamethoxam on activated charcoal derived from Iraqi date seeds and Koura clay as good absorbents

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Abstract:

In this study, activated charcoal extracted from Iraqi date seeds was used to study the effective removal of liquid thiamethoxam pesticide residues. Using Karwa clay to increase the adsorption capacity of thiamethoxam, activated charcoal made from Iraqi date kernel waste was produced using two different processes: chemical catalysis and physical catalysis treated with a phosphoric acid solution (5M). Several elements, including thiamethoxam concentration, mixing duration, contact time, amount of activated charcoal temperature, and pH of the medium, have been studied to influence thiamethoxam removal efficiency. The results showed that the maximum adsorption dose was 0.05 g/L, the dye concentration was 100 mg/L, and the adsorption duration for activated charcoal was 2.5 hours, which is the ideal condition for removal efficiency of 10-63%, while the adsorption duration for activated charcoal was 2.5 hours, which is the ideal condition for removal efficiency. 10-63%. The adsorption time on the Kora clay was 3.5 hours, which is the ideal condition for removal efficiency of 10-74%. Adsorption equilibrium was performed using Freundlich, Temkin, Harkins-Jura, Dupin, Elovitch, and Langmuir, and the results on the activated charcoal surface showed that the Harkins-Jura model with R2 values of 0.987 and the results on the kura clay surface showed that the Langmuir model with R2 values of 0.157 showed agreement. Best with experimental data for adsorption. According to thermodynamic analysis, the pesticide is endothermic, spontaneous, and indicates increased unpredictability at the adsorbent interface. It also indicates the pHZpc of the negatively charged carbon surface at pH = 2.0. Two pseudo-first-order models and two pseudo-second-order models were included in the kinetic analysis. The results indicate that the pseudo-second order model with R2 > 0.9661 on the activated charcoal surface fits the experimental data best. The results also indicate that the pseudo-second order model with R2 > 1 on the Kura clay surface fits the experimental data better. Density function theory, or DFT, was used to simulate thiamethoxam and help us determine the origin of the reaction.

Keywords: Thiamethoxam, Kinetics، Adsorption, pollution، pesticide, DFT and isotherms.

1-Introduction

Water pollution can be defined as causing changes in the nature, quality, and characteristics of water, as it is a basic source for all forms of life on Earth, which makes the water unfit for human use. This may occur as a result of the addition of other or Chemical and bacterial pollutants such as microorganisms, and even thermal or radiation energy. In addition, experts predict that by 2025, fifty percent of the world's population will reside in water-stressed areas [1]. Natural or human-caused negative interference can lead to water contamination. The primary cause of contamination in freshwater sources is thought to be nutrient pollution, which can include phosphates and nitrates from fertilization plants and farms. In addition to the rubbish that people discard, factory waste also adds to pollution.because of their toxicity, pesticides contaminate all aquatic systems and are naturally carcinogenic. Concerns have been raised by the discovery of pesticides in water and the need to find efficient ways to remove them from aqueous solutions and lower their toxicity to a manageable level [2]. When agricultural fertilizers are used carelessly and in excess of what plants need, they pollute water. They break down in water used for irrigation and disposed of in drains, where they accumulate until they eventually find their way into groundwater, which contains high concentrations of phosphate and nitrate compounds. What remains is carried by rainwater to the ground and to nearby streams [3].

Among the various neonicotinoid insecticide members, thiamethoxam (TMX) is widely used in agriculture to control pests leafhoppers, whiteflies, and aphids in various foods Crops[4]. Thiamethoxam is commonly used in seed dressing and spraying on various food crops and vegetables including cotton, maize, citrus, wheat, barley, maize, brinjal and sorghum which are major components of the food web. In addition, these pesticides pass through different ecosystems and enter aerobic and aquatic ecosystems due to their unique properties such as hydrolysis, non-volatile, bioaccumulation and poor degradation [5]. Thiamethoxam is reported to target central nervous system activities by blocking acetylcholine receptors, ultimately leading to the death of exposed insects[6]. Various adverse effects including developmental abnormalities, physiological changes, and reproductive changes due to exposure to thiamethoxam insecticides have been reported in non-target species [7].

Pesticides have been removed from aqueous liquids using a variety of techniques, such as oxidation, photocatalysis, electrochemistry, and adsorption. Alternative physical and chemical process [8]. Biosorption has many benefits, including being abundant, low-cost, simple, effective, and recyclable. Adsorption is an approach that involves complexation, chelation, and ion exchange. The rate of contaminant removal depends on several factors, such as the molecular structure of the contaminant, the type of biosorbent used, pH, temperature, and ionic strength [9].

In aqueous solutions of lignocellulosic industrial wastes, an environmentally friendly method for the disposal of thiamethoxam insecticide has been proposed. Using phosphoric acid from tangerine peels, porous activated carbon (TPAC) is produced. Particle size, adsorption process was evaluated using surface area, Fourier transform infrared and X-ray diffraction. Many variables are taken into account, such as pH, temperature, adsorbent dose, and initial adsorbent amount. With the examination of the properties of batch adsorption through the use of Freundlich and Langmuir isotherms. Exothermic and episodic adsorption was found to have an equilibrium time of 240 min and a theoretical adsorption capacity of 35.7 mg/g. After three cycles, TPAC was recovered and recycled because it is an affordable, high-yield and environmentally acceptable adsorbent for removing a drug called pesticide from aqueous solutions [10]. The palm tree belongs to the cactus family. It is a perennial tree with a thick stem, and the highest recorded height is (28.20) m. It is crowned with large feathery leaves (fronds), and its fruits are dates (colored and usually yellow), and dates, the last of which is dates [11]. The date fruit contains a nucleus called a seed. It is defined as a solid body, rectangular in shape, and pointed at both ends. It is located in the center of the fruit. Its dimensions are 12-20 mm in length, 6-15 mm in width, and 0.5-4 grams in weight. Typically, the duration of seed presentation is tripled [10]. There is no previous study that addressed the development of activated carbon using date seeds.

Koura clay is the material used in making bricks (koura). The primary components of the mineral compounds found in clay vary depending on the quarry and the geological composition of the soil. These differences affect the types of clay bricks that can be produced and the quantity of each component. It may be necessary to combine two different types of soil to produce a particular type of clay brick with a particular set of properties. Understanding the composition of raw materials is essential to understanding the properties of clay bricks [11].

The primary goal of this study is to purify water from pollutants. In the present study, porous activated carbon made from Iraqi date pit residue and kura clay was added as a biosorbent to remove thiamethoxam pesticides from the aqueous media. These agricultural wastes were chemically activated using basic NaOH and an acidic solution of HNO_3. This study used batch adsorption to test different variables, such as contact length, mass, pH, and starting thiamethoxam concentration. The removal capacity is verified by comparing the results of thermodynamic, kinetic and isothermal adsorption.

2- Methodology

2-1 Tools and chemicals

The materials used in this research, including thiamethoxam (≥94%), hydrogen nitrate (16%), sodium hydroxide (98%), phosphoric acid (35%), and Sodium nitrate $NaNO_3$ (98%), were all of excellent analytical quality (Table 1) : Chemical properties of the thiamethoxam used .

2-2 prepare the adsorbent surfaces

2-2-1Koura Clay surface

Koura Clay was ground and washed with distilled water several times to get rid of dust, salts and suspended impurities, and Next, as indicated in the following figure Koura Clay, the particles were filtrated, dried out, and the resulting clay was collected, ground once more, and filtered through a permeable sieve (200 µm). The results of chemical examination of Iraqi date seeds turned into Koura clay and carbonated charcoal are listed in Figure 1، Table 2.

Figure 1

Table 1 : Chemical analysis of koura clay.

Koura Clay		activated carbon derivate from Iraqi Date Seeds	
Constituent	(Wt%)	Constituent	(Wt%)
SiO_2	39.71	C	45.74
CaO	18.32	N	4.74
Al_2O_3	9.624	O	41.25
Fe_2O_3	6.905	P	8.26
MgO	5.063		
K_2O	1.343		
TiO_2	0.929		
Na_2O	1.357		

2-2-2 Iraqi Date Seeds (IDC) surface

Iraqi Date Seeds (IDC) are collected from the Iraq city dried (IDC) in the open air for 48 hours at 80 °C in an oven after being water-rinsed; the material is subsequently crushed to create a fine, nutty powder. The (IDC) powder is physically activated with carbonation in an oven at 500 °C for two hours, and chemically activated with the addition of phosphoric acid at a 5 ppm (1:1) 24 h . The powder is then dried, washed with hot water, and sifted to size through 600 µm[12]. As shown in Table 2.

Table 2: Chemical analysis of Iraqi date seeds that turn into carbonated charcoal.

2-2-3Evaluation of thiamethoxam removal efficiency in aqueous media

The batch method was used to evaluate the effectiveness of an activated charcoal derivative in removing thamethoxam from Iraqi date pits. Several important experimental parameters were studied, including the pH of the solution under study (2-10), the amount of labeled drug (10-100 mg/L) at an original concentration of 500 mg/L, and the amount of activated charcoal. (0.05 - 0.5 g) made from Iraqi date pits, and the reaction time is (0.5 - 3.5 hours). 20 ml of 100 mg per liter of drug called solutions and 0.05 g of activated charcoal were collected in a conical flask to test the effect of pH, temperature, contact duration and dose of activated charcoal on thiamethoxam. After continuous stirring at a rate of 200 rpm, the mixture was centrifuged. Next, the amount of thiamethoxam still present in the solution was measured using UV-visible spectrophotometry at a wavelength of 249 nm, its absorption maximum. The adsorption capacity of thiamethoxam (Qe, mg/g) was calculated using[13].

$$Qe=((Co-Ce)V)/m \qquad \text{………………. (1)}$$

Where m (mg) is the amount of activated carbon, V (L) is the volume of thiamethoxam solution, and C_0 (mg/L) and Ce (mg/L) indicate the original as well as equilibrium thiamethoxam concentrations, respectively.

3- Results and Discussion

3-1 The effect of contact time

This experiment was conducted to determine when the incorporated thiamethoxam would react most effectively with the outer layer of activated carbon made from existing Iraqi seeds. The pesticide has a neutral life of 2 hours, based on the results, during which time its absorption capacity increases in proportion to the contact time until saturation occurs. The relationship between time (h) and the amount of activated charcoal (mg/g) obtained from Iraqi date pit powder used as an adsorbent is shown in Figure (3,4) . This relationship is positive, which means that increasing any one of the variables will increase the other. For initial thiamethoxam levels of 100 mg/L, thiamethoxam absorption was measured at a given contact time with a different reaction time at (0.5-3.5 h). This is likely because there was initially more adsorption surface area available for adsorption of contaminants. At initial concentrations of 100 mg/L, shaking for approximately 2 hours was required to achieve the majority of maximum contaminant removal. The adsorption of pollutants increases with increasing contact time and remains constant after 30 min after reaching equilibrium for different starting concentrations [12]. The high initial absorption rate is due to the empty holes on the surface. However, the rate of adsorption decreases steadily once these gaps are filled with chemical ions, and ultimately depends on the transfer of electrons from the solution with water to the adsorbent surface .

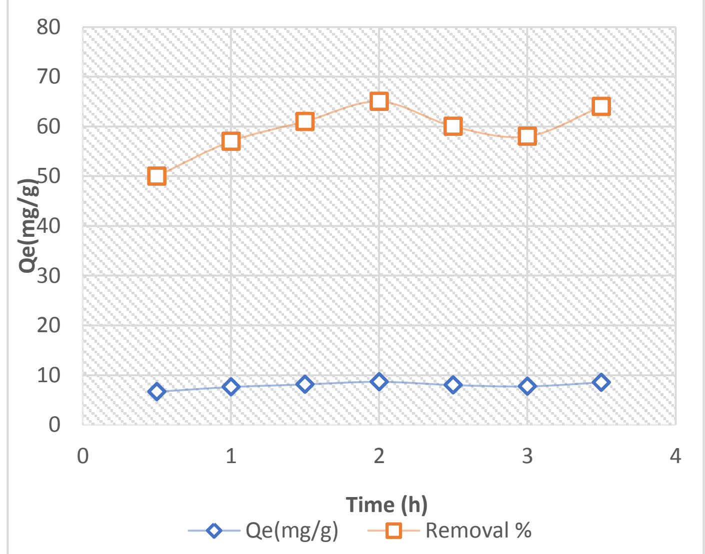

Figure 3 : Impact of contact time on the surface of effervescent charcoal made from Iraqi dates seeds at 318 k and pH = 7 for the adsorption of 20 mg/L of thiamethoxam .

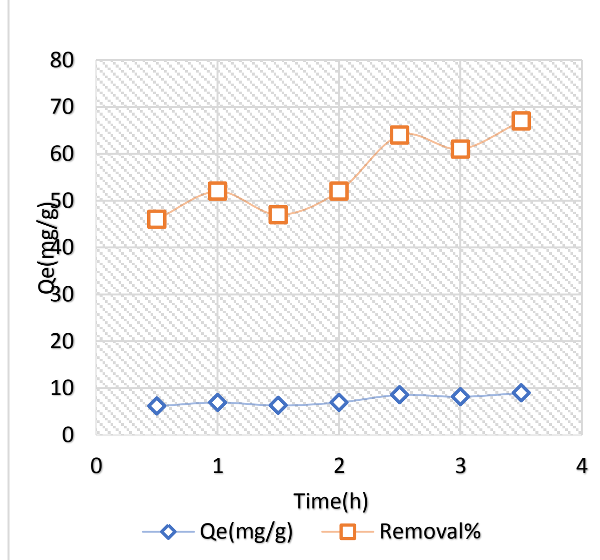

Figure 4 : Impact of contact time on Koura Clay surface adsorption of 20 mg/L of thiamethoxam at 318 k and pH = 7

3-2 The effect of Surface Weight on adsorption thiamethoxam

This effect was measured by applying different weights to the surfaces of activated charcoal made from Iraqi date pits, ranging from 0.05 to 0.5 grams. It was revealed that the surfaces used had better weights, which were 0.25 grams. This is because at these weights, the adsorption of thiamethoxam does not affect the increase in the number of adsorbed surfaces because all operational sites of the adsorption surface have reached the saturation limit (saturation limit) [13].The relationship between the external weight of adsorbent and the amount of adsorption (mg/g) for (318 K) and acid functional pH = 7 is shown in Figure 5. As the weight of the adsorbent increases, the removal of thiamethoxam decreases because the active sites become saturated with time[14]. The figure shows that the amount of adsorption decreases as the surface weight increases.

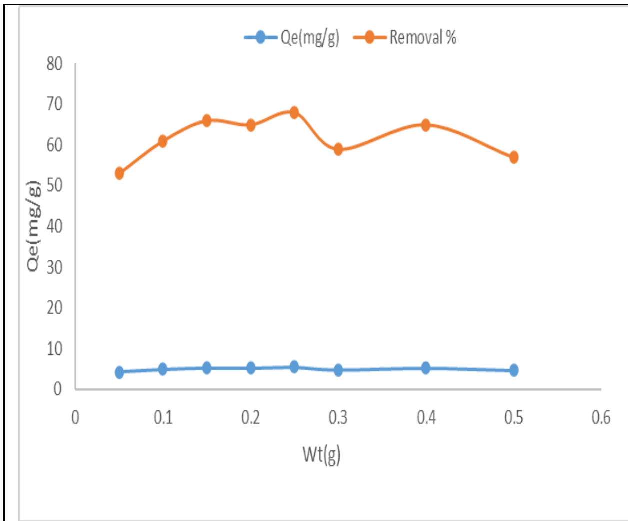

Figure 5 : shows how surface weight affects the amount of pesticide that can be adsorbed at a temperature of 318 k on carbonated charcoal made from Iraqi date seeds, when the weights of the charcoal vary. The acidic function is set at pH = 7.

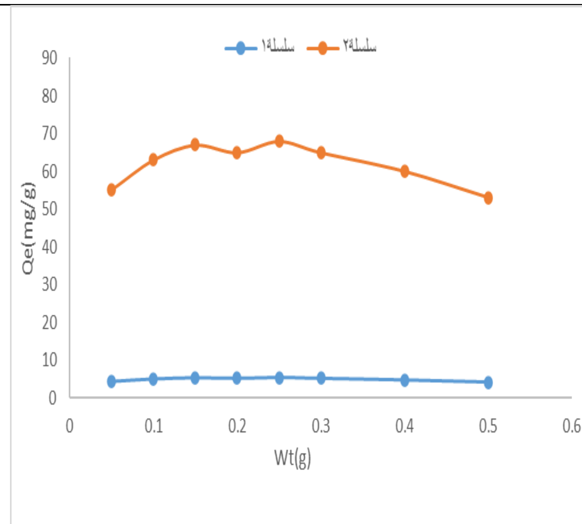

Figure 6 : Surface weight's impact on the adsorption of 15 mg/L of thiamethoxam pesticide at varying weights at Koura Clay's (318 k) temperature and acidic function pH = 7.

3-3 Temperature Effect

The efficiency of the adsorption process on the surface of activated charcoal depends greatly on temperature. These tests were performed at different conditions (318, 328, 338, and 348 K) to observe the extent to which this variable affects the ability of the thiamethoxam adsorption process to the surface. Figures (7) showed the extent of the effect of temperature on the adsorption of thiamethoxam, and the results showed that the adsorption of thiamethoxam increases with increasing temperature. This may be due to increased pore size or surface activation at high temperatures, as adsorption is an endothermic process [15].

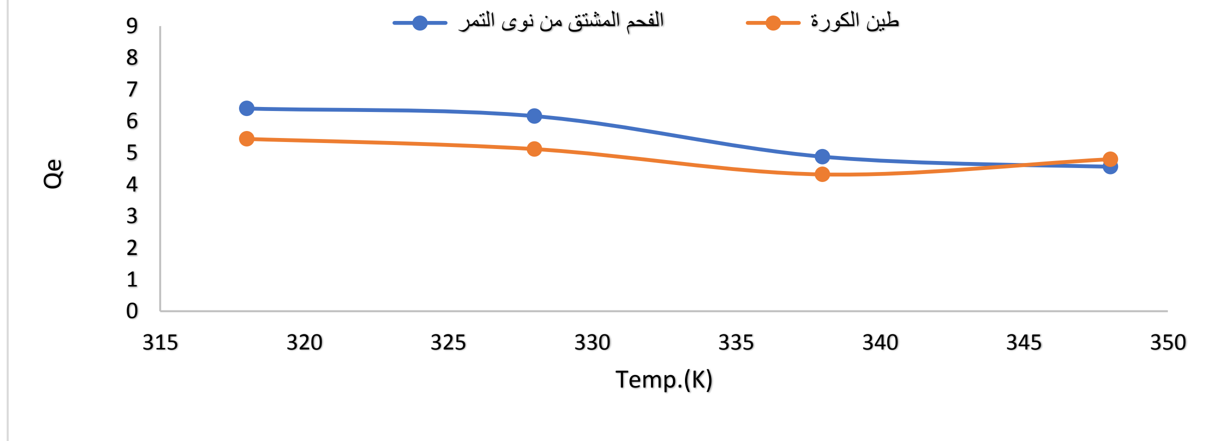

Figure 7 : The impact of temperature on the adsorption of 20 mg/L of thiamethoxam pesticide at varying weights, at 318 k temperature and pH = 7 acidic functions

3-4 Thermodynamic Parameters

The following formulas were used to calculate the enthalpy (ΔH), entropy (ΔS), and thermodynamic parameters [14]:

$\ln Keq = \Delta S0/R - \Delta H0/RT$ ……………… (1)

where T is the temperature in degrees Celsius (Kelvin), R is the universal constant for gases (8.314.10-3 kJ/mol. K-1), K is the constant of the Vant Hoff equation, and ln Xeq is a natural logarithm for the largest amount adsorbed (mg/g).

$\Delta G° = - RT \ln K$ …………………… (2)

$\Delta S° = \Delta H - \Delta G° / T$ ………………… (3)

l Kc against 1/T's Van't Hoff plot's slope and slope were used to calculate ΔH◦ and ΔS◦. (Figure 7, Table 2). Since an increase in 1 / T causes a decrease in Ln Keq, the relationship between the two quantities (1 / T and Ln Keq) is negative. The findings demonstrated that a positive value for ΔH◦ indicated the endothermic character of the adsorption, and a negative value for ΔG indicated a spontaneous reaction [16], as shown in Figure (7) and Table 2.

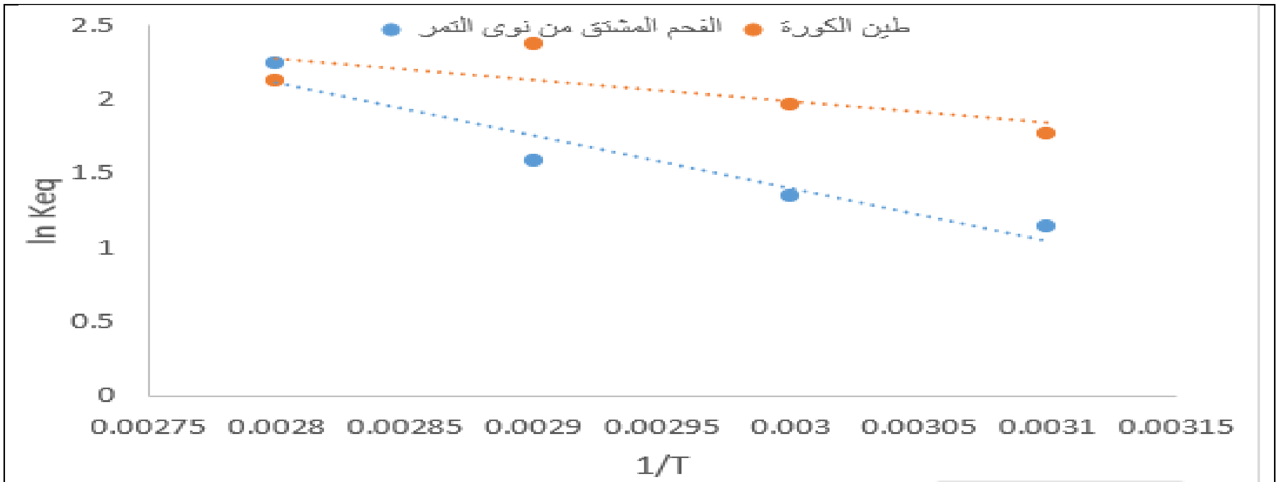

Figure 8 : shows how the equilibrium constants at 318 k C° with an acidic function with pH = 7 are related to temperature inversion.

Table 3 : Thermodynamic function values for the pesticide Thiamethoxam's adsorption on various surfaces

Values of thermodynamic	Activated charcoal	Koura clay
ΔG KJ.mol-1	-8.8460	-9.8166
ΔH KJ.mol-1	1.682	2.884
ΔS J.mol-1	27.823	30.878

3-5 Adsorption Equilibrium and Adsorption Isotherms Models

The slope as well as the intercept of the Ce/qe plot are used, respectively, to calculate the Langmuir qmax and KL (L/mg) variables, corresponding to Ce and qe values that are close to the tested values. Moreover, KL values increased with increasing temperature over time, indicating that adsorption became more effective[14]. Using the following formula, find the Freundlich coefficients Kf and n based on the connection of ln Qe versus lnCe (7,8)[14]: They are given in Table 3 and Figure 8,9

$$\frac{Ce}{Qe} = \frac{1}{Kl.qm} + \frac{Ce}{qm} \qquad \text{……………………………… (4)}$$

$$logQe = logKf + \frac{1}{n} logCe \qquad \text{… … … … . … … … . (5)}$$

$$ln\frac{Qe}{Ce} = ln\ K*Qm - \frac{1}{Qm.Qe} \qquad \text{……………………………..(6)}$$

$$\frac{1}{Qe2} = \frac{B}{A} - \frac{1}{A\,.log\,Ce} \quad ....(7)$$

Qe=B ln KT +B ln Ce

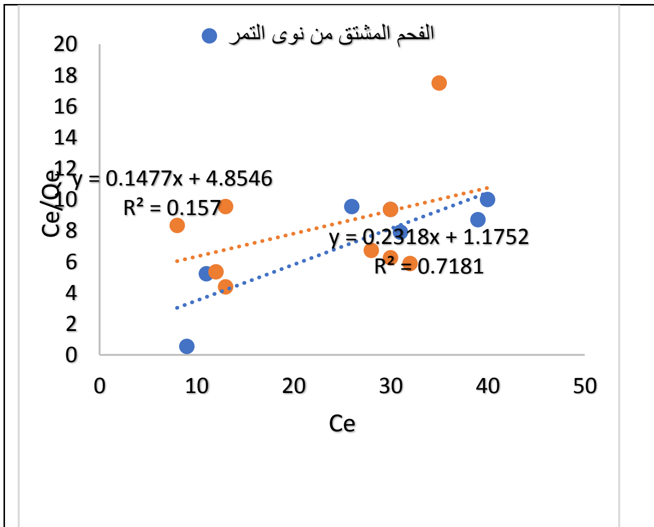

Figure 9 : The isotherm of Langmuir at 318 K and pH 7 thiamethoxam adsorption of 20 mg/L.

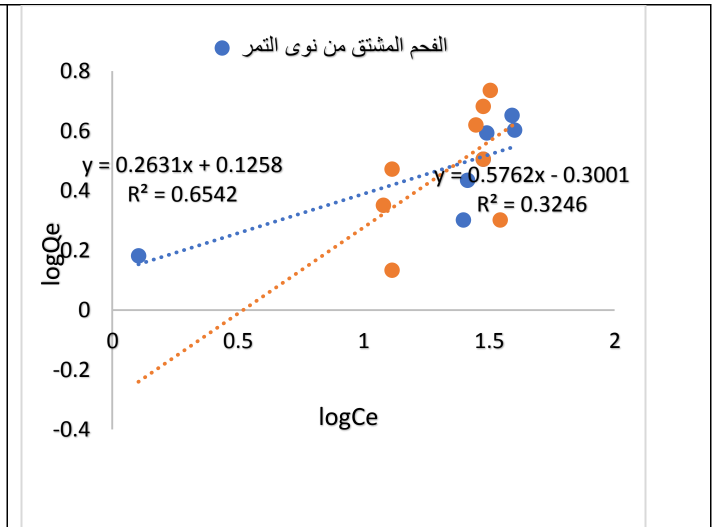

Figure 10 : Freundlich isotherm at 318 k for adsorption of 20 mg/L of thiamethoxam at PH =7

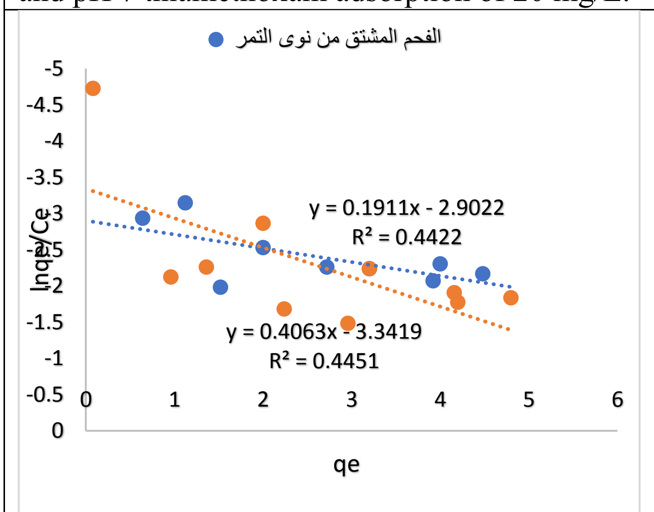

Figure 11 : Elovich equilibrium at 318 k for thiamethoxam adsorption at 20 mg/L at pH (7)

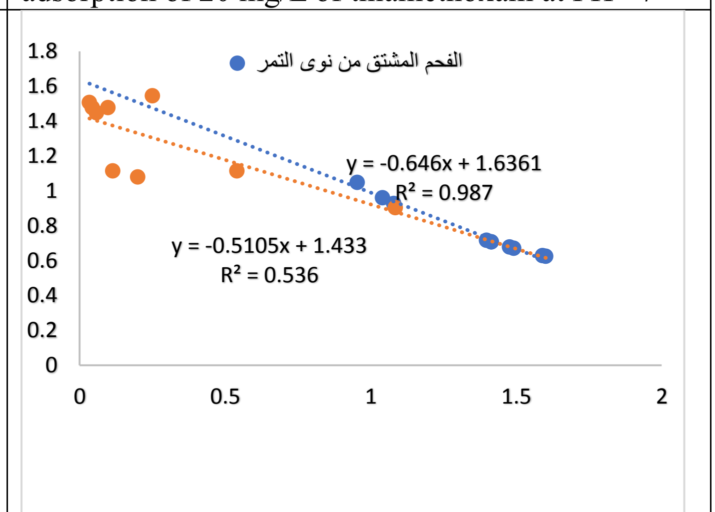

Figure 12 : Harkin-Jura isotherms for thiamethoxam adsorption at pH 7 at 318 k

Kinetic of Adsorption

The fictitious first-order equation was used to explain the kinetics of adsorption for the liquid-solid structure during this investigation [17]***:***

$$ln(q_e - q_t) = ln\,q_e - (K_1 - K_{-1})t \quad .... \quad (9)$$

In this example, qt is the amount of adsorbent material present at different times, K1 is the constant frontal contact velocity (min-1), and K-1 is the constant reverse interaction speed (min-1). Drawing ln(qe-qt) vs. t results in a straight line whose cross has a y-axis equal to lnqe and a slope equal to (K1+K-1). Using the following equation, define pseudo-second order [18]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \qquad \text{………………..} (10)$$

Where K2 is the constant of sorption velocity of a pseudo-second order (g.mg -1.min -1), and the following equations are used to obtain K2, qe from the drawing of t/qt vs. t:

$$K2 = \frac{Slop^2}{intercept} \qquad \text{……………..} (11)$$

$$qe = \frac{1}{slope} \qquad \text{………………} (12)$$

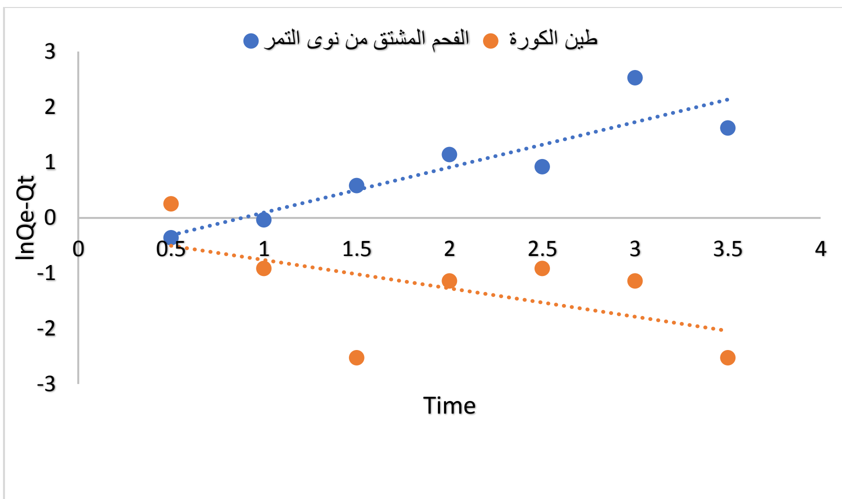

Figure 13 : First order fr adsorption of 20 mg/L of thiamethoxam at pH (7)

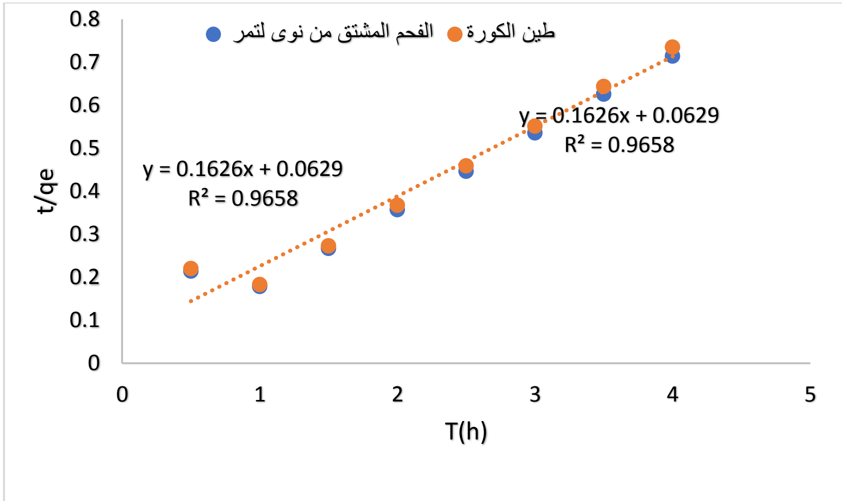

Figure 14 : second order for adsorption of 20 mg/L of thiamethoxam at pH (7)

Conclusions:

The results that obtained from experimental work could be drawn down as following:

●The results showed that the general behavior of the pesticide adsorption process follows the multilayer Freundlich isotherm. The values of the thermodynamic functions (Free energy ΔG, enthalpy ΔH, entropy ΔS) were also calculated based on the calculation of the values of the equilibrium constant Keq.

●The results showed that the adsorption process through the positive enthalpy ΔH value was (Endothermic), and positive values for entropy mean the randomness of the system due to an increase temperature.

References:

[1] A. Boretti and L. Rosa,[2019], “Reassessing the projections of the world water development report,” *NPJ Clean Water*, vol. 2, no. 1, p. 15.

[2] T. Ahmad, M. Rafatullah, A. Ghazali, O. Sulaiman, R. Hashim, and A. Ahmad,[2010] “Removal of pesticides from water and wastewater by different adsorbents: a review,” *J. Environ. Sci. Heal. Part C*, vol. 28, no. 4, pp. 231–271.

[3] N. Akhtar, M. I. Syakir Ishak, S. A. Bhawani, and K. Umar,[2021], “Various natural and anthropogenic factors responsible for water quality degradation: A review,” *Water*, vol. 13, no. 19, p. 2660.

[4] S. T. Gul *et al.*,[2017] , “Effect of sub lethal doses of thiamethoxam (a pesticide) on hemato-biochemical values in cockerels,” *Pak. Vet. J.*, vol. 37, no. 2, pp. 135–138.

[5] C. A. Morrissey *et al.*, [2015],“Neonicotinoid contamination of global surface waters and associated risk to aquatic invertebrates: a review,” *Environ. Int.*, vol. 74, pp. 291–303.

[6] S. E. M. Shalaby, A. R. H. Farrag, and G. S. M. El-Saed,[2010], “Toxicological potential of thiamethoxam insecticide on albino rats and its residues in some organs,” *JASMR*, vol. 5, no. 2, pp. 165–172.

[7] S. H. Yan, J. H. Wang, L. S. Zhu, A. M. Chen, and J. Wang,[2016], “Thiamethoxam induces oxidative stress and antioxidant response in zebrafish (D anio R erio) livers,” *Environ. Toxicol.*, vol. 31, no. 12, pp. 2006–2015.

[8] R. Rashid, I. Shafiq, P. Akhter, M. J. Iqbal, and M. Hussain,[2021] “A state-of-the-art review on wastewater treatment techniques: the effectiveness of adsorption method,” *Environ. Sci. Pollut. Res.*, vol. 28, pp. 9050–9066.

[9] M. Hassan, R. Naidu, J. Du, Y. Liu, and F. Qi,[2020], “Critical review of magnetic biosorbents: Their preparation, application, and regeneration for wastewater treatment,” *Sci. Total Environ.*, vol. 702, p. 134893.

[10] الفهداوي .ع .ز.,”[2019], تأملات في النخلة وثمارها من منظور قرآني“ J. Lit. *Ink*, vol. 1, no. 16.

[11] U. Konbr, W. Freewan, and R. Alshuk,[2016], “The Use of Mud Material in Desert Cities’ Construction as an Approach to Sustainability: Ghadames as a case study,",” in *Tanta University, the third international environmental forum*, pp. 1–13.

[12] J.-P. Simonin,[2016] “On the comparison of pseudo-first order and pseudo-second order rate laws in the modeling of adsorption kinetics,” *Chem. Eng. J.*, vol. 300, pp. 254–263.

[13] S. Suresh, R. W. Sugumar, and T. Maiyalagan,[2011], “Adsorption of acid red 18 from aqueous solution onto activated carbon prepared from murraya koenigii (curry tree) seeds,” *Asian J. Chem.*, vol. 23, no. 1, pp. 219–224.

[14] B. N. A. L. H. Khadim,[2022], “Study-Thermodynamic Adsorption of Bismarck Brown Y on Different Adsorbent Surfaces,” *NeuroQuantology*, vol. 20, no. 5, p. 672.

[15] E. S. Jawad and L. H. Khadim,[2022], “Adsorption of Safranin O and Bismarck Brawn Y Dyes on the Activated Charcoal Extracted from Iraqi Date Cores,” *NeuroQuantology*, vol. 20, no. 8, p. 1836.

[16] J. Fu *et al.*, [2015],“Adsorption of methylene blue by a high-efficiency adsorbent (polydopamine microspheres): kinetics, isotherm, thermodynamics and mechanism analysis,” *Chem. Eng. J.*, vol. 259, pp. 53–61.

[17] K. Shukla, A. Verma, L. Verma, S. Rawat, and J. Singh,[2020], “A Novel Approach to Utilize Used Disposable Paper Cups for the Development of Adsorbent and its Application for the Malachite Green and Rhodamine-B Dyes Removal from Aqueous Solutions,” *Nat. Environ. Pollut. Technol.*, vol. 19, no. 1, pp. 57–70.

[18] G. Hassani, M. Molaei, A. Jamshidi, and A. Raygan,[2023], “Removal of 17β-estradiol (E2) from Aqueous Solutions by Adsorption Using Oak Jaft and Tea Waste, Isotherm Investigation, and Adsorption Kinetics,” *Pakistan J. Anal. Environ. Chem.*, vol. 24, no. 1, pp. 13–30.