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Retraction

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IOP Publishing respectfully requests that readers consider all work within this volume potentially unreliable, as the volume has not been through a credible peer review process.

IOP Publishing regrets that our usual quality checks did not identify these issues before publication, and have since put additional measures in place to try to prevent these issues from reoccurring. IOP Publishing wishes to credit anonymous whistleblowers and the Problematic Paper Screener [1] for bringing some of the above issues to our attention, prompting us to investigate further.

[1] Cabanac G, Labbé C and Magazinov A 2021 arXiv:2107.06751v1

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Adsorption of the Toxin Pesticide (Thiophanate - Methyl) from its Aqueous solution on the Surface of Activated Olive Seed

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Abstract. The activated charcoal of olive seeds were used in this study to adsorb the toxin pesticide (Thiophanate-Methyl) from its aqueous solutions. The effect of the parameters such as initial concentration, contact time and temperature have been investigated. A thermodynamic analysis shows that the Thiophanate-Methyl removal by the olive seed's activated charcoal was an exothermic and spontaneous process. The Langmuir and Freundlich models describe the adsorption isotherms, especially Langmuir model according to correlation coefficients. The results show that removing Thiophanate-Methyl by activated charcoal of olive seed from aqueous solution was very effective and has great potential applications in environmental protection.

Keywords: toxin pesticide, olive seeds activated charcoal, Adsorption, Thermodynamic

1. Introduction

Agricultural pesticides of various varieties have an active role in increasing agricultural production globally but using these pesticides causes their accumulation in the food chain [1], water [2] and soil[3] , and down to groundwater. Therefore, environmentally friendly solutions have been found for the treatment and removal of agricultural pesticides in different waysincludingphoto-catalytic fragmentationcatalysis [4], solid-phase extraction [5] and adsorption [6].As a result of the high efficiency of adsorption technology [7] and its low cost in removing pollutants [8] from water solutions,activated olive nuclei were used as an adsorption surface for toxin pesticide (Thiophanate-Methyl). This pesticide is a therapeutic fungicide that eliminates a wide range of fungal diseases that affect fruit trees, vegetables and ornamental plants. It is also poisonous for fish. This study was carried out to remove this pesticide or reduce its toxicity to preserve fish wealth by adsorbing it on the surface of activated olive seeds [9, 10].

2. Materials

The toxin pesticide was used by Aresta Life Sciences/France and olive seeds

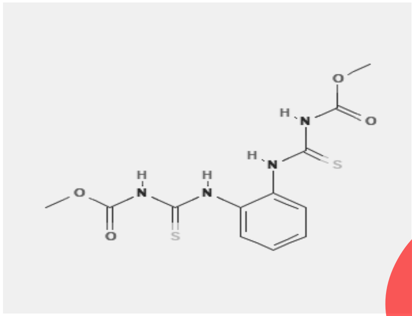

Figure 1. The structural formula of Thiophanate-Methyl

Table 1. Physico-chemical characteristics of the Thiophanate-Methyl

Parameters	Values
Molecular Weight	342.4g mol^{-1}
Molecular formula	$C_{12}H_{14}N_4O_4S_2$
Synonym	NF-44
Class	Dimethyl ester
λ_{max}	263nm

3. Procedure

3.1 Preparation of olive seeds activated charcoal

The collected olive seeds were cleaned dried and placed in a closed crucible in a muffle oven Figure1, which its temperature was raised to 650 C^{o}and kept there for 10 minutes. The resultant charcoal was left to cool and transferred to a mill to create affine powder of activated charcoal of olive seeds.

3.2. The maximum wavelength (λ_{max})(Table1),of the toxin pesticide was determined using a UV-visible device and the maximum wavelength (263nm) was as in Figure 2. The calibration curve was determined by preparing six consecutive concentrations within the range (5-30 ppm) of the study's used solution.The absorption of these concentrations was measured at the maximum wavelength (λ_{max}). After that, the curve which is absorption versus concentration was drawn according to Beer-lambert law (3).

The experiment was carried out by taking a temperature of 0.5 gm of olive seeds and placing them in contact with different pesticide concentrations within the range (3-30 ppm) as shown in figure 3.These samples were subjected to a shaking process using a temperature controlled vibrator at a temperature of 298k. The samples were then filtered at different times (3 - 24 min) to reach the equilibrium state. The temperature effect was then studied within the range (298 - 318 k) and it was found that the best temperature of 298k was studied at pH = 7.

To find adsorption isotherm, ten solutions of the toxin pesticidewere prepared with a concentration of (3-30 ppm) ,then 25ml of them were taken and placed in contact with 0.5gm of olive seeds. The samples were placed in a water bath with a controlled temperature shaker for half an hour at a temperature of 298K, thenthe material was left tostagnate. After that, the clear solution was taken and placed in test tubes placed in the centrifuge for half an hourand the absorption of the solutions was measured using a UV-visible spectrophotometer. The amount of adsorbent material was calculated according to the following equation 1.

$$Qe=V(Co-Ce)/m \qquad (1)$$

Where Co and Ce are the initial solution concentration (mg/L) and equilibrium concentration (mg/L), respectively;V is the volume of the solution; and) m)is the weight of the blends(g).

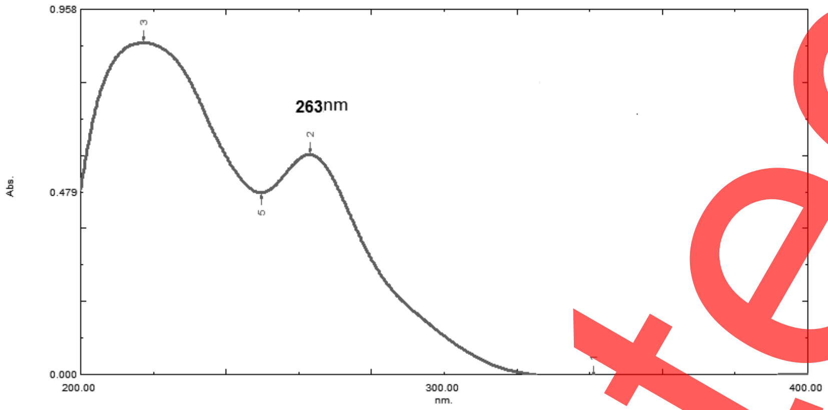

Figure 2. The spectrumof the toxin pesticide versus reagent blank.

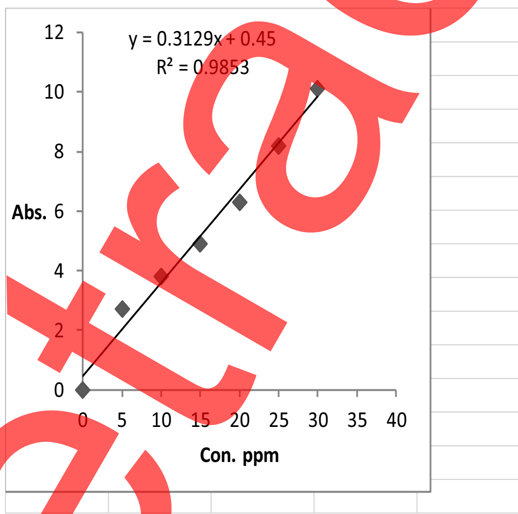

Figure3. Calibration curve of the toxin pesticide (5-30)ppm

4. Results and Discussion

4.1. Effect of concentration and contact time:

Figure 4 shows that the amount of adsorbent material increases with increasing concentration of pesticide within the range (3-30 ppm)where it was found that the best concentration at which the highest amount of adsorption is 30 ppm. Figure (5) shows that the best time at which the highest amount of adsorption is 15min and the reason for increasing the amount of adsorption within a short period to the large number of adsorption sites that are not occupied [11]. At time 18min and above, the stability can be observed at equilibrium time and this is due to the absence of unoccupied adsorption sites [12].

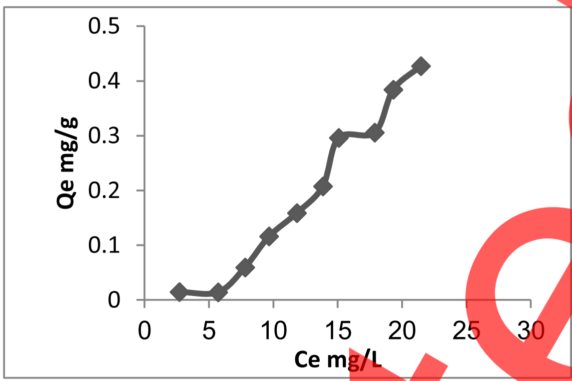

Figure 4. Effect of the concentration of adsorption of the pesticide on the surface of olive seedsactivated charcoal

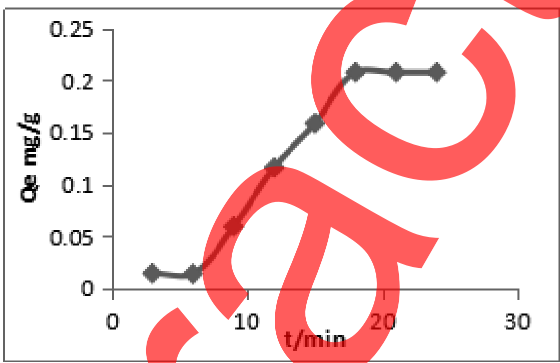

Figure 5. Effect of the equilibrium time of adsorption of the pesticide on the surface of olive seedsactivated charcoal

4.2. Temperature effect:

During this study, the effect of temperature on the adsorbed toxin pesticideon the surface of activated olive seedwas studied. The resultsin figure(6) shows that the adsorption of the pesticide decreases by increasing the temperature and this matches with the thermodynamic study and found that the best temperature is 298k [13].

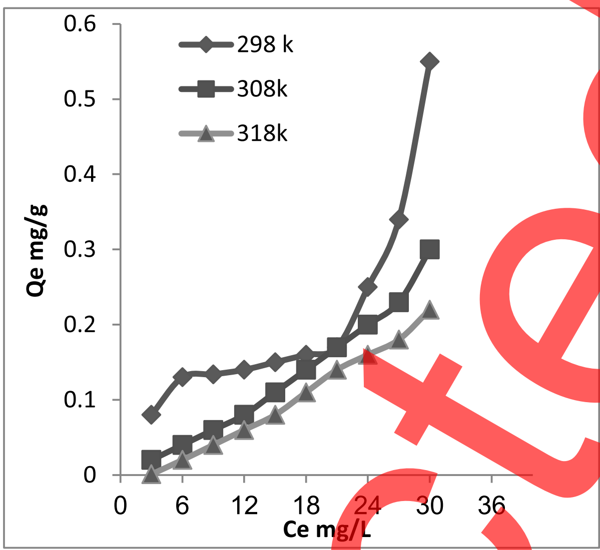

Figure 6. Temperature adsorptionoftoxin pesticideon thesurface of olive seedsactivated charcoal in the temperature range (298-318) K

4.3. Isotherm Adsorption:

The amount of adsorption corresponding to each of the values of equilibrium concentrations was calculated Figure(7) to give the general form of adsorption isotherms and it turned out to be S2 and S3 according to Gilesclassification.It is noted from these isotherms that adsorption increases by increasing the concentration of equilibrium and this shows that adsorption follows Freundlichand Langmuirmodels. These models are used to describe the interference behavior between the adsorbent and the adsorption surface. The Freundlichmodelassumes that the adsorption sites are not equal in their energy, allowing for multi-layer adsorption. Freundlich equation 2 can be represented as follows:

$$\log Qe = \log KF + 1/n \log Ce \quad (2)$$

By drawing $\log Q_e$ as inFigure (8) we get a straight line itsslope $\frac{1}{n}$ it is a measure of adsorption intensity andan intersection $\log K_F$ Which is a measure of adsorption capacity [14]

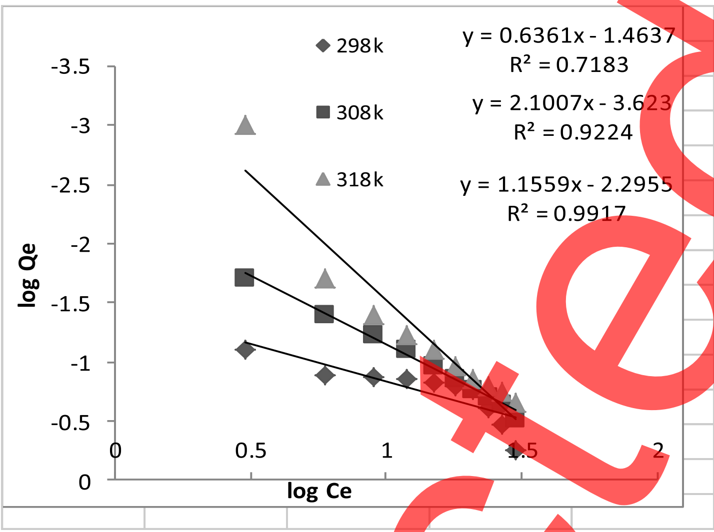

Figure 7. Frandlich adsorption isotherm fortoxin pesticide on the surface of olive seedsactivated charcoal at 298-318K and pH=7

Langmuir's model is a simplified theoretical expression for adsorption of one layer on a surface containing a specific number of adsorption sites with similar energies with no movement of the absorbent at the surface level. Langmuir equation 3 can be represented as follows:
Ce/Q = 1/ab +(1/a)Ce(3)

By drawing $\frac{C_e}{Q_e}$ opposite C_e as in figure 8 we get a straight line itsslope **1/a**andan intersection its amount 1/aband from the slope and intersection values, the Langmuir constants (a,b)can be calculated [15].

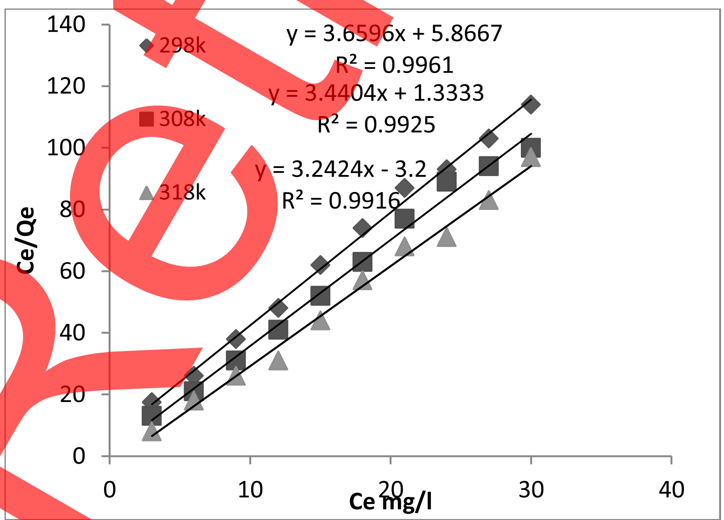

Figure 8. Langmuir adsorption isotherm for the toxin pesticide on the surface of olive seedsactivated charcoal at 298-318 K and pH=7

By applying the Freundlichand Langmuir models, adsorption appears to be consistent with both equations through R^2 values [16].

Table 2. The parameters of the Freundlichand Langmuir equations for adsorption of the pesticide on the surface of olive seedsactivated charcoal

Temp. K	Freundlich isotherm			Langmuir isotherm			
	Log Kf	n	R^2	a(mg/g)	b(mg/l)	R^2	RL
298	-1.46366	1.572149	0.6361	0.623795	0.106329	0.9961	1
308	-2.29551	0.865137	0.9224	2.580303	1.935227	o.9925	1
318	-3.62296	0.476026	0.9917	-1.01326	0.316643	0.9916	0.9

R^2 selection coefficient
1 / n The slope of the surface homogeneity is 0 <1 / n <1 where, in its smallness, the surface is not homogeneous
Kf is a constant returns to the total adsorption capacity and its unit is mg / g
a is a maximum adsorption capacity of the layer mg / g
b is a constant adsorption at equilibrium L / mg, indicating the intimacy of the interconnected sites as well as the surface energy
RL The separation factor, which is the thermal symmetry of the Langmuir, is given by equation 4
RL=1/[1+b Co] (4)
The values of RL are in the range of 0.1-0.99 means 0< RL> 1 representing extremely favorable adsorption process. Table 2shows thatthe adsorption data fit toLangmuir and Freundlich models.

Thermodynamic study

The highest adsorption was found at 298K. The diffusion speed of adsorption molecular on the surface decrease resulting in reduced interaction between the surface and the adsorption molecule and when the temperature increase, the bonds will separate. ΔH is calculated by draw Log xm vs. 1 / T K according to the equation (5) [17].

Log xm = **-** ΔH / (2.303 RT) + conc.(5)

A linear relationship was obtained as in figure 9 according to the results in table 3

Table 3. Values 1 / T K and Log Xm for adsorptionthe toxin pesticide on the surface of olive seedsactivated charcoal in the experimental range (298 – 318)

C°	Tk	1/T k	Xm	Log Xm
25	298	0.003356	4.50	0.653
35	308	0.003247	3.50	0.544
45	318	0.003145	3.00	0.477

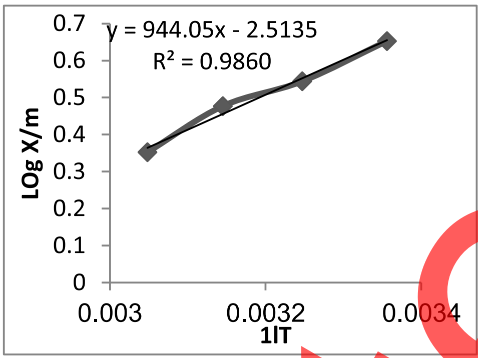

Figure 9. Log xm 1 / T K for adsorption of toxin pesticide on the surface of olive seedsactivated charcoal

$\Delta G = -RT\ lin[Qe / Ce]$ (6)

$\Delta\ G = \Delta H - \Delta T\Delta S$ (7)

The results illustrated in table (4)

Table 4. shows the values of ΔH, ΔG and ΔS for adsorption of the toxin pesticide on the surface of olive seedsactivated charcoalat 298K

ΔH ($KJ.mol^{-1}$)	ΔG ($KJ.mol^{-1}$)	ΔS ($kJ.\ mol^{-1}$)
-18.06	**4.87**	**- 0.07**

The negative value of ΔH and ΔS refers that the process is exothermic and the randomness decrease at the solid –liquid interface. The positive values of ΔG shows that the process is nonspontaneous. This indicates that the process is only adsorption [18-20].

5. Conclusion:

The possibility of the activated charcoal of olive seedusing in large quantities to remove toxin pesticide from their water solutions without cost. The highest concentration of toxin pesticide is 30ppm that can be adsorbed on (0.5g) of the activated charcoal of olive seeds at 298ºC. The process of adsorption is non-spontaneous and exothermic.

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