Retraction

Retraction: Adsorption of the Toxin Pesticide (Thiophanate - Methyl) from its Aqueous solution on the Surface of Activated Olive Seed (IOP Conf. Ser.: Mater. Sci. Eng. 1145 012049)

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This article (and all articles in the proceedings volume relating to the same conference) has been retracted by IOP Publishing following an extensive investigation in line with the COPE guidelines. This investigation has uncovered evidence of systematic manipulation of the publication process and considerable citation manipulation.

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 ways including photo-catalytic fragmentation/catalysis [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
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 Figure 1, which its temperature was raised to 650°C 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 ($\lambda_{max}$) (Table 1) of the toxin pesticide was determined using a UV-visible device and the maximum wavelength (263 nm) 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 ($\lambda_{max}$). 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 pesticide were prepared with a concentration of (3-30 ppm) each. 25 ml of them were taken and placed in contact with 0.5 gm of olive seeds. The samples were placed in a water bath with a controlled temperature shaker for half an hour. The adsorption of the solutions was measured using a UV-visible spectrophotometer. The amount of adsorbed material was calculated according to the following equation 1.

$$Q_e = \frac{V(C_0 - C_e)}{m} \quad (1)$$

Where $C_0$ and $C_e$ 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 spectrum of the toxin pesticide versus reagent blank.

Figure 3. 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 15 min 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 18 min and above, the stability can be observed at equilibrium time and this is due to the absence of unoccupied adsorption sites [12].
4.2. Temperature effect:
During this study, the effect of temperature on the adsorbed toxin pesticide on the surface of activated olive seed was studied. The results in figure (6) show 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 4. Effect of the concentration of adsorption of the pesticide on the surface of olive seed activated charcoal

Figure 5. Effect of the equilibrium time of adsorption of the pesticide on the surface of olive seed activated charcoal
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 Giles classification. It is noted from these isotherms that adsorption increases by increasing the concentration of equilibrium and this shows that adsorption follows Freundlich and Langmuir models. These models are used to describe the interference behavior between the adsorbent and the adsorption surface. The Freundlich model assumes that the adsorption sites are not equal in their energy, allowing for multi-layer adsorption. Freundlich equation 2 can be represented as follows:

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e$$

By drawing $\log Q_e$ as in Figure (8) we get a straight line its slope $\frac{1}{n}$ it is a measure of adsorption intensity and an intersection $\log K_F$ Which is a measure of adsorption capacity [14]
Figure 7. Freundlich adsorption isotherm for toxin pesticide on the surface of olive seeds activated 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:

\[ \frac{C_e}{Q} = \frac{1}{ab} + \frac{1}{a} C_e \]  

(3)

By drawing \( \frac{C_e}{Q} \) opposite \( C_e \) as in figure 8 we get a straight line its slope \( \frac{1}{a} \) and an intersection its amount \( \frac{1}{ab} \). 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 seeds activated charcoal at 298-318 K and pH=7
By applying the Freundlich and Langmuir models, adsorption appears to be consistent with both equations through R² values [16].

**Table 2.** The parameters of the Freundlich and Langmuir equations for adsorption of the pesticide on the surface of olive seeds activated charcoal

| Temp. (K) | K   | Log Kf | n | R²  | a (mg/g) | b (mg/L) | R²  | RL |
|-----------|-----|--------|---|-----|----------|----------|-----|----|
| 298       | -1.46366 | 1.572149 | 0.6361 | 0.623795 | 0.106329 | 0.6361 | 0.9961 | 1   |
| 308       | -2.29551 | 0.865137 | 0.9224 | 2.580303 | 1.935227 | 0.9224 | 0.9925 | 1   |
| 318       | -3.62296 | 0.476026 | 0.9917 | -1.01326 | 0.317664 | 0.9917 | 0.9   |

R² 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 2 shows that the adsorption data fit to Langmuir 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].

\[
\text{Log Xm} = - \Delta H / (2.303 \text{ RT}) + \text{conc.} (5)
\]

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 adsorption the toxin pesticide on the surface of olive seeds activated charcoal in the experimental range (298 – 318)

| C° | Tk  | 1/Tk | 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  |
\[ y = 944.05x - 2.5135 \]
\[ R^2 = 0.9860 \]

$\Delta G = -RT \ln\left(\frac{Q_e}{C_e}\right)$

(6)

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

(7)

The results illustrated in table (4)

Table 4. shows the values of $\Delta H$, $\Delta G$ and $\Delta S$ for adsorption of the toxin pesticide on the surface of olive seeds activated charcoal at 298K

| $\Delta H$ (kJ·mol$^{-1}$) | $\Delta G$ (kJ·mol$^{-1}$) | $\Delta S$ (kJ·mol$^{-1}$) |
|---------------------------|---------------------------|---------------------------|
| -18.06                    | 4.87                      | -0.07                     |

The negative value of $\Delta H$ and $\Delta S$ refers that the process is exothermic and the randomness decrease at the solid–liquid interface. The positive values of $\Delta G$ 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 seeds using 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 298°C. The process of adsorption is non-spontaneous and exothermic.

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