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# Effect of dissolved surfactants on sorption and desorption of Oxyfluorfen onto prepared activated Carbon

**Khalaf, Hussein A.**[1] **and Mohamed A. Balah**[2]

[1] Department of Chemistry, Faculty of Science, Omar Al-Mukhtar University, Al-Bayda, P.O 919, Libya, Email: hkhalaf70@yahoo.com

[2] Department of Plant Protection, Desert Research Center, El-Mataria, Cairo, Egypt, Email; mbaziz1974@gmail.com

## Abstract

The aim of the present work is to study sorption and desorption of oxyfluorfen herbicide from aqueous solution using activated carbon prepared from olive stones .The adsorption process has been done in absence and presence of nonionic (Tween40), cationic (TDMA) and anionic (SDBS) surfactants. Equilibrium adsorption levels were a function of contact time, surfactants type, and herbicides concentration. Different kinetic models have been studied in terms of pseudo 1st and 2nd order rate constants. The obtained results show higher amount of removal in case of SDBS (~95%) than others, Tween40 (~90%) and TDMA (~80%). The chemically and physically natural adsorption of the oxyfluorfen into activated carbon appeared in the presence of anionic / cationic and nonionic surfactants respectively. The Langmuir isotherm was better fitted for the experimental data. Moreover, the process involves pseudo 1st and 2nd order kinetics. The obtained results indicated that activated carbon of olive stones appeared to be a good material for removing of oxyfluorfen residues from aqueous solution effectively in the presence of ionic surfactants and may be suitable to control other diphenyl-ether herbicides leaching and preservation underground water from contamination.

**Keywords:** Olive stone; Activated carbon; Oxyfluorfen; Removal; Aqueous solution.

## 1.Introduction

The use of pesticides increased because of the need for improved agricultural production and the health of humans and animals protection. The annual world consumption of pesticides was 5.2 billion pounds in both 2006 and 2007 **(Grube *et al.*, 2007).** Herbicides are a weed control tactic in most cropping systems, and areas outside of crop fields. It can also be transported off crop fields in surface or subsurface water flow **(Patzold *et al.*, 2007and Reichenberger *et al.*, 2007).** Oxyfluorfen (trade name GOAL) is a diphenyl-ether herbicide used for pre and post-emergent control of annual broadleaf and grassy weeds. It is applicated not only in a variety of crops but also in non-agricultural ornamental, forestry and residential areas. However, oxyfluorfen is classified as a possible human carcinogen **(U.S, EPA, 2002).** Oxyfluorfen in soil environments is considered to be highly resistant to degradation since it is not hydrolyzed at pH 5, 7 or 9 (**U.S. EPA, 1992)** ' Oxyfluorfen hardly moves into silty clay soil and exhibited low run-off potential so it represents a low risk herbicide for the contamination of ground and adjacent water resources **(Mantzos *et al.*, 2014).** These data raise the necessity for further elimination from water and soils. The process of herbicide adsorption is influenced most by the chemical and physical properties of the specific herbicide, its formulations, the type and amount of clay, and the organic matter content of the soil **(Bailey and White, 1964).** Activated carbon is the most popular and widely used as a versatile sorbent for removal of various types of pollutants such as pesticides and many other chemicals (**Foo and Hameed, 2010).** The world adjuvant market is worth around US$500 million in 1995 - approximately 2.5% of the total pesticide market. The total world consumption of surfactants as adjuvants in agriculture was estimated at 60,000 tons in 1993 (**Rogiers, 1995).** Surfactants are amphiphilic molecules having two major components (moieties), a hydrophilic or water-soluble moiety (head group) and a hydrophobic, or water-insoluble, moiety (tail group) known as the critical micellar concentration (cmc), surfactants form self-aggregates (micelles) **(Rosen,**

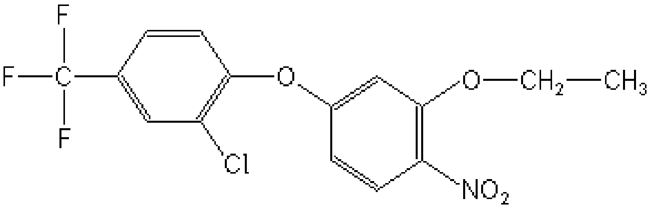
**1989).** Anionic or cationic compounds are chemically sorbed, where as nonionic compounds are physically sorbed. The negative correlation between sorption and mobility of pesticides has been well established **(Park *et al.*, 2002)**. An increase in efficiency in the desorption of residues of atrazine and linuron herbicides after different aging times in the soil in solutions of the surfactants SDS (anionic) and Triton X-100 (non-ionic) was recorded. While in water, the increase in the desorption of the herbicides in the water-surfactant system was greater for linuron than for atrazine, possibly owing to its more hydrophobic nature. The amount of herbicide desorbed being 10-fold (SDS) and 9-fold (Triton X-100) higher than that desorbed in water **(Rodriguez-Cruz *et al.*, 2006).** The kinetic and equilibrium studies involve anionic, cationic, non-ionic and mixed surfactants at the solid surface from the solution. Kinetics and equilibrium adsorption of surfactants at the solid – liquid interface depend on the nature of surfactants and the nature of the solid surface influences of different parameters such as molecular structure, temperature, salt concentration that are very important in surfactant adsorption **(Paria and Khilar, 2004).** The study carried out to investigate the sorption / desorption of oxyfluorfen on the activated charcoal prepared from olive stones in the absence and the present of surface active agent. The change of elimination rate of oxyfluorfen as influenced by using cationic, ionic and non ionic surfactant and contact time in aqueous system was determined.

# 2.Materials and methods

## 2.1. Materials:

### 2.1.1. Oxyfluorfen solution preparation:

Oxyfluorfen is a diphenyl-ether herbicide used for broad spectrum pre-and post-emergent control of annual broadleaf and grassy weeds in a variety of crops. Its molecular formula is $C_{15}H_{11}ClF_3NO_4$ (M.wt: 361.7 gm/mol). The stock solutions of oxyfluorfen standard **(**Sigma-Aldrich**)** was dissolved in absolute ethanol and further diluted with distilled water to obtain 120, 240 and 480 mg $L^{-1}$ prepared in deionized water and they were diluted when necessary.

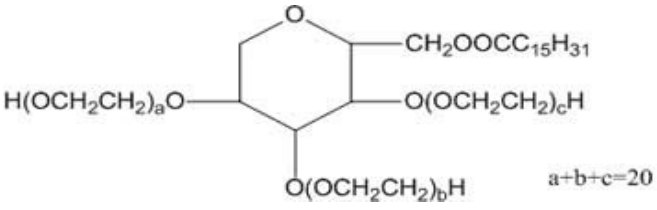


Oxyfluorfen

### 1.2. Surfactants used:

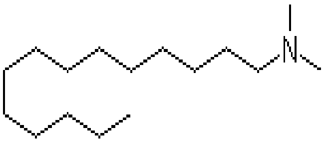
In this study, three types of surfactants have been prepared and used for investigation of their effects.

The first one is Tween40 (nonionic type). Tween 40 is, polyoxyethylene glycol sorbitan monopalmitate ($C_{62}H_{123}O_{26}$, M.wt: 1283.65 gm/mol):



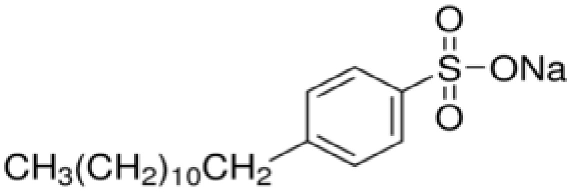
Tween40

The second is tetradecyl methyl amine (TDMA, Cationic surfactant) with formula: $C_{14}H_{29}NHCH_3$ and M.wt 241.5 gm/mol).



TDMA

The last one is sodium dodecyl benzene sulphonate (SDBS, Anionic surfactant) with formula $CH_3(CH_2)_{11}C_6H_4SO_3Na$, and M.wt 348.5 gm/mol.



SDBS

All three surfactants were prepare in two concentrations,; 0.1 and 0.2 gm/L in deionized water.

### 2.1.3. Synthesis of activated carbon

In brief, olive's stones were washed, dried, crushed followed by ethanol extraction overnight. Then, solid matter was dried at 378 K for 12 h followed by carbonization at 673 K for 3 h.

## 2.2. Batch adsorption studies:

By using bottle-point method, (**El-Geundi, 1990**) the adsorption isotherms were constructed, in which different concentrations were taken into various flasks (50 ml), shacked (120 rpm) for two hours at appropriate temperature. At the end, the activated carbon was separated by centrifugation (2000 rpm) and the amount of adsorbed matter was determined spectrophotometrically using DU800 Uv/Vis., at $\lambda_{max} = 220$ nm, these methods confirmed by **(He *et al.*, 2010)** which, oxyfluorfen were extracted twice with equal chloroform after centrifugation in a separatory funnel**.** Then, extract was evaporated to dryness and residue was determined using HPLC (SPECTRA SYSTEM, Thermo, USA) with analytical $C_{18}$ column and Ultraviolet detector at 280 nm**.**

**The studied parameters related to adsorption:**

**a. Contact time**; the contact time for oxyfluorfen-carbon system was determined by adding 0.1 g of carbon in 100 ml of oxyfluorfen solution with known concentration at different time intervals. The absorbance was measured at different time intervals. The amount of adsorption at time t, $q_t$ (mg $g^{-1}$), was calculated by:

$$q_t = \frac{V(C_o - C_t)}{m} \quad (1)$$

Where $C_o$ and $C_t$ (mg $L^{-1}$) are the initial and oxyfluorfen concentration at time *t*, *V* (L) is the volume of liquid phase and *m* is the mass of carbon (g).

**b. Oxyfluorfen concentration**; adsorption isotherms were obtained by contacting a constant mass (0.1 g) of carbon that was added to different concentrations of oxyfluorfen solution with continuous stirring for 2 hours. After that time, the samples were centrifuged and the absorbance of oxyfluorfen solution was measured. The adsorption capacity ($q_e$) of the carbon was determined from the concentration difference of the solution, at the beginning ($C_o$) and at equilibrium ($C_e$):

$$q_e = \frac{V(C_o - C_e)}{m} \quad (2)$$

## 2.3. Equilibrium isotherms:

In this study, two isotherms have been investigated including Langmuir and Freundlich.

*Langmuir isotherm*

This equation for the Langmuir (**Do, 1998)** is as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \quad (3)$$

Where $a_L$ and $K_L$ are the Langmuir isotherm constants.

*Freundlich isotherm*

Equation of this isotherm is as follows( **Do, 1998**):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

$K_F$ is the Freundlich constant and n is the Freundlich exponent.

## 2.4. Kinetic Sorption Study:

Kinetic model has been used to identify the possible mechanisms of oxyfluorfen adsorption process on to activated carbon. In this study, pseudo-first and pseudo-second order kinetic models **(Bello *et al.*, 2008)** have been proposed as follows to elucidate the mechanism of adsorption.

Lagergren proposed a pseudo-first order kinetic model as below. The integrated form of the model is:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 . t}{2.303} \quad (5)$$

where $q_t$ is the amount of oxyfluorfen adsorbed at time t (min), $q_e$ is the amount of oxyfluorfen adsorbed at equilibrium and $k_1$ is the rate constant of pseudo-first order adsorption.

The adsorption kinetics can also be given by a pseudo-second order reaction. The integrated linearized form of this model is:

$$\frac{t}{q_t} = \frac{1}{k_2 . q_e^2} + \frac{t}{q_e} \quad (6)$$

where $k_2$ is the pseudo-second order rate constant of adsorption.

The plot of t/q versus t of Eq. (6) should give a linear relationship, from which $q_e$ and $k_2$ can be determined from the slope and intercept of the plot, if second order kinetic equation is applicable.

# 3.Results and Discussion:

## 3.1.Removing of Oxyfluorfen in Presence and Absence of Surfactants:

Three concentrations, 120, 240 and 480 mg/L of oxyfluorfen were taken in presence and absence of surfactants (ionic and nonionic) with 0.1 gm activated carbon. The removing percent of oxyfluorfen from water with and without surfactants were shown in Table 1. From this table, it is clear that the removing % of oxyfluorfen from the aqueous solution by activated carbon is mostly considerable (52.7, 48.8 and 32.5% for concentrations 120, 240 and 480 mg/L, respectively) in absence of any surfactants. On the other hand, after the addition of surfactants (SDBS, Tween40 and TDMA), it is noticed that the removing % are increased comparable at both concentrations 0.1 and 0.2 gm/L for all added surfactants. Also, one can notice that the removal% in presence of anionic (SDBS) are higher than others, thus the order of removal% can written as:

Removing % (SDBS) > (Tween40) > (TDMA) > without surfactant.

**Table 1.** Removing % for oxyfluorfen from water in the presence and absence of surfactants.

| Oxy-fluorfen Conc. (mg/L) | With-out surfac-tants | SDBS (mg/L) | | Tween40 (mg/L) | | TDMA (mg/L) | |
|---|---|---|---|---|---|---|---|
| | | 0.1 | 0.2 | 0.1 | 0.2 | 0.1 | 0.2 |
| 120 | 52.7% | 93.7% | 94.9% | 87.0% | 90.0% | 78.3% | 75.8% |
| 240 | 48.8% | 84.1% | 84.7% | 81.7% | 85.2% | 67.2% | 69.0% |
| 480 | 32.5% | 63.3% | 63% | 66.1% | 67.0% | 57.9% | 59.0% |

## 3.2. Batch adsorption study

### 3.2.1. Effect of contact time on oxyfluorfen adsorption:

The amount of oxyfluorfen adsorbed (at initial concentration 240 mg/L) at various intervals of time in presence and absence of surfactants were shown in Figs. 1-3. These figures indicate the removal of the oxyfluorfen initially increases with time and the adsorption process was found to be rapid initially but attain equilibrium within 100 min. in case without surfactant. However, all equilibrium experiments were allowed to run for 2 hours. Moreover, the addition of surfactants has no effect on the time behavior but increases the amount of oxyfluorfen adsorbed. In comparison between the amounts of oxyfluorfen adsorbed in presence of surfactants, it is noticed that the addition of sodium dodecylbenzensulfonate resulted in increase in the amount of oxyfluorfen adsorbed and the addition of tetradecyl methyl amine has small effect on the amount of oxyfluorfen adsorbed as shown in Figs. 1-3. Also, one can say that there is no considerable variation between both surfactant's concentrations 0.1 and 0.2 mg/L. The adsorption capacity of the solid phase is important for characterizing the usefulness of the adsorption process and for determining the usefulness and applicability of a mathematical model.

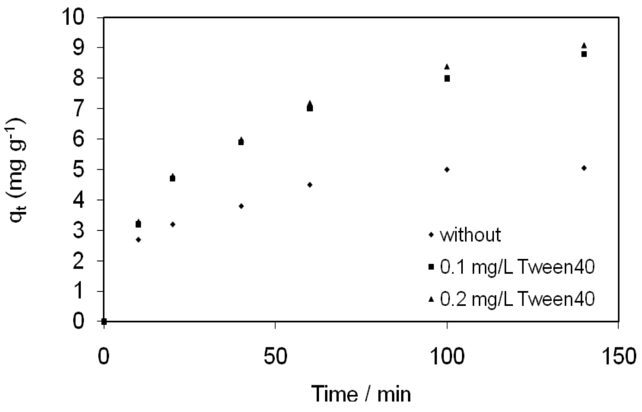


**Fig. 1.** Effect of contact time with and without Tween40 on adsorption.

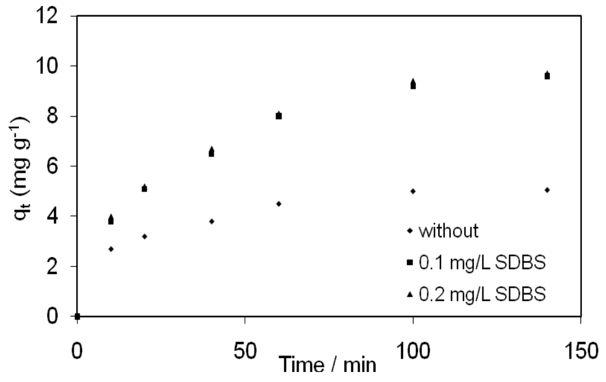


**Fig. 2.** Effect of contact time with and without SDBS on adsorption.

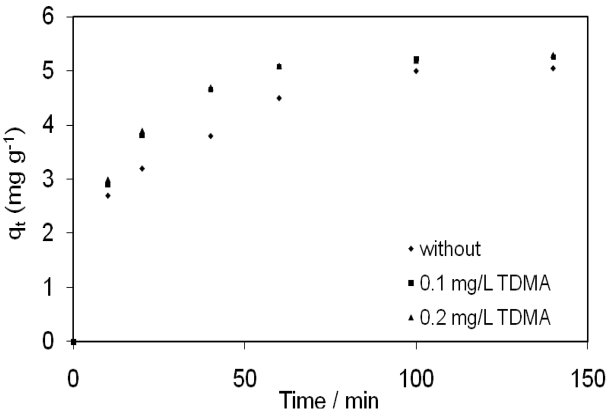


**Fig. 3.** Effect of contact time with and without TDMA on adsorption.

### 3.2.2. Oxyfluorfen adsorption isotherms:

Figure 4 shows the adsorption isotherm at 293 K for oxyfluorfen adsorbed onto activated carbon. Different concentrations of oxyfluorfen were taken with 0.1 gm activated carbon in 50 ml deionized water with and without surfactants (0.1 gm/L).

When the experimental data points of the adsorption of oxyfluorfen onto adsorbents were plotted as $q_e$ (mg/g) against $C_e$ (mg/L), the characteristic L-shape curves have been obtained as shown in Fig. 4. According to the shape of the curve, the isotherms corresponding to the oxyfluorfen may be classified as type-L (**Giles *et al.*, 1960),** which suggests moderate affinity of oxyfluorfen molecules for the active sites of the adsorbents.

The analysis of this isotherm is important to know which models are acceptable for design purposes. The first isotherm tested was that of Langmuir which may be represented by the equation:

$$C_e/q_e = 1/K_L + (a_L/K_L)Ce \qquad (7)$$

The plot of $C_e/q_e$ against $C_e$, Fig. 5, is seen to be linear over a certain concentration range. Values of $K_L$ and $a_L$ have been calculated using the least-squares method and are cited in Table 2. The value of the constant, $K_L/a_L$, corresponds to the maximum adsorption capacity ($q_{max}$) of the oxyfluorfen. Linear plots of $K_L/a_L$ against $C_e$ for the oxyfluorfen suggest the applicability of the Langmuir isotherm of the present systems, and demonstrate monolayer coverage of the adsorbate at the outer surface of the adsorbent (**Panday *et al.*, 1985**).

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless separation factor, R, which is defined by:

$$R = 1/(1+ a_L \cdot C_{ref}) \qquad (8)$$

Value of R for has been calculated and cited in Table 1. The R values (0.038, 0.038, 0.042 and 0.024) indicates that adsorption of oxyfluorfen onto activated carbon is very favorable (0< R <1) **(Attia *et al.*, 2008)**.

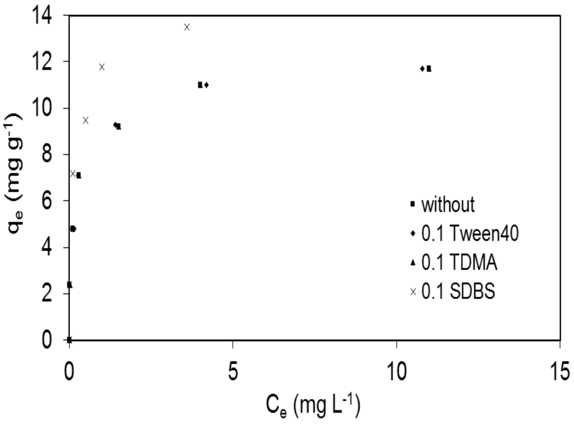


**Fig. 4.** Adsorption isotherm of oxyfluorfen onto activated carbon at 293 K

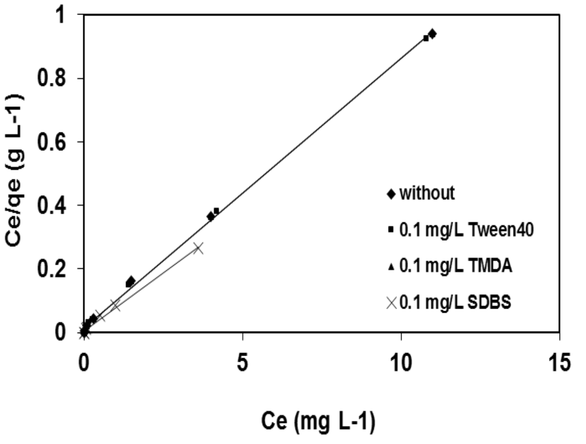


**Fig. 5.** Langmuir adsorption isotherm of oxyfluorfen onto activated carbon at 293 K.

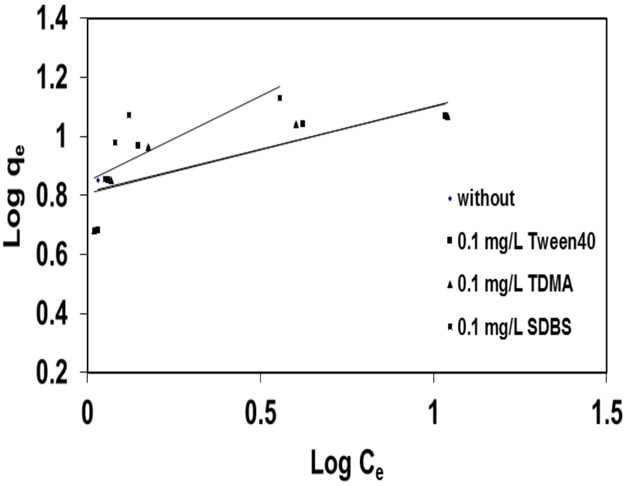


**Fig. 6.** Fruendlich adsorption isotherm of oxyfluorfen onto activated carbon at 293 K.

**Table 2.** Parameters in the Langmuir and Freundlich Adsorption Models.

| Sample | Langmuir isotherm | | | | | Freundlich isotherm | | |
|---|---|---|---|---|---|---|---|---|
| | $K_L$ | $a_L$ | $q_{max}$ | R | $r^2$ | $K_F$ | n | $r^2$. |
| without | 69.4 | 6.0 | 11.6 | 0.038 | 0.998 | 8.9 | 1.8 | 0.72 |
| 0.1 Tween40 | 71 | 6.0 | 11.8 | 0.038 | 0.998 | 6.5 | 3.47 | 0.63 |
| 0.1 TDMA | 63.7 | 5.4 | 11.8 | 0.042 | 0.999 | 6.4 | 3.38 | 0.66 |
| 0.1 SDBS | 156 | 11.4 | 13.7 | 0.024 | 0.996 | 7.1 | 1.75 | 0.50 |

The experimental equilibrium data for the adsorption of oxyfluorfen onto activated carbon has also been analyzed using the Freundlich isotherm as given by the following equation:

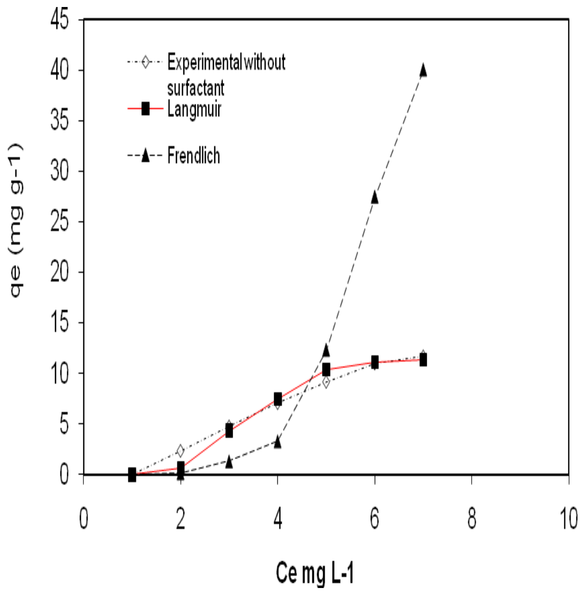
$$\text{Log } q_e = \text{Log } K_F + (1/n) \text{ Log } C_e \qquad (9)$$

Inspection of the results derived from the Freundlich analysis shows that a plot of log $q_e$ against log $C_e$ exhibits some curvature (Fig. 6). Certainly, two straight lines may represent the results. The Freundlich parameters, $K_F$ and n, for the heavy metals have been calculated using the least-squares method applies to the straight lines shown in Fig. 6 and are cited in Table 1. This shows that the values of n are higher than one, indicating that the tested oxyfluorfen is favorably adsorbed by activated carbon (**El-Guendi, 1991)**.

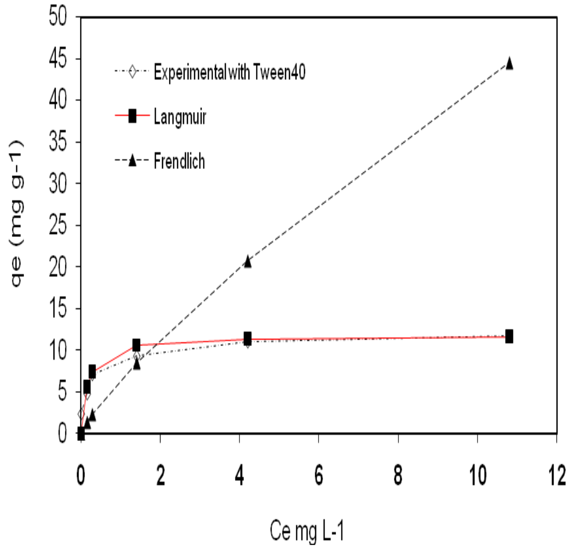
By using the appropriate constants of Langmuir and Freundlich equations, the theoretical isotherm curves were predicted using known values of $C_e$. Fig. 7 (a-d) show a comparison of the experimental points with Langmuir and Freundlich equations, in absence and presence of tested surfactants, to establish which equation yields the “best fit”. It is clear that Langmuir isotherm fits the data significantly better than Freundlich model.

### 3.3. Kinetic Sorption Study:

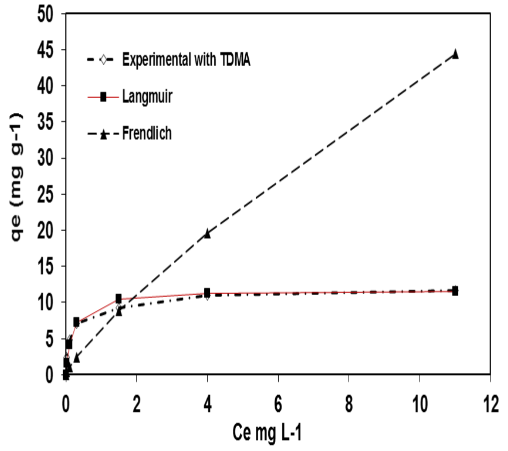
Kinetic equations have been developed to explain the transport of adsorbate onto various adsorbents. These equations 8 and 9 include the pseudo-first order equation (**Bello *et al*., 2008)** and the pseudo–second order (**Malik, 2004)**. These Kinetic models are only concerned with the effect of the observable parameters on the overall rate of adsorption.



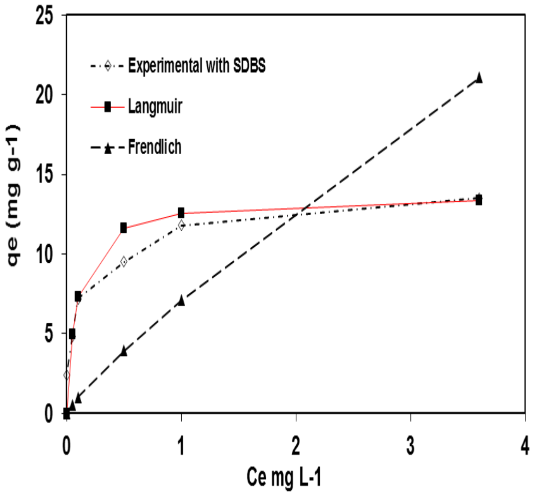
(a)



(b)



(c)



(d)

**Fig. 7.** Comparison between the experimental and theoretical isotherms in (a) absence of surfactants, (b) with Tween40, (c) with TDMA and (d) with SDBS.

$$\log(q_e - q_t) = \log q_e - \frac{k_1.t}{2.303} \qquad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2.q_e^2} + \frac{t}{q_e} \qquad (6)$$

where $q_e$ and $q_t$ are the amounts of oxyfluorfen adsorbed (mg $g^{-1}$) at equilibrium and at time t(min), respectively, $k_1$ the rate constant adsorption ($min^{-1}$) according to pseudo first order and $k_2$ is the pseudo second order rate constant ($g.mg^{-1}min^{-1}$).

For pseudo first-order derived by Langergren (**El-Geundi, 1990)**, values of $k_1$ have been determined from the plots of log ($q_e$-$q_t$) versus t for different concentrations of oxyfluorfen according to Eq. 6, Fig. 8.

**Table 3.** Rate constants of oxyfluorfen sorption onto activated carbon at 293 K.

| Temp. K | 1st order rate constant | | 2nd order rate constant | |
|---|---|---|---|---|
| | K ad (min-1) | $r^2$ | K ad (min-1) | $r^2$ |
| Without surfactants | 0.023 | 0.652 | 3.8 x 10-3 | 0.995 |
| 0.1 gm/L Tween40 | 0.021 | 0.855 | 19.6 x 10-3 | 0.934 |
| 0.1 gm/L TDMA | 0.085 | 0.944 | 0.289 | 0.929 |
| 0.1 gm/L SDBS | 0.044 | 0.965 | 15.1 x 10-3 | 0.235 |

ad= adsorption K=Constant $r^2$=correlation coefficient

The correlation coefficient values for the adsorption of oxyfluorfen in presence of TDMA and SDBS are higher (0.94 and 0.97, respectively) than others, Table 3. This shows that the adsorption of oxyfluorfen onto activated carbon produced from olive stones is first order only in the presence of ionic surfactants, TDMA and SDBS. The adsorption rate constants ($k_1$) have been determined from the slopes of the plots and the values were found to be: 0.085 and 0.044 $min^{-1}$ at 293 K for the adsorption in presence of TDMA and SDBS, respectively.

In the case of pseudo second order based on Eq. 6, if pseudo $2^{nd}$ order kinetics is applicable, then the plot of t /q versus t should show a linear relationship, Fig. 9. Both $q_e$ and $k_2$ can be determined from the slope and intercept of the plot. Also, this procedure is more likely to predict the behaviour over the whole range of adsorption. The linear plots of t/q versus t (Fig. 9) show a good agreement between experimental and calculated $q_e$ values only for the adsorption of oxyfluorfen in free of surfactant and in the presence of nonionic surfactant (Tween40), Table 3. Thus, second-order model is more suitable to describe the adsorption kinetics data in case of free and presence of Tween40.

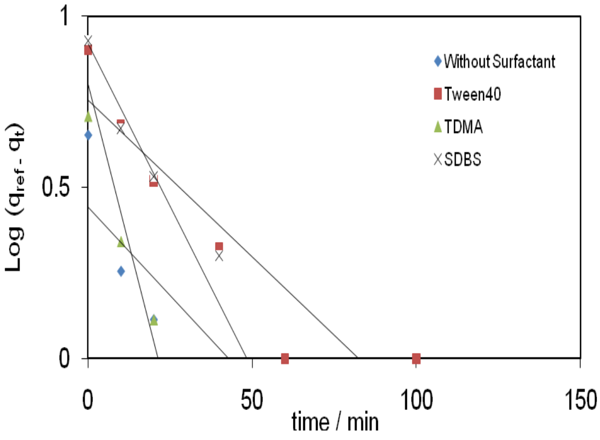


**Fig. 8.** First order for the adsorption of oxyfluorfen onto activated carbon with and without surfactants.

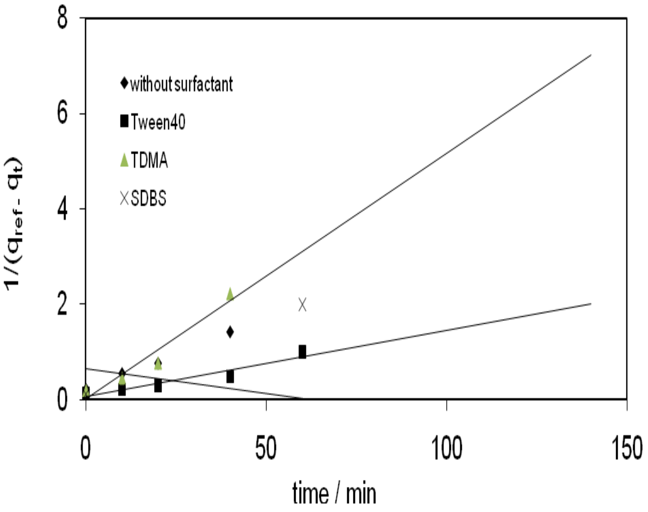


**Fig. 9.** Second order for the adsorption of oxyfluorfen onto activated carbon with and without surfactants.

## Conclusion:

The adsorption of oxyfluorfen herbicide with and without surfactant onto activated carbon prepared from olive stones which used as economically feasible removing method from water solution was studied and the following major points can be extracted from the results: The olive stones activated carbon is natural materials that are available in large quantities from olive production, may have potential as inexpensive adsorbent that has higher maximum adsorption capacity. The Langmuir isotherm better fitted the experimental data since the average percent deviations were lower than with Freundlich isotherm. Results show that all tested surfactant increased removing of oxyfluorfen, while the higher removing % in the presence of 0.1 g L-1 of SDBS (ionic surfactant), however, the lower removal % in the presence of cationic surfactant at the higher oxyfluorfen concentration.

These results obtained without any pH adjustment and in the room temperature (25 °C or 293 K ) and the availability of adsorptive sites is possible in the lower than the higher concentration of the herbicides. The Kinetics of the adsorption of oxyfluorfen was rapid in the initial stage followed by a slow rate. The higher adsorptive was correlated with the presence of both anionic and nonionic surfactants and appeared the naturally chemically and physically reaction of the herbicide into prepared activated carbon. The adsorption data indicated the applicability of the $1^{st}$ order reaction in presence of TDMA and SDBS but $2^{nd}$ order in presence and presence of Tween40.

## 4.Nomenclature:

$a_L$ parameter of Langmuir isotherm (L $mg^{-1}$)
$C_o$ initial oxyfluorfen concentration (mg $L^{-1}$)

| | |
|---|---|
| $C_e$ | equilibrium liquid-phase concentration ($mg.L^{-1}$) |
| $C_{ref}$ | reference liquid-phase concentration ($mg.L^{-1}$) |
| k1 | Pseudo 1st order rate constant ($min^{-1}$) |
| k2 | Pseudo 2nd order rate constant (g $mg^{-1}min^{-1}$) |
| $K_f$ | parameter of Freundlich isotherm ($dm^3.g^{-1}$) |
| $K_L$ | Parameter of Langmuir isotherm ($dm^3.g^{-1}$) |
| n | Freundlich exponent (dimensionless) |
| $q_e$ | equilibrium solid-phase concentration ($mg.g^{-1}$) |
| $q_{ref}$ | reference solid-phase concentration at onset of monolayer coverage ($mg.g^{-1}$) |
| $q_t$ | solid-phase concentration at time t ($mg.g^{-1}$) |
| $Q_e$ | dimensionless solid-phase concentration at equilibrium |
| $r^2$ | Correlation coefficient. |
| R | dimensionless separation factor, defined by equation (3). |

# References:

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