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Green Process for Adsorptive Removal of Ethion (*O,O,O′,O′*-Tetraethyl *S,S′*-Methylene Bis(Phosphorodithioate) from Agricultural Wastewater Using Modified Surface of Orange Peel and Apricot Kernel

Reda M. Abdelhameed[a],*, Fathia Mahdy[a], Hassan Abdel-Gawad[a], Bahira Hegazi[a]

[a] *Applied Organic Chemistry Department, Chemical Industries Research Division, National Research Centre, 33 EL Buhouth St., Dokki, Giza 12622, Egypt.*

Abstract

Smart absorber with engineered surface, low cost price becomes utmost importance for application in water treatment. Pesticide represents the fatal problem in water contamination due to large quantity misused by the farmers. Ethion is a common contaminated insecticide found in wastewater, so it is really important for removal of ethion from contaminant water. Here, the adsorption characteristics of ethion and its degradation products were studied using modified and functionalized low cost adsorbent. The modified agricultural wastes [orange peels (OP) and the outer crust of apricot kernel (AK)] were characterized and analyzed. Physical and chemical depositions of ethion residues on the surface of absorbers (OP and AK) were utilized.Theoretical calculations/modelling on surfaces of OP and AK were studied using Langmuir and Freundlich isotherm model. The results show that the removal efficiency of ethion increased when the pH of adsorption system increased then decreased at pH greater than 7. The using of different adsorbent doses found that the 95.5 % ethion removal was achieved when 16.5 g/L of the outer crust of apricot kernel. The kinetic model shows that the ethion uptake with the orange peels and apricot kernel adsorbents is a pseudo-second order adsorption.

Keywords: Ethion; Agricultural wastewater; Adsorbents; Kinetics; Isotherm

1. Introduction

The fetal problem in agriculture wastewater is containing high concentration of pesticides; among various types of pesticides, the most common used insecticide is ethion. The chemical name of ethion is *O,O,O′,O′*-tetraethyl *S,S′*-methylene bis-(phosphorodithioate) (I). Ethion has many applications against various foliar pests observed in fruit, vegetable, and cotton crops [1, 2]. The highly used of pesticides in agriculture for controlling pests is contaminating water resources daily [3]. They form a strong class of water pollutants. Moreover, pesticides are carcinogenic in nature [4]. The European Environment Agency stipulates a maximum residue levels (MRL) for pesticides in drinking water of 0.1 μgL−1 [5]. According to a report on the surveillance of pesticide residues in water in Egypt [6], there is a significant concentration (0.4–1.0 mgL^{-1}) of ethion residues in water samples. Toxicity of pesticides and their degradation products cause a potential hazard by contaminating the environment. The scientists do many efforts to eliminate pesticides from water [7-12].

Adsorption is one of the physico-chemical treatment processes found to be effective in pesticides removal from aqueous solutions. Adsorption is very likely process due to cheap or low-cost to get them from nature. Moreover, it requires little processing [13]. Searching about low

*Corresponding author e-mail: reda_nrc@yahoo.com.
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cost adsorbent nowadays is a big deal so plant wastes are more preferable because it is inexpensive and has high economic value. Recently, maize leaf [14], peanut hull pellets [15], rice husk ash and neem bark [16], grape stalk wastes [17] were used as matrix in adsorption process. The highly adsorption activity was found when orange peel was used in removal of carbofuran from aqueous solution [18].

Based on the availability of adsorbents in different places, it is obvious that more inexpensive and effective approaches need to be found for removal of ethion in water so that the strict regulation on the concentration of ethion in wastewater can be widely implemented. This research has aimed at investigating the adsorption efficiency of different low cost agricultural wastes (orange peels and the outer crust of apricot kernel) which easily available in Egypt for their abilities to remove ethion residues from water. Also, the kinetic study was examined.

2. Materials and methods

2.1. Materials

2.1.1. New protocol to Synthesis of ethion pesticide

Our modified protocol was designed to use commercially available material in Egypt for synthesis of ethion insecticide in large scale. The protocol was divided into two main steps; the first is synthesized of *O,O*-diethyl hydrogen phosphorodithioate (II) as intermediated and the second is synthesis of the final product (ethion) (I).

a) Preparation of *O,O*-Diethyl Hydrogen Phosphorodithioate intermediate

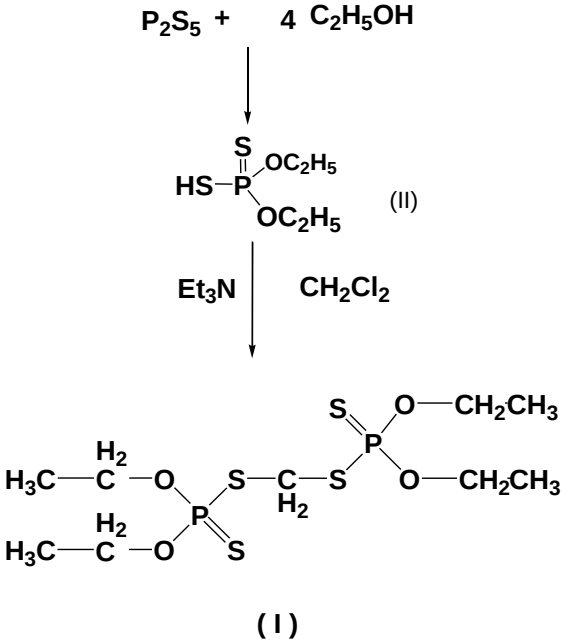
Phosphorus pentasulfide (P_2S_5, 10 g) was reacted with Ethanol (12 mL) in presence of anhydrous benzene (40 mL). The mixture was stirred at temperature for 3 hours and the final product was purified on silica gel column using hexane: acetone (98:2). The yield of purified intermediate is about 68% with rate of flow (Rf =0.68, n-hexane: ethyl acetate 98:2 v/v, Scheme 1).

IR (KBr) ν max/cm-1, 3400 (SH), 2851, 1580 (C-H aliphatic), 1022 (POC) and 722 (P =S); 1H NMR (CDCl3, 270 MHz), δ = 1.24 (t, J = 8.0 Hz, 3H, CH3CH), 2.80 (q, J = 8.5 Hz, 2H, CH2CH3), and 6.51 (s, 1H, SH); EI-MS (m/z), 186 (M+, 35.3%), 158 (68.7%), and 130 (91.5%);

b) Preparation of final product (ethion)

O,O-diethyl hydrogen phosphorodithioate (II) was reacted with methylene chloride (0.05 moles, 3.5 mL) in presence of triethylamine (0.1 mole, 13.5 mL). The mixture was stirred at 25 °C for 20 min, then heated until reflux then maintenance for 3 hours, filtered, evaporated and measured the yield (68%). The Rf value of purified ethion is 0.75 in solvent system n-hexane: ethyl acetate 98:2 (Scheme 1).

IR (KBr) ν max/cm-1, 2966, 1580 (C- H aliphatic), 1022 (POC), 720 (P S) and 670 (C- S); 1H NMR (CDCl3, 270 MHz), δ = 1.24 (t, J = 8.0 Hz, 3H, CH3CH), 2.80 (q, J = 8.5 Hz, 2H, CH2 CH3), and 7.30 (s, SCH2S); EI-MS (m/z), 385 (M+, 18.1%), 365 (9.1%), 231 (20.2%), and 153 (100%).



Scheme 1. Pathway of ethion synthesis.

2.2. Preparation of adsorbent

i) Orange peels were collected, cut, washed, and dried in an oven at 55°C.. The dried peels were grinding to fine particles. The granules were preserved in a vacuum descicator to be used as adsorbent for further analysis.

ii) Apricot kernels were collected from the local market, washed thoroughly with water to remove foreign impurities. They were dried in sunlight for four days; separate the outer crust of apricot kernel then grinding to fine particles and were stored in a vacuum descicator to be used as adsorbent for further analysis.

2.3. Characterizations:

Spectral analysis: the investigated products were determined using spectral analysis like 1H NMR (Jeol-EX, 270 MHz), EI –MS (Jeol JMS-AX500 mass spectrometer, 70 eV) and FTIR (KBr pellets, Nexus 670 FTIR spectrometer (Nicolet).

Chromatographic analysis: analysis of the prepared compounds was achieved by thin-layer chromatography (TLC) using silica gel 60 F254 thin-layer chromatoplates (20–20 cm, 0.25mm thickness, E. Merck). Prepared degradation products were run alongside as references and spots were detected under ultraviolet light at λ 254 nm and made visible by spraying the plates with a freshly prepared Hanes-Isherwood reagent.

Scanning electron microscope: the microstructures of the orange peels and the outer crust of apricot kernel were investigated using SEM Hitachi S-4800, Japan and the image was taken at 25KV operation condition. EDX mapping was analyzed using the unit connected to the microscope.

2.4. Batch sorption studies

Stock ethion solution of strength 7g/L was prepared. Batch studies were conducted for evaluating the adsorption potential of ethion on (orange peels and the outer crust of apricot kernel). Also, the kinetics and equilibrium parameters were studied. Adsorption experiments were carried out in an isothermal rotary shaking at 150 rpm and 30°C using a series of 10 mL polythene vial containing 6mL of initial concentrations of ethion solution. The initial pH values of the solutions were previously adjusted with buffer solutions of pH 1-11. The experiments were carried out at the original pH of the ethion solution (pH = 5). To start each adsorption test, ethion was added to water samples (6 mL) with predetermined conditions including initial ethion concentration, pH, adsorbent dosage, and the contact time. Ethion residues was then isolated from aqueous layers by extracting three times each with 25 mL of chloroform and sodium chloride solution (salting out, make separation easily) and was shaken for 2 min. The organic layers were dried over anhydrous sodium sulfate. The residual adsorbate (ethion) concentration was analyzed using a UV spectrophotometer (Shimadzu, Japan) at wavelength of λ 295 nm with Standard Methods.

2.5. Kinetic study

The adsorption kinetics study was performed by using 7g/L ethion concentration and with an adsorbent dosage of 16.5 g/L for (orange peels and the outer crust of apricot kernel). The samples were withdrawn at different pre-decided time intervals. All these samples were filtered, extracted and analyzed for residual concentrations of ethion as above.

2.6. Adsorption equilibrium and isotherm study

Separate isotherm studies were conducted for orange peels and the outer crust of apricot kernel with initial ethion concentration (7g/L) and adsorbent dosages of 4, 8, 16.5, 25 and 33 g/L. Equilibrium contact times determined from the kinetic studies aforementioned were used for these tests. After shaken for 24 hours, the samples were filtered, extracted and analyzed for residual ethion concentrations as previously. The effect of initial concentrations of ethion (1, 1.5, 3.5,5, 7, 9 and 12 mg/L) on the capacity of adsorption onto orange peels and the outer crust of apricot kernel was studied.

3. Results and discussion

3.1. FTIR spectroscopy of adsorbent

FTIR spectroscopy is the widely used technique to determine functional groups, structure determination, and identification of organic compound and study of chemical groups. Figures 1 and 2 show the FTIR spectroscopy for orange peels and the outer crust of apricot kernel. The peak at 727 cm−1 is due to C-C stretching, the absorption peaks at 3414 cm−1 -3472 cm−1 correspond to the stretch vibration of -O-H. The peaks at 2925 cm−1 and 2848 cm−1 related to CH2 stretch vibration. Peaks at 1746–1647 cm−1 correspond to the stretching vibration absorption of C=O and, the peak at 1116-1162 cm−1 is due to vibration absorption of C-O [19]. The FTIR of ethion gives absorption peaks at 2980, 2936 and 2901 cm−1 ascribed to aliphatic C-Hs. The sharp peak at 1016 cm−1is assigned to PO-Et and a band at 960 cm-1to POC-C. In addition, the bands at 816,796,651 and 505 cm−1 are assigned to P-OEt, P=S and P-S, respectively. The spectrum of ethion adsorbed fruits waste, Figures 1 and 2, exhibits the characteristic

bands of ethion at 2980 (aliphatic C-Hs), 1016(PO-Et), 960 (POC-C), and 651 (P=S) cm-1[20, 21].

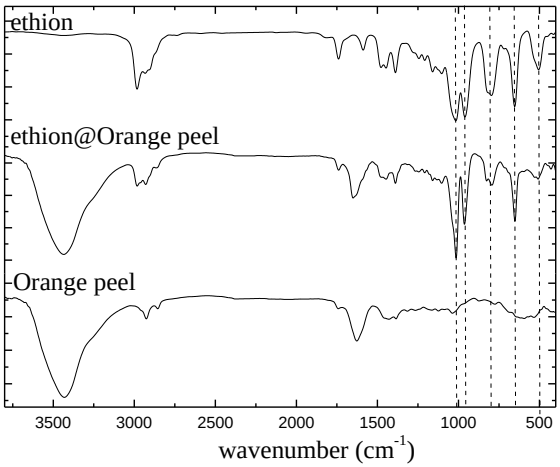


Fig. 1. FTIR spectrum of orange peel and ethion insecticide and orange peel after adsorption

3.2. *Microstructure screening by SEM/EDS*

SEM/EDS was represented the important technique for determination of the absorber materials because it providing more information about the surface structure of the orange peel and apricot kernel. The elemental composition of orange peel and apricot kernel was determined using microscopic analysis. Figure 3 showed the SEM image and EDX mapping of the outer crust of apricot kernel before and after adsorption of ethion from water. We concluded that the porosity of the outer crust of apricot kernel was decreased much after adsorption. Moreover, EDX of the outer crust of apricot kernel particles showed characteristics peaks related to carbon and oxygen. More interestingly is the appearance of peaks in EDX of the outer crust of apricot kernel after adsorption related to phosphorus and sulfur; these data confirm the presence of ethion insecticide in the pore of the outer crust of apricot kernel. The surface texture and elemental analysis of second absorber (orange peels) was also determined using SEM/EDS analysis. Figure 4 show highly cavity in the texture of orange peel, this texture was completely changed after ethion insecticide adsorption. Besides, EDX show excellent information about elemental composition of orange peels, it shows characteristic peaks related to carbon and oxygen. The more useful data comes from the elemental mapping is the appearance of phosphorus and sulfur element in the composition of the absorber; these confirm the uptake of ethion in the cavity of orange peels.

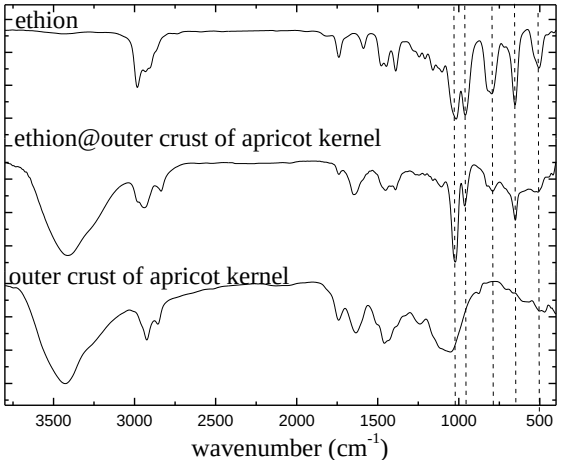


Fig. 2. FTIR spectrum of the outer crust of apricot kernel, ethion insecticide and the outer crust of apricot kernel after adsorption

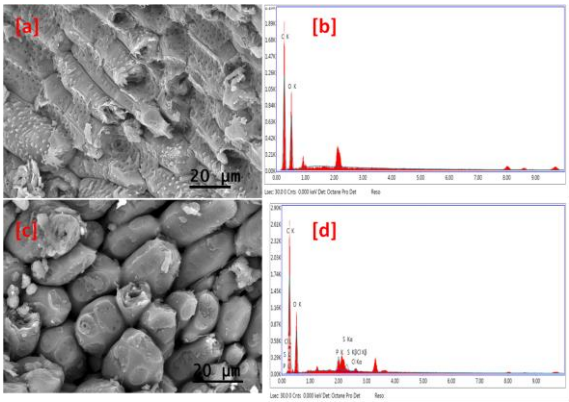


Fig. 3. [a, b] SEM image and EDX mapping of the outer crust of apricot kernel, [c,d] SEM image and EDX mapping of ethion insecticide adsorbed onto the outer crust of apricot kernel.

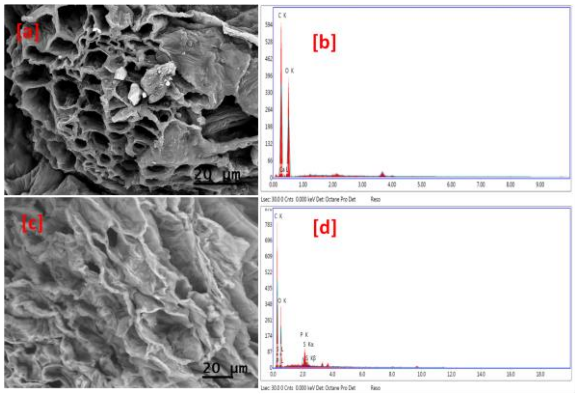


Fig. 4. [a, b] SEM image and EDX mapping of the orange peels, [c,d] SEM image and EDX mapping of ethion insecticide adsorbed onto the orange peels.

3.3. The factor affecting on the adsorption uptake

3.3.1. Effect of adsorbent dosage

The removal percentages of ethion as functions of dosages of the three adsorbents are shown in Fig. 5. Ethion removal increased with the increase in dosages of adsorbents up to certain levels and then leveled off. It was observed that, a 95.5 % ethion removal was achieved when the outer crust of apricot kernel dosage was 100 mg/6mL (stock solution with initial ethion concentration was 7g/L), but for orange peels, ethion removal was 78%.

3.3.2. Effect of pH

The pH of the solution plays an important role in the removal of ethion insecticide from wastewater because it effects on the surface charge of the orange peel and apricot kernel. The effects of pH on ethion removal with the two selected adsorbents were shown in figure 6. It seems that the ethion removal capabilities of outer crust of apricot kernels were increased by pH under the given test conditions. The adsorption of ethion with other absorbers was decreased when pH was higher 7. The difference in adsorption capacity of orange peels and the outer crust of apricot kernel at different pHs may be due to the difference in the concentrations of proton and hydroxyl ions in the solutions. The proton ions within low pH environments can neutralize those negative particles, reduce the hindrance to diffusions of ethion molecule and consequently increase the chances of their adsorption. High pH environments led to high concentration of OH^-, which can increase the hindrance to the diffusions of ethion molecules and thus reduce the opportunities of their adsorption [22-24].

3.3.3. Adsorption kinetics

The changes of ethion removal efficiency with contact time for various adsorbents at initial ethion concentration are shown in figure 7. The results show that t the removal rate followed the pseudo-second order model. Figure 7 also shows that about 83% - 87% ethion removal took place within the first 2 h of contact time in case of ethion- the outer crust of apricot kernel systems under the given conditions (i.e., the initial ethion concentrations 7g/L; adsorbent dosage: 16.5 g/L). After two hours the rate of removal was very slow. The removal profile of ethion by the outer crust of apricot kernel became flat after 6 h of adsorption. The results in figure 7 also indicated that due to the high availability of vacant sites in the outer crust of apricot kernel, and high affinity of organic compounds to the outer crust of apricot kernel, a high degree of concentration gradients and partitioning existed between solid and liquid phases. Once the availability of ethion diminished in the solutions, further uptakes were not observed.

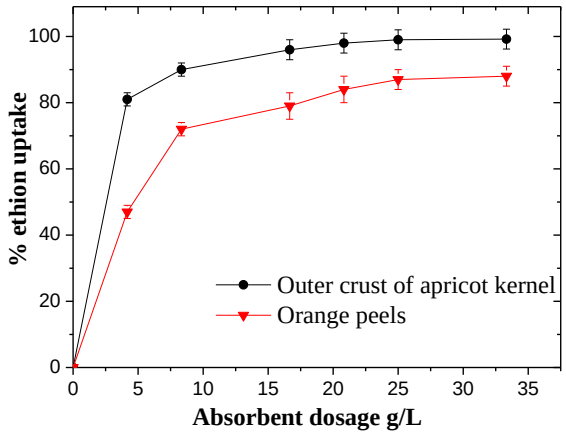


Fig. 5. Effect of adsorbent dose for ethion removal (ethion concentrations 7g/L, agitation speed = 150 rpm, pH 5, and temperature = 30 ◦C).

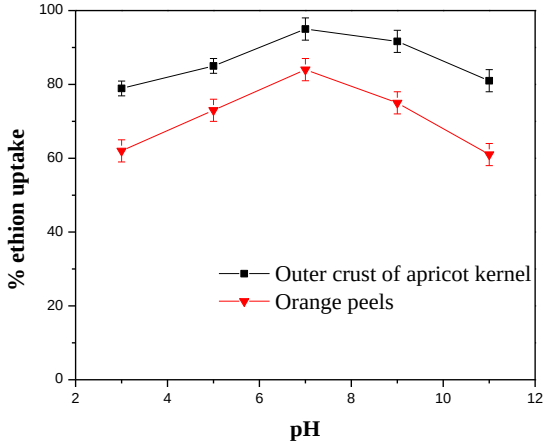


Fig. 6. Effect of pH on ethion removal (ethion concentrations 7g/L, adsorbent dose = 16.5 g/L, agitation speed = 150 rpm, and temperature = 30 ◦C).

3.3.4. Effect of initial ethion concentrations

Figure 8 shows that the adsorption capacity at low initial concentration of ethion is high. However, at higher concentration of ethion the adsorption capacity remained constant (Hameed et al 2009). Along with the increase of initial ethion concentrations from 1 to 12 mg/L using the three low cost adsorbents, the adsorption capacity increased from 58 to 378 mg/g;

however, the removal percentage decreased from 96 to 52 % for orange peels, the adsorption capacity increased from 48.4 to 283 mg/g; however, the removal percentage decreased from 99.8to 57 % for the outer crust of apricot kernel. A similar observation was reported for the adsorption of dyes and heavy metals on orange peel [22, 25, 26].

The adsorption kinetics of ethion onto low cost adsorbent was modeled using pseudo-second order [27].

$$\frac{t}{q_t} = \frac{1}{k_2\, q_e^2} + \frac{1}{q_e}\, t$$

Where q_t (mg g-1) is the solid loading at time t (min), q_e is the concentration at equilibrium (i.e., for t=∞), and k_2 (g mg-1 min-1) is the rate constant of the pseudo-second order equation (Figure 9).

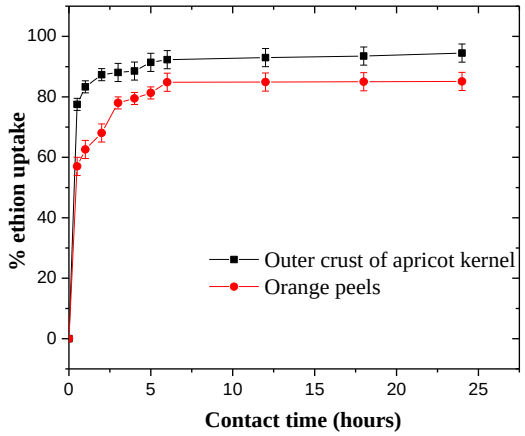


Fig. 7. Adsorption kinetics profiles for ethion removal (ethion concentrations 7g/L, adsorbent dose = 16.5 g/L, agitation speed = 150 rpm, pH 5, and temperature = 30 ◦C).

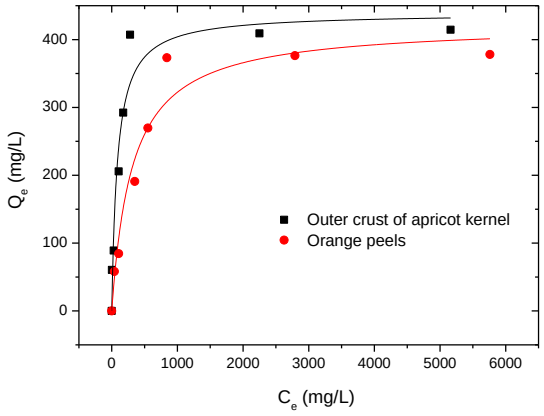


Fig. 8. Adsorption kinetics profiles for ethion removal with different initial concentrations

3.3.5. Adsorption isotherms

Experimental isotherm is useful for describing the adsorption capacity of orange peels and the outer crust of apricot kernel. The isotherm modeling is important in designing adsorption systems, the most widely model is Langmuir and Freundlich. The importance of Langmuir model is identification of monolayer adsorption on a surface [28, 29]. The linear form of the Langmuir isotherm was shown in the following equation [30].

$$\frac{C_e}{q_e} = \frac{1}{q_{max} k_L} + \frac{C_e}{q_{max}}$$

Where Ce (mg/L), qe (mg/g), kL and qmax are the equilibrium concentration of the orange peels and the outer crust of apricot kernel, the amount of ethion insecticide adsorbed per unit mass of a orange peels and the outer crust of apricot kernel, Langmuir constants, and maximum adsorption capacity, respectively.

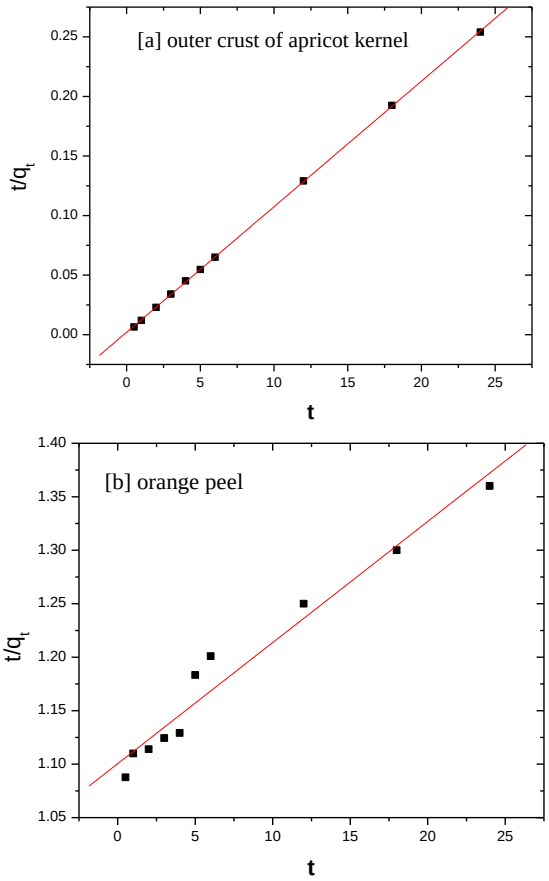


Fig.9. Pseudo-second order kinetics model fit for ethion adsorption

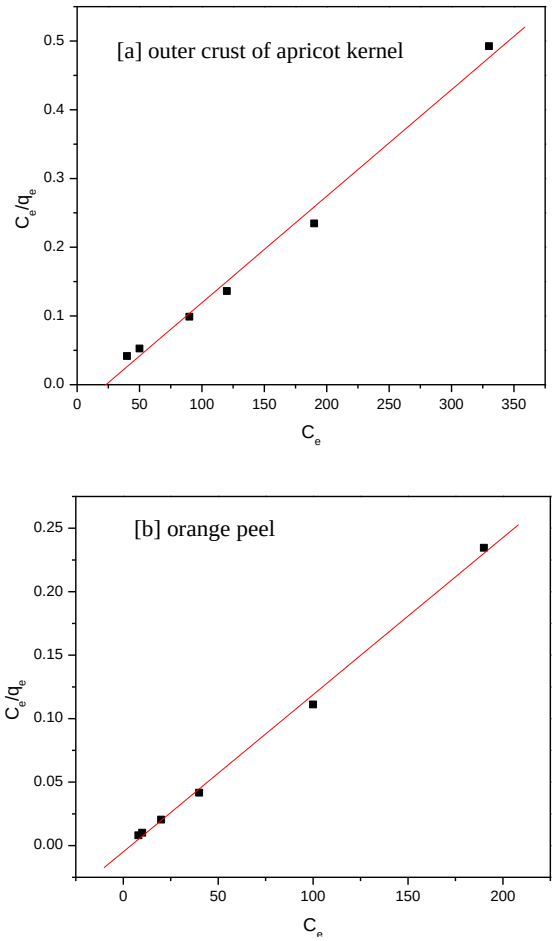


Fig.10. Langmuir isotherm for constant ethion concentration and varying adsorbent dose (ethion concentrations 7 g/L, 24 hours contact time, agitation speed = 150 rpm, pH 5, room temperature = 30 ◦C).

Figures 10 show a linear relationship of Ce/qe versus Ce using experimental data obtained, suggesting the applicability of the Langmuir model (R2 = 0.96-0.99). The mechanism of ethion uptake on orange peels and the outer crust of apricot kernel is monolayer significant coverage the outer surface. Values of qmax and kL calculated from the plot shown in figure 10 using the least square methods are listed in Table 1.

The Freundlich isotherm is given as [31].

$$\ln qe = \ln KF + (1/n) \ln Ce$$

Where KF ((mg/g), n are Freundlich constant and roughness indicator of the adsorption capacity, respectively. The relation between ln qe and ln Ce are shown in (Figure 11). The value of n was found to be 0.448-1.955, indicating that the adsorption condition was favorable.

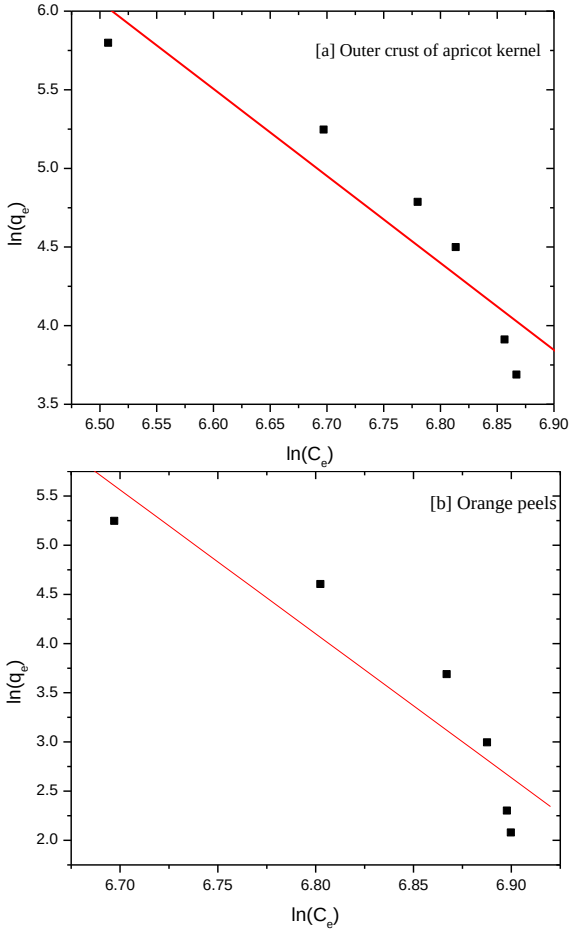


Fig.11. Freundlich isotherm for constant ethion concentration and varying adsorbent dose (ethion concentrations 7g/L, 24 hours contact time, agitation speed = 150 rpm, pH 5, room temperature = 30 ◦C).

Table 1 Langmuir and Freundlich parameters

Samples	Langmuir isotherm			Freundlich isotherm		
	q_{max} (mg/g)	k_L	R^2	n	k_F	R^2
Outer crust of apricot kernel	405	1.702	0.99	1.95	0.403	0.84
Orange peels	330	0.907	0.99	1.02	0.221	0.88

4. Conclusions

The collected orange peels and the outer crust of apricot kernel can be effectively used as adsorbent for the removal of ethion from aqueous solutions. The pH has highly effective on the absorption process towards ethion molecules. The removal efficiency of ethion increased when the pH of adsorption system increased then decreased at pH greater than 7. The best kinetic model fitted to obtained data is the pseudo-second-order equation. The Langmuir and

Freundlich isotherm models were used to express the sorption phenomena of ethion to the collected materials. Consequently, linear regression of the experimental data showed that the Langmuir equation best represented ethion adsorption data. The maximum adsorption uptake of ethion onto orange peels was 330 mg/g, however the higher adsorption uptake was found in presence of the outer crust of apricot kernel and amounted 405 mg/g. The experimental results indicated that the orange peels and the outer crust of apricot kernel were economically promising materials.

5. Acknowledgements

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6. Conflict of interest

The authors declare that they have no conflict of interest.

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