



## A comparative adsorption study with different agricultural waste adsorbents for removal of oxamyl pesticide

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### ABSTRACT

The use of cheap and eco-friendly adsorbents prepared from abundantly available pomegranate peel (Pomegranate activated carbons, PAC) and Banana peel (Banana activated carbons, BAC) compared with Commercial activated carbons (ACs) were used for the removal of an insecticide and nematicide oxamyl from aqueous solutions. The ACs were characterized by Fourier transform infrared spectroscopy, Scanning electron microscope, Transmission electron microscopy, and energy dispersive. The effects of initial pesticide concentration and contact time on the biosorption of oxamyl onto the three different adsorbents were investigated. The equilibrium data of kinetic studies were attained at 180 min. The experimental results show increasing adsorption of adsorbents with increasing oxamyl concentrations. The experimental isotherms data were analyzed using Freundlich, Temkin, and Dubinin–Radushkevich isotherm equations. The best experimental data were obtained for all adsorbents by the Freundlich isotherm model with high correlation coefficients ( $R^2 \geq 0.9699$ ). The results suggest that the oxamyl adsorption onto PAC, BAC, and Commercial AC is physical. Kinetic studies indicated that the pseudo-second-order fitted well to the experimental data. The results revealed that two adsorbents can be used as low-cost biosorbents for the oxamyl removal from aqueous solution.

*Keywords:* Activated carbon; Agricultural waste adsorbents; Oxamyl; Adsorption isotherm; Adsorption kinetics

### 1. Introduction

Pesticides are harmful to life because of their toxicity, carcinogenicity, and mutagenicity [1]. The harmful influence of pesticides on human health and the environment has resulted to the imposition of stringent legislation on drinking water quality in many countries [2]. Oxamyl, (N,N-dimethylcarbamoxyloxyimino-

2-(methylthio) acetamide), is a carbamate compound used in a wide range of agricultural situations. It is systemic and active as an insecticide [3] or a nematicide [4,5]. The risk of contamination of oxamyl is enhanced by its high solubility in water (280 g/L) and very low soil sorption coefficient. It is used for the control of nematodes in vegetables, bananas, pineapple, peanut, cotton, Soya beans, tobacco, potatoes, sugar beet, and other crops. The toxicity of pesticides

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and their degradation products make these chemical substances potential hazard by contaminating our environment [6]. Therefore, the removal of pesticides from water is one of the major environmental concerns nowadays.

There are several procedures available for pesticides removal from water which includes photocatalytic degradation [7,8], ultrasound combined with photo-Fenton treatment [9], advanced oxidation processes [10], aerobic degradation [11], electrodialysis membranes [12], ozonation [13], and adsorption [14]. Adsorption process using commercial activated carbons (ACs) is very effective for pesticides removal from wastewater, but its high cost limits its commercial application [15,16]. Thus, there is a growing need to find low cost and efficient, locally available materials for the pesticides removal. Lately, there has been an increase in the use of agricultural wastes as adsorbents which include: rice husk [17], pineapple stem [18], bagasse pith [19], maize cob [20], wood sawdust [21], hazelnut shell [22], papaya seeds [23], leaves [24], fruit peels [25], etc. The advantage of using agricultural waste materials as adsorbents is that it saves disposal costs while alleviating potential environmental problems [26]. Moreover, agricultural waste products are usually built up of lignocellulosic materials i.e. contain mainly cellulose, hemicellulose, and lignin, which are considered beneficial to adsorption [27].

Among the agricultural wastes, Pomegranate (*Punica granatum* L.) as an important fruit crop of many tropical and subtropical regions of the world, grown especially in the moderate climates of Mediterranean countries. It is widely consumed fresh and in processed forms as juice, jams, and wine. Pomegranate peel as a by-product of the pomegranate juice industry is inexpensive. Pomegranate peel material is composed of several constituents, including polyphenols, ellagic tannins, gallic, and ellagic acids [28]. Banana (*Musa* spp.) is considered as one of the most important favorable and popular fruits in Egypt and all over the world. In Egypt, the cultivated areas reach 45.802 thousand feddans which produce about 760.505 thousand tons of banana fruits [29]. The utilization of agro-wastes as adsorbents is currently receiving wide attention because of their abundant availability and low cost owing to relatively high fixed carbons and presence of porous structures.

The use of agricultural wastes as precursor for ACs will provide solution to environmental problems caused by wastes as well as they produce benefit products from low-cost materials. Therefore, the aim of this work is to assess the ability of low-cost adsorbents such as Pomegranate activated carbons (PAC) and Banana activated carbons (BAC) (in nanoscale)

compared with Commercial AC for removal of oxamyl from aqueous solution. Experimental parameters affecting the adsorption process such as initial oxamyl concentration and contact time were optimized. The isotherm and kinetic data of the adsorption were studied to describe the adsorption process.

## 2. Materials and methods

### 2.1. Adsorbate

The pesticide used as adsorbate in the experiments is oxamyl. Some properties and chemical structure of the pesticide are given in Table 1.

### 2.2. Adsorbents

Banana and pomegranate wastes were collected from local market in Egypt.

### 2.3. Biosorbent preparation

The waste peels of banana and pomegranate fruits were first washed with double distilled water and dried in an oven at 80°C overnight. The Commercial AC was purchased from Sigma-Aldrich. The dried adsorbents PAC, BAC, and AC were thermally activated at 500°C in a muffle furnace for 1 h. After activation, the ash contents were removed by washing with distilled water and dried in an oven at 110°C overnight [31]. The adsorbents will be ground in nanoscale using mechanical ball mill RWTC Planetary Ball mill type (RM400).

### 2.4. Adsorption experiments

The adsorption experiments of oxamyl onto PAC, BAC, and AC were carried out in a set of 150 Erlenmeyer flasks. The pesticide solutions (100 mL of each) of various initial concentrations in the range (500–2,500 mg/L) were added to separate flasks.

A fixed dose of 0.1 g/100 mL of the different adsorbents was added to each flask covered with glass stopper at normal pH (6.7) and room temperature (25°C ± 2), for contact time 24 h, with occasional agitation to reach equilibrium.

For kinetic studies of oxamyl onto PAC, BAC, and AC, 100 mL of the solution containing 500 mg/L with 0.1 g of each adsorbents was taken at different time intervals from 5 to 300 min to determine the equilibrium time. From the triplicate flasks, 40 mL of filtrate was transferred to a separatory funnel and extracted successively three times with 20, 15, and 10 mL

Table 1  
Some properties and chemical structure of oxamyl

Common name	Oxamyl
Chemical structure	$\begin{array}{c} \text{CH}_3\text{-NH} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{O} \end{array} \text{-O-} \begin{array}{c} \text{N}=\text{C} \\ \diagup \\ \text{SCH}_3 \\ \diagdown \\ \text{CON}(\text{CH}_3)_2 \end{array}$
Name	N, N-dimethyl-2-methylcarbamoyloxyimino-2-(methylthio) acetamide
Pesticide group	Carbamate
Activity	Systemic insecticide and nematicide
Molecular formula	C <sub>7</sub> H <sub>13</sub> N <sub>3</sub> O <sub>3</sub> S
MW <sup>a</sup>	219.3
S <sup>b</sup> (g/L)	280 g/L
Formulation	10% GR
Rate of application	20 kg/Feddan

Note: Data were obtained from [30].

<sup>a</sup>Molecular weight.

<sup>b</sup>Solubility in water at 25°C.

portions of dichloromethane. The combined extracts were dried on anhydrous sodium sulfate to remove moisture content and evaporated using a rotary evaporator on a water bath at 40°C. All samples were cleaned by filtration with Target Nylon (0.45 μm) prior to analysis in order to minimize the interference of the carbon fines with the analysis. The extracted samples were analyzed using HPLC with DAD.

Isothermal studies of oxamyl were conducted with an adsorbent quantity of 0.1 g with oxamyl concentration of 500, 1,000, 1,500, 2,000, and 2,500 mg/L in identical conical flasks containing 100 mL of distilled water. Blank solutions were treated similarly (without adsorbent).

The sorption capacity was determined using the following equation, taking into account the concentration difference of the solution at the beginning and at equilibrium [32]:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where  $C_0$  and  $C_e$  are the initial and the equilibrium oxamyl concentrations in mg/L, respectively,  $V$  is the volume of solution (mL), and  $W$  is the amount of adsorbent used (g). The removal percent of oxamyl from solution was calculated by the following equation (Eq. (2)):

$$\text{Removal}(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

## 2.5. Analysis of oxamyl

The concentrations of oxamyl in the solutions before and after adsorption were determined using an Agilent HPLC 1260 infinity series (Agilent technologies) equipped with a quaternary pump, a variable wavelength diode array detector (DAD), and an auto-sampler with an electric sample valve. The column was *Nucleosil C<sub>18</sub>* (30 × 4.6 mm (i.d) × 5 μm) film thickness. The mobile phase was 60/40 (V/V) mixture of HPLC grade acetonitrile/water. The mobile phase flow rate was 1 mL/min. The wavelength was 220 nm. The retention time of oxamyl was 2.4 min and the injection volume was 5 μL under the conditions.

## 2.6. Characterization of AC

ACs were analyzed by Fourier Transform Infrared (FTIR) on PerkinElmer 1720 FTIR in order to identify the functional groups that exist on the surface of the ACs.

The surface morphology of the ACs PAC and BAC was performed by a Scanning Electron Microscopy (SEM) (JEOL 5400), at 30 kV accelerated voltage. Prior to scanning, each adsorbent was coated with a thin layer of gold using a sputter coater to make it conductive. Transmission electron microscopy (TEM) samples were prepared by dropping diluted solutions of nanoparticles onto 400 mesh carbon-coated copper grids with the excessive solvent immediately evaporated. TEM at an operating voltage of 200 kV determined the morphology and electron diffraction pattern of the nanoparticles. In order to elucidate the biosorption

nature of PAC, BAC, and AC, the analyses of energy dispersive spectroscopy (EDX) (Jeol, JSM-5800) were used.

### 3. Results and discussion

#### 3.1. Characterization of adsorbents

The FTIR is an important technique to qualitatively determine the characteristic of functional groups, which make the adsorption behavior possible. The

FTIR spectra of the prepared adsorbents were shown in Fig. 1.

#### 3.1.1. FTIR analysis

Fig. 1 shows the FTIR spectra of the prepared nano banana (BAC) and nano pomegranate (PAC). The bands in the region of 3,427 and 3,286  $\text{cm}^{-1}$  are corresponding to phenolic OH stretching. Bands at 2,920 and 2,951  $\text{cm}^{-1}$  indicate C–H stretching, and peak

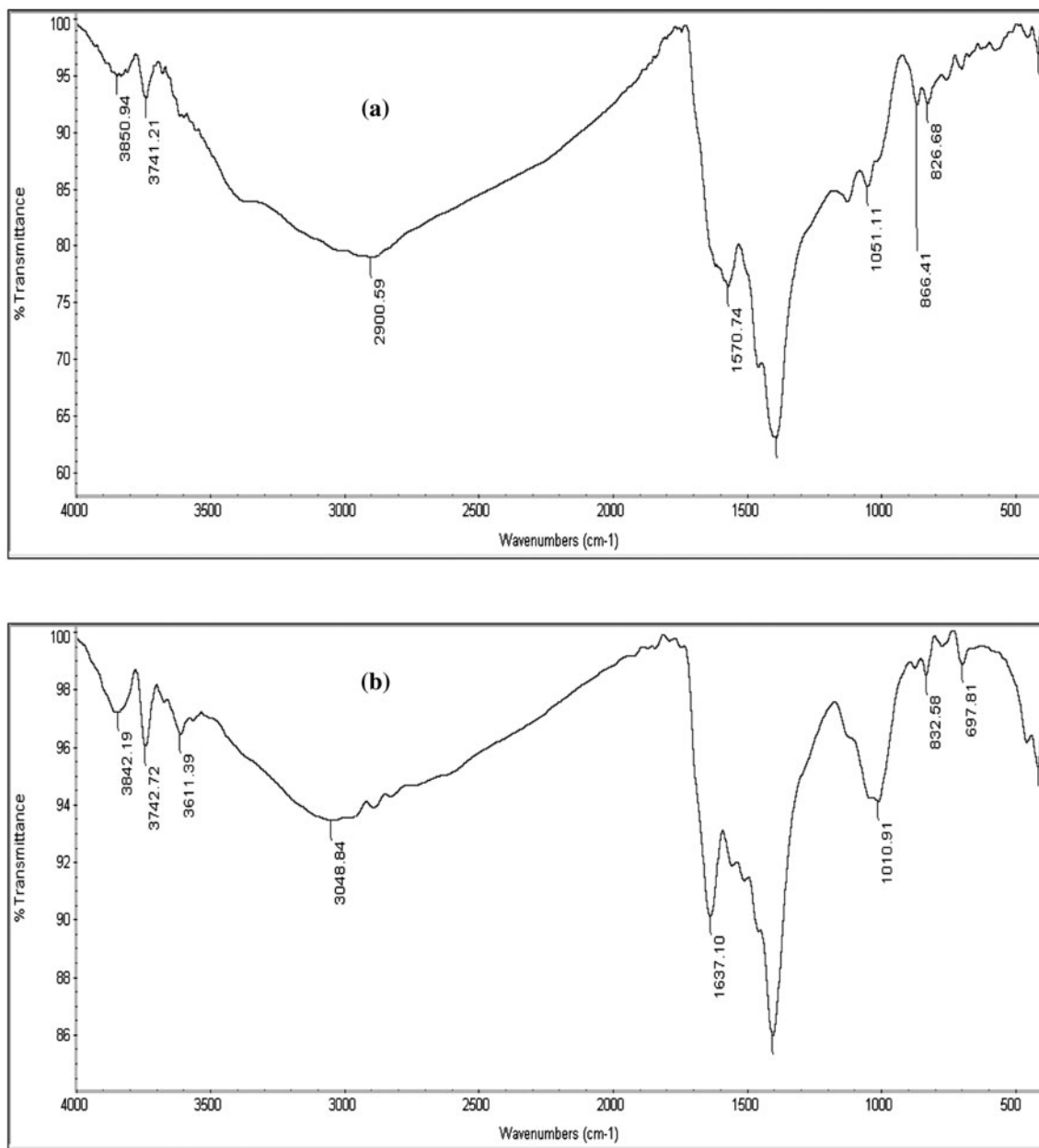


Fig. 1. FTIR spectrum of PAC (a) and BAC (b).

around  $1,570\text{ cm}^{-1}$  can be ascribed to C–C stretching vibration in aromatic rings [33]. The absorption at  $1,051\text{ cm}^{-1}$  indicates the existence of C–O stretching vibrations in alcohols, phenols, acids, ethers, or esters [34]. The weak band in the region of  $866\text{ cm}^{-1}$  is attributed to amine groups.

### 3.1.2. Morphology of the prepared BAC and PAC nanoparticles

A SEM was used to examine the surface of the two prepared (ACs) adsorbents.

Fig. 2 shows the SEM photographs of the prepared ACs obtained from BAC and PAC with  $500\times$  magnifications showing progressive changes in the surface of the particles. There are observed significant differences between the surface of BAC and PAC. Many pores are available on their surfaces whereas the external surfaces of pomegranate and banana have the pores with different sizes and different shapes. It can be seen from the micrographs that the external surfaces of the prepared ACs are full of cavities and quite irregular. The relatively smooth external surface of banana nanoparticles suggests that they are composed of countless tiny primary nanoparticles. The aggregation of these tiny primary nanoparticles can produce large numbers of intra-aggregated pores, resulting in a high microporous volume (as shown in Fig. 2(a)). This is inconsistent with the following TEM results. It is clear that prepared ACs appear to have numbers of pores, where there are good possibilities for oxamyl pesticide to be trapped and adsorbed onto these pores.

Fig. 3 presents the TEM image of the PAC nanoparticles, which appeared as homogeneous rod shapes  $50\text{--}120\text{ nm}$  in diameter. While BAC appeared as slightly spherical shape and ranged from  $25\text{ to }37\text{ nm}$  in diameter. The selected area of the electron diffraction patterns of the prepared samples show sharp spots that are indicative of single crystalline materials.

### 3.1.3. EDX analyses

In order to know the composition of banana and pomegranate peels, elemental analysis was done with the use of EDX analysis. The EDX analysis is shown in Fig. 4 which shows the presence of various elements along with a high amount of potassium.

### 3.2. Effect of contact time

The adsorption experiments were carried out for different contact time in the range of  $0\text{--}300\text{ min}$ . Fig. 5 shows the effect of contact time on the adsorption of oxamyl with initial concentration of  $500\text{ mg/L}$ , adsorbent dose ( $0.1\text{ g}/100\text{ mL}$ ), temperature ( $25 \pm 2^\circ\text{C}$ ), normal pH ( $6.7$ ) by PAC, BAC, and AC. The pesticide adsorption rate is high for the first  $30\text{ min}$  and finally equilibrium is established after about  $180\text{ min}$ . The rapid pesticide adsorption at the initial stages of contact time could be attributed to the abundant availability of active sites on the surface of adsorbents. Afterwards with the gradual occupancy of these sites, the adsorption became less efficient. Further increase in contact time did not enhance the adsorption, so, the optimum contact time was selected as  $180\text{ min}$  for further experiments.

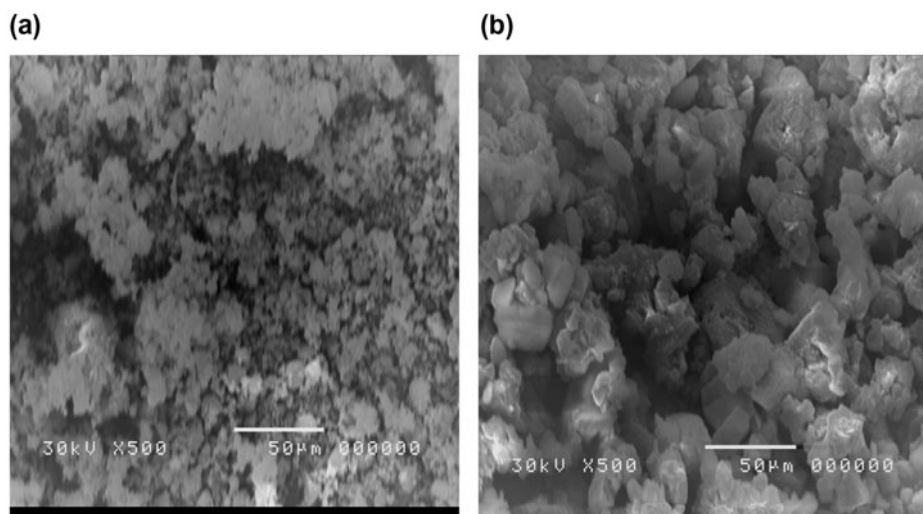


Fig. 2. SEM for the BAC (a) and SEM for the PAC (b).

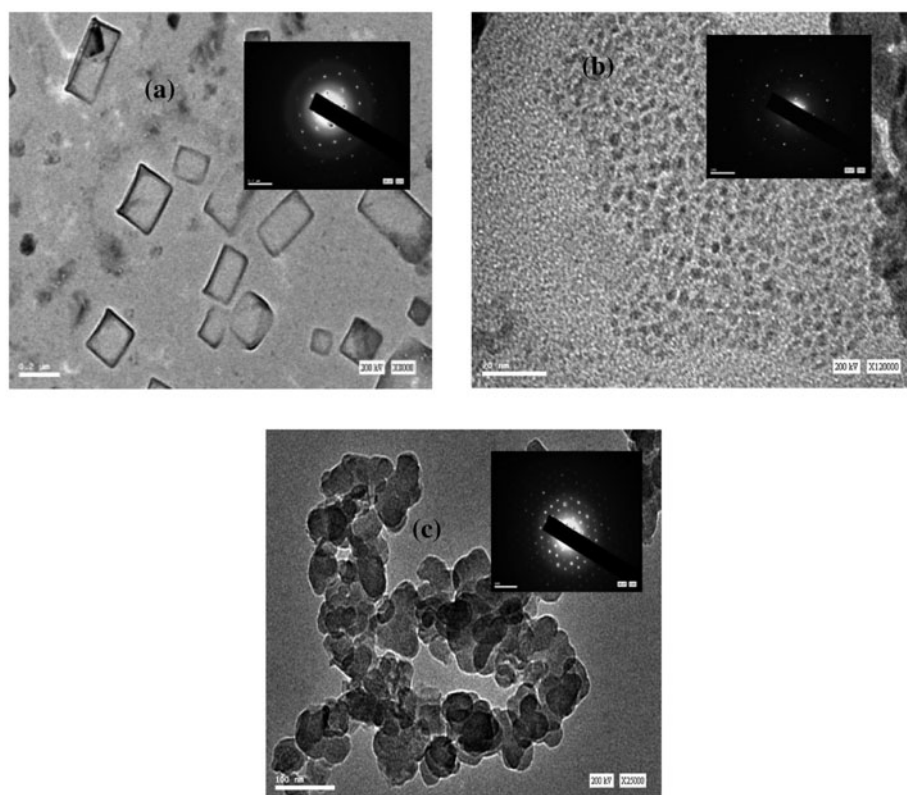


Fig. 3. TEM micrographs of BAC (a), PAC (b), and AC (c).

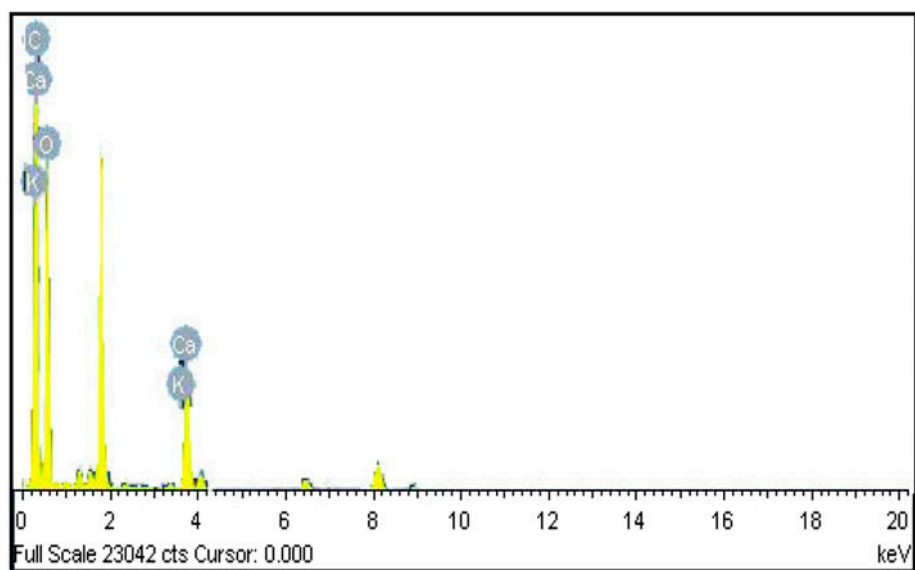


Fig. 4. EDX analysis of BAC.

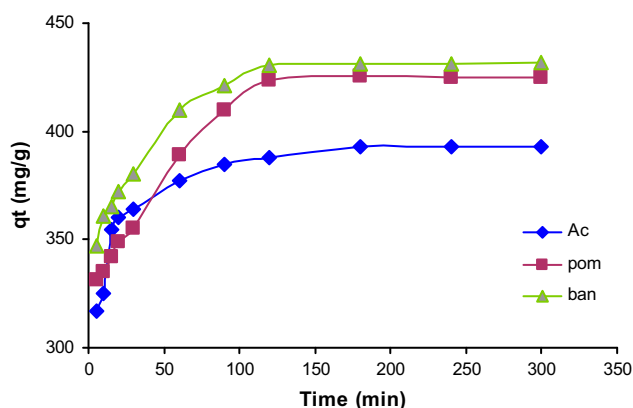


Fig. 5. Effect of contact time for removal of oxamyl by AC, PAC, and BAC ( $C_0 = 500$  mg/L, pH 6.7, temperature  $25 \pm 2^\circ\text{C}$ ).

### 3.3. Effect of initial concentration

The effect of initial pesticide concentration in the solution on the rate of adsorption onto three different adsorbents (AC, PAC, and BAC) was studied. The experiments were carried out at fixed adsorbent dose (0.1 g/100 mL) in the solution, temperature ( $25 \pm 2^\circ\text{C}$ ), normal pH (6.7), and at different initial concentrations of oxamyl (500, 1,000, 1,500, 2,000, and 2,500 mg/L). The wide range of initial concentration of oxamyl was used to observe the adsorption performance of oxamyl onto three adsorbents. The results are given in Fig. 6 indicating that equilibrium adsorption capacity increases with increase in initial concentration of oxamyl. This reveals an increase in equilibrium adsorption capacity from 412.27 to 2,125.4, 440.92 to 2,109.43, and 479.32 to 2,120.76 mg/g with increasing

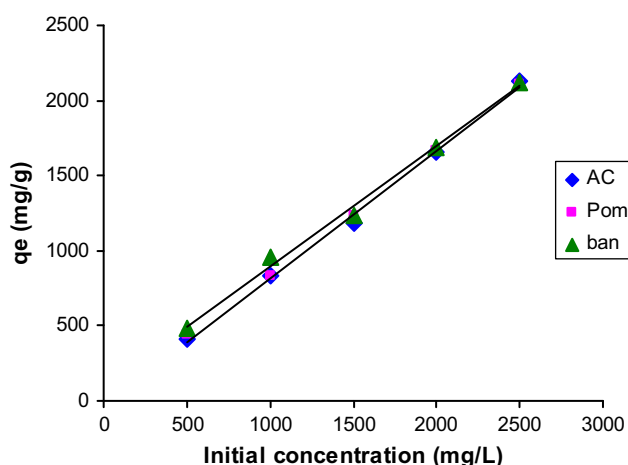


Fig. 6. Effect of initial concentration for removal of oxamyl on AC, PAC, and BAC.

initial pesticide concentrations from 500 to 2,500 mg/L for AC, PAC, and BAC, respectively. This is probably due to increase in the driving force of the concentration gradient. The effect of initial pesticide concentrations on the different adsorbents was found to be of considerable significance for the pesticide used.

### 3.4. Biosorption isotherms

The equilibrium isotherms are used to describe the experimental data. The adsorption isotherm is important from both theoretical and practical point of view. To optimize the design of an adsorption system for the adsorption of adsorbates, it is important to establish the most appropriate correlation for the equilibrium curves [35]. The equation parameters of these equilibrium models often provide some insight into the sorption mechanism, the surface properties, and the affinity of the adsorbent. Various isotherm equations like those of Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D–R) are used to describe the equilibrium characteristics of adsorption.

#### 3.4.1. The Freundlich isotherm

The Freundlich isotherm model assumes a heterogeneous adsorption surface with sites that have different energies of adsorption and provides no information on the monolayer adsorption capacity [36]. The Freundlich isotherm model has the form:

$$q_e = K_F C_e^{1/n} \quad (3)$$

Eq. (3) can be linearized in the logarithmic form (Eq. (4)) and the Freundlich constants can be determined:

$$\log q_e = \log K_F + 1/n \log C_e \quad (4)$$

where  $q_e$  (mg/g) is the equilibrium value for removal of adsorbate per unit weight of adsorbent,  $C_e$  (mg/L) is the equilibrium concentration of pesticide in solution, and  $K_F$  is the Freundlich constant (mg/g)  $(\text{L/mg})^{1/n}$  related to the bonding energy.  $K_F$  can be defined as the adsorption or distribution coefficient and represents the quantity of pesticide adsorbed onto adsorbent for unit equilibrium concentration.  $1/n_F$  is the heterogeneity factor and  $n_F$  is a measure of the deviation from linearity of adsorption. The data obtained from linear Freundlich isotherm for the adsorption of oxamyl onto AC, PAC, and BAC are presented in Fig. 7(a) and Table 2. The higher determination coefficients ( $R^2$ ) of the Freundlich isotherm for

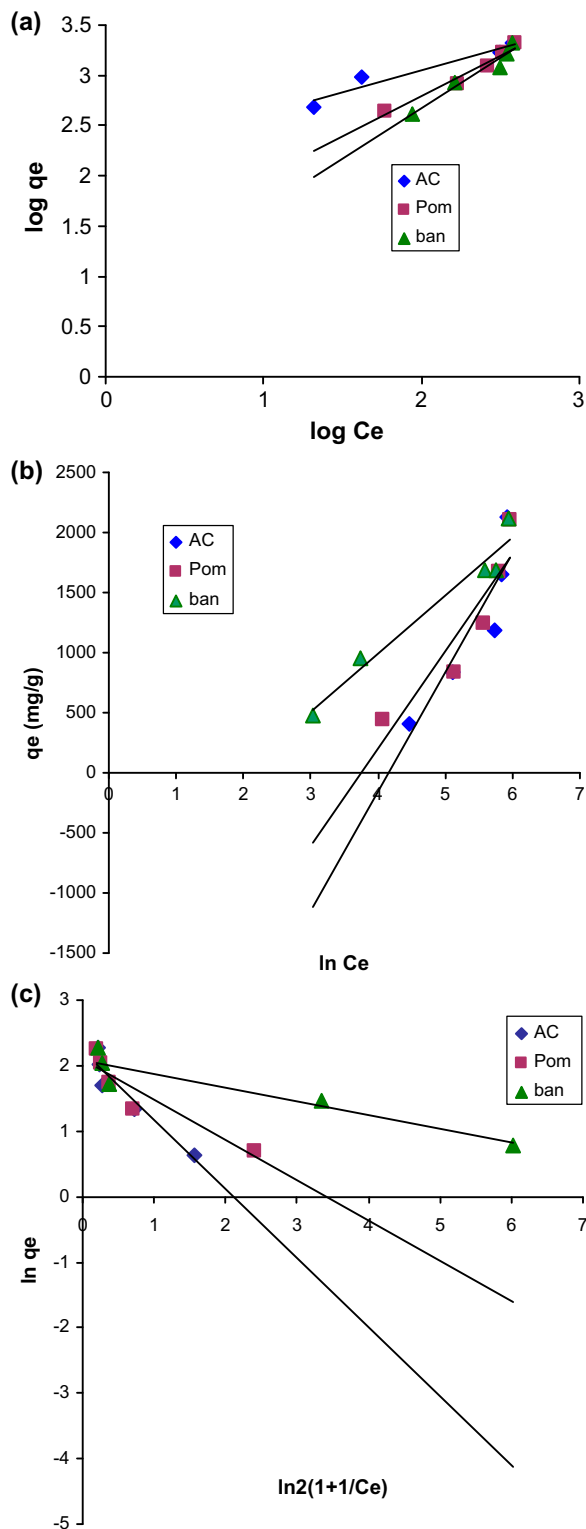


Fig. 7. (a) Freundlich adsorption isotherm for oxamyl adsorption on AC, PAC, and BAC; (b) Temkin adsorption isotherm for oxamyl adsorption on AC, PAC, and BAC; and (c) D-R isotherm for oxamyl adsorption on AC, PAC, and BAC.

the three adsorbents suggest that Freundlich isotherm can be used to fit the experimental adsorption data. Similar results have been reported for the adsorption of phosphate ions by pine cone [37].

#### 3.4.2. The Temkin isotherm

Temkin and Pyzhey [38] considered the effects of some indirect adsorbate or adsorbate interactions on adsorption isotherms and suggested that because of these interactions, the heat of adsorption of all the molecules in the layer would decrease linearly with coverage.

The linear form of Temkin isotherm is given as:

$$Q_{ad} = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e q \quad (5)$$

where  $RT/b = B$  is a constant related to heat of adsorption and  $b$  shows the variation of the adsorption energy (J/mol),  $T$  is the absolute temperature in Kelvin, and  $R$  is the universal gas constant, 8.314 J (mol/K). The constant  $b$  is related to the heat of adsorption.  $q_e$  (mg/g) and  $C_e$  (mg/L) are the amount adsorbed at equilibrium and the equilibrium concentration, respectively.  $A$  and  $b$  are constants related to adsorption capacity and intensity of adsorption. Plots of  $\ln C_e$  against  $q_e$  for the adsorption of oxamyl onto AC, PAC, and BAC are given in Fig. 7(b). The constants  $A$  and  $b$  are listed in Table 2. Examination of the data shows that the Temkin isotherm is not applicable to oxamyl adsorption onto AC, PAC, and BAC judged by low correlation coefficient  $R^2 \geq 0.831$ .

#### 3.4.3. The D-R isotherm

D-R proposed another equation used in the analysis of isotherms. D-R model was applied to estimate the porosity apparent free energy and the characteristic of adsorption [39]. The D-R isotherm do not assume a homogeneous surface or constant sorption potential and it has commonly been applied in the following form (Eq. (6)) and its linear form can be shown in Eq. (7):

$$q_e = q_m \exp(-K\epsilon^2) \quad (6)$$

$$\ln q_e = \ln q_m - \beta \epsilon^2 \quad (7)$$

where  $K$  is a constant related to the adsorption energy,  $q_e$  (mg/g) is the amount of pesticide adsorbed per g



Table 2  
Adsorption isotherms for removal of oxamyl by different adsorbents

Isotherm equation	Adsorbents		
	AC	Pom	Ban
Freundlich isotherm			
$K_F$ (mg g <sup>-1</sup> ) (mg L <sup>-1</sup> ) <sup>-1/n</sup>	147.706	15.251	4.572
$1/n$	0.4413	0.8062	1.0081
$R^2$	0.9345	0.9699	0.9481
Temkin isotherm			
$B$ (J/mol)	990.04	807.07	482.87
$A$ (L/g <sup>2</sup> )	64.071	42.355	6.939
$R^2$	0.8312	0.8504	0.9562
D–R isotherm			
$q_e$ (mg/g)	2,041.90	1,784.22	1,769.99
$E$ (kJ/mol)	1.70	2.231	3.818
$R^2$	0.9077	0.8491	0.8943
$\beta$	$1.723 \times 10^{-7}$	$1.004 \times 10^{-7}$	$3.429 \times 10^{-8}$

of adsorbent, and  $q_m$  represents the maximum adsorption capacity of adsorbent,  $\beta$  (mol<sup>2</sup>/J<sup>2</sup>) is a constant related to adsorption energy, while  $\varepsilon$  is the Polanyi potential that can be calculated from Eq. (8):

$$\varepsilon = RT \ln \left[ 1 + \frac{1}{C_e} \right] \quad (8)$$

The values of  $\beta$  and  $q_m$  can be obtained by plotting  $\ln q_e$  vs.  $\varepsilon^2$ . The mean free energy of adsorption ( $E$ , J/mol), defined as the free energy change when one mole of ion is transferred from infinity in solution to the surface of the sorbent, is calculated from the  $K$  value using the following relation (Eq. (9)) [40]:

$$E = \frac{1}{\sqrt{2\beta}} \quad (9)$$

The calculated values of D–R parameters are given in Fig. 7(c) and Table 2. The saturation adsorption capacities  $q_m$  obtained using D–R isotherm model for adsorption of oxamyl onto AC, PAC, and BAC are 2041.90, 1784.22, and 1769.99 mg/g, respectively. The values of  $E$  calculated using Eq. (9) are 1.70, 2.23, and 3.818 kJ/mol, respectively, indicating that the physico-adsorption process plays a significant role in the adsorption of oxamyl onto AC, PAC, and BAC. These  $E$  values are in agreement with [41] for the adsorption of oxamyl onto Egyptian Apricot Stone and [42] for the adsorption of dyes by loofa AC.

To study the applicability of the Freundlich, Temkin, and D–R isotherm models for the oxamyl biosorption by AC, PAC, and BAC are all calculated

parameters of these models and listed in Table 2. From the linear regression correlation coefficient  $R^2$ , it is shown that the equilibrium data could be well interpreted by the Freundlich isotherm.

### 3.5. Biosorption kinetics

The kinetic adsorption data were processed to understand the dynamics of adsorption process in terms of the order of rate constant. In the present study, we applied three important kinetic models viz. pseudo-first-order, pseudo-second-order, and Weber and Morris intraparticle diffusion model in order to investigate the mechanism of adsorption of oxamyl on different adsorbents.

#### 3.5.1. The pseudo-first-order

The pseudo-first-order rate equation can be expressed in a linear form as:

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303}(t) \quad (10)$$

where  $q_e$  and  $q_t$  are the amount of oxamyl adsorbed (mg/g) on the adsorbent at the equilibrium and at time  $t$ , respectively, and  $k_1$  is the rate constant of adsorption (L/min). Values of  $k_1$  were calculated from the plots of  $\log(q_e - q_t)$  vs.  $t$ . The application of this equation to the data of oxamyl on different adsorbents (data not shown) indicated the inapplicability of the model.

### 3.5.2. The pseudo-second-order

The pseudo-second-order kinetic model equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (11)$$

where  $K_2$  is the rate constant for the pseudo-second-order kinetics (g/mg min). The constants can be obtained from plotting ( $t/q_t$ ) vs.  $t$ . The initial sorption rate can be calculated using the following relation [43]:

$$K_0 = K_2 q_e^2 \quad (12)$$

The values of  $K_2$  and  $q_e$  are calculated from the intercept and slope of the linear plots of  $t/q_t$  against  $t$  and are presented in Table 3. Fig. 8 shows a graphical interpretation of the data for pseudo-second-order model. The corresponding correlation coefficients ( $R^2$ ) values for the pseudo-second-order kinetic model for the three adsorbents are close to unity, indicating the applicability of the pseudo-second-order kinetic model to describe the adsorption of oxamyl onto AC, PAC, and BAC. Similar results were also reported for the adsorption of 2,4 dichlorophenoxyacetic acid and carbofuran on carbon slurry, blast furnace slag, dust, and sludge, 2,4 dichlorophenol on the surface of maize cob AC and drin on the surface of acid treated olive stones [44].

According to the high regression coefficient, the adsorptions of oxamyl on the ACs generated from agricultural residues are best fitted by the pseudo-second-order kinetic model compared with pseudo-first-order kinetic model. It was recorded that commercial AC did not have a better behavior than manufacture AC PAC and BAC.

### 3.5.3. The intraparticle diffusion model

The intraparticle diffusion rate was also used for the adsorption of oxamyl on AC, PAC, and BAC. The

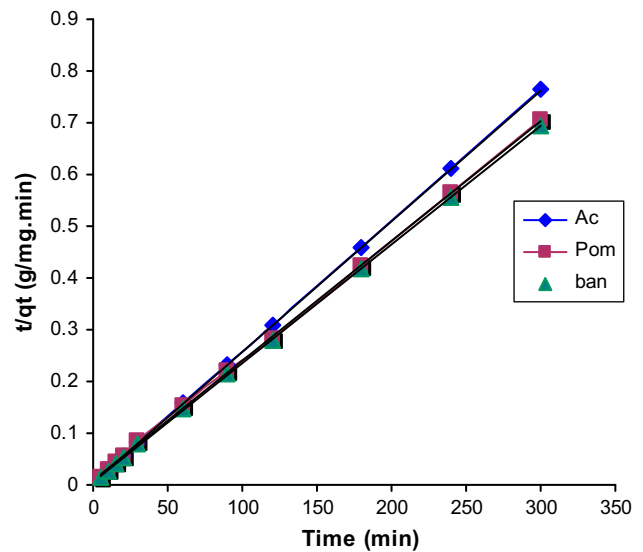


Fig. 8. Pseudo-Second-order kinetics for adsorption of oxamyl onto AC, PAC, and BAC ( $C_0 = 500$  mg/L, temperature  $25 \pm 2^\circ\text{C}$ ).

intraparticle diffusion was described by Weber and Morris [45]. The rate constants for the intraparticle diffusion ( $K_i$ ) are determined using the following equation:

$$q_t = k_i t^{1/2} + C \quad (13)$$

where  $K_i$  is the intraparticle diffusion rate constant ( $\text{mg/g min}^{1/2}$ ) and  $C$  (mg/g) is a constant that gives an idea about the thickness of the boundary layer i.e. the larger the value of  $C$  the greater the boundary layer effect. The intraparticle diffusion rate constants values are shown in Table 3. The plot of  $q_t$  vs.  $t$  (Fig. 9) could yield a straight line passing through the origin if the biosorption process obeys the intraparticle diffusion model. The line does not pass through the origin; therefore, intraparticle diffusion is not the only rate-controlling step.

Table 3  
Kinetic parameters for the removal of oxamyl by the three adsorbents

Kinetic model	Parameters	Values		
		AC	Pom	Ban
Pseudo-second-order	$q_e$ (mg/g)	400.00	434.782	434.782
	$K_2$ (g/mg min)	$1.179 \times 10^{-3}$	$5.688 \times 10^{-4}$	$8.138 \times 10^{-4}$
	$K_0$ (g/mg min)	188.640	107.523	153.836
	$R^2$	1.000	0.9997	0.9999
Intraparticle diffusion	$K_i$	10.976	10.588	11.024
	$R^2$	0.8187	0.9652	0.9899

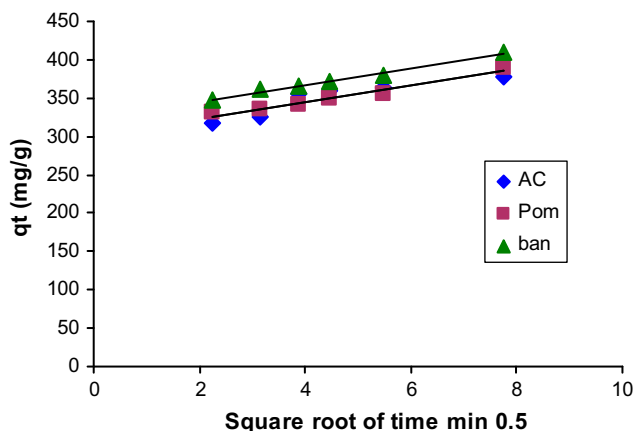


Fig. 9. Intraparticle diffusion for adsorption of oxamyl onto AC, PAC, and BAC ( $C_0 = 500$  mg/L, temperature  $25 \pm 2^\circ\text{C}$ ).

The results demonstrate that the values of coefficient of determination ( $R^2$ ) for the intraparticle diffusion are slightly lower than those of a pseudo-second-order kinetic model indicating that pseudo-second-order model is better obeyed than intraparticle diffusion model.

#### 4. Conclusion

The different materials of ACs, Pomegranate peel (PAC), and Banana peel (BAC) were used as agriculture waste adsorbents for the removal of oxamyl from aqueous solution compared with the commercial ACs. The Freundlich, Temkin, and D–R isotherm models are used to describe the isotherms and the Freundlich isotherm was shown to provide the best fitting. The values of energy of adsorption calculated from the D–R isotherm models are 1.70, 2.23, and 3.81 kJ/mol suggesting that the oxamyl adsorption on three adsorbents is physical. Different kinetic models are used to fit experimental data. The Kinetic studies of the equilibrium data showed that the pseudo-second-order model best describes the adsorption of oxamyl onto the three different adsorbents.

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