



Utilization of activated carbon prepared from agricultural waste for the removal of organophosphorous pesticide from aqueous media

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ABSTRACT

The current study aims to utilize activated carbon produced from agriculture waste to adsorb and remove malathion and profenofos as organophosphorous insecticides from aqueous solutions under different experimental conditions. Physicochemical properties of these materials were investigated by several procedures; elemental analysis, surface area, and texture porosity. A matrix effect analysis was applied to correlate the malathion and profenofos adsorption capacity to the agitation time, initial levels of each pesticide (1–10 mg/l), carbon dose (50–100 mg), pH (3–11), and different temperatures (15–45 °C). The maximum removal percentages of malathion and profenofos at equilibrium time were 97 and 98% for activated carbon derived from date stones (AC1), respectively, however, these values were 98 and 96% for Norit carbon as a reference carbon (AC2). At equilibrium time, the increase of temperature decreased the adsorption capacity of both AC1 and AC2 with malathion and profenofos. The adsorption capacity of both AC1 and AC2 to malathion and profenofos increased as the pH was increased.

Keywords: Organophosphorous insecticides; Malathion; Profenofos; Activated carbon; Date stones

1. Introduction

Man-made organophosphorous compounds have been widely distributed throughout our environment as pesticides since World War II. Several important studies indicated the relative persistence and toxicity of these compounds [1]. Once pesticides are introduced into the environment, whether by application, disposal, or spill, they can be influenced by many processes. These processes determine the ultimate fate of the pesticide by affecting its persistence and movement in the environment. In Egypt, the majority of populations live in the crowded cities and villages along the narrow green strip of land beside the River Nile. In this densely populated and limited area, about one million metric tons of commercial pesticides were used and injected into the environment since the beginning of the pesticide evolution in Egypt (ca. 1952) till 2003. Organophosphorous insecticides

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are of great significance in pest control and they represent more than 80% of total insecticides used in Egypt [2]. Of these insecticides, malathion and profenofos are well known and used for the control of agricultural pests [3,4]. These insecticides are frequently detected in surface and ground water [5]. Consequently, removal of pesticides from water and food web is one of the major concerns and several methods were reported [6,7]. A wide range of conventional treatment methods for the removal of organic and inorganic pollutants have been investigated intensively, such as chemical coagulation, carbon adsorption, electrochemical treatment, and photocatalysis [8-11]. However, an increasing attention has been focused on the adsorption technique due to their efficiency in the removal of pollutants from aqueous solution [12–14].

Nowadays, adsorption on activated carbon (AC) is considered the most widely used and effective physical methods for the removal of pesticides in industry, regardless of the expensive cost [15]. Therefore, several industrial and agricultural wastes have been used as cheap precursors for carbon to prepare AC for the removal of different pesticides from the aqueous solution. These include tea leaves, olive stones, cotton stalk, and rice husk [16–21]. The current study aims to use dates stones (DS) as an agriculture waste, renewable and low cost precursor for the production of AC and to test its ability to remove malathion and profenophos from aqueous solutions under different conditions.

2. Materials and methods

2.1. Materials and chemicals

High performance liquid chromatography grade solvents (n-hexane, diethyl ether, methanol, dichloromethane) and phosphoric acid (85%) were purchased from Merck (Darmstadt, Germany). NORIT Granular AC (NORIT GAC 1240 PLUS) was purchased from Norit Nederland BV (AC Amersfoort, Netherlands). The specification of Norit carbon (AC2) is shown in Table 1 as indicated by the producer. Malathion and profenofos were purchased from Nanjing Ronch Chemical Co., Ltd. (China).

2.2. Preparation of AC

Activated carbon (AC1) was prepared from DS collected from dates' factories in Upper Egypt. The DS were dried at 100° C in a drying oven for 1 day, then crushed and sieved to semi-fine particles (500–

850 μm). These particles were used for the production of AC through a single-step chemical activation using H_3PO_4 according to Girgis et al. [22]. In brief, 100 g of crushed DS was soaked in phosphoric acid in the ratio of 1:3 (w/w) and slightly agitated to ensure penetration of the acid throughout. The mixture was heated to 70 °C for 2 h and left overnight at room temperature. The impregnated solid was activated into muffle furnace and the temperature was raised to 500 °C for 2 h at the rate of 5 °C/min. The acid was removed by washing with distilled water till the pH reached 6.8. The carbon product was dried at 110 °C for 24 h using an electric oven.

The contents of carbon, hydrogen, nitrogen, and sulfur in raw DS, AC1, and AC2 were analyzed using carbon, hydrogen, nitrogen and sulfur elemental analyzer (Thermo Electron Flash EA 1112). The surface area and pore structural of AC1 and AC2 were examined from the adsorption–desorption isotherm of nitrogen at 77 K. The surface area (S_{BET}) was calculated by Brunauer–Emmett–Teller (BET) equation, the pore size distribution was calculated on the basis of desorption data by employing the Barrett–Joyner–Halenda method. However, the S_{BET} and pore structure for biomass of DS was characterized from CO₂ sorption at 273 K.

2.3. Adsorption equilibrium studies

To study the adsorption kinetics of malathion and profenofos, an amount of 0.1 g of DS, AC1, and AC2 was incubated with 100 mL of a mixture of malathion and profenofos (1 mg/L for each). The mixture was agitated at 100 rpm using water-bath shaker at 25 °C for 0.5, 1, 2, 3, 4, 6, and 8 h. The amounts of malathion and profenofos adsorbed at each time (Q_t , mg pesticide/g adsorbent) were calculated with the equation:

$$Q_t = (C_0 - C_t)V/m$$

where C_0 and C_t are the liquid-phase concentrations (mg/L) of the investigated pesticide at initial and at each time, respectively; *V* is the pesticide solution volume (L) and *m* is the adsorbent mass (g). The equilibrium condition was reached when no further decrease in the malathion and profenofos concentration occured in solution.

To investigate the effect of initial concentrations on the kinetics of pesticide removal, 100 ml of 1, 4, and 8 mg/L malathion and profenofos was placed in a 250 ml Erlenmeyer flask and incubated with 100 mg of AC1 and reference material AC2. The optimum shaking time was selected based on the sorption kinetics

Table 1 Specification of the Norit activated carbon (AC2)

Product specifications	Values		
According to producer Iodine number	950 mg/g		
Molasses number	210		
Iron, acid soluble, % as Fe	0.01%		
Moisture, % as packed	3%		
pH, water extract	5.0-8.0		
Mesh size			
Greater than 10 mesh (2.00 mm), $\%$	5%		
Less than 40 mesh (0.42 mm), $\%$	0.5%		
Density	0.50 g/ml		

study. The mixture was agitated using a shaking water bath at 100 rpm.

To study the effect of carbon dosage on the retention of malathion and profenofos from aqueous solution, three initial levels of carbon (50, 75, and 100 mg) were incubated with mixtures of malathion and profenofos (1, 4, and 8 mg/L) in 100 ml of aqueous solution. The mixtures were agitated using a thermostated shaker water bath at 100 rpm for 3 h (AC1) and for 4 h (AC2) at $25 \pm 1^{\circ}$ C and pH 7. The influence of temperature on the adsorption of malathion and profenofos by AC1 and AC2 in aqueous solutions was carried out using the same procedures under two additional temperatures (15 and 45°C). The influence of pH on pesticides adsorption at $25 \pm 1^{\circ}$ C was carried out using different mixtures of malathion and profenofos (1, 4, and 8 mg/L) in 100 ml water and incubation with 100 mg AC's at equilibrium time for each sorbent. The mixtures were agitated at 100 rpm. The pH was adjusted using NaOH (0.1 M) or HCl (0.1 N) and measured by pH meter (pH-meter 764 Multicalimatic). Malathion and profenofos were extracted from aqueous solution based on the methods described by Chatterjee et al. [14]. In brief, 100 ml of aqueous solution was extracted twice using a separating funnel with 50 ml of methylene chloride. The combined extracts were dehydrated by passing through column of anhydrous sodium sulfate and evaporated using rotary evaporator to ca. 1 ml. Then, the reduced extract was transferred to a vial and the volume was reduced to 0.1 ml by a stream of nitrogen for instrumentation.

2.4. Determination of malathion and profenofos

Malathion and profenofos were determined with GC (Varian 4000) equipped with Electron capture detector. The separation was accomplished on CP-Sil 8 CB ($30 \text{ m} \times 0.25 \text{ mm}$ i.e. $0.25 \mu \text{m}$ film thickness).

Splitless (0.5 min.) injection was used at 250 °C and the temperature of detector was 300 °C. Nitrogen was used as a carrier gas at a constant flow rate of 1 ml/min. The temperature program was performed as follows: initial temperature 100 °C held for 0 min, then increased to 280 °C at a rate of 20 °C/min and held constant for 7 min. The identification of malathion and profenofos was performed by the retention time and compared with certified standards at the same condition. The quantities of malathion and profenofos were calculated on peak area basis. The retention time for malathion and profenofos was 8.814 and 9.936 min, respectively.

2.5. Statistical analysis

All experiments were carried out in triplicates and the data were statistically analyzed using the general linear models procedure of the statistical analysis system. The significance of the differences among the treatment groups was determined by Waller–Duncan *k*-ratio. All statements of significance were based on a probability of $P \leq 0.05$.

3. Results and discussion

3.1. Physicochemical characteristics of the adsorbents

The elemental analyses for carbonaceous raw DS, AC1 and AC2 are presented in Table 2. The results indicated that DS contains higher hydrogen and oxygen content and the lowest carbon content compared with AC1 and AC2. However, AC2 showed a higher carbon and lower nitrogen, hydrogen, and oxygen content compared to that of AC1. It is well known that heteroatoms, which might have origin in the raw material or could be introduced during the preparation or further treatments, are deeply influenced by the charge, hydrophobicity, and electronic density of the AC surface [23]. Furthermore, the oxygens become primary adsorption centers due to their polarity and possibility to attract water via hydrogen bonding [24].

Table 2

Elemental analyses of activated carbons (AC1 and AC2) and dates stones (DS)

Sorbent	Elemental contents (%)					
agents	С	Ν	Н	S		
(AC1) DS	77.9 ± 0.60 49.3 ± 0.40	1.53 ± 0.04 1.14 ± 0.01	2.54 ± 0.07 6.80 ± 0.03	Nil Nil		
(AC2)	80.9 ± 6.25	0.67 ± 0.09	0.38 ± 0.03	0.41 ± 0.04		

S_{BET}	$V_{\text{tot.}}$ (cm ³ /g)	Pore size distribution (cm^3/g)				$V_{\rm mic\ DR}$	<i>L</i> _{N2} , nm	Е,	
(m²/g)		<2 nm	2–3 nm	3–5 nm	5–10 nm	10–50 nm			kJ/mol
873	0.791	0.339	0.075	0.111	0.119	0.148	0.298	2.55	15.63
385	-	-	-	-	-	_	0.141	0.56	29.70
1,082	0.555	0.401	0.030	0.037	0.029	0.059	0.368	1.06	21.59
	S _{BET} , (m ² /g) 873 385 1,082	$\begin{array}{ccc} S_{\text{BET,}} & V_{\text{tot.}} \\ (\text{m}^2/\text{g}) & (\text{cm}^3/\text{g}) \end{array} \\ \hline \\ 873 & 0.791 \\ 385 & - \\ 1,082 & 0.555 \end{array}$	$\begin{array}{c} S_{\text{BET},} & V_{\text{tot.}} & \text{Pore siz} \\ (\text{m}^2/\text{g}) & (\text{cm}^3/\text{g}) & \hline \\ \hline & \hline & \hline & \\ 873 & 0.791 & 0.339 \\ 385 & - & - \\ 1,082 & 0.555 & 0.401 \end{array}$	$\begin{array}{c} S_{\text{BET},} & V_{\text{tot.}} & \text{Pore size distribut} \\ (\text{m}^2/\text{g}) & (\text{cm}^3/\text{g}) & \hline & <2\text{nm} & 2-3\text{nm} \\ \hline & & & & \\ 873 & 0.791 & 0.339 & 0.075 \\ & & & & & & \\ 385 & - & & & & - \\ 1,082 & 0.555 & 0.401 & 0.030 \\ \hline \end{array}$	$\begin{array}{c} S_{\text{BET,}} & V_{\text{tot.}} \\ (\text{m}^2/\text{g}) & (\text{cm}^3/\text{g}) \end{array} \xrightarrow{\text{Pore size distribution (cm}^3/}{2 \text{ nm} 2-3 \text{ nm} 3-5 \text{ nm}} \\ \hline 873 & 0.791 & 0.339 & 0.075 & 0.111 \\ 385 & - & - & - & - \\ 1,082 & 0.555 & 0.401 & 0.030 & 0.037 \end{array}$	$\begin{array}{c} S_{\text{BET,}} & V_{\text{tot.}} \\ (\text{m}^2/\text{g}) & (\text{cm}^3/\text{g}) \end{array} \xrightarrow{\text{Pore size distribution (cm}^3/\text{g})} \\ \hline \hline & 2 \text{ nm} & 2 - 3 \text{ nm} & 3 - 5 \text{ nm} & 5 - 10 \text{ nm} \\ \hline & 873 & 0.791 & 0.339 & 0.075 & 0.111 & 0.119 \\ \hline & 385 & - & - & - & - \\ 1,082 & 0.555 & 0.401 & 0.030 & 0.037 & 0.029 \end{array}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$

Porous structure parameters of activated carbons (AC1 and AC2) and date stones (DS) determined by sorption at 77 K

*Pore structure characteristics from CO₂ sorption at 273 K.

Table 3

The carbon surface chemistry is influenced by the presence of heteroatoms and has a great influence on both, electrostatic and nonelectrostatic interactions [25]. The results presented in Table 2 also revealed that the element (C, H, S and N) contents of biomass DS are different from the other adsorbents.

The porosity and specific surface area (S_{BET}) of the tested adsorbents are given in Table 3. The characterization of the adsorbent agents revealed that the surface area (S_{BET}) of AC1 was higher than DS, but it was lower than the reference AC2. The data presented in Table 3 also show the Pore Size Distribution for the ACs (AC1 and AC2). Moreover, it can be observed that (a) V_{tot} for AC1 was greater than AC2 and the micropore distribution (d < 2 nm) represented 42.8% of the total pore volume for AC1, while it constitutes 72.1% for the reference AC2 (Table 3). Meanwhile, the mesopore distribution (d = 2-50 nm) was found to be systematically higher for AC1 than the reference AC2. The ratios of $V_{\text{mic}}/V_{\text{meso}}$ were 0.75 and 2.59 for AC1 and AC2; respectively.

3.2. Adsorption kinetics

The effect of contact time on the adsorption capacity is shown in Fig. 1(a-c). The maximum adsorption of malathion and profenofos was achieved within 2h for AC1 and recorded 97 and 98%, respectively (Fig. 1(a)). However, the maximum adsorption of the tested pesticides was observed within 5h for DS and recorded 61.4 and 65.8% for malathion and profenofos, respectively (Fig. 1(b)). For AC2, the maximum adsorption was achieved after 4 h and reached 98 and 96% for malathion and profenofos, respectively (Fig. 1 (c)). The current results were found to be in accordance with those reported by El Bakouri et al. [18], who reported that the equilibrium adsorption was achieved within 3.5 h for aldrin, dieldrin, and endrin using AC derived from DS. It has been noticed from the same data (Fig. 1(a) and (c)) that the removal percentage of malathion from aqueous solution reached 71% within 30 min for AC1. However, the removal percentage of malathion was only 34% for AC2 for the same time. Furthermore, the removal percentage of profenofos was around 80% for AC1 and reached 48% for AC2 within 30 min. From the reported results, it could be suggested that at the initial stage of the contact of ACs with pesticides, the adsorption of the investigated pesticides occurred rapidly and then comes to the second stages in which a slight decrease in the adsorption kinetics rate was noted. Thereafter, the adsorption reached the equilibrium stage when the amount of the investigated pesticides adsorbed on ACs was equal to the amount of pesticides desorbed. The rapid adsorption at the initial time mainly is due to the availability of a large number of vacant surface sites [26,27]. In the same concept, Kumar and Philip [28] mentioned that the rapid initial adsorption of pesticides is a surface phenomenon and it could be explained by the hydrophobic nature of the pesticides.

According to Hameed [26], the slow rate of pesticides uptake during the second stage can be attributed to the repulsive forces between the solute molecules and the decrease of vacant surface sites, besides, the adsorption at the exterior surface reached saturation at this time, then the solute molecules began to enter the pores of carbon and were adsorbed by the interior surface of the particles [27]. Furthermore, El Bakouri et al. [18,29] reported that during the second phase of adsorption of pesticides, there was a slight decrease in the adsorption kinetics rate of aldrin, dieldrin, and endrin pesticides and this behavior may be referring to the slow diffusion of the pesticide into the smaller pores and irregularities on the adsorbent surface.

3.3. Effect of initial adsorbent dosage on the adsorption capacity

The results presented in Figs. 2 and 3 showed the percentage removal and adsorption of malathion and profenofos by AC1 and AC2. These results revealed that the removal percentage of the initial concentrations



Experimental conditions: (100 mg of adsorbent; 1mg pesticide/l; pH 7; $T = 25 \pm 1$ °C).

Fig. 1. Effect of contact time on the adsorption of organophosphorous pesticides by AC1 (a), DS (b), and AC2 (c).

of malathion (1, 4, and 8 mg/L) at equilibrium using 50 mg of AC1 ranged from 58–92%. However, this value ranged from 47–88% for the reference AC2 under the same conditions (Fig. 2(a) and (b)). These data revealed that increasing the amount of AC1 and AC2 to 100 mg succeeded in removing the most available malathion from aqueous solution at all concentration levels (Fig. 2(a) and (b)). The maximum uptake of malathion at equilibrium was 10.46 mg/g at the initial concentra-

tion level of 8 mg/L using 50 mg of AC1 (Fig. 2(b)), while the maximum uptake of malathion at equilibrium was 8.25 mg/g at the initial concentration level of 8 mg/L using 75 mg of AC2 (Fig. 2(a)). Additionally, the results presented in Fig. 3(a) and (b) show the removal percentage of profenofos and adsorption capacity of the AC1 and AC2 at equilibrium phase. It could be observed that AC1 was more effective than AC2 in removing profenofos at all initial concentrations



Fig. 2. Percentage removal and adsorption capacity of malathion by AC1 (a) and AC2 (b).

(1, 4, and 8 mg/L) using 50, 75, and 100 mg of ACs. The maximum removal percentage of profenofos had occurred with the carbon dose of 100 mg for both AC1 and AC2 at all initial concentrations (1, 4, and 8 mg/L). These maximum values of removal percentage ranged between 90.7-99.6% (Fig. 3(a) and (b)). Moreover, the maximum uptake of profenofos at equilibrium was found to be 10.58 mg/g with AC1 compared with 7.98 mg/g with AC2 (Fig. 3(a) and (b)). Although the surface area of AC2 is greater than AC1, the adsorption capacity of AC1 for both insecticides tested was found to be higher than AC2. This could be due to the total pore volumes which recorded 0.791 cm³/g for AC1 compared with $0.555 \text{ cm}^3/\text{g}$ for AC2. The results shown in Table 3 illustrated that the mesoporosity (2–50 nm) of AC1 and AC2 constituted about 57 and 28% of the total pore volume, respectively, which may be available for those insecticides. It is a worthy to mention that not all the porosity of the AC has the same entrance dimensions. Thus, more porosity is open to molecules of smaller size than to molecules of larger size. Conversely, more porosity is closed to molecules of larger size than to molecules of smaller size. Consequently, closed porosity is defined as that porosity which is not accessible to a given adsorbate [30].

(a) 100 14 12 Adsorption capacity 80 10 % Removal 60 8 6 (mg/g) 40 4 2 20 0 0 75 100 50 75 100 50 75 100 50 mg mg mg mg mg mg mg mg mg AC1 (1 mg/L) AC1 (4 mg/L) AC1 (8 mg/L) Initial concentration of profenofos (mg/L) (b)¹⁰⁰ 10 8 80 Adsorption capacity 6 60 % Removal (mg/g) 40 4 2 20 0 0 50 75 100 50 75 100 50 75 100 mg mg mg mg mg mg mg mg mg AC2 (1 mg/L) AC2 (4 mg/L) AC2 (8 mg/L) Initial concentration of profenofos (mg/L) Experimental conditions: (50, 75, 100 mg of adsorbent; 1, 4, 8 mg profenofos/l; pH 7; T = 25± 1°C).

Fig. 3. Percentage removal and adsorption capacity of profenofos by AC1 (a) and AC2 (b).

3.4. Effect of temperature on the adsorption of malathion and profenofos

The data illustrated in Fig. 4(a) and (b) show the effect of temperature on the percentage removal and the adsorption capacity of adsorbent agents (AC1 and AC2) against different levels of malathion and profenofos at equilibrium time. The results indicated that decreasing the adsorption capacity of malathion and profenofos is associated with increasing the temperature from 25 to 45°C at equilibrium phase. It is well documented that temperature has three major effects on the adsorption process since (I) increasing the temperature is known to increase the diffusion rate of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle which was found to increase by increasing the temperature, (II) the viscosity of the solutions is decreased by increasing the temperature, and (III) the solubility of pesticides in water is increased as the temperature increased [31]. Moreover, the data presented in Fig. 4(a) and (b) showed that the uptake of malathion at initial concentrations (1, 4, and 8 mg/L) was decreased as the temperature increased from 15 to 45°C with both adsorbent materials AC1 and AC2.



Fig. 4. Effect of temperature on the percentage removal and adsorption capacity of malathion by AC1 (a) and AC2 (b).

However, the maximum adsorption capacity of malathion was achieved at 25 °C at an initial level of 8 mg/L, where they recorded 7.62 and 7.64 mg/g with AC1 and AC2, respectively. The maximum removal percentage of malathion from aqueous solution recorded 99.3% with initial concentration of 4 mg/L and 98.9% with initial concentration of 1 mg/L at 25 °C for AC1 and AC2, respectively (Fig. 4(a) and (b)).

The data presented in Fig. 5(a) and (b) show the adsorption capacity of AC1 and AC2 and the effect of temperature on the removal percentage of profenofos from the aqueous solution. These results indicated that, for both AC1 and AC2, the removal percentage of profenofos was increased as temperature increased up to 25° C, then the removal trend was decreased as the temperature was elevated up to 45° C. The maximum percentage removal recorded 99.5% at initial concentration of 4 mg/L for AC1 and 97.3% with initial concentration of 1 mg/L at 25° C for AC2 (Fig. 5(a) and (b)). Moreover, it has been noticed that the removal of both malathion and profenofos from aqueous solution followed the same trend. The results

presented in Fig. 5(a) and (b) also showed that the uptake of profenofos at initial concentration of 8 mg/L had the same trend of malathion where it decreased with increasing the temperature. The adsorption capacity has been decreased at initial concentration of 8 mg/L from 5.9 to 5.8 mg/g and from 4.5 to 3.8 mg/gwith AC1 and AC2, respectively as the temperature was increasing from 15°C to 45°C. The maximum adsorption capacity of profenofos was achieved at 25°C at an initial level of 8 mg/L and the recorded values were 7.82 and 7.53 mg/g with AC1 and AC2, respectively. The current results were in agreement with those obtained by Gupta et al. [32] who studied the adsorption isotherms of lindane and malathion using bagasse fly ash at three different temperatures and suggested that the adsorption is almost unaffected with rising temperature at lower concentrations of lindane and malathion, however, it decreased at higher concentration for both the pesticides. The adsorption in both cases follows the order $30^{\circ}C > 40^{\circ}$ C > 50 °C. However, the current study disagrees with the results obtained by Singh et al. [33] who reported that the adsorption of malathion by fly ash increased from 90 to 97.5% by increasing the temperature from 35 to 55°C at pH 4.50 and initial concentration of 10 mg/L.

The effect of temperature can be explained on the basis of solubility. With the increasing temperature, the solubility of both pesticides increases, therefore, exhibits lower tendency to go to the adsorbent surface and get adsorbed [34]. Moreover, the decrease in adsorption uptake in the higher temperature may be attributed to the weakening of adsorptive forces between the active sites of the adsorbent and adsorbate species as well as between the adjacent molecules of the adsorbed phase [35]. In addition, the effect of the exothermic nature of reaction exceeds the effect of increasing the diffusion rate as the temperature increase. According to these results, the adsorption performance achieved the maximum level at 25°C for both AC1 and AC2 towards the investigated pesticides.

3.5. Effect of pH on the adsorption of malathion and profenofos

Since the surface charge of the adsorbent could be modified by changing pH of the solution, pH is considered one of the most important parameters affecting the adsorption capacity of carbon towards pesticides. The effect of pH on the adsorption capacity of AC1 and AC2 was tested using 100 mg of each sorbent agent against different levels of malathion and profenofos (1, 4 and 8 mg/L). It is well known that



Experimental conditions: (100 mg of adsorbent; 1, 4, 8 mg profenofos/l;pH 7; T = 15, 25, 45 \pm 1 °C).

Fig. 5. Effect of temperature on the percentage removal and adsorption capacity of profenofos by AC1 (a) and AC2 (b).

malathion and profenofos are relatively stable under neutral and slightly acidic conditions. However, they are unstable under alkaline conditions, since the half-life of malathion and profenofos at pH 9 were found to be 5 and 5.7 h, respectively. So, all tests of the current study were carried out at pH 3 and 7 to avoid the effect of alkaline condition on the stability of these pesticides.

The results indicated that the retention of both insecticides onto the AC1 and AC2 had the same behavior (Figs. 6 and 7) and the percentage removal was increased as the pH elevated from 3.0 to 7.0 for all tested ACs. With the initial concentrations of malathion (1, 4, and 8 mg/L), the removal percentage at pH 3.0 ranged from 49 to 85% for AC1, while these percentages reached 95-99% when the solution pH was 7.0 (Fig. 6(a)). On the other hand, the removal percentage of malathion at pH 3.0 ranged from 41 to 79% and from 91 to 99% with AC2 at pH 3.0 and pH 7.0, respectively (Fig. 6(b)). Furthermore, the results presented in Fig. 7(a) and (b) revealed that the behavior of profenofos against all tested ACs had a similar trend. AC1 succeeded to remove more than 99% of profenofos (pH 7.0, initial concentration 4 mg/L) and the maximum removal percentage of profenofos reached 97% using AC2 at pH 7.0 and 1 mg/L initial concentration.

The results presented in Figs. 6 and 7 also indicated that AC1 and AC2 had the same maximum adsorption capacity for malathion and profenofos at pH 7. The maximum adsorption capacity of malathion reached 7.62 and 7.64 mg/g for AC1 and AC2, respectively at initial concentration of 8 mg/L (Fig. 6(a) and (b)). Meanwhile, the maximum adsorption capacity of profenofos at initial concentration of 8 mg/L was found to be 7.82 and 7.53 mg/g for AC1 and AC2, respectively at pH 7.0 (Fig. 7(a) and (b)). On the other hand, the adsorption capacity of both AC1 and AC2 had been diminished at pH 3.0 at all initial concentrations of both pesticides. The current results were found to be consistent with the results obtained by Chatterjee et al. [14] who studied the adsorption of malathion by Rhizopus oryzae biomass at pH range from 2 to 8 and concluded that the adsorption capacity increased at higher pH values. Furthermore, the findings of the present study were found to be in agreement with the results obtained by Singh et al. [33] who found that the adsorption of malathion by fly ash was increased from 96 to 99% at the initial concentration of 1 ppm and increased from 89 to 90% at 10 ppm at a high range of pH.



Experimental conditions: (100 mg of adsorbent; 1, 4, 8 mg malathion/l; pH 3, 7; T = 25 ± 1 °C).

Fig. 6. Effect of pH on the percentage removal and adsorption capacity of malathion by AC1 (a) and AC2 (b).



Experimental conditions: (100 mg of adsorbent; 1, 4, 8 mg profenofos/l; pH 3, 7; T = 25± 1 °C).

Fig. 7. Effect of pH on the percentage removal and adsorption capacity of profenofos by AC1 (a) and AC2 (b).

4. Conclusion

It could be concluded that the percentages of removal of both malathion and profenofos insecticides from aqueous solution as well as the adsorption capacity showed the same trend with all experimental factors. Moreover, AC prepared from DS (AC1) showed higher capacity to adsorb both insecticides than the reference activated carbon (AC2) under all tested conditions.

Conflict of interest

The authors declare that there are no conflicts of interest.

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