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PREPARATION OF ACTIVATED CARBON FROM REED PHRAGMITES AUSTRALIS (CAV.) AND A STUDY OF ITS EFFECTIVENESS IN ADSORPTION OF MALATHION

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ABSTRACT

Thermally Activated Carbon (TAC) was prepared by thermal treatment of a widely spread type of reed (Phragmites Australis (Cav.)) to obtain an environmentally friendly, efficient and low-cost adsorbent, and its adsorption behavior for malathion pesticide from water studied by the batch method. Characterization of TAC was investigated by "scanning electron microscopy" (SEM) and "Fourier trans form infrared spectroscopy" (FT-IR). The TAC performance was evaluated in removing Malathion under different experimental conditions. Langmuir and Freundlish isotherms were applied, its also applied two kinematic models, the "pseudo first order" and the "pseudo second order". The study revealed the following ; the maximum absorption capacity 12.33 mg/g , and that increasing the contact time(before reaching equilibrium) , adsorbent dose and the adsorbate initial concentration increase the efficiency of adsorption, as for increasing the temperature, it reduces this efficiency. It was also found that adsorption process is affected by the PH, and the adsorption data are well fit with the "Langmuir isotherm". The kinetic of adsorption is subject to a "pseudo-second-order model", The process also turned out to be exothermic and spontaneous.

KEYWORDS: *Adsorption, Malathion, Phragmites Australis, Environment, Isotherm*

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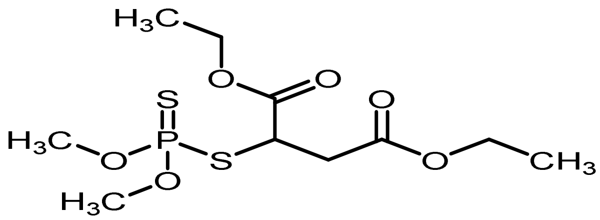
INTRODUCTION

Constantly growing population and consequently the increase in the Food consumption rate prompted Producers to step up efforts to increase the production of foodstuffs. And being a major component in this series, farmers are using increasing amounts of pesticides to preserve their crops [1, 2]. Pesticides are a very important part of growing crops, it is a chemical method used in agriculture to control insects, weeds and diseases in crops. It is a well-known and very effective technique for growing crops. Organophosphorous pesticides (such as malathion) are highly toxic agricultural chemicals used to protect plants. Malathion is a persistent and highly toxic ipesticide that has caused many serious environmental problems [3].

Malathion Molecular formula: $C_{10}H_{19}O_6PS_2$, Chemical name according to IUPAC: *S*-, 2-bis (ethoxycarbonyl) ethyl *O*,*O*-dimethylphosphorodithioate, formula weight (330 g/mo) l, solubility in water (145mg/L), Structural formula:



Malathion, a highly toxic pesticide registered in 1956, is widely used in agriculture as well as in public health to eliminate harmful organisms such as insects, worms, and others. Malathion is absorbed rapidly in many ways, such as in the digestive system, lungs, mucous membranes and skin, and causes blurred vision, increased salivation, headache, dizziness, vomiting, and nausea. It affects the nervous system, liver, adrenal glands and the immune system and is a carcinogen as well as toxic to birds, fish, bees and others [4].

Due to its toxic effect and health risks to humans, it is extremely dangerous and unsafe in nature [3].The World Health Organization (WHO) recommended that the pesticide level alone in drinking water should not exceed (0.1 μg / L) [5].There are several methods for removing pesticides, such as aerobic and photocatalytic degradation, advanced oxidation, biological oxidation , ozonation, nanofiltration and absorption [6].

The most commercially used technique for removing toxic water pollutants is adsorption, It is the phenomenon of the particles of a fluid mixture being attracted to the surface of an adsorbent, Associated with it by Physical links or chemical bonds. This technology is distinguished from other technologies by its low cost, simplicity of design, flexibility and ease of operation. Also, the adsorption process does not leave harmful residues [7].

Various natural or synthetic adsorbents; activated carbon (AC), polymers, agricultural and industrial waste, zeolite, and carbon nanotubes (CNTs) have been used as absorbents for treating polluted water [3].

AC is the most efficient and it is widely used in water treatment all over the world. It is also very inert, thermally stable and it works efficiently in a large pH range [8].

The adsorption efficiency is affected by the properties of carbon, surface area, particle and pore size, pollutant solubility, and the attraction of pollutants to the carbon surface. A variety of AC materials were used; Powdered and granular activated carbon, commercial activated carbon and black carbon from wheat tailings [7]. In this study, the AC was prepared from a reed plant called Phragmites australis which is available in huge quantities, thus obtaining a low-cost and environmentally friendly product.

Phragmites australis (Cav.) is a widespread plant found in swamp systems all over the world. This perennial is an erect plant that lasts throughout the seasons [9].

Phragmites australis can be found in a variety of humid to wet environments. Species can tolerate flowing and stagnant water, salt and basic conditions, and is commonly found in marshes, roadside ditches and other wet areas [10]. In Iraq, this plant is found in abundance and is considered one of the plant species of high biological and environmental value in three Iraqi marshes [11].

Figure 1: Phragmites Australis (Cav.).

EXPERIMENITAL

Material

Phragmites australis (Cav.) was collected from roadside ditches in southern Iraq. Malathion (57 % purity), NaOH and HCl (from Sigma) and Deionized water.

Methods

Adsorbents Preparation [12, 13]

The Phragmites australis (Cav.) was collected and dried in the air for a few days. After cutting it and washing it with regular water and then with deionized water several times, it is dried in the air again for a few hours and then transport to oven dried at 105^{o}C for 12 h, subsequently, crushed in a laboratory mill.

Thermal Activation

The resulting powder is transferred into an electric furnace and activated by heat at 250 C° for an hour under the least amount of oxygen and hydrogen possible. Cool the product to laboratory temperature, stir with fresh water, and filter several times and filtering until the filter becomes clear and reaches the neutral pH, then put in the drying oven at 105 C° until its weight remains constant, The result is cooled down and crushed and the resulting particles were sieved to obtain particle size (75µm). Then, it is kept in desiccators for further use. This Thermally Activated Carbon sample was named as (TAC).

a b

Figure 2: The Powder (a) Before Carbonization (b) After Carbonization.

ADSORPTION STUDY

A stock solution (1000 mg/L) of malathionpesticidein deionized water was prepared. Solutions with different concentrations were prepared from the above solution by dilution, after scanning with a spectrophotometer and determining the wavelength at which the maximum absorption occurs, the absorption of these concentrations was measured and the calibration curve was graphed.

Malathion adsorption was performed with activated carbon in the (100 ml) flasks, each containing (50 ml) of malathion solution, this study was conducted in a batch method, the influence of adsorbent dose, contact time, adsorbate initial concentration, temperature and PH was studied. The adsorption kinetic parameters were determined under the following conditions: Specific dose (0.25 g) of the activated carbon was transferred to (50 mL) of the (50 mg/L) malathion solution, in a (100 mL) flask. And when the equilibrium time has passed, the adsorbent was separated by a centrifuge. Then, the malathion concentration was analyzed spectrophotometrically by (UV-Visible Spectrophotometer 2100) [14].

To calculate the amount of malathion adsorbed at any time (qt mg / g) The following relationship has been applied:

$$q_t = (C_o - C_t)\ V/W$$

Where: C_o (mg/L): initial adsorbent concentrations, C_e (mg/L) :Final adsorbent concentration, V (L): volume of the adsorbate solution, W (g): weight the dose of the adsorbent.

The removal percentage (RE) of malathion by adsorbents was calculating by using the equation:

$$RE\% = \frac{C_0 - C_e}{C_0} \times 100$$

The adsorption capacity value was found using the following relationship:

$$q_e = (C_o - C_e)\ V/W$$

Where: $\mathbf{q_e}$ (mg/g) adsorption capacity at equilibrium.

RESULTS AND DISCUSSION

Characterization of the Adsorbent

FT-IR Analysis

Wood is a vegetable component that contains cellulose, hemicellulose and lignin as major ingredients. Therefore, different types such as–OH, -COOH and amine functional groups can participate in the adsorption [15]. FT-IR spectra of activated carbon prepared from Phragmites australis (Cav.) are shown in Figure 3.

The spectrum (TAC) show bands in (3421.12, cm^{-1}) for (-OH) stretching vibration. Peak observed in the (1712.79 cm^{-1}) indicate C=O stretching of carbonyls (carbonyl in -COOH or ester groups). The bands in (1604.77 cm^{-1}) is attributed to the aromatics C=C stretching; and in the (1103.28 cm^{-1}) can be traced back to C–O stretching [16].

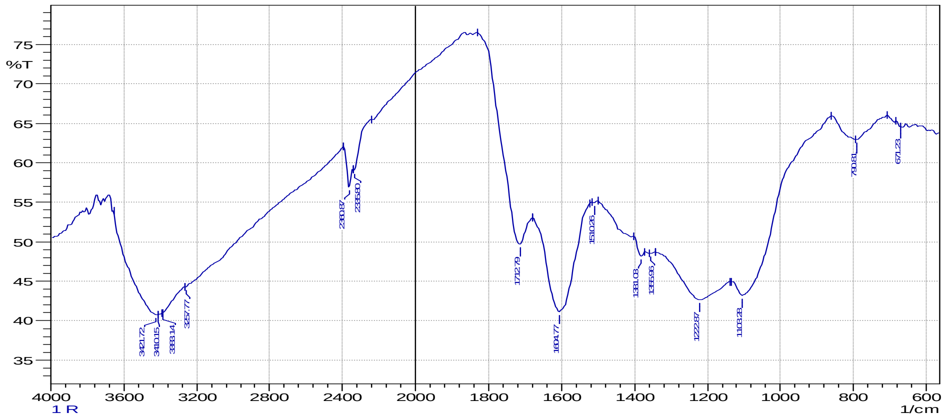
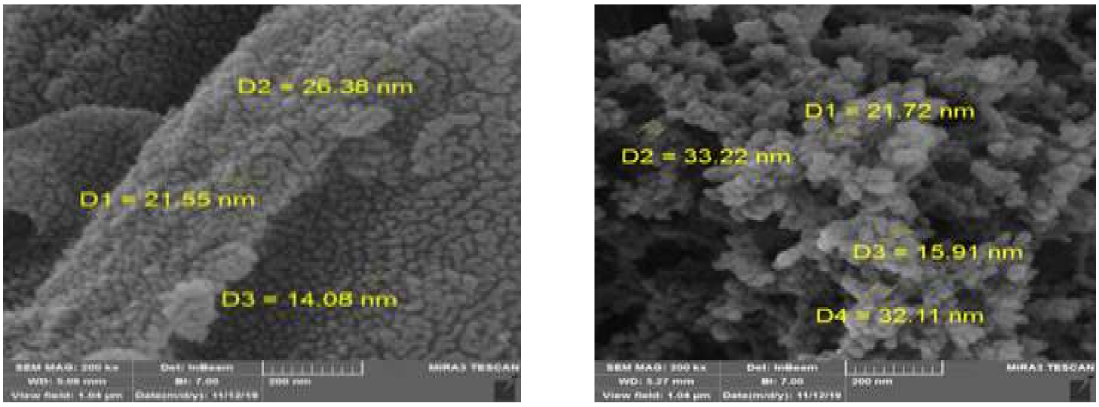


Figure 3: Spectrum (FT-IR) for TAC.

SEM Analysis

The surface morphology of TAC is carried out using SEM, this is because the SEM images enables us to directly observe to the changes in the surface microstructure of the TAC due to the modification [17]. Also, the surface morphology before and after adsorption are comparable [18]. Figure 4 (a and b) represent SEM images of TAC , It is noticeable in the SEM image (200nm) of TAC that the surface of a similar to the masses interspersed with holes and surrounded by cracks connected to each other to form what looks like valleys and this gives it the characteristic of porosity that the distribution of these blocks and holes in this surface is relatively homogeneous, as it shows the morphology of the surface and its porosity before and after adsorption, it is clear that malathion particles cover the TAC surface(Figure 4 (b))indicating that adsorption has occurred. The large surface area is evident from the small size of matter particles, as the dimensions of a portion of particles are within the nanoscale, and this enhances their ability to adsorb.



a **b**

Figure 4: Image of SEM for TAC Surface (200nm) (a) Before and (b) After Malathion Adsorption.

Adsorbent Dose Effect

Adsorbent dose is one of the key parameters effecting on adsorption capacity and balance point for contamination adsorption [(14)]. To study the adsorbent dosage effect, 0.1-0.75 g (2, 5, 10 and 15g / L) of TAC was treated separately with (50 ml) of the malathion solutions of (50 mg/L) ,the flasks were shaken at (150 rpm) at the Temperature of (25°C) for (24 h), 5 ml of sample was taken away by pipette and centrifuged to separate the adsorbent. Then the absorbance of the residual Malathion was measured. As is evident from Figure 5 (a).

Figure 3(a), shows the differences of removal percentage of malathion by TAC, the removal percentage increased with increase of adsorbent dose from 76.4% at the adsorbent dose (2 g / L) to 95% at the dose (5 g / L), Then removal became complete with the higher doses of TAC used. This change in the removal percentage is explained by the increase of adsorbent dose that increases the possibility of the adsorbate particles reaching the active sites, This leads to an increased the removal percentage [19].

In this study, 0.25 g was chosen as a suitable dose in which to study and compare the effect of change in other factors effecting adsorption.

Effect of Contact Time

In pollution treatment process it is preferable that the contact time required for the maximum level of adsorption efficiency be short. In this study, the contact time between (5-180 min) with time intervals was investigated, the adsorption percentage of Malathion by TAC increases with increasing the contact time till reach equilibrium about an hour later. Figure 5(b).

It is noted that the adsorption of malathion was very fast during the first 5 min and become slow after that gradually, until the equilibrium is established, This behavior is Attributed to the high rate of adsorption velocity at the beginning of the contact because there is an abundance of active sites available for the adsorption process and then gradually slows down until the equilibrium is stabilize [7].

Effect of Initial Concentration

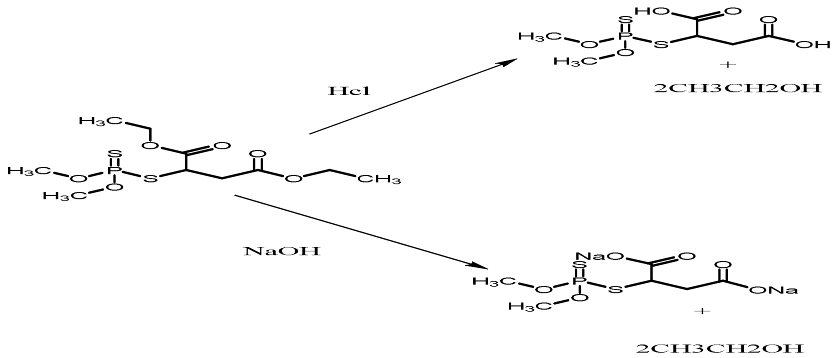
Parts of 0.25 g samples from the TAC were put in the series of flasks each containing 50mL from malathion solutions with concentrations (10, 20, 30, 40, 50, 60, 70 and 80 mg / L) at natural pH (7). These contents were shaken at (150 rpm) at the Temperature of (25 °C) for 90 min. After equilibrium, amount of solution were taken by a bibette and separated by the centrifuge To separate adsorbent particles from solution, Then the malathion residue was determined spectrophotometrically, Hence the amount of adsorbed is calculated Figure 5(c).

An increase in the adsorption capacity and a decrease in the removal percentage are observed increased concentration [20].

Effect of pH

The pH affects a lot in the adsorption process due to its effect on solute solubility and adsorption capacity of adsorbent surface [21]. The effect of pH is related to the nature of the adsorbent and adsorbate. In this exploration, pH studies were carried out in pH of (2–11) for 24 h. The pH value of the solution was controlled with NaOH and HCl solution. It is noted from Figure 5(d) that the removal efficiency had an increasing trend with increasing the pH in acidic conditions at pH 2 (87 %) to pH 7 (95 %) for TAC, Thus, there was a downward trend as the pH increased in alkaline conditions.

Decreased adsorption capacity of malathion at a pH below normal pH, , This can be attributed to the competition between protons and malathion molecules for the available active sites. But at pH 7 and the acidic values close to them, The increased adsorption capacity caused by the decrease in the number of protons that leads to a decrease in competition mentioned In addition to the abundance of oxygen atoms in the surface of activated carbon in the form of -COOH and -OH groups which are somewhat capable of electrostatic interactions with the positively charged adsorbate molecules, however, The basic conditions help to ionize some of the functional groups in TAC, and the functional groups of surface can become more deprotonated, and this leads to weakening of the interaction between the surface and the malathion molecules. The decrease in the adsorption efficiency when moving away from the natural PH value can be attributed to its effect on malathion, as when moving away to lower values than the natural PH, the acidity of the solution increases, so the hydrolysis of the ester groups that produce carboxylic acids increases, so the hydrogen bonding increases with water molecules, so the solubility increases and therefore the adsorption process decreases. However, when moving away from higher values than the natural PH, alkali of the solution increases, the hydrolysis in the base medium results in carboxylic acid salts, so the solubility increases, which leads to decreased adsorption.

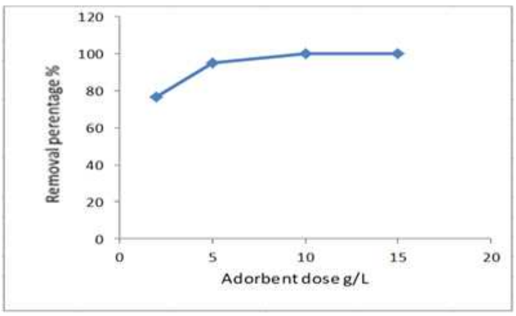


The pH value of 7 was chosen in this study because the pH value of the aquatic environment contaminated with malathion usually ranges between (6-8) [6].

Effect of Temperature

Temperature effect was studied by the Different temperature (15, 25, 35 and 45 °C). It was shown in Figure 5(e).

The figure shows that increasing the temperature from (15 ° C) to (45 ° C) led to a decrease in the percentage of malathion adsorption, This is due to the increase in the solubility of the pesticide with increasing temperature [7] or the weakening of vander waals attraction forces between the pesticide and the surface with increase in temperature [3].



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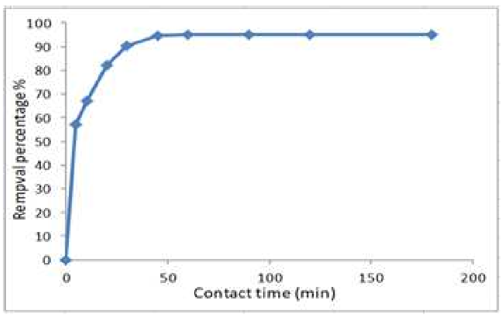

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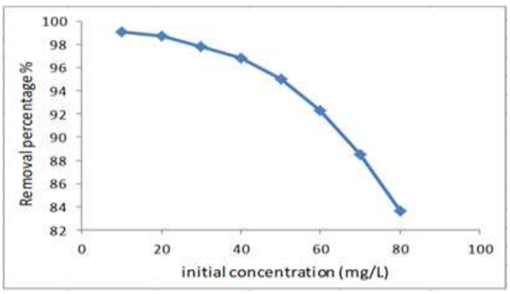

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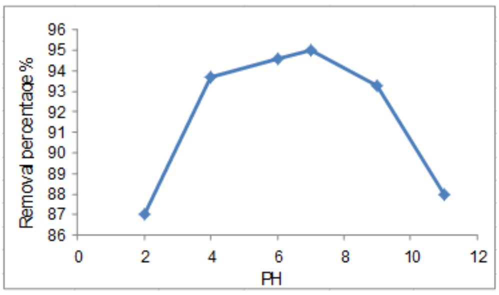

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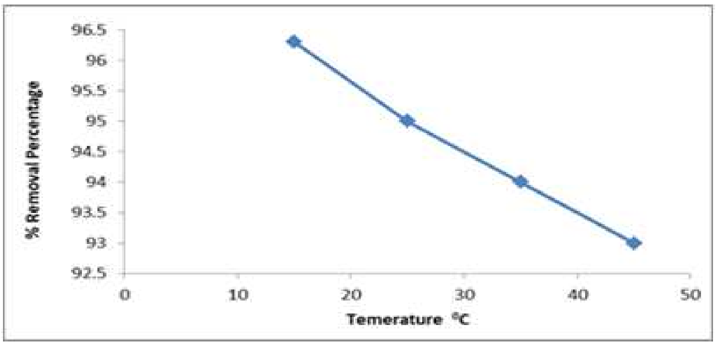


e

Figure 5: The Effect of (a) Adsorbent Dosage (b) Contact Time (c) Initial Concentration (d) pH (e) Temperature on the Removal Percentage.

Adsorption Isotherms

The study of adsorption isotherms gives information on the adsorption capacity, and therefore the study of these isotherms becomes necessary for the design of any adsorption system. [22]. Langmuir isotherm can be applied to adsorption from the solution in a manner almost identical to adsorption of gases on a hard surface, it remains confined to one layer, but in this case the adsorption is a competition between the solvent and dissolved molecules for the active adsorption sites [23]. The linear equation of Langmuir isotherm:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m\, b} + \frac{C_e}{Q_m}$$

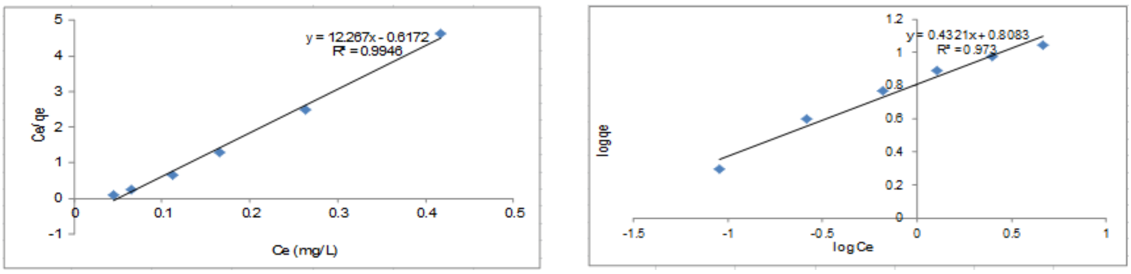
Where: Q_m: "maximum adsorption capacity" (mg / g), b: "Langmuir constant".

According to the Freundlich Equation, most for the adsorbent surfaces are heterogeneous, meaning that the adsorption sites in them possess different potential energies and different geometric shapes [24]. Therefore, the roll of these locations toward the same particles is different. In addition to adsorption on heterogeneous surfaces, this Equation deals with multilayer adsorption [25].Its logarithmic formula is:

$\log q_e = \log KF + n \log C_e$

Where K_f : adsorption capacity for Freundlich isotherm, n: Freundlich experimental constant.

In this study, these two isotherms were used to obtain necessary information on the conditions and nature of adsorption, the fitting of the Langmuir and Freundlich equation for the data on the adsorption process was investigated by graph (Ce/qe) versus (Ce) "Langmuir isotherm" and (log qe) versus (log Ce) "Freundlich isotherm" As shown in Figure 6 (a) and (b).



a b

Figure 6: Isotherm (a) Langmuir (b) Freundlich for Malathion Adsorption on TAC.

From the linear form to Langmuir isotherm, a and b constants are evaluated by the slope that is equal (1/a) and intercept that is equal (1/ab) of linear equation, whereas in the linear form to Freundlich isotherm the intercept was equal (lnKf) gives a measure and the slope was equal (1/n).These parameters computed from line plots using Langmuir equation and Freundlich equation, and R2 values are shown in Table 1

Table 1: Parameters of Langmuir and Freundlich Isotherm for Malathion Adsorption on TAC Adsorbent

Langmuir Isotherm	Q_m(mg/g)	b(l/mg)	R^2
	12.33	1.5902	0.9946
Freundlich Isotherm	**N**	**K_f**	**R^2**
	2.3142	6.431318	0.973

It is noted that the values of R^2 for the Langmuir equation were 0.9946 and Freundlich equation were 0.973, indicating the isotherm of Langmuir Best fit with experimental results.

The Langmuir isotherm is also expressed by equation: $R_L = 1/ 1+ bC_0$

Where R_L: "dimensionless constant separation factor".

Can the adsorption process be: unfavorable (R_L> 1), favorable ($0 < R_L<1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). In this study, the R_L obtained is (0.04); this result Indicates that a malathion adsorption process over TAC is favorable, and this is It may be related that this adsorbent has a large surface area [26].

Kinetic Studies

The study of adsorption Kinetics is important to infer its efficacy as well as to know the type of its mechanism:

Pseudo First Order Kinetic Model

This model was suggested by Largergren, the linear form for equation of this models is:

$$\ln (q_e - q_t) = \ln q_e – k_1t$$

Where: k_1 reaction rate constant of this model (L / min).

Pseudo Second Order Kinetic Model

The linear form for this models equation is: $t/q_t = tq_e + 1/ K_2q_e^2$

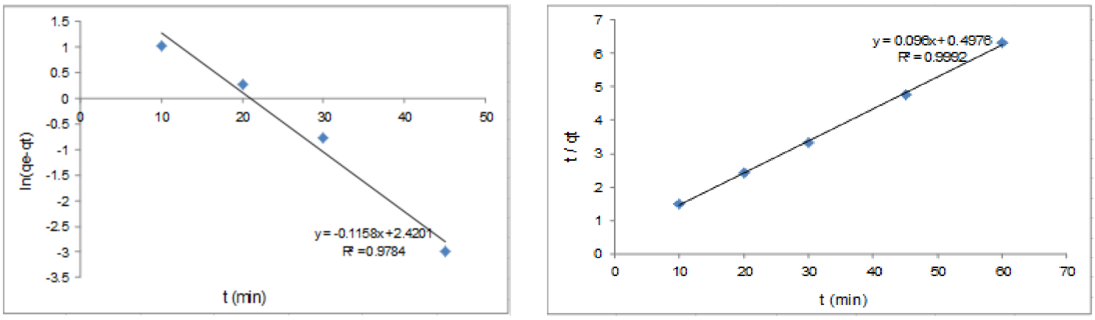
Where: k_2 reaction rate constant of this model (mg g^{-1} min^{-1}) .

The initial adsorption rate h (mg/g min), when $t \longrightarrow 0$ can be defined as:

$$h = k_2\, q_e^{\,2}$$

This model describes chemical adsorption. It is characterized by the ability to calculate the capacity from it without the need to know it through experiments, as well as the possibility of finding the initial adsorption rate from it. This information obtained from the kinetics model and others is necessary to design an adsorption process.

The values of ln (q_e - q_t) against the time t were plotted based on the linear relationship of the “Pseudo-first-orderequation”, and according to the linear relationship of the “Pseudo-second-orderequation”, the values of t/qt against the time t were plotted as in Figure 7.



a b

Figure 7: Experimental Values According to "Pseudo-First-Order Kinetics Model" (a) "Pseudo-Second-Order Kinetics Model" (b) In Its Linear form at Temperature (25°C),TCA Adsorbent Dosage (5 g / L), Initial Concentration (50 mg / L), pH (7).

From the data according to "Pseudo-first-order kinetics model", The k_1 value, adsorption capacity, and correlation coefficient (R^2) were calculated, And from the data according to "Pseudo-second -order kinetics model", the value of k_2, the adsorption capacity, and the R^2 were calculated, Table 2 indicates the parameters obtained by means of these two kinetic models [7].

Table 2: The Kinetic Parameters for Malathion Pesticide Adsorption on the TAC Adsobent

Pseudo-First-Order Kinetic Model		Pseudo-Second-Order Kinetic Model	
parameter	Value	parameter	value
q (exp) (mg/g)	9.5	q (exp) (mg/g)	9.5
q (cal) (mg/g)	11.247	q (cal) (mg/g)	10.416
$K_1(min^{-1})$	0.1158	$K_2(min^{-1}.g.mg^{-1})$	0.0185
R^2	0.9784	R^2	0.9992

It is noted from the values in the table that the "pseudo-second-order kinetic model" is more applicable to the adsorption process in the studied systems, because the value of R^2 and the lower deviation of the experimental value from the calculated value of the adsorption capacity is likely to match the adsorption with this model [6] Therefore, it was concluded that the "rate determination step" is a chemical absorption because this kinetic model agrees with this assumption[27].

Provides hydroxyl groups in the TAC which appears in the FT-IR spectrum, and the presence of electron-rich atoms (O, S, P) in the malathion molecules support the hypothesis of forming a hydrogen bonding between the TCA and the malathion molecules as one of the suggested mechanism of adsorption

CONCLUSIONS

This study demonstrated the feasibility of using low-cost activated carbon prepared from Phragmites Australis to remove the malathion pesticide from contaminated water through an adsorption process. Removal efficiency is affected by practical conditions such as initial concentration, contact time, pH, Adsorbent dose, and temperature. The results of the study showed that Qm = 12.33 mg/g and that the equilibrium data are well fit with the Langmuir isotherm and that the adsorption kinetic is subject to the "pseudo-second-order model", it has also been found that the adsorption is exothermic and spontaneous process.

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