

## Optimum Conditions for Adsorption of Lindane by Activated Carbon Derived from Date Stones

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**Abstract:** Trend of using economic products from agriculture waste in removing organic pollutants from water became highly accepted. So, the current study discussed the optimum experimental conditions to utilize activated carbon, produced from agriculture by-product, to adsorb and remove lindane from aqueous solutions. Date stones were used for preparation of activated carbon using chemical activation by impregnation with concentrated  $H_3PO_4$  (85%) at a ratio of 1:3 (w/w date stones:  $H_3PO_4$ ) followed by pyrolysis at 500°C for 2h (AC1). Norit activated carbon was used as a reference carbon (AC2). A matrix effect analysis was applied to correlate the lindane adsorption capacity to the agitation time, initial concentrations of lindane (1-10mg/L), carbon dose (50-100 mg/100 ml), pH (3-11) and different temperatures (15-40°C). Physicochemical properties were investigated by several procedures; elemental analysis, SEM and porosity characteristics. The maximum removal percentages of lindane at equilibrium time were 98.6% for AC1 (within 3hrs) and 94% for AC2 (within 4hrs). The decrease in pH from 11 to 3 leads to an increase in the lindane retention onto both ACs, whereas temperature had slightly effect on the adsorption capacity. It can be concluded that date stones activated with  $H_3PO_4$  is effective in the removal of lindane from aqueous media under different conditions. The experimental isotherm data were analyzed using Langmuir, Freundlich and Harkins-Jura isotherm equations. The error analysis demonstrated that the Langmuir equation was found to best represent the equilibrium data.

**Key words:** Adsorption • Activated Carbon • Date Stones • Lindane

### INTRODUCTION

Pesticides contamination has become an environmental concern worldwide because many pesticides have been used extensively for a number of years and they have harmful effects to human health and the environment. Lindane is one of the organochlorine pesticides (OCPs) which have been used as a broad spectrum insecticide and in the medicine field as scabicide since the early 1950s [1]. In Egypt, it is estimated that lindane used on the cotton in agriculture totaled around 11300 metric tons (MT) between 1952 and 1978 [2]. Substantial human exposure to OCPs has occurred due to its chemical stability, resistance to biodegradation in

combination of factors that include the large quantities applied since 1940s and bioaccumulation along the food web [3].

So research efforts dealing with the processes affecting the removal of pesticides from contaminated industrial effluents are critically needed in order to prevent further damage to surface and groundwater bodies.

The application of conventional biological treatments for the removal of organic refractory contaminants from aqueous solutions has proven to be ineffective; therefore, the satisfactory results obtained by using activated carbon (AC) led to their wide applications for the removal and control of synthetic and naturally occurring organic

chemicals in water[4,5]. Furthermore, a number of treatment technologies such as precipitation, coagulation-flocculation, ozonation, photo-Fenton degradation, catalytic wet oxidation, electrochemical treatment, biological methods, reverse osmosis membranes, evaporation and adsorption have been used for the removal of organic pollutants i.e. pesticides [6-8]. Despite the availability of the above-mentioned processes for the removal of organic pollutants, adsorption process is recognized as the most efficient and promising fundamental approach in the wastewater treatment processes as it can generally remove all types of organic pollutants and the effluent treatment is convenient due to its a simple design and easy operation [9]. Activated carbon, among a large variety of adsorbents, is still by far the most important one in environmental pollution control due to its large surface area, high adsorption capacity, porous structure and selective adsorption [10,11]. Moreover, it is established that the pore size distribution, surface chemistry and mineral matter content are the most important characteristics of AC in the adsorption of organic compounds. The adsorption capacity depends on the accessibility of the organic molecules to the microporosity which depends on their size. Thus, under appropriate experimental conditions, small molecules such as phenol can access micropores, natural organic matter can access mesopores and bacteria can only access macropores [5].

On the other hand, Egypt produces millions of tons of agricultural wastes and faces serious problems associated with burning of agricultural wastes in the open field. Therefore, there are many advantages of the use of these agricultural wastes as the volume of solid waste would be reduced, the treatment of wastewater by these AC would be achieved at reasonable cost. From the above considerations, the current study aimed to use date stones as agricultural wastes, renewable and low cost precursor for the production of effective sorbents (ACs) and tested as to their potential application to sequester lindane as organic pollutant from aqueous solutions under different conditions. A Norit activated carbon as a commercial carbon was chosen to evaluate the adsorption capacity of produced activated carbon.

## MATERIALS AND METHODS

**Materials:** Certified standard of lindane ( $\gamma$ -HCH) with purity greater than 99.8 % was purchased from Sigma-Aldrich Laborchemikalien, GmbH D-30918 Seelze. Hexachlorobenzene (HCB) was obtained from ALLTECH,

Applied. High grade solvents (n-hexane, diethyl ether and methanol) as well as phosphoric acid (85 %) were purchased from Merck, Darmstadt, Germany. A commercial MB was obtained from Tianjin Chemicals & Reagent Corp. China. Supelclean EVNI-18 SPE tubes 6 ml (0.5g) was provided by Supelco Company, (Bellefonte, PA). NORIT Granular Activated Carbon, NORIT GAC 1240 PLUS was purchased from the Netherlands.

**Preparation of Activated Carbon:** The Date stones were dried at 110°C for 24 h to reduce the moisture content. The dried date stones were then crushed and sieved. Size fractions of 1-2 mm were used in this study. The preparation of activated carbon was conducted in two steps: carbonization and activation. Both carbonization and activation were carried out in a stainless steel 316 reactor (length 700 mm and internal diameter 25 mm); the reactor was admitted into a vertical tube furnace. In the carbonization step, approximately 50 g of date stones was placed in the reactor and the furnace temperature was increased from room temperature to 500°C with a heating rate of 10°C/min and held at this temperature for 2 h under  $N_2$  flow. In the activation step, the resulting char was immersed in ortho phosphoric acid with different weight ratios [1:1, 1:2, 1:3, 1:4, DS:  $H_3PO_4$ , (W/W)] and the mixtures were kneaded with adding distilled water. The mixtures were then dried at 110°C for 24 h. The impregnated sample was placed in the reactor and heated up to 500°C under  $N_2$  flow for 2 h. After activation, the sample was cooled down under  $N_2$  flow, washed sequentially several times with hot distilled water until pH of water reached  $6 \pm 0.5$ , then the sample was dried for 24 h and finally kept in a tightly closed bottle.

**Methylene Blue Test (MB):** In order to establish the suitable impregnation ratio between the precursor and phosphoric acid. Date stones were impregnated with concentrated  $H_3PO_4$  (85%) at different ratios of 1:1, 1:2, 1:3 and 1:4 (w/w date stones:  $H_3PO_4$ ) and tested for the adsorption of MB dye as follows: adsorption of MB was determined by adding 0.2 g of AC to flasks containing 50 ml of MB solution (500 mg/l). The flasks were kept in thermostat shaker at  $25 \pm 2^\circ C$  for 48 hr. After that time the samples were centrifuged and the concentrations of the adsorbate were determined by spectrophotometer at the wave length for maximum absorbance of dye ( $\lambda_{max}=660nm$ ) [12]. The amount of MB was computed from the following equation:

$$q_e = (C_i - C_{48}) / m,$$

Where,  $q_e$  is the amount of MB adsorbed onto the activated carbon (mg/g),  $C_i$ , the initial concentration of MB (mg/l),  $C_{48}$  is the concentration of MB after 48 hrs (mg/l),  $V$  is the volume of liquid phase (l) and  $m$  is the mass of activated carbon (g).

**Characterization of Sorbent Agents:** The carbon, hydrogen, nitrogen and sulfur contents in date stones (DS), activated carbon and commercial activated carbon (Norit) were determined using a CHNS elemental analyzer (Thermo Electron Flash EA 1112).

The surface area and pore structural parameters of activated carbon (AC1) and Norit carbon (AC2) were examined from the adsorption-desorption isotherm of nitrogen at 77 K. The  $S_{BET}$  was calculated using BET equation and the pore size distribution was calculated on the basis of desorption data following the Barrett-Joyner-Halenda (BJH) method.

#### Batch Kinetic and Adsorption Isotherm Experiments:

AC1 and AC2 were characterized and tested for their potential application for the removal of lindane ( $\gamma$ -HCH) from aqueous solution.

An amount of 0.1 g of each carbon sorbents was incubated with a 100 ml solution of lindane (100  $\mu$ g/100 ml) using water-bath shaker at 25°C and agitated at 100 rpm for 0.5, 1, 2, 3, 4, 6, 8 and 24 h. After the agitation period, the samples were filtrated through a Whatman No. 40 filter paper and 10  $\mu$ g of hexachlorobenzene (HCB) was added to the supernatant as an internal standard and stirred for 10 min.

The amount of lindane adsorbed at each time ( $Q_t$ , mg lindane/g adsorbent) was calculated based on the following equation:

$$q_t = (C_o - C_t) V/m$$

Where  $C_o$  and  $C_t$  are the liquid-phase concentrations (mg/l) of the investigated pesticide at initial and at any time respectively;  $V$  is the pesticide solution volume (l) and  $m$  is the adsorbent mass (g). The equilibrium condition is reached when no further decrease in the lindane concentration occurred. Isotherm studies were conducted by adding the lindane solution (100 ml) of different concentrations (1, 2, 4, 6, 8 and 10 mg/l) and shaking with constant weight of adsorbents (100 mg) at pH=7 and 25°C for the equilibrium time.

**Conditions of Lindane Adsorbability:** To study the effect of carbon dosage on the retention of lindane from aqueous solution, three initial levels of carbon (50, 75 and 100 mg) were incubated with different concentrations of lindane (1, 2, 4, 8 and 10 mg/l, respectively) in 100 ml of aqueous solution. The mixtures were agitated using a thermostatic shaker water bath at 100 rpm for 3 h at  $25 \pm 1^\circ\text{C}$  for AC1 and for 4 h for AC2.

To study the influence of temperature on the adsorption capacity of AC1 and AC2 of lindane from aqueous solutions, the same procedures were followed under two additional temperatures: 15 and 40°C. In order to study the influence of pH on lindane adsorption at  $25 \pm 1^\circ\text{C}$ , different concentration levels of lindane (1, 2, 4, 6, 8 and 10 mg/l, respectively) in 100 ml water were incubated with 100 mg AC1 for 3 h and for 4 h for AC2. The mixtures were agitated at 100 rpm. The pH was adjusted using a NaOH (1.0 M) or HCl (1.0 N) and measured by pH meter (pH-meter 764 Multi-Calimatic).

**Extraction of Lindane from Aqueous Solution:** Extraction of lindane residue from aqueous solution was carried out using EVNI-18 SPE through three main steps: (I) Conditioning: the column was activated using 6 ml of hexane: diethyl ether (1:1) two times followed by 6 ml of methanol and then 6 ml of deionized water. (II) Sample extraction: the sample was transferred to the column and slowly passed through SPE using vacuum at flow rate of 10 ml/min. To ensure that the SPE packing does not dry between conditioning and sample addition, about 1 ml of deionized water was remained above the top of packing material. (III) Elution: The column was dried for 10 min under vacuum and lindane residues were eluted two times using 1.5 ml of hexane: diethyl ether (1:1). The eluate was evaporated under stream of nitrogen to 1.0 ml to be ready for analysis.

**Instrumentation and Analytical Conditions:** Lindane analysis was performed with GC/MS applied in full scan mode and MID (Multiple Ion Detection) was set for low concentrations. The separation was accomplished on ZB-5ms (30 m x 0.25 mm i.d, 0.25  $\mu$ m film thickness), Cat. Nr. 7HG-Go10-11, Phenomenex. Splitless (0.5 min) and injection temperature was 280°C. Helium was used as a carrier gas at constant flow of 1.2 ml/min. For full scan mode, the temperature program was performed as follows: initial temperature 35°C, held for 1 min; and then increased to 150°C at a rate of 20°C /min. Then it was increased to

260°C at a rate of 10°C /min and held constant for 5 min. For the MID method, initial temperature of 35°C was applied and held constant for 1 min; and then increased to 150°C at a rate of 20°C /min. Then it was increased to 320°C at a rate of 10°C /min and held constant for 5 min. The MS was started for acquisition after 3.7 min and stopped at 20 min for both methods. Full scan range was set between 40-450 m/s. For MID acquisitions selected diagnostic mass ions were: 181, 183, 217, 219, 284, 286 and 288.

## RESULTS AND DISCUSSION

**Effect of Date Stones to Acid Ratio on Adsorption of Methylene Blue:** Table 1 represents the variation of the Methylene Blue number of the prepared activated carbon samples with the activation time and temperature at specific date stones: acid ratios.

The results from table 1 illustrated that the maximum adsorption of methylene blue dye is obtained at an impregnation ratio of 1:3. Therefore, this ratio is the suitable impregnation ratio and selected for the production of activated carbon.

### Characteristics of the ACs

**Elemental Analyses of the Sorbent Agents:** The elemental analyses for AC1, DS and AC2 were presented in table 2.

It is well known that heteroatoms, originating from the raw material activated carbon or could be introduced during preparation or further treatments [13], are deeply influenced by the charge, hydrophobicity and electronic density of the AC surface. Furthermore, the presence of especially oxygen can activate primary adsorption centers [14], due to their polarity and possibility to attract water via hydrogen bonding. The carbon surface chemistry is, therefore, influenced by the presence of heteroatoms [15] and has a great influence on both, electrostatic and non-electrostatic interactions.

The results presented in table 2 revealed that the element contents of date stones (DS) for C, H and O are significantly different from the other adsorbents.

**Characterization of Porosity and Surface Area:** The porosity and specific surface area ( $S_{BET}$ ) of AC1 and AC2 were given in table 3.

The characterization of the adsorbent agents revealed that the surface area ( $S_{BET}$ ) of AC1 (date stones activated with  $H_3PO_4$ ) is found to be lower than the reference AC2. The isotherm of adsorption and desorption of nitrogen at 77K for AC1 and AC2 were shown in Fig. 1. Pore size distribution (PSD) according to BJH method and Kelvin equation (Fig. 2 a,b) showed that: a)  $V_{tot}$  for AC1 is greater than the reference material (AC2) and b) the micropore distribution ( $d < 2$  nm)

Table 1: Methylene blue number for different ration of date stones and phosphoric acid.

DS: $H_3PO_4$	1:1	1:2	1:3	1:4
Methylene blue number (mg/g)	105	108	123	112

Table 2: Elemental analyses for biomass and other activated carbon.

Sorbent agents	Elemental contents (%)				
	C	N	H	S	O*
(AC1)	77.9 ± 0.60	1.53 ± 0.04	2.54 ± 0.07	Nil	19.0 ± 0.3
(DS)	49.3 ± 0.40	1.14 ± 0.01	6.80 ± 0.03	Nil	42.8 ± 0.4
(AC2)	80.9 ± 6.25	0.67 ± 0.09	0.38 ± 0.03	0.41 ± 0.04	18.0 ± 6.2

AC1= Date stones activated with  $H_3PO_4$ ; DS= date stones; AC2 = Norit activated carbon. \* By difference.

Table 3: Porous structure parameters determined by sorption at 77 K.

Sorbent	Agents	S <sub>BET</sub> , (m <sup>2</sup> /g)	V <sub>tot</sub> , (cm <sup>3</sup> /g)	Pore size distribution (cm <sup>3</sup> /g)					V <sub>micDR</sub>	L <sub>N<sub>2</sub></sub> , nm	E,kJ/mol
				<2 nm	2-3 nm	3-5 nm	5-10 nm	10-50 nm			
AC1		873	0.791	0.339	0.075	0.111	0.119	0.148	0.298	2.55	15.63
AC 2		1082	0.555	0.401	0.030	0.037	0.029	0.059	0.368	1.06	21.59

AC1= Date stones activated with  $H_3PO_4$ ; DS= date stones; AC2 = Norit activated carbon.

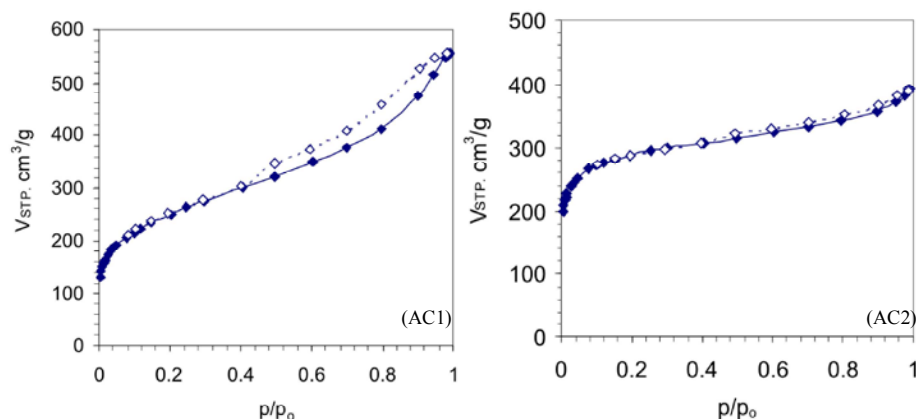


Fig. 1: Isotherm of adsorption (-♦-) and desorption (-◇-) of nitrogen at 77K for AC1 and AC2.

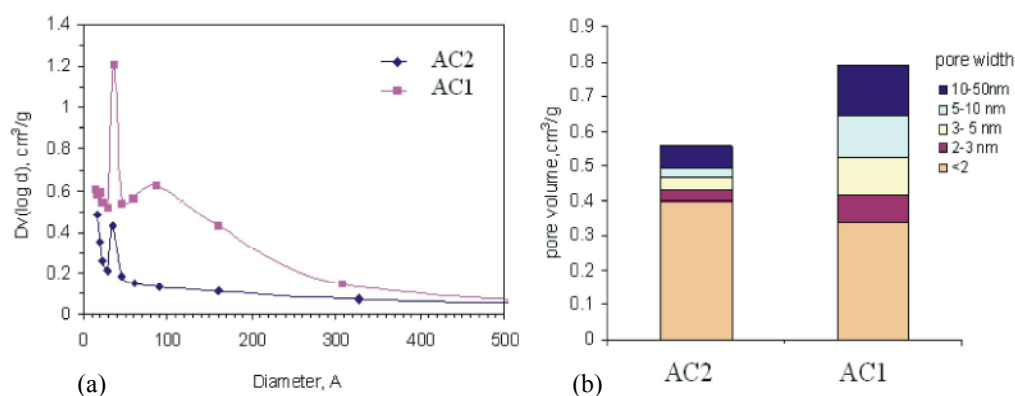


Fig. 2: Pore size distribution according to BJH method (A) and Kelvin equation (B).

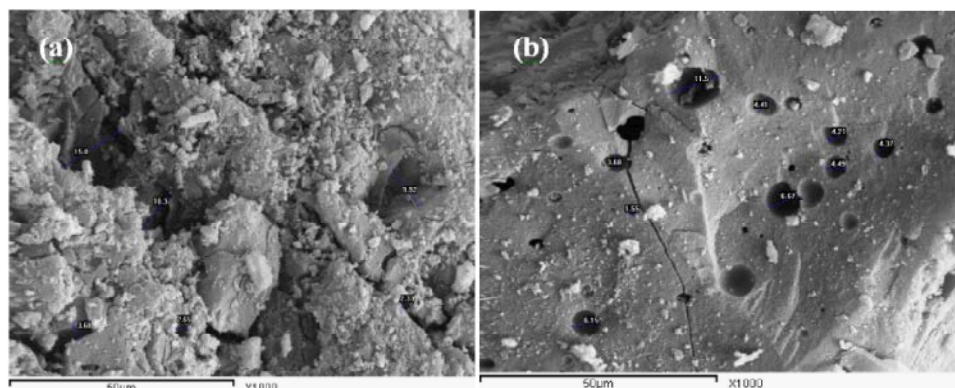


Fig. 3: SEM images at magnification of x1000 (a) AC1 and (b) AC2.

represents 42.8 % of the total pore volume for AC1, while it constitutes 72.1 % for the reference AC2. Meanwhile, the mesopore distribution ( $d = 2-50$  nm) was found to be systematic higher for AC1 than the reference AC2. The ratios of  $V_{mic}/V_{meso}$  were 0.75 and 2.59 for AC1 and AC2, respectively.

**Scanning Electron Microscope (SEM):** Scanning electronic microscopic images were shown in Fig. 3 corresponding to activated carbon derived from date

stones (AC1) and Norit carbon as a reference carbon (AC2). It can be observed that the external surface of the ACs was highly porous and full of cavities particularly AC1 and the pores had different size and shapes. This texture is beneficial for any adsorption process because large sized pores serve as feeder pores to lower dimension ones, i.e. meso- and micropores[16]. It was revealed that the chemical activation of sorbent agent results on a creation and developing of pores since Daifullah *et al.* [17] stated that phosphoric acid introduced into the

material is the main factor determining the porosity and pore size distribution of the obtained activated carbon.

**Kinetic Adsorption:** Data presented in Fig. 4 shows the kinetic of sorption for each sorbent agent and biomass against lindane. The results indicated that 82% adsorption of lindane from aqueous solution was achieved within 30 min for AC1. For AC2, the reference carbon, the adsorption of lindane was only 16.5%. The retention of lindane onto the both activated carbon was increased as the contact time increased. It is clear from the current results that the complete adsorption of lindane (98.6 %) is almost achieved within 180 min for AC1. However, for AC2 equilibrium is obtained much later (240 min) and only 94% retention is reached.

The current results are found to be in accordance with those reported by El-Bakouri *et al.* [18] who reported that the equilibrium adsorption is achieved within 3.5 h for aldrin, dieldrin and endrin using activated carbon derived from date stones.

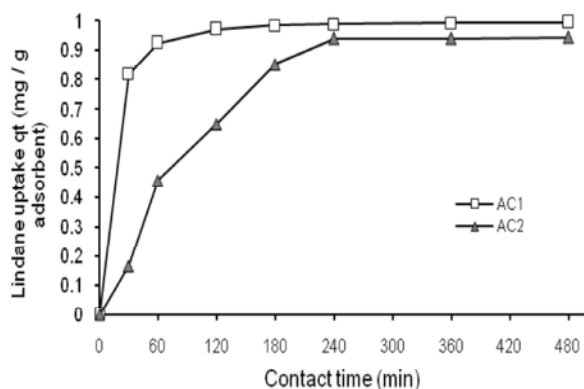


Fig. 4: Effect of contact time on the adsorbability of lindane to sorbent agents. Experimental conditions: (100mg of adsorbent, 1mg lindane/l, pH = 7, T = 25 ± 1°C).

According to Dias *et al.* [5], the adsorption process of AC could be occurred through an electrostatic or non-electrostatic interactions. When the adsorbate is an electrolyte that dissociates in aqueous solution,

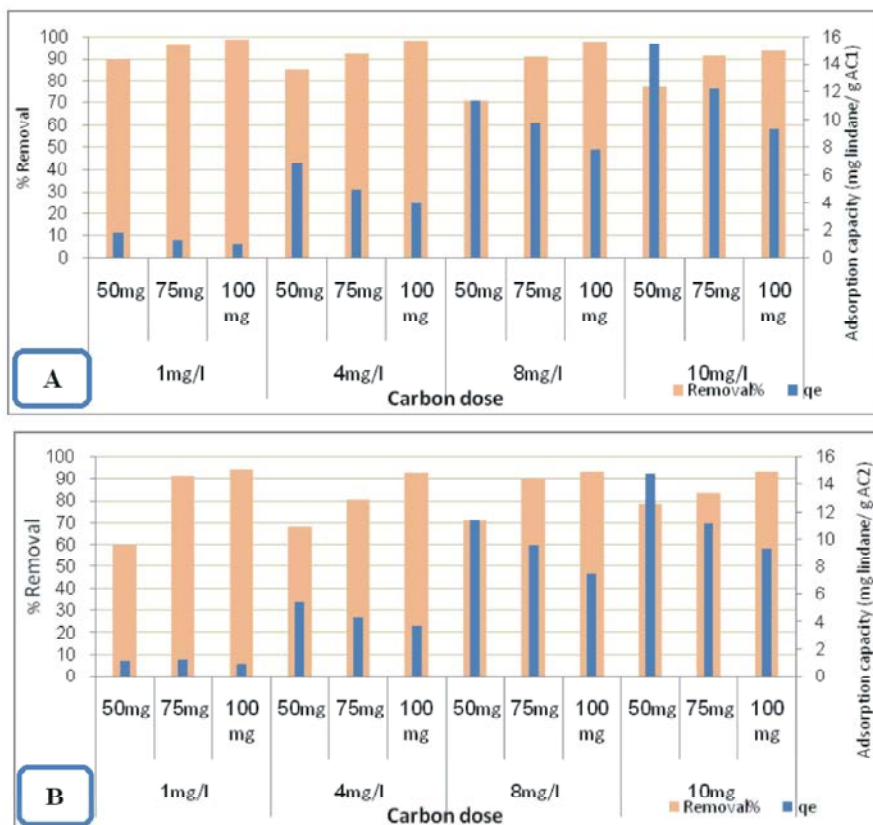


Fig. 5: Effect of initial carbon doses on % removal and the adsorption capacity of the ACs against lindane. (A: AC1 & B: AC2). Experimental conditions: (50, 75, 100 mg of adsorbent, 1, 4, 8, 10 mg lindane/l, pH 7, T = 25 ± 1°C).

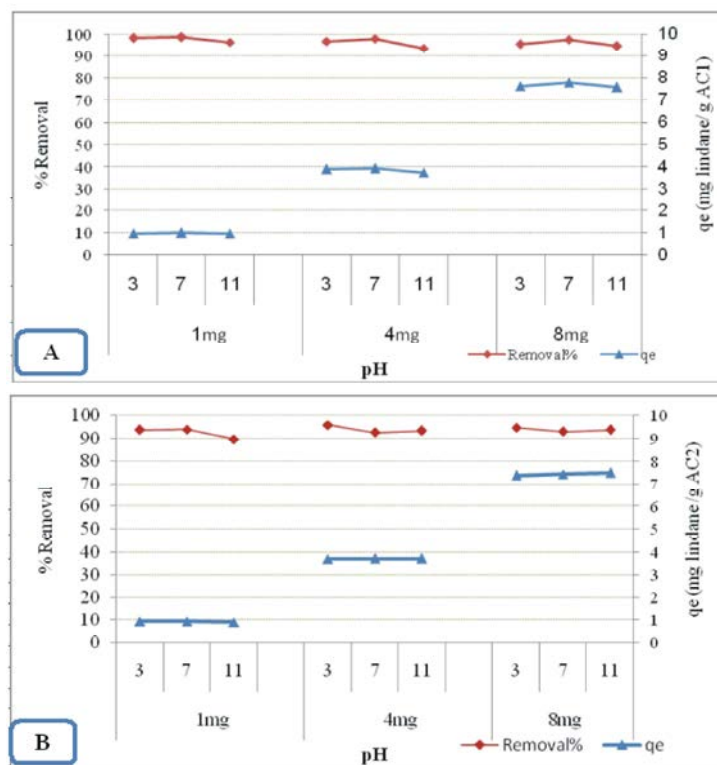


Fig. 6: The effect of pH on % removal and adsorption capacity of lindane from aqueous solutions (A: AC1 & B: AC2). Experimental conditions: (100mg of adsorbent; 1, 4, 8 mg lindane/l; pH = 3, 7, 11; and  $T = 25 \pm 1^\circ\text{C}$ ).

electrostatic interactions occur. The nature of these interactions that can be attractive or repulsive depends on: (i) the charge density of the carbon surface; (ii) the chemical characteristics of the adsorbate; and (iii) the ionic strength of the solution. Whereas, non-electrostatic interactions are always attractive and include: (i) van der Waals forces; (ii) hydrophobic interactions; and (iii) hydrogen bonding. Moreover, Moreno-Castilla [19] reported that the properties of the adsorbate that mainly influence the adsorption process in AC are: (1) molecular size; (2) solubility; (3) pKa; and (4) nature of the substituents (in the case of aromatic adsorbates).

#### Effect of Initial Carbon Dosage on Lindane Adsorption:

Data presented in Fig. (5 a, b) showed that the effect of initial carbon dosage on their adsorption capacity of different levels of lindane (1-10 mg/l) from aqueous media. The current results indicated that the removal percentage of lindane from aqueous solution using 50 mg of AC1 ranges from 70 to 90 % at different concentration levels (i.e. 1-10 mg/l). However, increasing the amount of AC1 to 100 mg succeeded to remove 93-99 % of lindane at the

same concentrations. When AC2 was used, the maximum adsorption of lindane ranged from 60 to 78.5 % at 50 mg while the percentage of removal was increased 1.56 folds with increasing carbon dosage to 100 mg and reached 94 %. This result is logic, considering the available surface area and the total pore volume including micro and mesopores.

In addition, the results presented in the same figures illustrate that, the uptake of lindane from aqueous solution reached 11.3 and 11.4 mg/g for AC1 and AC2; respectively with 50 mg from each sorbent at concentration level of 8 mg/l of lindane.

#### Effect of pH on Adsorption of Lindane to Activated Carbons:

Since the surface charge of the adsorbent could be modified by changing pH of the solution, pH is one of the most important parameters affecting the adsorption capacity of carbon towards lindane pesticide.

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 lindane. It was found that the retention of lindane onto the AC1 and AC2 has the same behavior (Fig. 6).

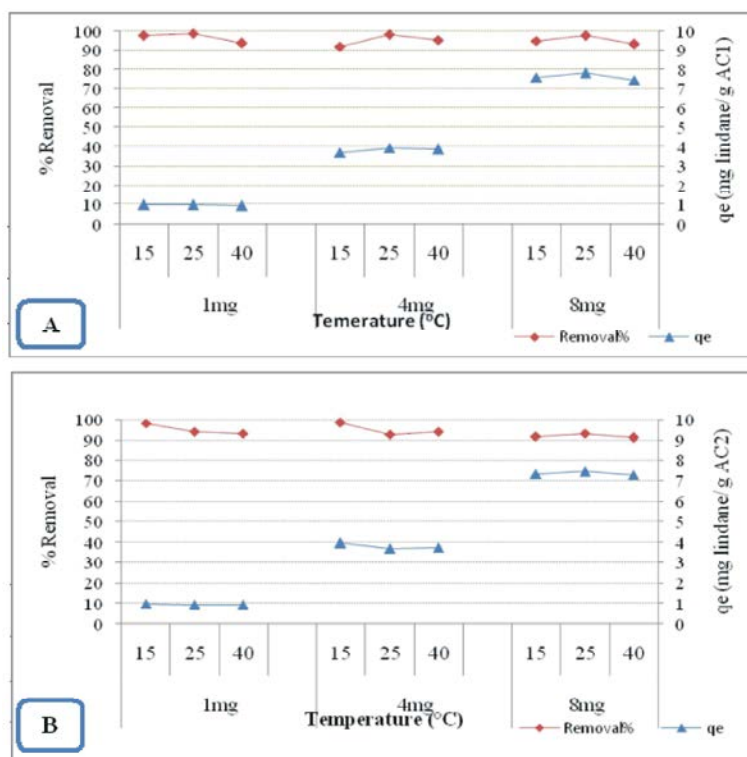


Fig. 7: The effect of temperature on % removal and adsorption capacity of lindane from aqueous solutions (A: AC1 & B: AC2). Experimental conditions: (100 mg of adsorbent; 1, 4, 8 mg lindane/l; pH 7;  $T = 15, 25, 40 \pm 1^\circ\text{C}$ ).

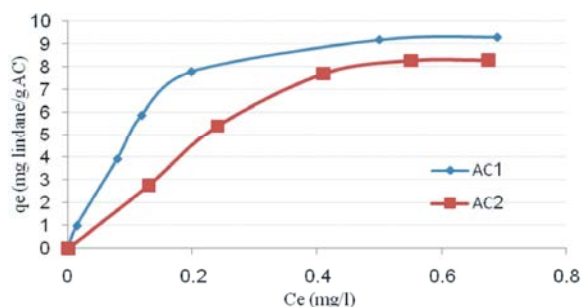


Fig. 8: Adsorption isotherm studies of lindane onto AC1 & AC2. Experimental conditions: (100mg of adsorbent; 1, 2, 4, 6, 8, 10 mg lindane/l; pH = 7;  $T = 25 \pm 1^\circ\text{C}$ ).

This can be explained by considering the effect of pH values on the surface properties of the sorbent as reported by Akhtar *et al.* [20]. At lower pH values, the surface of the sorbent would be surrounded by the hydronium ions, which may enhance the sorbents by greater attractive forces [21]. Furthermore, Daifullah *et al.* [17] illustrated that at low pH values, the surface of the carbon takes up the  $\text{H}^+$  ions from the solution and hence, increasing the acidity of the sorbent surface.

#### Effect of Temperature on Adsorption of Lindane to Activated Carbons:

The effect of temperature on the adsorption capacity of adsorbent agents against different levels of lindane was shown in Fig. 7 a,b. The results indicated that increasing temperature from  $15^\circ\text{C}$  to  $40^\circ\text{C}$  leads to a minor decrease of lindane adsorption at equilibrium.

The removal percentage of lindane from aqueous solution using AC1 at initial levels of 1, 4 and 8 mg/l reached between 92 and 98 % at the low temperature ( $15^\circ\text{C}$ ) however; at higher temperature ( $40^\circ\text{C}$ ), these percentages were slightly decreased and recorded between 93 and 95.5 % based on the initial concentration levels of lindane in the aqueous solution. The same trend was observed for AC2, the reference carbon, as the percentage of reduction recorded 91 and 98 % at  $15^\circ\text{C}$  while; it reached between 91 and 94 % at  $40^\circ\text{C}$ .

The results depicted in Fig 7 showed the adsorbability of lindane towards different types of ACs at three temperatures (15, 25 and  $40^\circ\text{C}$ ). These results suggested no significant difference on the adsorption capacity of the tested ACs which reached 7.60 and 7.33 mg/g for AC1 and AC2; respectively at  $15^\circ\text{C}$ .

However, the adsorption uptake decreased at 40°C to 7.45 and 7.28 mg/g for AC1 and AC2; respectively. It could be suggested from the current results that AC1 has the highest adsorption capacity for lindane followed by AC2; although, the maximum adsorption of lindane onto the ACs was achieved at room temperature (25°C ± 1).

Similar trend was observed by Fan *et al.* [22] who studied the adsorption uptake of 2,4,6-trichlorophenol (TCP) on AC derived from stalk of the scrap aquatic plant loosestrife and reported a decrease by increasing solution temperature from 20 to 50°C for all initial concentrations. In addition, our findings are in agreement with other studies of some pesticides adsorption onto various materials [4, 23]. In the same respect, El-Bakouri *et al.* [18] illustrated that a slight decrease of different drin pesticides removal efficiency is observed with increasing temperature.

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 [24].

**Adsorption Isotherms Analyses:** In order to assess the potential adsorption capacity of lindane onto the tested ACs (AC1 & AC2), the adsorption isotherm studies were done as given in details in the experimental part (Fig. 8).

Adsorption isotherms are described in many mathematical forms, some of which are based on a simplified physical model of adsorption and desorption, while others are purely empirical and are intended to correlate with the experimental data. Various isotherm equations, such as Langmuir, Freundlich and Harkins-Jura models have been used to describe the equilibrium characteristics of adsorption.

**Langmuir Isotherm Model:** The model assumed that adsorption occurs on a homogenous adsorbent surface of identical sites that are equally available and energetically equivalent with each site carrying equal numbers of molecules and no interaction between adsorbate molecules [25].

This model can be described by the following form:

$$q_e = \frac{k_l c_e}{(1 + \alpha_l c_e)} \quad (1)$$

Table 4: Langmuir, Freundlich and Harkins-Jura model parameters for the adsorption of lindane onto ACs.

	AC1	AC2
<b>Langmuir model</b>		
$a_l$	8.09	2.02
$k_l$	90.91	30.96
$R_L(-)$	0.001	0.003
SSE	1.253	1.233
HYBRID	5.35	6.766
<b>Freundlich model</b>		
$k_f$	15.35	12.39
$n(-)$	1.72	1.49
SSE	16.056	2.845
HYBRID	50.75	13.633
<b>Harkins-Jura model</b>		
$A(-)$	21.45	21.92
$B(-)$	- 0.064	0.081
SSE	35.898	1.904
HYBRID	134.9	11.95

Eq. (2) below represents the linearized form of Langmuir equation.

$$\frac{c_e}{q_e} = \frac{1}{k_l} + \left( \frac{a_l}{k_l} \right) C_e \quad (2)$$

where  $q_e$  is the solid phase equilibrium concentration (mg/g),  $C_e$  is the liquid phase equilibrium concentration (mg/l) and  $k_l$  (l /g) and  $a_l$  (l/mg) are the Langmuir constants.

The experimental data were plotted as  $C_e/q_e$  versus  $C_e$  and the values of Langmuir constants  $a_l$ ,  $k_l$  were obtained by linear regression method as presented in table 4.

The essential characteristics of the Langmuir equation can be expressed in term of a dimensionless separation factor,  $R_L$ , defined as Weber and Chakravorti [26].

$$R_L = \frac{1}{1 + C_0 k_l} \quad (3)$$

Where  $C_0$  is the highest initial solute concentration (mg/l).  $R_L$  values indicate whether the adsorption process is irreversible ( $R_L = 0$ ), favourable ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ), or unfavourable ( $R_L > 1$ ). Table 4 shows the values of  $R_L$  (0.001-0.003) are in the range of 0-1, confirming the favourable uptake of the lindane by the prepared activated carbon (AC1) and Norit carbon as a reference carbon (AC2).

**Freundlich Isotherm Model:** The Freundlich Isotherm was studied to understand the possibility of multi-layer adsorption and non-linear energy distribution for the adsorption sites of the same adsorbents.

- Freundlich equation is expressed as Freundlich [27]:

$$q_e = k_f C_e^{1/n}$$

where ' $k_f$ ' is the Freundlich constant (l / g), ' $n$ ' is the heterogeneity factor (-), ' $q_e$ ' is the amount of lindane adsorbed per unit mass of adsorbent (mg/g) and ' $C_e$ ' is the equilibrium concentration in mg/l. The logarithmic form of Freundlich equation can be expressed by:

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

Therefore, a plot of  $\log q_e$  versus  $\log C_e$  enables the constant  $k_f$  and exponent  $n$  to be determined.

It is clear from Table 4 that values of the Freundlich exponents  $n > 1$  represents a favourable adsorption condition [28].

**Harkins-Jura Model:** This model accounts for multilayer adsorption and also for the existence of heterogeneous pore distribution in the adsorbent [29]. The Harkins-Jura adsorption isotherm can be expressed as

$$\frac{1}{q_e^2} = \left(\frac{B}{A}\right) - \left(\frac{1}{A}\right) \log C_e \quad (5)$$

Where,  $B$  and  $A$  are the isotherm constants.

**Error Analysis:** Analysis of the isotherm is important in order to develop an equation that accurately represents the results and which could be used for design purposes. Error analysis method is employed to enable the optimization process and to evaluate the fitting of different isotherm equations to experimental data. The following functions were used in this study

- The sum of the squares of the errors (SSE) [30]:

$$SSE = \sum_{i=1}^P (q_{cal} - q_{exp})^2 \quad (6)$$

- The hybrid fraction error function (HYBRID) [31]:

$$HYBRID = \frac{100}{P - N} \sum_{i=1}^P \left( \frac{(q_{cal} - q_{exp})^2}{q_{exp}} \right) \quad (7)$$

Where  $P$  is the number of data points,  $N$  is the number of parameters within the model,  $q_{cal}$  is the capacity calculated from the used models and  $q_{exp}$  are the experimental adsorption capacities. The values of the error functions were calculated and presented in table 4.

By comparing the results listed in table 4, it was clear that Langmuir results represent the lowest values of error functions, which means that Langmuir model gives the best agreement with the experimental isotherm data obtained

## CONCLUSION

### From this Study we Can Conclude That:

- Date stones activated with  $H_3PO_4$  at ration of 1:3 (w/w) (AC1) was a good adsorbent and had a higher surface area (873  $m^2/g$ ) with high total pore volume ( $V_{tot}=0.791 \text{ cm}^3/g$ ).
- The equilibrium and total adsorption time of lindane was achieved much faster for AC1 than for the reference material AC2 in contrast to DS.
- Adsorption of lindane was found to be the maximum under neutral conditions.
- The experimental data have been modeled and evaluated by using three different models and two different error functions. The error functions for the nonlinear optimization that the langmuir isotherm gave the best correlation with experimental data.

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