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REMOVAL OF LINDANE AND MALATHION FROM WASTEWATER BY ACTIVATED CARBON PREPARED FROM APRICOT STONE

A. M. Hassan, M. Abed El-Moteleb and A. M. Ismael

Chemistry department, Faculty of Science, Al-Azhar University

ABSTRACT:

The powdered activated carbon, obtained from the apricot stone, has been used as inexpensive and effective adsorbent for the removal of lindane and malathion from wastewater. Apricot stones were treated with H_3PO_4 (1:1) then carbonized at 500°C for 3h. The ability of the powdered activated carbon to remove lindane and malathion from wastewater by adsorption was investigated. Batch adsorption experiments were conducted to observe the effect of contact time, weight of sample, pH, volume of an aqueous to mass of powdered activated carbon and concentration of studied pesticides on activated carbon. Equilibrium experiments results show that adsorption isotherms for lindane and malathion fit well to the Freundlich model.

INTRODUCTION:

Water pollution by organic and inorganic compounds is of great public concern. Adsorption technology is currently being used extensively for the removal of such pollutants from wastewaters. Among the various adsorbent systems available for the removal of pollutants from wastewaters, activated carbon is being widely used in developed countries[1-3]. Adsorption of some organochlorine pesticides (OCPs) onto solid substances, such as clay minerals or activated carbon, has been rather wide studied[4-7]. The adsorption onto activated carbon, have proved to be the most efficient and reliable method for the removal of aqueous-dissolved organic pesticides[8]. Active carbon has widely been utilized as a depurator for tap water and a scavenger of odor due to its strong adsorption capacity. Active carbon has been used for the analyses of water samples such as measurement of volatile organic compounds (VOC) in water[9] and the collection of water-soluble chemicals[10]. It has been reported that an activated carbon fiber filter (ACFF) is effective for the collection of pesticides in air[11,12]. ACFF has a large adsorptive capacity for many kinds of chemicals, and the adosrbates can be extracted easily with organic solvent. It is reported that activated carbon is stable in water dilute acids and bases. Activated carbon successfully has been tried for the removal of pollutants from aqueous solutions. In continuation, an attempt has been made to examine the utility of this material for the removal of lindane and malathion from water and waste water. The effects of various operating variables on removal have been studied to arrive at optimum conditions for the process. The results are presented and discussed in this communication.

EXPERIMENTAL METHODOLOGY:

Chemical and equipment:

All chemicals used were of analytical grade. Lindane (HCH-gammaisomer of 1,2,3,4,5,6-hexachlorocyclohexane) and malathion (Dimethoxy phosphino thioyl thio Buta-nedioic acid Diethyl Ester) were obtained from Sigma chemical Co., USA. Astock solutions of lindane and malathion were prepared by dissolving the required quantity in 50 ml of methanol then completed to liter of distilled water. A pH meter (Cole palmer series 5986, USA) was used for pH measurements. The specific surface area and porosity measurements were performed using pore size Micrometer-9320, USA. The microstructures of the carbon were observed by SEM (Philips XL30S-FEG, USA). The concentrations of lindane and malathion were determined by gas chromatography (GC) Agilent 6890N, USA.

The obtained data were presented in the form of:

$$\text{1-Adsorption uptake percent U\%} = \frac{[C_\circ - C_e]}{C_\circ} \times 100$$

$$\text{2-Adsorption capacity (qe)} = [C_\circ - C_e] \times \frac{v}{m} \text{ mg}$$

C_0 = is the initial concentration in aqueous phase in mg/l.
C_e = is the final concentration in the aqueous phase at equilibrium mg/l.
v = volume of water sample.
m =mass of activated carbon prepared from apricot stone.

Methods:

Chemical activation utilizes chemicals, such as H_2SO_4, H_3PO_4, $Zncl_2$, KOH and $CaCl_2$ that have dehydration and oxidation characteristics[13]. Activation and carbonization are usually carried out simultaneously in the chemical activation process.

Apricot stone were obtained from El-Amar village-Qulibia, (Egypt) which is famous of growing apricot stone. This apricot stone is collected as agriculture wastes.

Apricot stone was dried at 105ºC for 12 hrs. chemical activation by using (1M) H_3PO_4, then placed in an oven and heated to 500ºC for 3hr. after this the samples were allowed to cool to room temperature, washed with distilled water and soaked in 1% $NaHCO_3$ solution to remove any remaining acid. The samples were then washed with distilled water until pH of the activated carbon reached 6, dried at 105ºC for 5 hr[14]. then the activated carbon was ground in a micro hammer cutter mill (Glen Mills) and sieved to obtain the desired particle size (100-200 μm). The specific surface area and porosity measurements were achieved using Burunauer-emnett-tellrr nitrogen adsorption technique (BET). Characteristics of the prepared activated carbon are presented in Table (1). The size distribution of mciropores of activated carbon is under stood to be one of the critical factors determining its applicability[15].

Table (1): The characteristics of the activated carbon

Parameters	Value
Bulk density	0.84 g/ml
Porosity	47.10 %
Ash content	4.2 %
Surface area	642 (m^2/g)
Particle size	100-200 (μm)
pH	6.00(μ Sec.)

As shown in Fig. (1), the adsorbent had an irregular and porous surface, indicating relative high surface areas. This observation is supported by the Burunauer-emnett-tellrr nitrogen adsorption technique (BET) Surface area of the activated carbon[16].

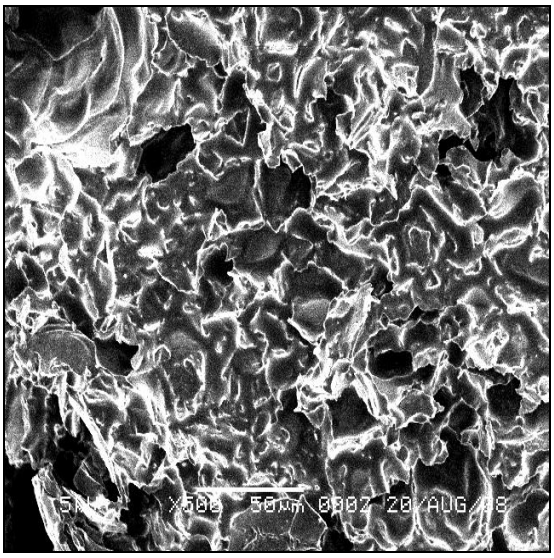

Fig. (1): SEM image of activated carbon

Adsorption experiments were carried out in Batch mode using a series of Erlenmeyer flasks of 50ml capacity covered with Teflon sheets to prevent contamination. The effect of contact time, pH, temperature, (V/M) and adsorbated concentration were studied. During these experiments, the solutions were shaken and the concentrations of lindane and malathion in the supernatant were determined.

Pesticides analysis:

Lindane and malathion were extracted from treated wastewater using n-hexane. The extracts were concentrated on water bath (40ºC) and water content removed using anhydrous sodium sulphate. The GC equipped with a Ni^{63} electron capture detector (ECD) and restek (7 m x 0.3 mm x 0.25 mm) Capillary column was used to detect and quantify Lindane[17]. Injector and detector temperature were 250ºC and 300ºC, respectively. The carrier gas was nitrogen at flow 35ml/min and temperature program was as follows: initial temperature 50ºC holding 1 min, increased from 50 to 230ºC at 15ºC/min and subsequently held for 2 min, increased from 230 to 300ºC at 10ºC/min subsequently held for 10 min. malathion were determined also by GC equipped with Flame Photometric Detector (FPD)[17]. The column used was pas 1701 (25 m x 0.32 mm x 0.25 mm). The chromatographic conditions were as below: initial oven temperature 170ºC (2 min) increasing by 5ºC/min to 240ºC (10 min). Injector temperature 260ºC and detector temperature 250ºC. The flow rate of nitrogen carrier gas was 3 ml/min. The analysis produced at Central Agricultural Pesticides Laboratory, Doki, Cairo.

RESULTS AND DISCUSSION:

1-Effect of weight samples of powdered activated carbon (PAC) on adsorption of pesticides:

To study the capacity of powdered activated carbon (PAC) for adsorption of lindane and malathion, experiments were carried out using initial concentration 0.671 mg/l and 2.1 mg/l for lindane and malathion respectively. The study of the sorption of selected pesticides (lindane and malathion) by batch techniques is carried out by determination the suitable weight sample of powdered activated carbon (PAC). In sorption studies the sorption uptake percent (%) of the respective pesticides was found to vary with different weight samples (0.1, 0.5, 1, 2, 3) g. From data which presented in Table (2), it is clear that the suitable weight of activated carbon is (2g). The adsorption uptake percent 95.53% and 95.23% for lindane and malathion respectively. This is consistent with the results obtained by Vinod *et al.*, (2002)[18].

Table (2): Variation of sorption uptake percent of lindane and malathion at different weight samples of powdered activated carbon (PAC)

	Ws	C_o (mg/l)	Ce (mg/l)	X (mg/l)	U (%)
Lindane	0.1	0.671	0.576	0.095	14.15
	0.5		0.462	0.209	31.14
	1		0.132	0.539	80.32
	2		0.03	0.641	95.52
	3		0.03	0.641	95.52
Malathion	0.1	2.1	1.7	0.4	19.04
	0.5		1.2	0.9	42.85
	1		0.4	1.7	80.99
	2		0.1	2	95.23
	3		0.1	2	95.23

Where :
Ws = weight of activated carbon per 50 ml of wastewater **Time = 6 hr**
pH= 6.0 M. Sec **temp.= 30°C**

2-Effect of contact time on sorption of lindane and malathion by (PAC):

Adsorption time of selected pesticides is one of the most important parameter were carried out. Variation of adsorption uptake percent (%) of the selected pesticides such as lindane and malathion as a function of contact time are presented in Table (3). From these results it is obvious that the sorption of lindane and malathion increases with time until to reach a nearly saturation level. However, the time of saturation totally equal with lindane and malathion. It is clear, that the 6 hr., (360 min.) is the specific time of saturation for lindane and malathion with adsorption uptake percent (95.52% and 95.23%) respectively. This is the same with the results observed by Myroslav *et al*., (2008)[19].

Table (3): Variation of adsorption capacity and uptake percent of lindane and malathion on powdered activated carbon at different contact time.

	Time (min.)	C_o (mg/l)	Ce (mg/l)	X (mg/l)	Qe (mg/g)	U (%)
Lindane	10	0.671	0.576	0.095	4.12	14.12
	30		0.323	0.348	8.7	51.86
	60		0.302	0.369	9.22	54.9
	120		0.201	0.470	11.75	70.04
	240		0.133	0.538	13.45	80.17
	360		0.03	0.641	16.02	95.52
	480		0.03	0.641	16.02	95.52
Malathion	10	2.1	1.6	0.5	12.5	23.8
	30		0.99	1.11	27.75	52.85
	60		0.8	1.3	32.5	61.9
	120		0.6	1.5	37.5	71.42
	240		0.4	1.7	42.5	80.99
	360		0.1	2	50.0	95.28
	480		0.1	2	50.0	95.28

Where:
weight of PAC = 2g per 50 ml of wastewater **pH= 6.0 M. Sec** **temp.= 30°C**

3-Effect of pH on sorption of lindane and malathion by (PAC):

Table (4) shows the effect of varying pH on the adsorption uptake percent (%) of Lindane and malathion. From these data, it is clear that the adsorption uptake percent (%) gradually increases by increasing the pH until to reach maximum value at (pH=6). The sorption uptake percent(%) of the investigated pesticides show the same previous rank. Meanwhile, the sorption of lindane and malathion very low below (pH=4) and increases rapidly at (pH= 5.50) coming to maximum at (pH=6.0). These results are similar to experiment obtained by Vinod *et al.*, (2002)[18], where maximum removal of lindane and malathion takes place at (pH= 6.0). At (pH =7) the degradation of lindane and malathion are expected to take place[20,21]. Finally the maximum uptake percent of lindane and malathion was (95.52% and 95.23%) respectively which takes place at (pH=6.0). The adsorption remains constant beyond this pH value.

Table (4): Variation of sorption uptake percent of lindane and malathion on powdered activated carbon with different pH

	pH	C_o (mg/l)	Ce (mg/l)	X (mg/l)	qe (mg/g)	U (%)
Lindane	2.31	0.671	0.631	0.04	1.00	5.96
	3.64		0.431	0.24	6.00	35.76
	4.23		0.213	0.458	11.45	68.25
	5.51		0.05	0.621	15.52	92.54
	6.0		0.03	0.641	16.02	95.52
	7.01		0.123	0.548	13.7	81.66
Malathion	2.31	2.1	1.9	0.2	5.00	9.52
	3.64		1.1	1.0	25.00	47.61
	4.23		0.7	1.4	35.00	66.66
	5.51		0.4	1.7	42.50	80.99
	6.0		0.1	2.0	50.00	95.23
	7.01		0.4	1.7	35.00	80.99

Where:
weight of PAC = 2g per 50 ml of wastewater **Time = 6 hr** **temp.= 30°C**

4-Effect of volume per mass of a powdered activated carbon ratio on sorption of studied pesticides:

The study of the adsorption of lindane and malathion by batch techniques is carried out by determination the ratio of the volume of aqueous phase to the mass of powdered activated carbon (V/M). In sorption studies, the sorption uptake percent (%) of the respective pesticides was found to vary with (V/M) ratio. Data are presented in Table (5). These data shows that, the sorption uptake percent, increases as (V/M) decreases, which this means an increasing of the mass of powdered activated carbon sample. An appropriate value for increasing uptake percent (%) of lindane and malathion is (25 ml/g), where 2gm of the activated carbon is mixed with 50ml of aqueous phase of studied pesticides.

Table (5): Variation of adsorption capacity and uptake percent of lindane and malathion with different (V/M) values

	V/M ml/g.	C_o (mg/l)	Ce (mg/l)	X (mg/l)	qe (mg/g)	U (%)
Lindane	500	0.671	0.576	0.095	82.46	14.15
	100		0.462	0.209	22.61	31.14
	50		0.132	0.539	204.16	80.39
	25		0.03	0.641	534.16	95.52
	16.66		0.03	0.641	355.96	95.52
Malathion	500	2.1	1.7	0.4	5.88	19.04
	100		1.2	0.9	18.75	42.85
	50		0.4	1.7	106.25	80.99
	25		0.1	2	500	95.23
	16.66		0.1	2	500	95.23

Where:
Time = 6 hr **volume of wastewater = 50 ml** **pH= 6.0 M. Sec** **temp.= 30°C**

5-Effect of lindane and malathion concentration on sorption by powdered activated carbon:

The relationship between the sorbed amount of lindane and malathion per gram, (X/M) against the equilibrium concentration [C] on a log-log scale shows straight lines as illustrated in Figs. (1 & 2) and Table (6). This linear relationship indicates that the sorption process can be described by a Freundlich type isotherm. Based on these data, it can be concluded that the sorption of the investigated pesticides by (PAC) takes place mainly through the formation of a single monolayer[22] of sorbed species. The following general equation is applied to describe the data in a quantitative way:

The amount of pesticides sorbed pergram (PAC)

Where:

C_o: is the initial concentration in aqueous phase (mg/l).

C_e: is the final concentration in aqueous phase (mg/l).

V: is the volume of the aqueous phase (ml).

M: is the weight of (PAC) (g).

X: is the amount of lindane and malathion sorbed on (PAC).

$$\text{Hence, } x/m = kc^{1/n}$$

$$\log (x/m) = \log k + 1/\log [c]$$

Table (6): Variation of adsorption capacity and uptake percent of lindane and malathion with the amount of them sorbed per gram on powdered activated carbon

	C_o (mg/l)	Ce (mg/l)	X (mg/l)	Log Ce	$X/M=C_0-Ce*V/M$	Log X/M
Lindane	2	1.7	0.3	0.2	7.5	0.87
	3.2	2.6	0.6	0.4	15	1.17
	6	4.8	1.2	0.6	30	1.47
	7	5.5	1.5	0.7	37.5	1.57
Malathion	2.5	2.0	0.5	0.30	12.5	1.096
	3.5	2.5	1	0.39	25	1.39
	4	2.4	1.6	0.38	40	1.60
	6	3.7	2.4	0.56	60	1.77

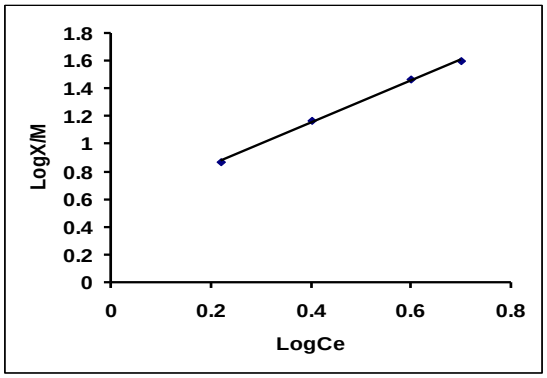

Fig. (2): Linear adsorption isotherm of Lindane onto powdered activated carbon according to Freundlich model

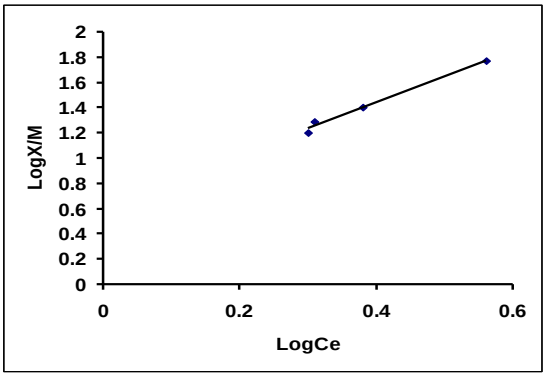

Fig. (3): Linear adsorption isotherm of Malathion onto powdered activated carbon according to Freundlich model

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إزالة مبيدات اللندين والملاثيون باستخدام الفحم المنشط المحضر من نوى المشمش

على مصطفى حسن، محمد عبد المطلب عبد الرحيم، أحمد محمد إسماعيل

كلية العلوم – جامعة الأزهر – مصر

تعتبر طريقة الادمصاص من أفضل التقنيات الحديثة المستخدمة فى إزالة الملوثات وبخاصة العضوية من المياه الملوثة، من خلال هذه الدراسة تم استخدام الفحم المنشط المحضر من أحد المخلفات الزراعية، وهو نوى المشمش بغرض إزالة مبيد اللندين – والملايثون من المياه الملوثة. تم تحضير محاليل من مياه ملوثة من خلال إذابة هذه المبيدات فى الماء بتركيزات مختلفة. تم خلط هذه المياه الملوثة الصناعية مع الفحم المنشط (بواسطة حمض أرثوفوسفوريك) مع الخلط لفترات كافية. تم تقدير هذه المبيدات الذائبة فى الماء الملوث الصناعى قبل إضافة الفحم المنشط ومرة أخرى بعد الرج مع الفحم المنشط وذلك باستخدام جهاز (GC). عند حساب السعة الادمصاصية للفحم المنشط وجد أنها كانت ١٦.٠٢ مليجرام/جرام لمبيد اللندين، ٥٠ مليجرام/جرام لمبيد الملايسون. تمت دراسة بعض العوامل المؤثرة على عملية الادمصاص للتوصل إلى أنسب الظروف يمكن معها الوصول إلى أعلى سعة ادمصاصية للفحم المنشط ما وجد أن معدل الإزالة لكلٍ من مبيد اللندين والملايسون ٩٥.٥٢%، ٩٥.٢٣%، كما وجد أن عملية الادمصاص للمبيدات التى تم دراستها تتبع نظام Freundlich Isotherm.