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Pesticides Removal from Drainage Waste Water Using Some Agricultural Wastes

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Abstract: The agricultural wastes proposed for the removal of water pollutants in this study are seeds of two Saudi date lines which are quite abundant in the Kingdom of Saudi Arabia, having high ion exchange capacity for organic compounds. Two goals can be achieved when using these type of date stones: the first is to evaluate the potentiality of date stones to sorb inorganic and organic pollutants from drainage water to render it suitable for irrigation of crops in the Kingdom and the second is to get rid of harmful agricultural wastes. Chemical and elemental analyses were carried out for date stones. Batch technique experiments were conducted to determine the adsorption properties of date stones to harmful pesticides such as Endrin, Lindane and Aldrin. Affecting parameters such as adsorbent weight, contact time and polluted water pH values were also studied to control and increase the efficiency of adsorption. The obtained results showed that the date stones can be considered as an efficient adsorbent for the investigated pesticides from prepared waste water. The resultant uptake efficiency was found to be more than 75% for the tested pollutants. Moreover, it was found that the adsorbed pesticides can not be disturbed from the loaded date stones. Comparative methods between the Saudi and Egyptian date stones were also studied.

Key words: Pesticides, water pollutants, Endrin, Lindane, Aldrin, Saudi date stones, adsorption

INTRODUCTION

The pesticides (such as Endrin, Lindane and Aldrin) are used to protect plants from insect infestations, to increase their productivity. On the other hand, these pesticides have adverse effects on water because part of these pesticides are carried down by the percolating water to the underground water. This causes significant pollution problems in the water systems. Therefore the need arises to eliminate or at least to decrease the concentration of the polluting materials to render the water suitable for irrigation purposes.

Therefore, the elimination of insecticide organic pollutants from waste water is an important subject for public health. Activated carbon has been widely used[1] however, it remains an expensive material and is not suitable for developing countries because of its high costs. For that reason research interest into the production of low cost alternatives to activated carbon has grown. Efforts were made to develop low cost adsorbents, for the removal of pesticides from aqueous solutions.

The selected adsorbents should be available, cheap, have high ion exchange capacity and have no effect on physical and chemical characteristics of the resultant water. Date stones have been proposed for this purpose.

MATERIALS AND METHODS

Adsorption process: Batch adsorption investigations[2] were carried out by contacting different masses of date stone with 10 mL of spiked aqueous solution, of an initial concentration of 0.88, 0.92 and 1.2 for Endrin, lindan and Aldrin respectively in tightly sealed glass bottles. The samples were shaken (1000 rpm using thermostated bath shaker of Shall Bath SBS-30 type from Stuart Scientific, UK) for a sufficient period of time (30 min). The sample was then centrifuged and concentrations of the studied pesticides were determined.

The progress of adsorption, during the experiment, was determined by taking a certain volume of adsorbate solution at the selected time intervals, centrifuging and subjecting. The centrifugation was performed using a IEC-HN-SII centrifuge from International Equipment Co., UK. Blank bottles without adsorbents were also prepared to determine any adsorption on the bottle walls.

The data can be represented in form of uptake percentage by:

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

where, C_o and C_e are the initial and final adsorbate concentrations in solution (mg L^{-1}), V is the solution volume and m is the adsorbent mass It is important,

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to mention that all chemicals and reagents used in all experiments are of analytical grade. Bidistilled water was used for dissolution, dilution and washing all glassware. Desorption or release experiments of the investigated pesticide was carried out on the loaded adsorbent.

A 1 mL of clear supernatant was left in the bottle together with solid phase 9 mL of disturbed solution was added and the closed polyethylene bottles where shaken for the descried time finally. The bottle was centrifuged for 15 min and desorption was evaluated using the following formula:

$$D\% = \{(ca - xce) / (co\text{-}ce)\}\ 100 \qquad (2)$$

where, ca: the activity of desoprtion solution x: is the volume fraction left initially with natural material sample.

Adsorbent: The raw materials used in this study as an adsorbent were date stones of types Saukary and Sakeie collected in Buraydah, Qassim, Kingdom of Saudi Arabia, in addition to the Egyptian dates of types Seman and Zaghlol collected from El-Kanaiate, Sharkia governate Egypt.

Date stones were prepared into a fine powder as follows:

- The date stones were ground into a fine powder in an electrical mixer.
- The powder was placed in an electrical oven set at a temperature of 80°C for 12 h to remove the roast so as to increase the adsorption efficiency.

The date stones were then subjected to a structural characterization using different techniques. The main physical and chemical properties were evaluated using elemental and chemical analysis. Also, the porosity and surface area of the date stones were investigated.

Adsorbate: The stock aqueous solutions of the studied pesticides were prepared at room temperature by percolating a certain weight of each compound into borosilicate glass bottles, with the desired bidistilled water volume. The equilibrium concentration of the tested pesticides was determined spectrophotometrically in the Ministry of Agriculture, Agriculture Research Center, Central Lab of Residue Analysis of Pesticides and Heavy Metals in Food, Cairo, Egypt. Fresh stock solutions were daily prepared. The equilibrium concentration of the studied pesticides was determined using gas chromatography of Perkin and Elmer type.

The traced contaminants were placed in direct contact with the applied adsorbent for a period of time to study the different variables affecting such systems.

RESULTS AND DISCUSSION

The data obtained in this investigation is divided into three main parts:

(a) The physical and chemical analyses of the two types of date stone samples.
(b) The study of the sorption behavior of some pesticides on date stones surface.
(c) A comparative evaluation of the types of Saudi and Egyptian date stones.

Physical properties of the date stones: Date stone samples were size-fractionated using standard sieve and stored in air-tight glass containers. Materials intended for immediate use were dried to a constant weight and stored in desiccator. Otherwise, the fines were used in adsorption experiments as it is. Sieves of 0.032-0.063 mm diameters to 0.28-0.31 mm diameter mesh sizes were used in the experiments reported in this study (Table 1). Surface area was evaluated for the various size fractions by the three point BET N_2 adsorption method using an Autosorb Gas Sorption System (Metallic Research Institute, Helwan, Egypt). The BET surface area and the pore volume of the investigated date stones were obtained using BET technique as an adsorption phenomenon of nitrogen gas on the adsorbent surface at 77°K (temperature of liquid nitrogen)[2] results are presented in Table 1.

Elemental and chemical analysis: From Table 2 and 3 it can be seen that the date stones contain low concentrations of heavy metals including the toxic Zr metal (arsenic compounds) so they cannot be used as an animals fodder. These concentrations although being very small (0.001-0.003%) their cumulative effect on animals can be very serious.

Adsorption of pesticides on date stones: The study of the adsorption of Endrin, Lindane and Aldrin by the Saudi (Saukary and Sakeie) and Egyptian (Seman and Zaghlol) date stones at a 1:1 weight ratio, were investigated. In preliminary experiments the Saudi stones showed a relatively higher ion exchange capacity than the Egyptian. This is due to the fact that at the beginning of fruiting the Saudi dates were softer and have higher moisture content than the Egyptian dates. Also, translocation of sugars and protein, (containing higher percentage of N, S, P and O) takes place from the dates to stones through the test. Hence the fully matured Saudi date stones become highly negatively charged than the Egyptian dates (Table 2). Figure 1 illustrates the adsorption process between the negatively charged date stones and the positively

Table 1: Physical Properties of the investigated date stones

Date stone types	Pore volume (cm^3 g^{-1})	Surface area (cm^2 g^{-1})
Saukary (Saudi)	0.015	2.2-2.6
Sakeie (Saudi)	0.013	2.1-2.3
Seman (Egyptian)	0.006	0.8-1.2
Zaghlol (Egyptian)	0.008	1.4-1.7

Table 2: Elemental analyses for different types of date stone

Items	C (%)	H (%)	N^2 (%)	S (%)	P (%)	Total heavy metals (%)	Zr (%)	Ash (%)
Saukary (Saudi)	62.91	5.36	9.21	8.92	11.2	0.03	0.002	1.2
Sakeie (Saudi)	65.12	4.22	7.10	10.20	12.1	0.01	0.001	0.8
Seman (Egyptian)	58.20	7.10	6.20	7.10	8.2	0.02	0.005	4.2
Zaghlol (Egyptian)	50.20	10.20	5.10	10.20	5.2	0.03	0.001	8.2

Table 3: Chemical analysis for date stone

Items	α-cellulose (%)	Lignin (%)	Pentosan (%)	Fat and oil (%)
Saukary	71.2	20.2	2.1	6.80
Sakeie	75.1	18.2	3.6	5.80
Seman	71.2	20.2	9.6	0.23
Zaghlol	67.3	18.3	10.2	6.20

Table 4: The percent uptake of pesticides after regeneration of the loaded date stone using salt solutions of NaCl, $MgCl_2$ and HCl

Elements	Uptake (%) Regeneration using: NaCl	$MgCl_2$	HCl
Endrin	8	4	71
Lindane	5	3	80
Aldrin	7	6	62

Weight of stone powder is 0.05 g, pH of the solution is 6.3, contact time is 120 min

charged pesticides through the electrostatic attraction between them. The positive charge on pesticides is due to the presence of chlorine atoms attached to the ring moiety of the pesticide that has an electron withdrawing effect producing a positively charged ring moiety. The adsorption of the pesticides as organic compounds depends mainly on the pore volume and surface area of the date stone. Table 1 and 2 show the highly negative charges of the Saudi date stones than that of the Egyptian due to increasing the percentage of the negative elements of N, S, P and also cellulose contents in Saudi dates.

The effect of different parameters affecting the sorption process were investigated.

Effect of contact time of Endrin, Lindane and Aldrin on date stones: To study the capacity of the Saudi (Saukary:Sakeie) and Egyptian (Seman: Zaghlol) date stones (at a 1:1 weight ratio) to sorb pesticides, experiments were carried out on samples using 0.92, 0.88 and 1.23 ppm solutions of Endrin, Lindane and Aldrin. From this Fig. 2, it is clear that the adsorption of Endrin, Lindane and Aldrin on the Saudi date stones increases with time to reach a nearly saturation level of the compounds species. As time increases, a good chance is created for entrance of pesticides molecules in the pore until a certain time, at which a saturation is developed in

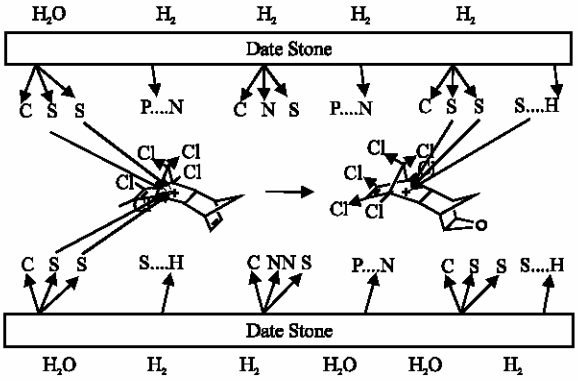

Fig. 1: The Electrostatic attraction between date stone and pesticides

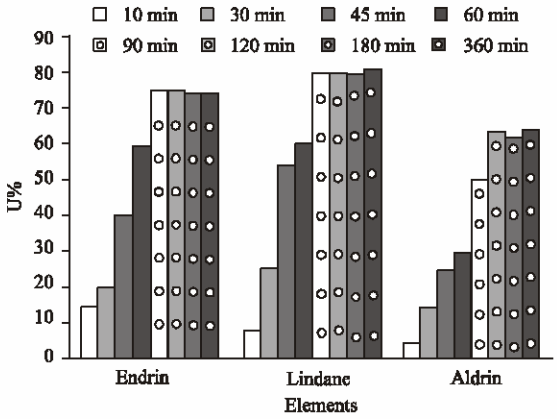

Fig. 2: Effect of contact time on the adsorption of the pesticides on Saudi date stone

all pores on the stone surface. At this time a stable state for uptake percent occur and no more increase with time is observed.

Also, it is clear that the studied date stone samples show high percent uptake for Lindane and Endrin and the maximum uptake was attained within 90 min which reaches about 80 and 70% uptake. Also, the maximum uptake of Aldrin was attained in 120 min and reached about 60%. Figure 3 shows that three hours are required for reaching the approximately 60% uptake of the studied pesticides.

Desorption of Endrin, Lindane and Aldrin from the loaded date stones: It is understood in these experiments, that the sorption of the respective compounds is supposed to take place mainly by electrostatic attraction between the stones surface as a negative charges and the ring moiety of the pesticide as a positive charge (Fig. 1). Some desorption experiments were carried out by batch technique to release the adsorbed compounds from the loaded date stones. The percent desorption of pesticides from date stones was very low and approaches zero.

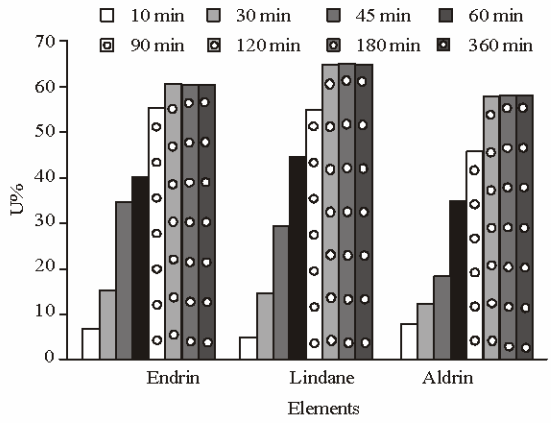

Fig. 3: Effect of contact time on the adsorption of the pesticides on Egyptian date stone

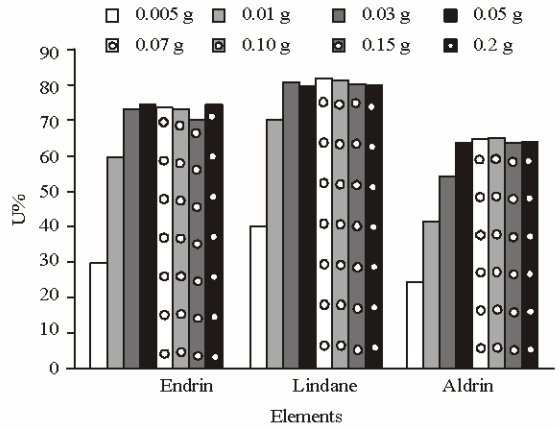

Fig. 4: Effect of weight of Saudi date stone on the adsorption process weight (g)

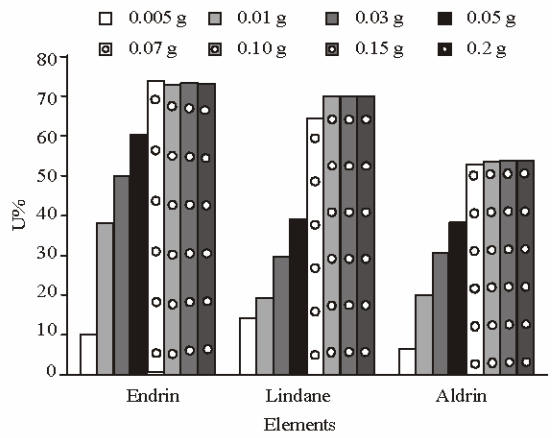

Fig. 5: Effect of weight of Egyptian date stone on the adsorption process weight (g)

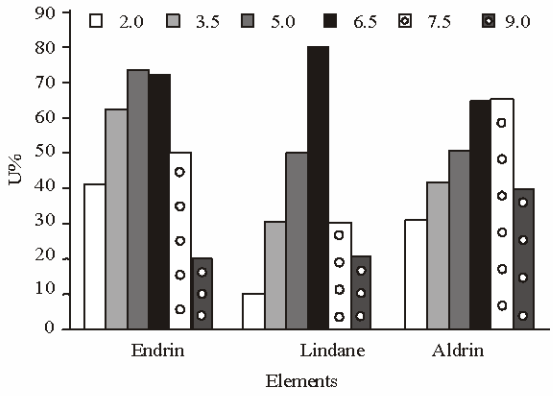

Fig. 6: The effects of pH of the pesticides solution on the adsorption process of the Saudi stones

Regeneration of date stones: The regeneration of the loaded date stones experiment was carried out using solutions of magnesium chloride, sodium chloride (to form Na or Mg-date stone) and hydrochloric acid solution (6 N) to transfer the date stones to the hydrogen form[3].

In the regeneration process using $MgCl_2$, NaCl and HCl, the pesticides loaded on the date stones were replaced by Mg, Na or H ions to form the stones salts which can be used for further adsorption investigations. Table 4 illustrates the data for using these methods. It appears that hydrochloric acid is one of the most suitable recommended methods for the regeneration process. As this material is of low economical value, the regeneration process is not needed costs.

Effect of weight on sorption of Endrin, Lindane and Aldrin on date stone: In all experiments, the solution containing the pesticides was contacted with the date stone until equilibrium was attained. The primary experiments were carried out to find out the required amount of the Saudi and Egyptian date stones that can result in reasonably high percent uptake. From these data (Fig. 4 and 5), it is clear that an appropriate value for weight is 0.03 g of the Saudi date stones mixed with 10 mL of aqueous phase Lindane and Endrin and 0.05 g was used in case of Aldrin, whereas 0.10 g were required for the Egyptian date stone. This is due to the fact that if the stone weight increased, the surface area will increase too and in turn the adsorption is increased to a limited level at which saturation will occur for the whole surface of the pesticides molecules. The low weight value of Saudi date stone than the Egyptian leads to the higher surface area of the Saudi one in addition to the higher pore volume of the Saudi stones.

Effect of pH on sorption of Endrin, Lindane and Aldrin on date stone: The adsorption process of pesticides on date stones depends largely on the concentration of the

hydrogen ion in solution. Increasing pH of solution (decrease in H^+ ion concentration) results in decrease in H^+ ion competition for vacant sites on the date stones. At a much higher pH values, the dissociation of counter compounds in the date stones matrix may increase resulting in a lower percent absorption of the given compounds[4]. Therefore the adsorption of the pesticides was studied in pH range 5-7.

From the Fig. 6, it is clear that the percent uptake of pesticides displayed a gradual increase with the increasing pH up to a maximum values around pH 6.0, followed by a gradual decrease.

Date stones are cheap, available and are highly efficient in removal of water pollutants. However, they cannot be used as an animal fodder due to their toxic effects in the long run.

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