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Peach nut Shells-An Effective and Low Cost Adsorbent for the Removal of Endosulfan from Aqueous Solutions

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Abstract

In the present studies the adsorption efficiency of peach nut shells for the removal of endosulfan from aqueous solutions has been investigated. The adsorption of endosulfan has been studied as a function of contact time, concentration and temperature. Maximum adsorption (95 ± 1%) was achieved for 0.24×10^{-4} mol dm^{-3} of endosulfan solution, using 0.1 g of adsorbent in 20 ml of solution for 30 min agitation time at pH 6. The Freundlich and Langmuir isotherms fit the equilibrium data satisfactory and their constants, sorption intensity 1/n (0.36), multilayer sorption capacity C_m 6.5 ± 0.26 mmol g^{-1}, and monolayer sorption capacity Q 0.27 ± 0.03 mmol g^{-1}, have been evaluated.Thermodynamics parameters namely change in enthalpy ΔH, Gibbs free energy ΔG and entropy ΔS, were calculated. The negative values of ΔG and positive value of ΔH indicate that the adsorption process is spontaneous and endothermic in nature and positive value of entropy ΔS confirms the possibility of favorable adsorption. The developed adsorption method has been employed to surface water samples.

Keyword: Peach nut shells; Endosulfan; Adsorption; Isotherms; Thermodynamics

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Introduction

In developing countries like Pakistan where the economy depends largely on agricultural products, one cannot afford to loose the harvest to pests. In Pakistan, 15–20% of the total harvest is destroyed by pests resulting in abandoned use of pesticides by the Pakistani farmers. According to EPA toxicity class, endosulfan is a highly toxic pesticide. It has been reported that endosulfan is genotoxic in mammalian cells [1, 2]. Due to the abundant usage and potential transport of endosulfan, contamination is frequently found in the environment at considerable distance from the point of application [3, 4]. Regulations for drinking water are required in order to limit human risks and environmental pollution. Turkish Drinking Water Standards (TDWS) (1988) [5] and the World Health Organization (WHO) (1984) [6] limit pesticides in water to 0.1 $\mu g\ l^{-1}$ for a single pesticide and 0.5 $\mu g\ l^{-1}$ for the sum of all pesticides.

The wide range of pesticides or herbicides in use makes research extremely difficult for producing a single method of removal for pesticides or herbicides that applies universally. Several methods for removal of these toxic chemicals may be required to solve this problem. Since adsorption is one of the best methods for removal of organic materials. Adsorption on activated carbon has been found to be an effective process for pesticides removal, but it is too expensive. Therefore, there is need to explore low cost adsorbents. As a result numerous low cost alternatives have been studied including Beech sawdust [7], eucalyptus bark [8], green algae (Ulothrix zonata) [9], seaweeds [10], coirpith [11], watermelon peels [12], zeolite tuff [13], rive bed sand [14, 15], bagasse fly ash [16], spent activated clay [17], etc. However, the literature is still insufficient to cover this problem, and there is need of more work and investigations in this field to develop some other locally available and economical adsorbents to eliminate pollutants from water.

In the present studies peach nut shells a cheap and abundant agricultural by-product in Pakistan have

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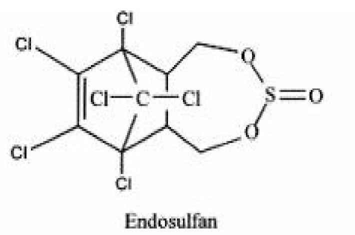
been investigated for the removal of endosulfan pesticide from water.



Experimental

Materials

All the reagents were of analytical grade. Endosulfan was obtained from Sigma Aldrich Co. (Seelze, 22 Germany). Methanol (HPLC grade) was procured from Fisher Scientific, UK. The adsorbent selected for the studies was collected from local market, Hyderabad.

Methods

Adsorbent preparation

Peach nut shells were washed several times with deionized water to remove foreign impurities and then dried in an oven at 110 ^{0}C for 6 h. The washed material was sieved in Ro-Tap type electrical sieve shaker. The sieved material was then treated with 0.1M nitric acid for 1 h, followed by soaking in methanol for 1 h to remove inorganic and organic matter from the surface of adsorbent and then heated in a closed muffle furnace (Phoenix, Sheffield, England, 1983) at 300^{0}C to increase the surface area [18] and it was found to be 83.3 m^2/g. This material was stored in a vacuum descicator to be used as an adsorbent for further analysis.

Batch adsorption experiments

Batch adsorption experiments were carried out by agitating 0.1 g of peach nut shells with 20 ml of endosulfan solution of desired concentration, temperature and pH with a constant speed of 100 rpm. At the end of predetermined time intervals, adsorbent was removed from the solution by filtration. The progress of the adsorption was assessed by residual concentration of endosulfan in supernatant by Hitachi model 6200 HPLC equipped with Licrosorb ODS column 5 μm (Ø250mm × 4 mm) UV–Visible detectors.

Results and discussions

Effect of pH

Optimization of pH of adsorption medium plays very important role in the adsorption studies. The adsorption of pesticide was studied over the range of pH 1-10 by using 0.1 g of the adsorbent per 20 ml of 0.24×10^{-4} mol dm^{-3} of the pesticide solution with the shaking speed of 100 rpm. It was observed that percent adsorption decreases with an increase in the pH as shown in Fig. 1. At lower pH the amino groups of protein and water molecules become protonated due to increase of H^+ ion concentration. As a result the adsorbent surface becomes positively charged and negatively charged S and O of endosulfan electrostatically attracted on surface. Whilist at higher pH, OH^- of polysaccharides groups become negatively charged consequently repulsion forces come to play between adsorbent surface and adsorbate molecules [19].

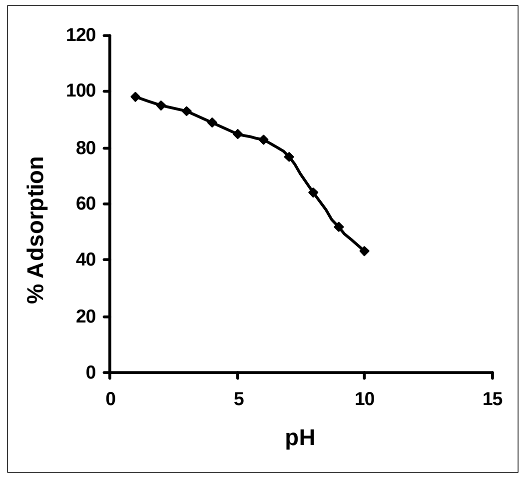


Figure-1. **Effect of pH for the adsorption of endosulfan onto peach nut shells**

Adsorbent dose

Adsorbent dose is an important parameter because it determines the capacity of an adsorbent for a given initial concentration of the adsorbate [20]. The effect of adsorbent dose on removal of pesticide was studied by varying the dose of adsorbent in the range of 0.01-1 g at fixed pesticide concentration. The result shows that as the adsorbent concentration increases, percentage adsorption generally increases, but as the amount of adsorbate is fixed, the amount adsorbed per unit mass of the adsorbent decreased due to adsorption sites that remaining unsaturated during the adsorption process. After 0.1 g of adsorbent percent adsorption was found almost constant.

Effect of contact time

In order to determine equilibrium time for maximum uptake 0.1 g of adsorbent was used over a contact time of 0–100 min, with 100 rpm shaking speed, for 20 ml of 0.42×10^{-4} mol dm^{-3} endosulfan solution. Adsorption experiments were carried out over 100 min to find the optimum contact time. It was found that contact time of 30 min is enough for maximum adsorption of pesticide (95%) from solution as shown in Fig. 2.

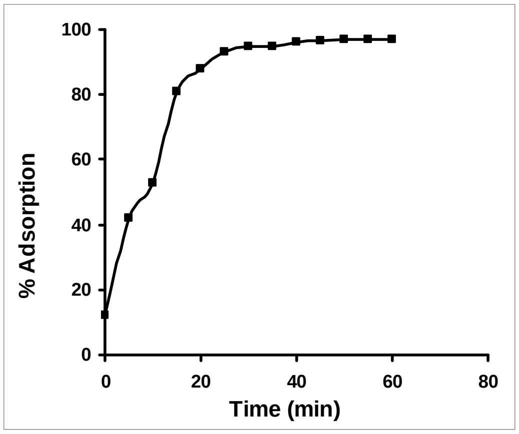


Figure-2. **Effect of contact time time for the adsorption of endosulfan onto peach nut shells**

Effect of initial pesticide concentration

For observing the effect of concentration of the adsorbate, the concentration range $(0.24\text{-}2.4)\times10^{-4}$ mol dm^{-3} was taken for the endosulfan at 30 ^{0}C by using 0.1 g of adsorbent under optimized conditions. It was observed that, an increase in initial concentration decreased the percentage binding. These observations can be explained by the fact that at very low concentrations of pesticide, the ratio of sportive surface area to the total endosulfan molecules available is high and thus, there is a greater chance for pesticide removal. Thus at low initial pesticide concentrations, the removal capacity is higher. When pesticide concentration is increased, binding sites become more quickly saturated as amount of adsorbent remained constant.

Adsorption Isotherms

Several isotherm models are available. In this study the Langmuir and Freundlich models were employed [21] The Langmuir equation assumes that adsorption is limited to monolayer; its linearized form can be represented as:

$$\frac{C_e}{C_{ads}} = \frac{1}{Qb} + \frac{C_e}{Q} \qquad (1)$$

where Q is the monolayer adsorption saturation capacity (mol g^{-1}), and b represents the enthalpy of adsorption (dm^3 mol^{-1}), independent of temperature. A plot of C_e/C_{ads} versus C_e yields a straight line with its slope of 1/Q and intercept of 1/Qb as shown in Fig. 3 and the results are enlisted in Table.1. The essential characteristic of the Langmuir isotherm can be explained in terms of a dimensionless constant separation factor (R_L), calculated using the equation $R_L = 1/(1 + bC_i)$ where C_i is the initial concentration of metal ions. R_L describes the type of the Langmuir isotherm [22] to be irreversible ($R_L = 0$), favorable ($0 < R_L > 1$), linear ($R_L = 1$) or unfavorable. The values of R_L calculated were between (0.053-0.36), indicating highly favorable sorption of endosulfan on the adsorbent surface.

Table-1. **Freundlich and Langmuir parameters for adsorption of endosulfan onto peach nut shells.**

Parameters	Value	R^2
Freundlich isotherm Cm ($mmolg^{-1}$)	6.5 ± 0.26	0.957 ± 0.07
1/n	0.36 ± 0.038	
Langmuir isotherm Q ($mmolg^{-1}$)	0.27 ± 0.029	0.966 ± 0.05
b (mol dm^{-3})	7.7×10^4	

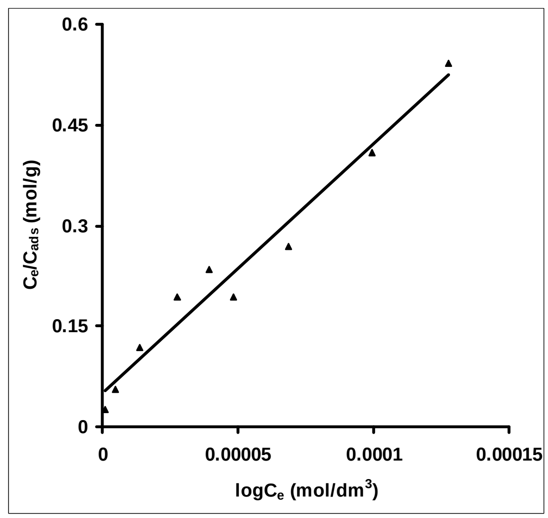


Figure-3. **Langmuir adsorption isotherm of endosulfan onto peach nut shells**

The Freundlich equation is an empirical relationship describing the adsorption of the solutes from a liquid to solid surface. Linearized form of Freundlich equation is:

$$\log C_{ads} = \log C_m + \frac{1}{n}\log C_e \qquad (3)$$

where 1/n is a characteristic constant related to adsorption intensity, C_{ads} is the adsorbed concentration of adsorbate onto adsorbent (mol g^{-1}), C_e represents equilibrium concentration of adsorbate in solution, and C_m is the multilayer adsorption capacity of adsorbent (mol g^{-1}). A plot of log C_{ads} versus log C_e would exhibit in a straight line with a slope of 1/n and intercept of log C_m as shown in Fig. 4 and the results are listed in Table.1.

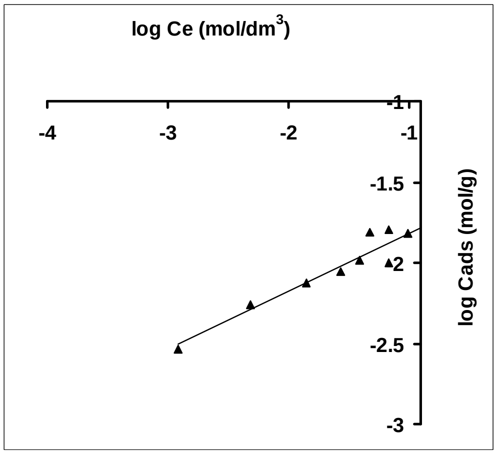


Figure-4. **Freundlich adsorption isotherm of endosulfan onto peach nut shells**

Thermodynamic studies

Effect of temperature was studies in detail to calculate various thermodynamic parameters, such as enthalpy ΔH, entropy ΔS, and Gibbs free energy ΔG. The values of these parameters were calculated at different temperature by using following relations [23, 24]

$$\ln K_c = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \qquad (4)$$

$$\Delta G = -RT \ln K_c \qquad (5)$$

The plot of ln K_c verses 1/K gives a straight line with coefficient of determination 'R^2' (0.91) as shown in Fig. 5.

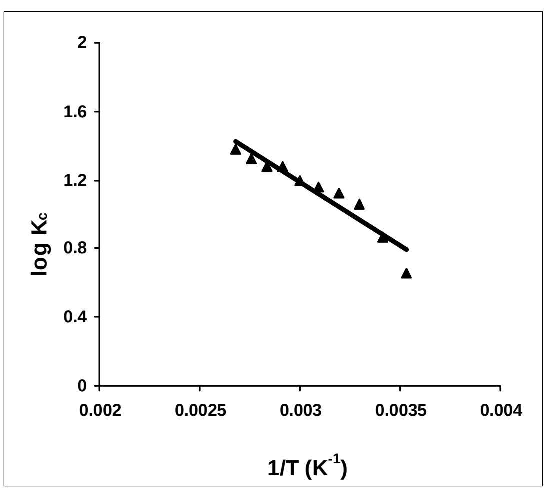


Figure-5. **Effect of temperature on adsorption of endosulfan on peach nut shells**

$K_c = F_e/(1-F_e)$, where F_e is the fraction adsorbed at equilibrium, while K is the temperature in Kelvin. From the slope and intercept of plot, the values of ΔH and ΔS have been computed, while ΔG is calculated using Eq. (5).

The negative value of free energy ΔG_{303K} (-6.15 kJ mol^{-1}) indicates the process of endosulfan removal to be spontaneous. The positive values of enthalpy change ΔH (14.22 kJ mol^{-}) further confirm the endothermic nature of the adsorption process and positive value of entropy ΔS (0.114 kJ mol^{-} K^{-1}) confirms the possibility of favorable adsorption.

Analytical Application

Surface water samples were collected from different agricultural areas of Sindh. The contaminated water samples were spiked with 10 μg ml^{-1} of the endosulfan pesticide. For the removal of endosulfan from contaminatedwater samples using peach nut shells at optimized experimental conditions, 100 ml portions of the spiked water samples were agitated for 60 min by using 0.5 g of adsorbent. 10 μl was injected to HPLC for the analysis by using adsorption procedure as stated in the experimental part.Endosulfan pesticide was successfully removed from contaminated water samples. The adsorbed amount of ensosulfan was recovered with 5ml of methanol by sonication on an ultrasonic bath for 10 min. The percent adsorptions along with percent recoveries are presented in Table 2.

Table-2. **Amount of endosulfan determined in surface water samples along with percent adsorption and percent recoveries using peach nut shells.**

Samples	Amount of endosulfan determined in surface water samples (μg ml^{-1})	% Adsorption	% Recovery
Matiari	0.82 ± 0.18	95 ± 1.0	92.0 ± 0.2
Hyderabad	0.65± 0.2	93.0 ± 1.5	88. ± 1.0
Hala	1.6 ± 0.15	94.0 ± 2.0	91.0 ± 2

Conclusion

The low cost peach nut shells were found to be effective for the removal of endosulfan pesticide from aqueous solutions. The value of 1/n from Freundlich adsorption isotherm proposes adsorption capacity of peach nut shells is better for lower concentration solutions rather than higher concentration solution, where as the R_L values from Langmuir adsorption isotherm depict favorable adsorption process. The thermodynamic quantities ΔH and ΔG indicate the endothermic and spontaneous nature of adsorption process. Endosulfan pesticide was successively removed from surface water samples. Methanol was found to be better solvent to desorb the adsorbed endosulfan from the surface of peach nut shells.

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