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Adsorption of Selected Pesticides from Aqueous Solutions Using Cost effective Walnut Shells

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Abstract:- In the present studies efforts are made to develop a low cost method to remove pesticides from water streams. Low cost walnut shells after chemical and thermal treatment are used to remove carbofuran and Chloropyriphos pesticides from aqueous solutions. The adsorption parameters i.e. pH, contact time, shaking speed and initial concentration have been studied. The adsorption was found to be rapid 97-99% within 30 min. The adsorption of pesticides on the adsorbent surface was found to be pH dependent. The adsorbent material was characterized by scanning electron microscopy (SEM) analysis and FT-IR spectroscopy. Elution experiments were performed to recover the adsorbed pesticide from the adsorbent surface. The Freundlich, Langmuir, D-R and Thomas models were used to study the partitioning behavior for the adsorption system along with kinetic and thermodynamic studies. The proposed adsorption method was utilized to remove carbofuran and Chloropyriphos pesticides from environmental water samples.

Key word: *Adsorption; pesticides; Walnut shell; Isotherms, Kinetics; thermodynamics.*

I. INTRODUCTION

Pesticides are being ever more used to control the loss of agricultural crops and improve yield. In developing countries like Pakistan, the use of pesticides is dispossessed to be so imperative that they are associated with growth of human benefit [1]. Extensive usage of pesticides is accountable for water contamination because of their leaching and runoff losses. Inappropriate discarding of the empty pesticide bottles, washing of spray instruments and unfettered discharge from manufacturing units are further sources of water resources contamination. In the past few years the existence of pesticide residues in ground water resources has experienced extensively and has turn out to be an intensive and burning issue of discussion [2].

Carbofuran (2,3-dihydro- 2,2-dimethyl-7-benzofuranyl-N-methylcarbamate) is a broad spectrum carbamates pesticide, used to control insects in a wide range of crops i.e. potatoes, corn and soybeans. WHO classified carbofuran as highly hazardous pesticide [3]. Carbofuran is highly toxic by inhalation and ingestion and moderately toxic by dermal absorption causes asthma, diabetes, cardiovascular disease etc [5]. Like wise Chloropyriphos (O,O diethyl O (3,5,6 Trichloro-2-pyridyl) an organophosphorous pesticide used against soil insects of field and vegetable crops. Chloropyriphos is more persistent than most organophosphates, possibly because it is stored in fatty tissues and released over time. Chloropyriphos when ingested by animals is converted to chloropyriphos-oxon which is more toxic than chloropyriphos itself.

Several methods are used to control contamination of water by organic pollutants i.e. biotreatment, air stripping, chemical oxidation, and adsorption by granular activated carbon [6].

However, nowadays adsorption by granular activated carbon is a broad spectrum technology. Yet owing the high cost of activated carbon, its use is restricted on economical contemplation. Alternatively low-cost adsorbents from agricultural by-products i.e. chestnut shells, watermelon peels, mango kernel, banana peel, orange peel, chickpea husk, hazelnut shell etc [7-13] have been investigated as a potential alternative to activated carbon. In the present work efforts have been made to develop low cost methods for water purification. The indigenously produced activated adsorbent from walnut shell is employed as low-cost adsorbent for the removal of pesticides from contaminated water streams.

II. MATERIAL AND METHODS

All chemicals and reagents used were of analytical grade and procured from Fluka /Merck (Germany). Pesticides were obtained from Sigma Aldrich Co. (Seelze, 22 Germany). Methanol (HPLC grade) was procured from Fisher Scientific (UK) and used for making synthetic aqueous solutions and for HPLC.

III. INSTRUMENTATION

Hitachi model 6200 HPLC equipped with a Licrosorb octadecylsilane (ODS) Inertsil column 5µm

(250×4 Ø mm) is used for analysis of pesticides. Water-methanol mixture (30:70) v/v was used as a mobile phase at a flow rate of 1 ml min^{-1}. The limit of detection (signal to noise ratio 2:1) was found to be 0.03 ng µl^{-1} and 0.07 ng µl^{-1} at selected wave lengths of 275 nm and 214 nm for carbofuran and chloropyriphos respectively.
Perkins Elmer UV/Vis spectrometer Lambda 2 is used for the determination of maximum wavelengths of carbofuran and chloropyriphos. The pH measurements are made on digital (InoLab pH level I) pH meter. The Gallenkamp automatic shaker model BKS 305-010 UK is used for the batch experiments. The surface area measurement was carried out by BET (Brunauer, Emmett and Teller) method using nitrogen as a standard by employing surface area analyzer (Quantasorb, QS-7) [15].
The IR spectra was acquired using a Thermo Nicolet Avatar 330 FTIR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector and KBr optics and controlled by OMNIC software (Thermo Nicolet Analytical Instruments, Madison, WI).

IV. ACTIVATION OF ADSORBENTS

The adsorption efficiency of adsorbets is depends upon the process of activation [16, 17]. To enhance the surface area and porosity the adsorbent was activated by chemical as well as thermal activation.

1.1. Chemical and Thermal Activation of walnut shells

The Walnut shells were washed carefully with deionized water to remove impurities and then dried. The sieved material (100 µm) was treated with 0.1 M nitric acid solution for 1 h to increase surface area of the adsorbents [18]. The material was washed with deionized then soaked in methanol for 4 h to remove organic matter from the surface followed by thermal activation in a closed muffle furnace (Phoenix, Sheffield, England, 1983) at 573 K for 1 h then kept in vacuum desiccators.

1.1.1. Surface Characterization of Adsorbents

The strength of adsorption possibly be affected by the physicochemical characteristics of the adsorbent such as surface area, pore size, surface functional groups, and composition [19]. Different activation treatments verify clearly different adsorption characteristics [20]. Consequently, an effective adsorbent should have a large surface area with the appropriate pore size to adsorb the targeted species.

4.2.1. BET (Brunauer, Emmett and Teller) Method

The surface area measurement was carried out by BET (Brunauer, Emmett and Teller) method. After chemical and thermal treatment surface area of the adsorbents was increased [12]. The specific surface area of unactivated walnut shells was found 32.4 ± 1.2 m^2/g, while, after activation it was increased as 83.3 ± 2.4 m^2/g.

4.2.2. FT-IR Spectroscopy

The FT-IR spectra of activated and unactivated walnut shells were recorded for determining the nature of surface groups responsible for binding of pesticides. The presence of a large number of peaks at different positions in FT-IR spectra **Fig. 1,** indicating the complex chemical nature of the material.

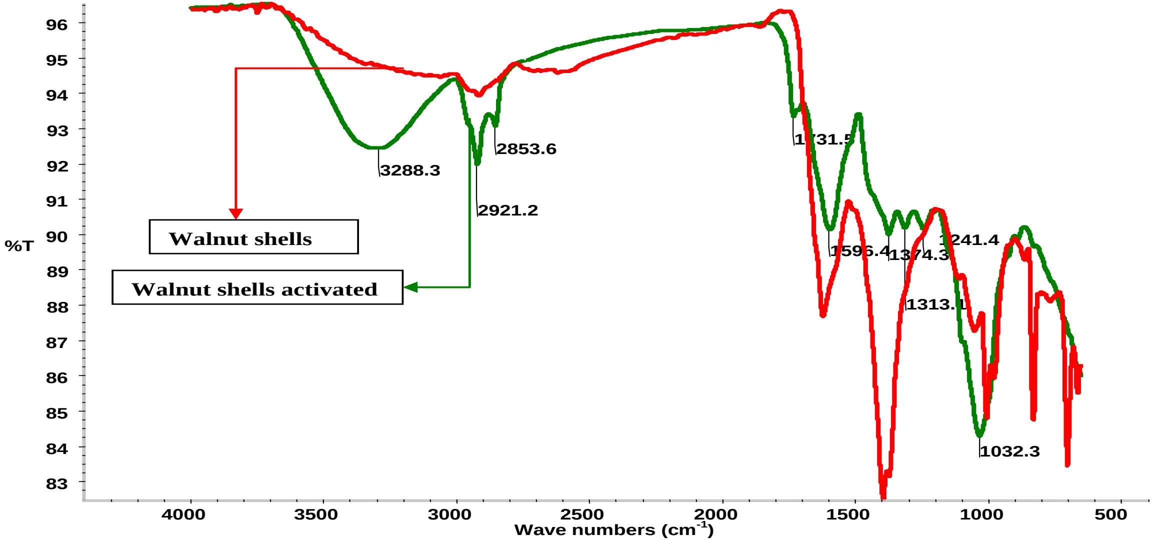

Fig. 1 FT-IR spectra of walnut shell

The results obtained by FT-IR analysis confirms the presence of functional groups such as alcoholic, carboxylic, carbonyl and ether groups in the structure of the biomass surface and carbonaceous material [21]. which may play a significant part to bind the pesticides on the surface of walnut shell at low pH.

4.2.3. *Scanning Electron Microscopy and Energy Dispersive X-ray analysis*

The surface area morphologies of adsorbents were studied with A Hitachi S2300 Scanning Electron Microscope (SEM) at 25 kV accelerating voltage. SEM images reveals that the porosity of walnut shell was increased after chemical and thermal activation as shown in **Fig. 2 a & b**.

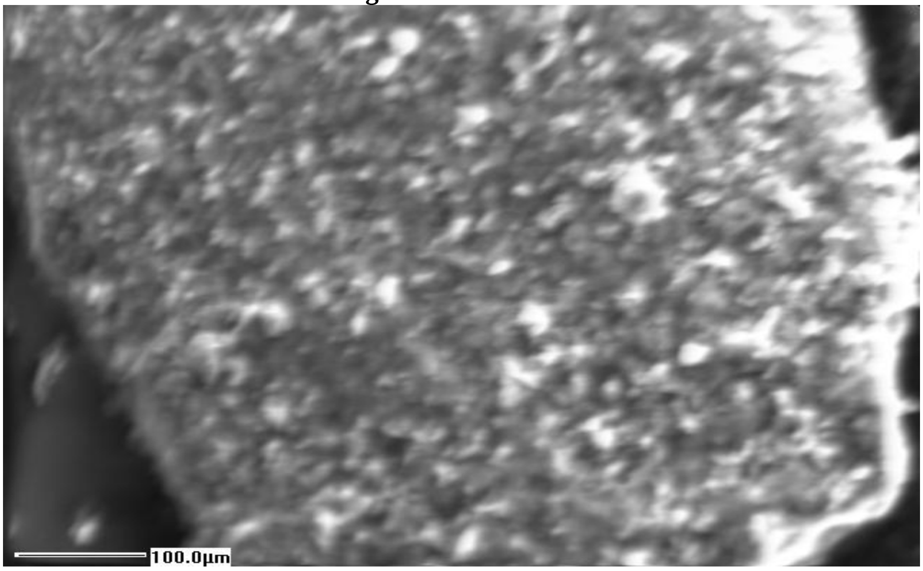

Fig. 2 (a) SEM image of untreated walnut shell

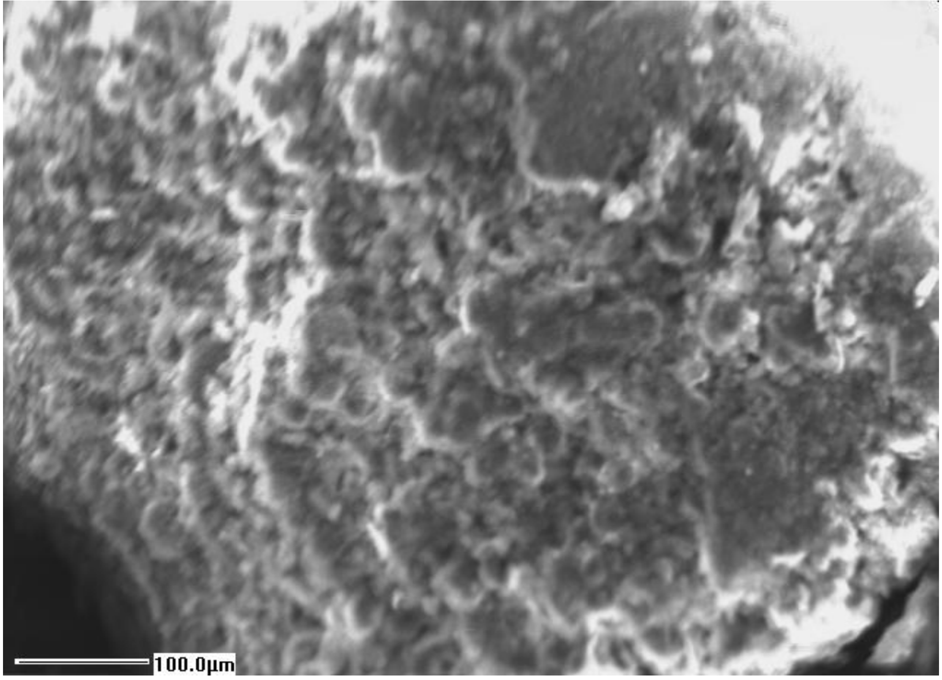

Fig. 2 (b) SEM image of chemically and thermally treated walnut shell

4.3. *Adsorption Method*

4.3.1. Batch Adsorption Method

An optimum amount of walnut shell was taken in a flasks containing pesticide solution and fitted to a thermostatic shaker at constant pH. The sample was filtered and was then injected to HPLC under optimized conditions.

3.1.2 Column Adsorption Method

Adsorbent material (5 g) was puted into a glass column (6 mm × 150 mm), by adjusting the pH of the pesticide solution with an optimum concentration, the solution was passed through the column at flow rates between 1-5 ml min^{-1}. Consequently the column was washed with distilled water followed by methanol to recover the adsorbed pesticides.

4.4. Data Manipulation

The % adsorption of pesticides was calculated using following equation:

$$\% Adsorption = \frac{C_i - C_e}{C_i} \times 100 \qquad (1)$$

where C_i (mol dm^{-3}) and C_e (mol dm^{-3}) are the initial and equilibrium concentrations of pesticide in aqueous solution, respectively.

5. Results and Discussions

5.1. Optimization of adsorption parameters

5.1.1 Effect of pH

Initially the experiments were carried out to select the most appropriate adsorptive medium to give maximum adsorption. The buffers of pH 1-10 at an interval of one unit were investigated to observe the effect of pH onto 0.1 g of adsorbent using 20 ml of 10 ppm solution of carbofuran and chloropyriphos separately with 100 rpm agitation speed for 60 min at 303 K. The percent adsorption was found to decrease with increasing pH as portrayed in **Fig 3**.At very low pH values, the surface of the walnut shell would be surrounded by the hydronium ions, which may enhance the pesticide interaction with binding sites of walnut shell to improve its attachment on polar adsorbent [22-23].

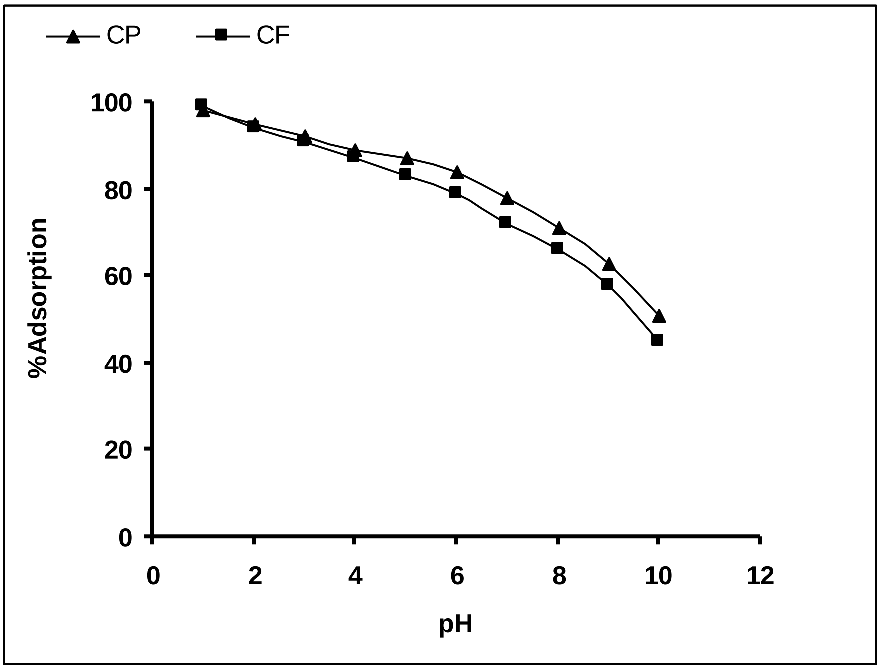

Fig. 3 Effect of pH for the adsorption of carbofuran and chloropyriphos

5.1.2 Effect of Adsorbent Dosage

The effect of amount of adsorbent in the range of 0.01-1 g on removal of pesticide was studied at optimum conditions As the mount of adsorbent increased, percentage adsorption was also increased to a limited value at which saturation take place.

5.1.3 Effect of contact time

The time study was carried out in the range of 5-60 min, and it was observed that with the increase of time pesticides uptake was also increased until certain limit (30 min) at which equilibrium was established. For further studies 30 min of contact time was applied.

5.1.4 Effect of initial concentration of carbofuran

The effect of concentration of the carbofuran and chloropyriphos was studied in the range of 10-100 ppm using 0.1 g of adsorbent. %adsorption of pesticide was increased with increasing concentration until the equilibrium is established at the solid–solution interface [24]. At the saturation point of adsorption on solid surface %adsorption decreases with the increase of initial concentration.

5.2 *Adsorption isotherms*

Langmuir, Freundlich and D-R isotherms were used to predict the equilibrium behavior of carbofuran and chloropyriphos adsorption onto walnut shells.

The Freundlich adsorption equation is the most widely used mathematical description of adsorption on aqueous systems. The linearized form of Freundlich isotherm is [25]

$$\log C_{ads} = \log K + \frac{1}{n}\log C_e \tag{2}$$

where 1/n is a characteristic constant related to sorption intensity, C_{ads} is the sorbed concentration of adsorbate onto adsorbent (mol g^{-1}), and K is the multilayer sorption capacity of adsorbent (mol g^{-1}).The Freundlich isotherm was plotted between the log C_{ads} and log C_e which is linear in case of all three adsorbents as shown in **Fig. 4**.

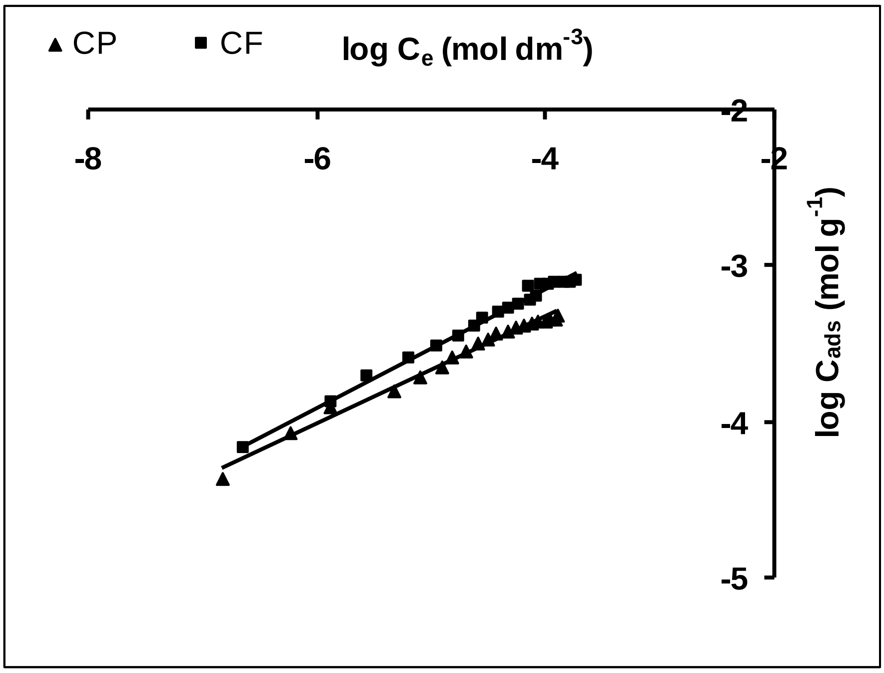

Fig.4 Freundlich adsorption isotherm of carbofuran and chloropyriphos

The Freundlich constant computed using slope of linear plots, 1/n <1 shows that adsorption is favorable at lower equilibrium concentrations [26]. The values of Freundlich constants are given in **Table 1.**

The Langmuir adsorption isotherm describes quantitatively the build up of a layer of molecules on an adsorbent surface as a function of the concentration of the adsorbed material in the liquid in which it is in contact [27]. Langmuir presented a general equation for the isotherm of localized adsorption,

$$\frac{C_e}{C_{ads}} = \frac{1}{Qb} + \frac{C_e}{Q} \tag{3}$$

where Q is the monolayer adsorption saturation capacity (mol g^{-1}), and b represents the enthalpy of sorption (dm^3 mol^{-1}), independent of temperature. The plot of C_e/C_{ads} against C_e presents a straight line as depicted in **Fig. 5.**

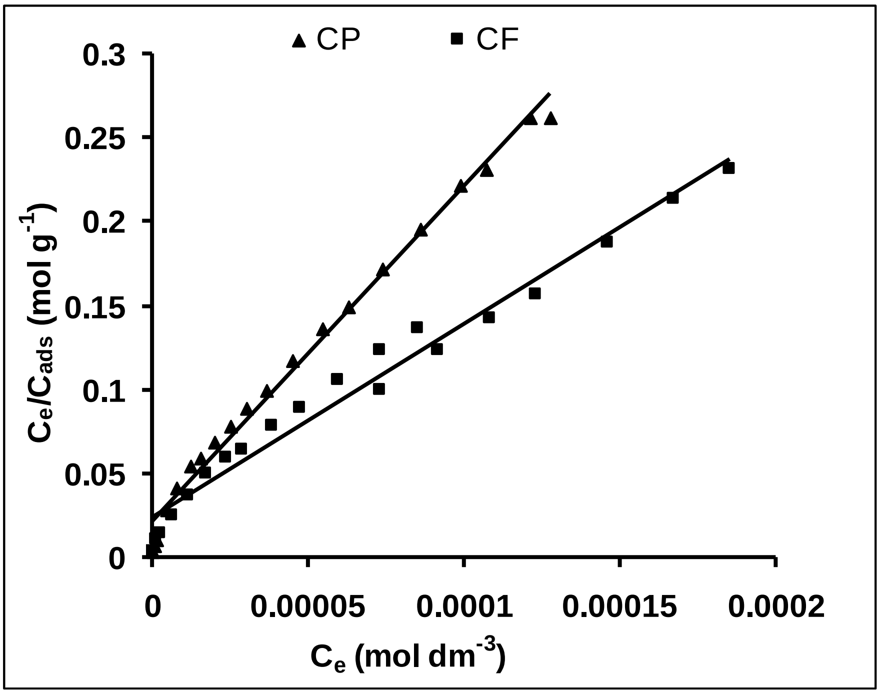

Fig. 5 Langmuir adsorption isotherm of carbofuran and chloropyriphos

R_L is an essential characteristic of Langmuir isotherm, it is the measure of the adsorbent capacity used given by the equation:

$$R_L = \frac{1}{1 + bC_i} \tag{4}$$

Table 1. Adsortion parameters for the adsorption of carbofuran and chlorophyriphos

Freundlich constants	1/n K (mmolg^{-1}) Regression coefficient (R^2)□ □ □	0.38 ± 0.008 22.9 ± 2.30 0.995 ± 0.015	0.34 ± 0.009 11.24 ± 1.16 0.993 ± 0.033
Langmuir constants	Q (mmolg^{-1}) b (L mol^{-1}) Regression coefficient (R^2)□ □ R_L (dimensionless factor)	0.89 ± 0.033 $(5.0 \pm 0.65) \times 10^4$ 0.988 ± 0.01 (0.043-0.47)	0.987 ± 0.016 $(1.23 \pm) \times 10^4$ 0.995 ± 0.008 0.026-0.35
D-R constants	X_m (mmolg^{-1}) E (kJ/mol) Regression coefficient (R^2)□	$(2.7 \pm 0.06) \times 10^{-4}$ 13.9 ± 0.02 0.994 ± 0.007	1.53 ± 0.003 14.7 ± 0.019 0.995 ± 0.062

The values of R_L are in the range of 0.1-0.99 means $0 < R_L > 1$ representing extremely favorable adsorption process [28]. The values of adsorption capacity and intensity of adsorption calculated from the slope and intercept of linear plots are also presented in **Table 1.**

A comparison of adsorption parameters of carbofuran pesticide, evaluated in present studies, with previously reported parameters is given in **Table 2.**

Table 2 Comparison of carbofuran pesticide adsorption with previous studies

Adsorbent	Adsorption capacities mg/g	References
Walnut shell	K = 508, R^2 = 0.995 Q = 0.19, R^2 = 0.976	This studies
GAC	K = 23.5, R^2 = 0.963 Q = 181.8, R^2 = 0.992	[29]
Fertilizer and steel industry waste	Q = 303, R^2 = 0.992	[30]
Banana stalks	K = 29.4, R2 = 0.817 Q = 161.3, R2 = 0.989	[31]

No work is previously reported on chloropyriphos pesticide**.** On the basis of adsorption capacity and regression coefficient values it is concluded that the adsorption data is best fitted to Freundlich adsorption isotherm
The D-R equation is an adaptation of the earlier Polanyi potential theory of adsorption [32,33]. The linear form of D-R isotherm is given here:

$$\ln C_{ads} = \ln X_m - ß\varepsilon^2 \qquad (5)$$

where X_m represents the maximum adsorption capacity of adsorbent (mol g^{-1}), β is a constant related to adsorption energy, while ε is Polanyi adsorption potential which can be evaluated by:

$$\varepsilon = RT \ln(1 + \frac{1}{C_e}) \qquad (6)$$

The D-R adsorption isotherm was studied by plotting ln C_{ads} versus ε^2 Polanyi potential) as shown in **Fig. 6.** The value of adsorption energy, E is calculated by.

$$E = \frac{1}{\sqrt{-2\beta}} \qquad (7)$$

D-R constants are also given in **Table 1.**

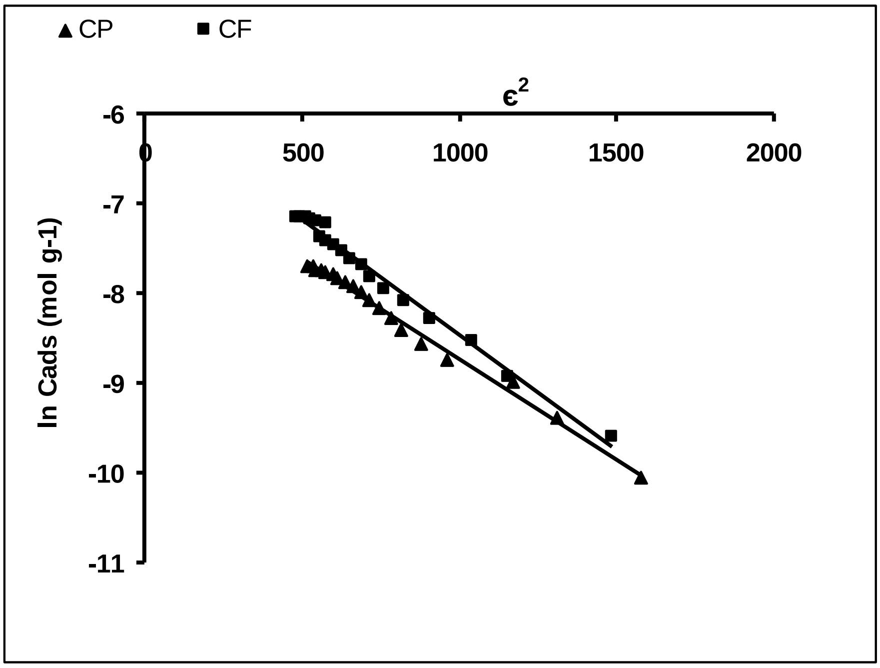

Fig. 6 D-R adsorption isotherm of carbofuran and chloropyriphos

5.3. *Kinetics of adsorption*

The Lagergren first order rate expression [34], is one of the most widely applied kinetic model to the adsorption processes. The specific rate constant k for any adsorbate-adsorbent system in equilibrium can be calculated from the first order rate equation, by plotting log (q_e-q_t) vs. time, t, as illustrated in **Fig. 7**. The adsorption of carbofuran as well as chloropyriphos follow first order rate and the findings are given in **Table 3**.

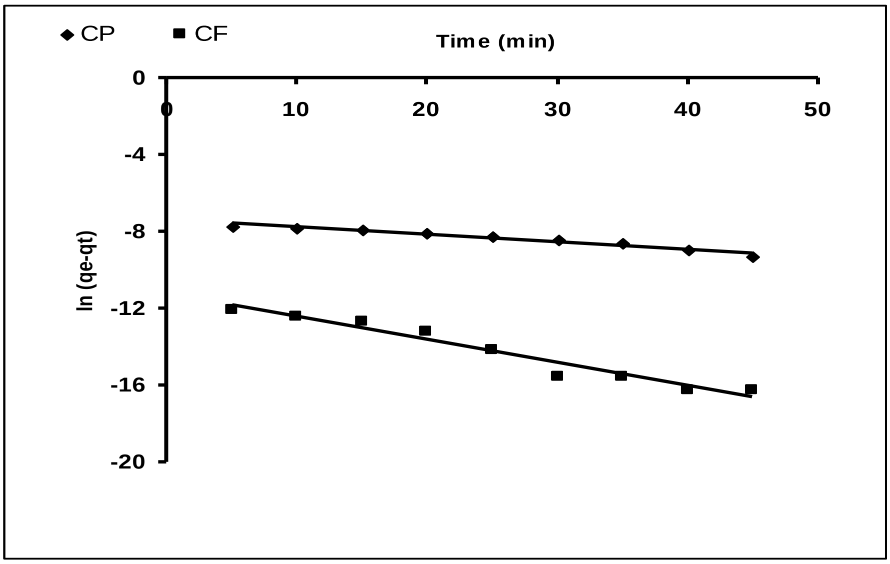

Fig. 7 Lagergren plots of carbofuran and chloropyriphos

Table 3 Kinetic parameters for the adsorption of carbofuran and chloropyriphos onto walnut shell

Kinetic Parameters	Carbofuran	Chloropyriphos
k (min^{-1})	0.14 ± 0.005	0.039 ± 0.003
Regression coefficient □ R^2□ □	0.96 ± 0.004	0.973 ± 0.012
R_d (μmol g^{-1} min^{-1})	0.13 ± 0.03	82.17 ± 5.20
Regression coefficient (R^2)□ □	0.93 ± 0.001	0.958 ± 0.022

To investigate the nature of adsorption mechanism by film diffusion or intraparticle diffusion mechanism, Reichenberg equation was used.

$$B_t = -0.4977 - \ln(1-Q) \tag{8}$$

If intraparticle diffusion occurs, the curve will be linear and if the plot passes through the origin, then the rate limiting process is only due to the intraparticle diffusion [35]. The plot of Bt versus time as shown in **Fig. 8** is not pasings through origin suggests the adsorption process is film diffusion process.

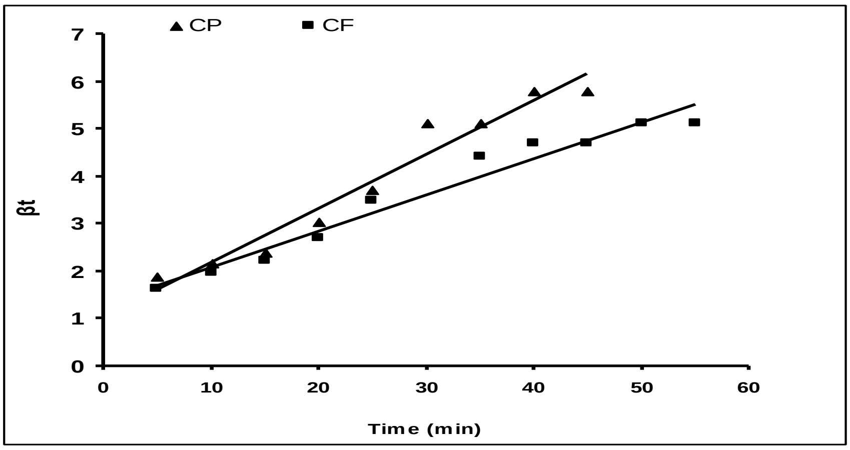

Fig. 8 Reichenberg plots of carbofuran and chloropyriphos

5.4 *Thermodynamics of adsorption*

The thermodynamic parameters i.e. ΔH, ΔG and ΔS were evaluated using following equations [36]:

$$\ln K_c = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{9}$$

$$\Delta G = -RT \ln K_c \tag{10}$$

From the slope and intercept of plots of log K_c versus 1/T as shown in **Fig. 9** ΔH and ΔS were calculated and the findings are listed in **Table 4**.

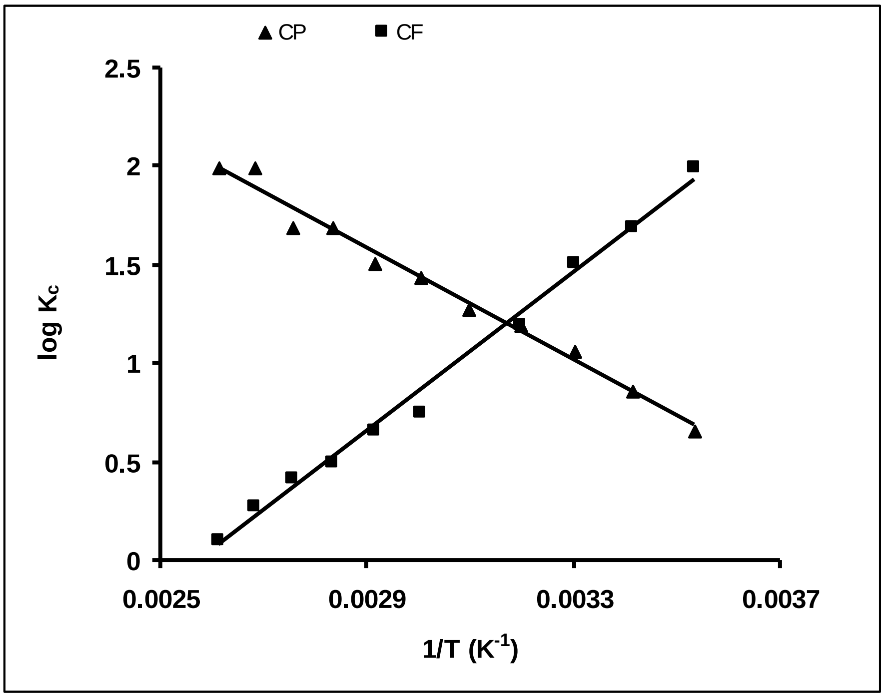

Fig. 9 Effect of temperature for adsorption of carbofuran and chloropyriphos

The positive value of ΔH in case of chloropyriphos shows that adsorption process is endothermic whereas negative ΔH value for carbofuran reveals the exothermic nature of adsorption process, while negative values of ΔG suggests the spontaneous nature of adsorption.

Table 4 Thermodynamic parameters for the adssorption of carbofuran and chloropyriphos onto walnut shell

Thermodynamic Parameters	**Carbofuran**	**Chloropyriphos**
□ H (kJmol^{1})	-38.05 ± 1.19	27.0 ± 1.09
□ S (kJmol^{1} K^{-1})	-0.10 ± 0.003	0.11 ± 0.003
□ $G_{303\ K}$ (kJmol^{-1})	-10.81	-6.15 ± 0.24
Regression coefficient (R^2)	0.99 ± 0.006	0.992 ± 0.055

5.5 Column Adsorption Studies

Column adsorption studies were performed in order to estimate the practical applicability of adsorbent i.e. walnut shells for the removal of carbofuran pesticide.

5.5.1 Effect of flow rate

The effect of flow rate on adsorption of carbofuran was examined at flow rate 1-6 ml min^{-1}. %adsorption was found maximum at flow rate of 2 ml min^{-1}.

5.5.2 Break through curves

In adsorption studies the break through is portrayed when the effluent concentration of species from the column is about 3-5% of the influent concentration. A solution containing 10 ppm of pesticides were passed through the column. The plot of concentration of pesticide vs aliquot volumes creates the breakthrough curve. The break through occurs at 5 dm^3 as shown in Fig 10. The breakthrough volume determines the maximum value of water sample containing pesticides introduced into the adsorbent. The sharp line of the curve **Fig. 10** illustrates the favorable equilibrium [37].

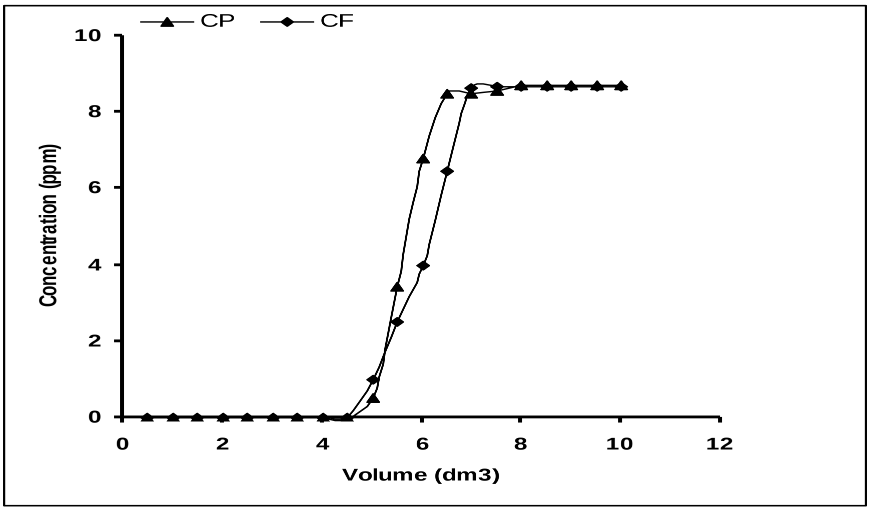

Fig. 10 Break through curve for the adsorption of carbofuran and chloropyriphos

The maximum adsorption capacity of adsorbent is calculated using Thomas model on the basis of column method.

Thomas Model

The Thomas model estimates the maximum solid phase concentration of adsorbate on the adsorbent surface and the rate constant of adsorption for column method [38]. The linearized form of this model is:

$$\ln\left(\frac{C_0}{C_{ads}} - 1\right) = k_{TH} C_0 t + k_{TH} \frac{q^t{}_{ac\,\max} m_s}{Q} \qquad (11)$$

The kinetic coefficient k_{TH} and the adsorption capacity of the bed $q^t{}_{acmx}$ were calculated by plotting ln $(C_0/C_{ads}-1)$ vs. time as shown in **Fig. 11**. The results are given in **Table 5**.

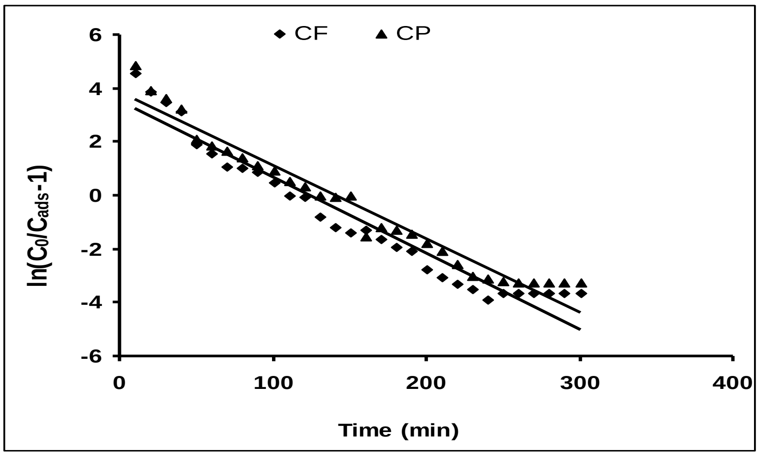

Fig. 11 Thomas model of carbofuran and chloropyriphos

Table 5 Thomas model parameters for the adsorption of carbofuran onto steam treated walnut shells

Analyte	Q (ml/min)	C_0 (mg/l)	k_{TH} (ml/(min mg))	q_{acmax} (mg/g)	R^2
Carbofuran	2	10	0.57	4.43	0.948
Chloropyriphos	2.5	10	0.46	4.26	0.957

5.6 Recovery of Carbofuran

Different solvents were used to desorb the adsorbed pesticides from the surface of walnut shells. It was found that 5 ml of methanol was used for ~98% recovery of carbofuran and chloropyriphos pesticides from adsorbent surface.

5.7 Reusability of Adsorbents

Several loading and elution experiments were takes place to test the stability of walnut shell. The adsorption efficiency was established practically constant (variation 1-5%) 6 cycles as shown in **Fig. 12**.

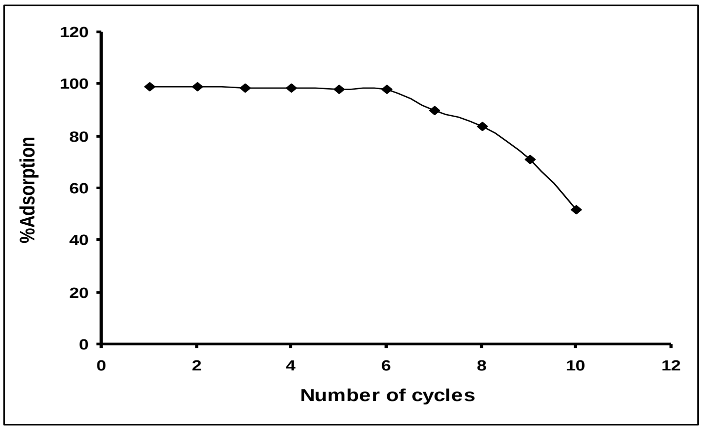

Fig. 12 Recycling of walnut shell for the adsorption of carbofuran and chloropyriphos

5.8 Analytical application to real water samples

To eliminate carbofuran and chloropyriphos pesticide from surface water samples were collected from agricultural areas of Sindh province, the column method was applied. Surface water samples were spiked with 10 ppm of carbofuran and chloropyriphos and analysed by HPLC. Using present method carbofuran and chloropyriphos pesticides were effectively removed from surface water samples. The results with %adsorption and %recoveries are revealed in **Table 6**.

Table 6 Percent adsorption and percent recoveries of carbofuran and chloropyriphos from surface water samples using walnut shell

Samples	Carbofuran			Chloropyriphos		
	Amount determined in surface water samples (µg L^{-1})	% Adsorption	% Recovery	Amount determined in surface water samples (µg L-1)	% Adsorption	% Recovery
Matiari	0.8 ± 0.2	98.0 ± 0.5	97.0 ± 0.2	0.8 ± 0.1	99 ± 1	98 ± 1
Hala	0.40 ± 0.05	99.0 ± 1.0	98.0 ± 0.5	0.60 ± 0.05	98 ± 1	97.0 ± 0.5
Tandojam	0.4 ± 0.1	98.0 ± 1.0	96.0 ± 0.2	0.45 ± 0.10	98.0 ± 0.5	96.0 ± 0.2
Sanghar	1.2 ± 0.2	99.0 ± 1.5	97.0 ± 0.5	1.0 ± 0.1	99 ± 1	98 ± 1

CONCLUSIONS

In the present work, attempt is made to develop a simplified adsorption method to remove toxic pesticides from water streams. Present work investigated indigenous, cost effective and effectual adsorbent i.e. walnut shell as a substitute of expensive adsorbents for the exclusion of pesticides. The effectiveness of the adsorbent was analysed by the conditions of pH, adsorbent dose, shaking speed, agitation time, temperature and concentration of pesticides solutions. The adsorption of pesticide on investigated adsorbents is a first-order process, controlled by film diffusion. Fruendlich adsorption isotherm is best fitted to the adsorption data. Proposed method was successfully employed to remove investigated pesticides i.e. carbofuran and chloropyriphos from environmental water samples. Methanol was found suitable solvent to recover the adsorbed pesticides from the surface of adsorbent. The adsorption capacity of adsorbent was found practically constant after repeated use of more than 6 times. It is, therefore, recommended that costly synthetic adsorbents may be reinstating by these inexpensive and abundant adsorbents for the removal of toxic pesticides from water streams on large scale.

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