# Parthenium Hysterophorous Weed: Novel Adsorbent for the Removal of Pesticides Mixture From Aqueous Solution

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**ABSTRACT** This work describes the potential applicability of chemically treated Parthenium hysterophorous leaf powder (PHLP) for removing pesticide (aldrin and dialdrin) from aqueous solution. The pesticides' determination was carried out by Gas Chromatography. Pesticides' removal was pH dependent and the maximum removal was found to be at pH 2.0. The maximum removal of pesticides was achieved within 100 min after the start of every experiment. The adsorption data were fitted to Langmuir, Freundlich, Temkin and Dubnin- Radushkevich (D-R) adsorption isotherm models to evaluate the models parameter. Experimental results showed that the Freundlich isotherm model best describes for the adsorption of aldrin, dialdrin. Pseudo-first order, pseudo-second order and Weber-Morris equations were applied to fit the kinetic results. aldrin and dialdrin fitted well in pseudo-first order model and Intra-particle diffusion was found to be the rate controlling the adsorption process.

## 2. Experimental Methodology
### 2.1. Adsorbent preparation

Parthenium hysterophorous leaves (PHL) were collected from the agricultural fields of district Bulandshaher, U.P, India and washed thoroughly with water to remove foreign impurities. It were then dried in an oven at 100⁰C. The dried material was sieved to mesh size BSS 72 (0.212mm) and rewashed thoroughly with deionized water to remove the fine particles and dried in an oven. The material was then chemically treated with 0.1M nitric acid for 1 hr, followed by soaking in methanol for 1 hr to remove inorganic and organic matter from the surface of adsorbent. The chemically treated parthenium was stored in a vacuum desicator and used as an adsorbent for further analysis.

### 2.2 Equipments and method of characterization

Remaining concentrations of pesticides mixture (i.e. Aldrin, and Dialdrin, ) were extracted from the water sample by using n-hexane. Water samples were extracted with 10 ml of n-hexane. The n-hexane layer was separated and the same procedure was repeated three times. Three fractions of extracted n-hexane were mixed together and a total volume of 30 ml extracted n-hexane was obtained. The combined n-hexane (30 ml) extracted was concentrated to 1 ml using rotary evaporator and was analysed by GC (model Agilent 7890A) with detector ECD. The temperature of the column, injector and detector were 100, 225 and 300 ⁰C, respectively. The mobile phase was nitrogen and used at 60 ml/min flow rate. The column used has specification DB-5 (30m × 250µm × 0.25µm). The chromatograms for pure pesticides i.e. Aldrin and Dialdrin were also recorded under the same experimental conditions for the qualitative and quantitative comparisions.

Characterization of the adsorbents was carried out by FESEM (model FEI Nova SEM 450) and surface area analysis. Scanning electron microscopic studies were conducted to observe the surface texture and porosity of the adsorbents. The surface area of the adsorbent was measured by BET (Brunauer–Emmett–Teller nitrogen adsorption technique).

### 2.3. Adsorption studies

In a typical batch study, solution of fixed initial concentrations of two different pesticides mixtures in double distilled water were taken in 100 ml conical flasks containing fixed amount of PHLP . The flasks were agitated at room temperature (28 ⁰C) at 120 rpm for a pre-determined time intervals using centrifuge. The parameter such as pH (2-10), time of contact (20-120 min.), adsorbent dose (1-10 mg), and pesticides concentration (1-50 mgl⁻¹) were varied during different sets of batch experiment. At equilibrium, the concentration of different pesticides was measured using Gas Chromatography. All experiments were repeated several times till reproducible results were obtained.

The amount of pesticides adsorbed onto PHL at equilibrium, qe (mg/g), was calculated using a mass balance relationship as given in Eq. 1

Where Co and Ce are the initial and equilibrium concentrations (mg/l) of pesticides in solution, V is the volume (l) and W is the weight (g) of the dry PHLP.

$$ qe = \frac{(Co - Ce)V}{W} $$

## 3. Result and discussion
### 3.1 Characterisation of Adsorbent

SEM micrographs which were obtained before and after treatment of PHLP with nitric acid-methanol, are presented in Fig. 1a and b. The scanning electron micrographs clearly reveal the surface structure of the sample. Fig. 1a, shows that the surface of the adsorbent is a continuous structure while Fig. 1b, shows a distorted structure which may be due to its treatment with nitric acid- methanol.

The BET surface area analysis of PHLP was performed with Quantachrome (Model Nova 2000e). The BET surface area of PHLP was found to be 250.785 m²/g , BJH Surface Area was found to be 145.045 m²/g, Pore Volume was 0.207

cc/g and Pore Radius was 18.024 Å.

## 3.2. Effect of adsorbate concentration and adsorption capacity.

For observing the effect of concentration on the adsorbate, the adsorption experiments were carried out using different concentrations of pesticides mixture (1, 10, 30 & 50 mg/L) at fixed pH (6.0), temperature (28⁰C) and contact time (100 min.). The pesticide adsorption capacity was investigated at four different concentrations by using 2.5mg of PHLP. Table.1 shows that the adsorption capacity increases with the increase in pesticide concentration as to the mass transfer driving forces become large[1].

## 3.3. Effect of pH

Optimization of pH of adsorption medium plays very important role in the adsorption studies. The adsorption experiment on mixtures of pesticide was studied over a range of pH 2-10 by using 2.5 mg of adsorbent per 10 ml of 10 mgL$^{-1}$ mixtures of pesticides by shaking it thoroughly. Fig.2 shows that percent sorption decreases with an increase in the pH. At low pH values, the surface of the adsorbent might be surrounded by the hydronium ions, which may enhance the adsorbate interaction with binding sites of the adsorbent with greater attractive forces improving its uptake for polar adsorbent[2]a viable eco-remediation technique based on the use of natural organic substances (NOS.

## 3.4. Adsorbent dose

The optimization of adsorbent dose was also carried out by varying amount of adsorbent with fixed concentration of pesticides mixture in the experiments. The adsorbent doses were varied from 1 to 10 mg at fixed pesticides mixture concentration (10 mgl$^{-1}$). The percentage adsorption increased from 48 to 98 % for aldrin and 47 to 98% for dialdrin when adsorption dose was increased, as the numbers of available sites increase with the increase in adsorption dose[3]temperature, pH and concentration on the adsorption of Cd(II

## 3.5. Effect of contact time

In order to determine equilibrium time for maximum uptake, 2.5 mg of adsorbent was used over a contact time of 10- 120 min, at pH 6 for 10 mgl$^{-1}$ mixture solutions of pesticides. The percentage adsorption of pesticides increases with time and attains the equilibrium at about 100 min. of contact time.

## 3.6. Adsorption isotherms

The adsorption isotherm basically reflects the interaction between solutes and adsorbents until the point where a state of equilibrium is reached. Various isotherm models, fitted to the isotherm data, have been reported in the literature [4] to optimize the effectiveness of adsorbents. In this work, the experimental equilibrium data of pesticides applied to PHLP were fitted to the Langmuir, Freundlich, Temkin and Dubnin-Radushkevich isotherm models. In order to evaluate the ability of the models to describe the adsorption process, the correlation coefficients (R$^2$) were calculated.

The Freundlich isotherm, assumes heterogeneous surface

energy for which the energy term in the Langmuir equation varies as a function of surface coverage. The well-known logarithmic form of the Freundlich isotherm is expressed by the following equation [5]:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e$$

Where qe is the solid phase equilibrium concentration (mg/g), Ce the liquid-phase equilibrium concentration (mg L$^{-1}$) and K$_F$ and n are Freundlich constants. n gives an indication of the facility with which the adsorption process takes place. K$_F$ (l/mg) is the adsorption capacity of the adsorbent (i.e. the adsorption or distribution coefficient) and represents the quantity of pesticides adsorbed onto PHLP per unit of equilibrium concentration. The slope of 1/n ranging between 0 and 1 is a measure of the adsorption intensity or surface heterogeneity, this value becoming more heterogeneous as it approaches to zero.

The corresponding linear plots of log q$_e$ against log C$_e$ are shown in Fig.3.The values of Freundlich Constants, K$_F$ and n with correlation coefficient (R$^2$) are given in Table.2.The values of 1/n less than 1 (n between 1 and 10) represent a favourable adsorption.

As seen in Table.2, the Freundlich isotherm fits quite well with experimental data for aldrin(correlation coefficient R$^2$=0.994), dialdrin(correlation coefficient R$^2$=0.994) whereas the low correlation coefficients (R$^2$< 0.990)show poor agreement of Langmuir, Temkin and Dubnin-radushkevich isotherms with the experimental data.

## 3.7. Adsorption kinetic experiments

The kinetic tests were carried out following the same procedure used for the equilibrium tests. Aqueous samples were taken at different intervals of time and the concentrations of pesticides were measured at the same intervals. The amount of pesticides adsorbed onto the Parthenium at time t; qt (mg g$^{-1}$) was calculated as follows:

$$q_t = \frac{C_o - C_t \times V}{C_o \times W}$$

Where $C_0$ and $C_t$ are the liquid-phase concentrations at an initial and pre-determined time t (mg L$^{-1}$), respectively, V is the volume of solution (L) and W is the dry weight of the added AC (g). The kinetic data were then fitted into the pseudo-first-order, pseudo-second-order and intraparticle diffusion models.

The rate constant of adsorption was determined from the pseudo-first-order equation proposed by Langergren and Svenska [6]:

*In(qe-qt= lh qe =k1t*

Where q$_e$ and q$_t$ (mg g$^{-1}$) are the amounts of pesticides adsorbed (mg g$^{-1}$) at equilibrium and at time t (h), respectively and k$_1$ is the adsorption rate constant (h$^{-1}$).

For the pseudo-first-order kinetic model, the plots of log (q$_e$-q$_t$) versus t for the pesticide mixture at initial concen-

trations of 1mgl⁻¹ are presented in Fig.4. The kinetic parameters from Eq. (4) are shown in Table 3. The $k_1$ values can be determined from the slope of the linear plots. The correlation coefficient values of pseudo-first order for aldrin($R^2$=0.97) and dialdrin($R^2$=0.95) are relatively greater than pseudo-second order and the experimental $q_e$ values agree with the calculated values obtained from the linear plots. This shows that the adsorption of aldrin and dialdrin follow the pseudo-first-order equation, rather it follows pseudo-second order equation.

The pseudo-second-order equation [7] based on the equilibrium adsorption is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e 2} + \frac{1}{q_e} t$$

Where $k_2$ (g mg⁻¹ h⁻¹) is the rate constant of second-order adsorption.

The kinetic parameters from Eq. (5) are shown in Table 3. The $q_e$ and $k_2$ values can be determined from the slope and the intercept of the linear plots of $t/q_t$ versus t, respectively.

An intraparticle diffusion model based on the theory proposed by Weber and Morris [8] was employed to identify the diffusion mechanism. This theory assumes an empirically based functional relationship, common to most adsorption processes, where uptake varies almost proportionally to $t^{1/2}$ rather than to the contact time t. According to this theory:
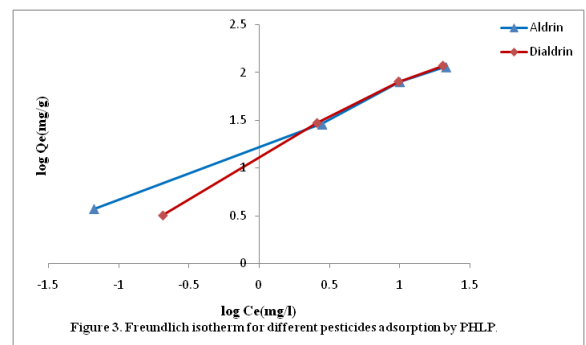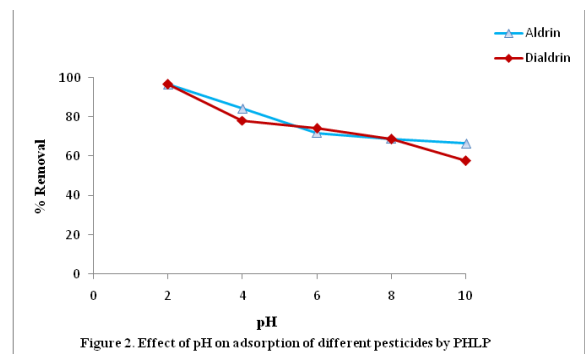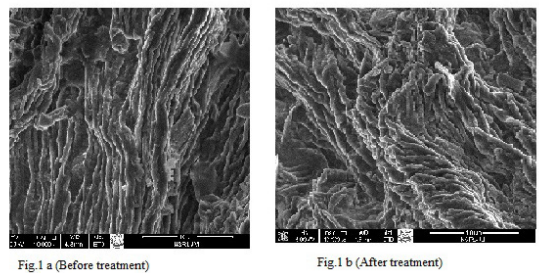
$$q_t = K_{id} t^{1/2} + I$$

For the intraparticle diffusion model, the plots of qt versus $t^{1/2}$ are presented in Fig. 5. The $K_{id}$ and I values can be determined from the slope and the intercept of the linear plots, respectively. The intercept value reflects the importance of the boundary layer thickness, i.e., the larger the intercept, the greater the thickness of the boundary layer [9]. The plots also present multi-linearity, indicating that two or more steps have taken place [10]. Fig. 5 indicates that three linear stages are involved with a moderate diffusion rate in the initial stage, due to external surface adsorption or instantaneous adsorption, followed by rapid diffusion, indicating that intraparticle diffusion is the rate-controlling adsorption process. Thus, predominantly, pesticides adsorption takes place rapidly by external mass transfer followed by intra-particle diffusion. The third step corresponds to the final equilibrium adsorption process, where the intra-particle diffusion starts to slow down due to the extremely low solute concentration in solution. As can be seen from Fig. 5, the linear line did not pass through the origin and this deviation from the origin (or near to saturation) might be due to the difference in the mass transfer rate in the initial and final stages of adsorption [11,12].

**4. Conclusion**
The present experiment shows that the treated PHLP can be used as a low cost adsorbent for pesticide removal from aqueous solutions, since 10 mg of PHLP

was able to remove more than 96 % of aldrin and dialdrin, from 10 ml of pesticides solution. The treatment of PHLP improves adsorption capacity because of increase in the surface area, as shown in SEM micrograph The removal efficiency of pesticide mixture decreased in the order Aldrin > Dieldrin. The Langmuir, Freundlich, Temkin and D-R isotherms are found to be applicable in the present pesticide mixture adsorption, which may be attributed to the formation of monolayer on the surface of the adsorbent. Aldrin and dialdrin fitted comparatively well in Freundlich isotherm. Different kinetic models were used to fit experimental data. The experimental result show that Psuedo-first order model best describes the adsorption of aldrin and dialdrin on PHLP in comparison to pseudo-second order model. These results demonstrate that PHLP, which is easily available, could be an effective and low cost adsorbent for the removal of pesticides from the aqueous solutions.
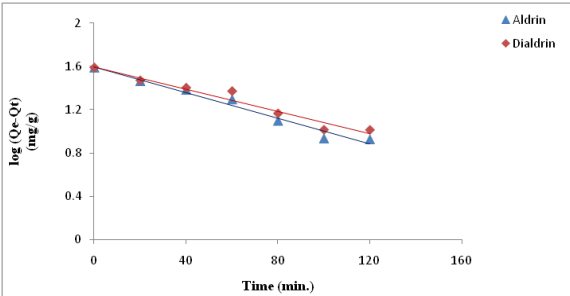


Fig.1 a (Before treatment)          Fig.1 b (After treatment)



Figure 2. Effect of pH on adsorption of different pesticides by PHLP



Figure 3. Freundlich isotherm for different pesticides adsorption by PHLP.

Figure 4. Plots of pseudo first-order kinetics for adsorption of different pesticides on PHLP: pH 2; initial concentration 1mg/L; adsorbent dosage 2.5 mg.
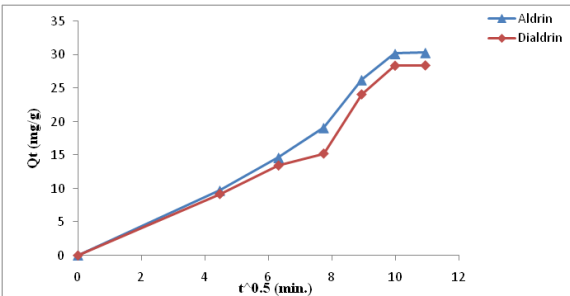
**Table 2: Langmuir, Freundlich, Temkin and Dubnin-Radushkevich isotherm model parameters and correlation coefficient for adsorption of pesticide mixtures onto PHLP**

| Pesticides | Langmuir Isotherm | | | Freundlich Isotherm | | | Temkin Isotherm | | | Dubnin-Radushkevich Isotherm | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $q_m$ (mg/g) | B (L/mg) | $R^2$ | n | $K_f$ (mg/g) | $R^2$ | $A_T$ (L/mg) | B | $R^2$ | $q_s$ (mg/g) | $K_{ad}$ (mol$^2$/kJ$^2$) | E (KJ/mol) | $R^2$ |
| Aldrin | 145.67 | 0.141868 | 0.8656 | 1.6704 | 18.0594 | 0.9948 | 10.0552 | 17.5041 | 0.8106 | 64.9687 | 5.9795×10$^{-8}$ | 2891.692 | 0.8626 |
| Dialdrin | 194.47 | 0.074528 | 0.9909 | 1.2501 | 12.1156 | 0.9941 | 1.1908 | 23.9492 | 0.8829 | 68.8252 | 1.5814×10$^{-7}$ | 1778.090 | 0.8903 |

**Table 3: Pseudo first order and Pseudo second order rate constants for adsorption of pesticide mixtures onto PHLP**

| Pesticides | $q_e$ expt(mg/g) | Pseudo first order | | | Pseudo second order | | |
|---|---|---|---|---|---|---|---|
| | | $q_e$(mg/g) | $k_1$ | $R^2$ | $q_e$(mg/g) | $k_2$ | $R^2$ |
| Aldrin | 38.703 | 39.544 | 0.031 | 0.97 | 38.127 | 0.0006 | 0.77 |
| Dialdrin | 38.709 | 39.519 | 0.027 | 0.95 | 35.671 | 0.0006 | 0.71 |



Figure 5. Weber and Moris Plots for adsorption of different pesticides on PHLP: pH 2; initial concentration 1mg/L; adsorbent dosage 2.5 mg.

| Pesticides | Pesticide concentration (mg/l) | | | |
|---|---|---|---|---|
| | 1 | 10 | 30 | 50 |
| Aldrin | 3.731708 | 28.75065 | 79.75964 | 114.2568 |
| Dialdrin | | 29.67742 | 80.64596 | 118.4454 |

**Table 1: The amount of pesticide adsorbed per gram of PHLP (Qe mg/g).**

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