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Kinetics and Equilibrium Isotherm Studies of Endrin and o, p DDT Adsorption on Low Cost Adsorbent, *Parthenium hysterophorous* Activated with Nitric Acid and Methanol

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Abstract: ***The efficiency of activated parthenium hysterophorous as an adsorbent for removing Pesticide mixture from water has been studied. Batch mode adsorption experiments have been conducted by varying pH, concentration, adsorbent dose and contact time. Pesticide removal was pH-dependent and found to be maximum 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 Langmuir isotherm model best describes for the adsorption of endrin and o,p DDT. Pseudo-first order, pseudo-second order and Weber-Morris equations were applied to fit the kinetic results. The kinetics data for the adsorption process obeyed second-order rate equation. The adsorbent was also characterized using FTIR spectroscopy to detect vibration frequency changes and BET to measure surface area, pore volume and pore radius of the adsorbent.***

Keywords: adsorption; organic pollutants; pesticides; kinetics; isotherm

1. Introduction

Organochlorine pesticides (OC) are considered one of the most dangerous products used in crop protection. A large number of these chemicals, such as DDT, technical hexachlorocyclohexane (HCH) and drin pesticides (aldrin, dieldrin and endrin), are used to control diseases like malaria, fi-lariasis, dengue, cholera, and Japanese encephalitis. These are also applied in industries to control vegetation, in forests and factory sites, for fumigation of buildings, ships etc. Organochlorine pesticides are known to be the most persistent organic micropollutants present in the environment and tend to accumulate in organisms. This characteristic, in combination with their toxicity and their high chemical and biological stability, makes organochlorine pesticides prone to bioaccumulation along the food chain, involving a wide range of trophic levels [1]. As a consequence, most of them have been listed as persistent organic pollutants (POP) by the United Nations Environment Program [2].

For the last few decades, different methods have been developed and used for water treatment [3]. Adsorption is considered as one of the suitable water treatment methods due to its ease of operation and the availability of a wide range of adsorbents. Besides, adsorption can also be applied for the removal of soluble and insoluble organic, inorganic, and biological pollutants.

In the present study attempts have been made to use Parthenium hysterophorous leaves powder (PHLP), a weed as a useful, effective and efficient low cost adsorbent. The adsorption of pesticides mixture (i.e Endrin and o,p DDT) has been studied in detail on the prepared adsorbent to assess its efficiency for the removal of pesticides from the aqueous solutions.

2. Experimental Methodology

Preparation and chemical treatment of Parthenium hysterophorous leaves Powder (PHLP) were described in previous paper [4].

FTIR spectroscopy was used to detect vibration frequency changes in the PHLP. The spectrum was collected by FTIR (model Bruker Alpha) in the range 400-4,000 cm^{-1} using ATR (Attenuated transmitted reflection) method. The surface area of the adsorbent was measured by BET (Brunauer–Emmett–Teller nitrogen adsorption technique). In a typical batch study, the same procedure is applied as described in previous paper [4]

3. Result and Discussion

3.1 Characterisation of Adsorbent

As the strength of the adsorption is proportional to the concentration, FTIR was used for some qualitative analysis. The FTIR spectrum of PHLP given in Fig. 12 (a) shows peaks at 3424.81 cm^{-1} (O–H stretch), 2923.17 & 2853.04 cm^{-1} (C–H stretch), 1731.31 cm^{-1} (C= O stretch), 1632.55 cm−1 (C=C stretch), 1537.49 cm^{-1} (C=C stretch),1453.93 cm−1 (symmetric bending of CH_3), 1382.59 cm−1 (C–O–H bend), 1248.83 cm−1 (C-O stretch), 830.95 cm^{-1} (C-H bend) and 661.39 cm−1 (C–O–H twist). It is clear that the adsorbent displays a number of absorption peaks, reflecting the complex nature of the adsorbent. Comparing Fig. 12(a) and (b), we can conclude that some of these peaks are shifted or disappeared (1658.04 cm^{-1}, 1650.88 cm^{-1}(C=C stretch), (1514.27cm^{-1}, 1548.23 cm^{-1}(C=C stretch); 1416.02cm^{-1}, 1433.85 cm^{-1} (symmetric bending of CH_3),1154.20 cm^{-1},1159.99 cm^{-1},1112.27 cm^{-1},1105.19 cm^{-1}, 1022.68 cm^{-1} (C-O stretch) and new peaks (2361.96 cm−1, 2342.48 cm−1 (N–H stretch); are also detected. These changes observed in the spectrum indicate the possible involvement of the functional groups present on the surface of the PHLP in sorption process.

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 m^2/g , BJH Surface Area was found to be 145.045 m^2/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 (28^0C) 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 the mass transfer driving forces become large[5].

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 the 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[6].

3.4 Effect of Adsorbent dose

The optimization of adsorbent dose was also carried out by varying the amount of adsorbent with fixed concentration of pesticides mixture in the experiment. The adsorbent doses were varied from 1 to 10 mg at fixed pesticides mixture concentration (10 mgl^{-1}). The percentage adsorption increased from 37 to 96 % for endrin and 42 to 98% for dialdrin when adsorption dose was increased, as the numbers of available sites increase with the increase in adsorption dose[7]

3.5 Effect of contact time

In order to determine the 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} solutions of pesticides mixture. 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 isotherms basically reflect 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 [8] 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 Langmuir isotherm presupposes monolayer adsorption onto a surface containing a finite number of adsorption sites via uniform strategies of adsorption with no transmigration of the adsorbate taking place along the plane of the surface. The linear form of the Langmuir isotherm model is described by the following equation [9]:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \left(\frac{1}{q_m}\right)C_e \tag{1}$$

where q_m (mg g^{-1}) is the Langmuir constant relating to adsorption capacity and b (L mg^{-1}) is the rate of adsorption, q_e is the amount of pesticides adsorbed at equilibrium (mg g^{-1}) and C_e is the liquid-phase equilibrium concentration (mg L^{-1}). Plots of C_e/q_e against C_e in Fig.3 shows linearity. Adsorption equilibrium therefore obeyed Langmuir equation. The corresponding calculated Langmuir constants, q_m ,b with correlation coefficient (R^2) are given in Table 2 . The essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor (R_L) [10]. This parameter is defined by:

$$R_L = \frac{1}{1 + bC_O} \tag{2}$$

Where b is the Langmuir constant and Co is the highest initial pesticide concentration (mg L^{-1}). The value of R_L indicates the type of isotherm: unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

In our case the value of R_L was found to be 0.07-0.80 and 0.07-0.79 for the initial concentration range 1-50 mgl^{-1} for endrin and o,p DDT respectively, it again confirms that the Langmuir isotherm adjusted well to the adsorption of pesticides on PHLP under these particular conditions.

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:

$$q_t = \frac{C_o - C_t \times V}{C_o \times W} \tag{3}$$

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 PHLP (g). The kinetic data were then fitted into the pseudo-first-order, pseudo-second-order and intraparticle diffusion models. The pseudo-second-order equation [11] based on the equilibrium adsorption is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 \bullet q_e 2} + \frac{1}{q_e} t \qquad (4)$$

Where k_2 (g mg^{-1} h^{-1}) is the rate constant of second-order adsorption.

For the pseudo-second-order kinetic model, the plots of t/q_t versus t for the pesticide mixture at initial concentration of $1mgl^{-1}$are presented in Fig. 4. The kinetic parameters from Eq. (4) 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, respectively. The correlation coefficient values of pseudo-second order for endrin(R^2=0.98) and o,p DDT(R^2=0.99) are relatively greater than pseudo-first order and the experimental q_e values agree with the experimental values obtained from the linear plots. This indicates that the adsorption process of endrin and o,p DDT onto the PHLP fits the second-order kinetic model.

An intraparticle diffusion model based on the theory proposed by Weber and Morris [12] 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:

$$q_t = K_{id} t^{1/2} + I \qquad (5)$$

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 [13]. The plots also present multilinearity, indicating that two or more steps have taken place [14]. 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 [15, 16].

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 endrin and o,pDDT from 10 ml of pesticides solution. The treatment of PHLP improves adsorption capacity because of increase in the surface area [1] and surface activation shown in FTIR spectra due to stretching of functional group. 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. Endrin and o,p DDT fitted comparatively well in Langmuir isotherm. Different kinetic models were used to fit experimental data. The experimental results show that Psuedo- second order model best describes the adsorption of endrin and o,pDDT on PHLP in comparison to pseudo first 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.

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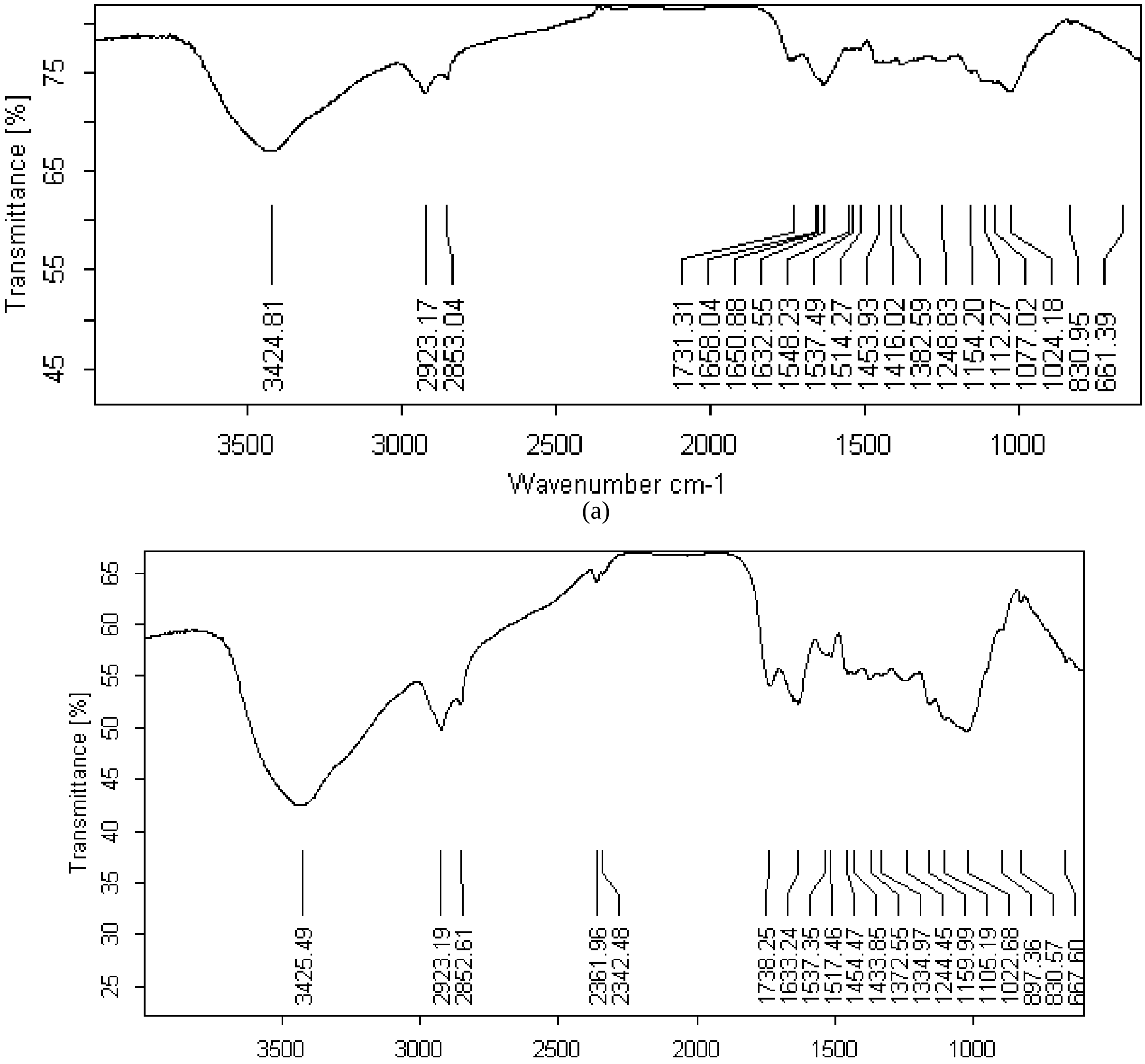

(a)

(b)

Figure 1: FT-IR spectra of (a) non treated PHLP and (b) nitric acid- methanol treated PHLP

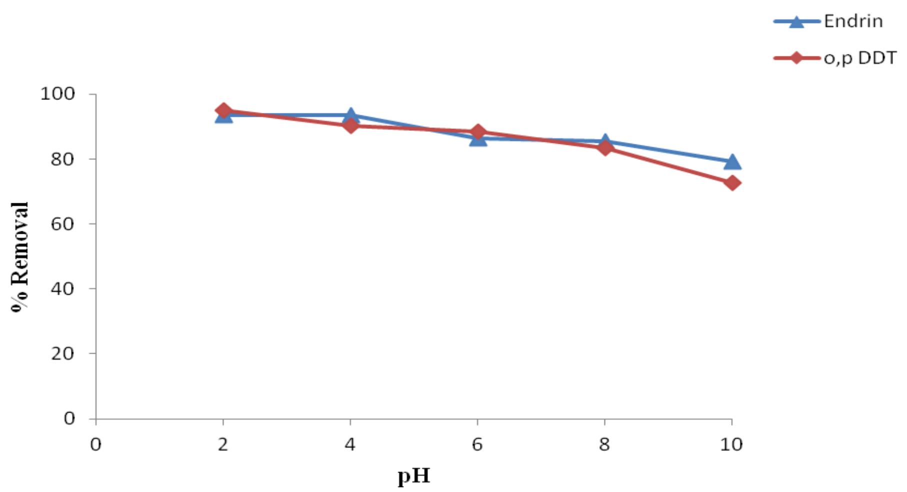

Figure 2. Effect of pH on adsorption of different pesticides by PHLP

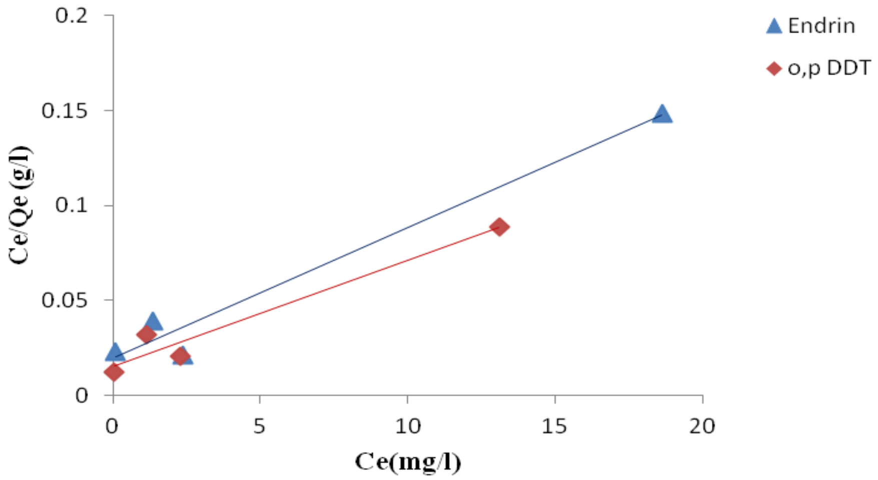

Figure 3. Langmuir isotherm for different pesticides adsorption by PHLP

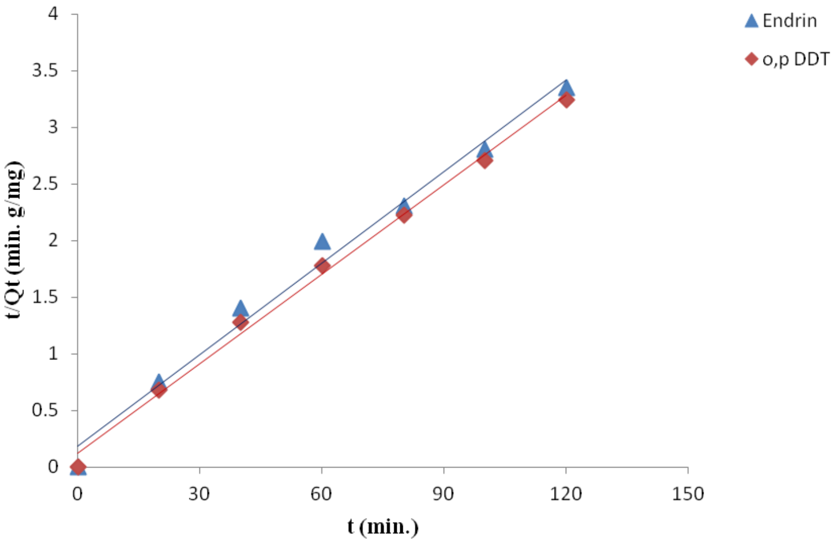

Figure 4. Plots of pseudo-second-order kinetics for adsorption of different pesticides on PHLP: pH 2; initial concentration 1mg/L; adsorbent dosage 2.5 mg.

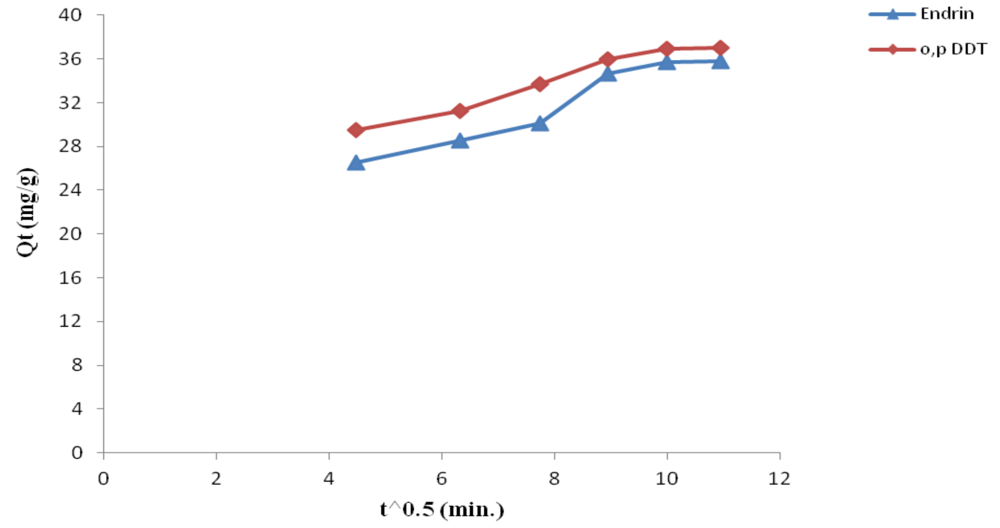

Figure 5. Weber and Moris Plots for adsorption of different pesticides on PHLP: pH 2; initial concentration 1mg/L; adsorbent dosage 2.5 mg.

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

Pesticides	Pesticide concentration (mg/l)			
	1	10	30	50
Endrin	3.808696	34.56311	92.18329	125.4567
o,p DDT	3.66154	35.43974	96.33803	147.5857

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
Endrin	152.07	0.242105	0.9707	1.4897	22.1030	0.8780	1.3154	22.4440	0.9258	78.2952	7.5931×10^{-8}	2566.109	0.9077
o,p DDT	182.85	0.259174	0.9509	1.5231	29.3789	0.9428	13.5376	23.8658	0.8585	84.1416	5.2381×10^{-8}	3089.546	0.8901

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

Pesticides	$q_e$expt	Pseudo first order			Pseudo second order		
		q_e(mg/g)	k_1	R^2	q_e(mg/g)	k_2	R^2
Endrin	37.411	26.356	0.058	0.93	37.167	0.0038	0.98
o,p DDT	38.045	22.520	0.065	0.93	37.992	0.0056	0.99