

diffusion models. The pseudo-second-order equation [11] based on the equilibrium adsorption is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} t \quad (4)$$

Where k_2 ($\text{g mg}^{-1} \text{h}^{-1}$) 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 1mg l^{-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:

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

For the intraparticle diffusion model, the plots of q_t 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 Pseudo- 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.

Acknowledgement

The authors are thankful to University Grant Commission (UGC), New Delhi India for providing Non-NET Fellowship to Firoz Ali Ansari.

References

- [1] Biziuk, M., Przyjazny, A., Czerwinski, J., Wierowski, M., Occurrence and determination of pesticides in natural and treated waters. *J. Chromatogr. A* 754(1996), 103–123
- [2] UNEP, 2001. Final act of the conference of plenipotentiaries on the Stockholm Convention on Persistent Organic Pollutants (POPs), United Nations Environment Program, Geneva, Switzerland. <<http://www.pops.int/>>.
- [3] Ali, I., New Generation Adsorbents for Water Treatment, *Chem. Rev.*, 112 (2012), 5073–5091
- [4] Firoz Ali Ansari, Masood Alam, Parthenium Hysterophorous Weed Novel Adsorbent for the Removal of Pesticides Mixture From Aqueous Solution, *Indian journal of applied research*.4 (2014) 439–442.
- [5] M. Salman, K.A. Al-saad, adsorption of 2, 4-dichlorophenoxyacetic acid onto date seeds activated carbon: equilibrium, kinetic and thermodynamic studies, *Int. J. Chem. Sci.* 10 (2012) 677–690.
- [6] H. El Bakouri, J. Morillo, J. Usero, A. Ouassini, Potential use of organic waste substances as an ecological technique to reduce pesticide ground water contamination, *J. Hydrol.* 353 (2008) 335–342.
- [7] M. Ajmal, R.A.K. Rao, R. Ahmad, M.A. Khan, Adsorption studies on Parthenium hysterophorous weed: removal and recovery of Cd(II) from wastewater., *J. Hazard. Mater.* 135 (2006) 242–8.
- [8] M. El-Guendi, Homogeneous surface diffusion model of basic dyestuffs onto natural clay in batch adsorbents, *Adsorp. Sci. Technol.* 8 (1991) 217–225.
- [9] W. Weber, F. DiGiano, *Process Dynamics in Environmental Systems*, 1st ed., John Wiley and Sons, Inc., New York, 1996
- [10] G. McKay, M. El Guendi, M. Nassar, Equilibrium studies during the removal of dyestuffs from aqueous solutions using bagasse pith, *Water Res.* 21 (1987) 1513–1520.
- [11] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, *Chem. Eng. J.* 70 (1998) 115–124.

- [12] Y. Onal, Kinetics of adsorption of dyes from aqueous solution using activated carbon prepared from waste apricot, *J. Hazard. Mater. B* 137 (2006) 1719–1728.
- [13] M. Sathishkumar, A.R. Binupriya, D. Kavitha, R. Selvakumar, R. Jayabalan, J.G. Choi, S.E. Yun, Adsorption potential of maize cob carbon for 2,4-dichlorophenol removal from aqueous solutions: equilibrium, kinetics and thermodynamics modeling, *Chem. Eng. J.* 147 (2009) 265–271.
- [14] F.C. Wu, R.L. Tseng, R.S. Juang, Comparisons of porous and adsorption properties of carbons activated by steam and KOH, *J. Colloid. Interf. Sci.* 283 (2005) 49–56.
- [15] I.A.W. Tan, A.L. Ahmad, B.H. Hameed, Adsorption of basic dye on high-surface-area activated carbon prepared from coconut husk: equilibrium, kinetic and thermodynamic studies, *J. Hazard. Mater.* 154 (2008) 337–346.
- [16] K. Mohanty, D. Das, M.N. Biswas, Adsorption of phenol from aqueous solutions using activated carbons prepared from *Tectona grandis* sawdust by ZnCl₂ activation, *Chem. Eng. J.* 115 (2005) 121–131.

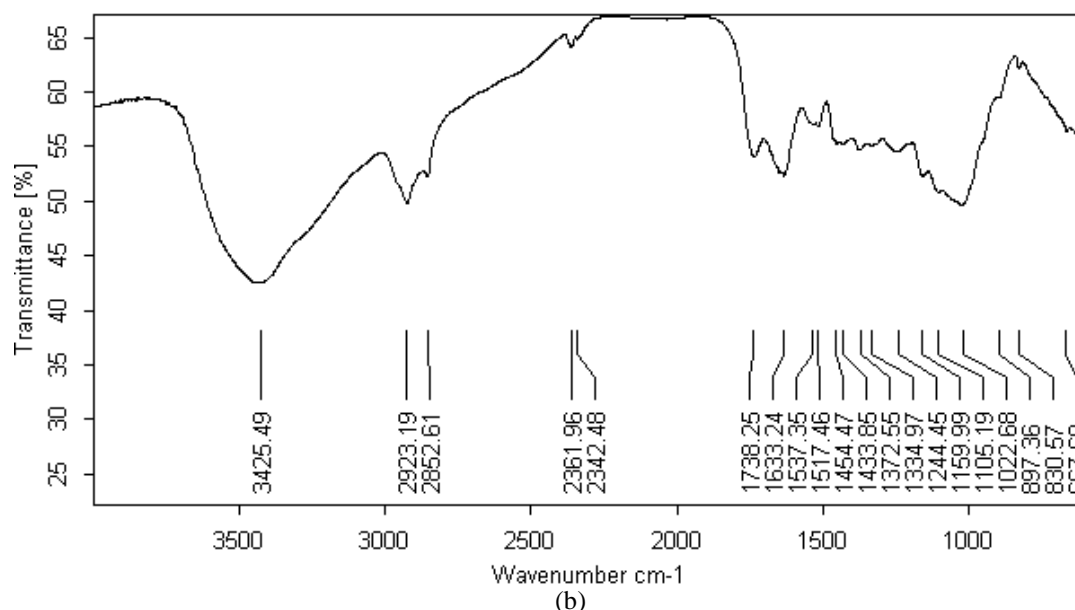
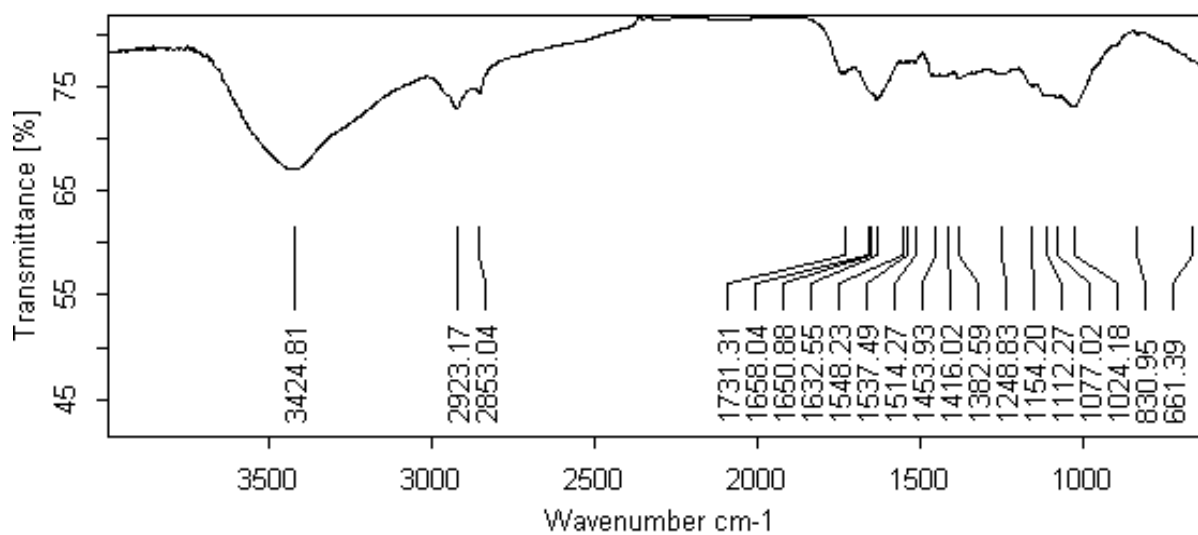


Figure 1: FT-IR spectra of (a) non treated PHLP and (b) nitric acid- methanol treated PHLP

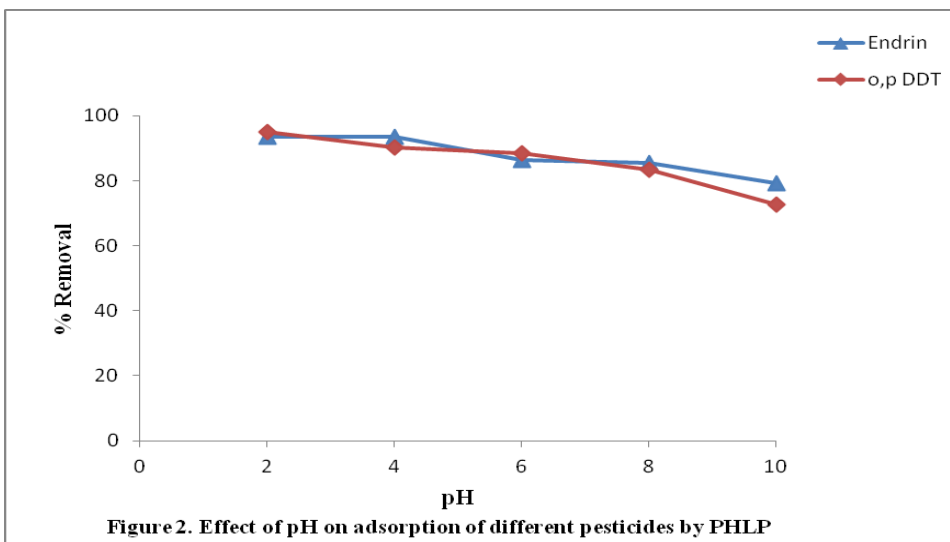


Figure 2. Effect of pH on adsorption of different pesticides by PHLP

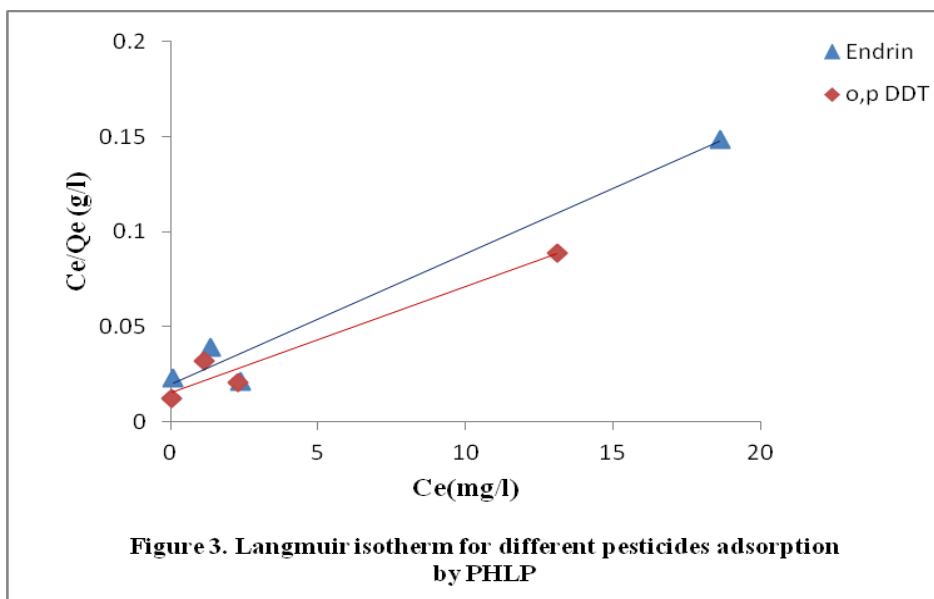


Figure 3. Langmuir isotherm for different pesticides adsorption by PHLP

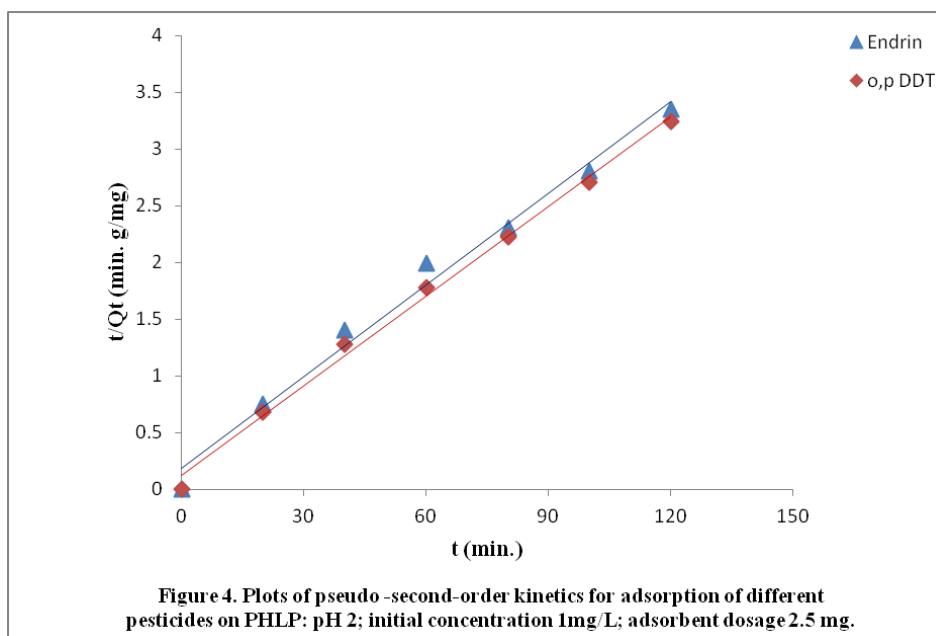


Figure 4. Plots of pseudo-second-order kinetics for adsorption of different pesticides on PHLP: pH 2; initial concentration 1mg/L; adsorbent dosage 2.5 mg.

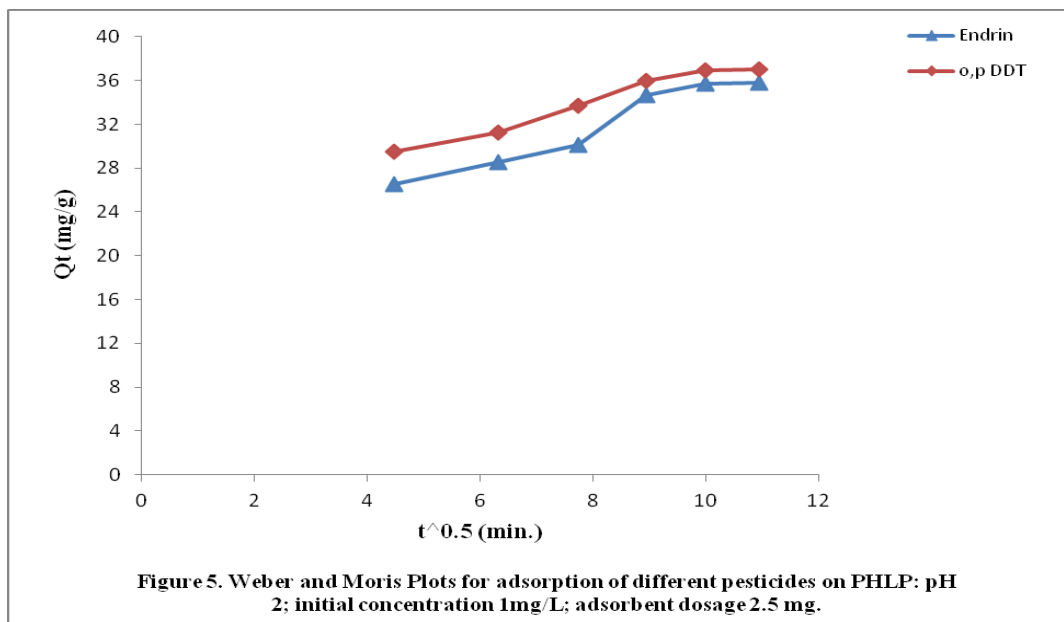


Figure 5. Weber and Moris Plots for adsorption of different pesticides on PHLP: pH 2; initial concentration 1mg/L; adsorbent dosage 2.5 mg.

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	1.35376	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