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Evaluation of Acid-Treated Palm Shell Powder for Its Effectiveness in the Adsorption of Organophosphorus Pesticides: Isotherm, Kinetics, and Thermodynamics

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ABSTRACT: We have investigated the adsorption behavior of two organophosphorus pesticides Monocrotophos and Chloropyrifos onto Acid-Treated Palm Shell Powder (APSP) prepared from palm shells (agro-waste). The effects of adsorbent dose, contact time, and concentration on adsorption were studied. The Freundlich and Langmuir isotherms were applied to the experimental equilibrium data. Monolayer adsorption capacities Q_m for spectrophotometric ((52.63 and 51.098) $\text{mg}\cdot\text{g}^{-1}$ for Chloropyrifos and Monocrotophos, respectively) and for COD measurements ((14.25 and 11.57) $\text{mg}\cdot\text{g}^{-1}$ for Chloropyrifos and Monocrotophos, respectively), have been evaluated. The calculated thermodynamic parameters ΔH, ΔS, and ΔG prove that Monocrotophos adsorption on APSP was feasible, spontaneous, and exothermic under the examined conditions, while Chloropyrifos did not show any appreciable change with temperature. The pseudo-first-order, pseudo-second-order, and intraparticle diffusion kinetic models were used to describe the kinetic data and evaluation of rate constants. The results of this study, with good correlation between spectrophotometric and COD measurements, imply the potential use of APSP as a low-cost adsorbent for removal of Chloropyrifos and Monocrotophos from industrial wastewater and runoff water from agricultural soils.

1. INTRODUCTION

Large amounts of pesticides are currently used throughout the world for agricultural and public health purposes. Numerous studies have reported that a great part of ground and surface water contamination is caused by direct losses (e.g., spills during filling operations, leakages of spray equipment, spray leftovers, spills of rinsing water of treatment equipment, etc.).[1,2] The potential environmental damage caused by pesticides provokes interest for remediation and/or prevention.

The organophosphorus and organochlorine pesticides are bioaccumulative and relatively stable, as well as toxic and carcingenic. They are used frequently for agricultural, forestry, and domestic activities.[3] They are leached to groundwater and runoff to surface water. Monocrotophos and Chloropyrifos are two of the widely used pesticides and are often found in surface and groundwater in residual form.[4]

A number of different methods for the removal of pesticides from water have been used which include membrane technology, solid phase extraction, ozone and chemical oxidation, fenton, combined photofenton and biological oxidation,[5] advanced oxidation processes,[6] aerobic degradation,[7] photocatalysis, and adsorption on various substances.[8−19] Adsorption on activated carbon is a well-known method for the removal of pesticides from water samples.[12,20,21] High-energy demands and consequently high costs are disadvantages of activated carbons. Therefore, alternative adsorbents are needed.

The recycling and use of agricultural waste materials and other low-cost adsorbents provide an economically viable solution for the abatement of pollutants from aqueous solutions.[22,23] Nowadays many low-cost adsorbents have been investigated as an alternative to activated carbon, for example, fly ash,[24] carbon cloth,[25] porous polymeric adsorbents,[26] wheat residue black carbon,[27] bleaching earth,[28] lignin,[22] riverbed sand,[29] wood charcoal,[30] waste tire rubber granules,[31] straw, woodchips, peat mix, garden waste compost, cow manure, coconut chips, chestnut shells, watermelon peel, charcoal, etc.[32−39]

Palm fruit is available in large quantity throughout coastal India. Palm shell is an agrowaste after the fruit is eaten. Therefore, the purpose of this work was to evaluate the adsorption potential of acid-treated palm shell powder (APSP) for Monocrotophos, an organophosphorous pesticide, and Chloropyrifos, an organochlorine pesticide. The effect of several physicochemical parameters, such as adsorbent dose, contact time, and pesticide concentration, was investigated. The Langmuir and Freundlich models were used to describe equilibrium isotherms. The equilibrium kinetics and thermodynamic parameters of the adsorption were then studied to understand the adsorption mechanism of the pesticides. It was decided to monitor the adsorption characteristics of APSP for the pesticides both by monitoring the concentration of pesticides and also by measuring the COD contributed due to the pesticides. The pesticides showed better adsorption capacities than those reported in the literature.

2. MATERIALS AND METHODS

2.1. Materials. The adsorbates used in this study were the pesticides Monocrotophos and Chloropyrifos obtained from Baroda Agrochemicals Limited, Vadodara. Their chemical structure and main physical properties are shown in Table 1. A stock

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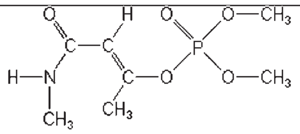
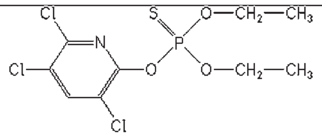
Table 1. Characterization of Pesticides

Pesticide	Monocrotophos	Chloropyrifos
Molecular Formula	$C_7H_{14}NO_5P$	$C_9H_{11}C_{13}NO_3PS$
Structural Formula		
IUPAC name	dimethyl (E)-1-methyl-2-(methylcarbamoyl)vinyl phosphate	O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate
pK_a	Non ionized	4.55
Log K_{ow}	-0.22	4.7
Molecular weight	223.2	350.62

solution of Chloropyrifos was prepared in acetonitrile since it provides complete solubilization, and subsequent dilutions to the required concentrations were made in double-distilled water. Stock solutions of Monocrotophos were prepared by dissolving accurately weighed amounts of Monocrotophos in double-distilled water and subsequently diluting to the required concentration.

2.2. Preparation of Adsorbent. Palm shells obtained from the coastal areas of Andhra Pradesh were washed, sundried for 24 h, and ground using a jaw crusher. They were then dried at 110 °C, and the cleaned powder was mixed with concd H_2SO_4 (sp. gr. 164) in a 1:1.5 weight ratio and allowed to stand in an oven maintained at (140 to 160) °C for 24 h. The resulting char was thoroughly washed with water followed by a 2 % solution of $NaHCO_3$ until effervescence ceased and then was left soaking in a 2 % solution of $NaHCO_3$ overnight. The acid-treated palm shell powder (APSP) was then separated, washed with water until free of bicarbonate, and dried at 105 °C. The adsorbents used in the study were characterized and communicated elsewhere.[40]

Batch Adsorption Experiments. The batch experiments were carried out at ambient temperature (~30 °C) in a thermostatted shaker at an agitation speed of ~150 rpm. A known mass of APSP was added to stoppered conical flasks filled with 25 mL of pesticide solution that were shaken for a fixed time interval. A blank, without APSP, was maintained to observe any adsorption of pesticides on the glass surface or degradation during the equilibration. The experiments were conducted at real pH values of pesticide solutions. In the studied concentration ranges, pH values of Monocrotophos and Chloropyrifos were 2.74 to 3.00 and 5.30 to 5.58, respectively. The initial and equilibrium pesticide concentrations were determined. After filtering the supernatants through Whatman filter paper no. 41, the COD and absorbance of the filtrate were measured.

For spectroscopic measurements, a calibration graph was prepared by taking known pesticide concentrations in 25 mL of aqueous solution and extracting with toluene (10 mL) for 1 min. After shaking, the samples were allowed to stand for 1 min, and 1 g of anhydrous sodium sulfate was added to each tube to remove any trace of moisture from the toluene. Pesticide concentrations in the toluene layer were analyzed spectrophotometrically after determining the wavelength that provided maximum absorbance. The wavelengths of maximum absorption for Monocrotophos and Chloropyrifos were (328.5 and 291.5) nm, respectively. A calibration graph for each pesticide was prepared, and the concentration of each pesticide residue after adsorption on APSP in further experiments was determined by referring to the calibration graph of the respective pesticide. The percentage removal of the pesticide and the amount adsorbed ($mg \cdot g^{-1}$) were calculated by the following relationship

$$q_e = (C_i - C_e)/m \qquad (1)$$

where C_i is the initial concentration of pesticide in $mg \cdot L^{-1}$; C_e is the equilibrium concentration of pesticide in $mg \cdot L^{-1}$; m is the mass of adsorbent in $g \cdot L^{-1}$; and q_e is the amount of pesticide adsorbed per gram of adsorbent.

COD measurements were done by closed reflux and titration according to the procedure outlined in standard methods,[41] and a calibration graph was prepared. The COD of the samples was estimated before and after adsorption by APSP, and the concentration of each pesticide was determined by referring to its respective calibration graph.

2.3. Kinetic Study. Three kinetic models were used to fit the experimental data. The first was the pseudo-first-order kinetic model; the integral form of this model is expressed by the following equation given by Lagergren[42]

$$\log(q_e - q_t) = \log q_e - K_1 t/2.303 \qquad (2)$$

where q_e and q_t are the quantities of pesticide adsorbed at equilibrium and at time t ($mg \cdot g^{-1}$), respectively; t is the time (min); and K_1 is the equilibrium rate constant of first-order adsorption (min^{-1}), which can be determined by plotting $\log(q_e - q_t)$ versus t.

The integral form of the pseudo-second-order kinetic model is expressed by the following equation

$$t/q_t = 1/(K_2 q_e^{\,2}) + t/q_e \qquad (3)$$

where K_2 is the pseudo-second-order kinetic rate constant $(\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1})$. The value of K_2 can be determined by plotting t/q_t versus t to obtain a straight line of slope $1/q_e$. The third model was the intraparticle diffusion model. This model, based on the theory proposed by Weber and Morris,[43] was tested to identify the intraparticle diffusion mechanism. The Morris–Weber equation is

$$q_t = K_i t^{0.5} \tag{4}$$

where K_i is the intraparticle diffusion rate constant $(\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{1/2})$. In each experiment, a pesticide solution of known concentration in a total volume of 25 mL was continuously stirred with 0.5 g of APSP at ambient temperature. Samples were collected at fixed time intervals, and the concentrations of the unadsorbed pesticide in the solution were determined after filtration as described above.

2.4. Adsorption Isotherms. The Langmuir isotherm and the Freundlich isotherm were tested for their ability to describe the experimental results. The Langmuir adsorption model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction between the adsorbed molecules.

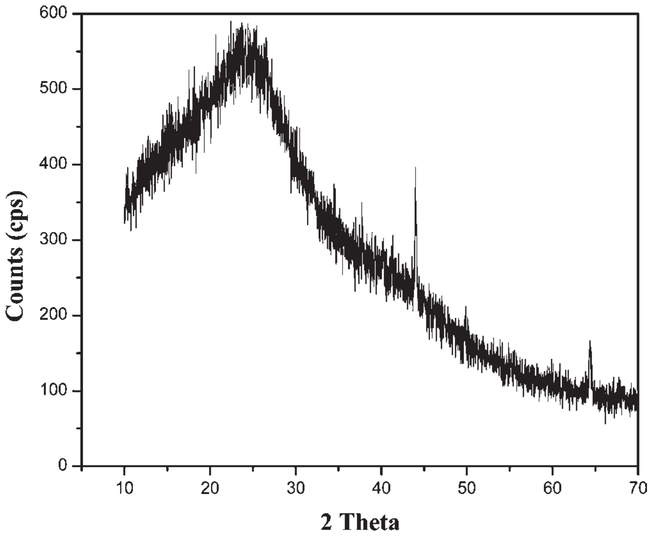


Figure 1. X-ray diffraction pattern of APSP.

The linear expression of the Langmuir model[44] is given by the following equation

$$\frac{C_e}{q_e} = \frac{1}{q_m}C_e + \frac{1}{K_a q} \tag{5}$$

where q_e $(\text{mg}\cdot\text{g}^{-1})$ and C_e $(\text{mg}\cdot\text{L}^{-1})$ are the amount of adsorbed pesticide per unit mass of adsorbent and pesticide concentration at equilibrium, respectively. q_m is the maximum amount of the per unit mass of adsorbent to form a complete monolayer on the surface bound at high C_e.

The Freundlich adsorption model determines the adsorption affinity between adsorbate and the adsorbent surface. The linear expression which provides the coefficients for the Freundlich model[45] is given by the following equation

$$\log q_e = \log k_f + \frac{1}{n}\log C \tag{6}$$

where q_e $(\text{mg}\cdot\text{g}^{-1})$ and C_e $(\text{mg}\cdot\text{L}^{-1})$ are the amount of adsorbed pesticide per unit mass of adsorbent and pesticide concentration at equilibrium, respectively. K_f and n are the Freundlich coefficients.

3. RESULTS AND DISCUSSION

3.1. Characterization of Adsorbent Material. The BET surface areas of APSP and PSP were measured by nitrogen adsorption isotherms using a BET surface area analyzer (Micrometrics ASAP 2020 V3.03 H). The BET surface areas for APSP and PSP were found to be 0.2979 $\text{m}^2\cdot\text{g}^{-1}$ and 0.6735 $\text{m}^2\cdot\text{g}^{-1}$, respectively. PSP and APSP also had a low pore volume of (0.00401 and 0.00315) $\text{cm}^3\cdot\text{g}^{-1}$, but their iodine numbers were found to be 146 and 238, respectively, which is indicative of good adsorption capacity. The pH values of PSP and APSP were found to be 6.0 and 8.5, respectively. The X-ray diffraction pattern of APSP (Figure 1) shows a peak centered around 21° corresponding to the 002 reflection of disordered packing of micrographites. The peak is broad suggesting an amorphous structure. The peak at 21° corresponds to an interlayer distance of 0.423 nm which suggested a disordered carbonaceous interlayer. The morphology of APSP was studied using scanning electron microscopy (Figure 2). The surface is magnified 1000 times which shows that the adsorbent has an irregular rough and porous surface with identifiable micropores and mesopores. The

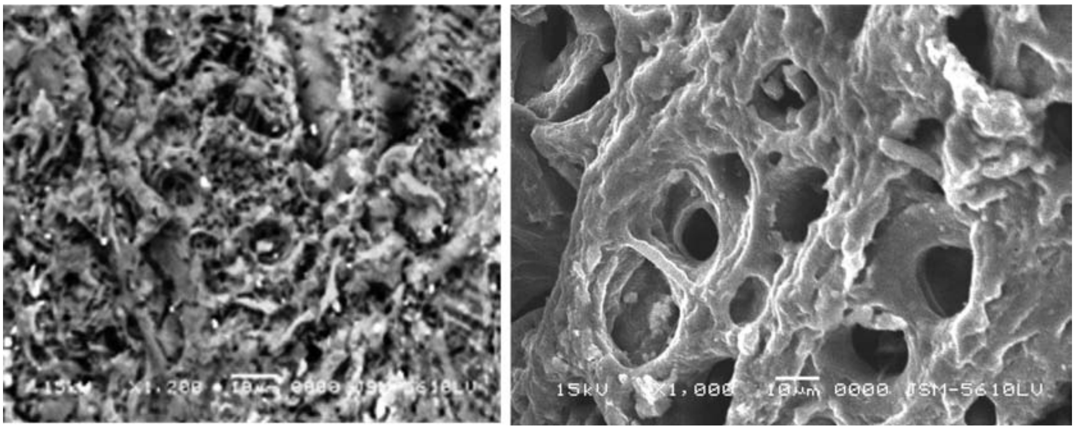


Figure 2. Scanning electron micrograph of PSP and APSP.

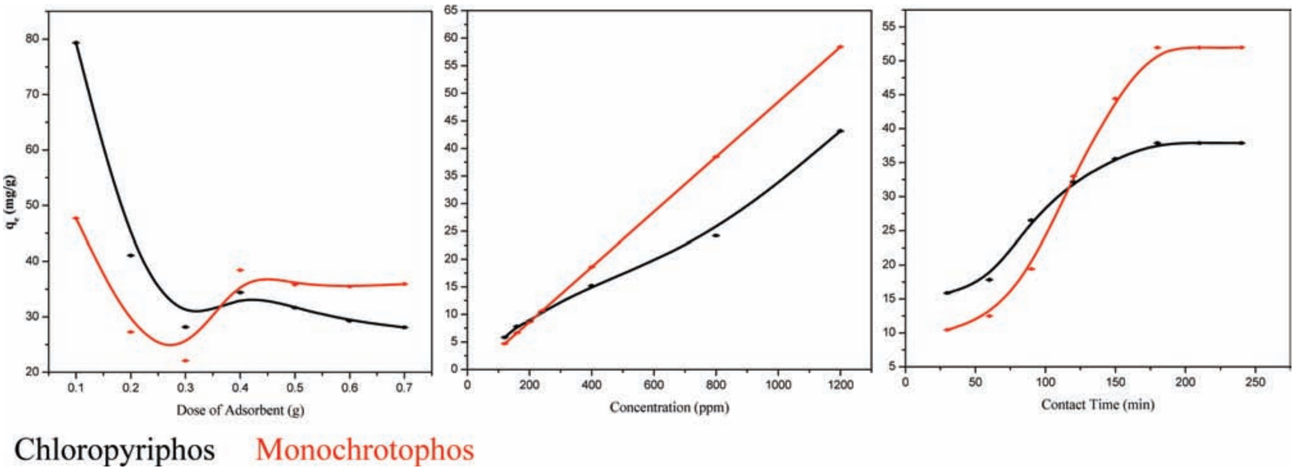


Figure 3. Effect of parameters on the amount of pesticide adsorbed on APSP by spectrophotometric technique.

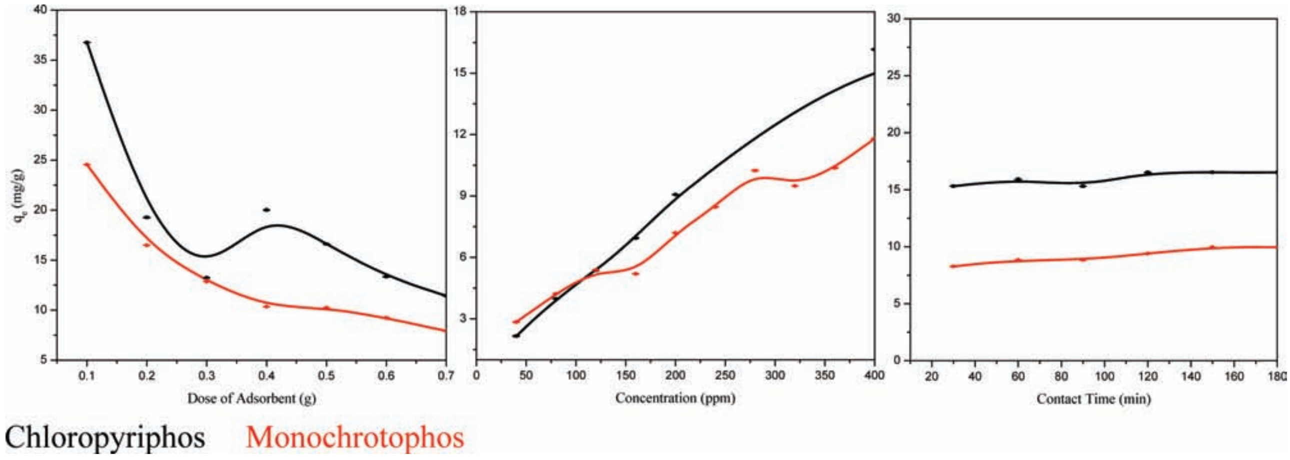


Figure 4. Effect of parameters on amount of pesticide adsorbed on APSP by COD.

morphology of APSP and PSP was studied using scanning electron microscopy (Figure 2). It is evident that the surface morphology of APSP is different from PSP. The micrograph shows that APSP has an irregular rough and porous surface with identifiable micropores and mesopores.

3.2. Effect of Time on Uptake of Pesticide. Figures 3 and 4 show the effect of contact time in the range (20 to 240) min on the percent adsorption of Monocrotophos and Chloropyrifos onto APSP using both spectrophotometric and COD measurements. Percent adsorption increases with increasing agitation time and is seen as a two-stage process in the case of Chloropyrifos acquiring equilibrium at 180 min. In the case of Monocrotophos also equilibrium was achieved within 180 min. It was decided to equilibrate for 240 min in all further investigations for both Chloropyrifos and Monocrotophos.

Chloropyrifos was transported into the macropores within 120 min of contact with APSP in the first phase. During the second phase (after ∼120 min), a slight decrease in the adsorption rate was noted, most likely because of slow diffusion of the pesticides into the smaller pores and irregularities on the adsorbent surface.[46] A number of adsorption studies have been published which show considerable variation in the time needed to establish equilibrium.[39] When equilibrium conditions are reached, the adsorbate molecules in the solution are in a state of dynamic equilibrium with the molecules adsorbed by the adsorbent. Overall, pseudo adsorption equilibrium was reached within 3 h for the pesticides under study. After pseudo equilibrium, less than a ∼2 % variation of pesticide concentration in the solution was observed even after keeping overnight. The results are consistent with those reported by El Bakouri et al.[47−49] for drin pesticide adsorption on modified organic waste residues and acid-treated agricultural stones for endosulfan and are also in accordance with results reported by Kyriakopoulos et al.[26] and Kumar and Phillip[50] for alachlor, amitrole, trifluralin, and prometryn adsorption on porous polymeric adsorbents and endosulfan adsorption on clay and composted Indian soils, respectively, where equilibrium was established in a period of around 4 h. Experimental data obtained from spectrophotometric and COD measurements for Monocrotophos and Chloropyrifos in the studied concentration range did not correlate well with each other. We are not able to explain this except that the differences could be because COD being a titrimetric technique is less sensitive than the spectrophotometric technique. Similar slight variations in data were also observed by Vergili et al.[56]

3.3. Effect of Absorbent Dosage. Figures 3 and 4 depict the effect of APSP dose on the adsorption of Monocrotophos and Chloropyrifos. Adsorbent dosage is an important parameter because this determines the capacity of an adsorbent for a given initial

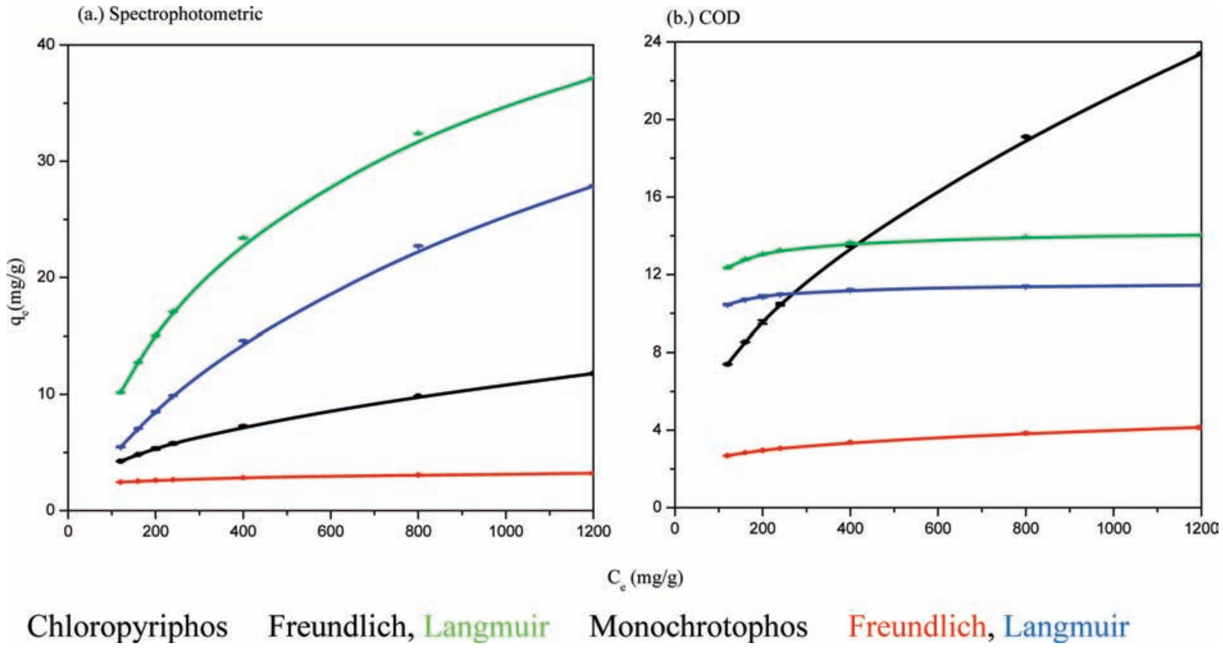


Figure 5. Isotherm. (a) Spectrophotometric and (b) COD.

Table 2. Isotherm Parameters and Thermodynamic Constants

		spectrophotometric		COD	
APSP	parameters	Clp	Mcp	Clp	Mcp
Freundlich	$K_f/(\text{mg}\cdot\text{g}^{-1})(\text{dm}^3\cdot\text{mg}^{-1})^{1/n}$	0.211	2.140	0.406	1.219
	$1/n$	1.021	0.272	1.151	0.434
	r^2	0.999	0.999	0.999	0.999
	SD	0.008	0.009	0.013	0.011
Langmuir	$q_m/(\text{mg}\cdot\text{g}^{-1})$	52.63	51.099	14.247	11.57
	$K_a/(\text{L}\cdot\text{mg}^{-1})$	0.002	0.001	0.0544	0.078
	r^2	0.999	0.999	0.999	0.995
	SD	0.015	0.011	0.007	0.008
Monocrotophos	thermodynamic parameters		303 K	313 K	323 K
	$\Delta G°/\text{kJ}\cdot\text{mol}^{-1}$		−11.44	−12.21	−12.59
	$\Delta H°/\text{kJ}\cdot\text{mol}^{-1}$		−9.771		
	$\Delta S°/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$		0.057		

concentration of adsorbate. Percent adsorption is found to increase with increasing amount of APSP. The increase in percentage removal of the pesticides can be attributed to the increase in adsorption surface area and the availability of free adsorption sites.

3.4. Effect of Initial Concentration. The adsorption of Monocrotophos and Chloropyrifos by APSP was studied at different initial concentrations [(100 to 1200) $\text{mg}\cdot\text{L}^{-1}$]. Figures 3 and 4 show the results for the effect of initial concentration on adsorption of both Monocrotophos and Chloropyrifos onto APSP by spectrophotometric and COD measurements. The equilibrium adsorption of Chloropyrifos and Monocrotophos by APSP (Figures 3 and 4) shows that the adsorption capacity of APSP increases with an increase in equilibrium concentration, while the percentage uptake was found to decrease (figure not shown) suggesting a limiting number of adsorption sites available for adsorption at higher concentration of adsorbate molecules which may be attributed to the increase in the concentration gradient and thus indicating the saturation of adsorption sites. At low concentrations, the ratio of surface active sites of adsorbent are more than the total adsorbate components and hence may interact with the adsorbent and be removed from the solution.[51]

3.5. Adsorption Isotherms. The Langmuir and Freundlich isotherms have been used to model the adsorption processes. In Figure 5 the plot of amount adsorbed (q_e) against the equilibrium concentration (C_e) shows that adsorption obeys the Langmuir model and Freundlich model for Monocrotophos and Chloropyrifos both by COD and spectrophotometric measurements. The parameters of the Langmuir and Freundlich adsorption isotherms, evaluated from the linear plots (figures not shown), are presented in Table 2 along with the coefficients of determination.

The slopes of the straight lines of the Freundlich isotherms give the values of $1/n$ (adsorption intensity), which is < 1

Table 3. Comparison of Adsorption Capacities of Agro-Based Adsorbents

adsorbent	pesticide	adsorption capacity	ref
water melon peel	Methyl parathion	24.3 μmol·g^{-1}	37
chestnut shells	Methyl parathion	22.5 μmol·g^{-1}	36
chestnut shells	Carbofuran	10.8 μmol·g^{-1}	36
wood charcoal	Atrazine	0.8 mg·g^{-1}	39
rubber granules	Atrazine	0.5 mg·g^{-1}	39
coal fly ash	Atrazine	3.3 mg·g^{-1}	39
coal fly ash	Metribuzin	0.6 mg·g^{-1}	39
coal fly ash	Metolachlor	1.0 mg·g^{-1}	39
activated carbon from date stones	2,4 D	238.1 mg·g^{-1}	57
acid-treated date stones	Aldrin	15.7 mg·g^{-1}	46
acid-treated date stones	Dieldrin	14.1 mg·g^{-1}	46
acid-treated date stones	Endrin	11.7 mg·g^{-1}	46
rice bran	Triazophos	0.01 mmol·g^{-1}	68
rice husk	Triazophos	0.03 mmol·g^{-1}	68
chick pea husk	Triazophos	0.01 mmol·g^{-1}	69
chick pea husk	Methyl parathion	0.03 mmol·g^{-1}	69
bamboo canes	Endosulfan sulfate	12.9 mg·g^{-1}	66
date stones	Endosulfan sulfate	13.5 mg·g^{-1}	66
olive stones	Endosulfan sulfate	11.1 mg·g^{-1}	66
peanut shells	Endosulfan sulfate	9.6 mg·g^{-1}	66
avocado stones	Endosulfan sulfate	8.7 mg·g^{-1}	66
wood sawdust	Endosulfan sulfate	6.7 mg·g^{-1}	66
straw	Endosulfan sulfate	5.6 mg·g^{-1}	66
sal wood charcoal	Endosulfan	1.0 μg·g^{-1}	67
APSP	Monocrotophos	51.1 mg·g^{-1}	present study
APSP	Chloropyriphos	52.6 mg·g^{-1}	present study

indicating the better removal efficiency of Monocrotophos at low concentrations. The slope value of < 1 indicated L-type isotherms, which are characterized by the decrease in the adsorption at higher aqueous concentration of compounds, and thus adsorption of Monocrotophos by APSP was concentration dependent.[52] These types of adsorption isotherms are observed when the molecules are adsorbed in a flat position, not suffering a strong competition from the water molecule, which explain the high affinity to the adsorbent for solutes at low concentration. However, as the concentration increases adsorption sites become limiting, leading to a decrease in adsorption. Earlier researchers[53−55] have reported L-type adsorption isotherms for pesticide adsorption in fly ash−soil mixtures and fly ash. The slope value is ~1 in the case of Chloropyrifos, suggesting an intensive adsorption process compared to Monocrotophos.

The values of q_m (mg·g^{-1}) are calculated from the slopes of the linear plots of the Langmuir isotherm. The results are shown in Table 2. The adsorption capacity of APSP used in present studies was 51.09 mg·g^{-1} and 52.63 mg·g^{-1} for batch and 11.57 mg·g^{-1} and 14.24 mg·g^{-1} for COD by the Langmuir isotherm and for Monocrotophos and Chloropyrifos, respectively. The q_m values for spectrophotometric and COD measurements are different which we are not able to explain. Similar observations have been reported by Vergili and Barlas in their studies on the removal of 2,4-D, MCPA, and Metalaxyl from water using Lewatit VP OC 1163 as an adsorbent which was monitored spectrophotometrically and by COD measurements.[56]

Comparison of q_m values for Monocrotophos and Chloropyrifos indicated that adsorption capacity of APSP for Chloropyrifos is higher than Monocrotophos. The higher adsorption of Chloropyrifos on APSP can be explained by its aqueous solubility as adsorption of organic compounds is generally inversely proportional to their aqueous solubilities.[57] Thus, Chloropyrifos which has a low aqueous solubility (2 mg·L^{-1}) was adsorbed more as compared to Monocrotophos which is completely soluble. Table 3 shows the comparison of maximum monolayer adsorption capacity of some pesticides on various adsorbents reported in the literature with acid-treated PSP used in this work. The adsorbent used in this work has adsorption capacity comparable to those cited in the literature.

3.6. Kinetics. The first-order kinetic model depends mainly on adsorbate concentration and gives a good description of the adsorption of contaminants at very low concentrations, while the second-order kinetic model is derived from adsorption processes where the rate-controlling step is an exchange reaction.[58] The correlation coefficients are closer to unity for the pseudo-second-order model by both COD and spectrophotometric measurements suggesting that both Monocrotophos and Chloropyrifos adsorption onto APSP is best described by this model. Hence this rate model was applied to understand the controlling mechanism of the adsorption process. Similar phenomena have been observed for the adsorption of phenol from aqueous solutions by activated carbon prepared from biomass material, by endosulfan adsorption using acid-treated agricultural stones,[59,60] and by Kuo et al.[61] for the adsorption of direct dyes by carbon nanotubes. The adsorption capacity q_e and the rate constant K_2 determined from the slope and intercept of the plot, respectively, are shown in Table 4.

To test the validity of the kinetic expression for intraparticular diffusion which is often the rate-determining step, proposed by Weber and Morris,[62] variations in q_t were plotted vs the square root of time. The plots do not pass through the origin suggesting that intraparticle diffusion is not the only mechanism operating. The plots (figure not shown) display more than one linear region where an initial portion is attributed to the diffusion of adsorbate through the solution to the external surface of the adsorbent or the boundary layer diffusion of solute molecules, with the second portion attributed to the gradual adsorption stage, where intraparticle diffusion is rate limiting. The third portion is attributed to the final equilibrium stage where intraparticles start to slow down due to extremely low adsorbate concentration in solution.[63−66] The slopes of the linear part corresponding to stage 2 and their coefficients of determination are given in Table 4. Figure 6 shows kinetic plots obtained for Monocrotophos and Chloropyrifos by both spectrophotometric and COD measurements. The adsorption coefficient or distribution coefficient K_d was calculated for each pesticide using the equation $K_d = C_{s,eq}/C_{l,eq}$. Comparing average K_d values calculated for each pesticide (Table 4) with the corresponding pseudo-second-order kinetic rate constant values (k_2) revealed that Chloropyrifos with higher kinetic rate constant values had higher K_d values and adsorbed faster compared to Monocrotophos. The same trend was observed by De Wilde et al.,[38] which suggests that strongly adsorbing pesticides (high K_d values) exhibit a fast kinetic adsorbing process (high kinetic rate constant values). K_d values

Table 4. Kinetic Parameters

		spectrophotometric		COD	
APSP	parameters	Clp	Mcp	Clp	Mcp
experimental	$q_e/(\mathrm{mg \cdot g^{-1}})$	43.157	51.936	16.524	9.959
pseudo 1st order	$q_e/(\mathrm{mg \cdot g^{-1}})$	7.078	12.109	202.755	1.456
	$K/(\mathrm{min^{-1}})$	0.024	0.024	0.186	0.012
	r^2	0.995	0.988	0.965	0.999
	SD	0.005	0.011	0.014	0.009
distribution coefficient	K_d	44.962	92.533	-	-
pseudo 2nd order	$q_e/(\mathrm{mg \cdot g^{-1}})$	47.393	60.607	16.94	10.537
	$K/(\mathrm{g \cdot mg^{-1} \cdot min^{-1}})$	0.0002	$9.86 \cdot 10^{-5}$	0.013	0.008
	r^2	0.995	0.998	0.999	0.998
	SD	0.014	0.019	0.017	0.015
intraparticle	$K_i/(\mathrm{mg \cdot g^{-1} \cdot min^{0.5}})$	3.53	8.365	0.219	0.406
	r^2	0.985	0.997	0.995	0.999
	SD	0.021	0.019	0.018	0.013

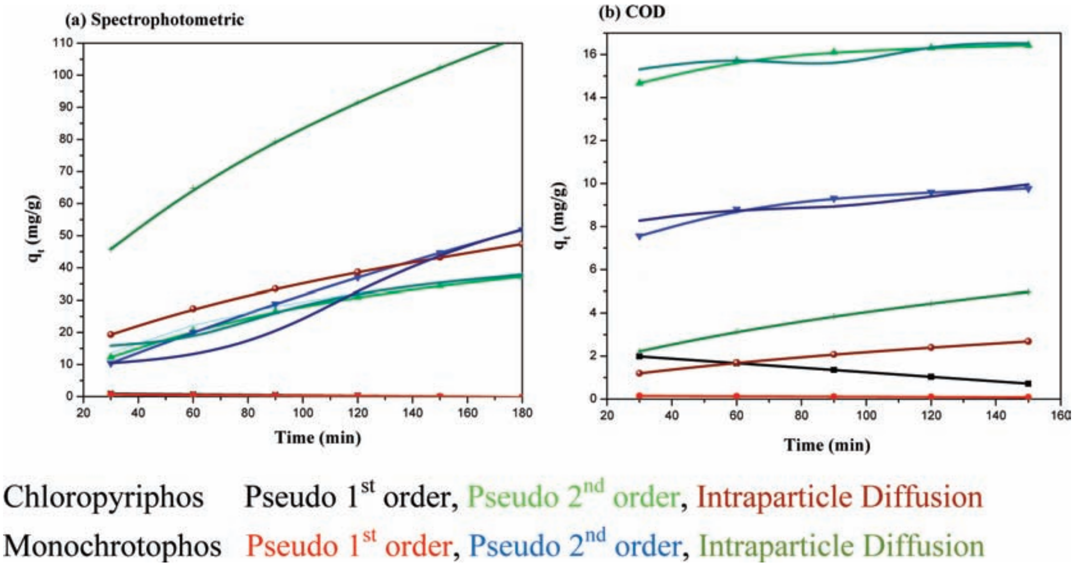


Figure 6. Kinetics. (a) Spectrophotometric and (b) COD.

indicate that the highest adsorption is for Chloropyrifos, which has a higher hydrophobic character (log $K_{ow} = 4.7$).

3.7. Adsorption Thermodynamics. The studies of temperature influence on the adsorption of Chloropyrifos and Monocrotophos revealed that Chloropyrifos adsorption did not show any appreciable change with temperature, while adsorption capacity of APSP for Monocrotophos decreased with increasing temperature (figure not shown). The thermodynamic parameters of the adsorption process could be determined from the experimental data obtained at various temperatures using the equations

$$\Delta G^\circ = -RT \ln K_d \tag{7}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{8}$$

where ΔG° is Gibbs energy; ΔH° is enthalpy of the reaction; ΔS° is entropy of the reaction; R is gas constant; T is temperature in K; and K_d is the distribution coefficient. The negative values of ΔH° indicate the exothermic nature of Monocrotophos adsorption on APSP and reveal that the adsorption is physical, involving weak forces of attraction. Similar observations have been reported by Memon et al.[36] for the adsorption of methyl parathion onto chestnut shells and El Bakouri et al. for drin pesticide on acid-treated agricultural stones. The negative ΔG° values suggest a spontaneous pesticide adsorption process for Monocrotophos.

4. CONCLUSION

APSP is a good adsorbent for the removal of Monocrotophos and Chloropyrifos from water. The process reaches equilibrium within 180 min and follows both the Freundlich and Langmuir isotherm model. Weak van der Waals interactions are mainly responsible for this adsorption process. The pesticide adsorption efficiency of APSP depended on the initial concentration of pesticide in the solution, and the maximum removal of pesticide was observed at concentrations which are generally encountered in wastewater and runoff from agricultural soils. The adsorption process of both Monocrotophos and Chloropyrifos onto APSP is best described by a pseudo-second-order model. Chloropyrifos with a higher kinetic rate constant value had higher K_d values as well as greater hydrophobic character compared to Monocrotophos. Chloropyrifos thus adsorbed faster and had greater adsorption capacity compared to Monocrotophos. The negative values of the thermodynamic parameters, i.e., ΔH and ΔG, indicate that adsorption is exothermic, feasible, and spontaneous in nature for Monocrotophos. The spectrophotometric and COD data for the pesticides showed similar trends except for the effect of time. APSP thus has potential use as low-cost adsorbent for the removal of pesticides under study from wastewater and runoff water from agricultural soils. It can also find use as a material in the preparation of biobeds to minimize environmental contamination from pesticide use.

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