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Development of Magnetic Nanoparticles from Poplar Sawdust for Removal of Pesticides from Aqueous Solution

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Abstract
A magnetic nano-adsorbent from widely available agricultural waste by-product viz. poplar sawdust (MNPSD) was successfully prepared by applying chemical co-precipitation method and was subsequently characterized for its unique properties of high surface area and nano-size particles. Adsorption studies were conducted in laboratory batch mode to evaluate its capacity to remove methoxychlor and methylparathion. Methoxychlor and methylparathion are organic based pollutants that are detected in the wastewaters due to their excessive usage in agriculture. The maximum adsorption efficiency of MNPSD for methoxychlor and atrazine were determined to be 163.9 mg/g and 77.5 mg/g respectively at contact time of 55min and pH of 2. Equilibrium, kinetic and thermodynamic studies further revealed the suitability of MNPSD for use as a cost effective, environmental friendly adsorbent for wastewater treatment especially for removal of hazardous pesticides.

Keywords- Pesticides; Sawdust; Magnetic Nanoparticle; Adsorption Isotherm; Adsorption Kinetics.

1. Introduction

Pesticides applied to agricultural activities in order to curtail the growth of pests and hence to increase the productivity of harvests has resulted in their presence in water bodies and are classed as hazardous pollutants (Gimba et al., 2010; Chang et al., 2011; Al-Zaben and Mekhamer, 2017). Because of their complex chemical structures, pesticides are difficult to degrade and hence are toxic to the human health and aquatic life (Valickova et al., 2013; Al-Zaben and Mekhamer, 2017). The maximum allowable discharge limit of such pesticides is 0.1µ/L (Cara and Jitareanu, 2015). Some of the adverse effect of pesticides to humans is evident via neural disorder, endocrine malfunction, toxicology to a fetus, genetic changes and reproductive effect etc. (Valickova et al., 2013).

Under this context, the need for wastewater treatment has necessitated the search for cost effective and environmental friendly technologies. Adsorption technology has received great attention for reducing various toxic organic/inorganic contaminants present in wastewater due to their low cost and high efficacy to bind to pollutants resulting in their separation (Deniz and Saygideger, 2010; Aksu and Tezer, 2005). Literature reveals the suitability of agricultural

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waste products/by products (Srivastava et al., 2009) as precursors for activated carbons mainly because of their abundance, organic nature and environmental friendliness. Also such waste products require less processing to achieve value-added products like activated carbons (Bulut and Zeki, 2007). Some of the widely studied agricultural residues are chestnut shell (Memon et al., 2007), rice bran, mango bark, ground nut (Chang et al., 2011), agricultural peels and other lignocellulosic materials for various types of contaminant removal from wastewater (Anastopoulos and Kyzas, 2014). Such lignocellulosic substrates have demonstrated adsorption efficiency comparable to other natural biomass.

Sawdust is a lignocellulosic material which is abundantly available and is a solid waste material from timber industry. Lignin, cellulose and hemicellulose are the main components of sawdust (Pekkuz et al., 2008). Various functional groups including hydroxyl, carbonyl and carboxylate present on sawdust are responsible for binding of toxic pollutants from wastewater (Bulut and Zeki, 2007). However, when these materials were used without modification as an adsorbent for wastewater treatment, various polyphenols and other organic substances were released leading to secondary pollution. Other disadvantages encountered were low adsorption efficiency and longer kinetics which was unsuitable for their use as adsorbent for wastewater treatment (Cheng et al., 2012). The adsorption efficiency of the lignocellulosic biomasses can be increased by physical and/or chemical treatment because such treatment leads to a splitting of the crystallite structure of lignin, cellulose and hemicellulosic component thereby enhance the surface area, porosity and chelating efficiency of adsorbent (Gaballah et al., 1997; Crini and Badot, 2008; Liao and Chen, 2002). But the disadvantage associated with physical and/or chemical treatment of biomass is the high consumption of energy, treatment time and high cost of chemicals. Nano adsorbents are known to demonstrate high efficiency for removal of pollutants on account of their nano size particles and high surface area. Also, the magnetic properties as demonstrated by Fe_2O_3 nano adsorbents can assist in the easy separation of the adsorbed pollutants along with the adsorbent from water (Banerjee and Chen, 2007). Because of their environmental friendliness, magnetic nanoparticles thus have received greater attention for contaminant removal.

In this study, magnetic nanoparticles were synthesized from sawdust followed by their characterization with FE-SEM, TEM and FTIR. They were finally used for assessing their removal capacity for methoxychlor and methyl parathion pesticides. The experimental data were further modeled using the standard isotherm modeling with the intention to find out the maximum adsorption efficiency. Kinetic models and thermodynamics parameters were used in order to find out the reaction rates, adsorption mechanism and feasibility of upscaling of the process.

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2. Materials and Methods

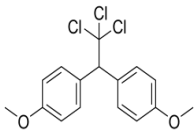
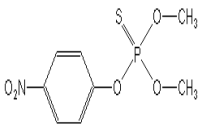
2.1 Collection and Storage of Poplar Sawdust

The poplar sawdust (*Populus*) for the synthesis of activated carbon was obtained from the local sawmill at Dehradun, India. The sawdust was cleaned with distilled water to eliminate surface impurity and dust. It was subsequently dried in a conventional oven for 24 h at 100ºC and at atmospheric pressure. Finally, the dried sawdust (RSD) was stored for further experimental work.

2.2 Chemicals and Reagents

Methoxychlor, methylparathion and other reagents ($FeCl_3$, $FeSO_4$ and NH_3) were of analytical grade and purchased from M/s Merck India. Some toxicological and physico-chemical properties of these pesticides are listed in Table 1. Stock solution (500 mg/L) was prepared and appropriate dilutions were made for the preparation of standard/sample solution. The glassware were washed with dilute nitric acid and repetitively rinsed with distilled water.

Table 1. Physico-chemical and toxicological properties of pesticides

Pesticides	Methoxychlor	Methyl parathion
Molecular Structure		
Molecular Formula	$C_{16}H_{15}Cl_3O_2$	$C_8H_{14}NO_5PS$
Molecular Weight	345.65 g/mol	263.20 g/mol
Pesticide type	Insecticide	Insecticide
Chemical family	Organo-chlorine	Organo-chlorine
Solubility in water (25˚C)	0.045 mg/L	60.0 mg/L
Log octanol-water partition coefficient	4.68-5.08	1.83-3.43
Environment fate	Highly persistent, non-mobile, high bio-accumulation	Moderately persistent and mobile, low bio-accumulation potential
Carcinogen class	Class D	Class A
Toxicity category	III (moderately toxic)	I (Highly toxic)
Use classification	Restricted and banned	Restricted and banned
EPA limit in drinking water	20 ppb	2 ppb

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2.3 Development of Adsorbent (MNPSD)

Magnetic nanoparticles of sawdust were synthesized following the methodology refs. (Gupta and Nayak, 2012). An approximate amount (6g) of $FeCl_3.6H_2O$ and 4g of $FeSO_4.7H_2O$ were dissolved in 100 ml of de-ionized water and heated to 90ºC followed by stirring for 30min. 1 gm of dried RSD suspended in 200 ml of de-ionized water and 40 ml solution of ammonium hydroxide (26%) were then rapidly added into the solution till the chemical precipitation started to occur. Throughout the process, an alkaline medium was maintained (pH 10) and stirred for a further 30min. Subsequently the solution was cooled to room temperature. The resultant black precipitate was separated by filtration and repeatedly washed with de-ionized water to neutral, followed by drying at 50ºC for 24 h. MNPSD samples thus prepared were then stored for further use.

2.4 Equipment for Characterization of Adsorbent and Adsorbate

The pH of sample solutions was measured by pH meter (Cyberscan 510, Singapore). A UV-Vis spectrophotometer (UV 10 HEDM218008, Thermo scientific) was used to quantify the concentration of pesticides in aqueous medium. The surface morphology of the both MNPSD and RSD were determined by using scanning electron microscope with energy dispersive X-ray spectroscopy (Leo Electronmikroskopie GmbH, Germany). Fourier Transform Infrared spectrophotometer (Model Perkin Elmer-1600 series) was performed to determine the active functional groups on MNPSD. Transmission Electron Microscope (FEITECNAI G2 microscope operating at 200 kV) studies were performed to determine the particle morphology and size.

2.5 Batch Equilibrium and Kinetic Studies

Adsorption studies under batch mode were carried out to assess the uptake capacity of the synthesized MNPSD and also to determine the effect of different parameters on the sorption process. The parameters that were considered in this study and that are known to have an influential effect on the adsorption efficiency were temperature, contact time, pH, initial metal ions concentration and adsorbent dose. For both isotherm and kinetic studies, approximately 100mg of the MNPSD was added to 100mL of solution containing pesticides of known concentration (10-50 mg/L) maintained at desired temperature and pH. The solution pH was maintained by adding 1M HNO_3 and 1M NaOH. A variation in the concentration of adsorbate solution was selected to determine the efficiency of the synthesized adsorbent under laboratory conditions. The flask containing reaction medium was agitated at 200 rpm for 180 min and at appropriate interval of time, aliquots were extracted and centrifuged for 20 min at 800 rpm on a centrifuge. The adsorption efficiency (mg/g) was calculated by using equation (1):

$$q_e = (C_o - C)\frac{V}{W} \quad (1)$$

Where, C_o= initial concentration of pesticides (mg/L),

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C= final concentration of pesticides (mg/L),
V = volume of solution (L),
W = weight of adsorbent (g).

3. Results and Discussion

3.1 Characterization of Adsorbents

In order to determine the efficiency of adsorbent to adsorb pesticides on to its surface from aqueous phase, the investigation of active functional groups on adsorbent surface is essential. The FTIR spectrum analysis of RSD sample exhibited the presence of various bands in the functional group region (Figure 1a, b). The presence of hydroxyl group (-OH stretch) is proved by the existence of broad band at 3500-3200 cm^{-1}, peak at 2931 cm^{-1}(alkyl C-H stretch), intense peak at 1642 and 1570 cm^{-1}(carboxyl C═O stretch conjugated with aromatic groups), intense peak at 1414 cm^{-1}(-OH stretch of phenols) and peak at 1270 cm^{-1}(carboxyl C-O stretch) and at 1118 cm^{-1} (C-O stretch). The peaks at 3432 cm^{-1}, 1642cm^{-1}, 1414 cm^{-1}, 1022 cm^{-1} on RSD (Figure 1a) showed a shift to 3418 cm^{-1}, 3267 cm^{-1}, 1636 cm^{-1}, 1413 cm^{-1} and 1020 cm^{-1} on MNPSD (Figure 1b) which revealed the successful interaction of RSD with MNP to form MNPSD. Various new peaks were observed on MNPSD at 566cm^{-1} which can be related to Fe-O group on MNPSD and thus indicates the existence of MNP (magnetic nanoparticles) on the surface of MNPSD. The peak at 1118 cm^{-1} which are found to be present in the spectrum of both RSD and MNPSD can be assigned to the –OH bends of lactones, ethers and phenols. Thus, carboxyl, hydroxyl and phenolic groups present on the MNPSD can enhance the affinity of pesticides towards adsorbent.

In order to assess the surface morphology of RSD and MNPSD, Fe-SEM analysis conducted revealed the absence of porosity on the surface of RSD (Figure 2a) whereas the surface of MNPSD (Figure 2b) reveals the presence of numerous irregular pores.

Results of TEM studies (Figure 3) reveal that MNPSD particle were mono-dispersed, fine, compact and having nano-particle diameter of 20-25 nm.

3.2 Effect of pH

Solution pH is an important parameter that is known to affect the physic-chemical interactions between the adsorbent and the adsorbate and hence on the uptake capacity of the adsorbent (Aksu and Gonen, 2004).

In the present study, the uptake of pesticides was studied at different pH (varying from 2-8) at 25ºC under constant adsorbent dosage and fixed adsorbate concentrations. The experimental results are shown in Figure 4. Figure 4 shows that highest uptake of the pesticides is obtained at pH of 2 while the uptake capacity decreases with an increase in pH. The adsorption capacity of MNPSD thus can be linked to its surface functionality. It is a well-known fact that the surface functionalities are known to protonate and de-protonate with a change in pH of

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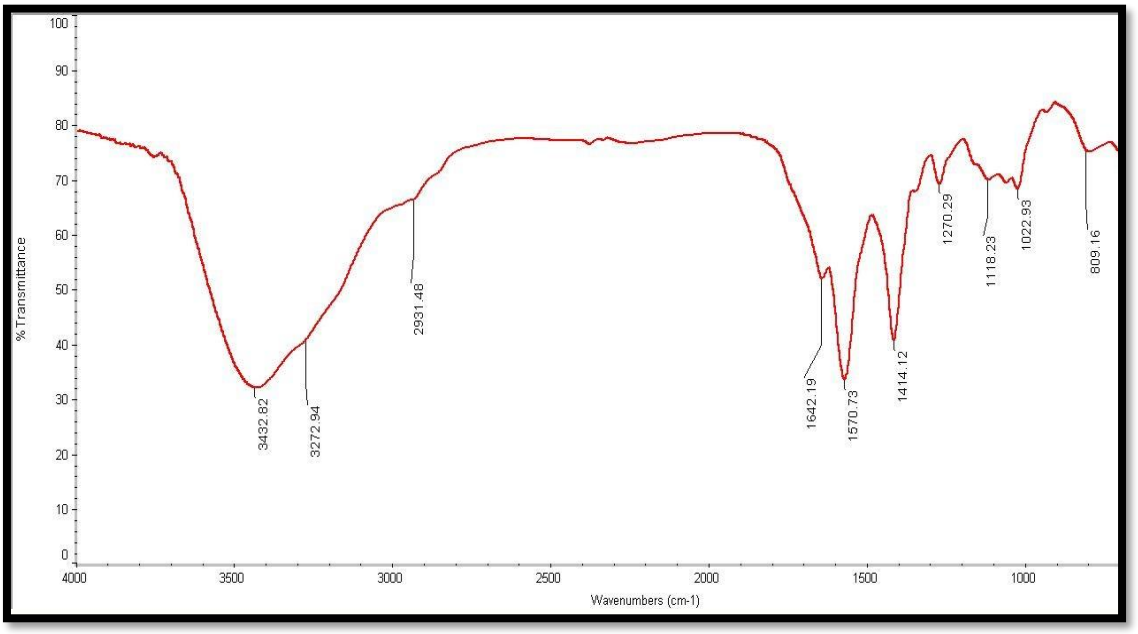
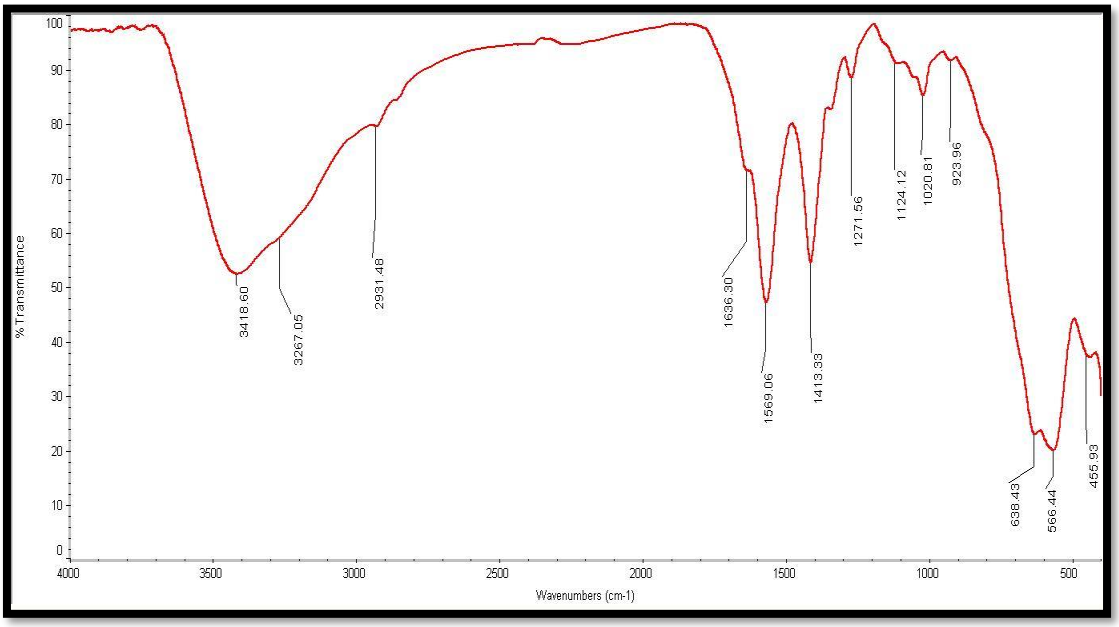
the medium (Gupta et al., 2011a; Gupta and Imran, 2008). The de-protonation of adsorbent surface increases with increase in the pH of the aqueous medium. This is responsible for a strong repulsion for the pesticides and hence a lower uptake capacity. On the other hand at lower pH values protonation of the surface of the adsorbent is enhanced leading to increased uptake of pesticides.



(a)



(b)

Figure 1. FTIR spectra of (a) RSD (b) MNPSD

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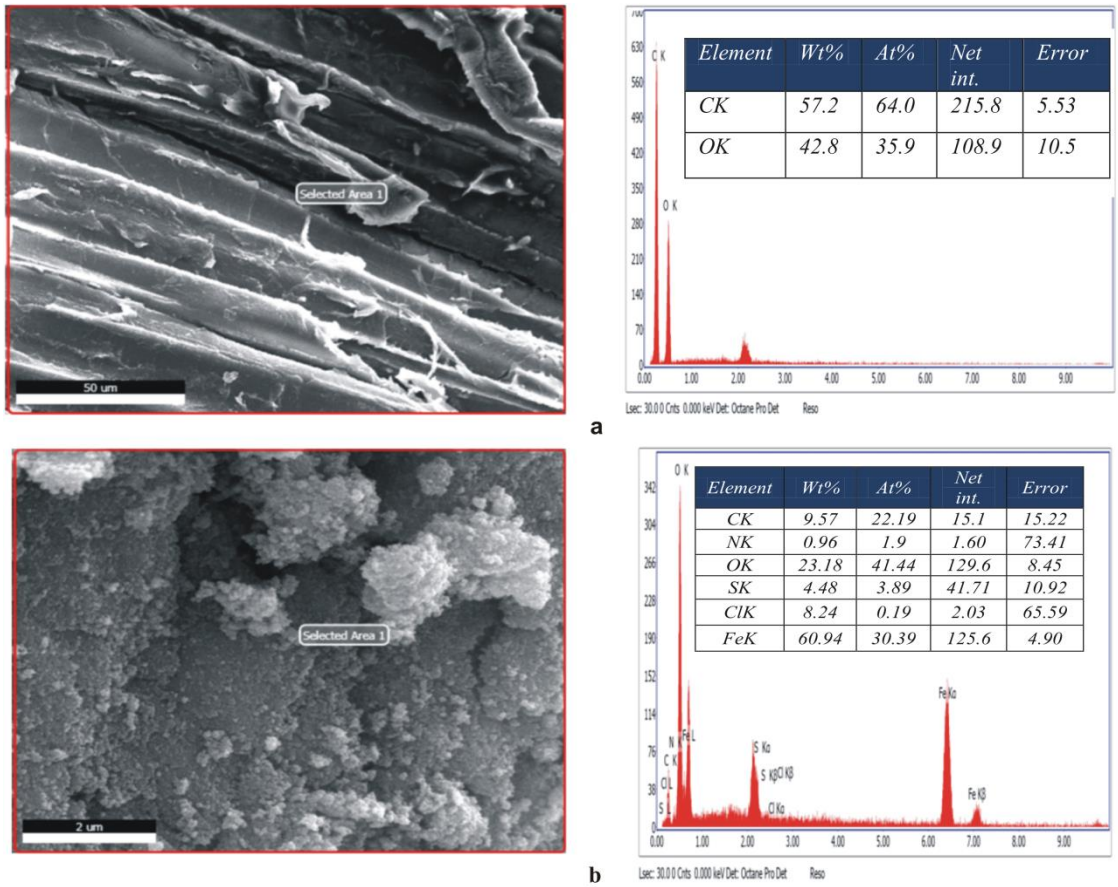

Figure 2. SEM micrograph and EDAX of (a) RSD (b) MNPSD

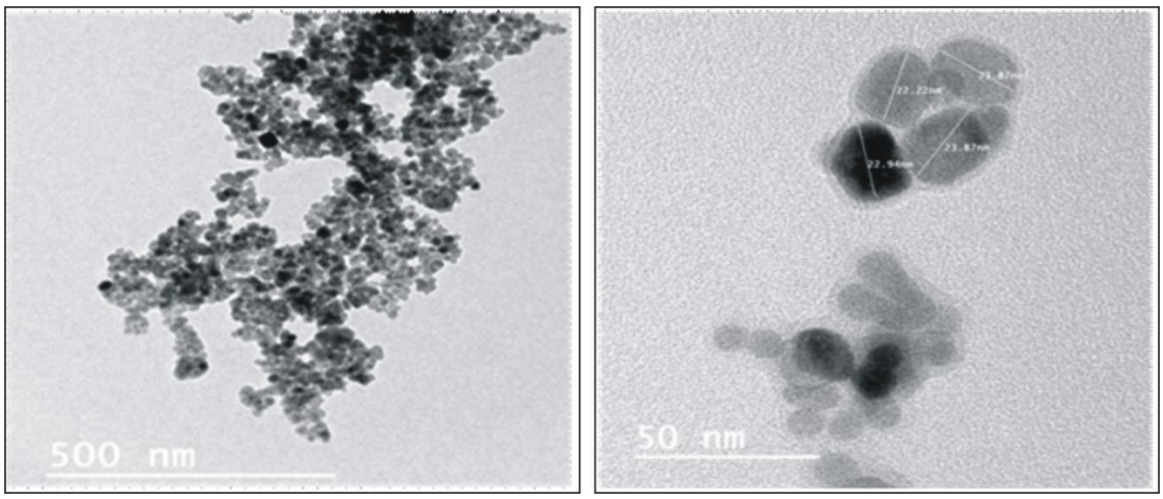

Figure 3. Transmission electron microscope (TEM) images for MNPSD synthesized

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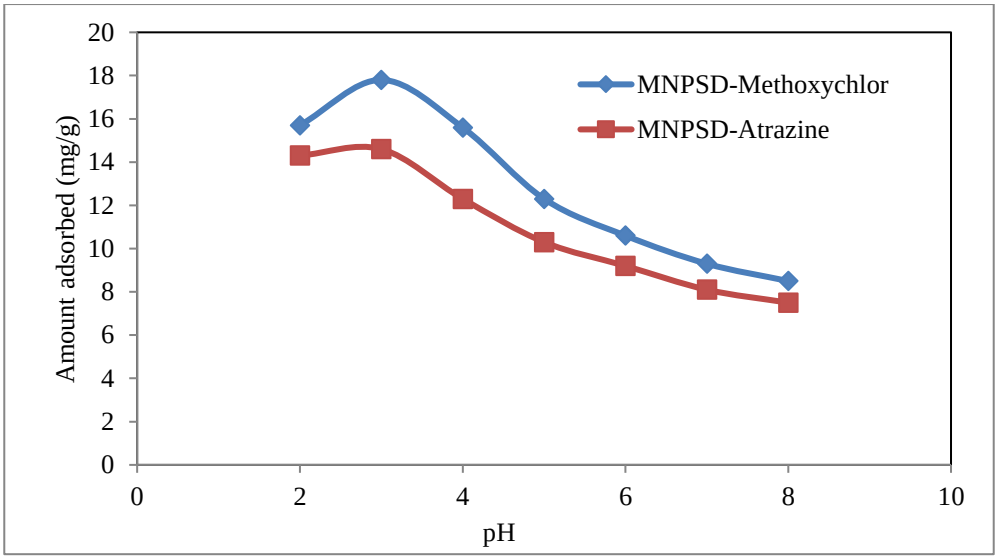

Figure 4. Effect of aqueous pH on the adsorption capacity of the MNPSD

3.3 Effect of Time of Contact and Initial Pesticide Concentration

Different concentration of pesticides was selected varying from 10-50 mg/L, in order to determine the performance of MNPSD for the removal of pesticides from wastewater. The simultaneous effect of initial pesticides concentration and contact time on the uptake performance of the MNPSD is shown in Figure 5. It was observed from the results that irrespective of the type of pesticides, the adsorption onto MNPSD was found to be very fast but steadily decreased after 55mins to reach equilibrium. A probable reason for an initial faster rate of pesticides uptake could be due to the availability of the active functionalities and pores on the surface of MNPSD (Gupta et al., 2011b). The adsorption of methoxychlor and methylparathion onto MNPSD showed an increase from 15.0 to 18.5 mg/g; and 9.37 to 11.6 mg/g respectively with an increase in the initial concentration of pesticides from 20 to 50mg/L. A possible reason is that higher concentration of adsorbate provides maximum diffusion rate of pesticides toward the adsorbent surface leading to an increase in extent of adsorption (Davis and Bhatnagar, 1995).

3.4 Adsorption Kinetics and Diffusion Studies

Lagergren's pseudo-first-order and pseudo-second-order model were used to model the batch experimental data in order to estimate the rate of reaction and mechanism of the binding process (Chien and Clayton, 1980; Ho and McKay, 1998).

The pseudo- first order kinetic model is given as follows:

$$log(qe - qt) = log\ qe\ k_1 \frac{t}{2.303} \quad (2)$$

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The pseudo-second order kinetic model is expressed as follows:

$$\frac{t}{qt} = \frac{1}{k_2}, ads + t\ \frac{1}{q_e} \quad (3)$$

Where, qt = amount adsorbed on adsorbent at time (t)

k_1 & k_2 = first-order and second order rate constant respectively,

qe = equilibrium sorption uptake

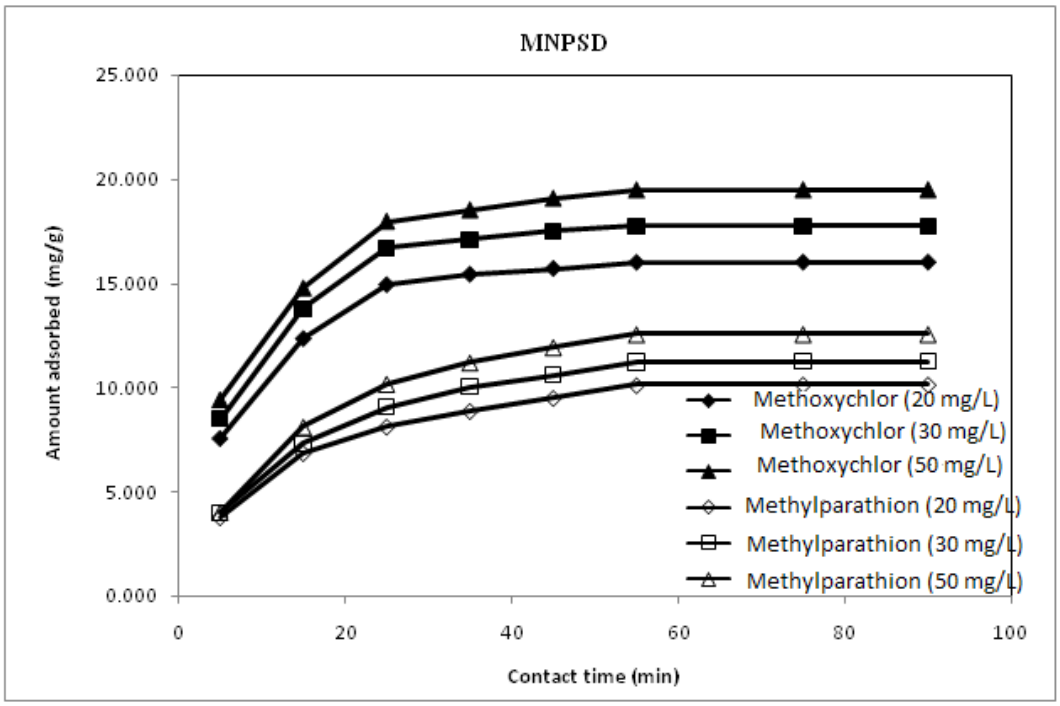

Figure 5. Effect of initial adsorbate concentration and contact time on the adsorption of methoxychlor and methylparathion on to MNPSD

The results of kinetics parameters and correlation coefficient (R^2) were calculated from the slope and intercept of plot log (qe-qt) and t/qt vs. t for pseudo first-order and second-order model respectively and outcome are listed in Table 2. Results reveal the high correlation coefficient (R^2) values for the studied MNPSD-pesticides system in the case of the pseudo-second-order model. Also, straight line plots were obtained (t/qt vs t) as can be seen in Figure 6a which indicates its relevancy for adsorption process kinetics.

"Weber and Morris" developed intra-particle diffusion model (qt vs. $t^{0.5}$) and which was used to evaluate the diffusion process of the pesticides in aqueous medium. It is expressed as follows (Weber and Morris, 1963; Wu, 2007):

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$$qt = ki\, t^{0.5} + C \quad (4)$$

Where, qt = amount of pesticides adsorbed at time (t),

k_i = diffusion rate constant (mg/g/min$^{1/2}$),
C = constant related to thickness of the boundary layer.

Table 2. Kinetic Parameters for the adsorption of pesticides onto MNPSD

Adsorbent	MNPSD					
Adsorbate concentration	Methoxychlor			Methylparathion		
	20mg/L	30 mg/L	50 mg/L	20 mg/L	30 mg/L	50 mg/L
qe (mg/g) (exp.)	15.0	16.8	18.5	9.37	10.4	11.5
Pseudo 1st order model						
q_e(mg/g) (theoretical)	17.3	19.4	20.5	12.8	13.3	14.5
k_1 (min^{-1})	0.104	0.094	0.091	0.088	0.085	0.083
R^2	0.89	0.92	0.88	0.84	0.89	0.81
Pseudo 2nd order model						
q_e(mg/g) (theoretical)	15.38	16.95	18.38	9.52	10.67	11.86
k_2 (g/mg/min)	0.016	0.011	0.010	0.012	0.010	0.008
R^2	0.997	0.998	0.997	0.997	0.997	0.998
Weber Morris						
k_i (mg/g/min$^{1/2}$)	0.43	0.44	0.68	0.85	0.889	1.02
C	12.7	14.2	14.6	4.22	4.92	5.57
R^2	0.99	0.99	0.99	0.99	0.99	0.99

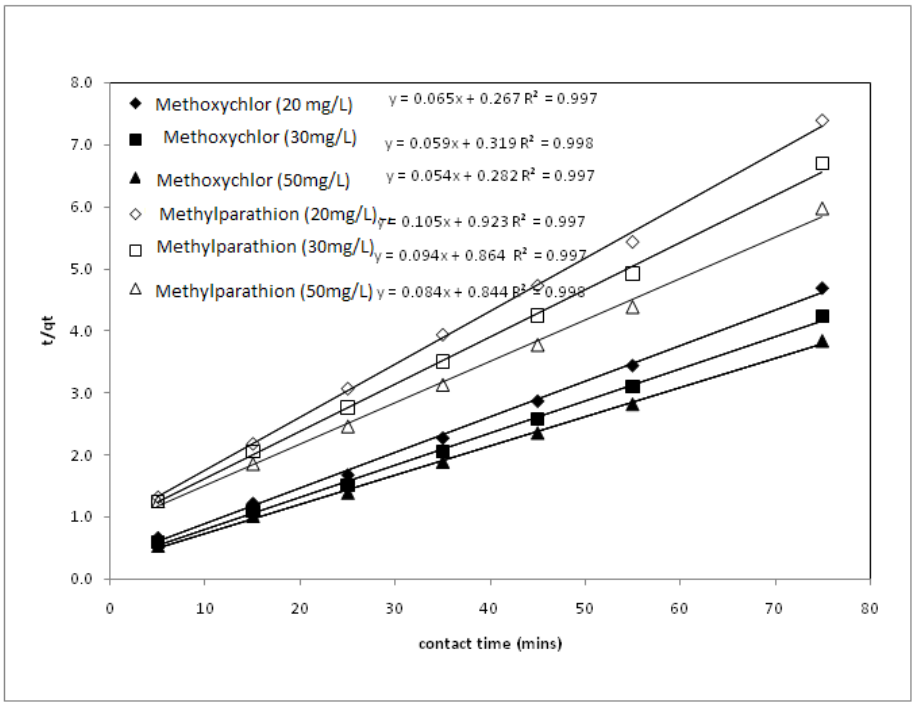

Figure 6a. Lagergren's pseudo-second-order plots at three different concentrations for MNPSD

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The model parameters were calculated from the slope and intercept of plot of qt vs. $t^{0.5}$ (Figure 6b). The diffusion of the pesticides seems to follow three distinct regions. The initial linear region signifies rapid pesticides transfer towards MNPSD which signifies the physical adsorption. The second linear region is the rate limiting step or slow step and indicates the fast diffusion of the pesticides towards MNPSD. The third linear slope shows the equilibrium region which indicates the saturation phase (Weber and Morris, 1963). In the MNPSD-pesticides adsorption system, the plots of qt vs t do not pass through the origin which implies the interplay of various mechanisms during the diffusion of the pesticides (Alhooshani, 2015).

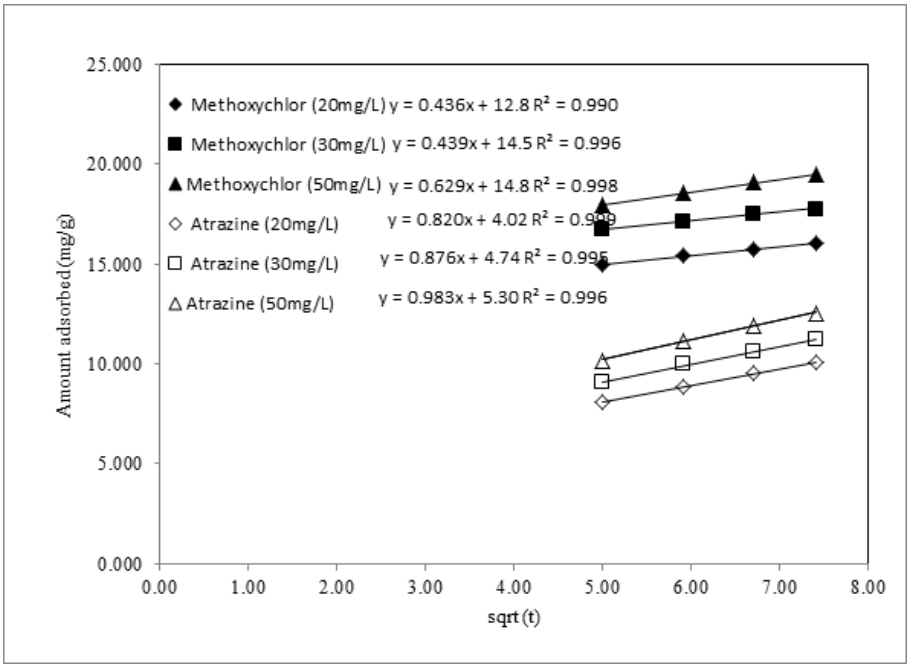

Figure 6b. Weber Morris plot of adsorption of pesticides onto MNPSD at three different concentrations

3.5 Adsorption Isotherm Studies

Isotherm plots were plotted from the experimental batch data under fixed temperature conditions of 25, 35 and 45°C and the results are shown in Figure 7. It is observed that MNPSD showed higher adsorption efficiency for the methoxychlor in comparison to that for methylparathion. The isotherm data of the pesticides were further fitted to Langmuir, Freundlich and D-R model (Allen et al., 2004; Ho and Ofomaja, 2005; Dubinin et al., 1947; Langmuir, 1916; Freundlich, 1906):

$$\text{Langmuir:} \frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{bq_o} C_e \quad (5)$$

Where, q_e = amount adsorbed on adsorbent (mg/g),

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$Q_\circ$ = maximum adsorption efficiency (mg/g),
C_e = concentration of adsorbate at equilibrium (mg/L),
b = constant related to energy (L/g).

Freundlich: $logq_e = logK_F + \frac{1}{n}\log C_e$ (6)

K_f = adsorption energy of adsorbent,
n = adsorption intensity of adsorbent.

Dubinin-Redushkevich: $\log qe = log\, q_D - 2B_D R^2 T^2 \log(1 + \frac{1}{C_e})$ (7)

B_D = energy of adsorption,
q_D = theoretical saturation capacity (mg/g),
R = gas constant (J/molK),
T = absolute temperature (K).

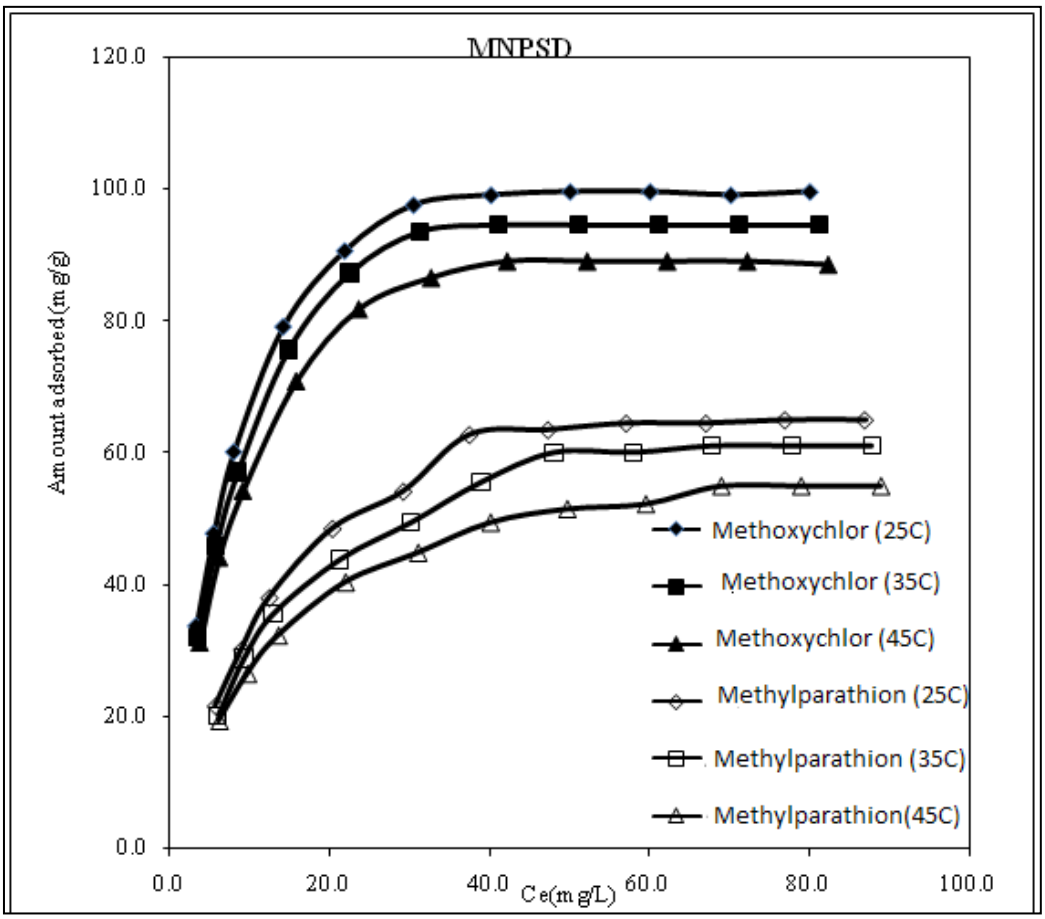

Figure 7. Adsorption isotherm for the uptake of pesticides onto MNPSD

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The regression coefficients and parameters for all pesticides derived from the plots of Langmuir, Freundlich and D-R model, are reported in Table 3. It is observed that at different temperatures the correlation coefficients are considerably higher for the Langmuir model (Figure 8) in comparison to the Freundlich and the D-R model (Figure not shown). The higher correlation coefficient (R^2) values and linear plot of 1/qe vs. 1/Ce reveals the applicability of Langmuir model (Table 3). The maximum adsorption efficiency of MNPSD for methoxychlor was 163.9 mg/g while the same for methylparathion was 77.5 mg/g at temperature of 25ºC and at pH 2.

Table 3. Isotherm model parameters for the adsorption of pesticides onto MNPSD at different temperature

Adsorbent	MNPSD					
	Methoxychlor			Methylparathion		
	25°C	35°C	45°C	25°C	35°C	45°C
Langmuir isotherm						
Q_o (mg/g)	163.9	120.5	107.5	77.5	71.9	63.3
b (L/mg)	0.099	0.101	0.103	0.075	0.077	0.078
R^2	0.995	0.993	0.992	0.992	0.994	0.998
Freundlich isotherm						
K_f	29.4	27.1	26.5	13.5	12.3	11.6
n	3.09	2.99	2.88	2.54	2.51	2.46
R^2	0.864	0.877	0.893	0.912	0.95	0.96
Intra-particle diffusion						
q_D (mg/g)	105.2	91.2	76.9	72.3	64.0	55.0
E_D	1.14	1.17	1.18	0.88	0.90	0.94
R^2	0.99	0.99	0.99	0.99	0.99	0.99
Thermodynamic studies						
-ΔG° (KJ/mol)	5.74	5.87	6.00	6.40	6.57	6.75
-ΔS° (KJ/mol)	1.23			1.91		
-ΔH° (kJ/Kmol	0.07			0.12		

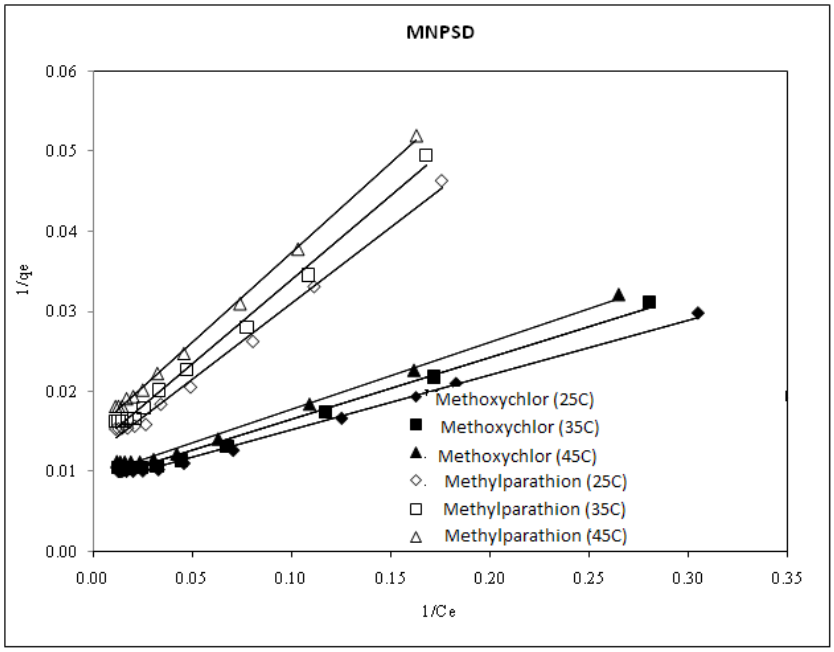

Figure 8. Langmuir adsorption isotherms of adsorption of pesticides onto MNPSD at three different temperatures

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Table 3 further reveals that the tendency to adsorb methoxychlor was higher onto MNPSD in comparison to methylparathion. The difference in the adsorption capacity of different pesticides onto adsorbent can be affected by various factors like the log-octanol-water partition coefficient (log K_{ow}) as has been documented by (Gupta et al., 2011a). The log K_{ow} is generally the measure of the water repelling capacity (hydrophobicity) of the compounds. Higher the log K_{ow} value as in the case of methoxychlor (Table 1), higher is its water repelling capacity and subsequently lesser is the solubility of methoxychlor. The result is the higher tendency of methoxychlor to adsorb onto MNPSD (Bedient et al., 1994).

3.6 Thermodynamic Studies

Figure 7 reveals that the adsorption of the pesticides was higher at 25°C and decreased with a rise in the temperature; thereby indicating an exothermic reaction for the MNPSD-pesticide system.

Thermodynamic parameters including Gibbs free energy change (ΔG^o), entropy change (ΔS^o) and enthalpy change (ΔH^o) were further calculated from the following and can be expressed as follows:

$$\Delta G^{\circ} = -RT\ ln\ b \tag{8}$$

$$\Delta S^{\circ} = (\Delta H^{\circ} - T\Delta S^{\circ}) \tag{9}$$

These parameters were evaluated at different temperature (25 - 45ºC). Exothermicity and spontaneity nature of the adsorption process was estimated from negative ΔH^o and ΔG^o values respectively as shown in Table 3.

4. Conclusion

Magnetic Nanoparticles (MNPSD) were successfully synthesized from sawdust which is an abundantly available timber industry waste having practically no utility. Characterization studies revealed the nanoporous morphology and a high surface area along with favorable surface chemistry in MNPSD which revealed its suitability as a adsorbent for wastewater treatment. Batch adsorption studies conducted on MNPSD revealed its higher efficiency to bind to methoxychlor in comparison to methylparathion. The reason for the higher binding efficiency for methoxychlor was attributed to its lower solubility. MNPSD revealed an efficiency of 163.9 mg/g for methoxychlor and 77.5 mg/g for methylparathion respectively at temperature of 25ºC and at pH 2. Adherence to Langmuir model revealed the adsorption to take place in a monolayer. The synthesized MNPSD demonstrated significant adsorption efficiency and faster kinetics for pesticides from aqueous phase. The system was found to be favorable with higher pesticides removal taking place at lower temperature.

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