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A GREEN TECHNOLOGY FOR THE REMOVAL OF PENDIMETHALIN FROM AQUEOUS SYSTEM USING ADSORPTION TECHNIQUE

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ABSTRACT

Pendimethalin (N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine) is a selective herbicide comes under dinitroaniline class which is used to control most of the annual grasses and many annual broad leaved weeds. Unlike other dinitroaniline herbicides, Pendimethalin shows persistence in soil up to 50 weeks. Among other water treatment techniques, adsorption processes are important wastewater treatment techniques because of its cost-effectiveness and availability of adsorbents. In this study adsorbing property of natural adsorbents like granular activated carbon, powdered activated carbon and carbon coated chitosan film were made use for the removal of Pendimethalin from the aqueous system. From adsorption studies it could be observed that powdered activated carbon shows better adsorption capacity compared to other adsorbents. The adsorption capacities of the absorbents used for the study are in the order of Powdered activated carbon (98% irrespective of pH) > carbon-coated chitosan film (91% at pH 7) > Chitosan (70% at pH 2) > Granular activated carbon (44.9% at pH7). To overcome the practical difficulties in the separation of powdered activated carbon from treated water, carbon-coated chitosan was used as an adsorbent for kinetics and adsorption isotherm studies. Isotherm studies confirm that adsorption processes of Pendimethalin over carbon-coated chitosan film favors Freundlich Adsorption Isotherm (multilayer adsorption). It was found that pseudo second order equation provided good correlation with experimental data for the adsorption of Pendimethalin over carbon-coated chitosan film.

KEY WORDS : Pendimethalin, Adsorption technique, Carbon coated chitosan film, Adsorption isotherm

INTRODUCTION

One of the milestones in pest control technology has been the introduction and extensive use of organic chemicals for weed control in agriculture and industry. Pendimethalin is herbicide which comes under dinitroaniline class. Pendimethalin is Orange –yellow crystals ($C_{13}H_{19}N_3O_4$). Pendimethalin is absorbed by the roots and leaves of plants, which dies shortly after germination or following emergence from the soil. The solubility of Pendimethalin in water is 0.33 mg/L at 20 ^oC. After the application of Pendimethalin in soil, it might have undergone N-dealkylation, nitroreduction, and cyclization (Marquis *et al*., 1979). Even though all dinitroaniline herbicides are having a very short life in the soil, Pendimethalin shows persistence up to 50 weeks (Pritchard *et al*., 1980). Pendimethalin quickly dissipates out of the water stream and gets bound to sediment and particulate matter. The degree of dissipation depends upon the organic matter present in the system. More than 50% of the water pollution due to pesticides occurs by leaching and mixing chemicals from agricultural practice (Anju Agrawal *et al*., 2010). A typical system for surface water treatment generally consists of pre-setting, coagulation/flocculation (sediment removal), granular filtration (sediment removal), corrosion control (pH adjustment or addition of corrosion inhibitors), and disinfection (USEPA). Various types of water treatment processes used all over the world to treat surface and groundwater towards safe drinking water standards are a) Coagulation/ Flocculation, b) Softening, c) Filtration, d) Disinfection / Chemical oxidation, e) Membrane Treatment, f) Ozonation, g) Adsorption.

Adsorption is a surface phenomenon in which common pollutants (organic and inorganic) get removed. Among other water treatment techniques, adsorption processes are important wastewater treatment techniques because of its cost-effectiveness and availability of adsorbents. Recent researches are focused on the adsorption with low cost and modified polysaccharide adsorbent (Grégorio Crini, 2005). When solute present in the solution comes in contact with solid adsorbent with a highly porous structure, a liquid-solid intermolecular force of attraction comes into force. This intermolecular force of attraction leads to deposition or concentration of solute over the solid surface (Mohamed Nageeb Rashed, 2013). This accumulation of adsorbate over the adsorbent is called adsorption. As the adsorption progresses, there exists an equilibrium between adsorbed molecules of pollutants and that in the solutionIn this study, the removal of Pendimethalin from the aqueous system was carried out using four different natural adsorbents. The natural adsorbents employed for the adsorption studies are granular activated carbon, powdered activated carbon, chitosan, and carbon-coated chitosan film

MATERIALS AND METHODS

Reagents and chemicals used for the study

- Chitosan deacetylation ≥ 75%
- Acetic acid
- Granular activated carbon
- Powdered activated carbon
- Carbon-coated chitosan film
- Dichloromethane HPLC grade
- Hexane HPLC grade
- Acetone HPLC grade
- Distilled water
- Sodium sulfate anhydrous

Equipments used

- Gas Chromatography (Agilent GC7890 A)
- Scanning electron microscopy (JEOL Model JSM-6390LV)

Preparation of carbon coated chitosan film

1g chitosan was added to 100 mL water containing 1% acetic acid under agitation. This was then subjected to degassing for 2 hrs. After that, the uniform solution of chitosan was filtered to remove any undissolved materials. The filtered chitosan solution was poured uniformly over the glass plate. Powdered activated carbon was uniformly spread over the chitosan layer made above over the glass plate, which was then dried in the oven for 20hrs under 70 ^{o}C. Dried chitosan film coated with powdered activated carbon along with a glass plate was kept in 2N NaOH solution for 30 minutes. The thin layer of chitosan film coated with powdered activated carbon was pealed out from glass plate and dried at 30 ^{o}C. This dried chitosan film coated with powdered carbon was used for the adsorption studies (Bhuvaneshwari, 2011).

Preparation of synthetic effluent water

Experimental solutions were prepared in the laboratory, by spiking distilled water with a known amount of standard stock solution of Pendimethalin in HPLC grade acetone. Standard stock solutions of Pendimethalin having a concentration of 100 ppm were prepared by dissolving 0.1g of Pendimethalin in HPLC grade acetone in a separate 1000 mL standard flask. Effluent water with the desired pH was achieved by adjusting the pH with dilute acid (H_2SO_4) or alkali (NaOH). Synthetic effluent water was prepared by adding a known quantity of the above-prepared stock solutions of individual pesticides into distilled water having the desired pH. This artificially prepared effluent water with required pH was used for the entire experiments.

RESULTS AND DISCUSSION

Removal of pesticides by adsorption techniques

In this study adsorbing property of natural adsorbents like granular activated carbon, powdered activated carbon and carbon coated chitosan film was made use for the removal of Pendimethalin from the aqueous system. To 100 mL of synthetic effluent water containing 1000 ppb Pendimethalin in separate 500 mL reaction flasks, known amount of one of the above natural adsorbents was added and shaken uniformly for 1hr in a wrist shaker. After 1hr of contact time adsorbent was separated from the system by filtration, the filtrate was then extracted as per the APHA method. Pesticide (Pendimethalin) remaining in the aqueous system was quantified by analysing the hexane extract in GC provided with micro ECD (Electron Capture Detector)

Optimisation studies in the dosage of adsorbents were carried out using adsorption studies by varying adsorbent dosage. Similarly, experiments were conducted for the optimisation of pH and contact time. Isotherm study was carried out under the optimum time, pH and optimum dose of an adsorbent. During the time study, samples were taken in a regular interval of time and analysed using GC. Kinetic data was generated by plotting the concentration of Pendimethalin remaining in the solution corresponding to the time.

Optimisation of adsorbent and pH in the adsorption of Pendimethalin from aqueous system

To the synthetic effluent water containing 1000 ppb of Pendimethalin, 0.1 g of granular activated carbon was added and agitated for uniform shaking. The shaking was continued for 1 hr and after 1 hr the adsorbent and adsorbate were separated by filtration and the filtrate was extracted as per APHA (2012) method. The same experiment was repeated with synthetic effluent water having different pH. The same experimental procedure was repeated with powdered activated carbon, chitosan, and carbon-coated chitosan film. The results obtained are depicted in Figure 1

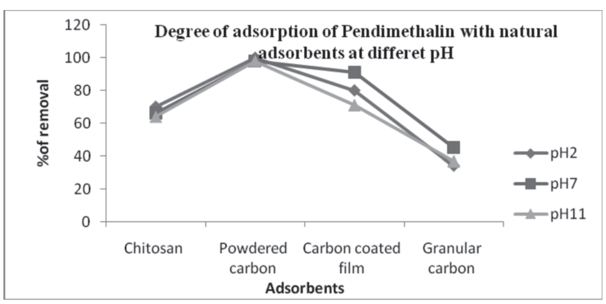

Fig. 1. Variation in the adsorption power of natural adsorbents for Pendimethalin at different pH

From Figure 1 it could be seen that more than 98% of Pendimethalin was removed from the aqueous system using powdered activated carbon. Since the particle size of powdered activated carbon was less than 0.18mm, removal from the water stream was very difficult,it required a more sophisticated filtration system. To overcome these difficulties in the removal of the adsorbent from the treated effluent water, chitosan film coated with carbon powder was chosen as the adsorbent for the removal of Pendimethalin from aqueous system. At pH 7 carbon-coated chitosan film was able to remove 91% of the Pendimethalin from synthetic effluent water. Kinetics studies and adsorption isotherm studies were conducted with carbon-coated chitosan film as an adsorbent at pH 7. The image of the carbon-coated chitosan film is depicted in Figure 2. Figure 3 represents the SEM images of carbon-coated chitosan film before and after adsorption of Pendimethalin.

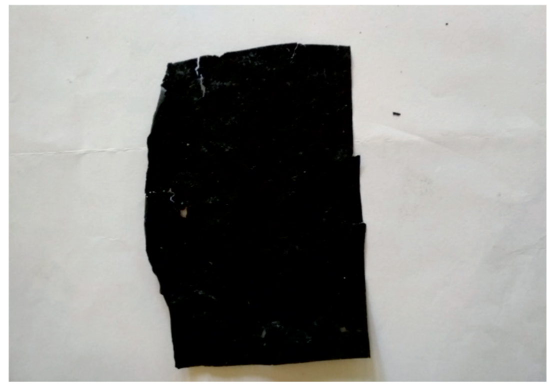

Fig. 2. Carbon coated chitosan film

The Scanning Electron Microscope (SEM) analysis shows that the surface of the carbon-coated chitosan film was rough and contains a number of irregular cavities. After adsorption, these cavities were coved with Pendiemthalin and hence surface became smooth.

Adsorption isotherm and kinetics model

A plot of adsorbate over adsorbent as a function of its concentration in solution at constant temperature is called adsorption isotherm. It is also the relationship between adsorbate in the liquid phase and adsorbate adsorbed on the surface of the adsorbent in equilibrium conditions and at constant temperature (Julius *et al.*, 2013, Mohamed, 2013). In this study, Langmuir and Freundlich isotherm models are used to interpret the adsorption behavior of Pendimethalin from aqueous system using carbon-coated chitosan film as adsorbent. All the experiments were carried out at optimum pH 7 and optimum dosage of carbon-coated chitosan film as adsorbent (0.1g/100 mL of synthetic effluent water) at an ambient temperature of 30 ^{o}C.

(a) Langmuir adsorption isotherm

According to Langmuir adsorption theory, all adsorption sites are equivalent and the ability of the adsorbate molecule to get bound to any one site is independent of whether or not the neighboring sites are occupied (Hanaor, 2014). There exist a dynamic equilibrium between the adsorbed molecules and the free molecules. The equation is as follows

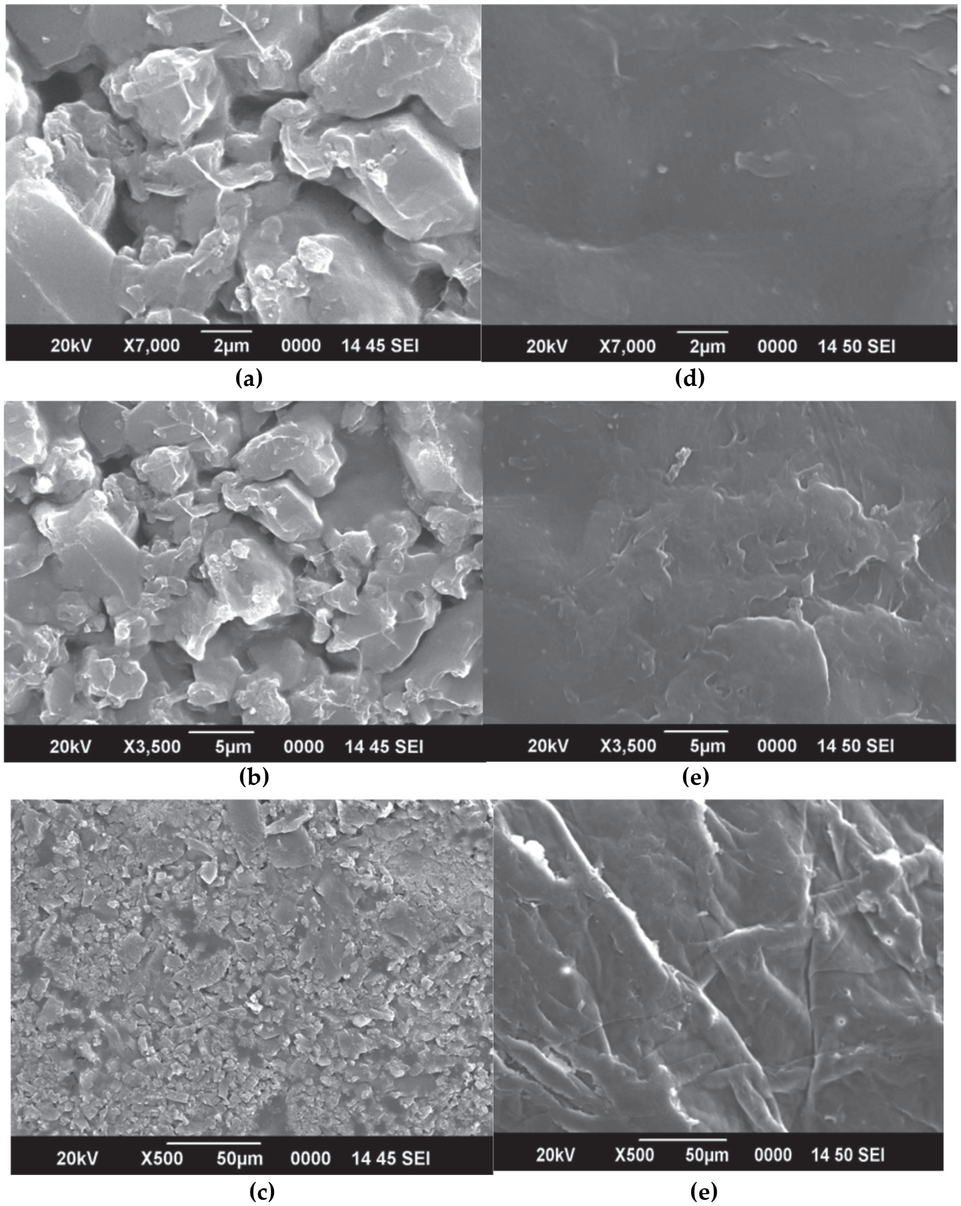

Fig. 3. (a), (b) and (c) represents SEM images of carbon-coated chitosan film and (d), (e), and (f) represents SEM images of carbon-coated chitosan film after Pendimethalin adsorption

$$Qe= QmKCe / 1 + KCe \quad .. (1)$$

Where Qe (mg of Pendimethalin per g of the carbon-coated chitosan film) is the adsorption density at equilibrium solute concentration Ce, and Ce is the equilibrium concentration of Pendimethalin in solution (mg/L). Qm (the mass of solute adsorbed per unit mass of adsorbent) is the maximum adsorption capacity corresponding to complete monolayer coverage. K is the Langmuir constant related to the energy of the adsorption (Pendimethalin per mg of the carbon-coated chitosan film). The above equation can be rearranged to a linear equation as follows. The plot of Ce/Qe against Ce (Langmuir adsorption isotherm) is shown in Figure 4. The Langmuir constant K and Qm can be calculated from the slope and intercept of the linear equation.

$$Ce / Qe = 1/Qm\,K + Ce / Qm \quad .. (2)$$

R^2 value, Qm and K value obtained from figure 4 are tabulated in Table 1.

(b) Freundlich adsorption isotherm

Freundlich isotherm is an empirical equation used for describing a multi-layer adsorption system. The equation is given below.

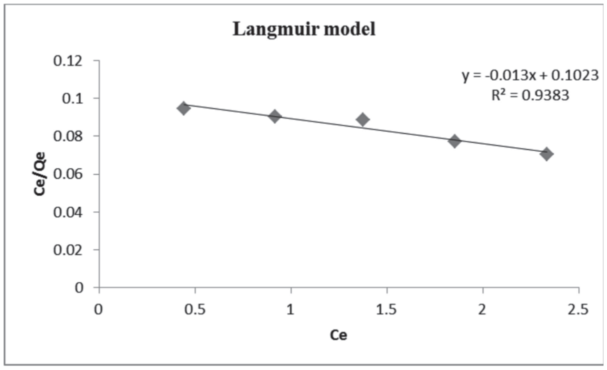

Fig. 4. Langmuir adsorption isotherm

$$x/m = KfCe^{1/n} \quad .. (3)$$

By taking logarithm on both sides

$$\ln (x/m) = \ln K_f + 1/n \ln Ce \quad .. (4)$$

The plot of ln(x/m) Vs lnCe is a straight line, and K_f and 1/n values can be obtained respectively from slope and intercept of the curve.

In this case,

'x' is the concentration of Pendimethalin adsorbed in mg

'm' is the mass of carbon-coated chitosan film used in g .

'Ce' is the equilibrium concentration of Pendimethalin in mg.

ln(x/m) is plotted against lnCe in Figure 6. The R^2 value, K_f and n values are tabulated in Table 1.

Isotherm data obtained from both Langmuir and Freundlich adsorption models are tabulated in Table 6.7. From this it was observed that the correlation coefficient value for the Freundlich isotherm model

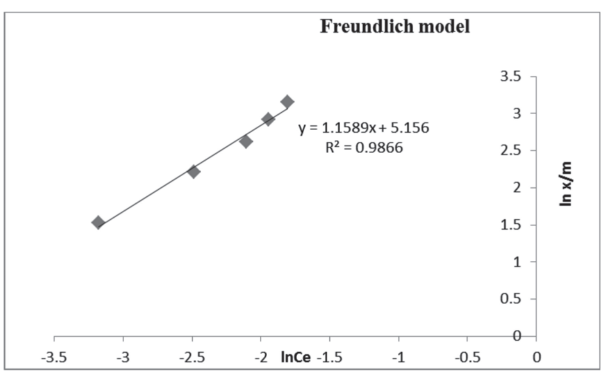

Fig. 5. Freundlich adsorption isotherm

is greater than the Langmuir adsorption isotherm model. This shows that adsorption of Pendimethalin over carbon-coated chitosan films more fitted with the Freundlich isotherm model. From Figure 5, 1/n was greater than 1 which indicates that the adsorption of Pendimethalin over carbon-coated chitosan film was cooperative (Itodo, 2011). Cooperative adsorption over a solid surface can be explained by multilayer adsorption in which there are adsorbate – adsorbate molecular interaction and

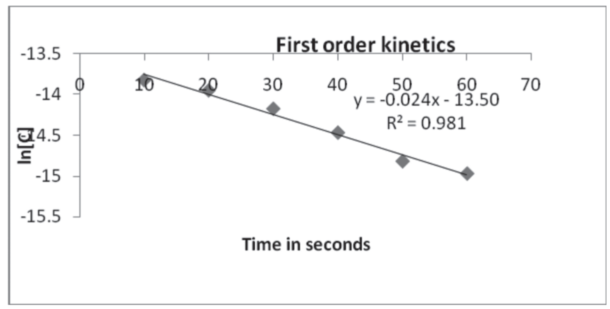

Fig. 6. First order kinetics of Pendimethalin adsorption over carbon-coated chitosan film

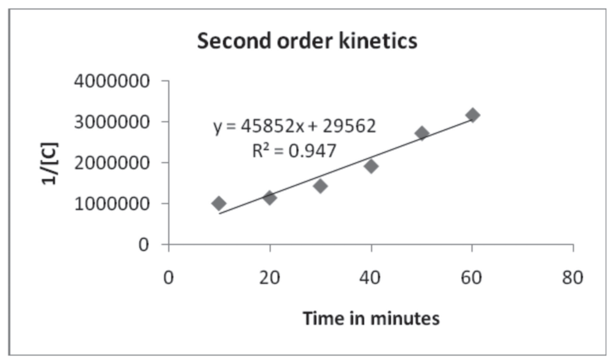

Fig. 7. Second order kinetics of Pendimethalin adsorption over carbon-coated chitosan film

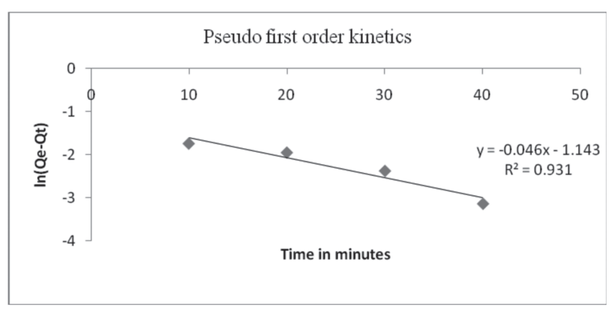

Fig. 8. Pseudo first order kinetics of Pendimethalin adsorption over carbon coated chitosan film

Table 1. Comparison of isotherm model

Isotherm Model	Equation	R^2	Qm	K	$\ln K_f$	n
Langmuir model	y=0.013x+0.1023	0.9383	76.9	0.127		
Freundlich model	y=1.1589x+5.156	0.9866			5.156	0.862

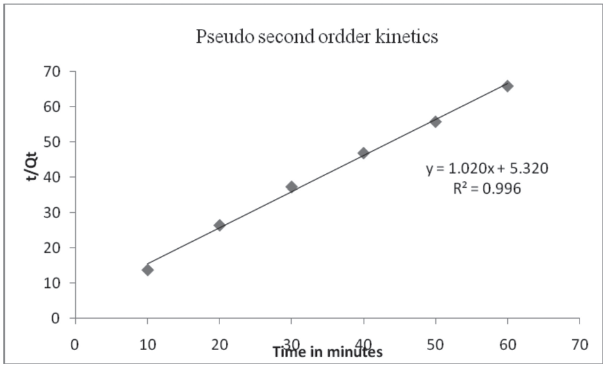

Fig. 9. Pseudo Second order kinetics of Pendimethalin adsorption over carbon coated chitosan film

Table 2. Comparison of Correlation coefficients from kinetics graph

Order of reaction	R^2 Value
First order kinetics	0.9818
Second order kinetics	0.9472
Pseudo-First order kinetics	0.9319
Pseudo-second order kinetics	0.9963

steric interaction (Shijie, 2015).

Kinetics of Pendimethalin adsorption over Carbon coated chitosan film

Kinetics graphs for Pendimethalin adsorption over

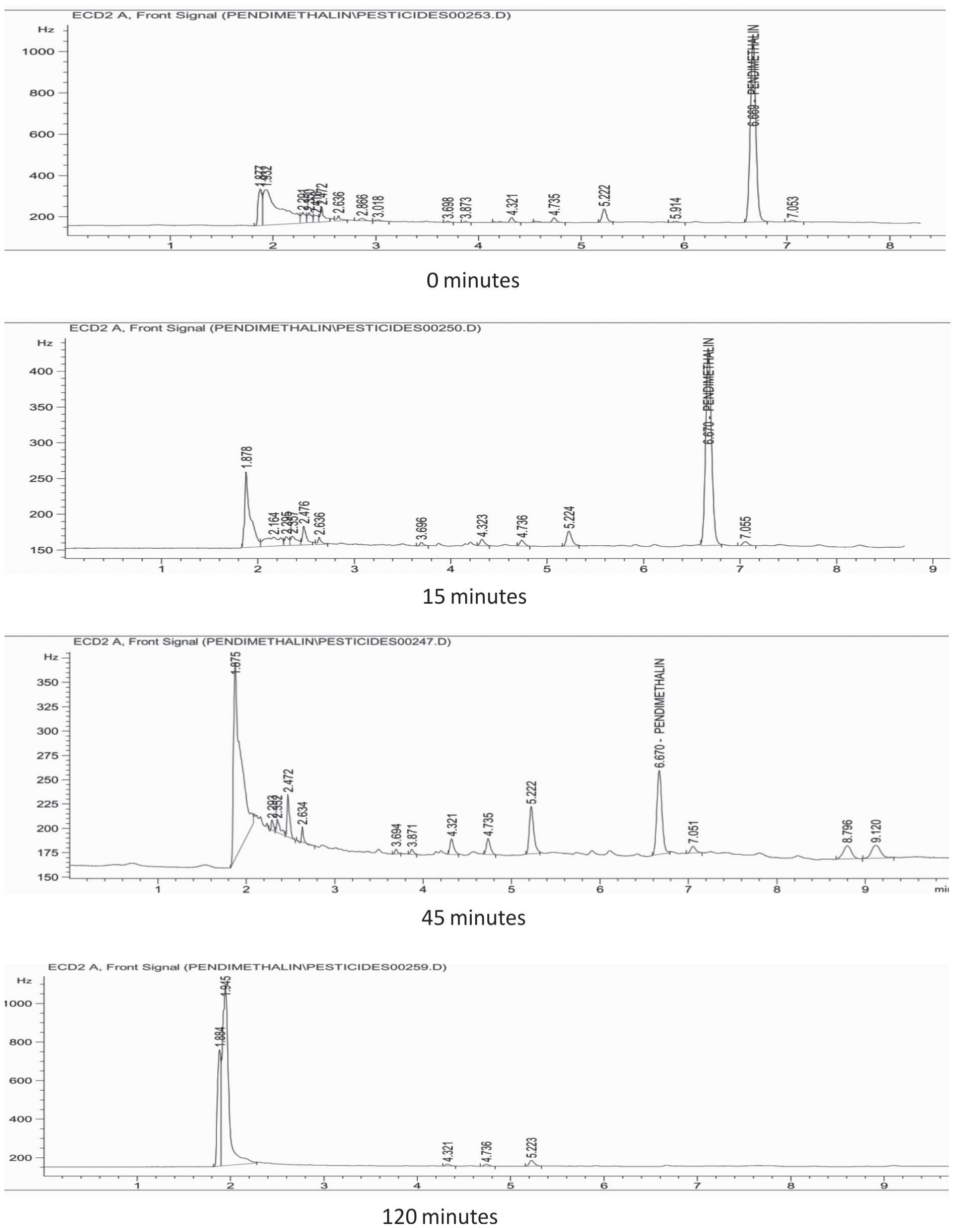

Fig. 10. Chromatograms for Pendimethalin Adsorption Isotherm over Carbon Coated Chitosan Film

carbon-coated chitosan film are given below. The correlation coefficient (R^2) obtained from the kinetics graphs are tabulated in Table 2. From graph, it was observed that the straight plot for the adsorption of Pendimethalin over carbon-coated chitosan film follows pseudo-second order kinetics.

CONCLUSION

From the adsorption studies of Pendimethalin from aqueous system using natural adsorbents (granular activated carbon, powdered activated carbon, chitosan, carbon-coated chitosan film) it could be seen that powdered activated carbon shows better adsorption capacity compared to other adsorbents. The adsorption capacities are in the order of Powdered activated carbon (98% irrespective of pH) > carbon-coated chitosan film (91% at pH 7) > Chitosan (70% at pH 2) > Granular activated carbon (44.9% at pH7). Even though the powdered activated carbon shows better adsorption capacity, its smaller particle size (0.18µm) demands more sophisticated filtration techniques for the separation of powdered activated carbon from the treated water system. To overcome these practical difficulties, carbon-coated chitosan film which is having a 91% adsorption capacity for the removal of Pendimethalin was used as an adsorbent for kinetics and adsorption isotherm studies. The Scanning Electron Microscope (SEM) analysis shows that the surface of the carbon-coated chitosan film was rough and contains several irregular cavities. After adsorption, these cavities were covered with layers of Pendimethalin and hence surface became smooth. Langmuir and Freundlich adsorption isotherm was used to describe adsorption based on the nature of surface coverage. It has been carried out by comparing Characteristic parameters of each isotherm and correlation coefficient for the adsorption of Pendimethalin over carbon-coated chitosan film. The R^2 value obtained from the isotherm data well suited with Freundlich adsorption isotherm. This implies that adsorption processes of Pendimethalin over carbon-coated chitosan film favor multilayer adsorption. Adsorption kinetic studies of Pendimethalin over carbon-coated chitosan film were performed using fist order kinetics, second order kinetics, pseudo first order kinetics and pseudo second order kinetics. It was found that pseudo second order equation provided good correlation with experimental data for the adsorption of Pendimethalin over carbon-coated chitosan film.

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