

Adsorption and Desorption Characteristics of Endosulfan Pesticide in Three soils in Palestine

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1. INTRODUCTION

Persistent Organic Pollutants (POPs) are a set of chemicals that are toxic, persist in the environment for long periods of time, and biomagnify as they move up through the food chain. POPs have been linked to adverse effects on human health and animals, such as cancer, damage to the nervous, reproductive disorders, and disruption of the immune system. Because they circulate globally via the atmosphere, oceans, and other pathways. POPs released in one part of the world can travel to regions far from their source of origin (Sandra et al. 2006).

With mounting evidence, indicating the long-range transport potential of these substances to regions where they have never been used or produced and the consequent threats they pose to the environment, the international community has called for urgent global actions to reduce and eliminate their release into the environment (Burger et al., 2001). Organochlorines (OCs), represent an important group of POPs which have caused worldwide concern as toxic environmental contaminants (Law et al. 2003, Covacia et al., 2005) and (Wurl and Obbard, 2005).

The lipophilic nature, hydrophobicity and low chemical and biological degradation rates of organochlorine pesticides have led to their accumulation in biological tissues and the subsequent magnification of concentrations in organisms, progressing through to the food chain (Tanabe, 2002). Specifically, one of the key environmental concerns, regarding some POPs, is their occurrence in polar regions, at surprisingly high levels.

Organochlorine pesticides (OCPs) are still widely distributed in the environment due to their persistency, semi-volatile nature resulting in long-distance transportation (Zhang H.B et al. 2006). Accumulation of OCPs also in the lipid content of animals is a common phenomenon due to their hydrophobic properties (Sijm and linde, 1995). Investigation of sorption phenomena of pesticides in soils is of great importance from environmental point of view. Pesticide sorption affects other processes like transport, degradation, volatilization, bioaccumulation, which influence the final fate of these compounds in the soil environment (Gao et al., 1998). All these processes influence the extent of surface water and ground water contaminations. Moreover, soils are a heterogeneous mixture of several components, many of which are organic and inorganic compounds of varying composition and surface activity. They can bind pesticides and reduce the bioavailability (Torrents and Jayasundera, 1997). Thus, knowledge of the pesticide adsorption–desorption characteristics of soil is necessary for predicting their mobility and fate in soil environments and also to understand whether bioremediation is a feasible option for the clean up of contaminated soil.

Numerous studies have been reported about the strong relationship between total organic carbon in the soil and the mobility of pesticides.

In this study, we focused on studying adsorption characteristics of endosulfan on various soils though they are of fundamental importance to quantify the transport of pesticides and the selection of proper remediation technique. The importance of organic matter, particle size, as well as pH of the soil for sorption has been emphasized by many workers (Gao et al., 1998).

These factors however, have not been studied in details for endosulfan, which is used widely in agriculture in Palestine. Therefore, investigation of these processes will provide a better understanding of its sorption and transport in soil environments.

2. Materials and Methods

2.1 Soil

Soil samples of most common soils of Palestine were selected for the study. The soils were identified and classified based on sieve analysis and hydrometer test (ASTM H-152) The organic matter of the soil was determined by chromic acid method (WREP-125 2nd Edition, 1998). The electrical conductivity was measured using conductivity meter (IS 2720 (part 21), 1977). Total soluble solids were estimated from electrical conductivity. The soil pH was measured by using a direct reading type pH meter with glass electrode and calomel reference electrode. The specific gravity was determined by pycnometer method (IS 2720(part3/sec 1), 1987). The moisture percentage of each soil was determined, and taken into account when an exact weight is required for analysis. The properties of the collected soils are given in table 1. The soils were sieved through IS (International Standard) sieve No. 10 (2mm aperture as per IS 2720(part 4), 1987). The fraction passing through the sieve was collected and preserved in air tight plastic containers for further studies.

2.2 Endosulfan standard solutions

A stock 100 ppm solution of endosulfan was prepared by transferring exactly 0.2875 mL of (0.350 g/mL) solution of endosulfan (Thionex®) into a one liter volumetric flask. The volume was completed to the mark with methanol: water solution (70 : 30 % v/v). The instrument used for analysis is the UV- Visible spectrophotometer (Shimadzu 1601PC), pH meter (3520 pH meter, JENWAY), conductometer (4510 conductivity meter, JENWAY), orbital shaker (Remi Instruments Ltd. US).

2.3 The pretreatment of the soil samples

The endosulfan content of the samples used in this work was high compared to the endosulfan concentrations used. Therefore, treating soil samples for desorption of their endosulfan content was necessary before they used. This was done by treating the samples with 0.1 M Perchloric acid (HClO₄) (this acid was chosen because of its ability to remove organic compounds and other metals from soil samples) many times until no traces was found in the extract. Soils were then washed thoroughly with distilled water and stored under distilled water. Portions of these treated samples were taken for the adsorption and desorption experiments.

2.4 Kinetic study

The adsorption kinetic study was carried out in batch mode using 250 mL conical flask with 5 g of appropriate soil (listed in Table 1) with a solid: solution mass ratio of 1:20) and 100 ml of 10 ppm of technical endosulfan solution. Sorbent masses were accurate to ± 0.001 g and solution volumes to ± 0.5 ml. The studies were conducted in triplicate for all soils on an orbital shaker (Remi Instruments Ltd.) at 150 rpm for a period of 24 h at room temperature ($25 \pm 2^\circ\text{C}$). From the triplicate flasks, 5 ml of sample was collected at time intervals of 0.25, 0.5, 1, 1.5, 2, 3, 4, 6, 8 and 24 h. The collected samples were filtrated and analyzed by UV-Visible -spectrophotometer.

2.5 Equilibrium study

Adsorption equilibrium studies were conducted for all soils with an adsorbent quantity of 5 g with technical endosulfan concentrations of 0.1, 0.2, 0.6, 0.8, 1, 2, 4, 6, 8 and 10 ppm in

identical conical flasks containing 100 ml of distilled water. A blank was maintained to determine the effect of endosulfan adsorption on the conical flasks. After the addition of soil samples, the reaction mixtures were agitated in an orbital shaker at 150 rpm for 3 h (estimated equilibrium time) at $25 \pm 2^\circ\text{C}$. After 3 h, 5 mL of sample was collected from each conical flask, the collected samples were filtrated and analyzed using UV- visible Spectrophotometer.

3. Results and Discussion

3.1 Calibration graph

Standard solutions of endosulfan 0.01, 0.6, 1, 2, 4, 6, 8, 10 ppm was prepared by transferring 0.05, 0.3, 0.5, 1, 2, 3 and 4 mL respectively, from 10 ppm standard solution of endosulfan into 5 ml volumetric flasks and completing the volumes to the mark with methanol: water solution (73:30%v/v). The absorbencies were measured at 214 nm (from previous studies like Wink o. 1985 and Balkom, 1995) against blank solution. A linear relationship was obtained between the absorbance and the concentration of endosulfan within the range (0.1-10 ppm). From the calibration curve (fig. 3.2) the detection limit was found to be 0.01 ppm with an absorbtivity of ($0.129 \text{ l. cm}^{-1}.\text{mg}^{-1}$). And relative standard deviation of (0.524 %) for 5 measurements of (4) ppm.

3.2. Adsorption

3.2.1. Adsorbent soil samples

The collected soil samples showed a wide variation in clay content Cambodian Agronomic Soil Classification System (CASC) starting from 2% to 46 %. Organic matter (OM) content varied from 0.32 % to 9.6% whereas insignificant variation of pH and specific gravity was observed, (Table 1).

3.2.2. Kinetic study

The adsorption kinetics exhibited an immediate rapid adsorption and reached pseudo-adsorption equilibrium within a short period of 1.5 h in sandy soil and 2.0 h in chalk soil and 3.0 h in red soil.

After pseudo equilibrium, less than 2% variation of endosulfan concentration in the adsorbate was observed even after 24 h. (Fig. 1). Beck and Jones (1996) studied the sorption of atrazine and isoproturon and they found that, the herbicides were removed from the solution within the first hour of the 24 h sorption experiments. The rapid initial adsorption of endosulfan is a surface phenomenon. Due to hydrophobic nature of endosulfan, the vacant sites in the soil particles were filled up rapidly in the initial stages and followed a linear variation. This is followed by a slow migration and diffusion of the compound (the rate of adsorption decreased drastically and reached the steady state) into the organic matter matrix and mineral structure (Gao et al., 1998). The same trend was observed by Parkpian et al. (1998) while studying the adsorption of endosulfan on Rangsit lowland soils and Phrabat upland soils, also by Kumar and Philip, (2006) while studying the adsorption and desorption characteristics of endosulfan in Indian soils.

From the results it is clear that, the sorption of endosulfan in soils is rapid in the initial period and the portion of pesticide participating in the long term behavior is insignificant as compared to that participating in the preliminary phase of rapid sorption.

The kinetic rates were estimated by Lagergren pseudo first order model (1898), and Ho's pseudo second order model (1995), given in Eq_s. below respectively.

$$\text{Log}(q_e - q_t) = \log q_e - k \cdot t$$

$$(1/q_t) = (1/h) + (1/q_e) \cdot t$$

where q_e is the amount of adsorbate sorbed at equilibrium; q_t is the amount of adsorbate sorbed on the surface of the sorbent at any time; k is the rate constant of sorption; t is the time and $h = k \cdot q_e^2$.

But none of the above models gave good fit for any of the specimens. This may be attributed to the nonhomogeneity of the soil. Hence, the data were plotted between square root of time ($t^{1/2}$) and equilibrium concentration (q_e).

A tangent starting from the origin was drawn as shown in (Fig. 2) and the rate of kinetic equilibrium was calculated as the slope of the tangent. The calculated rate constants for endosulfan $1.56 \text{ mg g}^{-1} \text{ h}^{-1/2}$ for red soil, $1.07 \text{ mg g}^{-1} \text{ h}^{-1/2}$ for chalk soil and $0.0390 \text{ mg g}^{-1} \text{ h}^{-1/2}$ for sandy soil. The kinetic rate constants for different soils are given in (Table 2).

3.2.3. Equilibrium study

In order to find the short term behavior of endosulfan in different types of soils, adsorption isotherm studies were conducted at $25 \pm 2^\circ\text{C}$ with an equilibrium time of 3 h. Using Langmuir [$(x/m) = (q_{\text{max}} b q_e / (1 + b q_e))$] and Freundlich [$(x/m) = K q_e^{1/n}$] equilibrium models, where (x/m) (mg/g) is the amount of pesticide adsorbed per gram of adsorbent; q_e (mg/l) is the equilibrium concentration in solution; q_{max} is the maximum adsorption capacity of the adsorbent; b is Langmuir's constant; K and $1/n$ are Freundlich's adsorption coefficient and adsorption constant. The isotherm constants and the maximum adsorption capacity of the soils were calculated for (0.1, 0.2, 0.4, 0.6, 0.8, 1, 2, 4, 6, 8, and 10 ppm) endosulfan concentrations to understand the behavior clearly. The relation between $1/q_e$ vs. $1/(x/m)$ is shown in (Fig. 3), the adsorption of endosulfan followed Langmuir isotherm better than Freundlich isotherm.

Although, the soil is a heterogeneous material, the adsorption data followed Langmuir isotherm, which is the representation of a monolayer, homogeneous/uniform adsorption. This may be due to the lower concentration of adsorbate in the solution, which was not sufficient to have a competition for the abundantly available adsorption sites in soil.

The maximum adsorption (q_{max}) of endosulfan concentrations occurred in red soil followed by chalk soil, and sandy soil (Table 3).

Same trend was reported by Torrents and Jayasundera (1997), who conducted the sorption study of non-ionic pesticides and found that the intensity of sorption was a function of herbicide and clay content. The q_{max} value of red soil for endosulfan was (0.387) mg / g of soil. Red soil has more vacant sites/surface area compared to sand particles (Gao et al., 1998). The organic matter in red soil was (9.6 %), which increased the endosulfan adsorption. On the other hand, sandy soil has fewer pores and adsorption sites (organic matter is 0.2%) which resulted in minimum endosulfan adsorption (0.075 mg / g of soil).

3.3 Effect of organic matter content (OM) on endosulfan adsorption.

The properties of chalk soil and red soil were nearly similar but there is difference in OM content (Table 1). Though the CASC in the red soil was only 61%; the adsorption of endosulfan was more (0.387 mg / g).

It was noticed that, the OM content in the red soil was 9.6%, which probably influenced the migration of endosulfan molecules to it, (Berglof et al., 2002; Yu and Zhou, 2005). Increase in organic contents increased sorption of nitroaromatic herbicide dinoseb by either non-specific partitioning or specific charge related mechanisms (Martins and Mermoud, 1998). In addition, the results are in accordance with Iraqi and Iraqi (2000), who demonstrated that beyond 2% organic matter in soils, the adsorption of parathion takes place almost entirely on the organic surfaces. The decrease in OM content which is 8.4% in chalk soil (as compared to red soil) reduced the adsorption rate of endosulfan from 0.387 to 0.213 mg g⁻¹ h^{-1/2} (Table 2). It is important to note that, the extent mineral's contribute to sorption depends on both the ratio of clay minerals and soil organic carbon contents (Hsieh and Kao, 1998; Spark and Swift, 2002). Soil rich in OM may retain the pesticides and reduce the possibility of contaminating the surface and groundwater sources.

3.4 Effect of pH of the soil samples on adsorption.

An attempt was made to investigate the significant role played by structure lattice in the adsorption process. The soil samples were digested with acid solution of varying concentrations to disrupt the structure. The pH of the soil samples were brought down to 1.5, 2, 3, 5, 6 and 7 with the use of concentrated HCl. Adsorption kinetic studies were carried out using the treated soil samples with an endosulfan concentration of 10ppm for a pseudo equilibration time of 3 h. The total amount of endosulfan adsorbed on each pH value was shown in (Fig. 4). No adsorption of endosulfan was observed at pH 1.5. Above which (between 2 and 3) it increased very slowly. Above pH 3.0 the trend in adsorption was differ according to soil type as shown in figure below.

Acid treatment destroyed the crystal lattice of the soil particles which might have reduced the adsorption (Kumar M., et al., 2006). To verify the above assumption, acid treated soil with a pH of 2 was neutralized (pH 7.0) and the kinetic study was conducted. The adsorption of endosulfan in the treated soil was only about 0.12 in red soil, (0.09 ppm) in chalk soil, and (0.03 ppm) in sandy soil. From the results the chance of suspicion about regaining of crystal lattice of the soil particles by pH adjustments was eliminated. The adsorption of endosulfan on glassware was insignificant compared to the adsorption of endosulfan in soil.

3.5 Effect of concentration of endosulfan on adsorption.

From the equilibrium study which was carried out for different concentrations of endosulfan, it was clear that as concentration of the endosulfan solution increased, the amount adsorbed increased as shown in (fig. 5).

Conclusion

The equilibrium rate constant for endosulfan adsorption on soils cannot be calculated by the existing pseudo first order and pseudo second order rate equations because of the non-homogeneity of the soil. Adsorption of endosulfan in all soils followed Langmuir isotherm and it is inferred that the adsorption was monolayer.

Both physical and chemical forces pronounced adsorption. The effect of chemical forces was predominant in red soil and chalk soil. The adsorption of endosulfan towards soil particles was highly influenced by CASC and OM content. Maximum desorption was achieved with ethanol but tap water and distilled water can effectively be used in the field. Narrow variations in the pH of soil medium did not have any influence on endosulfan adsorption or desorption. The decrease in pH of the soil reduced the adsorption and the increase in concentration increase the adsorption. The presence of clay, silt and OM

immobilizes endosulfan in the soil. Hence, increasing the CASC and OM content in the contaminated soil/zone can be an alternative solution to prevent the mobility of endosulfan.

Fig. 1 Kinetics of endosulfan adsorption on different soil samples

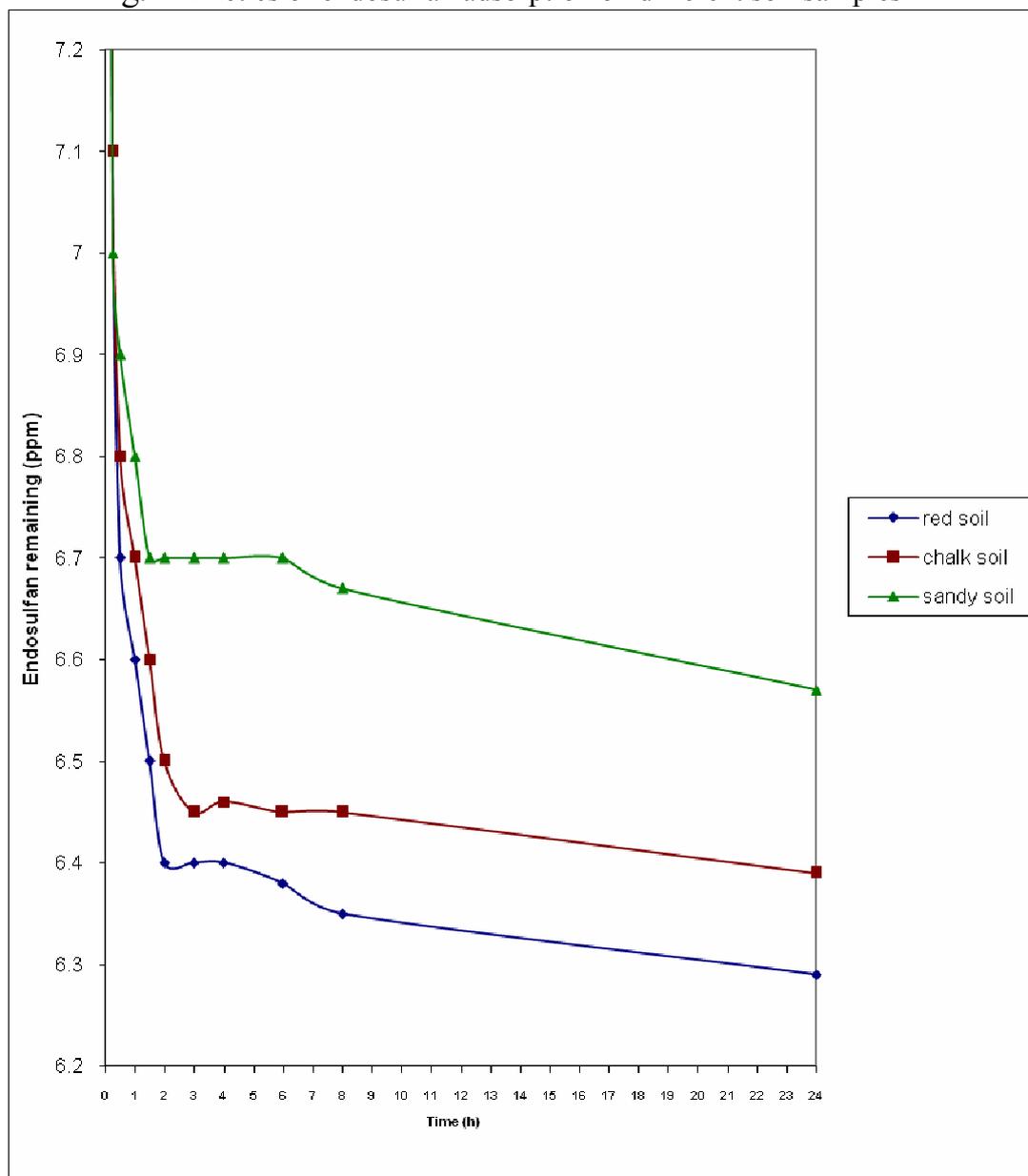


Fig. 2 Rate of adsorption of endosulfan on soil samples.

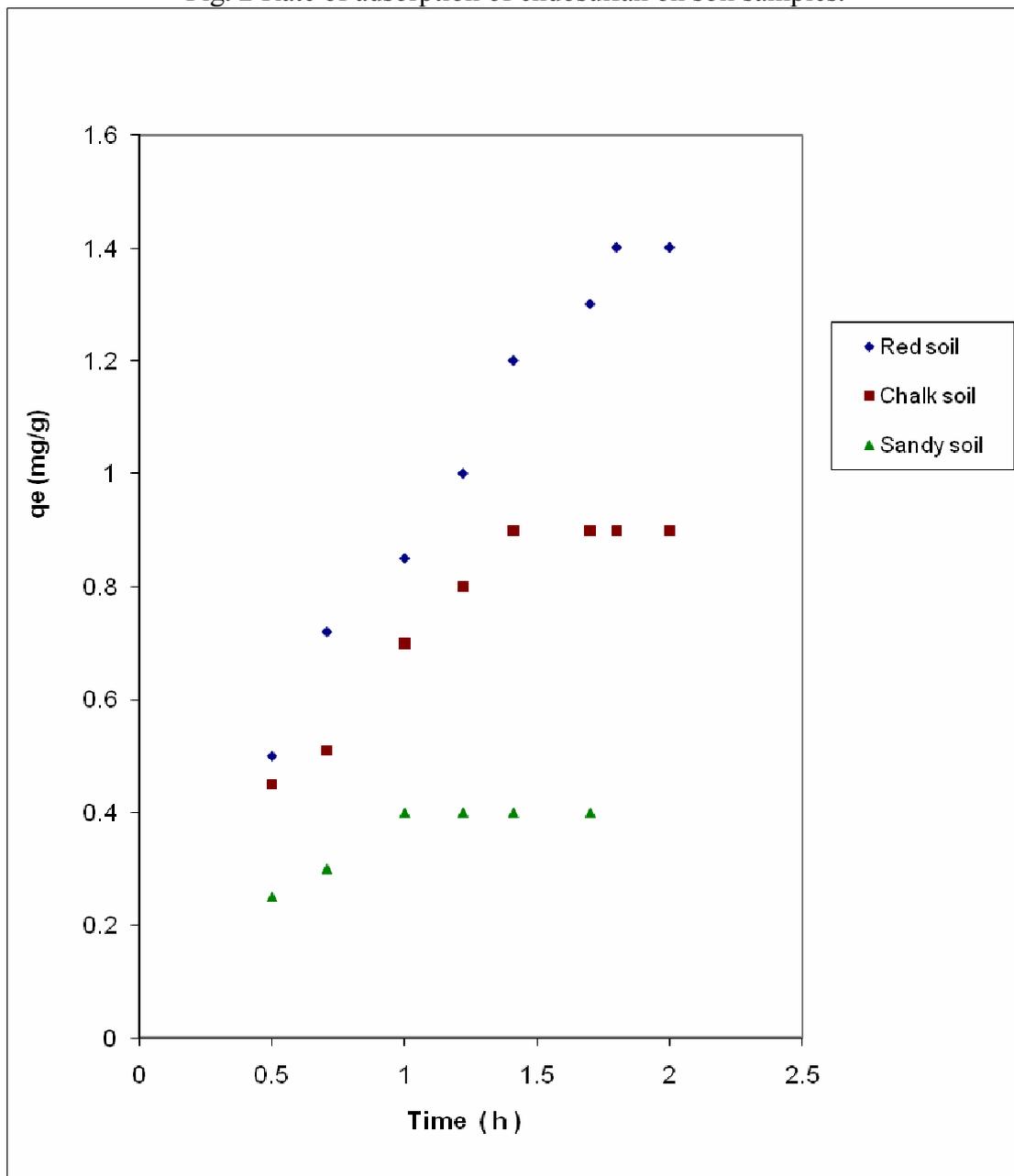


Fig. 3 Linearized Langmuir isotherm of endosulfan on (a) red soil, (b) chalk soil and (c) sandy soil.

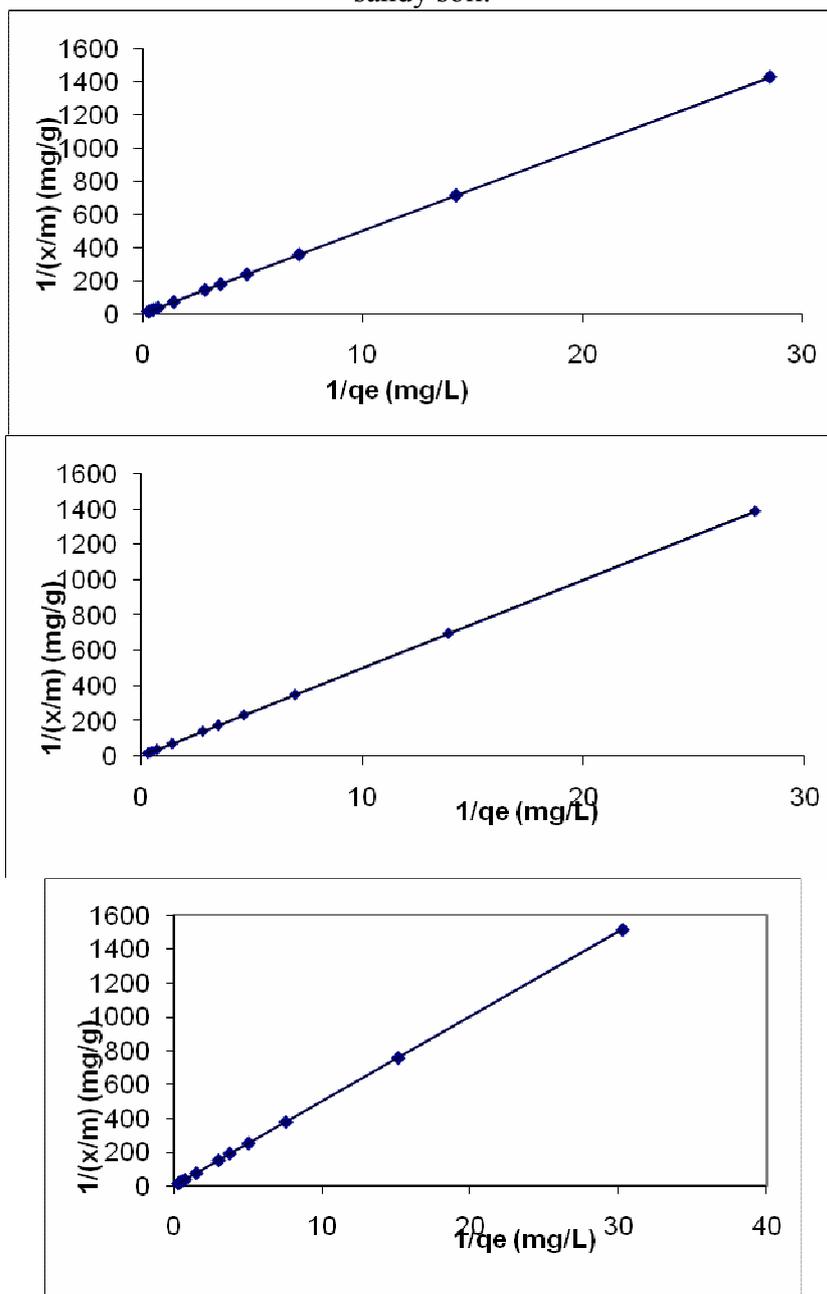
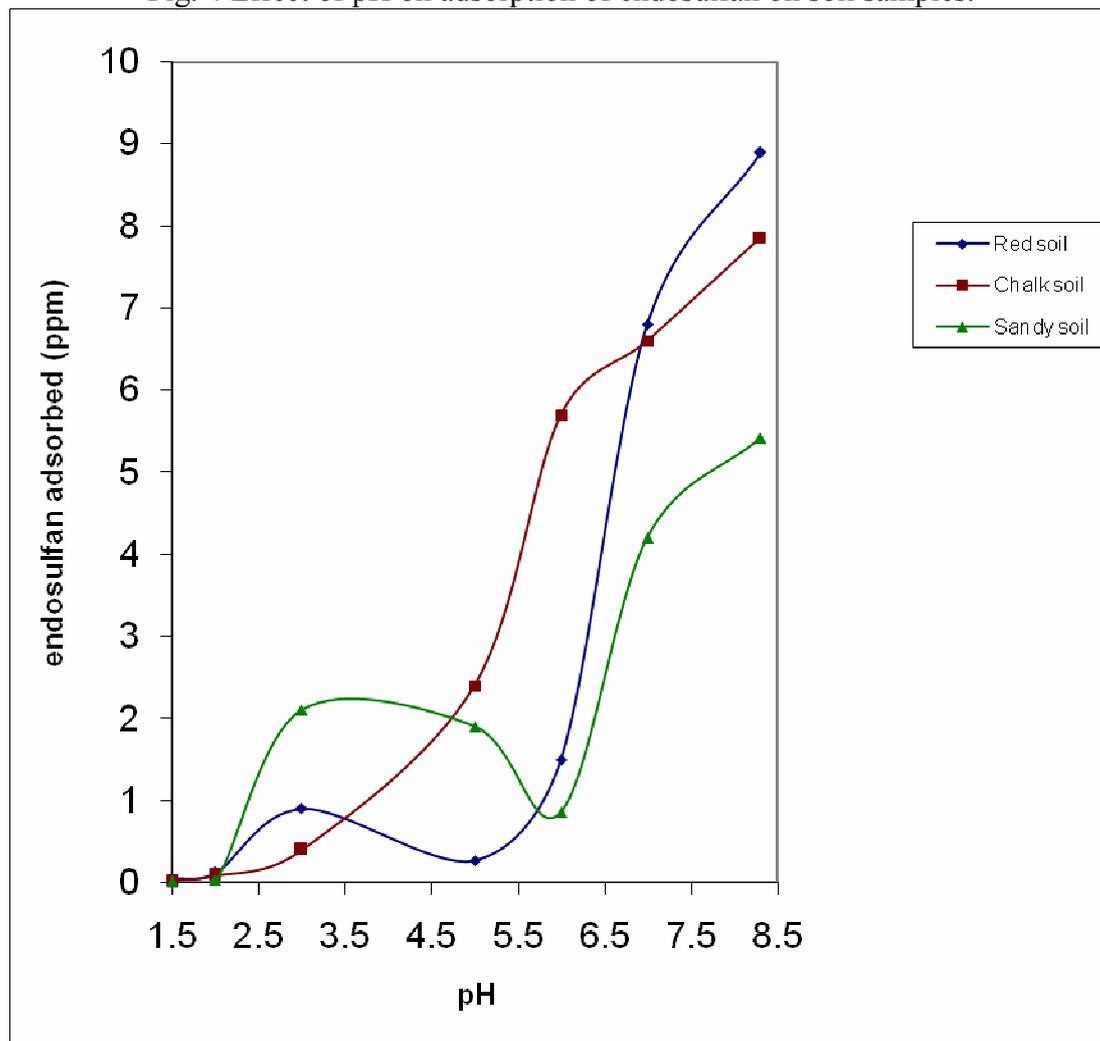


Fig. 4 Effect of pH on adsorption of endosulfan on soil samples.



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