

# Soil adsorption study of Dimethoate to evaluate its leaching potential by spectrophotometry

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Received June 02, 2013, Revised manuscript received July 24, 2013, Accepted September 12, 2013

## Abstract

With a view to study the leaching potential and consequently surface and ground water contamination, the adsorption of dimethoate on five soils of different characteristics has been carried out by using a batch equilibrium technique. A spectrophotometric methodology based on the reaction of thioglycolic acid, formed from microwave assisted alkaline hydrolysis of dimethoate, with carbon disulfide and nickel(II) acetate to form methyl isobutyl ketone extractable yellow colored nickel(II)-thioxanthate complex showing  $\lambda_{\max}$  at 378 nm has been developed for the purpose. The molar absorptivity ( $\epsilon$ ) and Sandell's sensitivity were found to be  $1.2 \times 10^3$  L/mol cm and  $0.19 \mu\text{g}/\text{cm}^2$  respectively. The leaching potential has been evaluated by Groundwater Ubiquity Score (GUS) and the values obtained in the range 1.85-2.45 classify dimethoate as a transition pesticide and thereby it poses a potential risk to the aquatic environment.

**Keywords:** Dimethoate, Environmental Pollution, Leaching, Soil-Adsorption Study, Spectrophotometry

## 1. Introduction

Pesticides pollute soil and water both by direct application to crops and through their residues [1]. These chemicals enter the soil in different ways; e.g., by washing of remaining deposits on crops by rain or irrigation water and incorporation with crop residues. In the soil environment, the pesticides get fractionated between the soil solution phase and the soil solid phase through adsorption on clay and organic fractions [2]. Adsorption of pesticides affects the various processes like mobility, persistence, volatilization, bioaccumulation, bioactivity and toxicity which influence the final fate of these compounds in the soil environment and determine the extent of contamination of surface water and groundwater [3]. A number of experimental studies on pesticide adsorption by soils have been performed to predict the pesticide movement in soils and aquifers [4-8].

Dimethoate (Dimethyl S-(methylcarbamoylmethyl) phosphorothiolothionate) is a broad spectrum organophosphorus insecticide exhibiting both contact and systemic action. It has been used against a wide range of insects and mites on various crops: citrus, cotton, fruit, olives,

potatoes, tea, vegetables etc. Dimethoate is used also to control household flies and on livestock [9,10]. Dimethoate is a moderately toxic insecticide and the oral  $\text{LD}_{50}$  value is 320 mg/Kg for rats [11]. The negative effects of this insecticide on the non-target organisms and the ecosystems are also reported [12-14]. Because of the wide range of uses and its toxic effects, there is a concern about potential effects not only on general population from dietary exposure to residues left on food crops, but also potential occupational health risks to workers who handle and often come in contact with these chemicals. This, therefore, necessitates convenient, reliable and sensitive method for the analysis of dimethoate in technical formulations and its residues on agricultural samples viz. food stuffs to check for health hazards.

Various analytical methods viz. HPLC, GC-MS, LC/LC-MS, voltammetric, spectrofluorometric, bioanalytical, spectrophotometric methods have been reported in the literature for the determination of dimethoate [15-23]. Spectrophotometric procedure can tolerate little interfering materials and the equipment being cheap and easily accessible in all the laboratories, it is most convenient method for the determination of the insecticide. Some spectrophotometric methods

involve the determination of insecticides by total phosphorus measurement, based on the formation of molybdenum blue using various reducing agents whereas some involve the oxidation of dimethoate and the determination of unreacted oxidant with dyes [20-23]. Some of these methods suffer from drawbacks such as poor sensitivity, instability of color, longer time required for color development, interference from foreign ions or absorption variations by the blank. To overcome these drawbacks, in the present study, a simple, rapid, selective and sensitive spectrophotometric method has been developed for the determination of dimethoate. The method is based on the microwave-assisted facile alkaline hydrolysis of the insecticide to form thioglycolic acid and latter can be transformed to methyl isobutyl ketone extractable yellow colored nickel(II)-thioxanthate complex showing  $\lambda_{\text{max}}$  at 378 nm. The proposed spectrophotometric method was successfully applied to the analysis of dimethoate in commercial insecticide formulation (for the purpose of quality control) and its recovery from vegetables and water samples (to monitor health hazards). The present method has also been validated to study the adsorption of dimethoate insecticide on five Indian soils of different soil characteristics. The various adsorption parameters viz. distribution coefficient or soil-adsorption coefficient ( $K_d$ ), soil organic carbon partition coefficient ( $K_{oc}$ ) and thermodynamic functions ( $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$ ) have been calculated. The pesticide leaching is an important process with respect to contamination risk to aquatic environment and the risk of leaching has also been evaluated for dimethoate in terms of Groundwater Ubiquity Score (GUS).

## 2. Materials and Methods

### Apparatus

All the spectrophotometric measurements have been made with carry 100 Bio UV-V is spectrophotometer. A microwave oven (Samsung Electronics, New Delhi, India) was used to carry out hydrolysis. The pH measurements were made on Cyber Scam 2500 pH meter (Eutech Instruments, Singapore). A shaking incubator (Genei, Bangalore, India) was used in the soil adsorption study.

### Reagents and Samples

Acetonitrile (Merck, Mumbai, India) was kept over phosphorus pentoxide (5 g/L) and distilled twice. The analytical standard of dimethoate (Fluka, Switzerland) was used. The purity was checked by a reported method [23] and its stock solution ( $1.0 \times 10^{-3}$  M) was prepared in acetonitrile. Acetic acid, carbon disulphide, methyl isobutyl ketone (MIBK), nickel(II) acetate and potassium hydroxide were obtained from Merck, Mumbai, India and were used as received. Sodium acetate-HCl buffer of pH  $\approx$  3 was prepared by mixing equal volumes of aqueous 0.2 M sodium acetate (Qualigen, Mumbai, India) and 0.2 M HCl (Merck, Mumbai, India). The soils used in the adsorption study were collected from Lahul-Spiti District of Himachal Pradesh, India.

### Preparation of Calibration Graph for Pure Compound

Aliquots (0.1-2.0 mL) of standard solution of dimethoate ( $10^{-3}$  M in acetonitrile) were taken in 10 mL measuring flasks and diluted to 3 mL with acetonitrile. Each solution was mixed with potassium hydroxide (1 mL,  $\approx$  1 M) and 3 mL of distilled water and kept in microwave oven for 60 seconds. The hydrolyzed solution was then mixed with one drop of carbon disulphide to form respective thioxanthate, then treated with acetic acid (2 mL,  $\approx$  1 M in water) not only to neutralize the excess alkali but also to make the condition slightly acidic. This solution was poured into a 100 mL separating funnel already containing 1 mL, 0.01 M nickel(II) acetate solution and 10 mL HCl-CH<sub>3</sub>COONa buffer (to maintained the pH of the solution at  $\approx$  3.0). The contents of the funnel were equilibrated two times with MIBK using 4 mL each time and total volume made to 10 mL with MIBK. The solution was dried by shaking with anhydrous sodium sulphate and the absorbance of yellow colored solution was measured at 378 nm against a reagent blank and calibration curve was prepared. The calibration characteristics viz. Beer's law range, molar absorptivity, Sandell's sensitivity, slope and intercept values and correlation coefficient calculated from calibration graph are given in Table 1.

**Table 1.** Spectrophotometric determination of dimethoate: Calibration characteristics

Optical characteristics	Corresponding value
$\lambda_{\max}$	378 nm
Beer's law range	2.29-45.8 $\mu\text{g/mL}$
Molar absorptivity ( $\epsilon$ )	$1.2 \times 10^3 \text{ L/mol cm}$
Sandell's sensitivity	$0.19 \mu\text{g/cm}^2$
Stability of color	300 min
Slope	0.0048
Intercept	0.0096
Correlation coefficient (R)	0.9942

### Formulation Analysis

An emulsifiable concentrate (EC), Rogor (Rallis India Ltd., Agrochemical Division, Mumbai, India), containing 30% active ingredient, procured from an authorised pesticide dealer was used. A single large sample of the formulation equivalent to 12.5 mg active ingredient was dissolved in 25 mL acetonitrile. The solution was further diluted 10 times with acetonitrile and suitable aliquots (0.5-0.8 mL) of this solution were taken and processed for analysis as described above for the pure compound. Table 2 gives the assay results.

**Table 2.** Assay of a commercial formulation of dimethoate (Rogor) containing 30% active ingredient

Amount taken ( $\mu\text{g}$ )	Recovery (%) <sup>a</sup>	
	Present method	Comparison method <sup>b</sup>
25	$94.6 \pm 0.6$	$91.6 \pm 0.8$
30	$97.2 \pm 0.4$	$95.3 \pm 1.3$
35	$92.9 \pm 1.2$	$90.8 \pm 0.9$
40	$95.8 \pm 0.8$	$93.7 \pm 0.7$

<sup>a</sup> Values are mean  $\pm$  standard deviation for 5 determinations; <sup>b</sup> Reference [23].

**Table 3.** Recovery of dimethoate from vegetable and water samples

Active ingredient added, $\mu\text{g}$	Recovery of active ingredient (%) <sup>a</sup>					
	Present method			Comparison method <sup>b</sup>		
	Cauliflower	Pea	Water	Cauliflower	Pea	Water
25	$90.7 \pm 0.86$	$78.9 \pm 1.02$	$91.4 \pm 0.64$	$82.2 \pm 1.08$	$76.5 \pm 1.02$	$90.6 \pm 0.90$
30	$87.6 \pm 1.01$	$83.2 \pm 0.89$	$92.3 \pm 0.56$	$84.8 \pm 0.92$	$81.8 \pm 0.92$	$88.8 \pm 1.02$
35	$90.9 \pm 0.97$	$92.3 \pm 0.90$	$94.7 \pm 0.82$	$91.5 \pm 0.90$	$84.8 \pm 0.86$	$90.8 \pm 0.90$
40	$92.4 \pm 0.64$	$95.6 \pm 0.48$	$97.3 \pm 1.06$	$90.2 \pm 0.72$	$87.6 \pm 0.82$	$92.6 \pm 0.86$

<sup>a</sup> Values are mean  $\pm$  standard deviation for 5 determinations; <sup>b</sup> Reference [23].

### Determination of Dimethoate in Vegetables and Water Samples

Dimethoate standard solution was prepared by dissolving 25 mg insecticide in 50 mL acetonitrile; this solution was further diluted 10 times with acetonitrile for a final concentration of 50  $\mu\text{g/mL}$  dimethoate. Suitable aliquots (0.5-0.8 mL) of this standard solution were added to 25 g portions of vegetables (cauliflower and pea) and were mixed thoroughly. These samples were blended with chloroform according to the general procedure of Schenk et al. [24] for the determination of dimethoate insecticide in vegetables. Sample (25 g) was taken in a blender cup and blended with 50 mL of chloroform. The sample was filtered through coarse filter paper and the filtrate was transferred into a 250 mL separatory funnel. NaCl (5 g) was added, the funnel was shaken for one minute and the phases were allowed to separate for 15 mins. The lower aqueous phase and any emulsion were discarded. Anhydrous sodium sulphate (4 g) was added to the separatory funnel, and the funnel was shaken for 30 s. The dried extract was filtered through coarse filter paper and evaporated to dryness. The residue was dissolved in 3 mL of acetonitrile and was processed for analysis as described above for the pure compound. Table 3 gives the assay results. The proposed method has also been applied to the determination of insecticide in spiked water samples. Aliquots (0.5-0.8 mL) of standard solution having a concentration 50  $\mu\text{g/mL}$  were added to 25 mL water samples and were mixed thoroughly. The samples were extracted with chloroform and processed for analysis in the same manner as described above. Table 3 presents the results.

**Table 4.** Characteristics of the different Indian soils used in the adsorption study of dimethoate

Soil samples	pH	Clay (%)	Organic carbon (%)	Cation exchange capacity (meq/100 g)
I	7.49	9.8	1.06	17.59
II	4.94	10.2	0.96	9.23
III	5.69	26.3	2.2	37.38
IV	7.43	16.3	0.59	8.8
V	6.87	12.5	1.32	12.2

**Soil Adsorption Study**

Dimethoate adsorption isotherms on five Indian soils of different soil characteristics (Table 4) were obtained by the batch equilibration technique using 50 mL conical flask at two different temperatures, i.e. 20°C and 30°C. Triplicate soil samples (2 g) were equilibrated with dimethoate solutions in the concentration range from 11.45-68.7 µg/mL on the shaker at 150 rpm at definite temperature for 6 h equilibrium time [25]. After equilibration, the suspensions were centrifuged and the equilibrium concentrations ( $C_e$ ) were determined in supernatants by the differential pulse polarographic procedure described above. Adsorption parameters for the adsorption process viz. distribution coefficient or soil-adsorption coefficient ( $K_d$ ), soil organic carbon partition coefficient ( $K_{oc}$ ) and Groundwater

Ubiquity Score (GUS) have been calculated by using equations 1-3 respectively [7,26].

$$K_d = \frac{X}{C_e} \tag{1}$$

$$K_{oc} = K_d \times \left( \frac{100}{\%O.C.} \right) \tag{2}$$

$$GUS = \log t_{1/2} [4 - \log(K_{oc})] \tag{3}$$

Where X is the amount of pesticide adsorbed mg/Kg of the adsorbent;  $C_e$  is the equilibrium solution concentration (mg/L);  $t_{1/2}$  = pesticide persistence (half life), OC = organic carbon content of soil. The GUS score is used to study the leaching behaviour of pesticides and these can be classified as leacher ( $GUS > 2.8$ ), transition ( $2.8 > GUS > 1.8$ ) and non-leacher ( $GUS < 1.8$ ) [26]. The thermodynamic parameters viz. Gibb's free energy ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) have also been calculated by using equations 4-6 respectively [27].

$$\Delta G^\circ = -RT \ln K_d \tag{4}$$

$$\ln \left[ \frac{(K_d)_2}{(K_d)_1} \right] = \frac{\Delta H^\circ (T_2 - T_1)}{R T_1 T_2} \tag{5}$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \tag{6}$$

where R = gas constant, T = absolute temperature.

**Table 5.** Adsorption parameters for the adsorption of dimethoate insecticide on five Indian soils at two different temperatures

Soil samples	20°C				30°C			
	$K_d$	$K_{oc}$	GUS	Isotherm	$K_d$	$K_{oc}$	GUS	Isotherm
I	1.54	145.03	2.21	S-type	1.29	121.55	2.30	S-type
II	1.81	188.37	2.07	S-type	1.50	156.47	2.17	S-type
III	2.39	108.61	2.36	S-type	1.87	85.00	2.45	S-type
IV	1.70	287.58	1.85	S-type	1.59	269.07	1.88	S-type
V	2.01	152.24	2.18	S-type	1.44	109.09	2.35	S-type

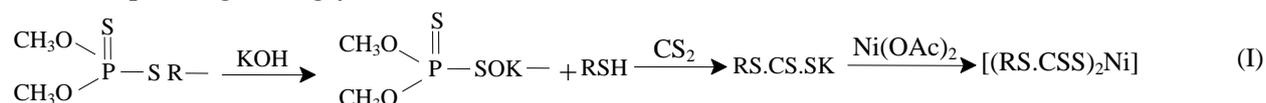
**Table 6.** Thermodynamic parameters for the adsorption of dimethoate on five Indian soils

Soil samples	$\Delta G^\circ$ (kJ/mol)		$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (kJ/K mol)
	20°C	30°C	25°C	25°C
I	-1.05	-0.64	-13.07	-0.0410
II	-1.44	-1.03	-13.89	-0.0424
III	-2.12	-1.59	-20.80	-0.0636
IV	-1.29	-1.16	-4.94	-0.0125
V	-1.70	-0.91	-46.13	-0.1504

All these parameters for the adsorption of dimethoate on five Indian soils of different soil characteristics were calculated and the results are shown in Tables 5 and 6.

### 3. Results and Discussions

The proposed method is based on the microwave-assisted hydrolysis of dimethoate into corresponding thioglycolic acid which



MIBK is an extracting solvent of choice because it is not only safe in comparison of commonly used toxic extracting solvents like benzene, chloroform, dichloromethane, ethyl acetate etc. and it relatively extract the coloured product quantitatively from aqueous solution. It is worth to mention here that thiophosphoric acid (other hydrolytic product) and nickel(II) acetate (colouring reagent) remain in aqueous phase having no affinity for organic phase.

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Effects of time of hydrolysis and pH on the development, stability and sensitivity of the color, vis-à-vis development of the proposed method has been studied before applying it to the analysis of dimethoate in commercial formulations and soil adsorption study. The hydrolysis of dimethoate to corresponding thioglycolic acid was carried out rapidly in microwave. Microwave heating has advantages over conventional heating such as greater speed, higher reaction rates and greater selectivity [28]. Microwave-assisted hydrolysis has also been demonstrated to be reproducible, time-saving and efficient [29]. The optimum time required for complete hydrolysis was obtained by varying the time of hydrolysis from 10-80 s and

reacts with carbon disulphide to form thioxanthate. The later is quantitatively transformed with nickel(II) acetate in water into yellow colored nickel(II)-thioxanthate complex (I) which is extractable into Methyl isobutyl ketone (MIBK). The analysis is accomplished by measuring the absorbance of the extract at 421 nm. The most plausible course of reaction is:

measuring corresponding absorbance of yellow nickel(II) complex at 378 nm. It has been observed that maximum color intensity and its stability was obtained corresponding to 60s hydrolysis time. It has been observed that yellow color is developed and stable in acidic medium (pH  $\approx$  3). The desired pH was maintained with the use of sodium acetate-acetic acid buffer in the whole experiment.

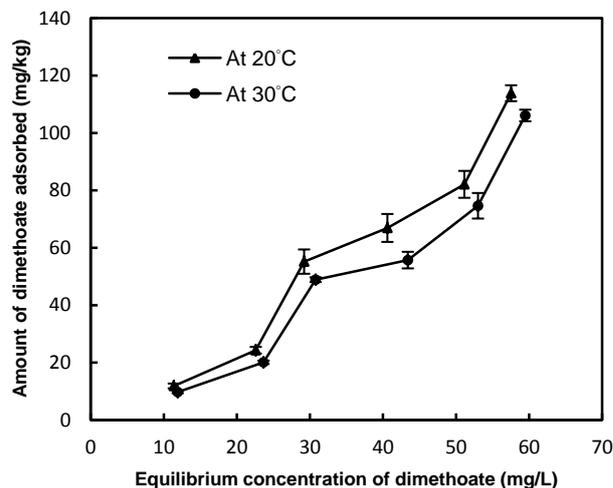
The kinetic stability of colored complex was studied with time and the color is found to be stable for at least 300 mins. Under the optimized experimental conditions, the proposed spectrophotometric method obeys Beer's law in the range of 2.29-45.8  $\mu\text{g/mL}$  for dimethoate. The method is quite sensitive and the molar absorptivity ( $\epsilon$ ) and Sandell's sensitivity were found to be  $1.2 \times 10^3 \text{ L/mol cm}$  and  $0.19 \mu\text{g/cm}^2$  at 378 nm. The method has successfully been applied to the analysis of a commercial formulation of dimethoate for its active ingredient content for the purpose of quality control. The recoveries were in the range 92.9-97.2%, with RSDs in the range 0.4-1.2% (Table 2). The results have, however, been compared with an independent method [23]. Recoveries of the insecticide from vegetables (cauliflower and peas) and spiked water samples were good, ranging from 78.9-97.3%, with RSDs ranging from 0.48-1.06% (Table 3). The validity of the method was assessed by investigating the effect of common cations like  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Fe}^{+3}$ ,  $\text{Pb}^{+2}$ , and  $\text{Cl}^-$ . These ions do not interfere in the method.

The adsorption isotherms of dimethoate insecticide on five Indian soils of different soil characteristics at two different temperatures are

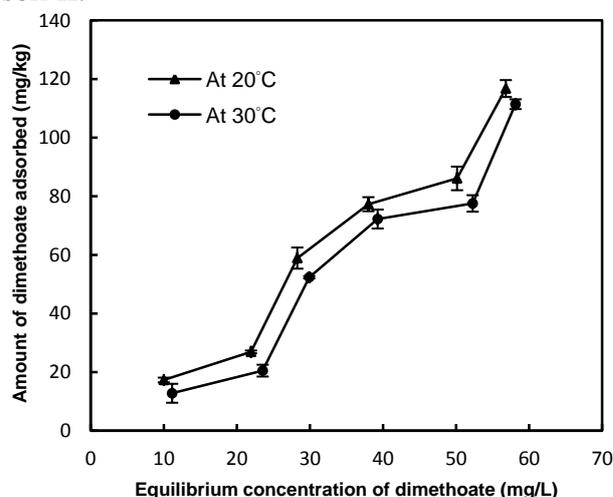
shown in Figs. 1 to 5. According to the initial portion of the curve, these isotherms can be classified as S-type of Gile's classification in all cases [30]. The S-types of isotherms are common and represent a system where a solid surface has a higher affinity for the solvent than for solutes [4]. Adsorption parameters such as the soil-adsorption coefficient ( $K_d$ ), soil organic carbon partition coefficient ( $K_{oc}$ ) and Groundwater Ubiquity Score (GUS) for the adsorption of dimethoate were also calculated and are presented in Table 5.  $K_d$  values for dimethoate were observed in the range 1.29-2.39 for all the soils. It has been observed that in general, the higher the  $K_d$  value, the greater is the pesticide adsorption [5]. From Table 5 it can be inferred that dimethoate is adsorbed maximally in case of soil III (with higher  $K_d$ ). The  $K_d$  for a pesticide is soil-specific and varies with soil texture and its organic matter content but the  $K_{oc}$  is less soil specific [31] and is calculated by normalizing adsorption coefficient ( $K_d$ ) with the organic carbon (OC) content of the soil. The value of  $K_{oc}$  for dimethoate adsorption on five soil substrates decreased with increased fraction of organic content, indicating that adsorption is not only due to organic matter content of soil but also influenced through some other factors [5]. The organic matter content of soils affects the adsorption of pesticide: the higher the organic matter contents, the higher the adsorption [3]. The cation exchange capacity (CEC) is another parameter that influences the adsorption of pesticide. The value of CEC is directly proportional to the hydrophobic nature of adsorbent: the greater the value of CEC of soil, the more hydrophobic is its surface. The organic pesticides, being more hydrophobic (low water solubility), have a higher adsorption affinity for the soils with higher CEC [32]. The thermodynamic parameters for the adsorption of dimethoate insecticide on five soils were also evaluated and are presented in Table 6. The negative value of entropy change ( $\Delta S^\circ$ ) is due to a decrease in randomness with adsorption. The value of Gibb's free energy ( $\Delta G^\circ$ ) and enthalpy change ( $\Delta H^\circ$ ) for the adsorption of dimethoate insecticide were also observed negative in all the cases suggesting the energetically favourable adsorption process [27]. From the negative values of enthalpy change ( $\Delta H^\circ$ ) it can be inferred that the value of soil-adsorption

coefficient ( $K_d$ ) decreased with rise in temperature. This is due to the effect of temperature on the weak binding between dimethoate and soil particles [33]. Because dimethoate has very weak adsorption in all the tested soils, it can lead to the penetration of this insecticide into groundwater.

**Figure 1.** Adsorption isotherm of dimethoate on soil I.



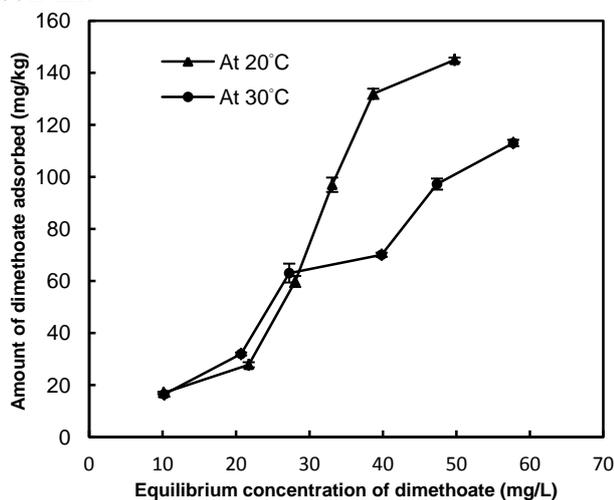
**Figure 2.** Adsorption isotherm of dimethoate on soil II.



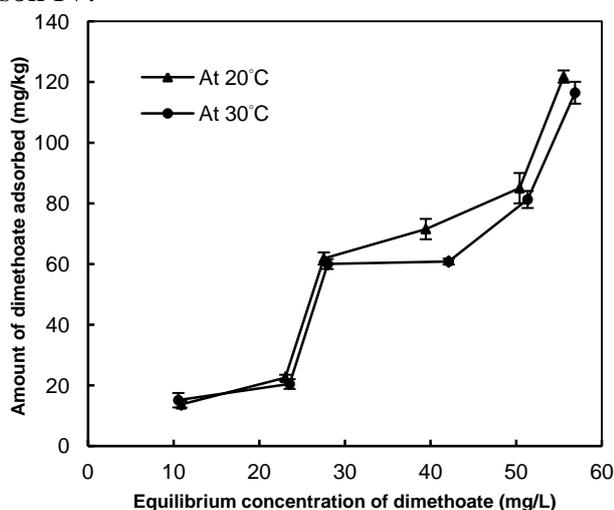
A number of models are available to evaluate the leaching potential of pesticide and the associated environmental pollution risk. The Groundwater Ubiquity Score (GUS) is the most commonly used model which relates pesticide persistence (half life) and adsorption in soil ( $K_{oc}$ ). The leaching potential of the insecticide in terms of the GUS index was determined by using the experimentally observed  $K_{oc}$  value for each soil sample and the reported half life of dimethoate [26]. The GUS score for dimethoate has been observed in the range 1.85-2.45 which classifies it as a transition insecticide. This

observation calls for the judicious use of this insecticide especially near the water bodies. The soils where dimethoate is maximally used should be amended with the addition of high organic matter content (manure, peat, municipal sewage sludge, etc.) in order to increase the insecticide's retention and reduce its mobility.

**Figure 3.** Adsorption isotherm of dimethoate on soil III.



**Figure 4.** Adsorption isotherm of dimethoate on soil IV.

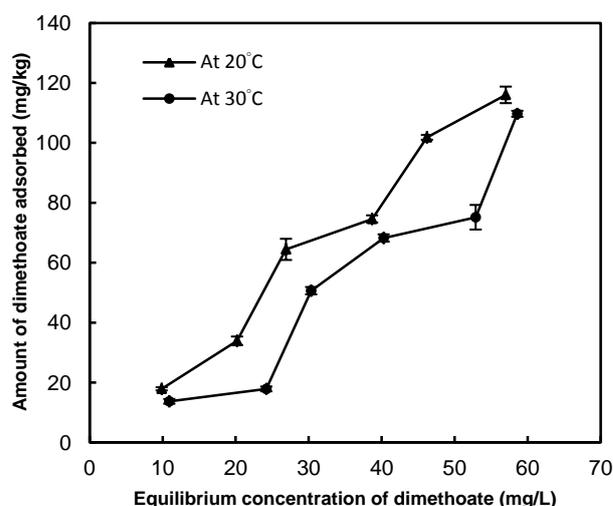


#### 4. Conclusion

The leaching of pesticide is an important risk with regard to the aquatic environment and this risk has been evaluated for dimethoate. It can be concluded that the insecticide has low values of soil organic carbon partition coefficient ( $K_{oc}$ ) suggesting its weaker adsorption in soil types and thus penetration into water sources. The GUS of the insecticide has been observed ( $2.8 > GUS > 1.8$ ), classifying dimethoate as a transition pesticide in terms of leaching behaviour and hence it should be used

judiciously to prevent groundwater contamination. Because pesticide adsorbed by soil is desorbed in relation to change in the concentration of soil constituents, there may also be undesirable side effects for subsequent crops, like phytotoxicity. The proposed spectrophotometric method is quite sensitive and obeys Beer's law in the range of 2.29-45.8  $\mu\text{g/mL}$  for dimethoate. The method has also been applied with success to the determination of this insecticide in residues on environmental samples where the recoveries are good.

**Figure 5.** Adsorption isotherm of dimethoate on soil V.



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