

Assessment of environmental toxicity of oxydemeton methyl by differential pulse polarography

Devender Kumar Sharma^{1*}, Atul Gupta² and Nisha Sharma¹

¹Department of Chemistry, Himachal Pradesh University, Shimla -171005, India

²Department of Chemistry, S.V.G.C. Ghumarwin-174021, India

*To whom correspondences should be addressed

E-mail: dksharma_dk@rediffmail.com

Received April 01, 2011, Revised manuscript received November 07, 2011, Accepted November 16, 2011

Abstract

In view of the potential hazards associated with the use of oxydemeton methyl- a widely used insecticide, its determination in environmental samples viz. soil, water and food stuffs has been studied to assess its environmental toxicity. A differential pulse polarographic method has been developed for the purpose. It is based on microwave assisted alkaline hydrolysis of the insecticide to 2-ethylsulfinyl-ethyl mercaptan which yields analytically useful diffusion controlled peak at -312 mV at dropping mercury electrode (DME). The peak is applicable to oxydemeton methyl determination in the linearity range 8.01×10^{-7} to 2.40×10^{-5} M with correlation coefficient 0.9948. The proposed method shows good precision and accuracy with maximum relative standard deviation (RSD) of 1.05%. The method has successfully been validated to the analysis of this insecticide in commercial formulations and its recovery from vegetables and water samples. The leaching potential of insecticide vis-à-vis associated environmental pollution risk was evaluated by the Groundwater Ubiquity Score (GUS) model. Its value has been observed < 1.8 which classifies oxydemeton methyl as non leacher pesticide in terms of leaching behaviour.

Keywords: oxydemeton methyl; differential pulse polarography; formulation analysis; soil-adsorption study; GUS

1. Introduction

Oxydemeton-methyl, S-[2-(ethylsulfinyl) ethyl]O,O-dimethyl phosphorothioate, is a systemic contact insecticide belonging to organophosphate family. It has been widely used in agriculture to control many insects primarily aphids, mites, jassids and sawflies on various crops primarily to mustard, broccoli and cauliflower [1,2]. The agro-environmental pollution caused by the extensive use of this indispensable chemical is of major concern because of its high toxicity. The oral LD_{50} value for oxydemeton-methyl is 10 mg/Kg for rats [3]. It has been reported to show central nervous system depressant activity, reproductive effects, genotoxic effects and mutagenic effects [4-6]. The pollution of soil, ground and surface water involves a serious risk to the environment and also to the human health due to direct exposure or through residues in food and drinking water [7]. There is an also potential occupational health risk to workers who often handle and come in contact with this chemical.

In general the fate of pesticide is mostly played out in the soil as the later is ultimate

reservoir for pesticides irrespective of their application target. These chemicals enter the soil in different ways i.e. with washing of remaining deposits on crops by rain or irrigation water and incorporated with crop residues. In soil environment, the pesticides get fractionated between soil solution phase (in free form) and soil solid phase through adsorption on clay and organic fractions (in bounded form) [8]. The adsorption of pesticides affects the various processes like bioactivity, mobility, persistence, toxicity, volatilization and bioaccumulation because all these phenomena are operative only on the unadsorbed fractions of pesticide [9]. All these processes influence the extent of surface and ground water contaminations. Therefore, from environmental point of view, thorough understanding of adsorption of this pesticide on soil is paramount for the prediction of its movement in soils and aquifers. Of no less importance is the determination of this insecticide in residues on environmental samples for the purpose of monitoring pollution and health hazards.

To accomplish above objectives, it is therefore, inevitable to find a simple, sensitive

and reliable technique of wide applicability for the analysis of oxydemeton methyl. Several analytical methods like GC-MS [10], GLC [11], LC-MS [12,13], bioanalytical methods [3] have been reported in the literature for the determination of oxydemeton-methyl. The electrochemical methods are now finding much greater use in pesticide analysis because the determinations can be done even at larger dilutions and with smaller volumes of solutions without any interference from inert carriers commonly present in their formulations. On the basis of accuracy of results and trace determination, differential pulse polarography (*DPP*) has emerged as a suitable technique among electrochemical methods of analysis. To the best of our knowledge, polarographic methods for the determination of oxydemeton-methyl have attracted little attention. In a significant effort in this context, we have been able to work out a remarkably sensitive differential pulse polarographic method to analyze oxydemeton methyl in the samples of environmental importance. Advantage has been taken of the microwave assisted facile alkaline hydrolysis of the insecticide to form 2-ethylsulfanyl-ethyl mercaptan and the reaction of later at dropping mercury electrode (*DME*) to yield analytically useful diffusion controlled peak at -312 mV in developing the method. Microwave assisted hydrolysis is advantageous than conventional heating in terms of higher reaction rates and greater selectivity and reproducibility [14,15]. The results have been calculated on the basis of calibration graph drawn between insecticide concentration and peak current. The method has been applied to the analysis of oxydemeton-methyl in commercial insecticide formulation (for the purpose of quality control) and its recovery from fortified vegetables and water samples (to monitor health hazards). The present method has also been validated to study the adsorption of oxydemeton-methyl 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 Groundwater Ubiquity Score (*GUS*) have been calculated. The thermodynamic parameters like Gibb's free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) for the

adsorption of insecticide have also been calculated.

2. Materials and methods

2.1. Apparatus

All Polarographic measurements were made with an Elico (India) Polarographic Analyser (model CL-362). The electrode system consisted of *DME* as working electrode, *SCE* as reference electrode and platinum as an auxiliary electrode. Domestic microwave oven, Samsung, India was used to carry out hydrolysis. The pH measurements were made on Cyber Scam 2500 pH meter. Genei (*TM*) shaking incubator, Bangalore was used in soil adsorption study.

2.2. Reagents and Samples

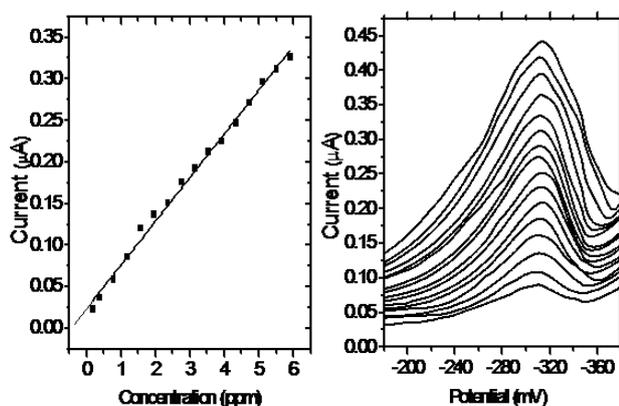
Acetonitrile (Merck) was kept over phosphorus pentoxide (5 g L^{-1}) and distilled twice. The analytical standard of oxydemeton-methyl (Sigma-Aldrich) was used. The purity was checked by reported method [16] and its stock solution ($2.0 \times 10^{-4} \text{ M}$) was prepared in acetonitrile. Potassium nitrate (Merck, AR, 0.1 M solution in water) was used as supporting electrolyte. Potassium hydroxide (Merck, LR), sodium acetate (Qualigen, AR) and acetic acid (Ranbaxy, LR) were used as received. Triton-x-100 (Merck), 0.002% in acetonitrile was used as suppressor.

2.3. Preparation of Calibration Graph for Pure Compound

The method for analyzing oxydemeton-methyl is standardized by optimizing experimental conditions viz. time required for complete hydrolysis and instrumental parameters like pulse amplitude and drop time variation etc. The calibration curve was prepared on the best optimized conditions. Aliquots (0.1-3.0 mL) of standard solution of insecticide ($2.0 \times 10^{-4} \text{ M}$ in acetonitrile) were taken in 25 mL measuring flasks and volume made to 3 mL with acetonitrile. Each solution was mixed with aqueous potassium hydroxide (1 mL, $\sim 0.1 \text{ M}$) and 5 mL of water and kept in microwave oven for 60 seconds. The hydrolyzed oxydemeton-methyl solution was then treated with aqueous acetic acid (2 mL, $\sim 0.1 \text{ M}$) and is mixed with aqueous KNO_3 supporting electrolyte (10 mL, 0.1M). Triton-x-100 (2 mL, 0.002 % in acetonitrile) was added

as suppressor and final volume made to 25 mL with sodium acetate-acetic acid buffer to maintain the pH of solution approximately at 4.5. Nitrogen gas was passed through each solution for 15 min. The differential pulse polarogram of each solution was recorded at room temperature (24 ± 1)°C with following instrumental parameters : initial potential = -100 mV; drop time = 2 s; pulse amplitude = 50 mV and scan rate = 3 mV/s. Calibration graph was constructed by plotting peak current (μA) (corresponding to -312 mV peak) versus concentration of oxydemeton-methyl ($\mu\text{g mL}^{-1}$) and is shown in Fig. 1.

Figure 1. Relationship between current and concentration (calibration graph) for oxydemeton methyl.



2.4. Determination of Oxydemeton Methyl in Vegetables and Water Samples

Oxydemeton-methyl 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 $\mu\text{g/mL}$ oxydemeton-methyl. Suitable aliquots 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. [17] for the determination of oxydemeton-methyl 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 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 minutes. The lower aqueous phase and any emulsion were discarded. Anhydrous sodium sulfate (4 g) was added to 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. Assay results are presented in Table 1. The proposed method has also been applied to the determination of insecticide in spiked water samples. Aliquots (0.2-0.8 mL) of standard solution having 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. The results are presented in Table 1.

Table 1. Recovery of oxydemeton methyl from vegetable and water samples

Amount taken (μg)	Recovery (%) ^a					
	Present method			Comparison method ^b		
	Cauliflower	Pea	Water	Cauliflower	Pea	Water
10.0	87.7 \pm 0.86	80.7 \pm 0.64	90.2 \pm 0.96	85.3 \pm 0.92	79.2 \pm 1.02	88.0 \pm 0.62
20.0	89.6 \pm 1.01	85.4 \pm 0.86	92.8 \pm 0.42	87.8 \pm 0.76	83.6 \pm 0.92	90.6 \pm 1.12
30.0	90.9 \pm 0.97	91.6 \pm 1.02	94.6 \pm 1.04	89.1 \pm 1.09	88.8 \pm 0.76	91.6 \pm 0.74
40.0	92.4 \pm 0.64	94.8 \pm 0.76	95.2 \pm 0.64	90.4 \pm 0.82	90.5 \pm 1.08	92.9 \pm 0.86

^a Values are mean \pm standard deviation for 5 determinations.

^b Reference [16].

2.5. Soil Adsorption Study

Oxydemeton-methyl adsorption isotherms on five Indian soils of different soil characteristics (Table 2) 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 oxydemeton-methyl solutions in the concentration range from 12.3-73.8 $\mu\text{g mL}^{-1}$ on shaker at 150 rpm at definite temperature for 6 h equilibrium time [18]. 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 isotherms were evaluated by using Freundlich's adsorption equation which is written as

$$X = K_f C_e^{n_f} \quad (1)$$

Where X is the amount of pesticide adsorbed mg/Kg of the adsorbent; C_e is the equilibrium solution concentration (mg L⁻¹); K_f and n_f are adsorption coefficients which are calculated from the least square methods applied to the linear form of the Freundlich's adsorption equation

$$\log(X) = \log(K_f) + n_f \log C_e \quad (2)$$

Table 2. Characteristics of the different Indian soils used in the adsorption study of oxydemeton methyl

SS	pH	Clay (%)	OC (%)	CEC (meq/100g)
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

SS: soil sample; OC: organic carbon; CEC: cation exchange capacity

Another parameters for the adsorption process viz. distribution coefficient or soil-adsorption coefficient (K_d) (in L/Kg of soil), soil organic carbon partition coefficient (K_{oc}) (in L/Kg of organic carbon content of soil) and Groundwater Ubiquity Score (GUS) have been calculated by using equations 3-5 respectively [19-21].

$$K_d = X/C_e \quad (3)$$

$$K_{oc} = K_d \times (100/\%OC) \quad (4)$$

$$GUS = \log(t_{1/2}) [4 - \log(K_{oc})] \quad (5)$$

Where $t_{1/2}$ = pesticide persistence (half life), OC = organic carbon content of soil. 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 ($GUS < 1.8$) [21]. The thermodynamic parameters viz. Gibb's free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) have also been calculated by using equations 6-8 respectively [22].

$$\Delta G^\circ = -RT \ln(K_d) \quad (6)$$

$$\ln \left[\frac{(K_d)_2}{(K_d)_1} \right] = \frac{\Delta H^\circ (T_2 - T_1)}{R (T_2 T_1)} \quad (7)$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \quad (8)$$

Where R = gas constant (J K⁻¹ mol⁻¹), T = absolute temperature (K).

All these parameters for the adsorption of oxydemeton-methyl on five Indian soils of different soil characteristics were calculated and the results are shown in Tables 3 and 4.

Table 3. Adsorption parameters for the adsorption of oxydemeton methyl insecticide on five Indian soils at two different temperatures

SS	K_f	n_f	K_d	K_{oc}	GUS	AI
20°C						
I	1.05	1.10	1.57	148.11	0.97	L-type
II	3.19	1.06	3.86	402.08	0.74	L-type
III	6.42	0.88	4.69	213.18	0.89	S-type
IV	0.90	1.47	4.08	691.53	0.61	S-type
V	3.58	1.06	4.32	327.27	0.79	L-type
30°C						
I	0.75	1.17	1.41	133.02	1.00	S-type
II	1.24	1.31	3.47	361.46	0.76	L-type
III	3.06	1.05	3.79	172.27	0.93	S-type
IV	0.93	1.43	3.89	659.32	0.63	S-type
V	1.14	1.36	3.72	281.82	0.82	L-type

SS: soil sample; AI: Adsorption isotherm; GUS: Groundwater Ubiquity Score

Table 4. Thermodynamic parameters for the adsorption of oxydemeton methyl on five Indian soils

SS	ΔG° (kJ mol ⁻¹)		ΔH° (kJ mol ⁻¹)		ΔS° (kJ K ⁻¹ mol ⁻¹)	
	20°C	30°C	25°C	25°C	25°C	25°C
I	-1.10	-0.87	-7.94	-0.023		
II	-3.29	-3.13	-7.86	-0.016		
III	-3.77	-3.36	-15.73	-0.041		
IV	-3.43	-3.42	-3.52	-0.0003		
V	-3.57	-3.31	-11.04	-0.026		

SS: Soil samples

3. Results and Discussions

The proposed method involves the microwave assisted alkaline hydrolysis of insecticide to 2-ethylsulfanyl-ethyl mercaptan [16] and the later yields analytically useful diffusion controlled peak at -312 mV at dropping mercury electrode (DME). The

optimum time required for complete hydrolysis (in microwave) of oxydemeton-methyl was obtained by varying the time of hydrolysis from 10-80s and measuring corresponding peak current at -312 mV. It has been observed that

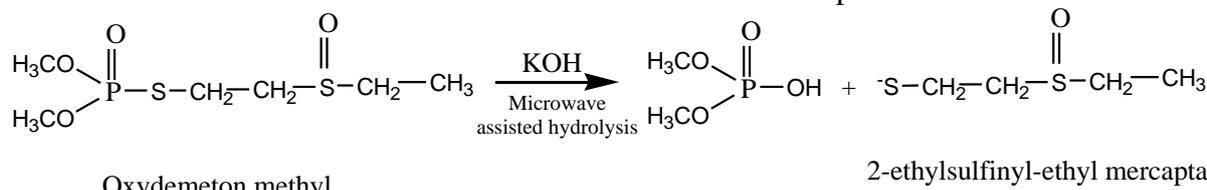
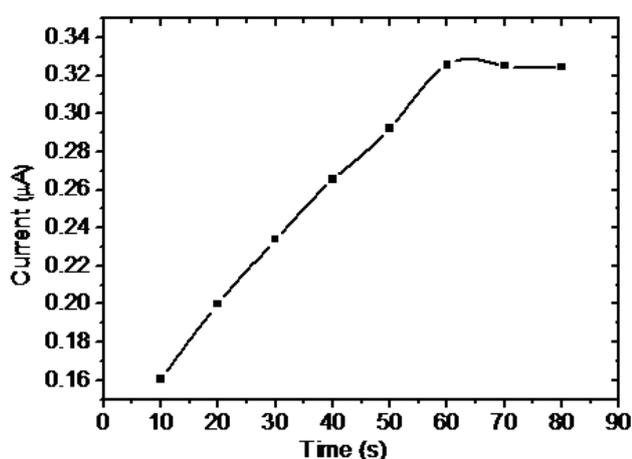
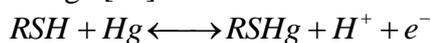


Figure 2. Effect of hydrolysis time on peak current.



The reaction taking place at the mercury electrode is supposed to involve the formation of mercurous mercaptide with one electron change [23].



The same is established by making the use of the equation of the polarographic wave [24].

$$E = E_{1/2} + \frac{0.0591}{n} \left[\log \frac{(i_d - i)}{i} \right] \quad (9)$$

It follows from the equation (9) that plot of $[\log (i_d - i)/i]$ against the corresponding potential (E), a straight line should be obtained with a slope of $0.0591/n$ for a reversible reaction. The value of n , the number of electrons taking part in the reversible reaction can be determined. In the present case a straight line with slope 0.081 is obtained indicating $n = 0.73$ (~ 1).

Under the optimized experimental conditions, the proposed method obeys the linear relationship between the concentration of insecticide and the peak current in the range 0.197-5.904 ppm (8.01×10^{-7} to 2.40×10^{-5} M). The linear regression equation has the value of slope and intercept as 0.05268 and 0.02318 respectively with correlation coefficient 0.9948. The proposed method shows good precision and

maximum peak current was obtained corresponding to 60 s hydrolysis time (Fig. 2). It may be mentioned that other hydrolytic product i.e. *O,O*-dimethyl phosphorothioic acid does not interfere in the present method.

accuracy with maximum relative standard deviation (*RSD*) of 1.05%. The validity of the method was assessed by investigating the effect of common cations like Na^+ , K^+ , Ca^{+2} , Fe^{+3} , Pb^{+2} , and Cl^- . These ions do not show any peak at this peak potential and hence do not interfere in the method.

The method has successfully been applied to the analysis of a commercial formulation of oxydemeton-methyl for its active ingredient content for the purpose of quality control. The recoveries were in the range 94.5-97.2%, with *RSDs* in the range 0.6-1.2%. The formulation analysis is essential not only to ensure the quality of marketed products of the pesticide but also to get reliable residue data. The method has been applied with success to the determination of this insecticide in residues on environmental samples for the purpose of monitoring pollution and health hazards. Recoveries of the insecticide from vegetables (cauliflower and peas) and spiked water samples were good, ranging from 80.7-95.2%, with *RSDs* ranging from 0.42-1.04% (Table 1). The results have, however, been compared with an independent method [16]. To check the validity of method on real samples, different vegetable samples were collected from the fields where the insecticide was sprayed. The oxydemeton methyl was extracted from these samples and analyzed as described above. The results were in good agreement with the reported method [16].

Soil Adsorption Study

The adsorption isotherms of oxydemeton-methyl insecticide on five Indian soils of different soil characteristics (Table 2) are shown in Figs. 3-7 respectively. According to the initial portion of the curve, these isotherms may be classified as S-type and L-type of Gile's classification [25] (Table 3). S-types of isotherms are common and represent a system where solid surface has high affinity for the

solvent than for solutes [26] where as L-types of isotherms represent a system where the solid surface has average affinity for the pesticide and the solvent is relatively inert i.e. there is no strong competition from solvent for adsorption sites [27]. The adsorption coefficients K_f and n_f were calculated for five soil samples from Freundlich's adsorption equation and results are presented in Table 3. The adsorption coefficient K_f represents the amount of pesticide adsorbed at an equilibrium concentration of 1 mgL^{-1} and n_f represents the variation in adsorption with varying concentration of pesticide [9]. Other 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 oxydemeton methyl were also calculated and are presented in Table 3. The soil-adsorption coefficient (K_d) values for oxydemeton methyl were observed in the range 1.41-4.69 for all the soils. Generally, higher the K_d value, the greater is the pesticide adsorption [9]. From table it can be inferred that oxydemeton methyl is adsorbed maximally in case of soil III (with higher K_d). The K_d for a pesticide is soil-specific and vary with soil texture and its organic matter content but the soil organic carbon partition coefficient (K_{oc}) is less soil specific [28] and is calculated by normalizing adsorption coefficient (K_d) with the organic carbon (*OC*) content of the soil. The value of K_{oc} for oxydemeton methyl 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 [9]. The organic matter content of soils affects the adsorption of pesticide: higher the organic matter contents, higher the adsorption [29]. The cation exchange capacity (*CEC*) is another parameter that influences the adsorption of pesticide. The value of *CEC* is directly proportional to hydrophobic nature of adsorbent i.e. greater the value of *CEC* of soil, its surface will be more hydrophobic. The organic pesticides being more hydrophobic (low water solubility) thus have higher adsorption affinity for the soils with higher *CEC* [30]. The thermodynamic parameters for the adsorption of oxydemeton methyl insecticide on five soils were also evaluated and are presented in Table 4. The negative value of entropy change (ΔS°) is

due to decrease in randomness with adsorption. The value of Gibb's free energy (ΔG°) and enthalpy change (ΔH°) for the adsorption of insecticide were also observed negative in all the cases suggesting the energetically favorable adsorption process [22]. From the negative values of enthalpy change (ΔH°) it can be inferred that the value of soil-adsorption coefficient (K_d) decreased with rise in temperature. This might be due to the effect of temperature on the binding of insecticide with soil particles [31]. Of the number of models available to evaluate the leaching potential of pesticide vis-à-vis associated environmental pollution risk, Groundwater Ubiquity Score (*GUS*) is the most commonly used model which relate pesticide persistence (half life) and adsorption in soil (K_{oc}). The leaching potential of oxydemeton methyl in terms of *GUS* index was determined by using experimentally observed K_{oc} value for each soil sample and literature reported half life of insecticide [32]. The *GUS* score for oxydemeton methyl has been observed in the range 0.61-1.00 which classifies it as non leacher insecticide.

4. Conclusions

The pesticide leaching is an important process with respect to contamination risk to aquatic environment and the risk of leaching has been evaluated for oxydemeton methyl. The values of soil organic carbon partition coefficient (K_{oc}) suggest greater adsorption in soil types and consequently inhibit its penetration into water sources. The leaching behaviour of the insecticide in terms of ground ubiquity score (*GUS*) was below 1.8, classifying oxydemeton methyl as non-leacher pesticide and hence it does not represent hazard to ground water contamination. It is further concluded that the toxicity due to this insecticide can also be reduced by adjusting the application dose according to soil properties. The soils with high organic carbon content increase pesticide adsorption and consequently reduce its leaching losses. The proposed method used to accomplish this study is simple, rapid, reliable and does not involve elaborate clean up procedures required with other methods.

Figure 3. Adsorption isotherms of oxydemeton methyl on soil I (a) at 20°C (b) at 30°C.

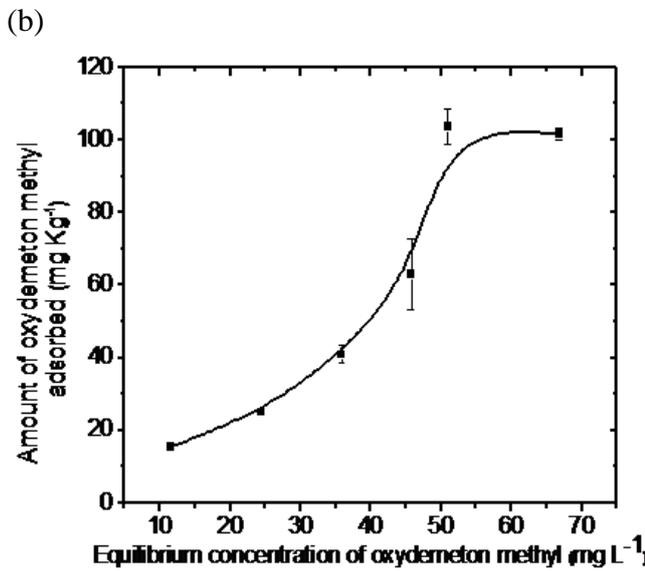
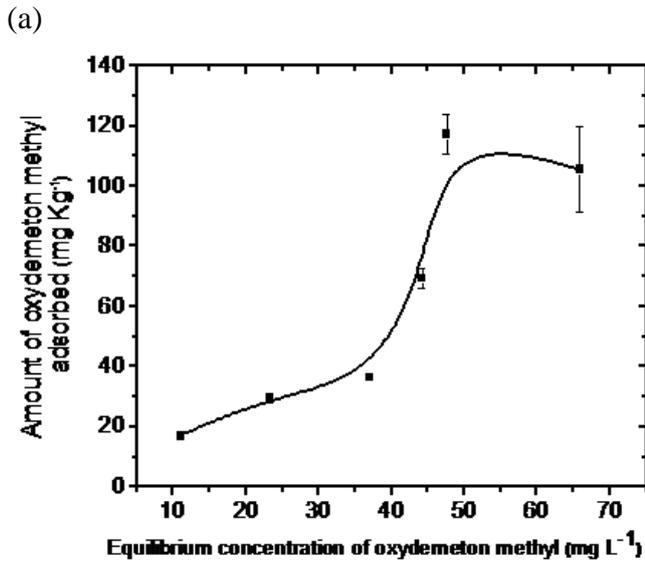


Figure 4. Adsorption isotherms of oxydemeton methyl on soil II (a) at 20°C (b) at 30°C.

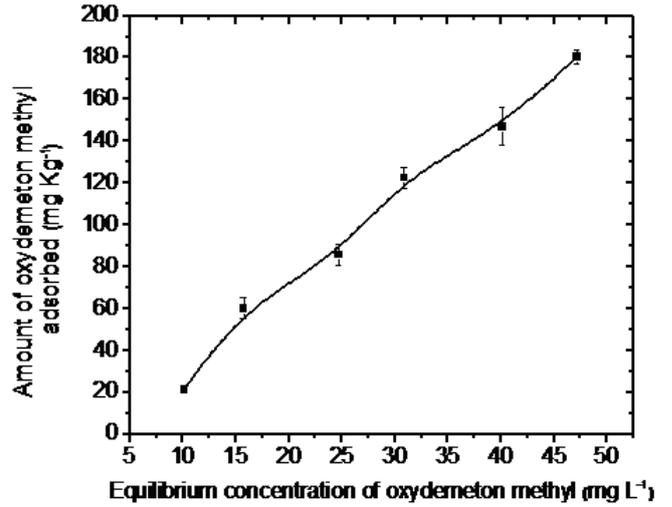
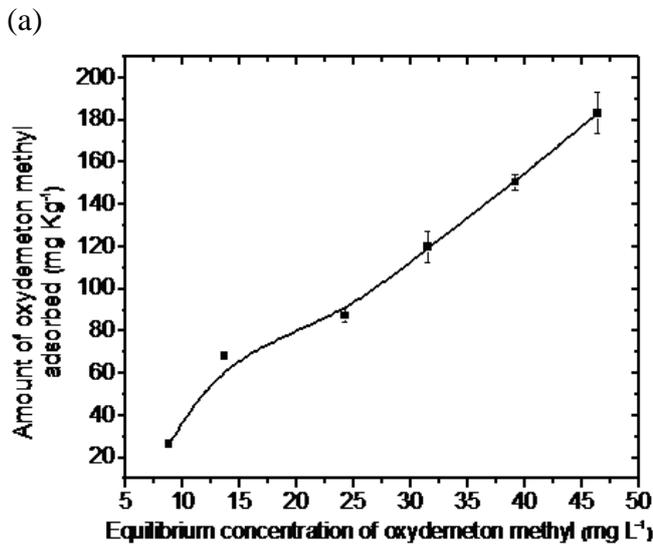


Figure 5. Adsorption isotherms of oxydemeton methyl on soil III (a) at 20°C (b) at 30°C.

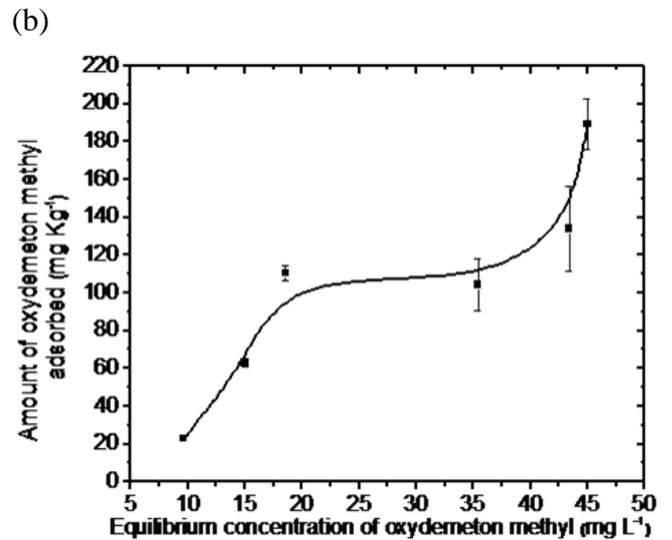
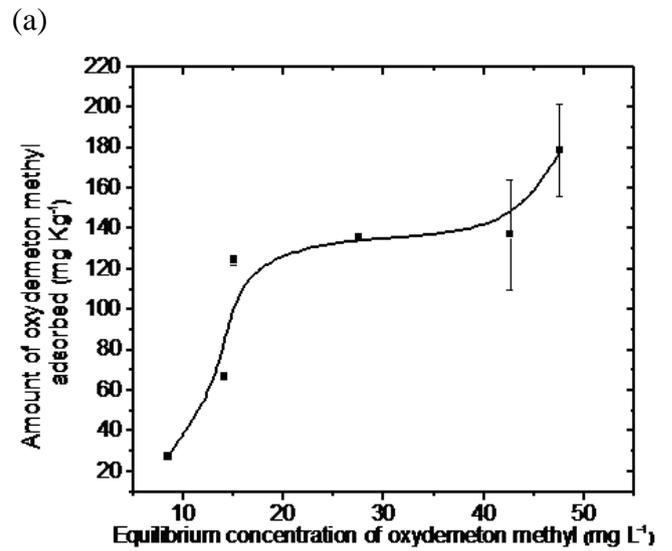


Figure 6. Adsorption isotherms of oxydemeton methyl on soil IV (a) at 20°C (b) at 30°C.

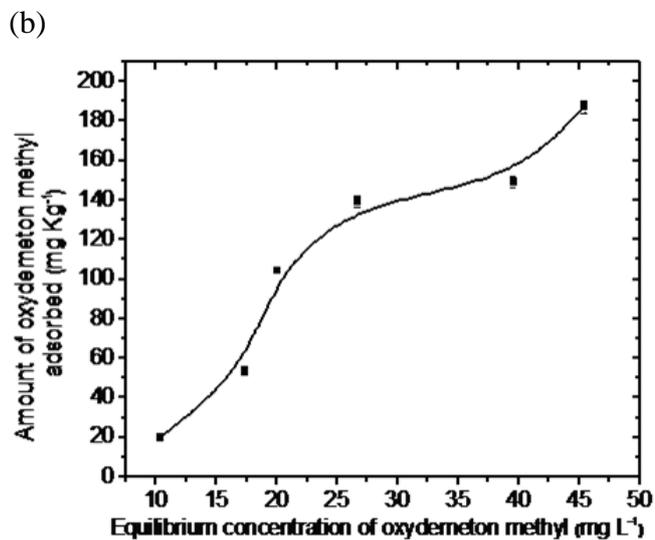
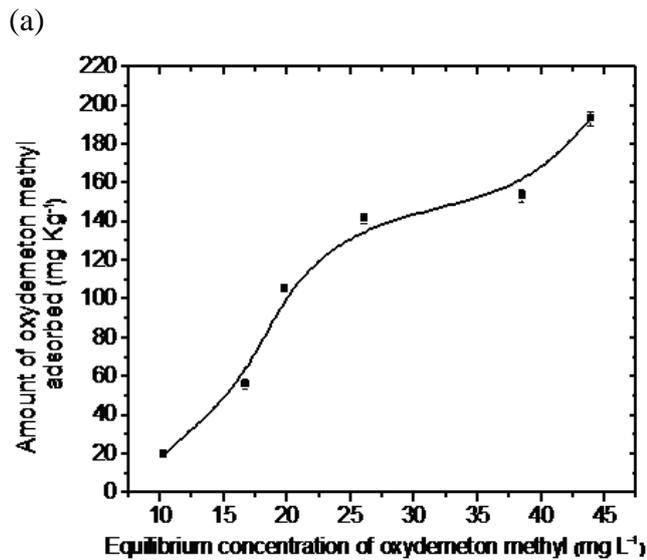
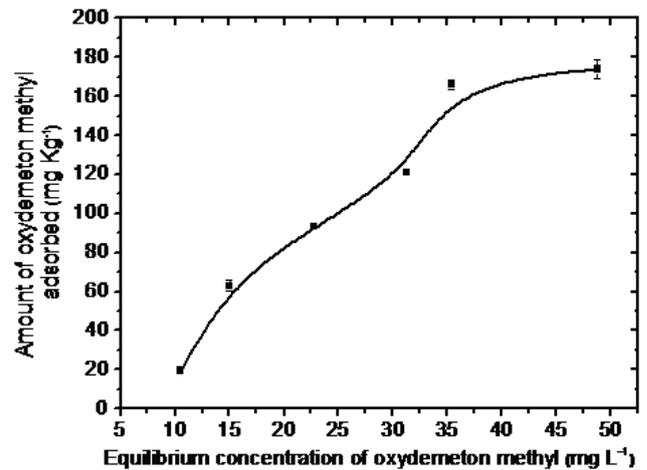
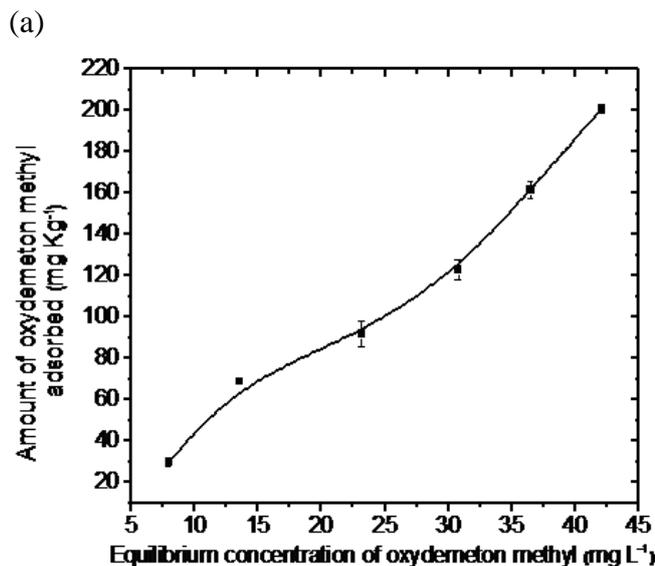


Figure 7. Adsorption isotherms of oxydemeton methyl on soil V (a) at 20°C (b) at 30°C.



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