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Spectrophotometric Study of Adsorption of Propoxur on Indian Soils

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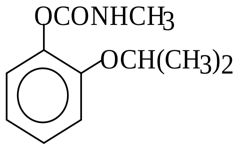
ABSTRACT: With a view to evaluate the leaching potential and consequently surface and ground water contamination, the adsorption of propoxur, a carbamate insecticide, on four soils of different characteristics has been studied using a batch equilibrium technique. To carry out adsorption study a spectrophotometric methodology based on the reaction of methyl amine, formed from microwave assisted alkaline hydrolysis of propoxur with carbon disulphide and cobalt(II) acetate to form methyl isobutyl ketone extractable yellow cobalt(II) methyldithiocarbamate complex showing λ_{max} at 360 nm has been developed for the purpose. The propoxur in commercial formulation and on four Indian soils of different soil characteristics has been determined by the proposed method. The leaching potential evaluated in terms of ground water ubiquity score (GUS) has values in the range 3.73-3.92 classifying it as leacher insecticide thereby posing a potential risk to both aquatic environment and human health calling for its judicious use.

Keywords: Adsorption; GUS; Leachability; Propoxur; Spectrophotometry.

INTRODUCTION: Though the application of pesticides to boost agricultural production is essential but their use also causes negative environmental effects which are viewed with increasing alarm. Pesticide when applied on crops only a small fraction of it reaches the target area[1] and rest is transported to various environmental components like soil and water. Soil however, is the ultimate reservoir for the species irrespective of their application. In the soil environment, the pesticides get fractioned between soil solution phase i.e. unadsorbed fraction (in free form) and soil solid phase through adsorption on clay and organic fraction (in bound form)[1]. 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[2]. All these processes influence the extent of surface and ground water contamination through leaching and have adverse effects on human health due to residues in drinking water[3]. Therefore, from environmental point of view, the study of adsorption phenomenon and evaluation of leachability of pesticides is of great importance to assess the ground water contamination.

Propoxur-(2-(1-methylethoxy) phenyl-N-methyl carbamate), a carbamate insecticide also known as Baygon, was introduced in 1959 [4,5 & 6]. Propoxur is a non-systemic insecticide with a fast knockdown and long residual effect used against turf, forestry and household pests and fleas.



(Structure of Propoxur)

It is also used in pest control for other domestic animals, anopheles mosquitoes, cockroaches, ants, gypsy moths and other agricultural pests[5&6]. It has been reported to show anti cholinesterse activity, reproductive effects, cytotoxic effects, genotoxic effects and carcinogenic effects[7,8,9,10,11 & 12]. It is moderately persistent and mobile in soils and is a potential contaminant of the aquatic environment and food sources due to its high solubility in water [4]. This, therefore, necessitates convenient, reliable and sensitive method for the adsorption study of propoxur in soils. Various analytical methods viz. chromatographic[13,14 &15], electrochemical[16], fluorescence[17] and spectrophotometric[18,19&20] have been reported in the literature for the determination of propoxur residues. Despite the development of many competitive analytical techniques, spectrophotometry continues to be very popular because of inherent ease and simplicity of technique coupled with the availability of inexpensive, reliable and now automated instruments and is still extensively used for the determination of the pesticides commonly used.

In the present work, a simple extractive spectrophotometric method based on microwave assisted alkaline hydrolysis of propoxur to methyl amine and its subsequent reaction with carbon disulphide and cobalt(II) acetate to form Methyl Isobutyl Ketone (MIBK) extractable yellow cobalt(II) methyldithiocarbamate product [$Co(DTC)_2$] (1) showing maximum absorbance at 360 nm has been developed. The method has been successfully applied to the analysis of propoxur in commercial formulation and subsequently validated to study its adsorption on four soils of different characteristics for the purpose of evaluation of its leaching potential and surface and groundwater contamination. The adsorption parameters viz. soil adsorption coefficient (K_d), soil organic carbon partition coefficient (K_{oc}) and Gibb's free energy(ΔG^o) have been calculated for evaluating the leaching behaviour of the insecticide in terms of groundwater ubiquity score (GUS) to assess the hazard to surface and ground water contamination.

MATERIALS AND METHODS:

Apparatus: The spectrophotometric measurements have been made with carry100 Bio UV-Vis spectrophotometer. Domestic microwave oven, Samsung was used to carry out hydrolysis. Genei (TM) shaking incubator, Banglore was used in soil adsorption study. A centrifuge (Labnet Z 150 A, Labnet International Inc Woodbride, NJ, USA) was used.

Reagents and samples: Acetonitrile (Merck) was kept over phosphorus pentaoxide (5 g L^{-1}) and distilled twice. The analytical standard of propoxur (Sigma-Aldrich) was used and its stock solution (10^{-3}M) was prepared in acetonitrile. Potassium hydroxide (Merck, LR, 0.1M), acetic acid (Ranbaxy, LR, 0.1M) were prepared in distilled water. Methyl isobutyl ketone (MIBK, Merck, AR)) was used as supplied. Cobalt (II) acetate (CDH, LR), its 0.01M solution in distilled water was prepared. Sodium sulphate anhydrous (Merck, AR) and Carbon disulphide (AR Merck) were used as received. The soils used in the adsorption study were collected from Solan District of Himachal Pradesh and were characterized at University of Horticulture and Forestry, Solan Himachal Pradesh.

Preparation of Calibration Graph for Pure Compound: The 7y6 prepared on the best optimized conditions. Aliquots (0.1-3.0 mL) of standard solutions of propoxur (10^{-3} mol L^{-1} in acetonitrile) were taken in 10 mL measuring flasks and diluted to 3 mL with acetonitrile. Each solution was mixed with aqueous potassium hydroxide (1 mL, ~0.1 mol L^{-1}) and 3 mL of distilled water. Each solution was mixed with one drop of carbon disulphide (~100 μL) and kept in microwave oven for 60 sec. Each solution was then treated with acetic acid (2 mL, ~0.1 mol L^{-1} in water) to neutralize the excess alkali and also to make the condition slightly acidic. The solution was poured into a 100 mL separating funnel containing 1mL, 0.01 mol L^{-1} cobalt(II) acetate solution. The contents of the funnel were equilibrated two times with MIBK using 2 mL each time and total volume made to 5 mL with MIBK. The solution was dried by shaking with anhydrous sodium sulphate and the absorbance of yellow coloured solution was measured at 360 nm against a reagent blank (Figure1). The calibration curve was prepared by plotting absorbance values against concentration of pure compound (Figure 2). The insecticide determined in the linearity range 4.18-58.6 μg mL^{-1} with correlation coefficient of 0.998.

Formulation analysis: The insecticide formulation "Laxmanrekhaa" an emulsifiable concentrates (EC) containing 2% active ingredient (Propoxur) was procured from an authorized pesticide dealer from local market. A single large sample of formulation equivalent to 10.45 mg active ingredient was dissolved in10 mL acetonitrile and diluted to a known volume (50 mL) with the same solvent. Suitable aliquots of the above solution were taken and processed for analysis in the same manner as described above for pure compound. The assay results are given in Table 1.

Soil adsorption study: Adsorption isotherms of propoxur on four Indian soils of different soil characteristics (Table 2) were obtained by the batch equilibration technique using 50 mL conical flask at 20°C temperature. Triplicate soil samples (2 g) were equilibrated with propoxur solution in the concentration range from 10.45-52.3 μg mL^{-1} on shaker at 150 rpm at respective temperature for 6 hr equilibrium time (estimated time required for equilibrium to be reached between propoxur adsorbed and in solution). After equilibration, the suspensions were centrifuged and the equilibrium concentrations (C_e) were determined in supernatants by the spectrophotometric procedure described above. Adsorption isotherms of propoxur were evaluated by using Freundlich's adsorption equation on four soils of different characteristics which is written as

$$X = K_f C_e^{nf} \qquad (1)$$

Where X is the amount of pesticide adsorbed mg/Kg of the adsorbent; C_e is the equilibrium solution concentration (mgL^{-1}); K_f and n_f are adsorption coefficients that characterize the adsorption capacity of adsorbent. The adsorption coefficients K_f and n_f are calculated from the least square methods applied to the linear form of the Freundlich's adsorption equation

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

Another 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 3-5 respectively[21,22 & 23].

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

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

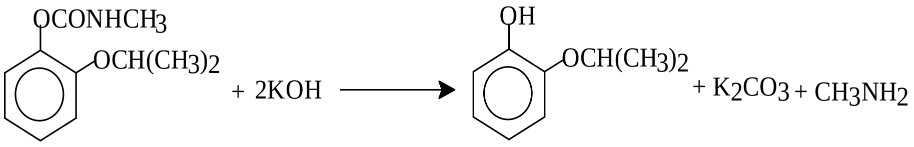
$$GUS = \log(t_{1/2})\,[4-\log(K_{oc})] \qquad (5)$$

Where R = gas constant, T = absolute temperature, $t_{1/2}$ = 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 in which GUS values are higher than 2.8, transition with GUS values between 1.8 and 2.8 and non-leacher pesticides with GUS values lower than 1.8[23].

$$\Delta G^o = -RT \ln K_d \qquad (6)$$

The thermodynamic parameter Gibb's free energy (ΔG^o) have also been calculated by using equation 6[24].

RESULTS AND DISCUSSION: The present spectrophotometric method is based on the colour reaction of methylamine (hydrolytic product of propoxur) with carbon disulphide to form methyl dithiocarbamate which reacts with cobalt(II) acetate in water to form yellow colored $[Co(DTC)_2]$ complex **(1)** showing maximum absorbance at 360 nm. The other hydrolytic products and excess of carbon disulphide and cobalt(II) acetate do not interfere in the proposed method.



$$2CH_3NH_2 + K_2CO_3 + 2CS_2 \longrightarrow 2CH_3NH.CS.SK + CO_2 + H_2O$$

$$2CH_3NH.CS.SK + Co(OAc)_2 \longrightarrow [(CH_3NH.CS.S)_2Co] + 2KOAc$$

(1)

Microwave assisted hydrolysis is an effective alternative to conventional procedure as it reduces the time of hydrolysis and problems associated to analyte losses and atmospheric contamination [25&26]. That methyl amine is infact formed from alkaline hydrolysis of propoxur [5, 27] and is quantitatively transformed into dithiocarbamates is well known[28].

Effect of various experimental parameters 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 propoxur in commercial formulation and soil adsorption study. The effect of time of microwave assisted hydrolysis and extracting solvent were studied and best results have been obtained corresponding to 60 sec hydrolysis time and methyl isobutyl ketone for extraction of the coloured product. Cobalt(II) acetate and other hydrolytic products are not extractable into MIBK and hence do not interfere in the method. The kinetic stability of the yellow product under optimized condition has been found to be 120 min. Under the optimized experimental conditions, the proposed spectrophotometric method obeys Beer's law in the range of 4.18-58.59 µg mL^{-1} of propoxur solution. The method is quite sensitive and the molar absorptivity (ε) and Sandell's` sensitivity were found to be 3.63×10^3 L $mol^{-1}cm^{-1}$ and 0.0576 $\mu g cm^{-2}$ at 360 nm. The method has subsequently been applied to the determination of propoxur in commercial formulation; the recoveries of the insecticide were in the range 92.3-95.6% of the nominal content with relative standard deviations (RSDs) in the range 0.7-1.2% (Table 1). The results have however been compared by an independent method[20]. The formulation analysis is essential not only to ensure the quality of the marketed samples of the insecticide but also to get reliable adsorption data. To assess the validity of the proposed method in soil adsorption study, effect of various common ions on the determination of the insecticide was studied. The method was found to be free from interferences due to common ions e.g. Na^+, K^+, Mg^{2+}, Ca^{2+}, Al^{3+}, Pb^{2+},OAc^-, PO_4^{3-}, NO_3^-, NO_2^-, CO_3^{2-}, SO_4^{2-}, Cl^- ions present in soil.

The major factors that determine the extent to which propoxur is adsorbed by soil includes various soil properties like soil pH, ion exchange capacity, clay content and organic matter. In view of this, the proposed method has been applied to study adsorption of propoxur on four soils of different soil characteristics to predict its leaching potential and contamination of ground water. The various adsorption and thermodynamic parameters are given in Tables 3 and 4 respectively.

Table 1: Assay of a commercial formulation of propoxur containing 2% active ingredient (Laxmanrehaa).

Amount taken (µg)	Recovery (%)[a]	
	Present method	Comparison method[b]
4.18	92.3±0.8	90.5±0.8
10.45	93.2±0.7	91.7±1.0
20.90	94.8±1.2	92.2±1.2
31.35	94.2±0.8	92.8±1.4
40.18	95.6±1.2	93.6±1.4

[a] *Values are mean ± standard deviation for 5 determinations*

[b] *Reference method*[20]

Table 2: Characteristics of the different Indian soils used in the adsorption study of propoxur.

Soil Sample	pH	Clay (%)	Organic carbon (%)	Cation Exchange Capacity (meq/100g)
I	7.38	9.3	0.7	12.2
II	7.41	18.2	1.0	12.9
III	7.44	32.6	0.6	13.1
IV	7.48	10.2	0.8	12.8

Table 3: Adsorption parameters for the adsorption of propoxur insecticide on four Indian soils at 20°C temperature.

Soil Sample	K_f	n_f	K_d	K_{oc}	GUS	Adsorption isotherm
I	0.27	1.31	0.76	108.67	3.73	S-type
II	0.42	1.22	0.86	85.87	3.92	S-type
III	0.17	1.36	0.55	92.33	3.86	S-type
IV	0.35	1.24	0.78	97.28	3.82	S-type

Table 4: Thermodynamic parameter for the adsorption of propoxur on four Indian soils at 20°C temperature.

Soil samples	I	II	III	IV
$\Delta G°$ (KJ mol^{-1})	0.67	0.37	1.44	0.61

The adsorption isotherms of propoxur on four Indian soils of different soil characteristics (Table 2) were drawn between the amount of propoxur adsorbed (mg Kg^{-1}) on soils and that in equilibrium suspension (mg L^{-1}) at a fixed volume of water respectively (Figure 3). According to the initial portion of the curve, these isotherms may be classified as S-type of Gile's classification [29] (Table 3). S-types of isotherms are common and represent a system where solid surface has high affinity for the solvent than for solutes[30]. The adsorption coefficients K_f and n_f were calculated for four 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 [2]. The Freundlich constant n_f is a measure of the deviation from linearity of the adsorption. The observed values of n_f were more than 1, (>1.0) in all four soils represent S-type isotherms, which infer that there is competition between pesticides and water molecules for the sorption sites on surface of the adsorbents [31].

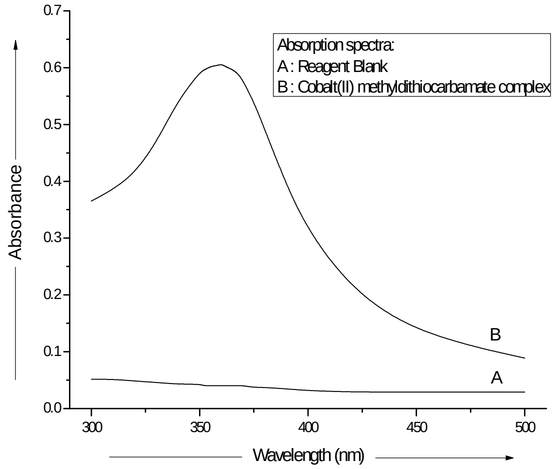


Figure 1: Absorbance maximum of Cobalt(II) methydilthiocarbamate complex.

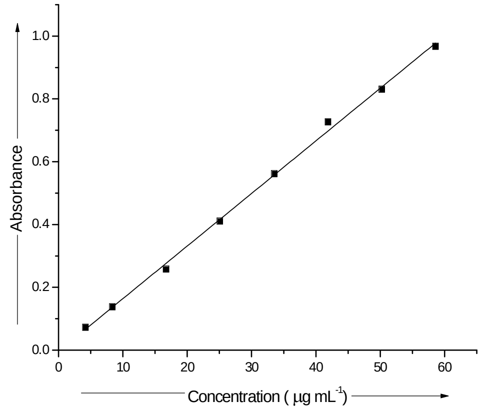


Figure 2: Calibration graph of propoxur (as cobalt(II) methyl dithiocarbamate) complex) at 360 nm.

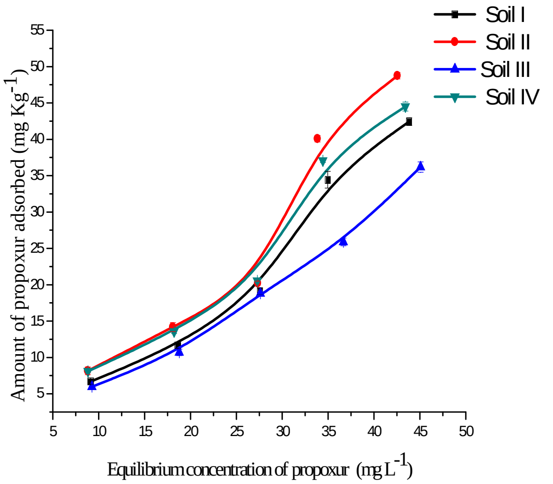


Figure 3: Adsorption isotherm of Propoxur adsorption on soils I– IV at 20^{O}C (error bars represent the standard deviation of three replicates).

The organic matter content and the clay of soils play a very important role in the sorption of pesticides on to the soil. It is found that the amount of pesticides sorbed by soils increases as the total soil organic carbon content and or clay content is increased[32]. This is because the particles of organic matter or clay provide soils with an increased number of adsorptive sites onto which pesticides molecules can bind. Another soil parameter is cation exchange capacity (CEC) which 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[33]. High adsorption of propoxur in soil II could be explained by its high percentage of organic carbon content. The value of K_d represents the extent of adsorption and in general higher the Kd value, the greater is the pesticide adsorption [2]. Hence, propoxur is adsorbed maximally in the case of soil II. Of the four soils of different characteristics studied the decreasing sorption order is: Soil II > Soil IV > Soil I > Soil III. The calculated K_d values are in conformity with the literature reported values[34]. Though Kd for a pesticide is soil-specific than soil organic carbon partition coefficient (Koc), but the latter give the more accurate results with regards to mobility of a pesticide in any kind of soil. The results of adsorption of propoxur on four Indian soils at 20^{o}C temperature are shown in Table 3 and Table 4. The ΔG^{o} values for adsorption of propoxur were positive at 20^{o}C indicating that adsorption of propoxur on soils is nonspontaneous in nature. The positive value of ΔG^{o} also shows that there is an energy barrier. When the ions enter from the solution into the particle surface, some of the water molecules forming hydration shell of ions are stripped off and simultaneously the degree of freedom of ions declines[35&36]. Groundwater Ubiquity Score (GUS) is the most commonly used model which relate pesticide persistence (half life) and adsorption in soil (Koc). The leaching potential of insecticides in terms of GUS index was determined by using experimentally observed Koc value for each soil sample and literature reported half life of propoxur[37]. The GUS for propoxur was from 3.73 to 3.92 classifying it as a leacher.

CONCLUSION: The proposed method for the determination of propoxur is simple, rapid and reliable and is of wide applicability especially by the laboratories of limited means. The experimental data indicate that propoxur adsorption on soils is very less. The low values of soil organic carbon partition coefficient K_{OC}, also suggest less adsorption in soil type and consequently its penetration into water sources. This is further supported by GUS values in the range 3.73-3.92. The observed GUS value of this insecticide which is more than 2.8 (of the Giles classification) for all soils used, classifying it as leacher pesticide in terms of leaching behaviour, thereby it poses potential risk to the aquatic environment. Hence, this insecticide should be used judiciously to prevent surface and groundwater contamination. The toxicity risk can be reduced by adjusting the application dose according to soil properties and amending the soils by increasing the organic carbon content of the soils. The latter aspect will not only reduce the mobility of the insecticide but also increase the fertility of the soil.

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