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Spectrophotometric Evaluation of Leaching Behaviour and Groundwater Contamination of Isoproturon Herbicide

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Abstract

*Concern about the environmental impact in terms of surface and ground water contamination due to excessive use of isoproturon herbicide prompted us to evaluate its leaching behaviour on soil in terms of Groundwater Ubiquity Score (GUS). A spectrophotometric methodology based on the microwave assisted hydrolysis of the herbicide with potassium tert.-butoxide to corresponding aniline and its subsequent deamination and nitration into acidic nitro phenol showing maximum absorbance at 370nm has been developed. Beers law is obeyed up to 41.26ppm of isoproturon solution and the determination can be made with a maximum RSD of 1.26%. GUS has been determined by using experimentally determined soil organic carbon partition coefficient for soil with literature reported half-life of isoproturon. GUS value of 2.73 classifies it a lecher herbicide representing a serious hazard to surface and groundwater contamination. With a view to reduce contamination risk the effect of farmyard manure on the adsorption of isoproturon on soil and consequently on GUS value has also been studied. The manure amendment not only reduced GUS value to 2.34 but also served as a source of nutrients, thus improving the soil fertility.***

Keywords: Isoproturon, spectrophotometry, soil adsorption study, leaching potential, GUS.

Introduction

Isoproturon is one of the most commonly used pre- and post- emergence selective herbicide and is used for the control of annual grasses and many broad leaved weeds in cereals. It is soluble in water and thus finds its way to water resources via. leaching. Like other pesticides, it has also been reported to have adverse effects on hepatic and reproductive systems and developmental processes[1-4]. This pesticide has high persistence and prolonged residual action. The pollution of soil, ground and surface water involves a serious risk to environment and also to human health due to direct exposure and through residues on foodstuffs and drinking water. Concern about the environmental impact of extensive use of pesticides has prompted research into the environmental fate of these chemicals which is strongly influenced by their interaction with soil as the latter is the ultimate reservoir for these species irrespective of their application target. In soil environment, the pesticides get fractioned between soil solution phase (in free form) and soil solid phase through adsorption on clay and organic functions (in bounded form). Pesticide adsorption by soil is a naturally occurring phenomenon which influences the extent of surface and ground water contamination. The presence of pesticides in surface and ground water has frequently been detected and has led to many workers[5-11] to carry out Experimental study on pesticide adsorption by soils because such studies could provide important information regarding the prediction of pesticide movement in soil and aquifers.

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To accomplish above objectives, it is therefore, ineviTable to find a simple, sensitive, cost effective and reliable technique of wide applicability for the analysis of isoproturon. Spectrophotometry, undoubtedly, is a versatile technique and methods based on this it have continued to flourish and find wide- acceptance by the laboratories of limited means. In the present work a new and sensitive spectrophotometric method has been developed for the determination of isoproturon to evaluate its leaching potential vis-à-vis contamination risk of surface and groundwater contamination. The method is based on the microwave assisted hydrolysis of the herbicide with potassium tert.- butoxide to the corresponding aromatic amine and deamination and nitration of latter to intense yellow acidic nitro phenol. The analysis is accomplished by measuring the yellow colour at 370 nm against a reagent blank. The method has subsequently been validated to study the adsorption of isoproturon on soil collected from Solan region of Himachal Pradesh where this herbicide is maximally used. The various adsorption parameters, namely soil-adsorption coefficient (K_d), soil organic carbon partition coefficient (K_{oc}), Gibb's free energy (ΔG^o) and groundwater ubiquity score (GUS) have been calculated It is well known that organic amendments such farmyard manure, compost etc. influence the adsorption of pesticides in soil and also improves the fertility by enhancing organic matter level. The proposed spectrophotometric method has also been applied to study the effect of farmyard manure of known characteristics on the soil adsorption of isoproturon.

Experimental

The analytical standard of isoproturon (99.7%), Gharda Chemicals Mumbai was used. A commercial formulation containing 75% isoproturon WP (PRIMILON-75) was procured from the local market. Acetonitrile (Merck, AR) was twice distilled from phosphorous pentaoxide 5g/L .Potassium tert. Butoxide (Loba Chem., AR), sulphuric Acid (SD fine Chem., AR), nitric Acid (Merck, AR), chloroform (Merck GR) and Sodium sulphate anhydrous (Merck, AR) were used as received.

Varian-Cary 100 Bio UV-Visible Spectrophotometer and Bausch and Lomb spectrophotometer (spectronic 20 D) with 1cm matched glass cells were used for absorption measurements. Microwave oven (Samsung), Incubator Shaker (PT-422) and Centrifuge (Sigma labrozentrifugen) were used for hydrolysis and soil adsorption studies.

Experimental **procedure.**

***Preparation of calibration graph for pure compound*:** Aliquots (0.1-2.0 mL) of standard aqueous solution of herbicide (10^{-3} M) were taken in 10 mL-measuring flasks and volume made to 2mL with acetonitrile. Each solution was mixed with 0.5mL of 0.02mol L^{-1} solution of potassium *tert.*butoxide (PTB) and kept in microwave for 60 seconds. Each solution was then mixed with 2mL of sulphuric acid and nitric acid mixture (1:3v/v). Final volume was made 10mL with distilled water and kept in microwave again for 60s. The absorbance was measured at the 370 nm against a reagent blank (spectrum of yellow coloured complex is illustrated in Fig. 1). The absorbance values are plotted against concentration of pure compound used and calibration curve prepared in usual way as shown in Fig. 2. The calibration characteristics i.e. Beers law range, molar absorptivity, stability, slope and intercept are given in Tables I.

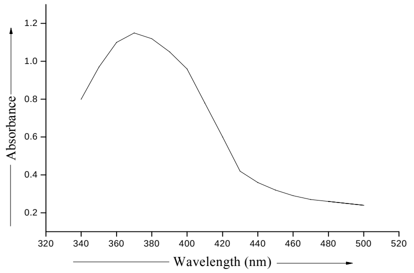

Fig. 1: Absorption spectrum of yellow acidic nitrophenol.

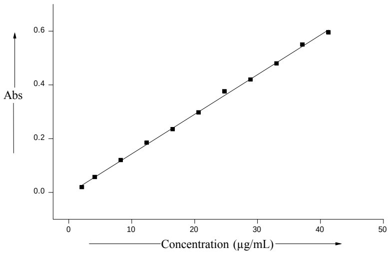

Fig. 2: Relationship between absorbance and concentration (calibration graph) for isoproturon.

Table I: Spectrophotometric determination of isoproturon as yellow coloured acidic nitro phenol: calibration characteristics.

Characteristics	Corresponding values
λ_{max}	370 (nm)
Beer's law range	up to 41.26 (µg mL^{-1})
Molar absorptivity(ε)	2.98×10^3 (L mol^{-1} cm^{-1})
Stability	120 (min)
Slope	0.0147
Intercept	-0.00388
Limit of Detection	0.70 (µg mL^{-1})
Limit of Quantification	1.03 (µg mL^{-1})

Formulation analysis: The herbicide formulation viz. Primilon-75 containing 75% isoproturon (W.P.) was used. A single large sample of this formulation was weighed, shaken with acetonitrile and filtered. The residue was washed 2-3 times with 5mL of acetonitrile. The filtrate and washing were diluted to a known volume (25 mL) with same solvent. SuiTable aliquots of the extracts of formulation were taken for analysis and processed in the same manner as described for pure compounds using both the methods. The assay results are given in Table II.

Soil adsorption study: Adsorption equilibrium studies were conducted for soil of H.P. by the batch equilibrium method. Triplicate soil samples (4g) were mixed with isoproturon solution in the concentration range from 186.41 - 433.23µg in 50mL conical flasks and contents were agitated by shaking mechanically at two temperatures (25±1)°C and (35±1)° C for 24 hours equilibrium time (the estimated time required equilibrium to reached between isoproturon adsorbed and isoproturon in solution). After 24 hours the herbicide was extracted from each conical flask with water, centrifuged and the supernatant was analyzed for isoproturon concentration in the solution by the procedure described above. The study has been carried out in the triplicate to minimize error.

The equilibrium concentration (**C_e**) was determined in supernatant by procedure described above. Adsorption isotherms were evaluated by using Freundlich's adsorption equation: $X=K_fC_e^{nf}$

Where '**X**' is the amount of herbicide adsorbed in mg/Kg of adsorbent; **C_e** is the equilibrium solution concentration (mg/L); **K_f** and **n_f** are adsorption coefficients that characterize the adsorption capacity of the adsorbent and have been calculated from the least square method applied to the linear form of the Freundlich's adsorption equation: $\text{Log } X = \log K_f + n_f \log C_e$

Other parameters for the adsorption process viz. distribution coefficient or soil-adsorption coefficient (K_d), Gibb's free energy ($\Delta G°$) and Soil organic carbon partition coefficient (K_{oc}) have been calculated by using calculated by using equations: $K_d = X/C_e$

$$\Delta G° = -RT \ln K_d$$

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

Where, 'R' is gas constant and 'T' is temperature, and OC is organic carbon content of the soil. The soil characteristics and results of adsorption study are summarized in Table III-IV. The adsorption isotherms are shown in Figs 3a-3b.

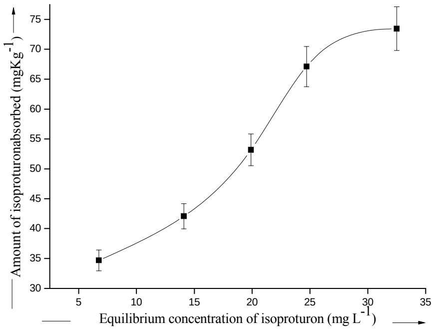

Fig. 3a: Adsorption isotherm of isoproturon on soil at 25°C± 1.
(error bars represents the standard deviation of three replicates).

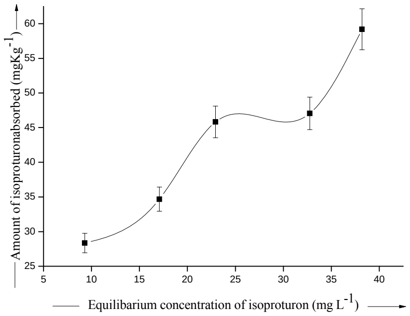

Fig. 3b: Adsorption isotherm of isoproturon on soil at 35°C± 1.
(error bars represents the standard deviation of three replicates).

Soil adsorption study amended with farmyard manure:

Adsorption isotherms on a soil amended with farmyard manure were studied by the batch equilibrium method. Triplicate soil samples (2g soil and 2g farmyard manure) were mixed with isoproturon solution in the concentration range from 186.41- 433.23 µg in 50mL conical flasks and contents were agitated by shaking mechanically at two temperatures (25±1) °C and (35±1)° C for 24 hours equilibrium time (the estimated time required equilibrium to reached between isoproturon adsorbed and isoproturon in solution). After 24 hours the herbicide was extracted from each conical flask with water, centrifuged and the supernatant was analyzed for isoproturon concentration in the solution by the procedure described above. The results of adsorption study are summarized in Table IV.

Results and discussion

Substituted aniline (hydrolytic product of the herbicide) can be deamminated and nitrated with sulphuric - nitric acid mixture (1:3v/v) to form corresponding intense yellow nitro phenol, has been made the basis of the proposed method. The analysis has been accomplished by measuring the yellow colour at 370 nm (Fig.1) .Beers laws is obeyed up to 41.26 µg mL^{-1} of isoproturon solution. The method is quite sensitive; as little as 1.03 µg mL^{-1} of isoproturon can be determined by the method. Isoproturon in the range 2.06 - 36.96 µg can be determined with maximum relative standard deviations (RSD) of 1.26 %. The method has also been applied to the determination of isoproturon in a commercial formulation containing 75% active ingredient. The recoveries of the insecticide were in the range 88.99 and 96.51% of the normal content with RSDs in the range 0.55 and 1.10 % respectively (Table II). The results have however been compared by an independent method[12]. Formulation analysis is essential not only to ensure the quality of marketed products in curing adulteration problems but also to obtain reliable residue data.

Table II : Assay results of a commercial formulation (Primilon) containing 75% isoproturon †

Active ingredient taken (µg)	Recovery of active ingredient*(%)
5.50	89.41 ± 0.81
11.10	92.35 ± 1.10
22.20	96.51 ± 0.91
33.30	94.27 ± 0.55

†Makers specification established by Ref. method [12]
*Values are mean of five determinations with standard deviation (±)

The proposed method for the determination of isoproturon possess advantages over the commonly used colorimetric method in terms of instantaneous development of colour, and its sufficient stability, non-extraction of coloured product and above all the simplicity, rapidity and reliability of the procedure.

The method has further been validated to study the adsorption of isoproturon on a natural soil. The relevant characteristics of the soil are given in Table III. The adsorption isotherms of isoproturon on soil were evaluated by Frenudlich's adsorption equation at two temperatures i.e. 25±1° and 35±1°C. The adsorption study at two temperatures is important to compare the binding between pesticide and soil particles. The result showed that increase in temperature caused decrease in adsorption for soil as well as for soil[13]. Adsorption isotherms of isoproturon on soil are shown in Figs 3a- 3b. The Frenudlich's adsorption coefficients $\mathbf{K_f}$ and $\mathbf{n_f}$ were calculated from the plot of log X versus log C_e (Figs 4-5) and data is presented in Table IV.

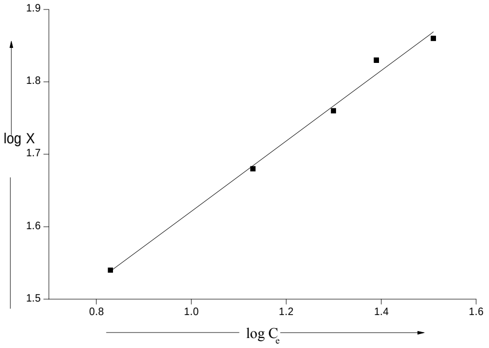

Fig. 4: Plot of logX versus log C_e for the evaluation of adsorption coefficients k_f and n_f of isoproturon on soil at 25°C

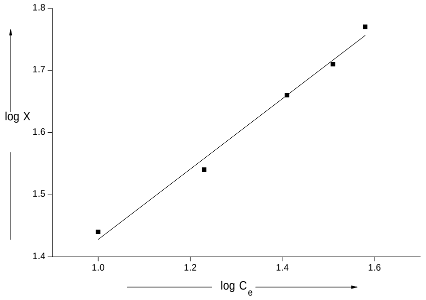

Fig. 5: Plot of logX versus log C_e for the evaluation of adsorption coefficients k_f and n_f of isoproturon on soil at 35°C

Table III: Characteristics of the soil used in the adsorption study of isoproturon.

Characteristics	Corresponding Value
pH	7.00
Clay	19.00(%)
Organic carbon (OC)	6.00 (%)
Cation exchange capacity (ECE) (meq/100g)	11.00

Table IV: Adsorption parameters for the adsorption of isoproturon on soil, and soil and manure at 25°C and 35°C ±1

Adsorption parameter	Soil		Soil and manure	
	25°C	35°C	25°C	35°C
K_f	1.10	0.96	1.30	1.31
n_f	0.51	0.49	0.53	0.40
K_d	3.15	2.01	7.11	4.45
Koc	52.50	33.53	118.43	74.16
GUS	2.51	2.73	2.12	2.34
□G^{o} (KJ mol^{-1})	-2.97	-1.79	- 4.86	-3.82

The adsorption coefficient K_f represents the amount of herbicide adsorbed at an equilibrium concentration of 1mg L^{-1} and represents the variation in adsorption with varying concentration of pesticide[14]. The observed value of $\mathbf{n_f}$ was less then1; indicating that with the increase in the concentration of herbicide, the percentage adsorption of the herbicide by the soil decreased. This might be due to the fact that at higher concentration, that is increased difficultly to access the adsorption site.

Other parameters such as soil adsorption coefficient (K_d), soil organic carbon partition coefficient (K_{oc}) and Gibb's free energy for adsorption process (ΔG^o) for the adsorption of isoproturon were also calculated and are represented in Table IV . The value of K_d represents the extent of adsorption and in general higher the K_d value, the greater is the pesticide adsorption[15]. The K_d for a pesticide is soil-specific and vary with the soil texture and its organic matter content, but the soil organic carbon partition coefficient (K_{oc}) is less soil specific and is calculated by normalizing adsorption coefficient (K_d) with the organic carbon (OC) content of the soil. The value of Koc was observed to be 52.5 and is very close to the literature reported value of 36 – 241[16]. The carbon exchange capacity (CEC) also influences the adsorption of pesticide. The value of CEC is directly proportional to hydrophobic nature of adsorbent. The organic pesticides being more hydrophobic (low water solubility) have higher adsorption affinity for soil with higher CEC. The organic matter content of soil also affects the adsorption of pesticide, higher the OC, higher will be the adsorption. The value of Gibb's free energy (ΔG^o) for adsorption of isoproturon was observed negative, suggesting the energetically favourable adsorption process.

Evaluation of leaching behaviour of isoproturon:

A number of models are available to evaluate the leaching behaviour of pesticides and associated environmental pollution risks. In the present study leaching potential of this herbicide has been evaluated in terms of groundwater ubiquity score (GUS) which is the most commonly used model and it relates pesticide persistence (half-life) and adsorption in soil (K_{oc}). The leaching potential of isoproturon in terms of GUS index has been determined by using experimentally observed K_{oc} value for each soil sample and literature reported half-life of isoproturon[17],

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

GUS value is used to study the leaching behaviour of pesticides, classifying them as lecher (GUS>2.8); non-lecher (GUS<1.8) and transition (2.8>GUS<1.8)[18]. The GUS score for isoproturon has been observed 2.73, which is above 1.8 thus classifies it as a lecher pesticide.

The toxicity due to this herbicide can be reduced by adjusting the application dose according to soil properties. The soils with higher organic carbon content increase its adsorption and consequently reduce its leaching losses. It is well known that organic amendments such as farmyard manure and compost not only influence the adsorption of pesticides but also improve the soil fertility and health by serving as source of soil nutrients[19]. In view of this, efforts have also been made to study the adsorption of isoproturon in soil in the presence of farmyard manure. The adsorption parameters for isoproturon in soil amended with farmyard manure are given in Table IV. It has been observed that with the addition of farmyard manure to soil, K_{oc} increased, suggesting increase in the adsorption of the herbicide. The GUS has also been found to be 2.34 which is less than without amendments (2.73). It is concluded that organic amendment in the form of farmyard manure has a double action, one it reduces the leaching potential by increasing adsorption of the herbicide and the second it also serve as the source of nutrients thus improving the soil fertility and maintain soil health and consequently soil productivity.

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