

Evaluation of Adsorption and Leaching Behaviour of Glyphosate Herbicide on Soils of Different Characteristics

AKHIL CHAUDHARY¹, SRISHTI SHEKHAR² and NISHA SHARMA^{*3}

¹⁻³ Department of Chemistry, Himachal Pradesh University, Shimla - 171 005, Himachal Pradesh, India

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Abstract

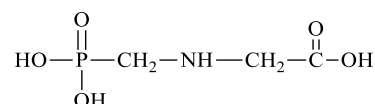
The risk of groundwater pollution by pesticides is affected by the nature and interaction of pesticides with soil, as soil is their ultimate reservoir regardless of the site of application. The current study is focused on the adsorption of glyphosate in three soils at 25 and 35 °C. The adsorption isotherms were fitted better by Freundlich's adsorption equation. The adsorption of glyphosate is positively correlated with organic carbon and clay content of soils. The negative magnitude of Gibbs free energy change (ΔG°) and enthalpy change (ΔH°) indicate exothermic, favourable and spontaneous nature of adsorption process. To assess the environmental toxicity of glyphosate a spectrophotometric method based on the formation and measurement of colored Ni(II) dithiocarbamate complex has been proposed. The Beer's law was valid within a concentration range of 0.4 - 7.4 µg/mL under optimized experimental conditions. The method is further validated on commercial formulations, food stuffs and water samples. The high recoveries from these samples indicate good accuracy and precision of the method. The leaching potential of glyphosate in terms of Groundwater Ubiquity Score (GUS) has values in the range 0.75 - 1.62, classify glyphosate as a non-leacher pesticide; thereby it does not pose potential risk to aquatic environment.

Key words: Glyphosate, Adsorption, Leaching potential, Formulation analysis, Residue analysis, Spectrophotometry

To fulfil the needs of ever-growing population pesticides have been used excessively to increase the production of high-quality agricultural products and to prevent the crop losses from harmful pests [1]. Pesticides when used in recommended dose are of tremendous benefits and exhibit numerous applications. But these chemicals are exceedingly hazardous, and their widespread usage poses harmful effects on human health, environment and other non-target species [2-4]. When pesticides are used, only a little portion reaches the site of action, with the larger proportion being lost via spray drift, off-target deposition, runoff, photodegradation, and ultimately accumulates in the soil and contaminate water resources [5]. The fate of pesticides in soils is influenced by adsorption-desorption phenomena as these processes affect their concentration in the soil solution leading to the contamination of aquatic biota [6]. The adsorption process also depends on the nature of pesticides, their water solubility, hydrophobicity and soil properties. Thus, it is important to investigate the interaction of pesticides with soil of various compositions to determine the fate of pesticides in soil to limit their impact on non-targeted organisms and ecosystems.

Glyphosate, (N-phosphonomethylglycine) is a broad-spectrum phosphorus containing amino acid-type herbicides [7] which is used widely on a number of crops, as well as in non-crop environments [8-9]. It has low mammalian toxicity but, when consumed orally, it causes digestive tract discomfort, eye and skin irritation, low blood pressure, and respiratory failure

[10-11] but the overdose of the herbicide may cause fatal effects [12].



Despite the enormous advantages of glyphosate, in public health and agricultural sectors, their erroneous usage leaves massive adverse impacts on human health and the environment [13-15]. Therefore, from environmental point of view, adsorption of glyphosate on soils is of great importance for predicting their movement in the soil and subsequent contamination of ground and surface water for ensuring their safe use. To monitor the pollution and health risks associated with the use of glyphosate herbicide, it is necessary to develop and validate quick, easy-to-use, cost effective and reliable analytical techniques for its evaluation.

Various instrumental methods to investigate glyphosate have been reported by chromatography [16-18], electrochemical [19-20], electrophoresis, enzymatic, chemiluminescence [21-23] and spectrophotometry [24-26]. Though chromatographic techniques are highly accurate and trustworthy, but the requirement of trained experts and highly specialized facilities with intricate sample pre-treatment procedures, restrict their application. Therefore, it is essential to develop quick, sensitive and cost-effective analytical approaches for the analysis of glyphosate herbicide.

***Correspondence to:** Nisha Sharma, E-mail: nishasharma581@gmail.com; Tel: +91 7018801452

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In the present work, a spectrophotometric method for the determination of glyphosate herbicide has been developed. The method is based on the measurement of a yellow colored Ni(II) dithiocarbamate, Ni(DTC)₂ complex, at 388 nm formed by the reaction of amino function of glyphosate with carbon disulfide and Ni(II) acetate. The proposed spectrophotometric method offers high sensitivity and involves a non-extractive procedure. The method has been suitably validated for the analysis of glyphosate in its commercial formulations and recovery from grains, vegetables and water samples. The method has also been validated to study the adsorption of glyphosate on three soils of different properties at two temperatures viz. 25 and 35 °C, to evaluate the risk of contamination to ground water through leaching.

RESULTS AND DISCUSSION

Apparatus: The spectrophotometric measurements were made on a Carry 100 Bio UV-Vis spectrophotometer (Varian Australia, Mulgrave-Victoria, Australia). A domestic microwave oven, (Samsung electronics, New Delhi, India) was used to carry out hydrolysis.

Reagents and samples: The analytical standards of glyphosate-ammonium, (95%) purity procured from Sigma-

Aldrich, (Bangalore) were used. Nickel (II) acetate (Central Drug House, Delhi, India, LR) was used to prepare, its 0.001 M solution in distilled water. Acetonitrile (Merck, Mumbai, India), carbon disulfide (AR grade, Merck, India), sodium bicarbonate (Merck, LR), glacial acetic acid (Merck, GR) was used as supplied. Glacial acetic acid (Merck, GR) with the concentration of, ~1 M, was prepared in distilled water. An herbicide formulation "Glyphos Dakar" containing 71% glyphosate was procured from the local market.

Preparation of calibration graph for pure compound by Spectrophotometric method

Aliquots (0.1-2 mL) of a standard solution of glyphosate (0.2 mM in distilled water) were taken separately in 10 mL measuring flasks, and the volume was made to 2 mL with distilled water. Each solution was mixed with 1.0 mL of, CS₂ (10% in Acetonitrile) followed by 1.0 mL of aqueous sodium bicarbonate (1 M), and then the volume was made to 5 mL with distilled water and kept in a microwave oven for 60 s (1000 W). Then, the solution was treated with 1 drop of acetic acid and 1 mL of, 0.001 M nickel (II) acetate solution, and the total volume was made to 10.0 mL with distilled water. The absorbance of yellow colored solution was measured at 388 nm against a reagent blank (Fig 1). The calibration curve was prepared by plotting absorbance values against concentration of the pesticide. The calibration characteristics are given in (Table 1).

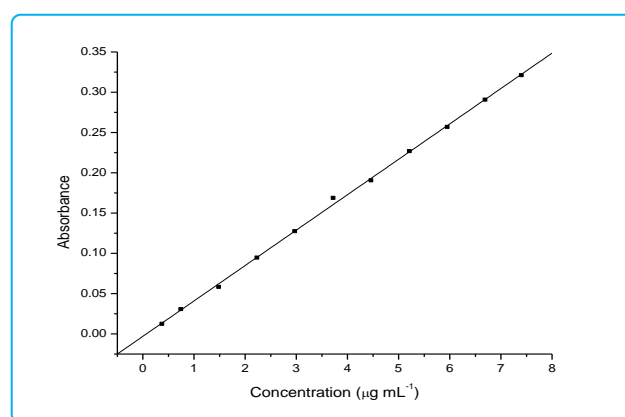
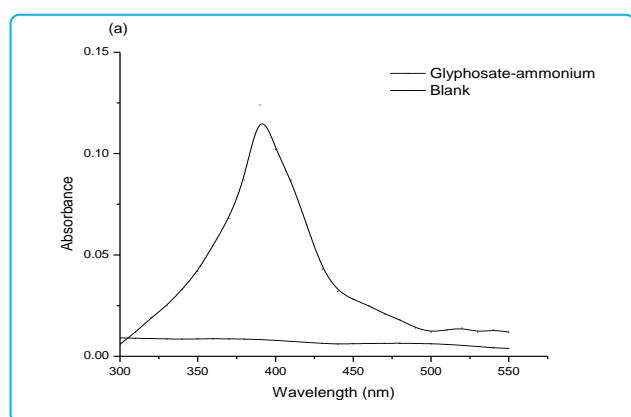


Fig 1 Absorption maximum for glyphosate (a) and Relationship between absorbance and concentration (calibration graph) for glyphosate as its nickel (II) dithiocarbamate complex (b)

Table 1 Calibration characteristics-for spectrophotometric determination of glyphosate as colored Ni(II) (DTC)₂ complex

Optical characteristic	Corresponding value
λ_{\max} , nm	388
Beer's law range, µg/ mL	0.4-7
Molar absorptivity, L/mol. cm	8.45×10^3
Sandell's sensitivity, µg/ cm ²	0.0220
Stability, min	300
Slope	0.0439
Intercept	-0.003
Determination coefficient (r^2)	0.999
LOD, µg/ mL	0.2
LOQ, µg/ mL	0.7

Formulation analysis

A formulation "Glyphos Dakar" containing, 71% active ingredient of glyphosate procured from an authorized pesticide dealer was used. A single large sample of glyphosate formulation equivalent to 10 mg of the active ingredient was dissolved and shaken with 10 mL of distilled water and filtered. The residue was washed 2–3 times with distilled water, and the

filtrate and washings were diluted to a known volume of 25 mL with distilled water. 2.5 mL of this solution was taken and further diluted to 100 mL. Suitable aliquots of the above solution were taken for analysis and processed in the same manner as described for pure compounds. The assay results are given in (Table 2).

Table 2 Assay results of commercial formulation of glyphosate "Glyphos Dakar" by spectrophotometric procedure

Amount taken, µg	Amount found, µg	Recovery, % ^a
1.0	0.98 ± 0.01	98.0 ± 0.8
2.0	1.97 ± 0.01	98.5 ± 0.6
3.0	2.97 ± 0.02	99.0 ± 0.5
5.0	4.97 ± 0.02	99.4 ± 0.4
7.0	6.94 ± 0.02	99.1 ± 0.3

^aValues are the mean of five determinations with standard deviation

Determination of glyphosate in grains, vegetable and water samples

Suitable aliquots of a standard solution of glyphosate having a concentration of 10 µg/mL were added separately to a

known weight (5 g) of grains (wheat and rice), vegetables (carrot and cauliflower) and water sample (25 mL). The samples (grains and water) were well mixed and extracted with 2–3 portions of chloroform (5 mL). The combined extracts were shaken for 5 min and filtered. In the case of vegetables after proper mixing, each sample was blended with 50 mL of chloroform in the same containers according to the general procedure of [27]. The samples were filtered through coarse filter paper (Whatman Grade No. 4), and each filtrate was transferred into 250 mL separating funnels. Sodium chloride (5 g) was added to each sample, the contents were shaken for one

minute, and the phases were allowed to separate for 15 min. The lower aqueous phase and any emulsion were discarded. Anhydrous sodium sulphate (4 g) was added, and the funnel was shaken for 30 s. The dried extract was filtered through coarse filter paper. The solvent from the filtrate (grains, vegetables and water) was removed by heating at 40°C in a water bath. The residue was dissolved in distilled water in glyphosate and processed for analysis as above by spectrophotometric methods. The amounts of glyphosate herbicide were calculated based on calibration graphs, and the results of recovery experiments are presented in (Table 3).

Table 3 Recovery (%)^a of glyphosate from fortified grains, vegetables and water samples by spectrophotometric procedure

Amount taken, µg	Wheat		Rice		Water		Carrot		Cauliflower	
	Found, µg	Recovery	Found, µg	Recovery	Found, µg	Recovery	Found, µg	Recovery	Found, µg	Recovery
1.0	0.94±0.01	94.0±1.3	0.91±0.01	91.0±1.2	0.95±0.02	95.0±1.5	0.94±0.02	94.0±1.7	0.94±0.01	94.0±1.2
2.0	1.91±0.02	95.5±1.2	1.85±0.02	92.5±1.1	1.95±0.03	97.5±1.2	1.91±0.03	95.5±1.4	1.91±0.02	95.5±1.1
3.0	2.82±0.03	94.0±1.0	2.78±0.03	92.7±0.9	2.89±0.03	96.3±1.0	2.8±0.03	93.7±1.0	2.82±0.03	94.0±0.9
5.0	4.73±0.05	94.6±0.9	4.55±0.04	91.0±0.8	4.86±0.04	97.2±0.8	4.73±0.04	94.6±0.9	4.74±0.04	94.8±0.8
7.0	6.54±0.05	93.4±0.7	6.37±0.05	91.0±0.7	6.87±0.05	98.1±0.7	6.5±0.05	93.4±0.7	6.53±0.05	92.8±0.6

^aValues are the mean of five determinations with standard deviation

Soil Adsorption Study

Batch equilibration technique has been applied to conduct adsorption studies of glyphosate on three soils with different soil characteristics (Table 4). Each soil type (2 g) in triplicate were equilibrated with glyphosate in the concentration range from 9.3–74.4 µg, on incubated shaker (Genie (TM), Bangalore, India) at 150 rpm at two temperatures viz. 25 and 35 °C for 8 hr equilibrium time (estimated time required for equilibrium to be reached between herbicide adsorbed and in solution). After equilibration, the suspensions were centrifuged and equilibrium concentrations (C_e) were determined in supernatants by the spectrophotometric procedure by taking suitable portions as described above. Freundlich's adsorption coefficients K_f and n_f were calculated from plot of $\log C_e$ versus $\log X$ (where X is the amount of pesticide adsorbed on soil) and Langmuir adsorption coefficients k and b were calculated from the intercept and the slope of the plot of C_e vs C_e/X . The various parameters of these models along with the values of coefficient of determination (r^2) were evaluated and presented in Table 5. The results indicated that data fitted better with Freundlich isotherm model and was used to calculate results of pesticides adsorption in soils according to the following equations as:

$$C_e^{n_f} \dots\dots\dots (1)$$

Where X , is the amount of pesticide adsorbed mg/kg on the adsorbent, C_e is the equilibrium solution concentration (mg/L), K_f and n_f are sorption coefficients that characterize the sorption capacity of adsorbent and are calculated from the least square methods applied to the linear form of the Freundlich's sorption equation.

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

The adsorption parameters viz. distribution coefficient or soil-adsorption coefficient (K_d), soil organic carbon partition coefficient (K_{oc}), thermodynamic parameters viz. Gibb's free energy (ΔG°), enthalpy change (ΔH°), entropy change (ΔS°) and leaching behaviour in terms of Groundwater ubiquity score (GUS) have also been calculated by using following equations reported in literature [28].

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

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

$$\Delta G^\circ = -RT \ln K_d \dots\dots\dots (5)$$

$$\ln \{ (K_d)_2 / (K_d)_1 \} = \Delta H^\circ / R \{ (T_2 - T_1) / T_1 T_2 \} \dots\dots\dots (6)$$

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ) / T \dots\dots\dots (7)$$

$$\text{GUS} = \log(t_{1/2}) [4 - \log(K_{oc})] \dots\dots\dots (8)$$

Where, R is gas constant, T is absolute temperature, $t_{1/2}$ is pesticide persistence (half-life, days) and OC is organic carbon content of the soil.

Table 4 Characteristics of the different Indian soils used in the adsorption study of glyphosate by spectrophotometric method

Soil type	Organic carbon (%)	Clay (%)	pH	Cation exchange capacity (meq/100 g)
I	0.12	21.4	7.11	8.5
II	0.65	23.5	7.45	8.8
III	1.68	26.2	6.53	9.8

Table 5 Spectrophotometric determination of adsorption constants and coefficient of determination (r^2) of glyphosate based on the Freundlich's and Langmuir equations

Temperature	Soil samples	Freundlich			Langmuir		
		K_f	n_f	r^2	k	b	r^2
25 °C	I	2.96	0.74	0.99	0.22	17.11	0.85
	II	3.61	0.64	0.99	0.37	14.24	0.94
	III	5.86	0.48	0.98	1.33	11.94	0.98
35 °C	I	2.72	0.77	0.99	0.18	18.09	0.81
	II	3.47	0.65	0.99	0.33	14.79	0.93
	III	5.60	0.49	0.96	1.70	11.99	0.92

RESULTS AND DISCUSSION

Standardization of the reaction conditions for the spectrophotometric method

The optimized experimental conditions required to achieve maximum absorbance and stability of colored complex has been studied before applying it to the determination of glyphosate in commercial formulation, grains, vegetables, water and soil samples.

Effect of time of hydrolysis

To achieve the maximum color intensity, the hydrolysis time in the microwave was varied from 10 to 100 sec. A hydrolysis time of 60 s gave the maximum color intensity and stability of the complex formed (Fig 2). Hydrolysis time of less

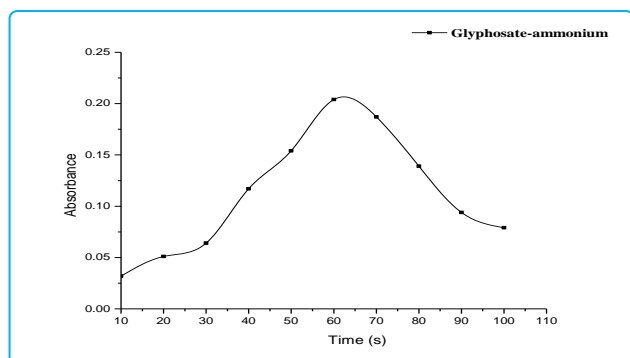
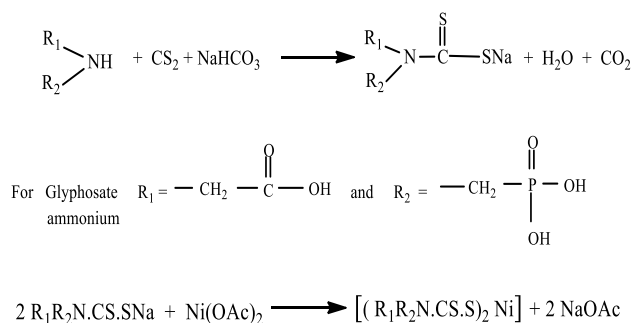


Fig 2 Effect of the time of hydrolysis in microwave on the absorbance value of glyphosate (as nickel(II) dithiocarbamate) complex (concentration = 5 μ g)

Quantification

Under the optimized experimental conditions, the proposed spectrophotometric method obeys Beer's law in the range of 0.4 – 7 μ g/mL with the stability of 300 min. The method is quite sensitive with molar absorptivity (ϵ) and Sandell's sensitivity values of 8.45×10^3 L/mol.cm and 0.02204 μ g/cm² for glyphosate at 388 nm. The limit of detection (LOD) and limit of quantification (LOQ) are 0.24 and 0.7 μ g/mL. To find the validity of the above method, it has subsequently been applied to the determination of glyphosate herbicide in commercial formulation, grains, vegetables and spiked water samples. The recoveries of glyphosate herbicide from commercial formulation were 98.0-99.4 % of the nominal content with relative standard deviations (RSDs) in the range of 0.3–0.8%. The recoveries of glyphosate herbicide from grains, vegetables and spiked water samples were good, ranging from 91.0% to 98.1% with RSDs in the range of 0.6 -1.7%.



Scheme 1 Proposed mechanism for the spectrophotometric method

Proposed mechanism for the spectrophotometric method for glyphosate-ammonium

than 60 s gives less intensity of the color, indicating non-completion of the reaction.

Effect of solvent

The effect of different diluting solvents such as water, ethanol, methanol, acetonitrile and acetone were studied. The maximum stability of the complex was observed to be obtained by taking water as a solvent for glyphosate herbicide.

Effect of carbon disulfide variation

The effect of different CS₂ concentrations has been studied, and it has been found that with an increase in the concentration of CS₂ the colour intensity increases. When the concentration is increased beyond 10%, the solution becomes turbid (Fig 3).

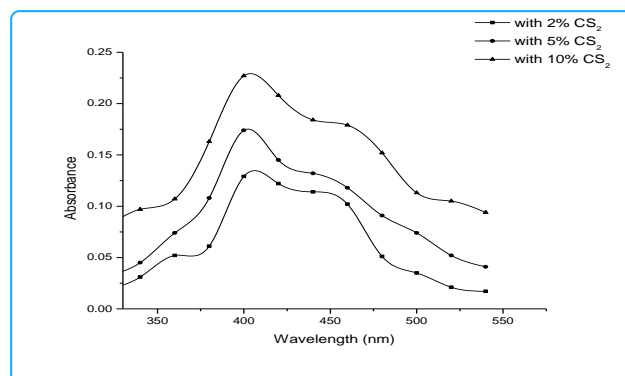


Fig 3 Effect of variation of carbon disulfide concentration on absorbance value in glyphosate

For the analysis of glyphosate, the primary step involves the alkaline hydrolysis of glyphosate to corresponding amino function, which subsequently reacts with carbon disulfide and forms sodium dithiocarbamate complex as shown in scheme 1. The sodium dithiocarbamate complex formed, on reaction with nickel (II) acetate in an aqueous acetonitrile medium forms yellow-colored nickel(II) dithiocarbamate [Ni(DTC)₂] complex [28], which is measured under optimized conditions at 388 nm (Scheme 1).

The reaction proceeds in 2:1 molar ratio has also been established by photometric titration of glyphosate with nickel(II) acetate in aqueous acetonitrile medium at 388 nm (λ_{max} of colored complex (Fig 1). The absorbance increases till glyphosate to nickel (II) molar ratio of 2:1 is achieved with the formation of yellow colored [Ni(DTC)₂] complex, and after that the absorbance becomes almost constant indicating that no more colored complex formed (Fig 4).

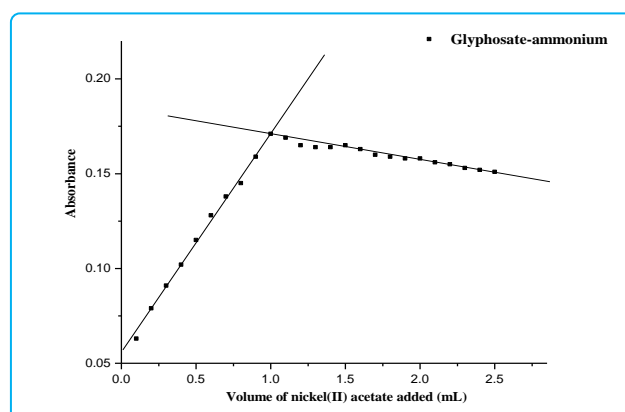


Fig 4 Photometric titration curves of glyphosate as nickel(II) dithiocarbamate complex

Soil adsorption study

To assess the leaching behaviour of glyphosate, adsorption studies were conducted on three different soils (Table 4) by above proposed method. The Freundlich's model fitted well with the adsorption data in comparison to Langmuir model (Fig 5-6) with higher value of coefficient of determination (r^2) (Table 5). To study the interaction between adsorbate and adsorbents the adsorption isotherms were studied [29]. The isotherms obtained for glyphosate are almost L type depending on the initial slope of the curve which is further supported by n_f values ($n_f < 1$), (Table 5). The L-type curves represent a relatively high affinity between the solid surface and solute at the initial stages of the isotherms (Fig 7) [30] and

indicates a gradual decrease in sites available for sorption as the concentration of the solute in the solution increases [31]. L-type curves also infer that there is minimum competition from solvent molecules for adsorption sites on the adsorbing surface [32]. The values of soil adsorption coefficients, K_d (Table 6) indicates higher adsorption of glyphosate in soil III on the basis of higher organic and clay content as they increase number of adsorptive sites, on which pesticide molecules can bind and enhance pesticide adsorption [33]. The thermodynamics parameters (ΔG° , ΔH° and ΔS°) for the adsorption of glyphosate on three soils at two temperatures viz. 25 and 35 °C were listed in (Table 6).

Table 6 Adsorption parameters for the adsorption of glyphosate on three Indian soils at three different temperatures

Temp.	Soil samples	K_d	K_{oc}	Log K_{oc}	Adsorption isotherm	GUS	ΔG° (KJ K^{-1} mol $^{-1}$)	ΔH° (30 $^\circ$ C)	ΔS° (30 $^\circ$ C)
25 °C	I	2.64	2198.92	3.34	L- type	0.75	-2.36	I= -6.95	I= -0.015
	II	3.27	696.48	2.84	L-type	1.33	-2.89		
	III	7.08	421.96	2.62	L- type	1.57	-4.77		
35 °C	I	2.41	2015.16	3.30	L- type	0.79	-2.15	II= -3.83	II= -0.003
	II	3.11	662.61	2.82	L-type	1.35	-2.77		
	III	6.47	385.16	2.58	L- type	1.62	-4.55		

The negative values of free energy change (ΔG°) and enthalpy change, (ΔH°), suggest the spontaneous, exothermic and physical nature of adsorption process. The negative values of entropy change (ΔS°), indicates decrease in randomness at the solid/ solution interface during the adsorption process [34-35]. The adsorption capacity of glyphosate on all three soil samples decreased with increase in temperature which is further suggested by adsorption coefficients values (K_d), as it also decreased with increase in temperature (Table 6). Therefore,

adsorption capacity for glyphosate on three soils decreases as soil III > soil II > soil I. The mobility and persistence of glyphosate, in groundwater can be assessed in terms of ground water ubiquity score (GUS), [36] which is a measure of leachability. The GUS values (Table 6) were calculated by reported method using experimentally observed K_{oc} values and literature reported half-life of glyphosate. The values of GUS in the range 0.75-1.62, classify it as non-leacher pesticide [36] thereby, it does not pose potential risk to aquatic environment.

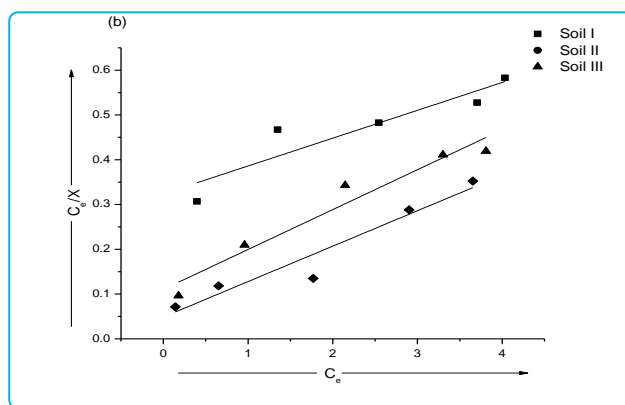
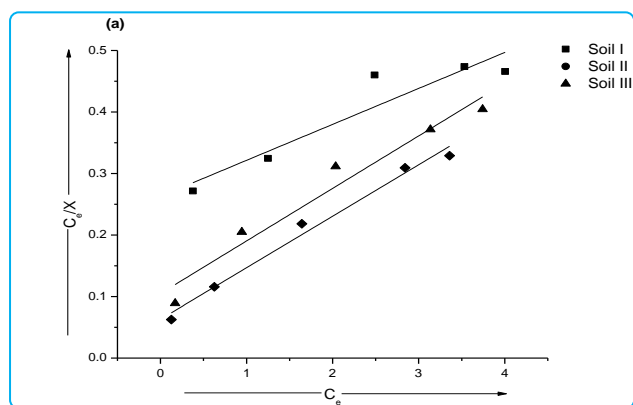


Fig 5 Plot of C_e/X versus C_e for the evaluation of Langmuir's adsorption coefficients k and b at 25 °C (a) and at 35 °C (b)

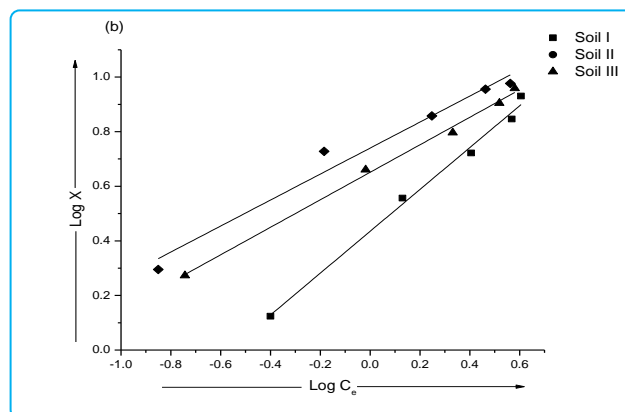
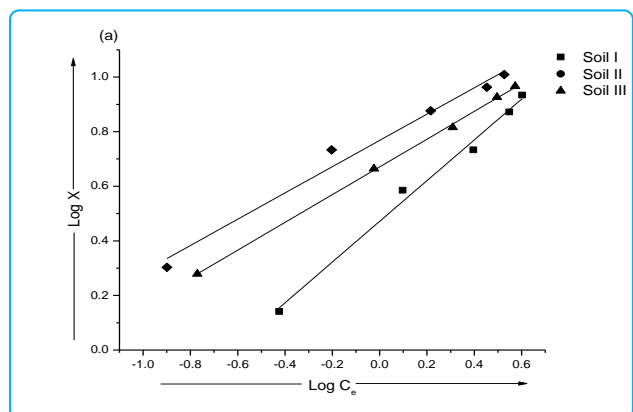


Fig 6 Plot of C_e/X versus C_e for the evaluation of Freundlich's adsorption coefficients k and b at 25 °C (a) and at 35 °C (b)

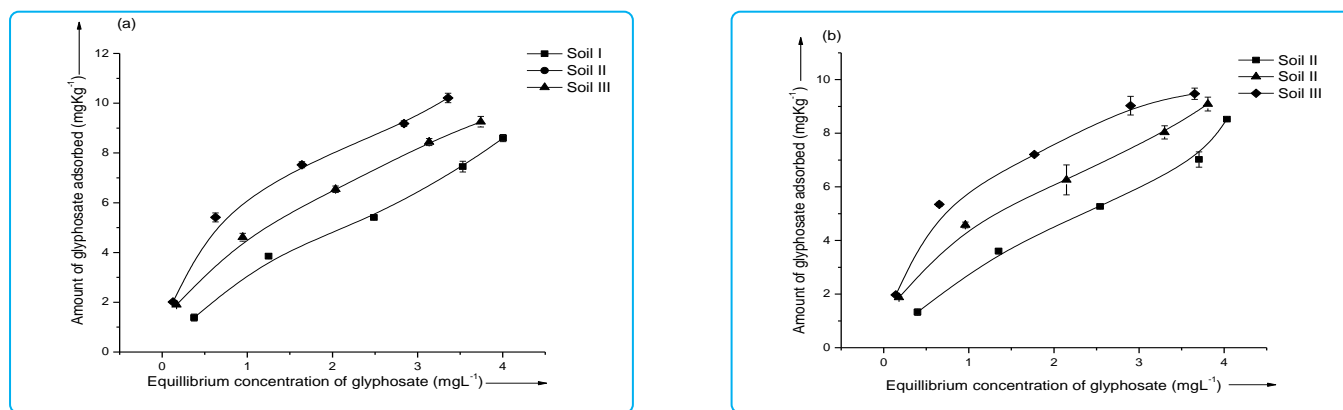


Fig 7 Adsorption isotherms of glyphosate adsorption on soils I-III at 25 °C (a) and at 35 °C (b)

CONCLUSION

The proposed spectrophotometric method is simple, sensitive, reliable and economical, allowing the determination of glyphosate herbicide in bulk as well as in commercial formulations. The high recoveries of glyphosate herbicide in formulation and residue analysis, with low relative standard deviation values show good accuracy and precision of the method. The thermodynamic parameters indicate the

spontaneous, exothermic and physical nature of adsorption process. Higher organic carbon and clay content of soils enhances the adsorption of glyphosate. The leaching potential for glyphosate in terms of GUS, classify it as non-leacher pesticide, therefore it does not cause potential risk to aquatic environment. However, to increase its adsorption and reduce the mobility the application doses can be adjusted according to soil properties and amending soils with clay and organic amendments.

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