



A Study of Adsorption and leachability of Monuron on Five Soils and Implications Concerning Groundwater Contamination

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Abstract

The aim of this study was to determine monuron herbicide contamination in surface and ground water. The adsorption of herbicide on five soils of different characteristics has been carried out by using a batch equilibrium technique at two different temperatures viz 25°C and 35°C. A spectrophotometric methodology has been developed based on the reaction of dimethyl amine (formed from hydrolysis of monuron with potassium tert.-butoxide) with carbon disulphide and nickel (II) acetate to form methyl isobutyl ketone (MIBK) extractable yellow nickel(II) dimethyl dithiocarbamate [Ni(DTC)₂] complex showing λ_{max} at 428 nm for this purpose. The molar absorptivity (ϵ) and Sandell's sensitivity were found to be 3.35×10^3 L/mol cm and $0.059 \mu\text{g}/\text{cm}^2$ respectively. The leaching potential has been evaluated by Groundwater Ubiquity Score (GUS) and the values obtained in the range 2.88-3.07 classify as leacherpesticide thereby could endanger live of aquatic environment and consumers. Thus, necessitate it for judicious use to reduce contamination risk to ecosystem.

Keywords: Spectrophotometry, Adsorption, Monuron, Leachability, GUS.

I. INTRODUCTION

Phenylurea compounds are used as selective herbicides and is one of the most important and extensively used class of herbicide worldwide. As a result of their intensive use, they can get into water via drift during pesticide spraying, by runoff from treated area, leaching through the soil thus detected as contaminants of rivers, streams, lakes, and seawater in many countries [1-6]. The contamination of water, residues on foodstuff and earth's atmosphere by pesticide are the areas of concern. Therefore, from environmental point of view, the examination of adsorption phenomenon and evaluation of leachability of pesticides is of great significance to assess the ground and surface water contamination. The adsorption study of pesticide on soils of different characteristics assists for the prediction of their movement in soils and aquifers.

Among the family of phenyl urea herbicides, monuron is used extensively to control weeds in agriculture as well as in non-cropped areas such as roads, train lines and sports pitches. Research on toxicity data have suggested that monuron herbicide as well as some of their degradation metabolites are unfavorable not only for animals, plants, algae and microbial activities but also for humans [7,8]. To estimate this herbicide in requisite environmental concentration, easy and reliable method is required. Of the various analytical methods viz. chromatographic [9-11], fluorescence [12,13], potentiometric [14] and the spectrophotometric methods [15] being simple, sensitive and find wide acceptance by laboratories of limited means. In view of the above, an extractive spectrophotometric method has been developed for the determination of

monuron and validated to study adsorption on five soils of different characteristics at two temperatures viz 25°C and 35°C, to evaluate its leachability and surface and ground water contamination, as the pollution of soil, ground and surface water involves a serious risk to the environment and also to human health by the way of direct exposure or through residues in drinking water.

The examination of this herbicide in farming produce and water for the purpose of anticipation of health hazards has also been approached in this study. In the present work the herbicide is hydrolysed with potassium *tert.*-butoxide (PTB) to dimethylamine in microwave and its subsequent reaction with carbon disulfide and nickel(II) acetate to form yellow coloured nickel(II) dimethyldithiocarbamate complex [Ni(DTC)₂].

II. MATERIAL AND METHODS

The analytical standard of monuron (Sigma, 99%) was used as received. A commercial formulation containing 80% monuron WP (Telvar) was procured from the authorised dealer. Acetonitrile (Merck, AR) was twice distilled from phosphorous pentoxide (5g/L). Potassium *tert.* butoxide (Loba Chem., AR) (Ranbaxy, SAS Nagar, Punjab, India, LR, 1 M solution in *tert.*-butanol) was used for hydrolyzing the herbicide. Methyl isobutyl ketone (MIBK, Merck, Mumbai, India, AR) was used as received. Nickel (II) acetate (Central Drug House, Delhi, India, LR), its 0.01 M solution in distilled water was prepared by dissolving 0.249 g of the compound in distilled water and standardized by EDTA titrations. Sodium sulphate anhydrous (Merck, AR) 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. 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.

2.1 Preparation of calibration graph for pure compound:

Aliquots (0.1-2.0 mL) of standard acetonitrile solution of the herbicide (10^{-3} M) were taken in 10 mL measuring flasks and volume made to 2mL with acetonitrile. Each solution was mixed with 0.7mL of 0.02mol L^{-1} solution of potassium *tert.*butoxide (PTB) followed by 0.3mL solution of water in acetonitrile (prepared by adding 1 drop (~100 μL) of distilled water in 10 mL of acetonitrile) and kept in microwave for 60 seconds. Each solution was mixed with one drop of carbon disulphide (~100 μL) followed by acetic acid (1 mL, ~1 M 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 1 mL, 0.01 M nickel (II) acetate solution. The contents of the funnel were equilibrated two times with MIBK using 2.5 mL each time and total volume of the MIBK extract was made to 5 mL with MIBK. The solution was dried with anhydrous sodium sulfate and the absorbance of yellow coloured solution was measured at 428 nm against a reagent blank and calibration curve was prepared (Fig.1) by plotting absorbance values against concentration. The calibration characteristics viz. Beer's law range, molar absorptivity, Sandell's sensitivity, slope and intercept values and correlation coefficient calculated from calibration graph and are given in Table 1.

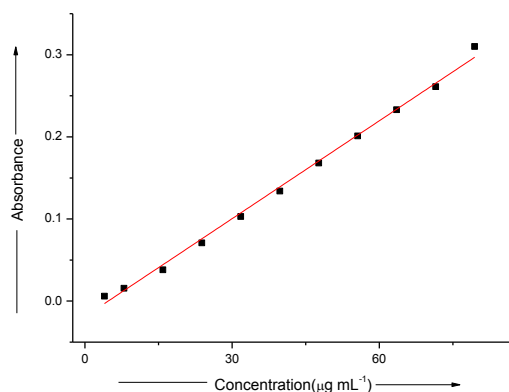


Figure 2. Calibration graph of monuron at 428 nm.

2.2 Formulation analysis:

The herbicide formulation viz. Telvar containing 80% monuron(W.P.) was used. A single large sample of this formulation equivalent to 10^{-3} M concentration 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 method described above. The assay results are given in Table 2.

2.3 Residue analysis: Determination of monuron in grains (Barley and Wheat) and water samples:

A known weight (5g) of grain (barley and wheat) was mixed with various amounts of herbicide formulation. The samples were well mixed and extracted with 2 - 3 instalments of 5mL of benzene. The combined extracts were shaken for 5 minutes and filtered. The solvent from the filtrate was removed by heating at 40°C in a water bath. The residue was transferred into a 10mL measuring flask with acetonitrile and processed for analysis as described above. The proposed method has also been applied to the determination of the herbicide in spiked water samples. Various amounts of herbicide formulation were added to 25 mL water samples and were mixed thoroughly. The samples were extracted with benzene and the extract processed for analysis in the same manner as described above. The results are given in Table 3.

2.4 Soil adsorption study:

Triplicate soil samples (2g) were taken in 50-mL conical flasks and were equilibrated with 3 mL acetonitrile solution of monuron in the concentration range from 15.89-79.46 $\mu\text{g mL}^{-1}$ and 7 mL distilled water. The contents of each flask were stirred to bring effective mixing by shaking mechanically at 140 rpm for 12 h equilibrium time (estimated time required for equilibrium to be reached between monuron adsorbed and monuron in solution) and placed in shaker at two different temperatures 25°C and 35°C. After 12 h the suspensions were centrifuged and equilibrium concentration (C_e) was determined in the supernatant in the same manner as described above for pure compound.

The adsorption parameters were evaluated using Freundlich (equation 1) and Langmuir (equation 2) adsorption models.

In Freundlich's adsorption equation, X is the amount of pesticide adsorbed mg/Kg of the soil; C_e is the equilibrium solution concentration (mg/L). The adsorption isotherms are shown in Fig.3 at 25°C and Fig.4 at 35°C. The adsorption coefficients K_f and n_f are related to the adsorption capacity and adsorption intensity respectively. Their values were calculated from the intercept and the slope of the straight line of the linearized form of the Freundlich isotherm. In case of Langmuir isotherm equation, constant k is related to the free energy of adsorption and b reflects the equilibrium constant for the adsorption process and is an indication of the affinity of the adsorbent for pesticides. The values of k and b were calculated from the intercept and the slope of the straight line of the linearized form of the Langmuir isotherm.

Other parameters for the adsorption process viz. soil-adsorption coefficient (K_d) and soil organic carbon partition coefficient (K_{oc}) were calculated as;

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

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

Where OC is organic carbon content of soil [16,17]. The leachability of monuron in five soil types has been evaluated in terms of the GUS index which is an experimentally calculated value that relates pesticide half-life and K_{oc} [18-20].

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

$t_{1/2}$ is pesticide persistence (half-life). The results of soil characteristics and adsorption studies are presented in Table 4 and 5 respectively.

The thermodynamic parameters viz. Gibbs free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) have also been calculated [21].

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

$$\ln[(K_d)_2 / (K_d)_1] = \Delta H^\circ (T_2 - T_1) / R(T_1 T_2) \quad (7)$$

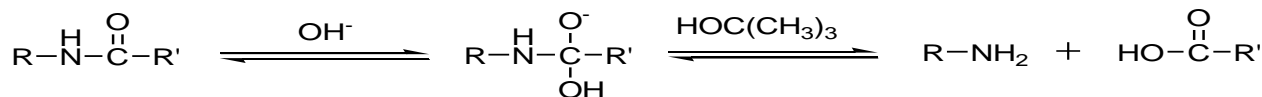
$$\Delta S^\circ = \Delta H^\circ - \Delta G^\circ / T \quad (8)$$

where R is gas constant and T is absolute temperature.

III. RESULTS AND DISCUSSION

In present study, the spectrophotometric method is based on the color reaction of dimethylamine (hydrolytic product of monuron) with carbon disulphide to form dithiocarbamate which reacts with nickel (II) acetate in water to form MIBK extractable yellow coloured $[\text{Ni}(\text{DTC})_2]$ complex. The proposed method for the determination of monuron possess advantages over the commonly used colorimetric method [15] in terms of instantaneous development of colour, its sufficient stability, and above all the simplicity, rapidity and reliability of the procedure.

It is important to mention that above hydrolysis of monuroninfect involves the cleavage of its amide function. Though amides are susceptible to both acidic and alkaline hydrolysis but owing to their acid sensitivity and thermal liability, hydrolysis with a base is preferred. However, in either case, the hydrolysis of amide is frequently an inefficient process [22,23] requiring long time heating and high temperature. Gassman et al.[24] reported the use of potassium *tert*.butoxide (PTB) for selective hydrolysis of amides at room temperature. The reagent has double base action i.e. first the hydroxylation of a carbonyl group followed by dehydrogenation of hydroxyl group. The strong nucleophilic and poorly solvated hydroxide adds to carbonyl of amide group and its subsequent deprotonation by *tert*.butoxide as:



In the present work PTB in *tert*.butanol has been found a suitable hydrolyzing agent for the amide group present in the above herbicide and consequently in developing proposed spectrophotometric method. The hydrolysis by this reagent has been carried out by 0.7 ml of 0.02 molL⁻¹ PTB in *tert*.butanol followed by 0.3 mL solution of water in acetonitrile (prepared by adding 1 drop (~100 µL) of distilled water in 10 mL of acetonitrile, optimum concentration of hydrolyzing agent) in a microwave. Microwave-assisted hydrolysis is an effective alternative to conventional procedure as the former not only reduces the hydrolysis time but also the problems associated with analyte losses and atmospheric contamination [25].

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. Nickel (II) acetate and other hydrolytic products are not extractable into MIBK and hence do not interfere in this method. The kinetic stability of the yellow coloured product under optimized condition has been found to be 120 min. The calibration curves for monuron under the optimized conditions were obtained by plotting absorbance corresponding to different concentration of herbicide and was found to be linear in the range 3.97-79.46 µg mL⁻¹ of monuron solution. The optical and calibration characteristics are summarized in Table 1. Linearity was indicated by high correlation coefficient (r²) obtained. The r² value found to be 0.994 indicating good linearity. The method is quite sensitive and the molar absorptivity (ε) found to be 3.35×10³ L mol⁻¹cm⁻¹ at 428 nm. The maximum relative standard deviation (RSD) calculated from the pooled data of all the five runs made with 7.90-71.51 µg of pure monuron was 1.12% (Table 2). The method was subsequently applied to the determination of monuron in commercial formulation and in residues on grains (barley and wheat) and spiked water samples. When applied to the assay of a commercial formulation containing 80% active ingredient, the recoveries of the active ingredient were in the range 92.31-97.80% of the normal content with RSDs in the ranges 0.41-1.17 % (Table 2).The recoveries of the herbicide from spiked water and fortified grains samples ranged from 88.74-96.66% and 82.74-93.21% with RSDs in the ranges 0.49-0.98 % and 0.41-1.01% respectively (Table 3). The formulation analysis is essential not only to ensure the quality of its marketed products but also to obtain reliable residue/adsorption data. The results, have however, been compared by an independent method[15]. The validity of the method was assessed by investigating the effect of common cations generally present in soil and water like Na⁺, K⁺, Ca²⁺, Mg²⁺, Al³⁺, Fe²⁺, Pb²⁺, Cl⁻

, SO_4^{2-} , CO_3^{2-} , NO_2^- , NO_3^- , SCN^- , PO_4^{3-} , CH_3COO^- . These ions do not obstruct in the present method.

Table 1. Spectrophotometric determination of monuron as colored $\text{Ni}(\text{DTC})_2$ complex: calibration characteristics.

Optional Characteristics	Corresponding Values
λ_{max}	428nm
Beer's law range	3.97-79.46 $\mu\text{g mL}^{-1}$
Molar absorptivity(ϵ)	$3.35 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$
Sandell's sensitivity	$0.059 \mu\text{g cm}^{-2}$
Stability	120 min
Slope	0.0039
Intercept	-0.019
Correlation coefficient (r^2)	0.994

Table 2. Assay of a commercial formulation containing 80% active ingredient.

Active Ingredient Taken (μg)	Recovery of Active Ingredient (%)	
	Present Method ^a	Comparison Method ^b
7.90	92.31 \pm 1.04	93.32 \pm 0.65
23.83	92.54 \pm 1.01	93.20 \pm 0.43
39.73	97.80 \pm 0.97	95.32 \pm 0.79
55.62	96.55 \pm 1.12	92.86 \pm 1.21
71.51	94.21 \pm 0.41	96.01 \pm 1.37

^aValues are mean of five determinations with standard deviation (\pm).

^bReference method¹⁵.

Table 3: Recovery of monuron from grains (Barley and Wheat) and water samples.

Monuron (μg)	Recovery* (%)					
	Present method			Comparison method ^b		
	Barley	Wheat	Water	Barley	Wheat	Water
9.93	87.29 \pm 0.69	86.74 \pm 0.63	96.66 \pm 0.49	89.99 \pm 0.64	85.29 \pm 0.53	94.99 \pm 0.98
19.86	90.67 \pm 0.95	85.01 \pm 1.01	91.65 \pm 0.81	94.01 \pm 0.34	87.65 \pm 1.09	89.99 \pm 0.89
29.80	93.21 \pm 0.78	82.74 \pm 0.77	88.74 \pm 0.98	88.36 \pm 0.91	85.09 \pm 0.83	87.74 \pm 1.11
39.73	91.53 \pm 0.41	88.37 \pm 0.95	96.12 \pm 0.65	91.10 \pm 0.59	90.01 \pm 1.34	95.01 \pm 0.75

*Values are mean of five determinations with standard deviation (\pm).^bReference method¹⁵

The adsorption of these herbicides on five soils has been studied by the proposed spectrophotometric method and characteristics of five soils used in the adsorption study of monuron are given in Table 4. Using batch equilibrium procedure for soil adsorption study, two isotherm models Freundlich and Langmuir were used to fit the experimental data. The various parameters of these models for the adsorption of monuron on to soil samples along with the values of coefficient of determination (r^2) were evaluated and are given in Table 5. The results of the adsorption isotherms showed that the value of coefficients of determination is high ($r^2 > 0.89$) for Freundlich isotherm than Langmuir isotherm ($r^2 > 0.40$), indicating that data fitted better with Freundlich isotherm model and consequently can explain satisfactorily the results of adsorption in soils. So, the adsorption isotherms have been evaluated by Freundlich equation.

Table 4: Characteristics of five soils used in the adsorption study of monuron.

Soil Sample	pH	Clay (%)	Organic Carbon (%)	Cation Exchange Capacity (meq/100 g)
I	6.90	10.2	0.7	12.8
II	7.40	5.0	0.8	12.7
III	7.50	26.3	0.9	13.1
IV	7.62	18.2	1.0	12.9
V	6.50	20.0	1.5	11.5

Table 5: Adsorption constants and coefficient of determination (r^2) of monuron on five Indian soils at two temperatures based on the Freundlich and Langmuir equations

25°C	Freundlich				Langmuir		
	Soil	K_f	n_f	r^2	k	b	r^2
	I	29.8	2.24	0.96	0.15	148.40	0.86
	II	31.1	2.25	0.89	0.16	152.22	0.79
	III	32.1	2.28	0.91	0.16	152.34	0.62
	IV	33.9	2.35	0.96	0.17	152.52	0.81
	V	38.1	2.53	0.98	0.20	152.11	0.78
35°C	I	31.5	2.30	0.91	0.16	147.75	0.82
	II	32.9	2.32	0.97	0.17	150.75	0.77
	III	34.9	2.41	0.91	0.18	150.00	0.40
	IV	36.4	2.47	0.97	0.19	150.56	0.72
	V	40.5	2.65	0.96	0.23	148.31	0.80

Adsorption parameters such as the soil-adsorption coefficient (K_d), soil organic carbon partition coefficient (K_{oc}) and Groundwater Ubiquity Score (GUS) for the adsorption of monuron were also calculated and are presented in Table 6.

Table 6: Adsorption parameters for the adsorption of monuron on five Indian soils at two different temperatures.

Soil Sample	25°C				35°C			
	K_d	K_{oc}	GUS	ΔG^0 kJ(mol ⁻¹)	K_d	K_{oc}	GUS	ΔG^0 kJ(mol ⁻¹)
I	8.50	500.12	2.88	-5.21	8.84	491.39	2.9	-5.31
II	8.95	497.50	2.89	-5.34	9.31	489.8	2.91	-5.43
III	9.20	484.45	2.91	-5.41	9.67	483.49	2.92	-5.53
IV	9.60	497.82	2.92	-5.51	10.12	476.99	2.93	-5.61
V	10.46	418.32	3.06	-5.72	10.89	418.74	3.07	-5.82

The strength of sorption of pesticides to soils is related to two basic parameters K_d and K_{oc} of the pesticide. The values of K_d , soil-adsorption coefficient represents the extent of sorption and in general higher the K_d value, greater is pesticide sorption[26]. Soil organic carbon partition coefficient (K_{oc}) relates to the hydrophobicity of the pesticides. Based on these parameters, the order of sorption in five soils of different characteristics studied is: Soil V > Soil IV > Soil III > Soil II > Soil I. In soil IV and Soil V, the high organic content is soil V is responsible for higher sorption[27]. The cation exchange capacity (CEC) is another parameter that influences the adsorption of pesticide. The value of CEC is directly proportional to the hydrophobic nature of adsorbent: the greater the value of CEC of soil, the more hydrophobic is its surface. The organic

pesticides, being more hydrophobic (low water solubility), have a higher adsorption affinity for the soils with higher CEC[28].The adsorption isotherms of monuron on five Indian soils of different soil characteristics at two different temperatures are shown in Fig.2 and Fig.3.

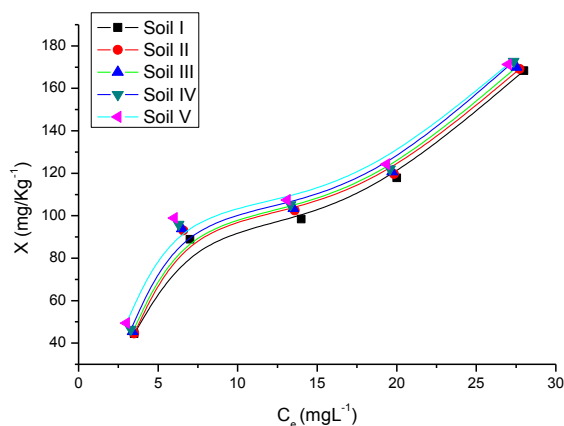


Figure3: Adsorption isotherm of monuron sorption on soils I–V at 25 °C

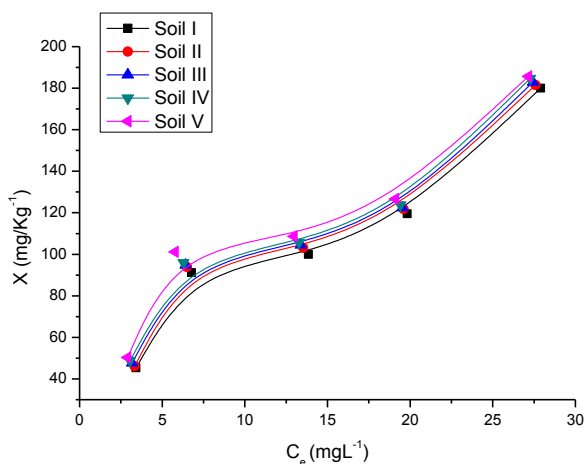


Figure 4: Adsorption isotherm of monuron sorption on soils I–V at 35 °C

The thermodynamic parameters for the adsorption of monuron herbicide on five soils were also calculated and are presented in Table 7. The value of Gibb’s free energy (ΔG°) and enthalpy change (ΔH°) for the adsorption of monuron were observed negative in all the cases suggesting the energetically favourable adsorption process[21]. The negative value of ΔS° shows decreased randomness at the adsorbent and solution interface[29]. The adsorption of herbicide decreased with the increase in temperature. Generally, with the rise in temperature, the pesticide becomes more soluble and the adsorbate-adsorbent bonds also got weakened. As monuron has very weak adsorption in all the tested soils, it can lead to the penetration of this herbicide into groundwater[30,31].

Table 7: Thermodynamic parameters for the adsorption of monuron on five Indian soils.

Soil samples	ΔG° (kJ/mol)		ΔH° (kJ/mol)	ΔS° (kJ/Kmol)
	25°C	35°C		
Soil I				
Soil II				
Soil III				
Soil IV				
Soil V				

I	-5.21	-5.31	-1.27	-0.042
II	-5.34	-5.43	-1.28	-0.043
III	-5.41	-5.53	-1.62	-0.053
IV	-5.51	-5.61	-1.71	-0.057
V	-5.72	-5.82	-1.30	-0.043

Groundwater Ubiquity Score (GUS) is the most frequent used model which relates pesticide persistence (half life) and adsorption in soil (K_{OC}). The leaching potential of herbicide in terms of GUS index was determined by using experimentally observed K_{OC} value for each soil sample and literature reported half life of monuron [20]. GUS index for monuron was 2.88-3.07 (Table 6), which is higher than 2.8, which corresponds to a high-leacher compound. Present study shows that the toxicity due to this herbicide can be reduced by adjusting the application dose according to soil type especially near the water bodies. Other alternatives such as soil should be amended with farmyard manure and compost which are rich in organic matter content in order to increase the herbicide retention and thus reducing its mobility. These amendments not only reduced GUS value but also served as a source of nutrients, thus improving the soil fertility [32].

IV. CONCLUSION

Phenyl Urea pesticides are the most important pesticide group not only in agricultural but also in non-cropped areas. Thus they are prime source of pollution of soil, ground and surface water and poses a serious risk to both environment and human health due to direct exposure or through residues in food and drinking water. The applied pesticide enters into soil and detected in aquatic environment by leaching thus resulting into surface and ground water contamination. The threat of leaching of monuron has been evaluated by assessing its adsorption on five soils of different soil characteristics at two different temperatures viz. 25 °C and 35 °C by the proposed method. The present study showed that monuron is adsorbed maximally at soil V among the five soils as it has maximum organic content. The observed GUS values in the range 2.88-3.07 classifying it as a leacher pesticide in terms of leaching behaviour, thereby it constitute potential risk to the ground water as well as to aquatic environment. Hence it should be used judiciously to prevent groundwater contamination. The present method has also been applied with success to the determination of this herbicide in residues on environmental samples where the recoveries are good thus validating the present method.

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