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Supramolecular solvent microextraction of phenylurea herbicides from environmental samples

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ABSTRACT

An efficient microextraction method was developed for extraction and determination of phenylurea herbicides (monuron, linuron and isoproturon) in water and rice samples followed by analysis with high performance liquid chromatography (HPLC). The proposed method based on microextraction of herbicides in supramolecular solvent (SUPRAs, 400 mg decanoic acid; 15% THF) for 1.0 min of centrifugation. Factors affecting the extraction efficiency of herbicides like pH, amount of decanoic acid (DeA), volume of tetrahydrofuran (THF), composition of SUPRA, centrifugation time and sample amount were studied. Limit of detection (LOD) and quantification (LOQ) were 30 $ngmL^{-1}$ and 10 $ngmL^{-1}$ for monuron, 10 $ngmL^{-1}$ and 30 $ngmL^{-1}$ for linuron, 30 $ngmL^{-1}$ and 100 $ngmL^{-1}$ for isoproturon with linear range of 0.3–20 (10^3) $ngmL^{-1}$. The inter-day RSD values were 2.5–3.7%, 4.2–5.5% and 5.2–7.2, while for intra-day the obtained RSD values were 3.2–4.1%, 4.3–5.2% and 5.2–6.5% for 5,10, 15 (10^3 $ngmL^{-1}$), respectively. The proposed method has been applied successfully to the spiked water and rice samples and recoveries in the range of 91.1–99.0 % for tape water, 82.5–94.0% for canal water and 80.0–85.5% for rice samples were obtained.

Keywords: Phenylurea herbicides; Supramolecular solvent; Microextraction; Decanoicacid

1. Introduction

Contamination of agricultural products with various pesticides is quite frequent due to the use of high amounts of pesticides to protect crops from diseases and pest. The intake of these pesticides can cause birth defects, cancer, severely affect endocrine, nervous and immune systems etc. The extent of the damage to human health depends largely on the toxicity and amount of contaminants consumption. Therefore, the control of these pesticides in consumer products is of major concern [1].

Phenylurea herbicides are commonly used to control many broad leaves perennial and annual weeds [2]. Among these, monuron (MRN), linuron (LRN) and isoproturon (IP) have been reported to be carcinogenic; and their annual consumption in Europe has been included in the European ''black list' [3]. Because of water solubility and persistent of their soil-based residues, for several months, they can easily enter into the food chain. These herbicides also migrate to groundwater depending on surface run-off, rainfall pattern and soil properties which leads to the accumulation of these herbicides to toxic level. Slow degradation process and absence of microbial activity leads to their persistence in soil and water for several months [4,5]. The structures and some properties of the monuron, linuron and isoproturon herbicides are given in Table 1.

Phenylurea herbicides have been detected in wastewater treatment plant effluents and raw drinking water sources in concentrations that exceed the drinking water quality value proposed by the EU; i. e. 0.1 μgL^{-1} for each individual pesticide and 0.5 μgL^{-1} for the total concentration of pesticides and related products, foreseen in the European Drinking Water Directive 98/83. Due to their potential risks even at low concentrations, such as toxicity and possible carcinogenic properties for humans and wildlife, the removal of phenylurea herbicides constitutes a priority objective in the water industry. Toxicity of phenylurea herbicides has been

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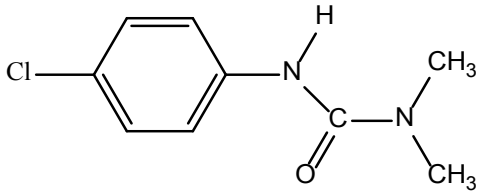
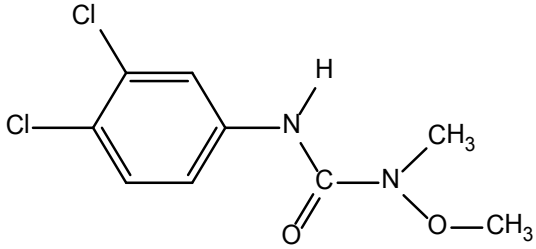
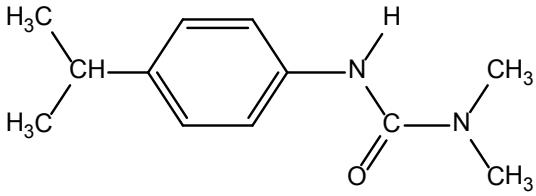
Table 1
Chemical structures, LD_{50}, octanol-water partition coefficients (log $K_{o/w}$), ionization constants (pK_a) and numbers of donor acceptor groups of selected herbicides

Pesticide	Chemical structure	LD_{50} (mg Kg^{-1}) [6]	Log $pK_{o/w}$ [a]	pK_a [a]	H donor and acceptor sum
Monuron		1053	1.93	14.2	2
Linuron		1146	3.21	12.1	3
Isoproturon		1826	2.82	15.1	2

[a]source : soft cambridge

quantified in terms of LD_{50}, i.e., the amount of a material, given all at once, which causes the death of 50% (one half) of a group of test animals. The LD_{50} is one way to measure the short-term poisoning potential (acute toxicity) of a material in experimental animals. These herbicides can be found for any route of entry or administration to the biota but dermal (applied to the skin) and oral (given by mouth) administration are the most common. Based on the LD_{50} values (Table 1), these herbicides are classified to be toxic and had been included in the list of endocrine disruptors chemicals [6].

Different conventional techniques have been developed for the extraction of different herbicides. These techniques include microwave-assisted extraction (MAE) [7,8], pressurized liquid extraction, (PLE) [9], supercritical fluid extraction (SFE) [10], hollow fiber-based liquid-phase microextraction (HF–LPME) [11], matrix solid-phase dispersion (MSPD) [12,13], solid-phase microextraction (SPME) [14] and stir-bar sorptive extraction (SBSE) [15]. However, there is a gap in the development of microextraction techniques for the treatment of various agricultural based samples, mainly due to the low extraction efficiency of organic solvents and their complex matrices [16]. The recent trends in analytical chemistry is towards the use of microscale methods for analysis. For the extraction of smaller concentrations of analyte from environmental samples, microscale liquid–liquid and liquid–solid extraction methods have been developed as environmentally friendly, cost effective, fast and easy to handle the samples [17–19].

Supramolecular solvents (SUPRAs) are water immiscible nanostructured liquids made from amphiphilic molecules through self-assembly processes having outstanding properties for analytical extraction at the microscale [14,20]. These are three-dimensional ordered aggregates with sites of different polarity offering a number of interactions for analyte solubilization (i.e., hydrogen bond, dipole–dipole, π-cation, hydrophobic interactions, etc.) making them suitable for extraction of organic molecules in a wide polarity range. Thus, a large number of binding sites, permits to develop a simple, fast and efficient sample treatment methods with high extraction efficiency [17,21,22].

The supramolecular solvent proposed in the present work has been used first time for the simultaneous monitoring and extraction of mixture of monuron, linuron and isoproturon from agricultural products and water samples. The solvent was produced from decanoic acid (DeA) in tetrahydrofuran (THF) having large surface area which permits good extraction and high sensitivity. The type of interaction involved in extraction process is also discussed in detail. The obtained results in optimization studies, evaluation of analytical parameters and applications to real samples are presented and discussed.

The aim of the proposed method is to develop an extraction procedure for mixture of herbicides, in non-fatty foods, that could be very useful for developing countries whose laboratories are not equipped with expensive instruments. Green chemistry approach was also adapted for developed method using "Analytical Eco Scale"concept.

2. Experimental

2.1. Reagents

Analytical grade chemicals were used as supplied without further purification. HPLC-grade methanol (99.9%) was supplied by BioM Laboratories, Cerritos, USA, Chemical Division (Malaysia) and acetonitrile (99.9%) by Lab-Scan Analytical Sciences, Asia Co. (Pathumman, Bangkok, Thailand). Decanoic acid (DeA) and Tetrahydrofuran (THF) were purchased from Merck Schuchardt OHG 85662 Hohenbrunn, Germany and Sigma Aldrich (89555St. Louis, MO, USA), respectively. High purity (>98%) pesticide standards i.e. monuron [3-(4-chlorophenyl)-1,1-dimethylurea], linuron [3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea] and isoproturon [3-(4-isopropylphenyl)-1,1-dimethylurea] were obtained from Sigma-Aldrich, Laborchemikallen GmbH, Germany. Hydrochloric acid (HCl) was purchased from BDH Laboratory supplies Poole Bh15 1TD, England. Stock solutions of 1.0×10^5 ngmL^{-1} for each pesticide were prepared in methanol and stored at 4ºC. Different concentrations of standard solutions in a mixture were prepared daily by the dilution of stock solution in methanol.

2.2. Instruments

For separation of herbicides, the chromatographic measurements were performed on high performance liquid chromatography (HPLC) series 200 equipped with a stationary phase C_{18} column (5 µm × 15 cm × 4.6 mm) from California, USA, and UV-VIS detector at 245 nm. A vortex oscillator (Zenith lab Model-XH-C Korea) was used to assist the supramolecular solvent production and extraction. A centrifuge machine 800 (made in China) was used for phase separation process. pH values of solutions were measured with a WTW pH 422 lab pH meter (West Germany).

2.3. Supramolecular solvent production

The recommended procedure for formation of supramolecular solvent (SUPRA), used for microextraction of herbicides samples, reported in the literature was used with a modification [16]. Decanoic acid (400 mg) was dissolved in THF (15%) in a 50 mL tube. Then, 1700 µL of hydrochloric acid aqueous solution (pH = 2) was added and the mixture was stirred with vortex oscillator for 1.0 min. The supramolecular solvent (SUPRA), which is less dense than water, spontaneously formed as an immiscible liquid into the bulk solution. The mixture was centrifuged at 4000 rpm for 1.0 min to complete the separation of SUPRAs. Afterward, it was withdrawn using a micosyringe and transferred to a close storage tube to prevent THF losses. The resulting SUPRA solvent was stored at 4ºC for further extraction process (Fig. 1a).

2.4. Optimization studies

The experimental variables effect on the extraction efficiency of herbicides related to the extractant (e.g. volume and composition of the supramolecular solvent) and operational parameters (e.g. pH, vortex stirring time) were investigated. All optimization studies were performed in triplicate and selection of optimum condition was based on area values obtained from the chromatograms. The optimized conditions were then applied for the microextraction of herbicides from samples.

2.5. Determination of MRN, LRN and IP in rice and water samples

2.5.1. Sample collection and preservation

Canal water (located near industrial area) and laboratory tap water from chemistry laboratory (University of Peshawar) were selected for the extraction study. Water samples were collected in clean containers and transported to the lab. All water samples were filtered through 7–9 µm filter paper for removing suspended solids. The pH of filtered water samples were adjusted to 2 by the addition of concentrated HCl, and were stored at 4ºC until analysis [23]. Spiking of water samples were made by adding a known concentration 10, 15 and 20 µgmL^{-1} of the working standard solution of mixture of herbicides to the collected water samples and recovery experiments were performed in triplicate.

Rice sample was purchased from local market of Peshawar (Pakistan) and known amount (30 g) was ground and homogenized to obtain a representative and reasonable sub-sample for extraction process. Then, portions of 100–350 mg of sample were taken for analysis and recovery experiments were performed in triplicate. Spiking of samples were made by adding a known concentration 10, 15 and 20 µgmL^{-1} of the working standard solution of mixture of herbicides to a portion of powder rice and further homogenized by mechanical shaking. Spiked samples were allowed to stand at room temperature for 15 min before analysis.

2.5.2. Coacervate-based extraction of real samples

Decanoic acid (400 mg) was dissolved in THF (15%) in separate tubes. Afterwards, spiked water sample (1700 µL) at pH 2 was added, which induces the formation of a water immiscible coacervate. The mixture was stirred by vortex oscillator (800 rpm, 1.0 min) to enhance the extraction rates of analytes. After measurement of volume of SUPRA formed, standing at the top of the solution in the tube, an aliquot (20 µL) was withdrawn using a microsyringe and was injected into the HPLC system for analysis.

Rice sample was spiked with mixture of herbicides and mixed with 800 µL of SUPRAs. Sample dispersion was achieved by vortex oscillator at 800 rpm for 1.0 min. Then, it was centrifuged at 4000 rpm for 1.0 min to completely separate the solvent and the solid residue (rice sample). Finally, 20 µL of the SUPRAs containing the target herbicides was withdrawn and injected into the chromatographic system [24]. A schematic procedure for the sample treatment is presented in Fig. 1b.

2.5.3. HPLC analysis

The mixture of herbicides, IP, MRN and LRN were separated and quantified using isocratic reverse phase HPLC analysis. Mixture of acetonitrile, methanol and water

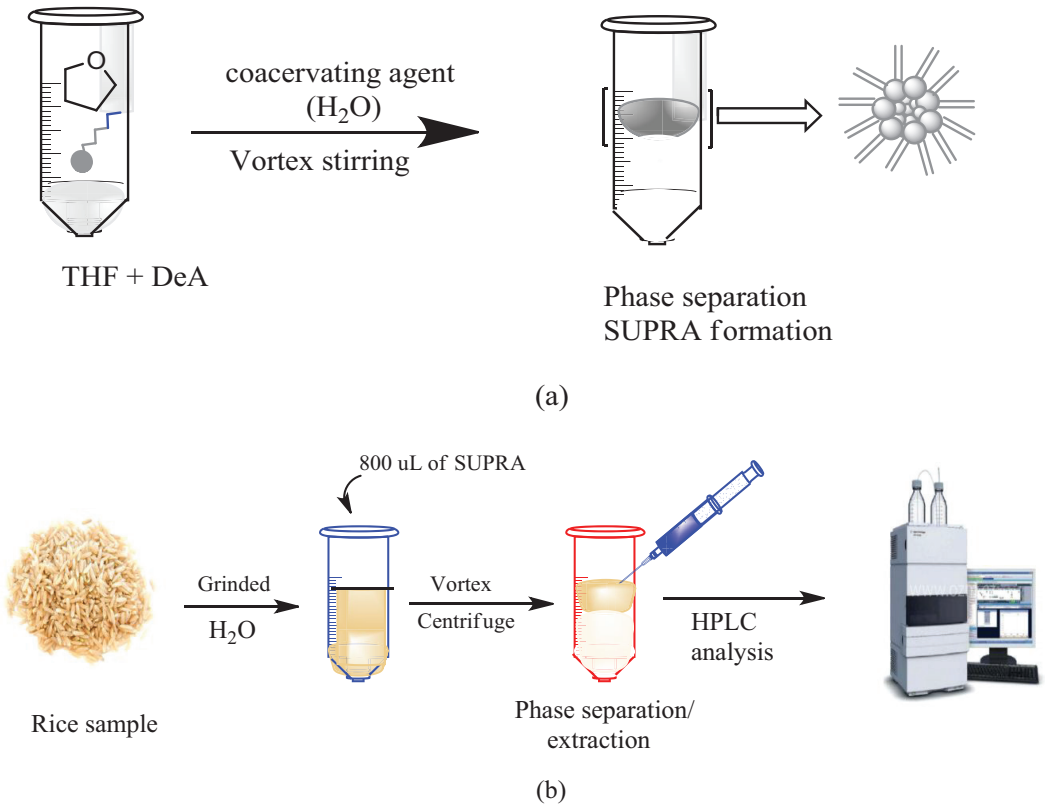


Fig. 1. Schematic procedure for (a) SUPRA formation using DeA and THF, (b) Rice sample extraction using SUPRA.

(ACN:MeOH:H_2O) in a ratio of 8:7:5 was used as mobile phase at a flow rate of 1 mL/min. The column effluents were monitored at 245 nm using UV detector. Quantification of herbicides were performed measuring peak area. Retention time of MRN, IP and LRN were 2.0, 2.3 and 2.9, respectively. Calibration curves for IP, MRN and LRN were constructed in the concentration range of 5–20 μgmL^{-1}.

3. Results and discussion

3.1. Coacervated extraction of herbicides

3.1.1. Description and binding capabilities of reverse micelle-based coacervates

Decanoic acid (DeA) dissolved in THF formed reverse micelles according to a self-association sequential-type procedure. The addition of coacervating agent (i.e. H_2O) to the binary system, resulted in partial desolvation of the aggregates, making their interaction easier and elevated the formation of bigger aggregates of reverse micelles [25,26]. Therefore, supramolecular solvent (SUPRAs) produced, dispersed in a THF: water continuous phase, consists of reverse micelles with a wide size distribution range in nano and micro scale [27,28]. As phase separation was produced from the protonated decanoic acid (pKa = 4.8 ± 0.2), thus pH values below 4 are required for the formation of SUPRAs [29].

The structure and nature of the functional groups present in MRN, IP and LRN molecules (Table 1) suggest the possibility of several types of interactions. The better understanding about the interactions of analytes with SUPRAs is important for setting up an efficient extraction scheme [30]. These three pesticides are neutral (p*Ka* for IP, LRN and MRN are 15.1, 12.1 and 14.2 respectively) at the pH range of coacervates formation (pH < 4) and relatively polar hydrophilic compounds (see log $K_{o/w}$ values in Table 1) containing hydrogen donors and acceptors atoms [31]. Accordingly, solubilization of analyte molecules in reverse micelles of decanoic acid is favored by two fold mechanism based on hydrophobic and Van der Waals interactions with the hydrocarbons tails and hydrogen bonds of the carboxylic acid polar groups of the surfactant.

The LRN is slightly soluble in water and presents higher value of log $K_{o/w}$ which suggest higher hydrophobic character. Such hydrophobic character is responsible for LRN persistent in the environment and also responsible for hydrophobic-hydrophobic interaction between LRN and SUPRAs. The IP has both hydrophobic and hydrophilic characters with log $K_{o/w}$ lower than LRN while MRN in the group is more water soluble due to low value of log $K_{o/w.}$ Therefore, its interaction with SUPRs may be lower due to high hydrophilic character of MRN.

3.1.2. Optimization of coacervated extraction process

Extraction recoveries for phenylurea herbicides were dependent on selection of the optimum conditions. The investigated variables were: DeA amount, THF percentage,

composition and volume of SUPRAs, pH, sample volume, time required to attain equilibrium conditions.

pH of solutions is important for the supramolecular extractions because it affects the formation of supramolecular solvent and also the dissociation of analytes (herbicides) with acid-base properties. The pH was investigated by synthesizing supramolecular solvent as immiscible aggregates from water solution, the pH of which was adjusted between 1–4 (Fig. 1a) with hydrochloric acid (HCl). As phase separation is produced from the protonated decanoic acid (pKa = 4.8 ± 0.2), therefore, pH values below 4 are required for the formation of SUPRAs. Hence, pH 2 was selected for further extraction process because of adequate extraction of IP, MRN and LRN herbicides.

The vortex assisted microextraction time was optimized and the effect of extraction period on recoveries was investigated at six levels; 0.5–5.0 min. The results exhibited no appreciable change in recovery from 1.0 to 5.0 min of extraction time for all selected herbicides (Fig. 1b). For this reason, 1.0 min was selected for further extraction process.

The effect of centrifugation time on the microextraction of phenylurea herbicides in the sample for complete phase separation was checked at 800 rpm for 1.0–5.0 min. The phase separation and quantitative recovery obtained for all three herbicides was with 1.0 min. of centrifugation time. After 1.0 min, there was no significant increase in recovery therefore 1.0 min of centrifugation time was selected for separation and extraction process.

Supramolecular solvent (SUPRAs) containing decanoic acid (DeA) as reverse micelles in 10% THF phase. Therefore, different amounts of DeA were optimized in the range between 200 and 1000 mg and the extraction recoveries obtained are shown in Fig. 3a. The extraction efficiency of herbicides increased with the use of lower amount of DeA (300 mg), the signal of LRN was higher than IP and it was higher than MRN. As a fact with increase in amount of DeA there is decrease in extraction efficiency due to the reduction of micellar solubilization sites. On the other hand, SUPRAs produced using THF percentage from 5% to 30% were also studied. It was clear from recoveries that the extraction efficiency increased with increase in THF concentration up to 15%, which leads to improved dispersion and solubilization, after that it decreased (Fig. 3b).

The effect of SUPRAs composition on recovery of herbicides was investigated by synthesizing SUPRAs from a constant amount of decanoic acid (400 mg) dispersed in variable ratio of water/THF continuous phase. The highest recoveries were obtained with 15:85 ratio of THF: H_2O (Fig. 4a). The volume of SUPRAs used for extraction was also optimized as it influences the recovery of three studied

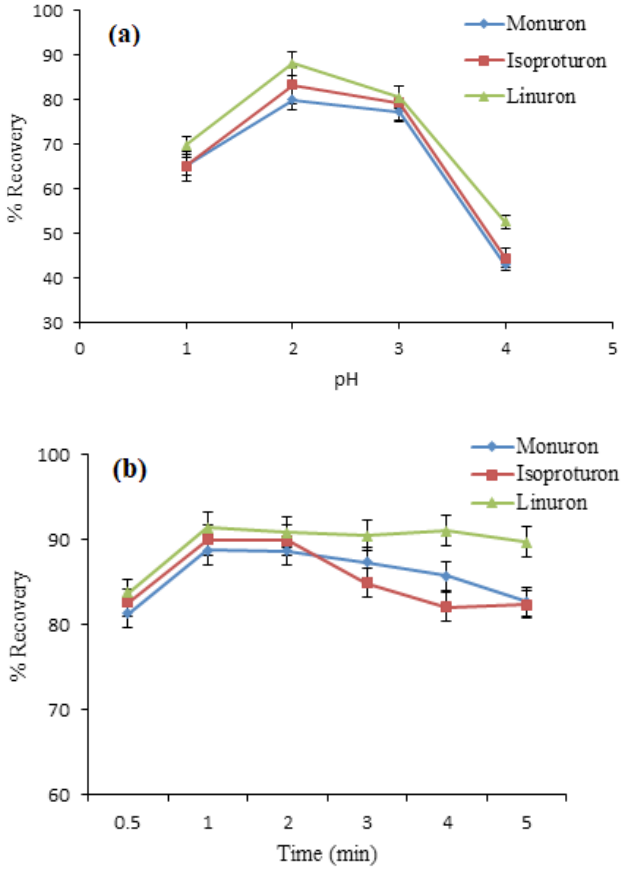


Fig. 2. Percentage recovery obtained for phenylurea herbicide using SUPRA microextraction at (a) different pH values, (b) different time interval.

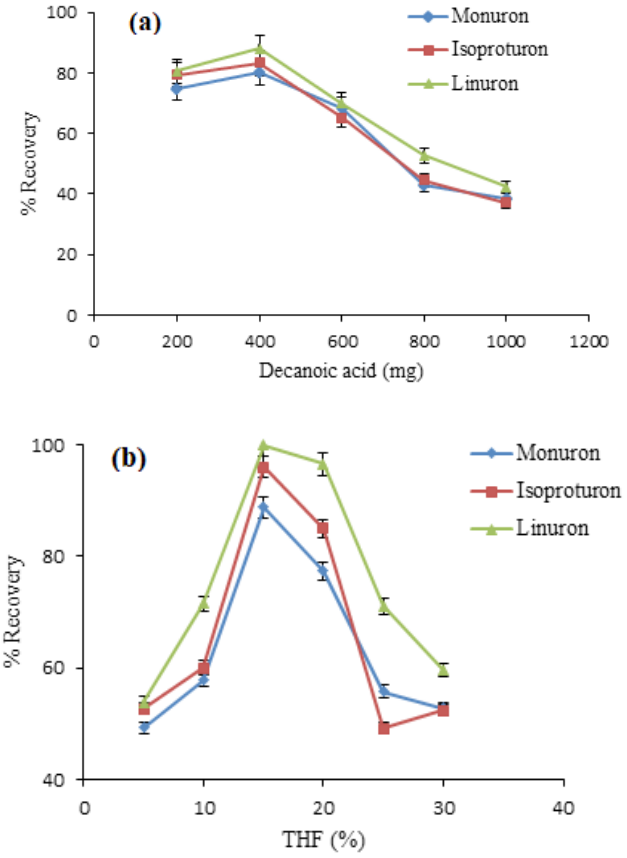


Fig. 3. Recoveries obtained for phenylurea herbicides using SUPRAs prepared from (a) different amount of decanoic acid (b) variable THF (%).

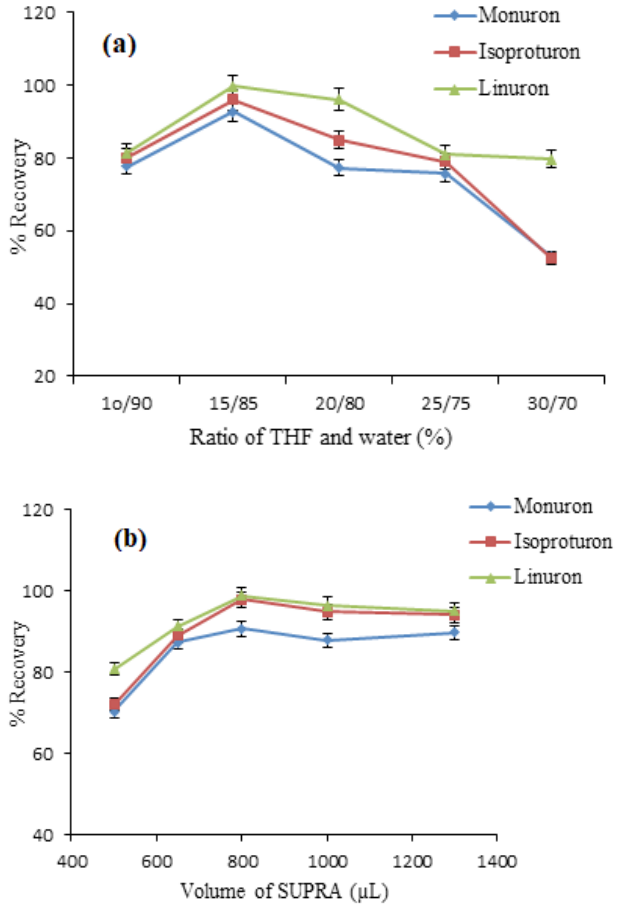


Fig. 4. Recovery obtained for herbicides using SUPRAs microextraction as a function of (a) the THF/water ratio used for self-assembly, (b) the volume of SUPRAs.

Table 2
Optimized parameters for extraction of phenylurea herbicides using SUPRA microextraction

Parameters	Optimized values
pH	2.0
Vortex time (min)	1.0
Decanoic acid (mg)	400.0
THF (%)	15.0
Volume of SUPRA (mL)	0.8
THF:H_2O ratio	1:6

herbicides. In order to evaluate, volumes of SUPRAs added to analyte solution for recovery were studied from 500 to 1300 µL. Recoveries equal to or above 90% were obtained for SUPRA volume 800 µL or above (Fig. 4b). Therefore, 800 µL aliquots of SUPRA solvent was chosen as optimum. SUPRA volume less than 800 µL was insufficient for the sample extraction and large volume of SUPRAs makes the phase diluted and as a result decrease in signal obtained.

Table 3
Recoveries (%) of selected herbicides as a function of amount of sample analyzed

Sample amount (mg)	Solvent volume/ sample amount (µL/mg)	Recovery (%)		
		Monuron	Linuron	Isoproturon
100	8.0	94.1	99.7	95.9
150	5.3	93.9	97.8	94.7
200	4.0	90.7	94.1	91.8
250	3.2	84.9	85.9	85.4
300	2.6	78.3	83.7	80.1
350	2.3	75.9	78.9	76.7

Time of extraction: 1 min, Volume of SUPRA: 800 µL

The optimized values of experimental parameters are given in Table 2.

The influence of matrix components on recoveries was investigated by extracting different quantities (100–350 mg) of rice samples (Table 3). Quantitative recoveries obtained up to around 200 mg, and then the recoveries progressively decreased as the amount of sample increased due to the inefficient solvation of the sample at solvent volume/sample amount ratios below around 4.0. Therefore, maximum amount of 200 mg of rice sample with 800 µL of SUPRAs is recommended for the extraction of herbicides.

3.2. Analytical performance

Under the optimized experimental conditions, various analytical parameters like linearity range, correlation coefficient, limits of detection (LOD), PF and precision calculated as relative standard deviation (RSD%) for interday and intraday were determined at three different concentrations. Calibration curves for all three herbicides were made using standard solutions (0.5–20 mgL^{-1}) prepared in methanol and obtained by least squares linear regression analysis of the peak area against concentration of each herbicides. Table 4 shows the calibration curve ranges, the coefficient of determination, retention times for analyte. Good linearity was obtained with correlation of determination ranging from 0.9904 to 0.9725. The limit of detection (LOD) was determined by analyzing four blank samples on signal to noise ratio of three. The method showed a low detection limits of 10, 30 and 10 ng mL^{-1} for MRN, IP and LRN, respectively. While limit of quantification (LOQ) was calculated by analyzing four blank samples on signal to noise ratio of ten and LOQ values of 30, 100 and 30 ng mL^{-1} were found for MRN, IP and LRN, respectively. No appreciable differences in retention times were observed for the herbicides injected in methanol or SUPRA.

The interday precision was evaluated over four daily replicates, spiked at three different concentration levels (Table 4) for three days and the intraday precision was evaluated over four replicates, spiked at three concentration levels (Table 4) within one day. The interday and intraday precision (RSD, %) were in the range of 3.2–6.5% and 2.5–

Table 4
Analytical parameters of the proposed method

Analyte	Linear range ($\times10^3$ ngmL^{-1})	R^2	Retention time (min)	LOD (ngmL^{-1})	LOQ (ngmL^{-1})	Concentration ($\times10^3$ ngmL^{-1})	Precision (% RSD)		PF
							Interday	Intraday	
Monuron	0.5–20	0.9901	2.0	10.0	30.0	5.0	3.3	3.4	25
						10.0	4.5	5.5	
						15.0	6.1	7.2	
Isoproturon	0.5–20	0.9725	2.3	30.0	100.0	5.0	4.1	3.7	
						10.0	5.2	5.6	
						15.0	6.5	7.2	
Linuron	0.5–20	0.9904	2.9	10.0	30.0	5.0	3.2	2.5	
						10.0	4.3	4.2	
						15.0	5.2	6.8	

LOD: limit of detection, LOQ: limit of quantification, RSD: relative standard deviation, n = 4, PF: Preconcentration factor

7.2%, respectively. The results show low variation between measurement.

Preconcentration factor (PF) for the proposed method was calculated based on the following equation

$$PF = \frac{Csup, final(mL)}{Caq, initial(mL)}$$

where C_{sup}, *final* and C_{aq}, *initial* are the final and initial concentrations of herbicides in SUPRAs and sample solution, respectively. *Csup,final* was obtained from the calibration curve. The preconcentration factor (PF) for the proposed method was found 25.

3.3. Green chemistry in SUPRA extraction procedures

An ideal approach to green analytical practice would be to reduce the number of steps involved in a given analytical procedure (less energy use and low volume of waste production) and to search for more environmentally benign analytical methodology. This green approach will be a key parameter in "Analytical Eco-Scale"concept, proposed by Van Aken [32], assumed that an ideal procedure, which uses less chemicals, conducted at room temperature and is safe both for operator and the environment, has a score of 100 in the Eco-Scale. For each parameter which differs from ''the ideal value'', penalty points are assigned, lower the total score. The higher the score, the greener and more economical is the procedure. This concept can be adapted to evaluate green analytical methods. The sum of penalty points should be included in the Eco-Scale calculation, according to the following formula: Analytical Eco-Scale = 100 - total penalty points

The result of calculation is ranked on a scale, where the score:

>75 = excellent green analysis,

>50 = acceptable green analysis,

<50 = inadequate green analysis.

Results of penalty points calculations are given in Table 5 for the proposed procedure and applied green chemistry involving "Analytical Eco-Scale". Analytical Eco-Scale total score was found 79 which is a value higher than 75 indicates excellent green analysis.

Table 5
Penalty points (PPs) calculations for SUPRAs microextractions

Reagents		
Penalty points (PPs)		
Decanoic acid (DeA)	<10 mL (g)	01
Tetrahydrofuran (THF)	<10 mL (g)	06
HCl	<10 mL (g)	02
Methanol	<10 mL (g)	06
Acetonitrile	<10 mL (g)	04
∑ 19		
Instruments		
Penalty points (PPs)		
LC	≤1.5 kWh per sample	01
Vortex	<0.1 kWh per sample	00
Centrifuge	<0.1 kWh per sample	00
Occupational hazards	No severe hazards	00
Waste	<1 mL (g)	01
∑ 02		
Total penalty points = 21		
Analytical Eco-Scale total score = 79		

3.4. Analysis of real environmental samples

To assess the applicability of proposed method in real samples extraction, experiments were performed using rice and water samples (tap and canal water). All the samples were spiked at concentrations of 10–15 (10^3) ngmL^{-1} of each phenylurea herbicide in a mixture. Fig. 5 shows chromatograms of the unspiked and spiked samples at optimized conditions. The results of recoveries are listed in Table 6 and shows that 80.05 to 99.01% recoveries were obtained. High values of recoveries from water and rice samples revealed

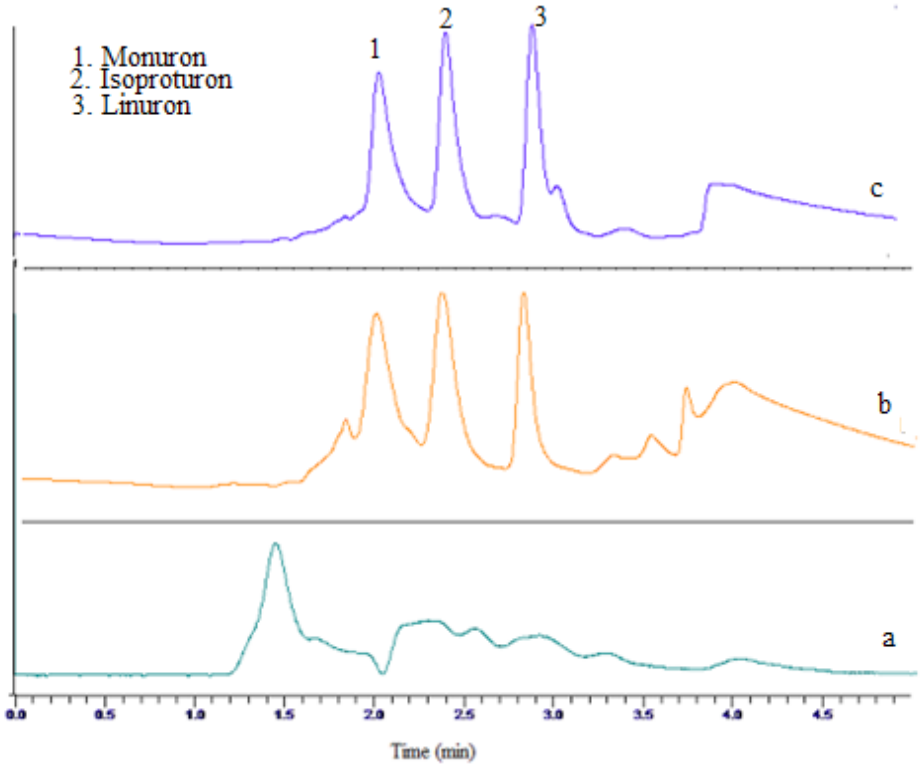


Fig. 5. Chromatograms obtained from; (a) unspiked samples, (b) spiked with 10 mg L^{-1} and (c) spiked with 15 mg $L^{-1}$of mixture of herbicides using SUPRAs microextraction.

Table 6
Determination of phenylurea residues and recoveries for tap water, canal water and rice sample

Herbicides	Spiked ($\times 10^3$ ngmL^{-1})	Tap water		Canal water		Rice	
		Found	R (%)	Found	R(%)	Found	R(%)
Monuron	0.0	n.d.	–	n.d.	–	n.d.	–
	10.0	9.5	95.1	9.2	92.0	8.2	82.0
	15.0	14.1	94.1	13.1	87.3	12.0	80.0
	20.0	18.2	91.1	15.8	89.1	15.1	85.5
Isoproturon	0.0	n.d.	–	n.d.	–	n.d.	–
	10.0	9.5	95.0	9.20	92.0	8.2	82.1
	15.0	14.2	94.7	13.8	92.0	12.2	81.3
	20.0	18.5	92.5	16.5	82.5	16.0	80.0
Linuron	0.0	n.d.	–	n.d.	–	n.d.	–
	10.0	9.9	99.0	9.40	94.0	8.5	85.0
	15.0	14.6	97.3	13.3	88.7	12.5	83.3
	20.0	18.5	92.5	17.2	86.0	16.4	82.0

n.d.= not detected

that the matrix from real samples had no significant effects on the extraction of selected herbicides.

3.4. Comparison of SUPRA with other reported methods

The main analytical features of the proposed method were compared with other reported methods for the determination of phenylurea herbicides in real samples (Table 7). The reported methods mostly involved high volume of solvents and extraction time while lower volume of sample and some of them have high values of LOD. The proposed method exhibited low volume of solvent and extraction time as well as high volume of solvent with good PF. Extraction of selected herbicides with SUPRAs microextraction has the advantage of low solvent consumption for the extraction, good values of LOD and LOQ

Table 7
Comparison of proposed method with other reported methods for extraction of monuron, linuron and isoproturon

Herbicide	Extraction method	Detection technique	Number of analytes	Extraction Time (min)	Solvent volume (mL)	Sample volume (mL)	Linear range ($\times 10^3$ ngmL^{-1})	LOD (ngmL^{-1})	RSD (%)		Sample type	Ref
									Interday	Intraday		
Monuron Linuron	SPE (Biosorption)	HPLC-DAD	2.0	2880	–	6.0	–	116.0 66.0			Soil	[33]
Monuron Linuron Isoproturon	SPME (PDMS–DVB and CW–TPR fibres	HPLC-UV	3.0	40.0	100.0	3.0	–	500.0 510.0			Water	[34]
Linuron	LL-MAE	LC-PDA	1.0	60.0	20.0	2.0	10.0–500	70.0			Vegetable	[35]
Monuron Linuron Isoproturon	SPME (PDMS, PA)	GC-NP	3.0	60.0	–	2.0	1–250	100.0 40.0 60.0			Water	[36]
Monuron	SPME(CW/TPR, PDMS/DVB, PA	LC-MS	1.0	90.0	100.0	1.0	0.05–5	5.0	7.0	4.0	Fruit juice	[37]
Isoproturon Linuron	*LLE (USE)*	GC-MS	2.0	20.0	60.0	2.0	7–1400	90.0 50.0			Soil	[38]
Monuron Linuron Isoproturon	LLE	HPLC-UV	3.0	10.0	100.0	0.1	1–10	2.0 1.0 2.0			Water	[39]
Monuron Linuron Isoproturon	SPE (silica-based C18 , polymeric sorbents)	LC-DAD-UV	3.0	28.0	100.0	2.0	0.05–5	21.0 34.0 24.0			Water	[40]
Linuron	LL (DLLME) QuEChERS	GC-MS	1.0	15.0	1.0	0.1	0.025–2	24.0			Maize	[41]
Monuron Linuron Isoproturon	LLE (MASE)	HPLC-UV	3.0	10.0	20.0	1.0	10–100	20.0 20.0 20.0			Soil	[42]
Linuron Isoproturon	(SPE) MIP	HPLC-UV	2.0	120.0	5.0	1.0	0.1–500	–			Corn	[43]
Monuron Linuron Isoproturon	SUPRA	HPLC-UV	3.0	1.0	0.8	20.0	0.3–20	30.0 10.0 30.0	3.3 3.2 4.1	3.4 2.5 3.7	Water, Rice	Present work

Solid phase extraction (SPE), Polydimethylsiloxane–divinylbenzene (PDMS–DVB), Carbowax–templated resin (CW–TPR) fibers, Polydimethylsiloxanes, polyacrylate fiber (PA), microwave-assisted solvent extraction (MASE), Ultrasonic solvent extraction (USE) Dispersive liquid–liquid microextraction (DLLME), Molecular imprinted polymer (MIP), Solid phase microextraction (SPME), Liquid-liquid extraction (LLE).

which helps in quantitative determination of herbicides in real samples.

4. Conclusions

Supramolecular solvents (SUPRA) have outstanding properties for microextraction due to wide polarity range and solubilizing sites that interacts with solutes arising from the multiple binding sites it provides (i.e. hydrogen bonds, dipole–dipole, dispersion, etc.). These properties have been exploited for the microextraction of phenylurea herbicides (monuron, linuron and isoproturon) in water and agricultural samples. The proposed sample treatment process is rapid, simple, eco-friendly and less-expensive and does not require special laboratory equipment and evaporation of solvents before HPLC analysis. The time and cost are the advantages of the use of SUPRA rather than large volume of solvents and more time as in conventional LLE. High extraction recoveries (%) were achieved in 1.0 min for all herbicides using low SUPRA (0.8 mL) volumes. The extraction efficiencies of these herbicides are in order; linuron > isoproturon > monuron depending on their octanol–water (log $K_{o/w}$) constants [monuron = 1.94, isoproturon = 2.82, linuron = 3.21]. Additionally, the method provides advantages of high extraction efficiency, good precision and accuracy. The developed method proved high efficiency compared with other methods.

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