Asian Journal of Chemistry; Vol. 24, No. 5 (2012), 2042-2044

ASIAN JOURNAL OF CHEMISTRY

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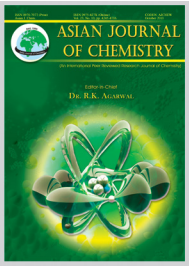

Simplified Approach for the Extraction of Quinclorac From Soils

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(*Received*: 14 April 2011; *Accepted*: 12 December 2011) AJC-10823

A simplified version of the QuEChERS method for the extraction of quinclorac from soil samples was proposed. Optimum results were obtained dispersing soil in water, followed by the addition of 1 % acetic acid in acetonitrile, magnesium sulfate and sodium acetate as a modification of the quick, easy, cheap, effective, rugged and safe (QuEChERS) method. Liquid chromatography/ultraviolet (LC-UV) detector was then used to analyze the extracts without any other sample pretreatment. The result showed the recovery ranged from 73.8 to 106.4 % and 66.6 to 87.3 % with the relative standard deviations of 1.9 to 15.7 % and 4.7 to 9.3 % in two soil samples, respectively. The limit of detection (LOD) of the method was 0.05 mg kg^{-1}. The limit of quantification (LOQ) was 0.5 mg kg^{-1}. The half life period of quinclorac was 65.7 and 36.5 days in soil of Changsha and Nanning in China, respectively.

Key Words: QuEChERS, Quinclorac, Soil.

INTRODUCTION

Quinclorac (3, 7-dichloro-8-quinoline-carboxylic acid) is a class of highly efficacious auxin herbicides used widely for problem weeds in rice. It was active against dicot and monocot weeds, particularly barnyard grass[1-3]. The widespread use of quinclorac had led to controversy with respect to water and soil pollution. Several studies reported that following rotational crops may be injured by quinclorac residue in soil[4-6]. In addition, some reports had indicated that quinclorac has adverse effects on hydrophyte, aquatic animal and even cause harm to the livers and kidneys of mammals[7]. Han *et al.*[8] reported quinclorac has potential threat to human. Hence, quinclorac residues in soil may act as potential environmental hazards and it is necessary to develop analytical methodologies to monitor quinclorac in the environment.

Separation methods most commonly used for the determination of quinclorac include gas chromatography (GC)[4], liquid chromatography (LC)[9] and capillary electrophoresis (CE)[10]. Traditionally, sample preparation method has based on a large of solvent extraction. These methods often require large solvent volumes, use a lot of glassware and take much time and labor, which reduce the laboratory efficiency and sample throughput. However, development of solventless (or at least with low solvent consumption) sample preparation techniques constitutes a pillar of green analytical chemistry[11] and has taken a rapid development during last years.

QuEChERS (quick, easy, cheap, effective, rugged and safe) sample preparation was introduced by Anastassiades *et al.*[12]. It has mainly been used for different food matrices with high water content[12,13]. To the best of our knowledge the use of QuEChERS in soils is very limited[14] but with very good results. A simplified version of the QuEChERS method for the extraction of chlorinated pollutant compounds from soil samples[15].

In this paper, the simplified version of QuEChERS sample preparation method for the analysis of quinclorac residue in soils is proposed. This method has been evaluated in terms of their stable from different soil matrices with HPLC-UV. It is simple, rapid and can be applied routinely to quinclorac residue analysis in soils.

EXPERIMENTAL

Quinclorac standard (98 %) was obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Methanol (MeOH) and acetonitrile (MeCN) liquid chromatography grade was purchased from Tedia (USA). Sodium acetate tri-hydrate ($NaOAc{\cdot}3H_2O$), glacial acetic acid (HOAc) magnesiumsulfate ($MgSO_4$) anhydrous and sodium sulphate (Na_2SO_4) anhydrous were provided by from Sinopharm Chemical Reagent Co. Ltd., (Shanghai, China). The purity was not taken into account when making acid solutions, thus the % indicates the volume fractions of acid solutions (*e.g.* 1 % AcOH in MeCN was prepared by mixing 10 mL glacial AcOH with 990 mL MeCN). The two

different types of soils (0-10 cm) were collected from agricultural fields in Changsha and Nanning, China. No quinclorac in soil samples was validated using traditional analysis method. Soil samples were ground to powder after air drying and passed though a 2 mm sieve, then stored in 4 ºC until analysis.

Analytical procedure: For extraction, 5 g samples were transferred into a 50 mL polypropylene centrifuge tube. 2 mL of ultrapure water was added and mixed using a Vortex mixer for 1 min. Subsequently, 10 mL of MeCN (1 % AcOH) were added, the mixture was shaken vigorously for 2 min. 3 g of magnesium sulfate and 0.9 g of $NaOAc{\cdot}3H_2O$ were added, shaken as quick as possible to prevent formation of $MgSO_4$ conglomerates and centrifuged for 5 min at 5000 rpm. A 9 mL aliquot was filtered through a Na_2SO_4 column and dried under a stream of nitrogen, then redissolved in 1.0 mL of MeOH for HPLC-UV analysis.

Dissipation of quinclorac residues: To study the dissipation of quinclorac from soil, 3.4 g quinclorac (50 % WP) was applied to the flooded rice plots 7 days after transplanting rice seedlings. The experimental treatment consisted of three replicate plots and a control plot that were separated by irrigation channels; the area of each plot was 20 m^2. Plant samples were collected at 0 (2 h after spraying), 1, 3, 7, 14, 21, 30, 60, 120, 150 and 300 days after spraying and stored at -20 ºC until further analysis.

Chromatographic conditions: Quinclorac concentrations were determined on an SHIMADZU 20 AT LC, equipped with an SPD-20A UV detector and an autosampler, a column oven. Analytical separations for the pesticides were achieved on CNW C_{18} column (250 × 4.6 mm i.d., 5 µm particle size) at 30 ºC. The mobile phase used was water (containing 0.2 % acetic acid)/methanol (45/55, v/v) with a flow rate of 0.8 mL/min. The detections were performed at 240 nm and the injection volume was 20 µL.

RESULTS AND DISCUSSION

This study was part of an overall research project to investigate the fate of the herbicides assayed within the rice production ecosystem. As pointed out before[4-6] due to the peculiarities of the rice rotating system, residues from quinclorac may persist in the soil and may damage following crops. This fact makes it necessary to analyse the presence of the herbicide in soil. In the application of the method to dry matrices, it is very common to add a volume of water to the samples, prior to the extraction step, to hydrate them and make the pores in the sample more accessible to the extraction solvent[16-18]. Sieved soil sample was weighed in a glass centrifuge tube with screw cap, which keeps the tube closed for most of the process of sample preparation to avoid as much as possible losses of volatile compounds during this stage. Soil samples, in contrast with fruits and vegetables, do not have high contents of lipid materials. Different soil types are characterized by their mineral fraction (variable percentages of sand, silt and clay) and organic matter fraction (10-15 %) mainly composed by humic substances (Table-1). Therefore, two different soils were evaluated in this paper.

Modified QuEChERS method validation: The standard calibration curve of quinclorac during HPLC-UV analysis was constructed by plotting the analyte concentration *versus* peak area. The regression equation of the standard calibration curve (Fig. 1) was y = 694034x -15828 (R^2 = 0.9988). Therefore, the calibration curve showed excellent linearity in the concentration range 0.1-10 mg L^{-1}.

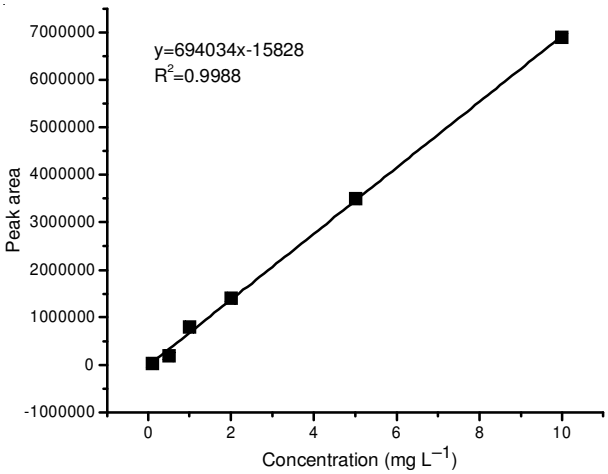

Fig. 1. Standard curve for quantification of quinclorac

TABLE-1
PHYSICAL AND CHEMICAL PROPERTIES OF SOILS

Area	Soil type	pH value	Organic material (%)	Cation exchange capacity(cmol kg^{-1})
Changsha	Alluvial soil	5.83	9.2	9.43
Nanning	Purple soil	7.13	13.4	33.46

Limits of detection and quantitation: The limit of detection (LOD) of quinclorac was defined as the minimum concentration of quinclorac that was detected with acceptable certainty. The limit of detection was estimated to be 0.05 mg kg^{-1} for soil. The limits of detection (LODs) of the proposed method were determined at a signal-to-noise (S/N) ratio of 3 for the individual herbicides in soil by LC-UV, whereas the limits of quantitation (LOQs) were obtained as the lowest spiked level with acceptable recovery and RSD. The limits of quantitation values were estimated to be 0.5 mg kg^{-1} for soil, corresponding to the lowest spiking level used.

Recovery: Based on the original QuEChERS method, some parameters were slightly modified. Good recoveries were obtained for quinclorac using 5 g soil. Soil blanks were fortified at 0.10, 0.5 and 1.0 mg kg^{-1} and processed as described above. The modified QuEChERS methods (as described in the materials and methods section) gave good results, showing high recoveries (66.6-106.4 %) and low relative standard deviation (RSD) (15 %) (Table-2). However, Niell *et al.*[19] reported that quinclorac presents a very low recovery (10 %) when QuEChERS was used to determine herbicides in rice.

Dissipation of quinclorac residues in soil: In this paper, we showed a new version of QuEChERS method for extraction of quinclorac from actual soil samples incubated with the herbicide. Residue concentration and half-life of quinclorac were calculated by the first-order kinetics equations, $C_t = C_0e^{-kt}$ and $t_{1/2} = \ln 2/k$, respectively. The variables are defined as follows: C_t denotes the concentration of the pesticide residue at time (t), C_0 denotes the initial concentration, k is the rate

TABLE-2
PERCENT RECOVERY OF QUINCLORAC EXTRACTED WITH THE MODIFIED QUECHERS METHOD FROM SOILD

Sample	Spiked level (mg kg^{-1})	Recovery (%)					Average recovery (%)	RSD (%)
		1	2	3	4	5		
Changsha soil	0.1	63.1	74.1	61.7	69.7	100.3	73.8	15.7
	0.5	91.9	102.7	93.5	78.1	78.3	88.9	10.6
	1.0	106.9	104.4	108.6	107.7	104.5	106.4	1.9
Nanning soil	0.1	60.8	66.3	72.1	63.5	70.5	66.6	4.7
	0.5	80.1	77.0	79.7	86.9	99.5	84.6	9.1
	1.0	94.1	89.5	75.3	97.4	80.1	87.3	9.3

constant and $t_{1/2}$ is the half-life[20]. Fig. 2 showed the dissipation curve of quinclorac in the soil under field conditions. Concentrations were reduced by more than 90 % after application 150 days in Changsha and 120 days in Nanning. Half-life period ($t_{1/2}$) and other statistical parameters of dissipation were calculated from the experimental data and are summarized in Table-3. Hill *et al.*[4] reported DT_{50} of quinclorac was 48 week in Lethbrige soil. Resgalla *et al.*[21] also reported residues of the herbicide quinclorac detected in samples of water collected in the 1998/1999 and 1999/2000 rice crop seasons in seven hydrographic basins in Santa Catarina (SC) State. From these results, it was evident that quinclorac have potential threat to soil, water and human.

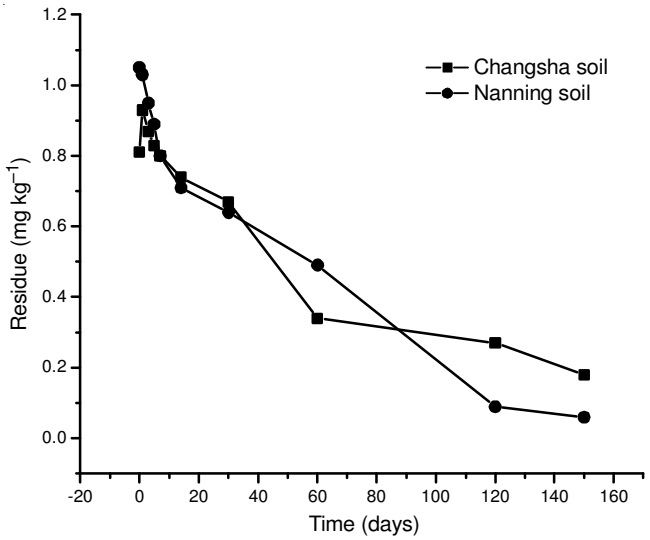

Fig. 2. Dissipation of quinclorac residues in soil samples under field conditions in Changsha and Nanning

TABLE-3
DEGRADATION OF KINEMATIC EQUATIONS, CORRELATION COEFFICIENT AND HALF-LIVES QUINCLORAC OF IN SOILS

Sample	$c = c_0e^{-kt}$	Correlation coefficient	Half-life period (days)
Changsha soil	$c = 0.8578e^{-0.0105t}$	0.961 6	65.7
Nangning soil	$c = 1.0333e^{-0.0189t}$	0.977 2	36.5

Conclusion

A modified and simplified QuEChERS approach has been evaluated for the determination of quinclorac in soil matrices. Residue and decline of quinclorac were evaluated in soil samples used the QuEChERS method.

ACKNOWLEDGEMENTS

The authors are grateful to National Natural Foundation of China (30971936) (31071716) for supporting this research.

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