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Spectroscopic Determination of Permethrin Insecticide in Environmental and Agricultural Samples Using Leuco Crystal Violet Reagent

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Abstract

A new sensitive spectrophotometric method for the determination of permethrin insecticide in environmental and agricultural samples has been developed. The reaction mechanism is based on complexation followed by coupling of permethrin with leuco crystal violet (LCV). This method is based on the measurement of red shift of absorbance band of LCV in the UV-Visible region of 200-800 nm. The resulting complex absorption spectra was observed at λ_{max} = 580 nm. The color of permethrin was changed from colorless to violet by the addition of LCV. The effects of various pesticides and metal ions on the selective determination of permethrin were also studied. The analytical parameters were improved and effectively employed for permethrin assessment in a variety of environmental samples including water, soil and vegetables. The purpose of the present research was to design a method for the color complexation determination of permethrin. We have employed LCV as a reagent to form a complex with permethrin. The limit of detection was 0.34 µg mL^{-1} and the limit of quantification was 1.06 µg mL^{-1}. The Sandell's sensitivity is found 0.29×10^{7} µg cm^{-2} and molar absorptivity of the colored system is 3×10^{-5} L $mol^{-1}cm^{-1}$. The advantages of using present method are its simplicity, selectivity and sensitivity towards the analysis of permethrin using LCV in water, soil and vegetable samples.

Keywords: Spectrophotometry; Permethrin; Leuco crystal violet; Environmental samples

Introduction

Pesticides are synthetic or natural substances, which are meant to destroy, control or prevent pests, weeds and pathogens for improving food quality and reducing crop production losses (Tang et al., 2019; Fantke and Juraske, 2013; Mahajan and Randhawa, 2023). In fact, a small amount of pesticide can reach the target. However, the rest enters the environment needlessly, causing a risk to human health, animals and environmental pollution (Xu et al., 2017; Farha et al., 2018; Kaushal and Singh, 2022; Singh et al., 2023). Insecticides are one of the largest parts of pollutants in agricultural products and groundwater. Among them, pyrethroids are one of the important classes of insecticides with good environmental compatibility and outstanding bioactivity compared to carbamate, organophosphorus and organochlorine. It is very important in the control of mites and pests as well as crop pests (Kim et al., 2006; Feo et al., 2012). Pyrethroids are synthetic pyrethrin derivatives from the flowers of *Tanacetum cinerarieafolium*. In the last few years, the pyrethroid residues may exist in products that are made from the infected produce, such as fruit, vegetables, and beverages. However, residual problems have regularly been attracted due to their broad application; mostly pyrethroids can cause harmful effects on human health and environmental problems (Qian et al., 2019; Lopez et al., 2001).

Permethrin is a synthetic pyrethroid insecticide that is similar to naturally occurring compounds with insecticidal capabilities (Proctor et al., 2019). Permethrin is chemically known as (3-phenoxybenzyl 3-(2,2 dichlorovinyl) 2,2dimethyl cyclopropane carboxylate) It is a broad-spectrum insecticide, used to kill a variety of insects (Zhan et al., 2018). Permethrin is used to control a variety of pests on a variety of crops, including nut, vegetable, fruit, ornamental, cotton, mushroom, potato, and cereal crops. It is used in greenhouses, home gardens and for termite control (Ahmed, 2023). Permethrin is a kind of non-systemic pyrethroid insecticide with some repellent effects (Amin et al., 2017). Its residues in cereals and other agricultural products represent a serious risk to human health causing cancer, infertility, nerve disorders and immunological disorders (Pirsaheb et al., 2018). Due to their adverse effect, it is necessary to determine Permethrin in vegetables, soil and water samples. In the last few years, many techniques used to determine Permethrin from environmental samples such as liquid chromatography with UV detection (Tehrani et al., 2013), High-performance liquid chromatography (Ganzera et al., 2006), flourier transform infrared spectroscopy (Sahu et al., 2020), gas chromatography-mass spectroscopy (Garrido et al., 2005), tandem mass spectrometry (Lehotay, 2007), Solid-liquid extraction (Sharma et al., 2022), Liquid-liquid extraction (Katsumata et al., 2005), solid-phase extraction (SPE) (Henze and Comeau, 2008; Clara et al., 2005), microwave-assisted extraction (Mineau et al., 2011). But they all are very expensive and time-consuming methods. Many researchers have detected permethrin in environmental samples. Vega et al. have reported the safety of permethrin and pyriproxyfen in dogs treated with vet guard plus (Vega et al., 2016).

Drago et al. (2014) have reported the acute permethrin neurotoxicity and its variable presentations and high index of suspicion. Kaneko investigated in his report pyrethroid chemistry and metabolism that all the pyrethroid insecticides so far are rapidly metabolized in mammals and their metabolites are almost completely excreted in the urine and faeces within several days of single oral or subcutaneous administration except their cyano moiety (Kaneko, 2010). Michelle et al. proposed the method for the analysis of pyrethroid insecticides in water and sediment using Gas Chromatography/Mass Spectrometry (Michelle et al., 2009). Diaz et al. detected the resolution of deltamethrin, permethrin, and cypermethrin enantiomers by high-performance liquid chromatography (HPLC) with diode-laser polarimetric detection (Diaz et al., 1998). WHO also reported the specifications and evaluations for public health pesticides permethrin (25:75 cis:trans isomer ratio) (WHO, 2012).

In the present work, the UV-Visible spectrophotometric method has endeavoured for easy and rapid determination of permethrin from water, soil and vegetable samples. The spectrophotometric method is utilized here to record absorbance of samples following analyte deposition and UV-Visible spectrophotometer processing. The analytical factors such as pH, reaction time, temperature, the effect of reagent by developing novel reaction method were optimized for the determination of analyte from sample solution through UV-Visible. The advantages of proposed method are quick, rugged, cheap, inexpensive, portable, highly sensitive, simple and accurate analytical techniques for the determination of pesticides in environmental samples. This method has been successfully applied for analysis of permethrin insecticide in water, soil and vegetable samples i.e., rice, cabbage, tomato, red long beans, brinjal, onion, potato and bottle gourd.

Experimental Design

Chemicals and reagents

All chemicals used were in analytical grade so no further purification by chemical method was needed. Permethrin (purify 98%) and leuco crystal violet (LCV) (4,4′,4″-methylidynetris, N,N, -dimethyl aniline) (HPLC grade), bromine water, potassium iodide and potassium iodate were procured from Sigma-Aldrich (ACS reagent, ≥99%, St. Louis, MA, USA). Besides, other pesticides and metal ions used in the selectivity test were also purchased from Merck. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were purchased from Hi-Media (AR reagent, 99% Mumbai, India). The concentration of permethrin was determined through a UV-Visible spectrophotometer. All glassware was thoroughly cleaned with freshly prepared 3:1

HCl/HNO_3 (aqua regia) and rinsed using ultrapure water with conductivity around 18 MΩ cm^{-1}. All the solutions were prepared in ultrapure water and the same was used throughout the studies. Stock standard solution of permethrin (100 µg mL^{-1}) was prepared in an appropriate amount of analyte with dissolving ultrapure water. All sample solutions were stored at room temperature until the analysis. The 3D structure of permethrin insecticide is given in Fig. 1.

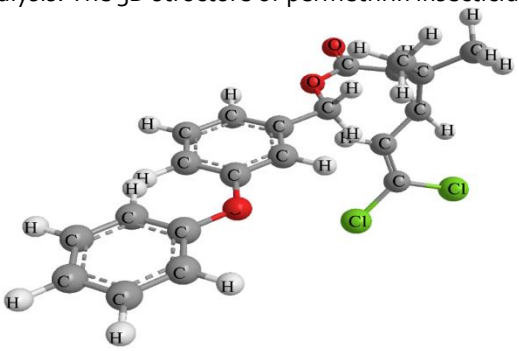

Fig.1. 3D structure of permethrin insecticide

Apparatus

UV-Visible spectrophotometer (Cary 60 UV-Vis, Agilent Technologies) was used for all spectral measurements. The absorption spectrums were recorded in the range of 200-800 nm for the determination of permethrin. A digital pH meter (model 335, Systronics, India) was used for the pH measurements. A REMI R-4C centrifuge force of 5000 rpm with permanent swing-out rotors was used for centrifugation. Thermo Fisher Scientific Barnstead smart2 pure water system was used to obtain ultrapure water for the solution preparations. A micropipette (10 to 1000 µL, Glaxo Smith Kline Pharmaceuticals) was also used for the measurement of variable amounts of all liquid samples. The surface modification and structural characterization of permethrin and permethrin with dye was confirmed by using FTIR spectrometer (Nicolet iS10, Thermo Fisher, Scientific Madison, USA).

Samples collection and preparation for determination of permethrin using LCV

Solid samples

Vegetable Samples

The samples (water, soil and vegetable samples) were collected from different agricultural sites of Chhattisgarh, India. After collection, the samples were crushed into small pieces. Next, in a beaker 5.0 g of vegetable sample and 3 µg mL^{-1} solution of permethrin were mixed to each other. The prepared solution mixture was centrifuged at 10,000 rpm for 2 min. Afterwards, the filtrate part of the sample was taken in a glass vial and then 0.5 mL of bromine water was added into the filtrate with continuous shaking. Next, 2-3 drops of formic acid and 0.5 mL of KI + KIO_3 mixture solutions were gently mixed into it. Now, 0.5 mL of LCV solution was added into the above solution mixture with heating for 10 min and the solution was allowed to cool at room temperature. Afterwards, the sample solution was made up of 10 mL of distilled water into the volumetric flask. Finally, the prepared samples were utilized for the quantitative determination of permethrin using the LCV as a spectrophotometric analysis. Flow diagram of sample pre-treatment procedure for the detection of permethrin in vegetable samples is shown in Fig. 2.

Soil Samples

Environmental soils were collected using clean polyethylene bags and washed several times with water. Subsequently, 5 gm of soil sample was taken into 50 mL conical flask and 20 mL of 0.3% H_2SO_4 along with 10 mL of 0.6% m/v H_2O_2 and 0.5 mL glycerin solution were added to it. Next, the solution mixture was boiled at 160-180˚C for 20 min onto a sand bath. The 2 mL of 0.6% m/v H_2O_2 solution was again added into the above solution with continuous boiling for 10 min. Then it was diluted with 50 mL of distilled water and stood for cooling at room temperature. Afterwards, the supernatant part of sample was filtered using Whatman filter paper (0.45µm pore size) and 0.1 mL of 0.01 M $KMnO_4$ solution was added into it and made into 250 mL with ultrapure water. After that, 5 mL sample solution was pipette out into a beaker and 0.5 mL of bromine water, 4 drops of formic acid and 0.5 mL KI + KIO_3 solution were mixed to each other

and then it was makeup in 10 mL with the help of distilled water into a volumetric flask. The samples were stored in a refrigerator at 4°C for 24 h until spectrophotometric analysis. Flow diagram of sample pre-treatment procedure for the detection of permethrin in soil samples is shown in Fig. 2.

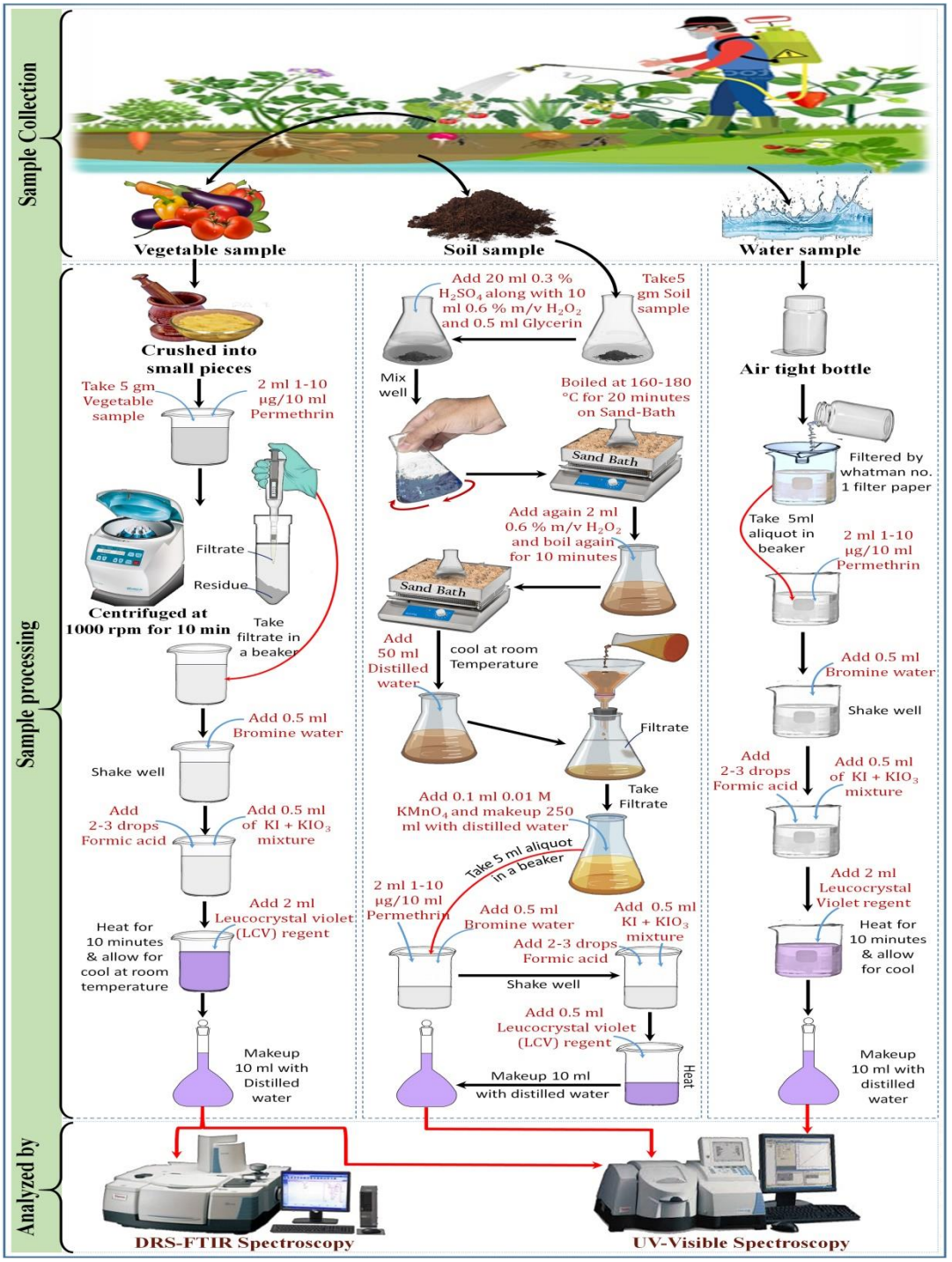

Fig. 2. Flow diagram of sample preparation/pre-treatment procedure for the detection of permethrin using LCV enriched spectrophotometry method in vegetable, soil and water samples.

Liquid samples

The water samples were collected in polyethylene air-tight bottles from rural areas of Raipur city, Chhattisgarh, India. The water samples were directly filtered through Whatman filter paper

No. 1 to prevent the adsorption of any chemical substances onto the surface of suspended elements. Then 5 mL of diethyl ether was added and vaporized into dryness. After that the residue were dissolved with 5 mL ethanol and makeup in 10 mL by using distilled water. Finally, the prepared samples were used for the quantitative determination of permethrin employing spectrophotometric analysis (Sharma et al., 2020). Flow diagram of sample pre-treatment procedure for the detection of permethrin in liquid samples is shown in Fig. 2.

Results and discussion

Characterization

The UV-Vis spectrophotometric approach is employed in this study to analyse and quantify complex mixtures. UV-Vis spectrophotometry was used to determine the absorbance band of LCV complexation on the basis of color change. A strong band of permethrin and LCV gives the absorbance band at λ_{max} = 240 nm and λ_{max} = 285 nm respectively. After adding the both solutions caused the complexation of particles resulting in a change of solution color from colorless to violet. That is appearance as red shit (higher wavelength) at λ_{max} = 580 nm in UV-Vis analysis, indicated in Fig. 3 (a-c). The appearance of new peak in UV-Vis spectra could be attributed to the complex formed due to the coupling of particles. Probably, the reaction mechanism behind it was catalytic oxidation of crystal violet in the presence of permethrin, which leads to the color change of the solution. The pure permethrin and after the addition of LCV reagent complex solution with permethrin were also characterized by FTIR technique.

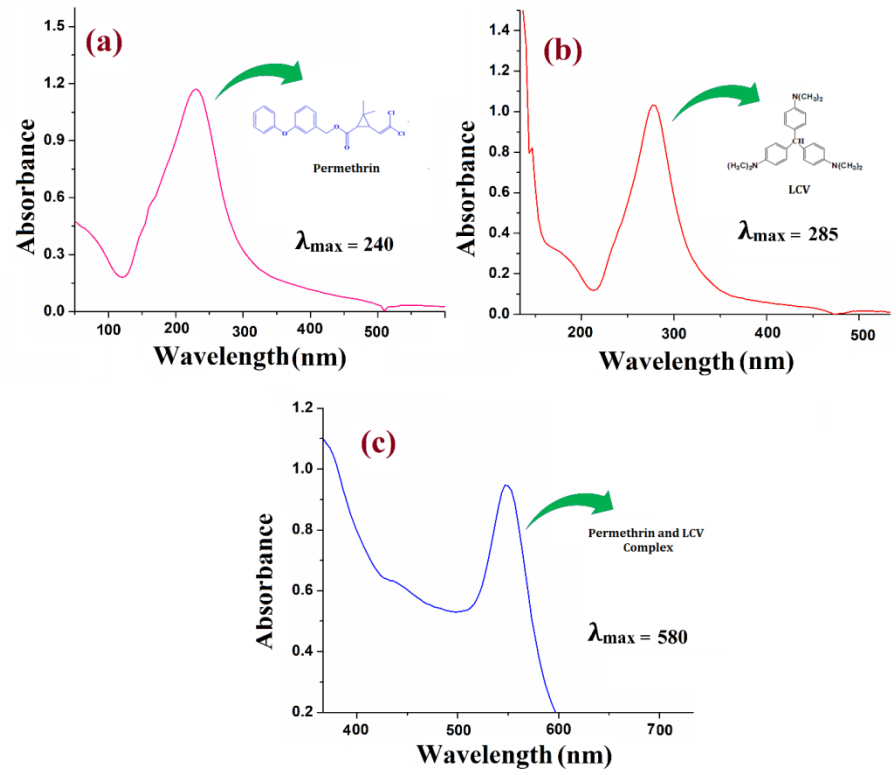

Fig. 3. UV-Vis spectra of (a) permethrin, (b) LCV and (c) permethrin with LCV

FTIR is a simple and quick analytical and non-destructive method for identifying, characterization, and quality assurance of components based on functional groups, molecular structures, and chemical bonding of chemical compounds (Saha et al., 2021; Saha et al., 2022). FTIR is a conformational analysis of the complexation between violet and LCV. FTIR findings for permethrin are similar to UV-Vis results. Complexations between LCV and permethrin to form a violet color dye, and due to these processes, different functional groups are involved in the complexing process. Permethrin spectrum exhibits a very strong band at 1730.15 cm^{-1} which is assigned to C=O stretching vibration indicating the presence of carbonyl groups. The absorption bands obtained at 1472.23 and 1448.53 cm^{-1} correspond to C=C bending and CH_3 stretching

vibrations, respectively and the absorption band at 1123.63 cm^{-1} arises due to the C-C stretching. The absorption bands at 978.89 cm^{-1} is assigned to O-C-O symmetric stretching and at 858.60 cm^{-1} is due to =C-H stretching. The absorption band at 796.33 cm^{-1} arises due to the Cl-C-Cl stretching (Yao et al., 2013). Fig. 4 (a-c) shows the LCV spectra of symmetrical stretching absorption band is C-N 1452.32 cm^{-1}, NH-CN band is 1340.60 cm^{-1}, CH_2 bending 1234.44 cm^{-1}, NH_2 rocking band is 1158.45 cm^{-1}, C-C stretching absorption band is 1068.23 cm^{-1}, C-N stretching band 785.20 cm^{-1}, CH_2 stretching band is 2866.18 cm^{-1} and C-H scissoring vibrational CH_3N^+ is observed at 1555.50 cm^{-1}. The absorption band at 2934.91 cm^{-1} was assigned to the stretching vibrations of C-H bonds. The absorption band at 1051.23 and 1318.25 cm^{-1} were attributing to the bending vibration of C-H bond in the pyrrole ring and C-N stretching vibration. The absorption bands at 1550.12 and 1461.76 cm^{-1} belong to C-C asymmetric and symmetric stretching vibrations of the LCV respectively. The absorption band at 1755.32 cm^{-1} belong to C=O vibrations and the absorption bands at 1484.11 and 1143.20 cm^{-1} belong to C=C and C-C cm^{-1} vibrations, respectively. These results indicate that LCV has been successfully complexation between the permethrin. The shifting of the infrared band is a complexation conformation study. In the entire process, mostly groups and functional groups are switched to the complexation process.

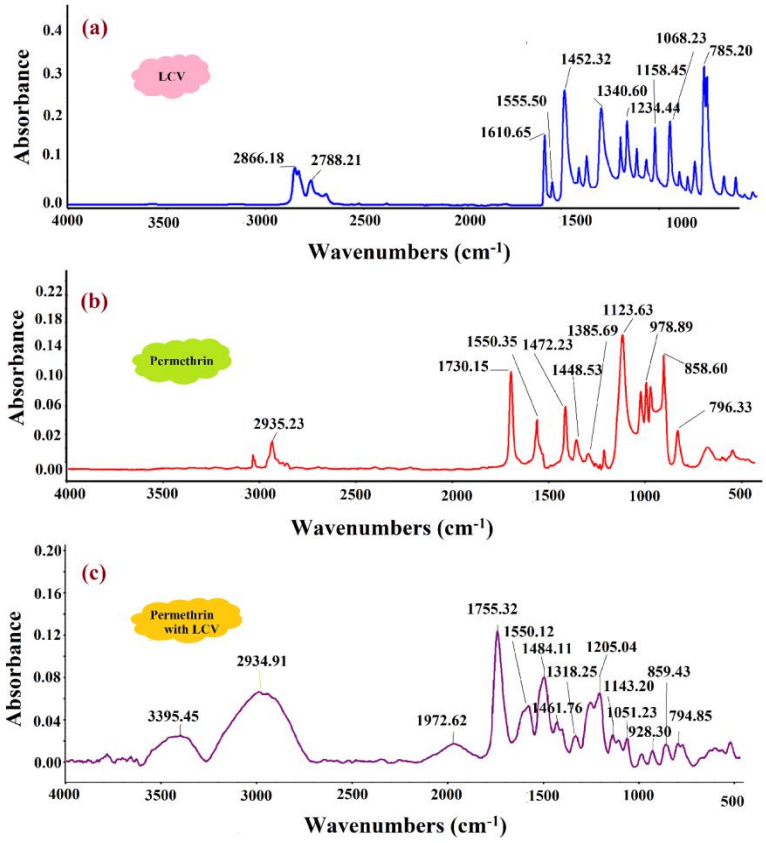

Fig. 4. FTIR spectra of (a) leucocrystal violet (b) permethrin and (c) leucocrystal violet with permethrin.

Mechanism for the detection of permethrin using the LCV reagent complex

The reaction involved in the present method was completed in stepwise process. Firstly, bromine water was added in permethrin solution to produce dibromopermethrin and an excess amount of bromine water was removed by adding 1 to 2 drops of formic acid. After that, potassium iodide and potassium iodate solution (5:1) was introduced into the reaction mixture, which reacts to release the hydrogen iodide in solution. In the next step, an aliquot of LCV was added into the reaction mixture, which resulting the oxidation of LCV and formation of crystal violet dye with permethrin. Further, the mixture was kept in a room temperature and diluted with water and then the absorption spectrum was taken using UV-Vis. An absorption band was observed at 580 nm, owing to the formation of dye (Fig. 3c).

Effect of physical variables and their Optimization

Several parameters such as effect of pH, volume of bromine water, volume of LCV and KI & KIO_3 were optimized in present work for determination of permethrin. The efficient detection of permethrin was obtained when pH sample solution was 6.0 at volume of bromine water of 1 mL, KI & KIO_3 of 2.5 mL using 3 mL volume of LCV. The results are shown in Fig. 5 a-e.

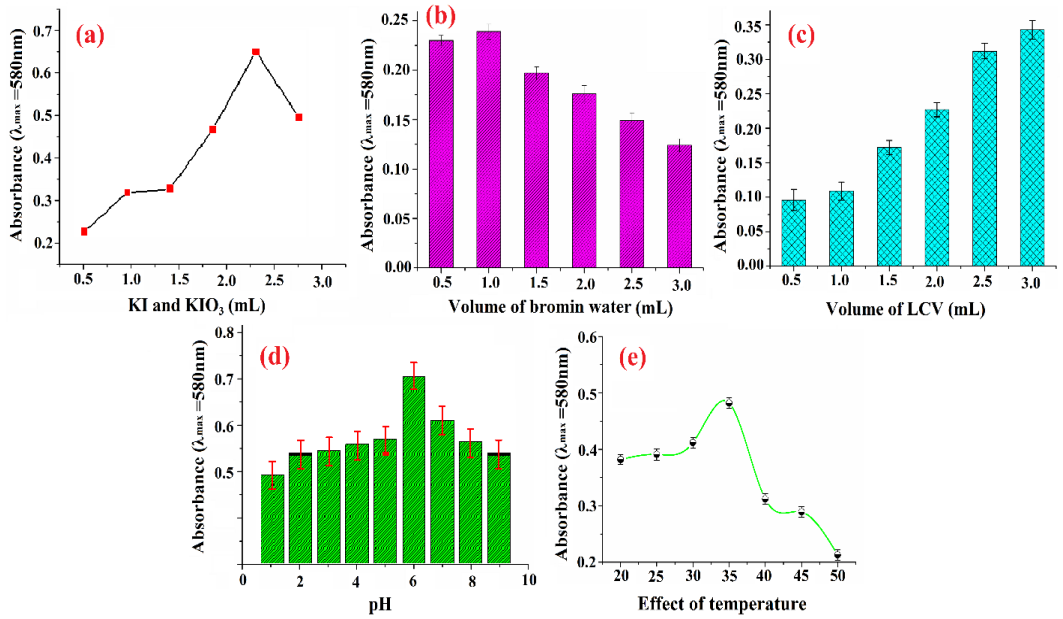

Fig. 5. Optimization parameters: (a) effect of KI & KIO_3, (b) volume of bromine water, (c) volume of LCV, (d) effect of pH and (e) effect of temperature [number of repetitions: 5].

Effect of KI and KIO_3 volume

The KI and KIO_3 volumes were also studied for determination of permethrin for chemical reaction between permethrin and LCV. It was found that the absorbance value increased with the increasing of KI and KIO_3 volume and reached the maximum when 2.5 mL was used. It demonstrated that the use of 2.5 mL KI and KIO_3 was adequate for the extraction of permethrin. Therefore, 2.5 mL volume of KI and KIO_3 was selected as an optimized condition, the results are shown in Fig. 6 a.

Effect of bromine water volume

The bromine water volume was investigated in the proposed work. The effect of bromine water volume was evaluated by increasing the volume ranging from 0.5 to 1.0 mL keeping the other parameters constant. Maximum absorbance was obtained when 1.0 mL of bromine water was used. The absorbance decreased when bromine water volume was increased up to 3.0 mL as shown in Fig. 6 b. Therefore, the bromine water volume at 1.0 mL was set for the determination of permethrin.

Effect of LCV volume

To study the effect of LCV volume, the experiment was performed between 0.5-3.0 mL of LCV for the determination of permethrin at pH 6.0. The results are given in Fig. 6 c. The results showed that the absorbance value first increased when the volume of LCV was increased and then after a point it became stable. It took 10-12 min for the complete reaction, but the color of the product remained unchanged for several days. Hence, an LCV volume of 3.0 mL was selected for the present experiments.

Effect of pH

The effect of pH on the interaction between permethrin and LCV was studied over the pH range from 1.0-9.0 and the pH adjustment were performed by addition of appropriate amounts of

diluted HCl or NaOH solution. As illustrated by Fig. 6 d, the absorbance increased in the pH range of 1.0-6.0 and the absorbance decreased in the pH range of 7.0-9.0. Since, the reaction mechanism involved was the catalytic oxidation of LCV in the presence of permethrin, which leads to color change of the solution mixture. At pH 6 (acidic medium) the color of the solution becomes intense. Therefore, the sample solution was maintained at pH 6.0 for the determination of permethrin using LCV by UV-Vis spectrophotometry.

Effect of temperature

The effect of temperature on the reaction was studied by the varying temperature range from 25°C to 60°C for the determination of permethrin and found that the 30°C to 35°C temperature was sufficient for the complete reaction and formation of color complex (Fig. 6 e).

Effect of diverse substances

The effect of various diverse substances and other pesticides that may be present in solid and liquid samples is evaluated for selective determination of permethrin with using LCV. In order to examine the specificity and selectivity of the complexation between permethrin and LCV, we selected several potentially interfering compounds which are associated with food, soil and water samples including permethrin (glyphosate, buprofezin, phenthoate, kitazin, bifenthrin), metallic ions (Na^{2+}, K^{+}, Zn^{2+}, Ba^{2+}, Ca^{2+}) to evaluate the selectivity for determination of permethrin using LCV based spectrophotometry. In this work, the determination of permethrin was carried out by standard spiked with different concentrations of diverse ions and other pesticides at pH 6.0 followed by analysis with spectrophotometry. The possible interfering chemical substances with their tolerance limits in the determination of permethrin are given in Table 1 and Fig. 7. The absorbance value of permethrin remained unchanged even in the presence of the test following the chemical process mentioned above at the optimized conditions of the proposed methodology

Table 1. Effect of foreign species (concentration of permethrin 3 µg/mL)

Foreign Species/Ions	Tolerance limit
Glyphosate	500
Buprofezin	800
Phenthoate	700
Kitazin	600
Bifenthrin	100
Na^{+}	500
K^{+}	950
Ca^{2+}	100
Zn^{2+}	700
Ba^{2+}	600

The tolerance limit is the amount of foreign species that results in a ±2% mistake in absorbance value.

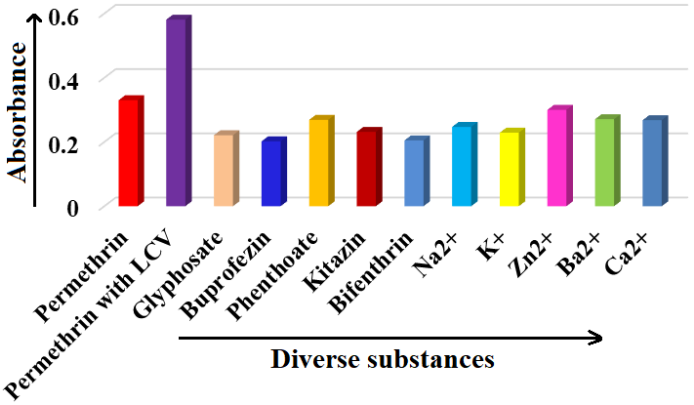

Fig. 7. Effect of the diverse substances in the presence of the LCV and LCV with analytes for selective determination of permethrin.

Analytical evaluation for determination of permethrin using LCV

Important parameters such as linearity range, correlation coefficient (R^2), limit of detection (LOD), limit of quantification (LOQ), selectivity, accuracy and precision for the determination of permethrin were estimated to determine the plausibility of complexation with LCV. The calibration curve was prepared for permethrin by adding various concentrations of permethrin 1-10 µg in 10 mL in different glass vials. The statistical parameters were included in the regression equation (y = mx+c) derived from the calibration graphs, as well as the standard deviation (SD) of the slope and intercept on the ordinate and the SD residuals (SDy/x). The linearity of calibration graphs was demonstrated by high values of the correlation coefficient (r) and modest values of the regression equations y-intercepts. The absorption spectrum of the violet color permethrin/LCV complex is shown in Fig. 8 with maximum absorption at 580 nm.

Table 2 shows the apparent molar absorptivity of the produced colored complex and the RSD% of response factors for each suggested spectrophotometric technique. Beer's law was followed, and the linearity graph in the concentration range of 1-10 µg mL^{-1} of permethrin solution is given in Fig. 8. In this present work the molar absorptivity and Sandell's Sensitivity were also calculated as show in Table 2. The results of the present work have been validated by making a comparative analysis using a standard reported HPLC method (Khalkho et al., 2022), as shown in Table 3. The recovery % was determined by adding different amounts of permethrin to the real sample. Table 4 shows an excellent recovery % of 97.6-100.2 % for permethrin determination in real samples. The LOD was also determined by adding a minimum amount of permethrin into the LCV solution and using three times the standard deviation with the slope of the curve (3SD/slope) (khalkho et al., 2022). LOQ is the lowest concentration of analyte at 10 × SD by acceptable precision at a similar concentration, i.e., LOQ = 10SD/slope (Saha et al., 2021; khalkho et al., 2022). The values of LOD and LOQ in the present work were calculated to be 0.34 µg mL^{-1} and 1.06 µg mL^{-1}, respectively. The precision of the method was obtained by calculating the relative standard deviation percentage (RSD %) by six replicate analysis of the samples under the optimized conditions. The SD and RSD for determination of permethrin were found to be ±0.007 and 3.30 %, respectively, showing a good precision of the method for determination of permethrin in sample solution.

Table 2. The suggested method's analytical parameters and optical properties

S. No.	Parameters	Values for the reaction
1.	λ_{max}, nm	580
2.	Linearity range, µg mL^{-1}	1-10
3.	Molar absorptivity, L $mol^{-1}cm^{-1}$	$3x10^5$
4.	Sandell's sensitivity, µg cm^{-2}	$0.29x10^{-7}$
5.	Quantitation limit, µg mL^{-1}	1.06
6.	Detection limit, µg mL^{-1}	0.34
7.	Regression equation (y=mx+c)	0.066x +0.089
8.	Relative standard deviation (%)	3.30
9.	Slope (y)	0.066
10.	Intercept (c)	0.089
11.	Correlation coefficient (R^2)	0.966

Applications to the determination of permethrin using LCV in environmental samples

The LCV reagent solution was successfully used for the determination of permethrin in environmental samples (water, soil and vegetables) obtained from different sites of Chhattisgarh, India. In a glass vial containing 2 mL of filtered water/soil/food sample, 1.0 mL aliquots of LCV was added at pH 6.0. The solution mixture was allowed to react for 4 min while maintaining the pH of the sample solution. Then the solution was used for spectrophotometric analysis due to the development of color complex. An absorbance band appears at 580 nm in UV-Vis analysis was used for determination of permethrin from real samples. The coupling product's color visibly turned to violet. It is clearly observed that the pure permethrin spectrum at 240 nm and after the adding LCV reagent solution of gives red shift at 580 nm due to the complexation. In this work, quality control experiments were performed on each sample, which included a linear calibration standard in matrix, a spiked and a blank sample for the chemicals

compound. A good recovery % range, i.e., 97.6-100.2 % found for the determination of permethrin in real samples using LCV reagent displayed remarkable selectivity of the chemical complexation for detection of the target analyte. The results on the permethrin contents of all positive samples are given in Table 4.

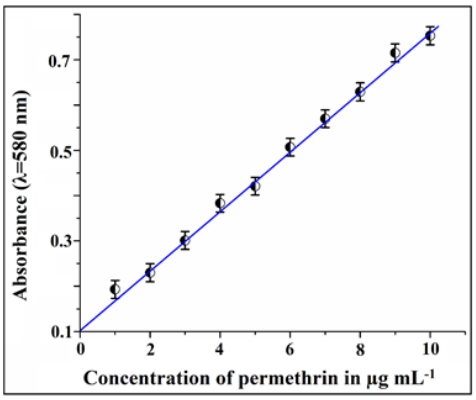

Fig. 8. Calibration curve for different concentrations of permethrin.

Table 3. Determination of permethrin in real samples analysed by the present and reported HPLC method

Statistical Parameters	Statistical data for permethrin detection	
	UV-Visible spectroscopy (Present method)	High performance liquid chromatography (Reference method)
Linear range (µg mL^{-1})	1-10	0.55-4.40
RSD (%)	3.30	2.56
Correlation estimation (R)	0.983	0.999
Correlation Coefficient (R^2)	0.966	0.999
LOD (µg mL^{-1})	0.34	0.16
LOQ (µg mL^{-1})	1.06	0.497
Recovery (%)	97.6-100.2	93.95-96.58

Table 4. Recovery percentage (%) for determination of permethrin using LCV in real samples

Samples	Permethrin originally found (µg)	Permethrin Added (µg)	Total Permethrin Found* (µg)	Difference (µg)	Recovery (%)
Water**	0.25	10	10.01	9.76	97.6±0.5
Soil**	0.38	10	10.34	9.96	99.6±0.8
Rice***	0.31	10	10.24	9.93	99.3±0.4
Potato***	0.24	10	10.22	9.98	99.8±0.5
Cabbage***	0.43	10	10.39	9.96	99.6±0.7
Red long beans***	0.52	10	10.54	10.02	100.2.±0.8
Brinjal***	0.43	10	10.42	9.98	99.8±0.7
Onion***	0.24	10	10.24	10.00	100.0±0.5
Tomato***	0.34	10	10.28	9.94	99.4±0.6
Bottle gourd***	0.53	10	10.29	9.76	97.6±0.8
*Mean of three replicate analysis; **Amount of samples 10 mL; ***Amount of samples 5gm					

Comparison of present method and other reported methods for determination of permethrin

The linearity range, LOD, RSD, and recovery % values obtained by newly developed LCV reagent complex were compared with other reported methods for the determination of permethrin in different types of samples, given in Table 5. The LOD value obtained by the present method was found lower than with High Performance Liquid Chromatographic, Gas chromatography-mass spectrometry, Solid-Phase Extraction, Liquid-liquid microextraction combined with gas chromatography and SERS on optical fiber fabricated by laser-assisted photochemical method

(Kim et al., 2006). These previously published approaches need a time-consuming sample preparation procedure, trained personnel and expensive chemical reagents. The present spectrophotometric method based on LCV reagent chemical complex is very simple, rapid, sensitive, selective, cost-effective, and also minimum quantity of chemical reagents are required as compared to other sophisticated analytical instruments. The good recovery ranging from 97.6-100.2 % was comparable to that obtained with other sophisticated methods.

Table 5. Comparison of the present method with other reported methods for determination of permethrin

Method	Linearity range	(R^2)	LOD ($\mu g\ mL^{-1}$)	LOQ ($\mu g\ mL^{-1}$)	RSD (%)	References
High performance liquid chromatography	0.55 –4.40	0.999	0.164	0.497	2.56	Harshit et al., 2017
Gas chromatography-mass spectrometry	0.01 –250	0.999	2.8	9.43	3.5	Shishovska et al., 2010
Solid-Phase extraction combined with dispersive liquid-liquid microextraction	0.2– 400 ng g^{-1}	0.998	2.02	1.06	1.8	Shiran et al., 2019
Liquid-liquid microextraction combined with gas chromatography	0.5-100	≥ 0.999	1.01	2.6	< 4	Shiran et al., 2016
SERS on optical fbre fabricated by laser assisted photochemical method	2.5-200 ng/mL	0.991	0.35	0.1	<3	Noori et al., 2017
UV-Vis spectroscopy	1-10 µg mL^{-1}	0.966	0.34	1.06	3.30	**Present work**

Conclusion

In this present work, LCV reagent complexes were successfully applied for the determination of permethrin in water, soil and vegetable samples (rice, potato, cabbage, red long beans, brinjal, onion, tomato and bottle gourd) using the spectrophotometric method. The permethrin/LCV complex is particularly sensitive for determining permethrin at low concentrations, and it is immediately detectable with the naked eye because of the significant color difference of the sample solution with and without analytes. Thus, the present spectrophotometric method is a simple, cost-effective and does not need particular sample preparation for improved extraction, leading to enhanced extraction and recovery % in UV-Vis region during the analysis. The consequence of our study is the prospect of accurately and especially monitoring the sprayed pesticide residue in vegetable samples before marketing. Thus, the proposed method is found to be simple, sensitive, and rapid for the analysis of permethrin. Also, it used less toxic substance as reagents for the analysis. This method can be considered as one of the good alternatives to most of the high-costing, delicate apparatus which need much more maintenance. In this method detection of limit is calculated very low as compared to other expensive and time-consuming techniques. It can be very efficiently applied for the determination of permethrin in other food and environmental samples.

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