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Experimental design optimization of RP-HPLC method for simultaneous estimation of metsulfuron-methyl, chlorantraniliprole and chlorimuron-ethyl residues in stems of *Oryza sativa*

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Abstract

Background: The study aims to develop a chemometrics optimized D-optimal mixture design approach assisted RP-HPLC method for the determination of pesticide residues of metsulfuron-methyl, chlorantraniliprole, and chlorimuron-ethyl in the stems of *Oryza sativa*. Chromatographic separation was achieved on a C18 column using a mobile phase consisting of a pH 3.5 phosphate buffer and acetonitrile in the ratio 85:15.

Results: The optimized HPLC method gave a sharp resolution of metsulfuron-methyl, chlorantraniliprole and chlorimuron-ethyl at a retention time of 2.599 min, 3.805 min and 4.661 min respectively. Linearity was observed in the range 100–500 µg/mL for metsulfuron-methyl ($r^2 = 0.999$), 4–20 µg/mL for chlorantraniliprole ($r^2 = 0.999$) and 100–500 µg/mL for chlorimuron-ethyl ($r^2 = 0.999$). The developed method was validated as per ICH guidelines.

Conclusion: The proposed chemometrics optimized RP-HPLC method was found to be successful in the resolution of pesticide residues in the stems of *O. sativa*. The developed method can be applied to routine quantification of metsulfuron-methyl, chlorantraniliprole and chlorimuron-ethyl.

Keywords: Pesticides, *Oryza sativa*, Metsulfuron-methyl, Chlorantraniliprole, Chlorimuron-ethyl, Chemometrics, Validated

Background

Pesticides and herbicides are used to destroy the insects or other organisms harmful to cultivated plants in modern agricultural practices to enhance the yield and upgrade the quality of the agricultural crops. Nearly 30% of the food production is lost in third world countries due to insects, pests, plant pathogens, weeds, rodents, birds during storage. However, the unregulated and

indiscriminate application of pesticides has raised serious concerns regarding environmental pollution and human health issues [1–6]. The pesticides ought to be checked for viability, natural, and toxicological tests to get enrolled by the government for legitimate use in determining applications. Sustained accumulation of pesticides in agrarian items is a matter of grave concern for its far-reaching adverse health consequences [2–4]. *Oryza sativa* is the most widely consumed cereal grain as a staple food for a large part of the world's human population, especially in Asia.

Metsulfuron-methyl (CAS 74223-64-6, molecular formula $C_{14}H_{15}N_5O_6S$, and MW 381.37) is methyl

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2-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)carbamoylsulfamoyl]benzoate (Fig. 1a). It is a herbicide, xenobiotic and an environmental contaminant [7]. Chlorantraniliprole (CAS 500008-45-7, and molecular formula $C_{18}H_{14}BrCl_2N_5O_2$, MW 483.1) is 5-bromo-N-[4-chloro-2-methyl-6-(methylcarbamoyl)phenyl]-2-(3-chloropyridin-2-yl)pyrazole-3-carboxamide (Fig. 1b). It is an organobromine compound and acts as insecticide, a ryanodine receptor agonist and employed to protect a wide variety of crops, including rice [8]. Chlorimuron-ethyl (CAS 90982-32-4, molecular formula $C_{15}H_{15}ClN_4O_6S$, and MW 414.8) is ethyl 2-[(4-chloro-6-methoxy-pyrimidin-2-yl)carbamoylsulfamoyl]benzoate (Fig. 1c). It is an agrochemical, proherbicide for chlormuron, acetolactate synthase inhibitor and used as herbicide for the control of weeds in peanuts, beans, and other crops [9].

Different spectroscopic, chromatographic and hyphenated techniques are available for the detection of multi-residue pesticide analysis and their contamination levels [9–14]. However, to the best of our knowledge, no reported HPLC method is available for simultaneous determination of metsulfuron-methyl, chlorantraniliprole, chlorimuron-ethyl in rice (*Oryza sativa*) crops. Therefore this research was aimed to develop and validate an RP-HPLC method for the detection of three pesticides in the stems of *Oryza sativa*, the chromatographic conditions optimized by the D-optimal mixture design approach of chemometrics [15, 16].

Methods

Materials and reagents

Metsulfuron-methyl, chlorantraniliprole, chlorimuron-ethyl were obtained from Pharma Train, Hyderabad, India. KH_2PO_4 was obtained from Finer Chemical Ltd, Mumbai, India. Acetonitrile was from Molychem, India

and HPLC grade methanol and orthophosphoric acid was sourced from Merck, Mumbai, India.

Instrumentation

UV–visible spectrophotometer (UV 3000⁺, Labindia, Mumbai, India), Waters[®] 2695 HPLC System with separation module, PDA Detector and Empower[®] software (Waters Corporation, Milford, USA), weighing scale (Afcoset[®] ER-200A, Hyderabad, India), reversed phase Inertsil[®] ODS C18 column (4.6 × 250 mm, 5 μ) (GL Sciences, Inc., California, USA), rotary evaporator (Buchi R100, Germany) and pH meter (Adwa-AD 1020, Adwa Instruments, Inc., Szeged, Hungary). All glass apparatus were sourced from Borosil[®] (Borosil Glass Works Ltd., Mumbai, India).

Software

Experimental design, data analysis and generation of surface plots were performed by using Design Expert[®] Trial Version 13, State-Ease Inc., Minneapolis, MN, USA.

Chemometrics optimized development of chromatographic parameters

Any developed new experimental methodology is acceptable when it can be performed in considerably less time with the simultaneous saving of material and personal cost. Chemometric tools like Response Surface Methodology (RSM) using desirability function is a good statistical analysis tool for extracting the maximum amount of complex information, for proper optimization of any process technology and determining the values of process parameters at which response reaches its optimum level which can be maximum, minimum or a desired region where the response is stable over a range of parameters [14, 15]. In this research paper D-optimal mixture design

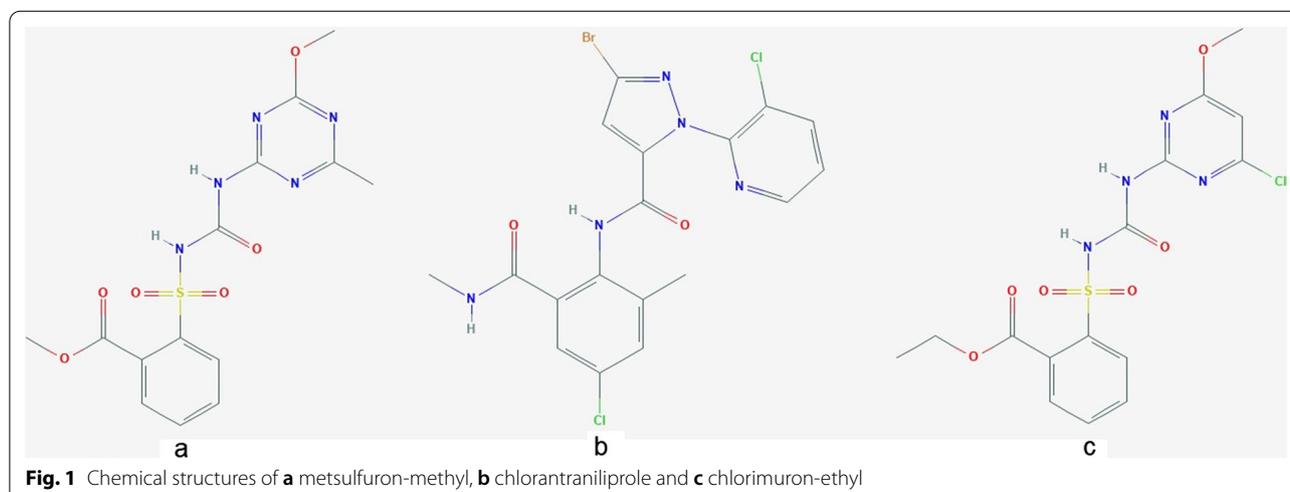


Fig. 1 Chemical structures of **a** metsulfuron-methyl, **b** chlorantraniliprole and **c** chlorimuron-ethyl

approach has been applied for optimizing the RP-HPLC chromatographic conditions for detection of pesticides in stems of *Oryza sativa*; mobile phase composition, and flow rate were considered as the input variables.

Standard solution preparation

A 50 mg of metsulfuron-methyl, 2 mg of chlorantraniliprole and 50 mg of chlorimuron-ethyl working standard were accurately weighed and transferred into a 100 mL cleanly dried volumetric flask, 7 mL of mobile phase was added, sonicated to dissolve it completely and volume made up to the mark with the same solvent i.e. Stock solution. A 0.6 mL of the above stock solutions were further pipetted into a 10 mL volumetric flask and volume was adjusted up to the mark with mobile phase.

Sample preparation

The commonly used herbicide and insecticide together for the rice crop in the east and west Godavari districts of India are DuPont Almix[®], a herbicide which contains metsulfuron-methyl and chlorimuron-ethyl, and used for weed management; and DuPont Ferterra[®], an insecticide which contains chlorantraniliprole, used for white ear incidence in rice plants. The stems of *Oryza sativa* were collected from dried agriculture fields of the Rajahmundry region of India, dried, powdered, macerated in ethanol, filtered, and subjected to drying using a rotary evaporator (Buchi R100, Germany). The dried powder served as the test sample. The test samples were dissolved in mobile phase prior to injection into the HPLC system.

RP-HPLC analysis under optimized chromatographic conditions

Analysis was carried out in gradient elution HPLC system (Waters[®]) with auto-sampler and PDA detector in reversed phase Inertsil[®] ODS C18 column (4.6 × 250 mm, 5 μ) (GL Sciences, Inc., California, USA) at ambient temperature; the optimized mobile phase composition consisted of phosphate buffer:acetonitrile (85:15) maintained at pH 3.5, the flow rate was kept at 1 mL/min, detector wavelength at 281 nm, injection volume 20 μL and a run time of 15 min. The developed method was validated as per International Conference on Harmonization (ICH) Guidelines for Validation of Analytical Methods [17]. Various parameters were evaluated including linearity, the limit of detection (LOD), the limit of quantification (LOQ), accuracy, precision and robustness as per the ICH guidelines.

Preparation of calibration curve

Appropriate volumes of aliquots (0.2, 0.4, 0.6, 0.8 and 1.0 mL) from standard stock solutions of metsulfuron-methyl, chlorantraniliprole and chlorimuron-ethyl were

transferred to different 10 mL volumetric flasks. The volume was made up to mark with the mobile phase to obtain various concentrations of 100, 200, 300, 400 and 500 μg/mL for metsulfuron-methyl and chlorimuron-ethyl; and those of 4, 8, 12, 16 and 20 μg/mL for chlorantraniliprole. The absorbance of resultant solutions was measured at 281 nm. The calibration curve was constructed by plotting the absorbance versus concentration.

Forced degradation studies

The International Conference on Harmonization (ICH) guideline entitled stability tests of new drug substances and products that require stress testing to elucidate the inherent stability characteristics of the active substance [17]. Stress degradation studies on the metsulfuron-methyl, chlorantraniliprole and chlorimuron-ethyl were done for the proposed method.

Acid degradation

From the standard stock solution, 5 mL was transferred into a 50 mL volumetric flask, 1 mL of 5 N HCl was added and kept at 60 °C for 6 h and then neutralized with 1 mL of 5 N NaOH and diluted to marked volume with mobile phase and mixed properly. The solution was filtered with 0.22 μ syringe filters, suitably diluted and injected into HPLC system and analyzed.

Alkali degradation

From the standard stock solution, 5 mL was transferred into a 50 mL volumetric flask, 1 mL of 5 N NaOH was added and kept at 60 °C for 6 h and then neutralized with 1 mL of 5 N HCL, mixed properly and volume adjusted with mobile phase. The solution was filtered with 0.22 μ syringe filter, suitably diluted and injected into HPLC system and analyzed.

Oxidative degradation

From the standard stock solution, 5 mL was transferred into a 50 mL volumetric flask, 1 mL of 30% hydrogen peroxide was added and heated to 70 °C for 1 h on a water bath. The flask was removed from the water bath and allowed to cool at room temperature and after volume adjustment with mobile phase was mixed thoroughly. The solution was filtered with 0.22 μ syringe filter, suitably diluted and injected into HPLC system and analyzed.

Reduction

From the standard stock solution, 5 mL was transferred into a 50 mL volumetric flask, 1 mL of 10% sodium bisulphate was added and heated at 70 °C for 1 h on a water bath. The flask was removed from the water bath and allowed to cool at room temperature, volume adjusted with mobile phase and mixed properly. The

solution was filtered with 0.22 μ syringe filter, suitably diluted and injected into HPLC system and analyzed.

Assay

The sample solution prepared from the *Oriza sativa* was injected as described under experimental work. The corresponding chromatogram obtained is noted and the amounts of metsulfuron-methyl, chlorantraniliprole and chlorimuron-ethyl were determined using calibration curves.

Results

In this research D-optimal mixture design approach was applied for optimizing the RP-HPLC chromatographic conditions for detection of pesticides in stems of *Oryza sativa*; mobile phase composition, and flow rate were considered as the input variables. Considering the retention time of metsulfuron-methyl, chlorantraniliprole and chlorimuron-ethyl as three different responses, the software generated ANOVA tables and 3D-surface plots are presented in Tables 1, 2 and 3 and Figs. 2, 3 and 4 respectively. The normal probability plot of the residuals displays the residuals versus their expected values when the distribution

Table 1 Software generated ANOVA table considering retention time of metsulfuron-methyl as Response 1

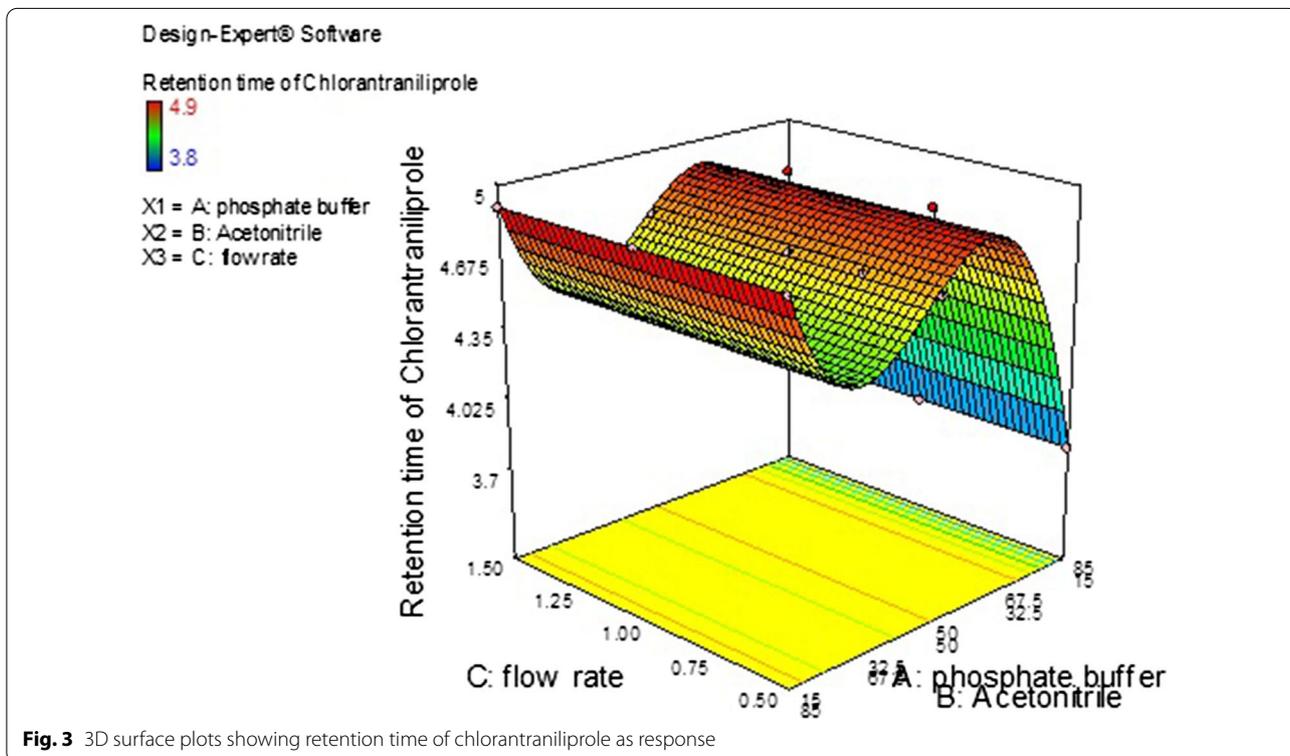
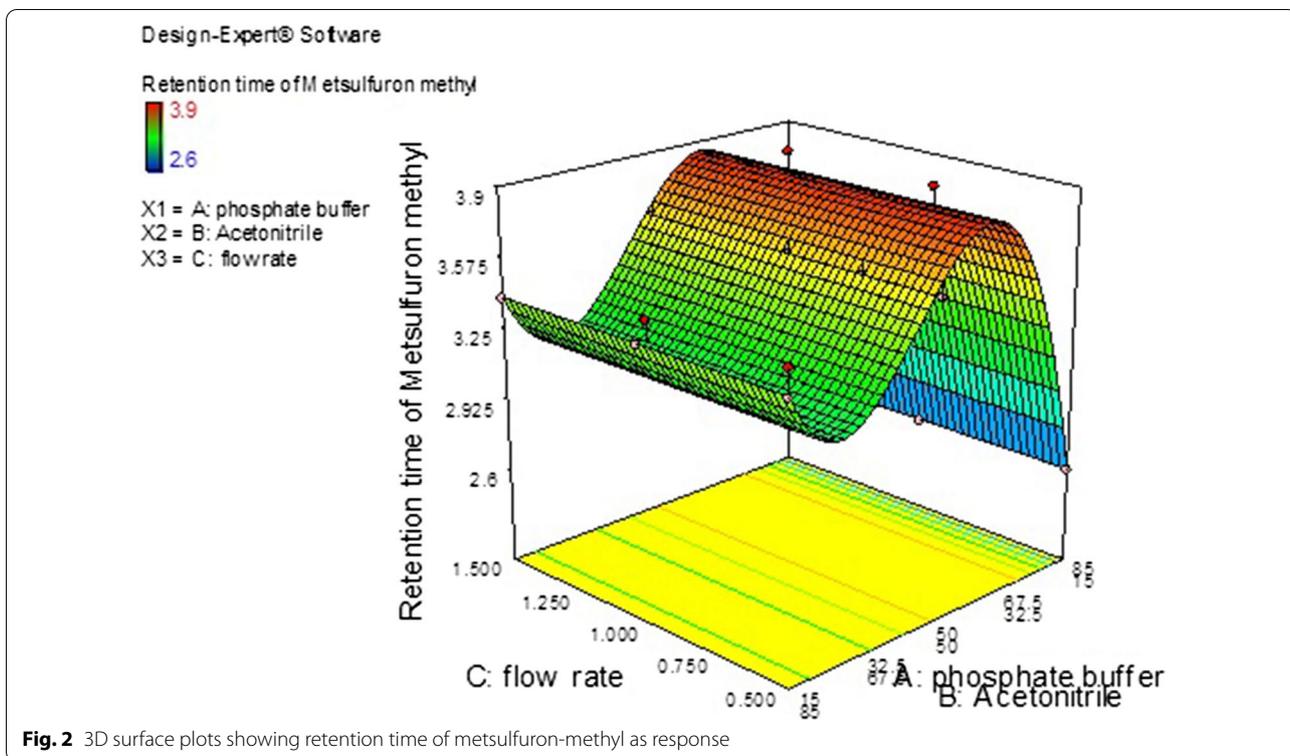
Source	Sum of squares	df	Mean square	F value	p value Prob > F	
Model	3.92	3	1.31	345.65	< 0.0001	Significant
Linear mixture	1.36	1	1.36	359.48	< 0.0001	
AB	1.60	1	1.60	424.04	< 0.0001	
AB (A-B)	0.92	1	0.92	242.43	< 0.0001	
Residual	0.057	15	3.784E-003			
Lack of fit	0.057	10	5.677E-003			
Pure error	0.000	5	0.000			
Cor total	3.98	18				

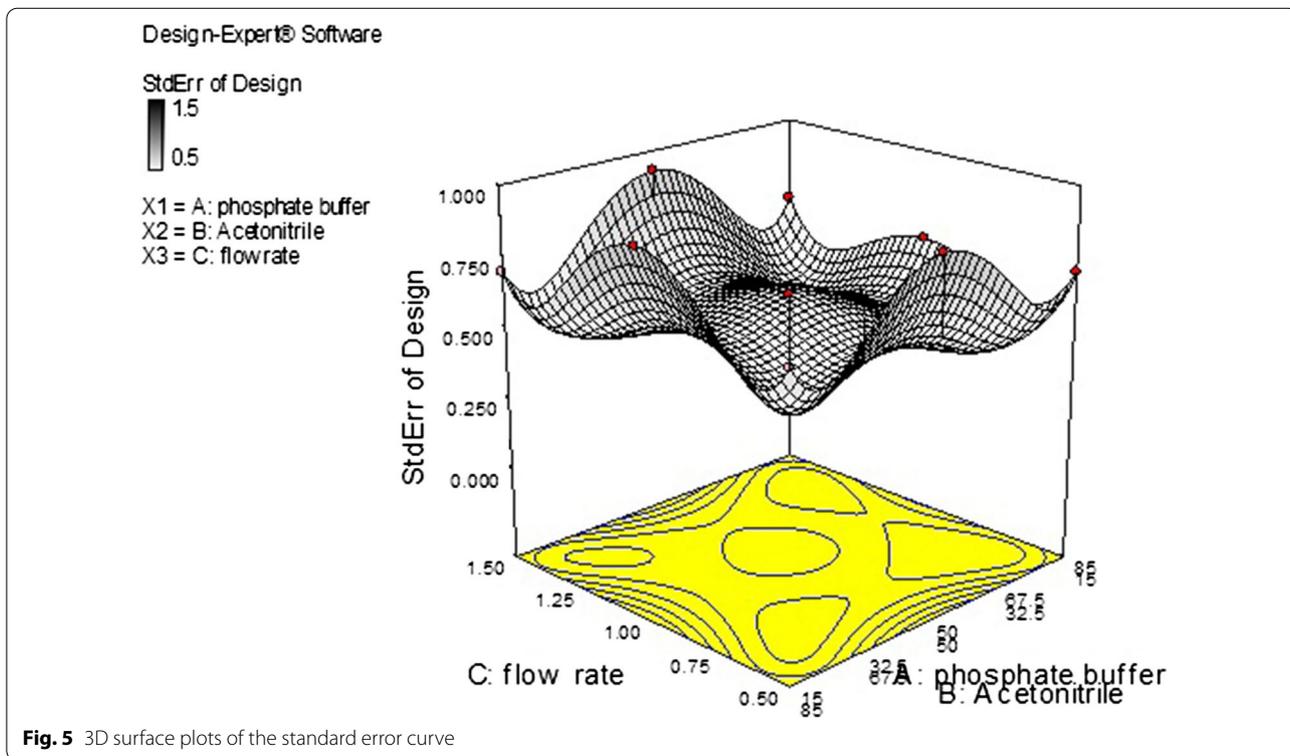
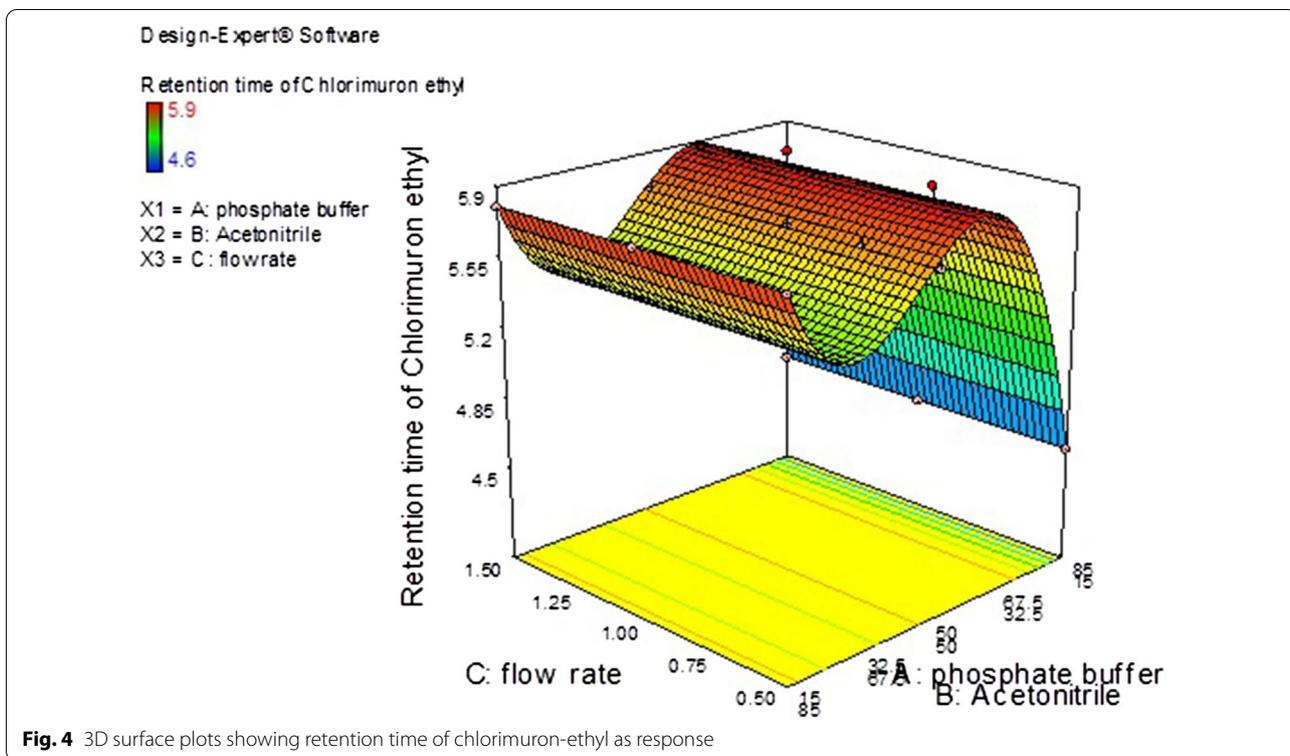
Table 2 Software generated ANOVA table considering retention time of chlorantraniliprole as Response 2

Source	Sum of squares	df	Mean square	F value	p value Prob > F	
Model	4.18	3	1.39	1082.42	< 0.0001	Significant
Linear mixture	2.79	1	2.79	2162.72	< 0.0001	
AB	0.55	1	0.55	424.04	< 0.0001	
AB (A-B)	0.83	1	0.83	642.60	< 0.0001	
Residual	0.019	15	1.288E-003			
Lack of fit	0.019	10	1.932E-003			
Pure error	0.000	5	0.000			
Cor total	4.20	18				

Table 3 Software generated ANOVA table considering retention time of chlorimuron-ethyl as Response 3

Source	Sum of squares	df	Mean square	F value	p value Prob > F	
Model	5.47	3	1.82	694.05	< 0.0001	Significant
Linear Mixture	3.41	1	3.41	1295.93	< 0.0001	
AB	1.11	1	1.11	424.04	< 0.0001	
AB (A-B)	0.92	1	0.92	349.01	< 0.0001	
Residual	0.039	15	2.628E-003			
Lack of fit	0.039	10	3.942E-003			
Pure error	0.000	5	0.000			
Cor total	5.51	18				





is normal. The standard error curve is provided in Fig. 5 and the normal plot of residuals showed linearity with very little scattering in all three responses. This random pattern indicates that a linear model provides a decent fit to the data. The software generated final equation presented in terms of actual components and actual factors considering retention time of metsulfuron-methyl as response 1 is given below:

$$\begin{aligned} &\text{Retention time of metsulfuron-methyl} \\ &= -2.37271E - 003 * \text{Phosphate buffer} \\ &+ 0.048760 * \text{Acetonitrile} \\ &+ 5.40642E - 004 * \text{Phosphate buffer} * \text{Acetonitrile} \\ &+ 1.55613E - 005 * \text{Phosphate buffer} * \text{Acetonitrile} \end{aligned}$$

And the final equation in terms of pseudo components and coded factors is:

$$\begin{aligned} &\text{The retention time of metsulfuron-methyl} \\ &= +2.61 * A \\ &+ 3.41 * B \\ &+ 2.65 * A * B \\ &+ 5.34 * A * B * (A - B) \end{aligned}$$

The software generated final equation presented in terms of actual components and actual factors considering retention time of chlorantraniliprole as response 2 is:

$$\begin{aligned} &\text{The retention time of Chlorantraniliprole} \\ &= +0.012823 * \text{phosphate buffer} \\ &+ 0.066236 * \text{Acetonitrile} \\ &+ 3.15375E - 004 * \text{Phosphate buffer} * \text{Acetonitrile} \\ &+ 1.47788E - 005 * \text{Phosphate buffer} * \text{Acetonitrile} * \end{aligned}$$

And the final equation in terms of pseudo components and coded factors is:

$$\begin{aligned} &\text{The retention time of Chlorantraniliprole} \\ &= +3.80 * A \\ &+ 4.91 * B \\ &+ 1.55 * A * B \\ &+ 5.07 * A * B * (A - B) \end{aligned}$$

The software generated final equation presented in terms of actual components and actual factors considering retention time of chlorimuron-ethyl as response 3 is:

$$\begin{aligned} &\text{The retention time of chlorimuron-ethyl} \\ &= +0.017909 * \text{Phosphate buffer} \\ &+ 0.074747 * \text{Acetonitrile} \\ &+ 4.50535E - 004 * \text{Phosphate buffer} * \text{Acetonitrile} \\ &+ 1.55593E - 005 * \text{Phosphate buffer} * \text{Acetonitrile} * \end{aligned}$$

And the final equation in terms of pseudo components and coded factors is:

$$\begin{aligned} &\text{The retention time of chlorimuron-ethyl} \\ &= +4.61 * A \\ &+ 5.81 * B \\ &+ 2.21 * A * B \\ &+ 5.34 * A * B * (A - B) \end{aligned}$$

The UV spectrum selection of analytes where all three exhibited a sharp response as detector wavelength is given in Fig. 6 and the standard chromatogram obtained (Fig. 7) basing on the chemometrics assisted developed RP-HPLC chromatographic conditions showed proper resolution of the analytes. The chromatogram obtained for the sample solution was shown in Fig. 8 which indicates consistency of the three peaks. The results of system suitability parameters were found within the limits as per ICH guidelines, such as the resolution between samples was not less than 2, theoretical plates were not less than 2000, and tailing factor was less than 2 as shown in Table 4. The optimized HPLC method gave a sharp resolution of metsulfuron-methyl, chlorantraniliprole and chlorimuron-ethyl at retention times of 2.599 min, 3.805 min and 4.661 min respectively. Linearity was observed in the range 100–500 $\mu\text{g/mL}$ for metsulfuron-methyl ($r^2=0.999$), 4–20 $\mu\text{g/mL}$ for chlorantraniliprole ($r^2=0.999$) and 100–500 $\mu\text{g/mL}$ for chlorimuron-ethyl ($r^2=0.999$). The validation and stability parameters of the chemometrics optimized RP-HPLC method are summarized in Table 5. ICH guidelines mandatory oblige the

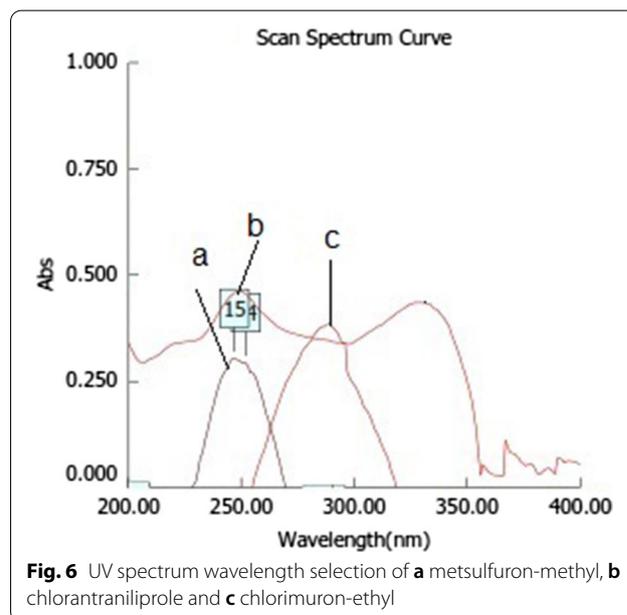


Fig. 6 UV spectrum wavelength selection of **a** metsulfuron-methyl, **b** chlorantraniliprole and **c** chlorimuron-ethyl

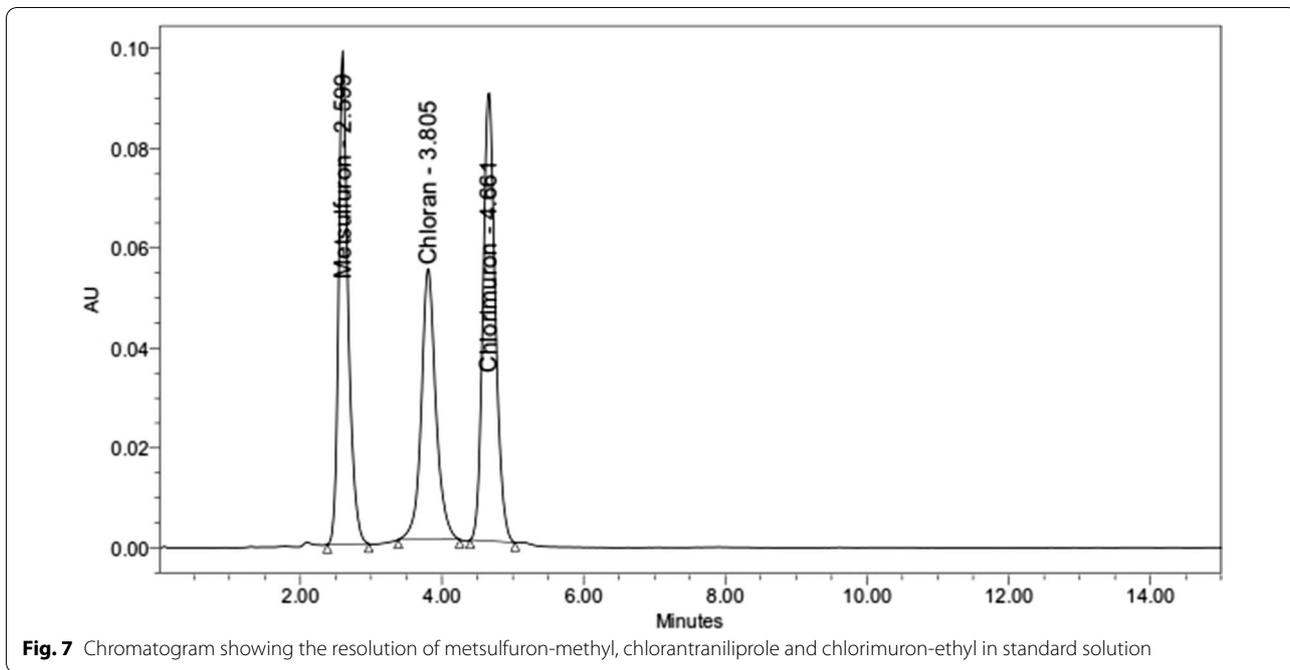


Fig. 7 Chromatogram showing the resolution of metsulfuron-methyl, chlorantraniliprole and chlorimuron-ethyl in standard solution

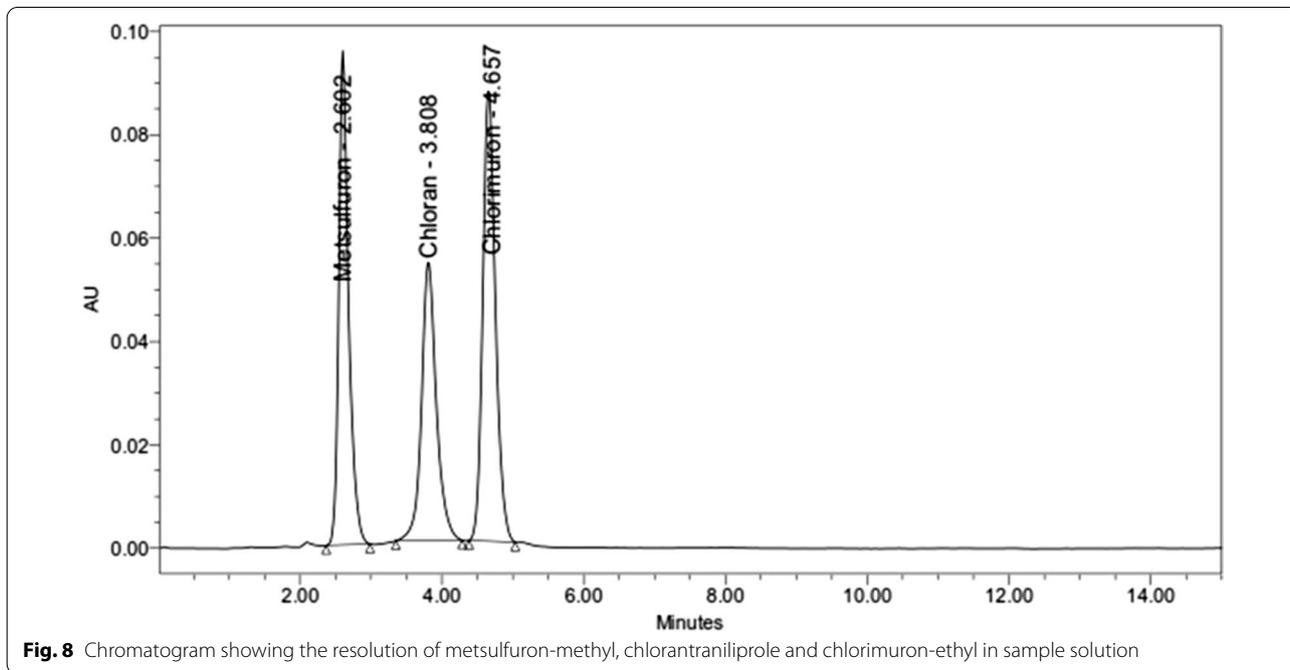


Fig. 8 Chromatogram showing the resolution of metsulfuron-methyl, chlorantraniliprole and chlorimuron-ethyl in sample solution

Table 4 System suitability parameters of the developed RP-HPLC method

Pesticide	RT (min)	Area ($\mu\text{V s}$)	Height (μV)	USP resolution	USP tailing	USP plate count
Metsulfuron-methyl	2.605	910,536	96,742	–	1.37	3925.26
Chlorantraniliprole	3.818	749,206	54,411	4.08	1.13	4822.14
Chlorimuron-ethyl	4.677	1,078,666	87,396	2.92	1.18	3360.73

Table 5 Validation and stability parameters of the chemometrics optimized RP-HPLC method

Parameters	Metsulfuron-methyl	Chlorantraniliprole	Chlorimuron-ethyl
Linearity correlation coefficient	Slope = 2966.9 Intercept = 13,062 (R ²) = 0.999	Slope = 62,403 Intercept = 13,062 (R ²) = 0.999	Slope = 3513.5 Intercept = 13,062 (R ²) = 0.999
Precision	Mean = 934,911.8 SD = 7337.7 %RSD = 0.8	Mean = 743,186.5 SD = 2511.5 %RSD = 0.3	Mean = 1,107,995.2 SD = 8554.2 %RSD = 0.8
Intermediate precision	Mean = 960,417.7 SD = 8148.4 %RSD = 0.8	Mean = 934,911.8 SD = 3655.2 %RSD = 0.5	Mean = 934,911.8 SD = 3722.7 %RSD = 0.3
Accuracy (Mean recovery)	99.95	99.86	100.27
LOD (S/N ratio)	3.00	2.96	3.02
LOQ (S/N ratio)	9.98	10.02	10.00
Acid degradation (%)	3.26	2.50	10.89
Base degradation (%)	1.58	1.05	9.99
Oxidative degradation (%)	3.83	5.19	10.52
Reduction (%)	1.71	3.85	8.21

forced degradation studies under a range of conditions [17]. Results of forced degradation studies of the analytes are shown in Table 6 and Fig. 9. For metsulfuron-methyl, highest degradation was found during oxidation (3.83%) and lowest during alkali degradation (1.58%). Chlorantraniliprole degraded most in peroxide (5.19%) and least in alkali (1.05). Finally chlorimuron-ethyl was influenced nearly equal by both acid (10.89%) and peroxide (10.52%) environments.

Discussion

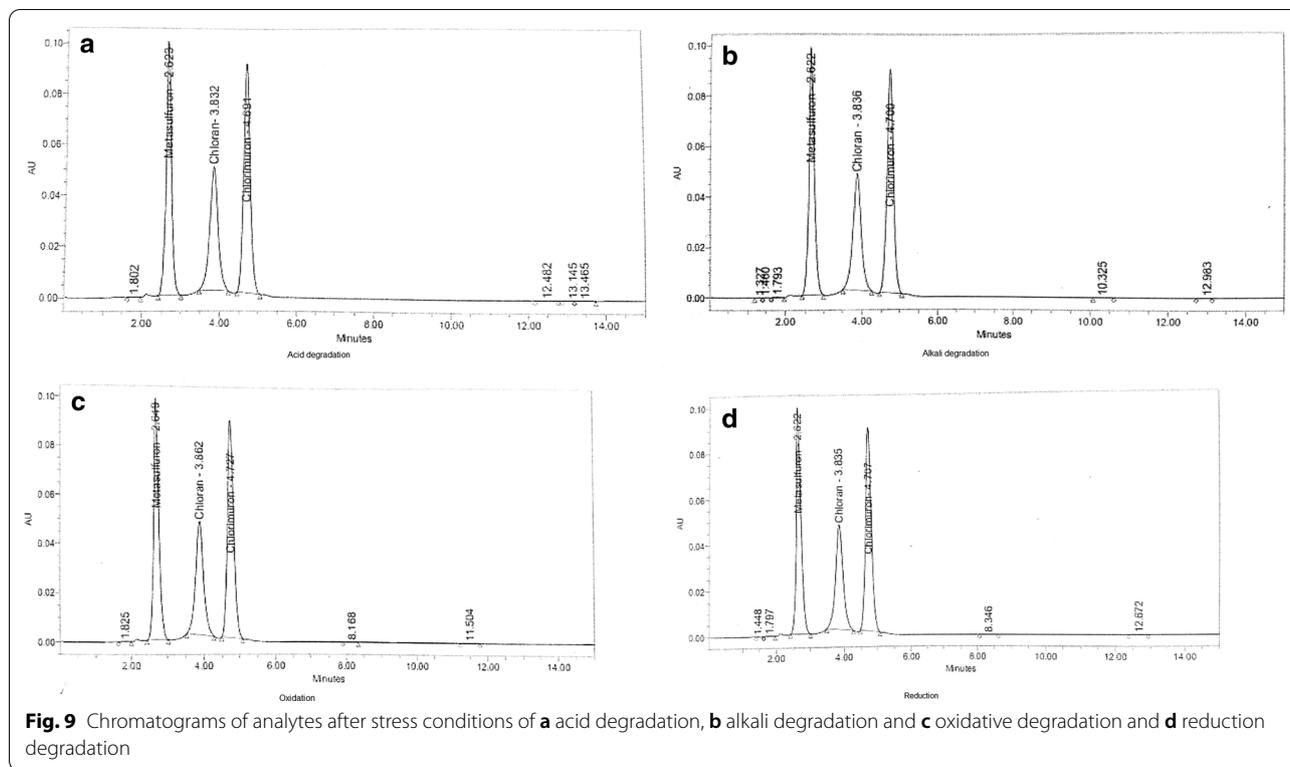
The purpose of this research was to develop and validate chemometrically optimized simple, precise and reliable RP-HPLC method for simultaneous determination of three pesticide residues of metsulfuron-methyl, chlorantraniliprole and chlorimuron-ethyl in stems of *Oryza sativa*. In earlier studies, chemometrics for the optimization of analytical method development was successfully applied [18, 19]. In the present research, the results of the chemometric tools such as response surface methodology and ANOVA were tested for optimization of each factor. The D-optimal mixture design approach

has been applied for optimizing the RP-HPLC chromatographic conditions. From the software generated final equations in terms of actual components and actual factors considering retention time of three analytes, positive coefficients were obtained for phosphate buffer and acetonitrile, such as 2.61 and 3.41 for metsulfuron-methyl; 3.80 and 4.91 for chlorantraniliprole; and 4.61 and 5.81 for chlorimuron-ethyl respectively. This indicates that the concentrations of phosphate buffer and acetonitrile influence the retention time.

Standard protocols of ICH Q2 (R1) guidelines were followed for the analytical method development and validation. The results of system suitability parameters were found within the limits as per ICH guidelines, thus developing precise and accurate results [17]. The developed method was validated for linearity, precision, accuracy and robustness, LOD and LOQ. The RSD values of precision and intermediate precision of developed method were less than 2% which indicates that the method is precise and repeatable. The recovery of three analytes was found in the range of 100 ± 3% which shows that the method is accurate and capable of reproducibility.

Table 6 Results of forced degradation studies for the analytes

Stress condition	Metsulfuron-methyl (300 µg/mL)		Chlorantraniliprole (12 µg/mL)		Chlorimuron-ethyl (300 µg/mL)	
	Area	Degradation %	Area	Degradation %	Area	Degradation %
Standard	912,303	–	754,473.7	–	1,082,565	–
Acid	882,563	3.26	735,622	2.5	964,622	10.89
Alkali	897,865	1.58	746,565	1.05	974,452	9.99
Peroxide	877,382	3.83	715,326	5.19	968,643	10.52
Reduction	896,677	1.71	725,442	3.85	993,645	8.21



Further the LOD values were found between 2.96–3.00, and LOQ values were found between 9.98 and 10.00, and were within the limits. The result of this method was in consonance with reported methods of these pesticides in other combinations in terms of reproducibility, rapid resolution, sensitivity and selectivity [20–22].

Results of forced degradation studies of the three analytes showed that the degradation was less than 15% and was within the limits, indicating stability of the analytes under stress conditions. The developed method can be successfully applied to routine quantification of metsulfuron-methyl, chlorantraniliprole and chlorimuron-ethyl in the food industry since it is reproducible, stable and rapid.

Conclusion

Based on the reported experimental results, this developed chemometrics assisted the new RP-HPLC method for simultaneous estimation of three pesticide residues: metsulfuron-methyl, chlorantraniliprole and chlorimuron-ethyl in stems of *Oryza sativa*. This method was found simple, accurate, precise and rapid and making it more viable and acceptable and successfully applied for routine analysis in the quality control departments of food industries and government-approved food testing laboratories.

Abbreviations

RP-HPLC: Reversed-phase high-performance liquid chromatography; %RSD: Percentage recovery; LOD: Limit of detection; LOQ: Limit of quantification; ICH: International Council for Harmonization of Technical Requirement for Pharmaceutical for Human Use; MW: Molecular weight; ACN: Acetonitrile.

Acknowledgements

The authors are thankful to Pharma Train, Hyderabad for providing the necessary facilities to carry out the research work.

Authors' contributions

SKA and PK contributed equally for literature survey, design, execution, data acquisition/processing, and manuscript preparation. FHA has conceived the research, guided in experimental design, manuscript preparation and editing. All authors read and approved the final manuscript.

Funding

This project is not funded by any funding agency.

Availability of data and materials

Available data and material is available upon request. <https://database.ich.org/sites/default/files/Q2%28R1%29%20Guideline.pdf>. <https://pubchem.ncbi.nlm.nih.gov/compound/Metsulfuron-methyl>. <https://pubchem.ncbi.nlm.nih.gov/compound/Chlorantraniliprole>. <https://pubchem.ncbi.nlm.nih.gov/compound/chlorimuron-ethyl>.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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Received: 28 July 2021 Accepted: 19 October 2021

Published online: 26 October 2021

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