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RESIDUE DYNAMICS AND EFFECTS OF DIFFERENT HOUSEHOLD PROCESSES IN REDUCTION OF FENPROPATHRIN RESIDUES IN CHILLI (*CAPSICUM ANNUUM* L.)

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Abstract

Spraying of chilli crop with fenpropathrin @ 75 and 150 g a.i./ ha led to the initial residues ranging from 0.12 to 0.14 and 0.19 to 0.22 mg/kg, respectively. Fenpropathrin residues in chilli dissipated below the limit of quantification after 3 and 5 days at low and high doses. The half-life of fenpropathrin in chilli was calculated to be 2.41 and 1.92 days. Residues of fenpropathrin on chilli collected 0 day after spray was below MRL following application @ 75 g a.i./ ha. Among various household processing methods, $KMnO_4$ solution reduces 72.50 per cent residue washing, boiling, dipping in sodium bicarbonate solution, salt solution and acetic acid solution, respectively after 0 (2 hrs after spray) day of fenpropathrin @ 75 g a.i./ ha after third spraying in chilli.

Introduction

Chilli (*Capsicum annuum* L.), popularly known as *'mirch'* in Hindi, belonging to Solanaceae originated in Latin America. Different varieties of chilli are grown for different purposes including pungency. World's leading producer of chillies as well as consumers is India. Chilies seem to be the most widely grown spice throughout India. The production, as well as productivity of chilli is hindered by the losses caused due to insect pests. The crop is under the ravage of more than 21 pests which are major limiting factors to chilli production (Dey *et al.* 2001). In general, the pests that occur in chilli are aphids *Aphis gossypii* Glover,

Myzus persicae (Sulzer); mites *Polyphagotarsonemous latu*s (Banks); whitefly *Bemisia tabaci* (Gennadius); thrips *Scirtothrips dorsalis* Hood; chilli pod borers *Spodoptera litura* (Fabricius); *Helicoverpa armigera* (Hubner); blossom midge *Asphondylia capsici* Barnes. Among all the sucking pests attacking chilli, whitefly, *B. tabaci* and thrips, *S. dorsalis* are dominant pests. The estimated loss due to sucking pests was 30 to 50 per cent (Varadharajan 1994).

Fenpropathrin is a novel insecticide implemented by Sumitomo Co. Ltd. It is a pro-synthetic pyrethroid compound. It is a synthetic pyrethroid insecticide, which is more photostable than synthetic pyrethroids developed from the naturally occurring pyrethrum. It is 4th generation of synthetic pyrethroid, resistant to sunlight, air and highly persistent. It is used as broad-spectrum insecticide which is useful to control mainly the pests of field crops, vegetables, fruit trees. Fenpropathrin functions as non-systemic, contact and stomach poison at the same time acts as sodium channel modulator. It is used as an acaricide and insecticide as well. It is effective against mites, whiteflies, leaf miners, armyworms, loopers, aphids, cutworms, stem borers. Patel (2013) reported that pyriproxyfen + fenpropathrin @ 500 ml/ ha reduced the infestation of jassid in brinjal after emamectin benzoate @ 10 g a.i./ ha.

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Because of invariable presence of residues, the consumers are at risks in consuming various commodities treated with pesticides, if suitable waiting period not followed. The rational recommendation for an insecticide must need effective control of target pest as well as residues which are left on the produce should be toxicologically unobjectionable. Therefore, in the present study attempts were taken to estimate fenpropathrin residues in chilli at different time intervals for suggesting waiting periods and to study the impact of different household procedures for minimisation of fenpropathrin residues in chilli and also dietary risk assessment can be calculated under Bihar, Indian condition.

Materials and Methods

Standard stock solution of fenpropathrin was prepared with HPLC grade hexane which was further diluted to have different concentrations and injected into instrument to see the linearity by plotting a calibration curve. The storage temperature for all these standard solutions was kept around -4^0C prior to use.

A field experiment with 3 treatments and 3 replications for each test insecticide was carried out at the "University Apiary" of "Dr. Rajendra Prasad Central Agricultural University, Pusa". Chilli (var. Pusa Jwala) was raised in randomized block design according to the recommended agronomic practices for this region. Seedlings were transplanted on 21st October, 2019 at a spacing of 75 x 50 cm in plots size of 50 m^2.

Fenpropathrin 30 EC was applied on chilli crop at dosages of 75 and 150 g a.i./ ha, accordingly using high volume Aspee Hand Knapsack Sprayer holds capacity of 15 l. The first spray was carried out at 50 per cent flowering and subsequent two sprays with 10 days interval. The amount of volume used while spraying was 500 l/ ha. About 250 g samples of chilli fruits were analysed before and 0 (2 hrs after spraying), 1, 3, 5, 7, 10 and 15 days after third treatment with insecticide. Samples were processed immediately. Samples of red chilli were sampled 20 days after final application.

"Quick, Easy, Effective, Rugged and Safe (QuEChERS)" techniques with slight modification was used for processing of chilli samples for residue analysis. A macerated chilli sample (10 g) was transferred to 50 ml polypropylene centrifugal tube and kept it overnight in refrigerator. Samples were taken from refrigerator and 20 ml of acetonitrile (HPLC grade) was added to each tube. To each centrifuge tube, sodium chloride (10 ± 0.1 g) was added and shaken for 10 min at 50 rpm on rotospin (Tarson®). Samples were centrifuged for 3 min at 2500 rpm. Moisture if any was removed from aliquot of acetonitrile by anhydrous sodium sulfate followed by clean-up through "dispersive solid phase extraction (DSPE)". For this, a polypropylene tube constituting "0.15 ± 0.01 g PSA sorbent, 0.90 ± 0.01 g anhydrous $MgSO_4$ and 0.05 ± 0.01 g graphitic carbon black" was prepared for an aliquot of 6 ml which was thoroughly mixed by vortex spinix (Tarson®). Once again centrifuged for 3 min at 2500 rpm and finally a 3 ml aliquot was taken and evaporated to near dryness. The terminal volume was marked up to 3 ml with hexane for residue analysis.

The estimation of fenpropathrin was carried out through gas-liquid chromatography (GLC) equipped with an electron captured detector and a glass capillary column (length: 30 metre, 25mm i.d., film thickness: 0.25 mm). The conditions to operate for fenpropathrin residues were: detector temperature (280^0C), injector temperature (260^0C) and oven temperature (240^0C) with carrier flow @ 30 ml/min. The residues of fenpropathrin in chilli samples were matched with the "retention time" of respective standards, whereas, estimated by "peak heights". "Retention time" for fenpropathrin was observed to be 4.73 min., correspondingly when injected under above-mentioned conditions.

The theoretical maximum residue concentration (TMRC) is determined by multiplying the maximum residue (residue in mg/ kg) within every chilli sample by the *F i.e.*, estimated national daily per capita consumption of the food commodity on each sampling day (kg/person/ day). The TMRC is compared with maximum permissible intake (MPI), computed for a 55 kg average Indian by multiplying acceptable daily intake (ADI) value of the insecticide and 55 kg.

To study the effect of different household processes in reduction of residue of fenpropathrin in chilli, samples (2 kg) taken 0 (2 hrs after spraying) and 1 day after third application were subjected to different treatments as follows:

T1: Washing with tap water

T2: Dipping in 2% salt solution for 10 min. followed by washing

T3: Dipping in 0.1% sodium bicarbonate solution for 10 min. followed by washing

T4: Dipping in 0.2% $KMnO_4$ solution for 10 min. followed by washing

T5: Dipping in 4% acetic acid for 1 min. followed by washing

T6: Cooking/Boiling

T7: Control

All the samples were analysed and compared with control (no household process) prior to analysis.

Results and Discussion

The full-scale deflection was obtained with 3 ng of the standard of fenpropathrin. Chromatograms for fenpropathrin and spiked samples of chilli are presented in Fig. 1. Samples of chilli were processed and terminal volume was composed to 3 ml and again concentrated to 0.5 ml from where 2 µl of sample was injected to observe the maximum load of samples can be analysed without any interference peak in the area relating to the compound estimated. The LOQ of fenpropathrin was observed to be 0.05 mg/ kg and LOD resulted to be 0.02 mg/ kg.

Mean per cent recoveries of fenpropathrin in chilli samples spiked with 0.05, 0.25 and 0.50 mg/ kg levels ranged from 82.07 to 89.51 per cent and found to be more than 80 per cent, so the results obtained are expressed without application of any correction factor (Table 1, Fig. 2). The repeatability (RSD_r) for fenpropathrin in chilli at 0.05-0.50 mg/ kg ranged from 4.79 to 6.26 per cent, respectively (Table 1). The between-batch recoveries and reproducibility (RSD_R) were examined at 0.05 mg/ kg for fenpropathrin in chilli. The reproducibility of fenpropathrin in distinctive substrates was found to range about 6.15 to 10.48 per cent and all measurements are within 15 per cent at all concentrations.

The application of fenpropathrin was started at fruit initiation stage followed by, subsequent two applications at 10 days intervals. After last application @ 75 g a.i./ ha the mean initial deposit of fenpropathrin in chilli was determined to be 0.12 mg/ kg. The residues dissipated to a mean level of 0.09 mg/ kg, hence indicating a loss of 25 per cent in chilli samples collected one day after spray. After 3 days of application fenpropathrin residues resulted less than the quantitative limit of 0.05 mg/ kg (Table 2).

Application of fenpropathrin @ 150 g a.i./ ha resulted residues of 0.21 mg/ kg in samples collected 0 (2 hrs) after third spray. The residue levels of fenpropathrin were observed to be 0.14 and 0.07 mg/ kg, thus resulting 33.33 and 66.66 per cent dissipation in samples collected after 1 and 3 days, respectively. Samples collected after 5 days showed residue less than the quantitative limit of 0.05 mg/ kg (Table 2). The present results are different from the observation made by Patil *et al.* (2019) who investigated an initial deposits of 1.58 mg/ kg fenpropathrin residues on chilli

and half-life 8.14 days following application of fenpropathrin 30 EC @ 150 g a.i./ ha. This might be due to different climatic conditions, spray patterns, etc.

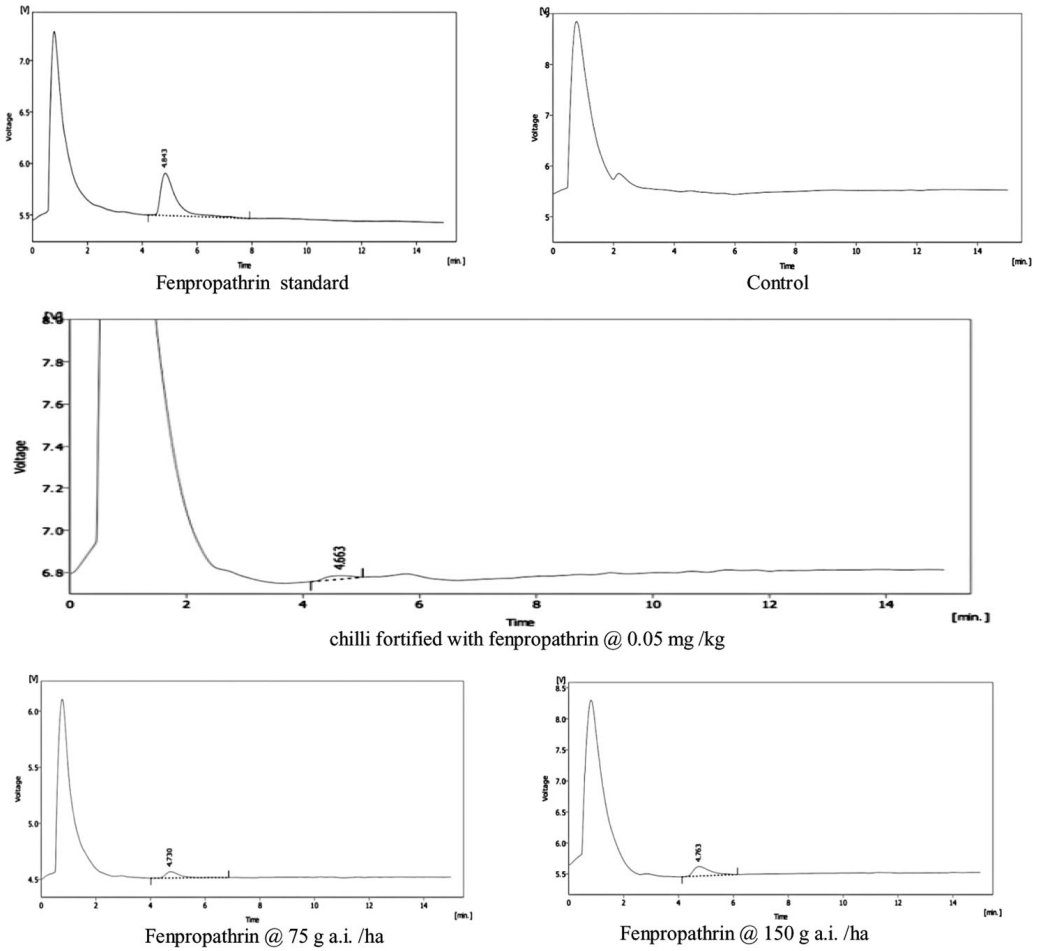

Fig. 1. GLC Chromatograms for chilli samples after third application

Table 1. Amount of pyriproxyfen recovered from spiked chilli samples.

Substrate	Spiked level (mg/kg)	Amount recovered * mean ± SD	RSD_r
Chilli	0.50	89.51 ± 5.60	6.26
	0.25	87.52 ± 4.80	5.48
	0.05	82.07 ± 3.93	4.79

*Mean of six replications, SD = "Standard Deviation", RSDr = "Relative Standard Deviation" (Repeatability)

Table 2. Residue (mg/kg) of fenpropathrin in chilli following its third spray.

Days after treatment	Residue level @ 75 g a.i./ha		Residue level @ 150 g a.i./ha	
	Mean ± SD	Per cent dissipation	Mean ± SD	Per cent dissipation
Before spray	<LOQ	-	<LOQ	-
0 (2hrs after spray)	0.12 ± 0.010	-	0.21 ± 0.015	-
1	0.09 ± 0.015	25.00	0.14 ± 0.021	33.33
3	<LOQ	-	0.07 ± 0.015	66.66
5	<LOQ	-	<LOQ	-
20 (Red chilli)	<LOQ	-	-	-

LOQ = Limit of Quantification (0.01 mg/kg)

Initial deposits of fenpropathrin @ 75 g a.i./ha in chilli fruits were below MRL of 0.2 mg/ kg. In case, double dose, residues of fenpropathrin in chilli fruits was below MRL after 1 day of application. Therefore, the present investigations suggest a waiting period of 1 day at recommended dose for fenpropathrin-treated chilli crops following Good Agronomic Practices (Table 3). Determination of dissipation kinetics regarding residues of fenpropathrin on chilli is expressed in the form of semi-logarithm graph (Fig. 2). For both single and double the recommended dosages, the half-life of fenpropathrin in chilli following third application was found to be 2.41 and 1.92 day, respectively. Similar findings were observed by Ahmed and Mohammed (2014) who reported deposits of 1.53 and 1.76 mg/kg in squash fruit along with garden rocket following treatment of fenpropathrin 20 EC @ 238 g a.i./ha with half- life values of 1.78 days besides 1.85 days, accordingly. Singh *et al.* (2015) suggested that spraying of cypermethrin @ 50 and 100 g a.i./ha, the residual deposits were found to be 1.46 and 3.11 mg/ kg declined below its LOQ of 0.05 mg kg^{-1} after 25 days with $T_{1/2}$ of 4.43 days as well as 4.70 days, respectively. So, it is suggested that a waiting period of one day is required to reduce the risk for safe consumption of chilli fruits. Pandher *et al.* (2012) stated that with the application of deltamethrin @ 17.5 g a.i./ha, the half-life values ranged over 0.36 to 1.99 days in green chillies and observed to be less than its determination limit of 0.01 mg/kg in red chilli, accordingly.

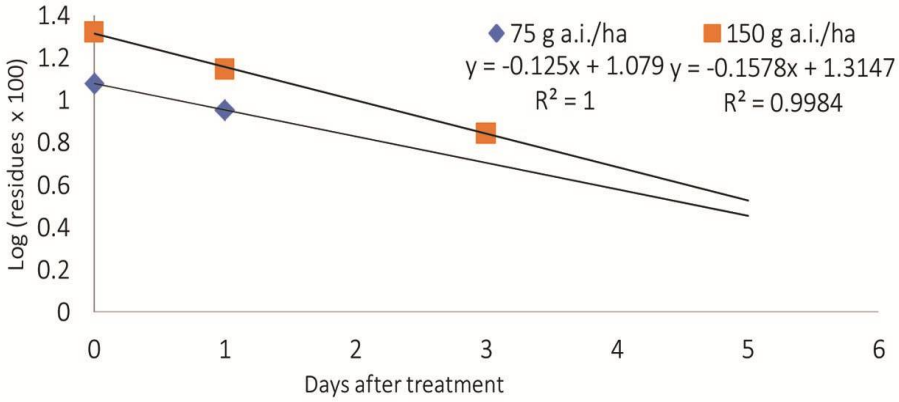

Fig .2. Semi-logarithm graph showing dissipation kinetics of fenpropathrin in chilli

The prescribed ADI of fenpropathrin is 0.03 mg/kg body weight/ day. The MPI of the insecticide was assessed to be 1.65 mg person/ day based on the average Indian body weight of 55 kg. The TMRC calculated by taking the consumption of chilli and maximum residues present in chilli samples after 1 days of application was well below the MPI making the suggested waiting period more practical from consumer point of view.

The studies on processing consider the effect of washing, dipping in salt solution, sodium bicarbonate, $KMnO_4$, acetic acid and cooking/boiling. Results related to the effect of different household processes on the reduction of fenpropathrin residues from 0 and 1 day samples of chilli after 3rd spray.

As a result of washing the mean initial deposit was observed to be 0.12 mg/kg of fenpropathrin on chilli was reduced to 0.053 mg/kg; which accounted a loss of 55.83 per cent by the application of fenpropathrin @ 75 g a.i./ha. After 1 day of application the samples were taken and washed well, thereby washing reduced fenpropathrin residues to BDL showing a loss of 100 per cent with respect to control *i.e.*, without washing.

Table 3. Dissipation parameters of fenpropathrin residue in chilli after 3nd spray.

Dissipation parameters	Rate of application (g a.i./ha)	
	75	150
K_1 (b)	-0.125	-0.157
K_2 (a)	1.079	1.314
$T_{1/2}$	2.41	1.92
T_{MRL}	1.00	1.00
R^2	1.00	0.998
Y	-0.125x + 1.079	-0.157x + 1.314

K_1= "Slope of the regression line", K_2 = "Initial deposit obtained as in the regression equation", $T_{1/2}$ = "Residual half life (in days)", T_{MRL} = "Time (in days) required for the pesticide residue to reach below the maximum residue limit, R^2 = "Coefficient of determination.

Dipped in 2 per cent salt solution for 10 min. subsequently by washing reduces fenpropathrin residues by 50 per cent while 1 day after application, residue reduces by 100 per cent.

Chilli fruits collected two hours after spray @ 75 g a.i./ha when dipped in 0.1 per cent sodium bicarbonate ($NaHCO_3$) solution around 10 min. followed by washing had 0.057 mg/kg fenpropathrin residues as compared to control which was 0.12 mg/kg, thus removing 52.50 per cent residues. However, 100 per cent residue was removed from 1-day samples.

Dipping in 0.2 per cent $KMnO_4$ solution subsequently by washing reduced the fenpropathrin residues in chilli samples drawn 0 day after application by 72.50 per cent while 100 per cent in samples collected after 1 day application.

Chilli samples collected 0 day after application when subjected to dipping in 4 per cent acetic acid for 1 min. subsequently by washing removed residues of fenpropathrin by 41.67 per cent in comparison to control. The samples collected 1 day after application resulted a loss of 100 per cent as compared to control.

The mean initial deposit of 0.12 mg/ kg of fenpropathrin on chilli samples when applied @ 75 g a.i./ha, was degraded to 0.057 mg/kg as a result of boiling; showed a loss of 52.50 per cent. Chilli samples were collected after 1 day of application, boiling reduced fenpropathrin residues by

100 per cent as compared to control. But with respect to 1-day samples, the mean residue for fenpropathrin on chilli were decreased to BDL hence, accounted the loss of 100 per cent.

Yuan *et al.* (2009) stated that washing was the determinative means for the removal of pesticide residues in cabbage. Elbashir *et al.* (2013) found that application of fenpropathrin on tomatoes; the residues were usually greater than the MRL but on washing one time or several times in most cases removed the residues below the respective MRL.

Patil *et al.* (2018) suggested that the effect of dehydration on fipronil, λ-cyhalothrin, ethion, cypermethrin, fenpropathrin and fenazaquin and found that residues concentrated in sun dried chilli powder to a factor of 5.02 to 9.13 with respect to green chilli fruits. Begum *et al.* (2016) revealed that after dipping in 2 per cent salt solution for 15 min, eventually washing with tap water + cooking was the best treatment to eliminate residues of majority of insecticides from both brinjal and chilli.

The mean initial deposits of fenpropathrin after the third application in chilli @ 75 and 150 g a.i./ha ranged over 0.12 to 0.14 mg/ kg and 0.19 to 0.22 mg/ kg, respectively. The $T_{1/2}$ of pyriproxyfen in chilli was calculated to be 2.41 and 1.92 days. A waiting period of 1 day was suggested through present investigations when fenpropathrin applied @ 75 g a.i./ha in chilli following good agricultural practices. Household processing plays an important role in reducing pesticide residues from the food stuff. Among various household processing methods, highest reduction was observed while $KMnO_4$ solution with 72.50 per cent reduction and least at dipping in acetic acid solution.

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