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Residue Evaluation of Controlled-Release Formulations of Imidacloprid Against Rice Leaf Folder

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Imidacloprid (1-(6 chloro-3-pyridinyl methyl)-N-nitro imidazolidin-2-ylideneamine is a new systemic insecticide possessing potential activity and novel mode of action (Kagabu et al., 1992; Moriya et al., 1992; Shiokawa et al., 1992). This insecticide is effective for controlling aphids, white flies, thrips, scales, psyllids, plant bugs and various other harmful pest species, including resistant strains. It is used as seed dressing, soil treatment and foliar treatment in different crops, including rice, cotton, cereals, maize, sugarbeet, potatoes, vegetables, citrus fruits, pome and stone fruits. However, according to the US Environmental Protection Agency (EPA), imidacloprid has the tendency to leach to ground water.

To prevent repeated applications, evaporation and leaching losses, and harmful effects on the environment, controlled-release formulations of imidacloprid polyvinyl chloride (PVC) granules and imidacloprid carboxy methyl cellulose (CMC) granules were evaluated and compared with imidacloprid seed dressing for their efficacy against the leaf folder on rice during the rainy seasons of 2002 and 2003. Their residual toxicity behavior was also studied.

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Materials and Methods

Field experiments were conducted to assess the bioefficacy and residual behaviour of imidacloprid controlled-release formulations and seed dressing against the leaf folder, *Cnaphalocrocis medinalis* (Guenee) on rice during the rainy seasons of 2002 and 2003. A rice crop (Pusa Sugandh-3) was raised in 2×2 m plots, adopting the recommended agricultural practices. Three formulations of imidacloprid viz., polyvinyl chloride (PVC) granules, carboxy methyl cellulose (CMC) granules and seed dressing with 70 WS were used in the study (Table 1). There were eight treatments, including untreated control, which were thrice replicated. Controlled-release formulations (CRF) were applied as broadcast in standing crop 20 days after transplanting (DAT) while imidacloprid seed dressing was carried out at 15 g/kg seed before sowing in the nursery. The leaf folder infested leaves and total number of leaves were counted, one day prior to insecticide application and at 10-day intervals thereafter, on ten randomly selected hills in each plot. The samples of rice grain and straw collected at crop harvest were analyzed for imidacloprid residues with HPLC, as per the procedure: A representative chopped sample (20 g) of rice straw was homogenized twice with 200 mL acetonitrile/water mixture (80:20 v/v) for two minutes. The homogenized material was filtered through a Buchner funnel, the acetonitrile was evaporated, and saturated NaCl solution (50 mL) was added to the aqueous remainder.

The aqueous phase was partitioned twice with 100 mL of hexane, the hexane layer was discarded each time. Subsequently, the aqueous phase was extracted thrice with 70 mL dichloromethane. The dichloromethane phase was washed with 70 mL potassium carbonate solution (0.05 M)

Table 1 Treatments and doses

Sample	Treatment	Dose	Time of application
1	T_1 -Imidacloprid seed dressing	15 g kg^{-1} seed	20 DAT
2	T_2 -Imidacloprid PVC granules	2.2 g/4 m^2	20 DAT
3	T_3 - Imidacloprid PVC granules	4.4 g/4 m^2	20 DAT
4	T_4 - Imidacloprid PVC granules	6.6 g/4 m^2	20 DAT
5	T_5 - Imidacloprid CMC granules	2.2 g/4 m^2	20 DAT
6	T_6- Imidacloprid CMC granules	4.4 g/4 m^2	20 DAT
7	T_7 - Imidacloprid CMC granules	6.6 g/4 m^2	20 DAT
8	T_8 – Untreated control	–	–

DAT, days after transplanting; PVC, polyvinyl chloride; CMC, carboxy methyl cellulose

to remove the acidic co-extractives. The dichloromethane phase was further dried by passing through a 2-cm layer of anhydrous sodium sulphate. The solution was evaporated to dryness on a rotary evaporator. The residue was dissolved in 4 mL of n-hexane ethyl acetate mixture (1:1 v/v) and subjected to column chromatography. The grain sample (10 g) was ground into powder and processed in the same way as given for straw.

The sample solution was passed through a column (45 × 1.5 cm) packed with 10 g of silica gel over 2-cm layer of anhydrous sodium sulphate. The column was sequentially eluted with 60 mL mixed solvent, comprising of n-hexane/ethyl acetate (1:1 v/v) and 20 mL ethyl acetate, and elutes were discarded.

The imidacloprid residue was collected from the subsequent fraction of sample solution eluted with another 60 mL ethyl acetate and concentrated to 2 mL using a rotary evaporator at 40°C. The residue was dissolved in 2 mL water/acetonitrile (80:20 v/v) mixture and 20 μL of the solution was then subjected to high-performance liquid chromatography (HPLC) analysis.

Imidacloprid content was estimated using a Shimadzu HPLC fitted with SPDM6A photodiode detector and a data system. Samples were resolved isocratically on a 15 cm × 3.9 mm i.d. RP-18 column using acetonitrile/water (80:20) at 1 mL/min as the mobile phase. The absorbance was recorded at 270 nm, at a sensitivity of 0.05 AUFS, by injecting a volume of 20 μL. Retention time of imidacloprid was 4.3 min; the limit of detection was found to be 0.006 mg kg^{-1}.

Untreated plant samples (both rice straw and grain) were spiked with known amount of pesticide (1000 ppm) and equilibrated for 1 hr prior to extraction and subsequently subjected to the extraction procedure described above. The extraction efficiency of imidacloprid in grain and straw based on the mean value of three replications were 92 and 78 per cent, respectively.

$$\text{Residue of imidacloprid } (\mu g\, g^{-1}) = As/Astd \times M/M1 \times V/V1 \times f$$

Where, As = peak area of the sample; $Astd$ = peak area of the standard; M = volume of standard injected (μL); M_1 = weight of the sample (g); V = volume of the final extract (mL); V_1 = volume of the sample injection (μL); and f = recovery factor; 100 per cent mean recovery.

Results and Discussion

During the rainy season 2002, all the treatments were found to be effective against the leaf folder as these suffered 18.0–23.7% leaf damage as compared to 27.1% in the untreated control at 80 DAT (Table 2). However, imidacloprid PVC granules at 6.6 g (T_4) was considered the best treatment followed by imidacloprid seed treatment (T_1), imidacloprid PVC granules at 4.4 g (T_3), imidacloprid CMC granules at 6.6 g (T_7), imidacloprid CMC granules at 4.4 g (T_6), imidacloprid CMC granules at 2.2 g (T_5) and imidacloprid PVC granules at 2.2 g (T_2), in the decreasing order of bioefficacy. Effectiveness of imidacloprid (Confidor 200 SL) at 25 a.i. ha^{-1} against the leaf folder has also been reported by Singh and Singh (1999) and Krishnaiah et al. (2002).

Likewise in 2003 (Table 3), various treatments recorded less leaf damage (25.2–30.0%) in comparison to the untreated control (37.7%) at 80 DAT. Imidacloprid CMC granules at 6.6 g (T_7) proved to be the best treatment followed by imidacloprid PVC granules at 6.6 g (T_4), imidacloprid seed treatment (T_1), imidacloprid CMC granules at 4.4 g (T_6), imidacloprid PVC granules at 4.4 g (T_3), imidacloprid CMC granules at 2.2 g (T_5) and imidacloprid PVC granules at 2.2 g (T_2) in the diminishing order of efficacy. In general, higher doses of insecticides proved more effective against the leaf folder than lower ones.

Imidacloprid PVC granules at 6.6 g (T_4) and imidacloprid CMC granules at 6.6 g (T_7) exhibited better efficacy against the leaf folder during 2002 and 2003, respectively, than imidacloprid seed dressing (T_1) perhaps because of the sustained insecticide release from these formulations. Present findings are in agreement with that of Kumar et al.

Table 2 Effect of imidacloprid on rice leaf folder during rainy season 2002

Treatment	Pre- treatment count	30 DAT	40 DAT	50 DAT	60 DAT	70 DAT	80 DAT	Grain yield/plot (kg)
T_1 - Imidacloprid seed dressing (15 g)	2.8 (8.4)	3.1 (9.8)	7.8 (15.7)	11.5 (19.6)	13.9 (21.7)	18.3 (25.3)	19.2 (25.9)	2.6
T_2 - Imidacloprid PVC granules (2.2 g)	4.0 (11.3)	5.0 (12.8)	9.0 (17.3)	14.4 (22.2)	18.3 (25.3)	22.5 (28.3)	23.7 (29.1)	2.3
T_3 - Imidacloprid PVC granules (4.4 g)	1.3 (6.2)	3.3 (10.4)	8.1 (16.0)	11.7 (19.9)	16.2 (23.6)	20.1 (26.6)	20.3 (26.7)	2.6
T_4 - Imidacloprid PVC granules (6.6 g)	2.5 (7.9)	3.1 (9.3)	6.7 (14.9)	10.5 (18.9)	14.0 (21.9)	17.1 (24.4)	18.0 (25.1)	2.9
T_5 - Imidacloprid CMC granules (2.2 g)	2.3 (8.0)	4.1 (11.7)	9.2 (17.5)	13.9 (21. 9)	15.8 (23.4)	20.7 (27.1)	22.1 (28.0)	2.5
T_6 - Imidacloprid CMC granules (4.4 g)	1.6 (7.2)	2.3 (8.7)	8.5 (16.9)	11.9 (20.1)	13.2 (21.3)	20.1 (26.6)	21.9 (27.9)	2.8
T_7 - Imidacloprid CMC granules (6.6 g)	2.5 (8.9)	2.1 (8.3)	6.7 (14.9)	11.3 (19.7)	12.7 (20.8)	18.3 (25.3)	21.1 (27.3)	3.0
T_8 - Control	2.4 (8.5)	6.7 (15.0)	13.4 (21.4)	17.1 (24.4)	22.1 (28.1)	26.6 (31.1)	27.1 (31.4)	2.1
SEM±	1.0	0.9	1.5	1.3	1.1	1.2	1.3	0.1
CD (0.01)	–	3.6	6.3	5.5	4.4	5.2	5.5	0.5

DAT, days after transplanting; PVC, polyvinyl chloride; CMC, carboxy methyl cellulose; values in parentheses are arc sin transformed values

Table 3 Effect of imidacloprid on rice leaf folder during rainy season 2003

Treatment	Pre-treatment count	30 DAT	40 DAT	50 DAT	60 DAT	70 DAT	80 DAT	Grain yield/plot (kg)
T_1 - Imidacloprid seed dressing (15g)	2.8 (9. 7)	5.5 (13.6)	12.4 (20.7)	13.8 (21.8)	21. 7 (27.7)	25.4 (30.3)	27.9 (31.9)	2.3
T_2 - Imidacloprid PVC granules (2.2 g)	2.8 (9.1)	7.1 (15.4)	11.1 (19.4)	14.1 (22.0)	21.9 (27.9)	26.4 (30.9)	30.0 (33.2)	2.1
T_3 - Imidacloprid PVC granules (4.4 g)	3.1 (9.9)	6.4 (14. 7)	11.1 (19.4)	13. 7 (21.7)	21.6 (27.7)	26.0 (30.7)	28.8 (32.4)	2.2
T_4 - Imidacloprid PVC granules (6.6 g)	2.1 (6.7)	6.1 (14.3)	10.9 (19.2)	12.5 (20.7)	21.1 (27.4)	24.7 (29.8)	26.8 (31.2)	2.3
T_5 - Imidacloprid CMC granules (2.2 g)	3.8 (10.8)	6.9 (15.2)	13.2 (21.3)	14.2 (22.1)	22.5 (28.3)	26.8 (31.2)	30.0 (33.2)	2.3
T_6 - Imidacloprid CMC granules (4.4 g)	2.1 (7.6)	5.8 (13.9)	10.0 (18.4)	13.9 (21.9)	20.3 (26.8)	26.2 (30.8)	28.2 (32.1)	2.4
T_7 - Imidacloprid CMC granules (6.6 g)	1.4 (5.5)	5.0 (12.9)	8.9 (17.4)	11.8 (20.1)	17.5 (24.8)	23.4 (28.9)	25.2 (30.1)	2.5
T_8 - Control	4.5 (10.5)	9.1 (17.5)	15.1 (22.9)	17.8 (24.9)	25.6 (30.4)	33.0 (35.1)	37.7 (37.9)	1.9
SEM ±	1.4	0.5	0.6	0.4	0.8	0.9	0.9	0.1
CD (0.01)	–	2.1	2.4	1.8	3.5	3.6	3.8	0.5

DAT, days after transplanting; PVC, polyvinyl chloride; CMC, carboxy methyl cellulose; values in parentheses are arc sin transformed values

(2003), who found Phorate PVC-10 at 0.75 kg a.i. and Profenphos at 7.5 kg a.i. ha^{-1} superior to Phorate PVC-10 at 0.5 kg a.i. ha^{-1} and Thiamethoxam at 12.5 g a.i. ha^{-1} in controlling the rice leaf folder. Similarly, Panwar et al. (1999) reported that PEG 6000, phorate and starch Xanthate-based 10% phorate formulation (SX-10), proved as effective as Thimet 10G and Furadan 3G, even at half the dose (0.5 g m^{-1} furrow) against the maize shoot fly.

During 2002, imidacloprid CMC granules at 6.6 g (T_7) followed by imidacloprid PVC granules at 6.6 g (T_4), imidacloprid CMC granules at 4.4 g (T_6), imidacloprid seed treatment (T_1) and imidacloprid PVC granules at 4.4 g (T_3) had significantly higher yields than the untreated control (Table 2). On the other hand, yield in plots treated with imidacloprid CMC granules at 2.2 g (T_5) and imidacloprid PVC granules at 2.2 g (T_2) was statistically at par with that in

Table 4 Residues of imidacloprid in rice grain and straw after harvesting

Treatment	Dose (g plot^{-1})	Residues (mg kg^{-1})	
		Grain	Straw
T_1 -Imidacloprid seed dressing	15 g kg^{-1}	0.017 ± 0.002	0.025 ± 0.001
T_2 - Imidacloprid PVC granules	2.2	0.011 ± 0.006	0.014 ± 0.004
T_3 - Imidacloprid PVC granules	4.4	0.013 ± 0.004	0.019 ± 0.002
T_4 – Imidacloprid PVC granules	6.6	0.015 ± 0.002	0.021 ± 0.001
T_5 - Imidacloprid CMC granules	2.2	0.012 ± 0.003	0.017 ± 0.001
T_6 - Imidacloprid CMC granules	4.4	0.016 ± 0.001	0.020 ± 0.003
T_7 -Imidacloprid CMC granules	6.6	0.022 ± 0.001	0.034 ± 0.019

the untreated control. During 2003, only imidacloprid CMC granules at 6.6 g (T7) and 4.4 g (T6) recorded significantly higher yields that the untreated control. In other treatments, yield was at par with that in the untreated control (Table 3). The treatments that proved more effective against the leaf folder also yielded higher than others.

The maximum residue (0.022 mg kg^{-1}) of imidacloprid was observed with CMC granules at 6.6 g (T7) followed by imidacloprid seed dressing (T1) and imidacloprid CMC granules at 4.4 g (T6), which had 0.017 and 0.016 mg kg^{-1} residue, respectively. The residue of imidacloprid PVC granules at 6.6 g (T4) was detected as 0.015 mg kg^{-1} in rice grain. Between imidacloprid PVC granules at 2.2 g (T_2) and imidacloprid CMC granules at 2.2 g (T_5), the former left less residue (0.011 mg kg^{-1}) on rice (Table 4). Information about the residues of imidacloprid when applied as CRF in rice is lacking. However, Ishii et al. (1994) and Iwaya et al. (1998) reported the imidacloprid residue in rice grains to be 0.002 mg kg^{-1} when it was applied as 2% granules at 200 g a.i. ha^{-1} at 2–3 leaf stage. Gopal et al. (2002) reported that imidacloprid residues in mustard seed samples at harvest were below detectable limit when it was used as Confidor 200 SL at 20 and 40 a.i. ha^{-1}. In the present study, the mean residue values of imidacloprid were higher in straw samples as compared to grains. The least residue, 0.011 mg kg^{-1}, was recorded with imidacloprid PVC granules at 2.2 g (T2) in grains. The residues in rice grain and straw samples were below the MRL value of 0.05 mg kg^{-1} as specified by *codex alimentarius* for imidacloprid in cereal plants. Ishii et al. (1994) reported the imidacloprid residues 94 DAT to be 0.007 and 0.002 mg kg^{-1} in rice leaves and sheaths, respectively, when used as 2% granular formulation.

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