Controlled Release of Oxyfluorfen from the Variously Complexed Formulations

II. Selection of Promising Formulations

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數種 結合劑型으로부터 Oxyfluorfen의 放出制御 硏究

II. 有用한 放出制御型의 選拔

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ABSTRACT

Thirty formulations of oxyfluorfen(2-chloro-2, 2, 2-trifluoro-p-toyl 3-ethoxy-4-nitrophenyl ether) were manufactured by adsorption and substitation. Of them 16 formulations were selected because they showed rekatuvely high activity and long durability in the bioassay with (*Brassica campestris* V.L.) Then, the formulations selected and 4 commercial formulations were tested using *Monochoria* in pots. As the result, the formulations of polymer 11, elvan 7/40, coal-slag 7/40, zeolite(A), and bentonite(A) were selected because they showed almost complete inhibition of *Monochoria* even up the 73 days after treatment.

INTRODUCTION

The authors(1) have previously reported that Oxyfluorfen, a highly active herbicide of diphenylethers, provided a promise to use in rice by split applications or formations of controlled-release. When oxyfluorfen is applied in flooded paddy soils, it can induce crop injury (bleaching) by quick, excess release of oxyfluorfen right after treatment(3) on young rice leaves, and hence the herbicidal activity of oxyfluorfen on annual and perennial weeds which emerge in mid-seasons for a long period in transplanted rice is decreased by releasing active ingredient in a short period after treatment (2). This is a reason in which development of controlled release of many herbicides is interesting recently.

Development of controlled-release formulations is emphasized in terms of residual effects, improvement of efficacy, economic use, and decrease of crop injury and environmental pollution(4, 5). The manufacturing processes of controlled-release formulations include monolithic or depot system diffusing herbicides in polymer carriers or binding herbicides to polymers, erosive polymer herbicides releasing by microorganisms, utilization of porous materials such as fibers, porous plastic, and foaming agents, utilization of conjugated compounds, or pumping action of saturation pressure(4). Peterson *et al*.(2) tested the formulations of oxyfluorfen such as sand core granules, slowly dissolving urea-formaldehyde fertilizer, and pumice. Yoshimoto *et al*. (6) studied the bioactivities by changing chemical structure. Also the authors have developed controlled-release formulation of 2, 4-D by binding 2, 4-D to rice hull lignin (7, 8).

The objectives of this study were to reduce rice injury (bleaching) from oxyfluorfen by controlling quick, excess release when applied in flood water right before rice transplanting, and to select the

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controlled-release formulations of oxyfluorfen that were durable for 40 days after transplanting.

MATERIALS AND METHODS

This experiment was carried out to evaluate the residual activity of various oxyfluorfen formulations in terms of water solubility, soil adsorption, releasing, and formation of treated layer on flooded soil surface. Experiment was conducted using test tubes and or petri-dish, and pots. The formulations of oxyflourfen included 13 types of complexed polmers, 3 of adsorbed elvans, 3 of adsorbed briquet ashes, 2 of adsorbed zeolite, 1 of seasand coated, 2 of adsorbed bentonite and 2 of substituted-OH or $-NH_2$ group. (Table 1.).

And also the formulations of 0.25G, 1G, 3G and 23.5EC commerciallized were included as the control. Test plant was *Brassica campestris* L. (cv), Hybrid Hanra) which had no dormancy and almost 100% germinability in the preliminary study, and was a gift from the branch station of crop experiment at Mokpo.

Experiment I. Selection of formulations in test tube/petri dish test.

To select appropriate formulations of oxyfluorfen by evaluating the releasing from soil adsorption after treatment, 40 ml of distilled water (PH 6.6) or 20g of paddy soil mixed with 40ml of distilled water were placed in test tubes (2cm in diameter). After that, all formulations tested were applied at the final concentration of 25 ppm.

Table 1. Various oxyfluorfen formulations tested in Experiment I.

No.	Formulations	ai%	Type
1	Polymer-1	20.0	Diffusion promoter
2	Polymer-2		Adhesive form
3	Polymer-3		
4	Polymer-4	20.0	
5	Polymer-5	20.0	Adhesive form－pin-hole
6	Polymer-6	14.29	
7	Polymer-7	16.67	0% polymer
8	Polymer-8	16.53	1% polymer
9	Polymer-9	16.32	2.5% polymer
10	Polymer-10	16.67	% of polymer
11	Polymer-11	13.79	0.5% polymer
12	Polymer-12	13.56	0.75% polymer
13	Polymer-13	13.33	1.0% polymer
14	Elvan 7	0.06	< 7 mesh
15	Elvan 7/40	0.04	7-40 mesh
16	Elvan 40/120	0.04	40-120 mesh
17	Coal slag 7	0.06	< 7 mesh
18	Coal slag 7/40	0.04	7-40 mesh
19	Coal slag 40/120	0.04	40-120 mesh
20	Zeolite(A)	0.04	Use on Alachlor
21	Zeolite(B)	0.04	Use on Pumansa
22	Seasand	0.04	20-30 mesh
23	Bentonite(A)	0.04	Pumice type
24	Bentonite(B)	0.04	Use for Alachlor granule
25	$-NH_2$ type	95.0	NO_2 reduction
26	-OH type	95.0	C_2H_5 transformed
27	Oxyfluorfen 0.25G	0.25	Clay absorption
28	Oxyfluorfen 1G	1.0	Sand coating
29	Oxyfluorfen 3G	3.0	Sea sand coating
30	Oxyfluorfen 23.5EC	23.5	Market use

*No. 1-13 : COE/CNU manufactured, No. 14-21 and No. 24-26 : COA/CNU manufactured, No. 23, 24 : KRICT manufactured, and NO. 27-30 : Rohm and Haas Co. manufactured, respectively.

The clay paddy soil was finely ground, washed and precipitated in distilled water to remove undesirable matters. The soil was air-dried again and seived with 1-mm mesh. The test tubes treated with oxyfluorfen were shaken at 150 rpm for 20 min at room temperature. Then they were incubated at the cons tant temperature pf 30℃ in dark, Each petri dish with filter papers reseiv ed 10ml of the supenatants from the test tube, and 25 seed of *Brassica campestris* (cv. Hanra) were placed in each petri dish. The same amount of distilled water was added again. In the same way above mentioned, the supernatent was taken at 1, 7, 11, 21, 29, 36 and 43 days after oxyfluorfen application, and the bioactivity was assayed. Four days after sowing, germinability and root elongation of young seedlings were measured, and the inhibition rate of growth was calculated to select better formulations in terms of durability of herbicidal activity.

Experiment II. Selection of formulations in pot test.

Twenty formulations of oxyfluorfen, selected from Experiment I, were tested using pots ($L^{15} \times W^{5} \times H^{10}$ cm) in a growth chamber (Table 2). The pots were filled with autoclaved clay loam soil that seived with 100 mesh, and then were watered with distilled water and was left for 24hr. the water was kept 1cm deep and each formulation was applied in the water at the final concentration of 100ppm. After draining from the bottom of the pots for 24hr at 0, 1, 2, 3, 4, 5, 6 and 7 weeks after oxyfluorfen application, 10 seed of rape were seeded and incubated for 4 days in a growth chamber. The dada obtained were similar to those of experiment I.

Table 2. Various oxyfluorfen formulations tested in experiment.

Formulations	ai %	type
Check	—	—
Pol. 1	20	Diffusion promoter
Pol. 6	14.29	—
Pol. 7	16.67	0% polymer
Pol. 9	16.32	2.5% polymer
Pol. 11	13.79	0.5% polymer
Elvan 7	0.06	< 7 mesh
Elvan 7/40	0.04	7-40 mesh
Coal slag 7	0.06	< 7 mesh
Coal slag 7/40	0.04	Use on Alachlor
Coal slag 40/120	0.04	40-120 mesh
Zeolite (A)	0.04	Use on Alachlor
Sea sand	0.04	20-30 mesh
OH type	95	C_2H_5 transform
Bentonite (A)	0.04	pumice type
Bentonite (B)	0.04	Use for Alachlor
0.25 G	0.25	Clay absorption
1G	1	Sand coation
3G	3	Seasand coating
23.5EC	23.5	Market use

RESULTS AND DISCUSSION

Experiment I. Selection of formulation in test tube/petri dish test.

The supernatant taken from shaken test tubes after oxyflourfen application in water was used to test bioactivity of various oxyfluorfen formulations. This indicates the measurement of dissolved amount of oxyfluorfen in water by bioassay. When oxyfluorfen was applied to water with soil, oxyfluorfen released was taken out at time intervals to test the durable activity by bioassay. Of 30 different formulations tested, 20 formulations were selected by evaluating the activity on rape when applied in water only and water with soil. The growth inhibition of rape seedlings by oxyfluorfen was much higher when treated in water only than when treated in water with soil. The products of Goal 0.25G, 1G, 3G and 23.5 EC manufactured by Rohm and Haas Co. showed excess release of oxyfluorfen right after treatment and thereafter the amount of oxyfluorfen realeased was decreased with time when applied in water. However, when but when applied in water/soil, they were showed the decreased activity from 21 days after treatment. Although oxyfluorfen is known as a herbicide that is little soluble in water (9), that it showed high activity continuously when applied in water in this test was due to extremely high bioactivity of oxyfluorfen and puddling soil with enough water after oxyfluorfen treatment.

According to Peterson (2), when applied to soil, oxyfluorfen released from media within a few minutes is about 20%, which is readily adsorbed to adjacent soil, so that oxyfluorfen activity is hard to be durable. However, in this study oxyfluorfen showed

Table 3. Promising formulations of oxyfluorfen selected

(Unit. : Inhibition % of the check)

No. and code	water treatment (DAT)							water−soil treatment (DAT)						
	1	7	11	21	29	36	43	1	7	11	21	29	36	43
Polymer-1	40	36	33	34	31	29	17	29	27	21	19	18	15	13
Polymer-6	15	16	16	19	20	22	11	12	11	10	20	16	23	15
Polymer-7	26	33	25	31	13	11	−	7	4	10	7	6	8	−
Polymer-9	31	47	27	26	27	28	16	23	16	13	12	12	5	4
Polymer-11	49	47	21	8	6	5	6	57	53	23	23	18	13	8
Elvan-7	58	51	47	29	28	13	6	45	40	16	12	16	19	16
Elvan 7/40	94	79	61	57	41	22	5	96	99	88	40	19	11	17
Elvan 40/120	100	100	100	82	76	52	6	100	100	97	79	21	12	16
Coal-slag-7	62	65	40	44	18	15	6	83	87	76	44	16	11	8
Coal-slag-7/40	76	57	45	28	39	13	7	85	69	73	24	24	17	19
Coal-slag-40/120	70	69	60	33	39	18	6	87	63	53	21	22	21	27
Zeolite(A)	56	49	25	25	28	23	11	39	46	21	22	16	13	11
Seasand	78	85	64	52	58	43	13	42	33	31	26	20	23	20
-OH type	88	100	100	100	88	85	50	23	16	17	19	8	10	−
Bentonite(A)	82	87	83	87	79	76	80	85	87	83	89	85	80	61
Bentonite(B)	28	27	26	24	20	23	16	26	24	21	19	16	18	16
0.25G	77	65	52	64	69	44	13	42	43	43	51	26	28	27
1G	100	100	100	100	82	94	40	34	36	40	30	20	17	9
3G	100	99	100	100	90	46	17	47	41	61	53	50	41	13
23.5EC	100	100	91	100	71	30	28	44	53	64	60	66	66	21

* Inhibition percentage of the check : calculated as the rate (%) in fresh weight of emerged seedlings to the check at a given date.

considerably high residual activity which was also similar in both treatments of water and water/soil. This suggested that the herbicidal activity of oxyfluorfern granular(G) or emulsifiable concentrate (EC) applied in water with soil is slowly decreased from 40~50% of the activity but is much more decreased from the lower activity when not shaken the treated test tubes. Therefore, formulation with bentonite(A), coal-slag type and 7/40 or 40/120 mesh of elvan, which showed higher activity than G or EC types commerciallized and seemed practically to be more desirable. As a result, it was thought that the formulations having herbicidal action right after application and slow-releasing action for a long time were ideal for reducing crop injury and for increasing herbicidal efficacy in rice. Form this standpoint. 16 formulations selected primarily from the experiment I were shown in Talbe 3, except for products of Rohm and Hass Co.

Experiment II.Selection of formulations in pot tests.

Rape was used for Experiment I using petri dishes or test tubes, but for simulating paddy fields in Experiment 2 pot tests were carried out using *Monochoria*, on aquatic weed of rice, and also the chemicals were applied to the water.

Because oxyfluorfen is basically not a germination inhibitor, *Monochoria* normally germinated in all treatments, but germination phenomena were not visual due to the activity by sunlight at germination. As shown in Table 4, all formulations tested inhibited germination of test plant seeded by 23 days after treatment, but from 30 days after treatment the germination inhibition varied among formulations. However, the formulations that inhibited germination completely when seeded by 73 days after treatment included elvan, coal-slay, and bentonite formulation. Also, the formulations of polymer 9, polymer 11, and zeolite showed similar effects. The similar results were obtained on the number of plants emerged, fresh weight and inhibition rate (Table. 6). In other words, they showed excellent inhibition for a long period (up to 73 days after treatment), compared with sand coated formulation (1G and 3G), adsorptive formula-

Table 4. Variation in visual rates(check=0, complete death=9).

Formulations	Days after application						
	12	23	30	37	45	61	73
Check	0	0	0	0	0	0	0
Pol. 1	9	9	8.5	8.5	7	5	6
Pol. 6	9	9	9	9	8	2	2
Pol. 7	9	9	8	8.5	8	3	0
Pol. 9	9	9	8.5	8	9	7	9
Pol. 11	9	9	9	9	9	9	7
Elvan 7	9	9	9	9	9	9	8.5
Elvan 7/40	9	9	8	9	9	9	9
Coal slag 7	9	9	9	9	9	9	8
Coal slag 7/40	9	9	9	9	9	9	9
Coal slag 40/120	9	9	9	9	9	9	9
Zeolite(A)	9	9	9	9	9	9	8
Sea sand	9	9	9	7.5	9	6	7
OH type	9	9	6	6.5	5	3	4
Bentonite (A)	9	9	9	9	9	9	9
Bentonite (B)	9	9	9	9	9	9	9
0.25 G	9	9	8	9	3	0	0.5
1G	9	9	7	6.5	1	1	3
3G	9	9	7	7	4	1	2
23.5 EC	9	9	6.5	4.5	5	0	0

Table 5. Variation in No. of indivisuals and fresh weight(mg) per pot.

Formulations	12 DAA			23 DAA			30 DAA			37 DAA		
	NO*	WT**	IR***	NO	WT	IR	NO	WT	IR	NO	WT	IR
Check	25	31.1	0	22	26.2	0	21	46.0	0	23	58.7	0
Pol. 1	1	0.5	98.4	0	0	100	1	0.3	99.3	2	0.8	98.6
Pol. 6	1	0.8	97.4	0.5	0.1	99.6	0	0	100	0	0	100
Pol. 7	1	0.1	99.7	1	0.1	99.6	2	1.6	96.5	1.5	0.5	99.1
Pol. 9	0	0	100	0.5	0	100	2	0.9	98	6	5.5	90.6
Pol. 11	0	0	100	0	0	100	0	0	100	0	0	100
Elvan 7	0.5	0.05	99.8	0	0	100	0	0	100	0	0	100
Elvan 7/40	0	0	100	0	0	100	0	0	100	0.5	0.05	99.9
Coal slag 7	0.5	0.05	99.8	0	0	100	0	0	100	0	0	100
Coal slag 7/40	0	0	100	0	0	100	0	0	100	0	0	100
Coal slag 40/120	0	0	100	0	0	100	0	0	100	0	0	100
Zeolite (A)	0	0	100	0	0	100	0	0	100	0	0	100
Sea sand	0	0	100	0	0	100	0	0	100	3.5	6.4	89.1
-OH type	0	0	100	0	0	100	9	5.0	89.1	8	8.8	85
Bentonite (A)	0	0	100	0	0	100	0	0	100	0	0	100
Bentonite (B)	0	0	100	0	0	100	0	0	100	0	0	100
0.25 G	0.5	0	100	0	0	100	0.5	0.1	99.8	3	3	94.9
1 G	0.5	0.1	99.7	0	0	100	2	1.4	97	6	6.7	88.6
3 G	0.5	0.3	99.0	0.5	0	100	5	2.7	94.1	7.5	15.5	73.6
23.5 EC	1	0.5	98.4	1	0.1	99.6	7	9.7	78.9	11	22.7	61.3

* : Numbers of individuals per pot.
** : Total fresh weight(mg) per pot.
*** : Inhibition rate on fresh weight to the untreated check.

tion(0.25G) and emulsifiable concentrate(23.5EC).

Although this high, durable activity of the formulations selected did not explain the evidence of controlled release by controlling excessive release

Table 6. Variation in No. of individuals and fresh weight (mg) per pot.

	45 DAA			61 DAA			73 DAA		
	NO	WT	IR	NO	WT	IR	NO	WT	IR
Check	19	55.3	0	37.5	80.5	0	37.5	106	0
Pol. 1	6	4.1	92.6	19	25	88.9	15	16.2	84.7
Pol. 6	3	2.7	95.1	15	43.2	46.3	31	55.1	48
Pol. 7	6	7.7	86.1	32	54.1	32.8	40	96.4	9.1
Pol. 9	7	12.4	77.6	26	20.8	72.8	0	0	100
Pol. 11	0	0	100	0	0	100	13	11.4	89.2
Elvan 7	0	0	100	0	0	100	2	2.3	97.8
Elvan 7/40	0	0	100	0	0	100	0	0	100
Coal slag 7	0	0	100	0	0	100	6	27	74.5
Coal slag 7/40	0	0	100	0	0	100	0	0	100
Coal slag 40/120	0	0	100	0	0	100	0	0	100
Zeolite(A)	0	0	100	0	0	100	5	4.3	95.9
Sea sand	0	0	100	6	4.2	94.8	7	7	93.4
-OH type	6	9.7	82.5	20	25.6	68.2	26	41.2	60.9
Bentonite (A)	0	0	100	0	0	100	0	0	100
Bentonite (B)	0	0	100	0	0	100	0	0	100
0.25 G	7	14.5	73.8	27	9.3	88.4	29	79.9	24.6
1 G	20	43.5	21.3	25	7.3	90.9	25	44.7	57.8
3 G	6	9.8	82.3	1	0.9	98.9	31	21.9	79.3
23.5 EC	5	5.3	90.4	38	145.2	0	41	75	29.2

Abb. : refer to Table 4

immediately after treatment, we can inter the durability of the formulations by controlled release.

Because the formulatios of elvan, coal-slag, and bentonite all showed high activity and durability regardless of materials and processes, further research was requried to study the properties in detail.

The formulations of polymer 11, elvan 7/40, coal-slag 7/40, zeolite(A), and bentonite(pumice type) were selected from Experiment II because they showed high activity even when seeded at 73 days after treatment.

摘　要

Oxyfluorfen(2-chloro-2, 2, 2-trifluro-p-toyl 3-ethoxy-4-nitrophenyl ether)의 徐放型 模型化를 위하여 各種 吸着 및 置換型2 30種을 만들고 유채를 檢定植物로 하는 in vitro test를 實施하여 比較的 活性이 높고 持續性이 認定되는 16種製型을 選拔할 수 있었다. 따라서 이들 16種의 製型을 旣存製型 4種과 並行公試하여 pot實驗을 遂行하였다. 檢定植物로는 물달개비를 使用하였고, 處理後 73日 까지 定期的으로 除草活性의 變動樣相과 持續性을 判斷한 結果 Polymer 11, Elvan 7/40, Coal slag 7/40, Zeolite (A), Bentonite(A)의 5種을 選拔할 수 있었다.

이들의 除草活性은 處理後 73日까지 無處理對比 100%에 가까운 Biomass inhibition rate를 보였다.

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