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Optimization of self-dispersible floating granule (UG) of flucetosulfuron and its herbicidal performance

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Abstract : This study was conducted to optimize formulation factors of a self-dispersible floating granule of flucetosulfuron that can be used at a low application volume (5 kg ha^{-1}). SPA and xanthan gum were selected as a binder because blending of them showed good granulation and floatation. Potassium chloride selected as a filler also showed good granulation, floatation and disintegration properties. Among wetters and dispersants, Surfynol 440 gave the best dispersibility. The optimum granule size was determined to be 1.0 mm considering floating time and dispersibility. Flucetosulfuron was mixed with the blend of SPA and xanthan gum, potassium chloride, and Surfynol 440 and formulated as a floating self-dispersible granule at 1.0 mm in diameter. Indoor and outdoor field experiments showed that the floating granule of flucetosulfuron performed well, covering long range from the application spot up to 15 m in weed control. Therefore, this floating technology may be used for laborsaving herbicide formulation development and help to reduce workloads for herbicide application. (Received February 15, 2006; accepted March 20, 2006)

Key words : *Echinochloa crus-galli,* floating granule, flucetosulfuron, formulation factor, laborsaving

INTRODUCTION

Granule (GR) is a typical formulation for rice herbicide in Korea and Japan, and 3 kg GR package for 0.1 ha is still the most common formulation, accounting for 73% of rice herbicides in Korea (Korea Crop Protection Association, 2005). In Japan, which has a similar herbicide application system to Korea, the proportion of 3 kg GR dramatically decreased from 82% in 1994 to 22% in 2000 (Takeshita and Noritake, 2001). With the reduction of 3 kg GR, lighter formulation types such as 1 kg GR, jumbo GR, and flowable suspension concentrate (SC) have replaced its place, occupying 35%, 22% and 7%, respectively (Takeshita and Noritake, 2001). Although the dependence on 3 kg GR is still high in Korea, Korea is now experiencing the similar transition from 3 kg GR to new types of formulations; the proportion of the lighter formulation types such as SC, water dispersible granule (WG) and self-dispersible floating granule (i.e. Up-granule or UG) increased from 2% in 2000 to 15% in 2004 (Korea Crop Protection Association, 2005a).

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The application of 3 kg GR is normally made in the paddy field or along the levee with a backpack sprayer or by hand, but requires rather heavy workloads, particularly for old or female farmers. In Korea, the percentages of rice farmers over 65 years of age and female farmers reached now 36% and 50%, respectively, in 2004 (Ministry of Agriculture & Forestry, 2005). Moreover, farmers cultivating rice in large paddy fields greater than 3 ha have also increased. In these circumstances, the 3 kg GR is considered too heavy. Therefore, demands on lighter formulations to reduce the quantity of herbicide and workloads are now very high. The lighter formulations developed so far are flowable SC, WG, UG and jumbo GR. Trials to compare workload for application of 3 kg GR with that of a lighter formulation, jumbo GR, showed that the total application time per 0.1 ha was 6 min for 3 kg GR and 1.5 min for jumbo GR (Takeshita *et al.*, 1994). As the lighter formulations can significantly reduce labor time for herbicide application, they are now called as

Table 1. Inert ingredients used in this study

Category	Formulation ingredients
Binder	Aarabic gum, dextrin, gellan gum, guar gum, locust bean gum, PEG6000 (polyethyleneglycol), sodium alginate, tara gum, xanthan gum, Na-CMC (sodium carboxymethylcellulose), PVP (polyvinylpyrrolidone), SPA (sodium polyacrylate), PVA (polyvinyl alcohol)
Water-soluble filler	Potassium chloride, ammonium chloride, sodium sulfate, ammonium sulfate, urea, sodium benzoate, glucose, lactose
Wetter / dispersant	EP4C (sodium di-ethylhexylsulfosuccinate), Surfynol 440 (ethoxylated 2,4,7,9-tetramethyl-5-decyn-4,7-diol), Q2-5211 (polyoxyethylene modified polydimethyl siloxane)

laborsaving formulations.

Flucetosulfuron is a new sulfonylurea herbicide that controls *Echinochloa crus-galli* effectively as well as other annual and perennial weeds at 20~30 g a.i. ha^{-1} (Kim *et al.*, 2003). This biological property has been waited for long in sulfonylurea chemistry since the introduction of bensulfuron-methyl as an essential component of the one-shot herbicide application. Flucetosulfuron is now registered in Korea with a trade name of Fluxo® by LG Life Sciences, Ltd (Korea Crop Protection Association, 2005b), and became the first herbicide registered as a solo one-shot herbicide without other grass-killer partners such as carbamates and aryloxyphenoxy propionic acids. Presently six products are registered in Korea, but all of them are GR formulations. Due to increasing demands on laborsaving formulations, it has been necessary to formulate flucetosulfuron as these types of formulations, which may enable farmers to apply the formulation from levee by hand or application equipment. For flucetosulfuron to be applied from levee, the formulation must float very quickly after its application and then release flucetosulfuron. The released flucetosulfuron then must disperse to a long distance.

In this paper, we describe a self-dispersible floating 500 g (the application volume for 0.1 ha) granule of flucetosulfuron without water-soluble pack as a type of laborsaving formulations. This floating granule submerges down to the soil surface immediately after application, then floats up onto the water surface, and releases the active ingredient as the granule disperses rapidly across a long distance. This study was conducted to select appropriate formulation ingredients for each characteristic, floating capacity or dispersibility, and thus to make the granule physico-chemically more self-dispersible and biologically stable and effective to cover wide and long range in rice paddy field.

MATERIALS AND METHODS

The self-dispersible floating 500 g granule containing flucetosulfuron of 2.1 g (0.42% w/w) requires specific characteristics; submerging after being applied, floating within a few minutes, dispersing to a long distance within a short period of time (defined as long distance dispersal) and finally releasing or diffusing active ingredients (defined as short distance dispersal). To optimize these characteristics, this study was conducted by examining formulation ingredients (Table 1) and granule size for each characteristic of them.

Formulation preparation

To evaluate the effects of binders on granulation and floatation, various polymers as listed in Table 1 were added into a template granule formulation, which contains the same amount of potassium chloride, EP4C, and so on. After the dry ingredients and flucetosulfuron were blended using a Ken mixer (KM-600, AICOH Co, Japan), sufficient water (10~13% w/w) was added, and then a wet blending was carried out. Blended samples were then transferred to a laboratory extruder (KAR-75, Tsutsui Co, Japan) for granulation by extruding them through the screen with holes of different sizes. The extruded granules were dried at 50℃ for about 3 min in a laboratory fluid bed drier (TG100, Retsch Co, Germany).

Measurement of floatation

To evaluate the influence of ingredients and granule sizes on floatation, experimental granules containing different binders or water-soluble fillers were prepared with different sizes, 0.7, 1.0, 1.2, and 1.5 mm in diameter. Five granulelets of a uniform size in each granule sample were placed gently into a 500 mL beaker containing tap water at 5 cm depth. Then, the floating time of each granulelet was recorded.

Measurement of dispersal of flucetosulfuron

To evaluate the influence of the wetters/dispersants and granule sizes on dispersion of flucetosulfuron, granule samples were formulated at different sizes. The granule samples contained the same binder and filler selected on the basis of floating time in the above study. To quantify the dispersed flucetosulfuron without clean-up process, 90 g a.i. ha^{-1} of flucetosulfuron, about four times higher than the recommended dose, was applied. An accurate weight of granules containing about 18.9 mg of flucetosulfuron was spot-applied at the top front of a specially designed Styrofoam box (0.3 m×10 m) laid with black vinyl sheet containing 150 L of tap water (5 cm in water depth).

At different time intervals, 1 mL aliquots of water were sampled at 1 cm water depth of three different points at 7 m away from the treated spot. Water samples were filtered and analyzed using a high performance liquid chromatography (Waters, USA) to quantify flucetosulfuron. The column was Capcell Pak C_{18} UG120 (Shiseido, Japan), 250 mm × 4.6 mm i.d., 3 µm particle size, with a guard column, and all maintained at 40 ℃. The mobile phase was 30% of acetonitrile and 70% of 0.02 M ammonium acetate and 0.1 M acetic acid in water.

Flow rate was 1 mL min^{-1} and detection was made by using Waters 2487 detector (Waters, USA) at 254 nm of wavelength. Retention times for threo and erythro isomers of flucetosulfuron were 18.2 min and 22.5 min, respectively.

Biological evaluation

Indoor and outdoor field experiments were conducted to evaluate the biological performance of the floating 500 g granule selected in the above studies and compared with the 3 kg GR containing 0.07% of flucetosulfuron (Fluxo®, LG Life Sciences, Ltd).

An indoor paddy field system was designed to be 0.32 m deep × 0.3 m wide × 13 m long using Styrofoam box filled with paddy soil (sandy loam) up to 20 cm. Top soil was puddled after top irrigation and seeds of *E. crus-gall* were sown at 3 days after puddling. As soon as the seedlings emerged, the water depth was set and maintained at 5 cm throughout the experiment period.

At the 3-leaf stage of *E. crus-galli*, the floating granule and the 3 kg GR, equivalent to 21 g a.i. ha^{-1} of flucetosulfuron, were applied at the front of each system by hand. Efficacy was visually assessed at 30 days after application.

An outdoor field experiment was conducted at the research farm of LG Life Sciences, Ltd in Daejeon Korea. Each plot size was 1.5 m wide and 20 m long. Rice (*Oryza sativa* cv. Ilpoom) seedlings at 17 days of age were transplanted on May 17, 2002. Just prior to herbicide application, plots were flooded to 5 cm water depth. And then in the half of plots chopped rice straw as an artificial obstacle preventing herbicide dispersal was placed at 5 m from the application spot with 50 cm width and in the other half plots no straw was placed.

The floating granule and the 3 kg GR of flucetosulfuron were applied by scattering up to 2 m front of the plot from the levee by hand. After herbicide application, additional irrigation was made at different timings, 3 and 7 days after herbicide application (DAA). Visual assessment was made to measure efficacy against naturally established *E. crus-galli* and *Monochoria vaginalis* and phytotoxicity to the transplanted rice at 30 DAA.

Statistical analysis

All measurements were initially subjected to analysis of variance (ANOVA). Non-linear regression analysis was used to fit the logistic model to visual efficacy against weeds in order to estimate the maximum distance to achieve weed control greater than 90%. All statistical analyses were conducted using Genstat 5 (Genstat Committee, 1993).

Table 2. Granulation and floatation properties of the granules containing different binders

Binders	Degree of granulation	Floating time (s)
Na-CMC	Intermediate	Not detected (soluble in water)
Dextrin	Good	Not detected (soluble in water)
PVA	Intermediate	Not detected (soluble in water)
SPA	Poor	239
PVP	Good	Not detected (soluble in water)
PEG6000	Good	Not detected (soluble in water)
Sodium alginate	Good	Not detected (soluble in water)
Xanthan gum	Poor	117
Gellan gum	Poor	Not detected (soluble in water)
Tara gum	Poor	Not detected (soluble in water)
Locust bean gum	Good	Not detected (soluble in water)
Arabic gum	Intermediate	Not detected (soluble in water)
Guar gum	Good	Not detected (soluble in water)

RESULTS AND DISCUSSION

Selection of binder

To select the most suitable binder, the floating granules were made using the same template containing flucetosulfuron, EP4C, and potassium chloride and varying binders (5.0%), and then their degree of granulation considering the goodness of extrusion and floating time were compared. All the granules containing different binders listed in Table 1 did not float (collapsed or soluble in water) except for those contained SPA (sodium polyacrylate) and xanthan gum (Table 2). The reason for floating capacity of these granules using SPA and xanthan gum may be due to the capacity of keeping airs in the network or matrix structure within a granule (Mikio *et al.* 1991). Although both xanthan gum and SPA helped the granule to float readily, dispersal after floatation was different. The granules containing 5% xanthan gum disintegrated slowly. The granules containing 5% SPA disintegrated rapidly although its shape in water was somewhat distorted. When they were blended, the floating capacity improved slightly with increasing xanthan gum at a fixed content of SPA, but the floatation was delayed with increasing SPA at a fixed content of xanthan gum (Fig. 1). Based on this result, the contents of SPA and xanthan gum were fixed at 0.8 and 0.5%, respectively, for further studies.

Selection of water-soluble fillers

To examine the suitability of potassium chloride in comparison with other fillers, potassium chloride was

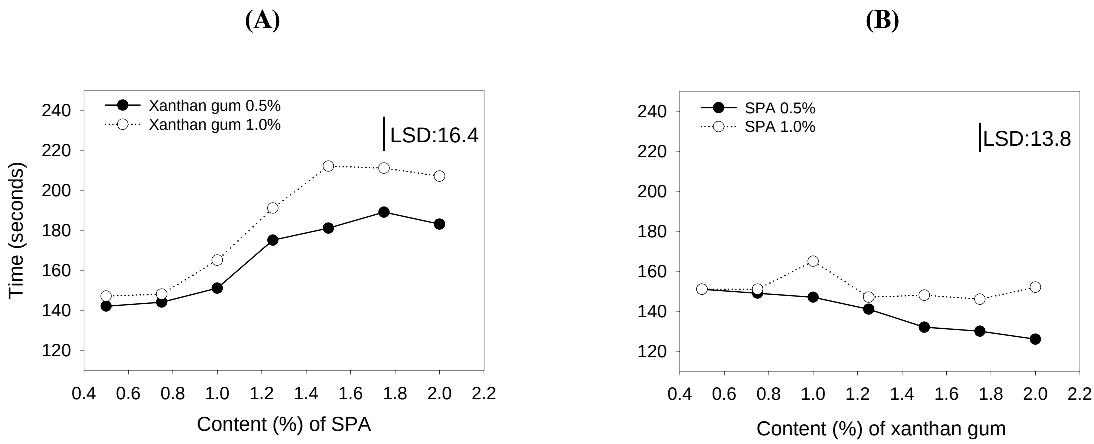

Fig. 1. Floating times of the granules as affected by the contents of SPA (A) and xanthan gum (B). These granules were made using the same template containing flucetosulfuron, EP4C, and potassium chloride and varying the relative content of SPA and xanthan gum.

Table 3. Granulation, floatation and disintegration of the granules containing different fillers

Filler	Degree of granulation	Floating time (s)	Disintegration of granules after flotation
Potassium chloride	Good	142	Disintegrated immediately
Ammonium chloride	Good	357	Disintegrated 2~3 seconds later
Sodium sulfate	Intermediate	792	Disintegrated 2~3 seconds later
Ammonium sulfate	Good	Not floated	Not applicable
Urea	Good	122	Not disintegrated
Sodium benzoate	Poor	154	Disintegrated 2~3 seconds later
Glucose	Good	230	Disintegrated 2~3 seconds later
Lactose	Good	Not floated	Not applicable
$LSD_{0.05}$		81.5	

Template formulation : flucetosulfuron, EP4C, SPA, xanthan gum and fillers to 100%.

replaced with other soluble fillers. For granulation, most fillers were good except sodium sulfate and sodium benzoate (Table 3). Regarding floating time, the granule containing urea floated most quickly taking 122 seconds, followed by those containing potassium chloride, sodium benzoate, and glucose, while those containing ammonium sulfate and lactose failed to float. After floatation, the disintegration property was best with potassium chloride, disintegrating immediately. From this study, it was suggested that potassium chloride was the most appropriate filler among the tested fillers. Additionally, potassium chloride is commonly used as a carrier in this type of formulation (e.g. Choi *et al.*, 1998) and easy to obtain. Therefore, we decided to use potassium chloride as a main filler in further studies.

Selection of wetter/dispersants

It is thought that the spreading and dispersal of an active ingredient after floatation is firstly due to the driving force generated by repulsive power of inert ingredients during the disintegration of granules on the water surface. In generating such a driving force, surfactants such as wetters and dispersants can contribute as a spreading agent. Dispersal capacity was assessed by measuring the concentration of flucetosulfuron at 7 m apart from the applied spot at different time intervals. In all the formulations, the maximum concentration was reached at about 72 h after application; however, the concentration of flucetosulfuron was almost instantaneously (within 1 h) reached at 60 to 80% of the maximum in the formulations containing 1% of EP4C, Surfynol 440, or Q2-5211 (Fig. 2). By comparison, in the 3 kg GR, the concentration of flucetosulfuron was initially very low and increased linearly until 72 h, suggesting dispersion was solely dependent on diffusion of the active ingredient. Therefore, it is evident that these surfactants contribute greatly to the dispersal of the disintegrated particles on the water surface. Among the surfactants, Surfynol 440 gave the best dispersibility, so this was selected for further studies.

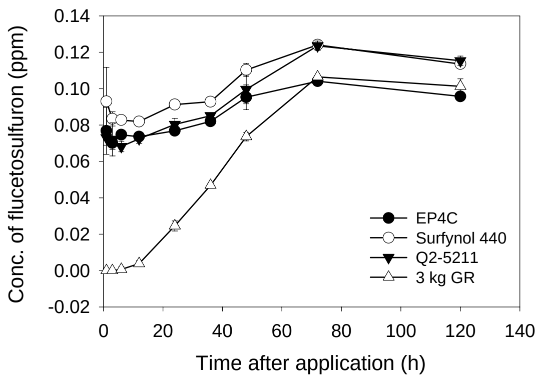

Fig. 2. Time-course change in flucetosulfuron concentration at 7 m apart from the application spot of granular formulations containing different wetters and dispersants. Template formulations for the granules containing EP4C, Surfynol 440, or Q2-5211: flucetosulfuron, wetter/dispersant, SPA, xanthan gum, potassium chloride to 100%, and for the 3 kg GR: flucetosulfuron, EP4C, sodium lignosulfonate, dextrin, Na-bentonite, talc to 100%. Theoretical maximum concentration of flucetosulfuron: 0.126ppm.

Effects of granule size on floatation and dispersal

It was assumed that granule size would affect the

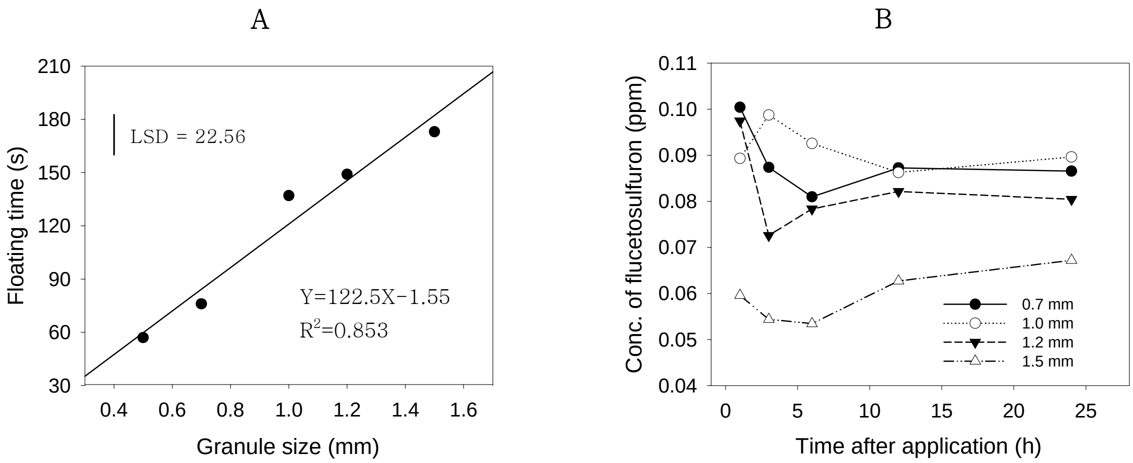

Fig. 3. Floatation of the floating granules (A) and dispersal of flucetosulfuron (B) as affected by granule size. The concentration of flucetosulfuron was measured at 7 m apart from the application point. Template formulation: flucetosulfuron, Surfynol 440, SPA, xanthan gum, and potassium chloride to 100%.

floatation and dispersal of granules. In general, the 3 kg GR package contains many small particles (1000 particles/g) of about 0.8 mm in diameter (Takeshita and Noritake, 2001). As the granule size of the 3 kg GR also ranges from 0.7 to 1.2 mm in diameter, we tested the experimental granules ranged from 0.5 to 1.5 mm in diameter. The smaller the granule size, the faster its floating time; and the dispersal of granule also varied with its granule size (Fig. 3). Floating time was proportionally increased with increasing granule size with linear relationship between them (Fig. 3A). The concentration of flucetosulfuron at 7 m apart from the application point was affected by granule size and 1.0 mm granule showed the best dispersibility, followed by 0.7 mm, 1.2 mm and 1.5 mm (Fig. 3B).

Considering floating time and dispersal, a smaller granule appears to be better. However, a small-sized granule is difficult to broadcast and its fall can be influenced by wind. Therefore, we determined the optimal diameter of the granule to be 1.0 mm for the biological efficacy test.

Biological performance of the floating granule

Based on above studies, we formulated the one floating granule containing 0.42 % of flucetosulfuron and other selected inert ingredients, SPA, xanthan gum, Surfynol 440, and potassium chloride, for biological evaluations. Biological performance of the floating granule was then compared with the 3 kg GR.

In-door experiment

When the 3 kg GR of flucetosulfuron was spot-applied, *E. crus-galli* was controlled up to about 6 m away from the application spot; however, herbicidal efficacy was decreased dramatically in the farther distance, showing no effect from 9 m. By comparison, the floating granule showed perfect control of *E. crus-galli* up to about 9 m and still high efficacy in the region farther than 9 m (Fig. 4). Choi *et al.* (1998) reported that the effective control greater than 90% of *E. crus-galli* by the floating granule of molinate +

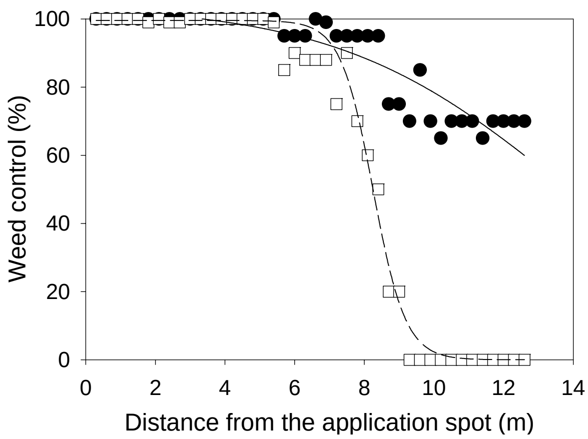

Fig. 4. Efficacy of the floating granule (●) and the 3 kg GR (□) of flucetosulfuron against *Echinochloa crus-galli*. Herbicide application was made at the front of the indoor paddy field system designed to be 0.3 m wide×13 m long using Styrofoam box. The dose rate of flucetosulfuron was 21 g a.i. ha^{-1}.

simetryn was achieved up to 5 m. Although it is difficult to directly compare their result with our result, our result suggests that flucetosulfuron has a good diffusion potential even in the 3 kg GR formulation system and our floating granule technology increases the dispersal of flucetosulfuron significantly.

Outdoor field experiment

Fig. 5 showed efficacy of the floating granule against *E. crus-galli* and *M. vaginalis* and its phytotoxicity to rice when chopped rice straw was placed as an artificial obstacle on water surface and the first irrigation after herbicide application was made from the region of herbicide application at 3 DAA (days after application) and 7 DAA. The first irrigation at 3 DAA ((Fig. 5A and B) showed better efficacy and rice safety than 7 DAA (Fig. 5C and D). When the first irrigation was made at 3 DAA, *E. crus-galli* and *M. vaginalis* established 17 m and 20 m apart from the application point, respectively, was completely controlled, and these efficacy was not affected by chopped straw placed at 5 m from the application spot with 50 cm width (Fig. 5A and B). However, in case of the first irrigation at 7 DAA, overall efficacy was significantly reduced and also affected by the chopped straw. With no straw, *E. crus-galli* and *M. vaginalis* established about 14 m were well controlled (Fig. 5D). By comparison, with straw as an obstacle placed on water surface, the floating granule achieved effective control only up to 10 m and 15 m apart from the application point for *E. crus-galli* and *M. vaginalis*, respectively (Fig. 5 C). Although phytotoxicity to rice appeared to be slightly greater when the first irrigation was made at 7 DAA, no significant damage on rice was observed in this study. Our results thus indicated that the time of the first irrigation and obstacles on water surface may affect performance of the floating granule. Nevertheless, our results clearly demonstrated that the self-dispersible floating granule of flucetosulfuron performed well, covering long range from the application spot in weed control.

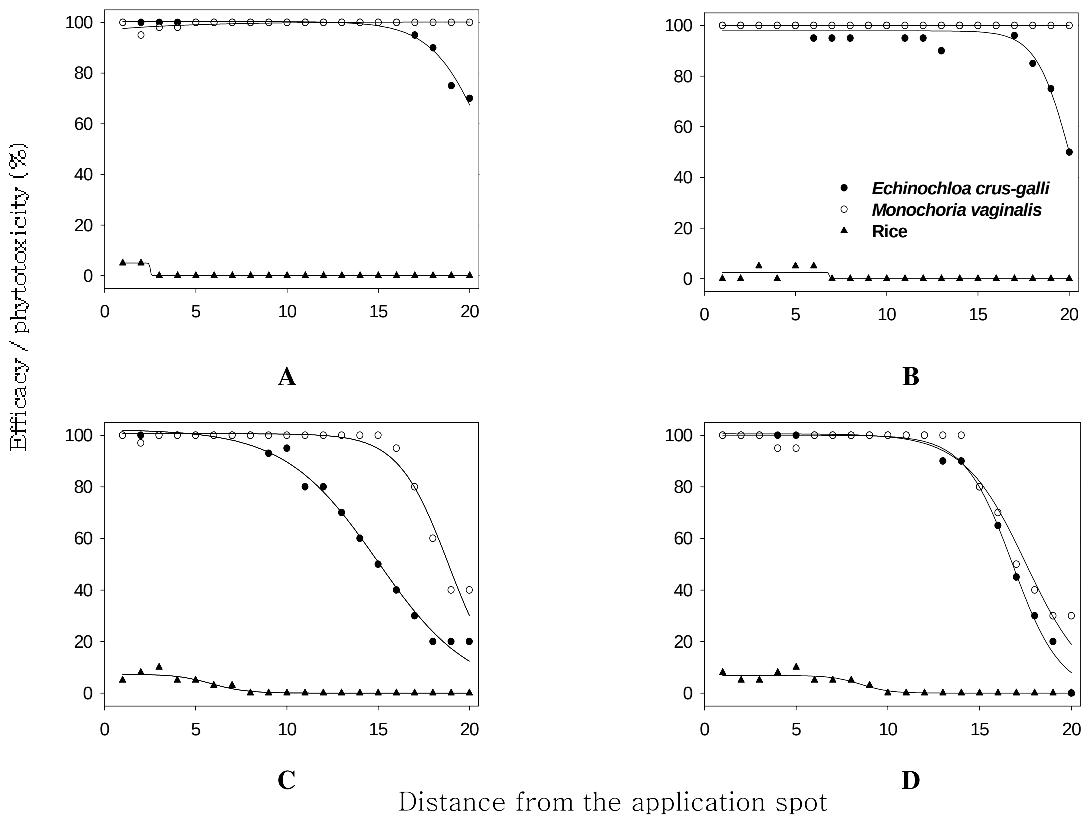

Fig. 5. Efficacy of the floating granule of flucetosulfuron against *Echinochloa crus-galli* and *Monochoria vaginalis* and its phytotoxicity to rice. Before herbicide application, chopped rice straw was placed at 5 m from the application spot with 50 cm width (A and C). After herbicide application, additional irrigation was made at 3 (A and B) and 7 (C and D) DAA.

The dispersal of herbicide is also affected by water depth, algae, and surface soil separation, wind and water temperature. Takeshita and Nortake (2001) showed that deeper water is better than shallow water for dispersion of herbicide due to water movement. Recently Kim *et al.* (2005) reported that wind direction and water temperature affected dispersal of herbicide active ingredient. Therefore, further works in various conditions may provide more useful information for practical use of this floating granule of flucetosulfuron in current rice cropping systems. When these works are completed, the floating granule can be used to save labor for herbicide application but also overall costs for formulation delivery and storage as compared with the 3 kg GR.

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Flucetosulfuron 수면부상형 입제의 최적화 및 제초효과

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요약 : Flucetosulfuron 수면부상성 입제의 제형요소 및 효능을 최적화하기위한 일련의 실험을 실시하였다. SPA와 xanthan gum을 혼합하여 입제로 제제한 경우 조립성과 부상성이 우수하여 점착제로 선발하였으며 증량제는 조립성, 부상성 및 붕괴성이 우수한 KCl을 선발하였다. 또한 습윤 및 분산제로는 분산성이 가장 우수한 Surfynol 440을 선발하였다. 입제의 입경은 부상성과 분산성을 고려 1.0 mm로 결정하였다. 본 연구로 선발된 부제를 이용해 조제한 flucetosulfuron 수면부상성 입제를 실내 간이 포장 및 야외 포장에서 제초활성을 평가한 결과 잡초를 처리지점에서 15 m에 다다르는 지점까지 우수하게 방제하였다. 따라서 본 수면부상성 입제 기술은 flucetosulfuron을 비롯한 노동력 절감형 제초제 개발에 사용될 수 있을 것으로 기대된다.

색인어 : 수면부상성 입제, 제형요소, 노동력 절감형, 물피, flucetosulfuron.

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