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Article

Effect of Chitosan Molecules on Paraquat Herbicidal Efficacy under Simulated Rainfall Conditions

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Abstract: Unexpected rainfall before herbicide absorption by plants can wash away herbicides from plant tissue surfaces, which may reduce the herbicidal efficacy and increase the adverse effects on nontarget organisms and the environment, including water networks. The objective of this study was the evaluation of the effect of chitosan on paraquat efficacy under simulated rainfall conditions. Simulated rainfall within 3 h after paraquat application decreased its herbicidal efficacy. A mixture of paraquat (280 g a.i./ha) and chitosan (0.05% *w*/*v*) significantly increased the herbicidal efficacy against *Ageratum conyzoides* L. (21% increase), *Borreria alata* Aubl. (15%) and *Paspalum conjugatum* Bergius (8%) under the rainfall conditions. The chemical structure of chitosan may contribute to the penetration of paraquat into plant tissues. However, a mixture of paraquat and chitosan did not affect the herbicidal efficacy against *Imperata cylindrica* (L.) Beauv. The morphological characteristics of *I. cylindrica* may interfere with the enhancement effect of chitosan. Chitosan is a degradable, nontoxic and easily available and low-cost material made from crustacean shells. These results suggest that chitosan may increase paraquat efficacy against some noxious weed species under rainfall conditions, which may reduce the risk of paraquat contamination into the environment. Therefore, the application of herbicides with chitosan may provide the economic and environmental benefits. Chitosan may enhance the efficacy of other herbicides under unexpected rainfall conditions; however, this possibility requires further investigation.

Keywords: chitosan; herbicide efficacy; nanoparticle; paraquat; rainfall

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1. Introduction

The herbicide paraquat (1,1′-dimethyl [4,4′-bipyridine]-1,1′-diium dichloride) is classified as a methyl viologen, and is normally synthesized in the form of a dichloride salt from pyridine [1,2]. It is a quick-acting, nonselective and post-planting contact herbicide with plant surfaces [3,4]. It works as a photosystem I electron diverter and leads to rapid leaf wilting and desiccation [5,6]. Paraquat is one of the most common herbicides and has been used worldwide for post-emergence weed management in crop fields such as rice, tobacco and cotton [5,7]. However, the herbicide can contaminate the environment, including water networks, because of its high aqueous solubility, and threatens aquatic animals and algae [8]. Paraquat also causes lung and renal problems in humans [9,10]. The herbicide binds to soil easily, and its half-life varies from 16 months to 13 years [11,12]. Thus, paraquat has been banned in some countries due to its potential for environmental contamination and toxicity to humans [9,10,13,14].

The application of nanoparticles has been investigated in the production of effective herbicide formulations with less potential for toxicity and environmental contamination [15–17]. It is considered that nanoscale molecules penetrate plant surfaces easily and into their cells through cell membranes [18,19]. Chitosan is one of the potential nanoparticles for the formulation of herbicides [20–22]. It is a linear polysaccharide obtained by deacetylation of chitin, which is produced from crustacean and arthropod shells [23,24]. Chitosan is a degradable, nontoxic, easily available and low-cost material [25]. It works as a herbicide carrier by increasing herbicide contact areas with the plant surface and reducing herbicide absorption time by plant tissues [18,21,26,27].

The full dose of an applied herbicide does not always reach the targeted weed species, and some of the applied herbicide can reach nontarget organisms and soil and water resources, thus causing environmental contamination [28,29]. It is also possible to receive unexpected rainfall after herbicide application in crop fields. Rainfall can wash away herbicides from plant tissue surfaces before they are absorbed, which may reduce their herbicidal efficacy and increase the adverse effects on the environment [30,31]. The objective of this study was the evaluation of the effect of chitosan on paraquat efficacy under simulated rainfall conditions. We selected *Ageratum conyzoides* L., *Borreria alata* Aubl., *Paspalum conjugatum* Bergius and *Imperata cylindrica* (L.) Beauv. as target weed species. These species have been naturalized in many parts of the world, and also often infest agricultural lands, forests and plantations. A mixture of paraquat and chitosan was applied to these weed species under simulated rainfall conditions, and paraquat herbicidal efficacy against the targeted weeds was then determined.

2. Materials and Methods

2.1. Plant Materials

The broadleaf weeds *Ageratum conyzoides* L. and *Borreria alata* Aubl. and grass weeds *Paspalum conjugatum* Bergius and *Imperata cylindrica* (L.) Beauv. were selected as test weeds. Sample weeds with 2–3 leaves were collected from a palm oil plantation in Lampung area, North Sumatra, Indonesia in July 2021. Three weed plants each were transplanted into plastic pots (20 cm in diameter) filled with 2.5 L soil and grown in a greenhouse for 1 month.

2.2. Herbicides Dose–Response Experiment

After 1 month of incubation in a greenhouse as describe above, the weeds in plastic pots were moved into experimental plots (4 $\times$ 4 m) as designed in Figure 1. Then, a mixture of paraquat dichloride (Pataniquat 140 SL, CV Central Aneka Agro: Kubang Jaya, Indonesia) and chitosan (Kitosan, Chitosan Pharma: Cirebon, Indonesia) was applied using a semi-automatic knapsack sprayer and nozzle T-jet with a working pressure of 15–20 P.S.I. for a volume of 400 L per h. Water supply from sprinklers was adjusted to be 13 mm per day based on the average rainfall in the Lampung area, North Sumatra, which was measured by a rain gauge (20 cm in diameter), as shown in Figure 1.

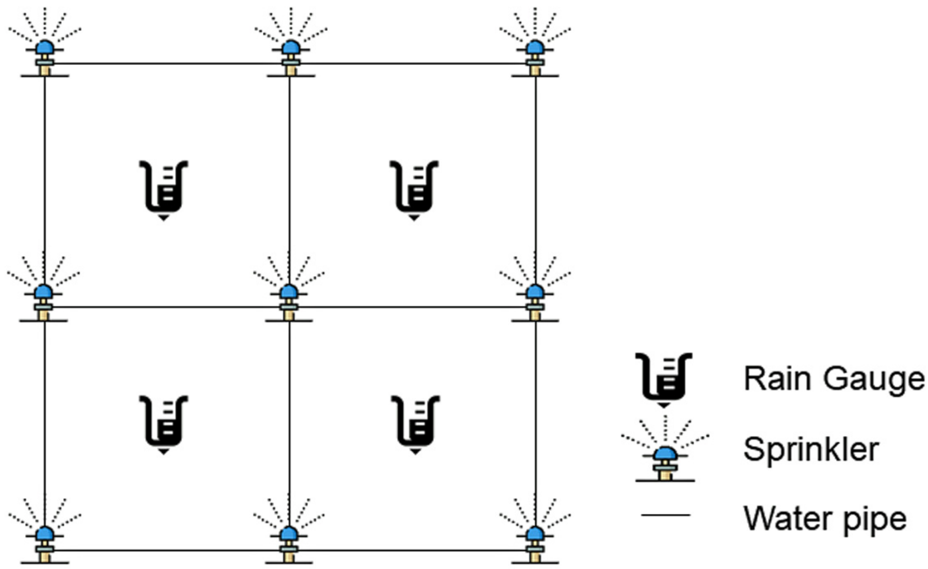

Figure 1. The layout of sprinklers and rain gauges on experimental plots (4 × 4 m).

The treatment was a split-plot design consisting of four main plots and six sub-plots with three replications. The main plots were treated with a mixture of paraquat (140 g/L; final application, 280 g a.i./ha) and different concentrations of chitosan: paraquat and no chitosan; paraquat + 0.05% (*w*/*v*) chitosan, paraquat + 0.1% (*w*/*v*) chitosan, and paraquat + 0.15% (*w*/*v*) chitosan. The subplots were exposed to rain intervals after application of a mixture of paraquat and chitosan: rainfall just after herbicide application (0 h), rainfall at 1 h after herbicide application, rainfall at 2 h after herbicide application, rainfall at 3 h after herbicide application, rainfall at 4 h after herbicide application, and no rainfall after herbicide application.

Three weeks after herbicide application, aerial parts of the weed specimens were harvested and dried in an oven at 80 °C for 48 h. Herbicide efficacy (weed damage by herbicide) was calculated by comparing the dry weight of the treatment with the control by the following equation:

$$[1 - (\text{dry weight of treatment})/(\text{dry weight of control})] \times 100\%.$$

2.3. Statistical Analyses

The obtained results were assessed by analysis of variance with the F-test, and the averages among the treatments were compared by LSD test at 5% value. When there was an interaction between two factors, the average data from each treatment combination were presented with a two-way table notation of significance. When the results of the analysis did not show an interaction, then the average data for each treatment were presented in a table of independent significance notation. The independent significance notation table was produced by averaging the whole efficacy values of each treatment including the efficacy values of the combination treatments.

3. Results

3.1. Paraquat Activity on Ageratum conyzoides

Paraquat at g a.i./ha completely killed *A. conyzoides* (Figure 2A, no rain). Simulated rainfall within 3 h after the paraquat application suppressed its herbicidal efficacy. No effect of rainfall on efficacy was observed at 4 h after application. Chitosan (0.05%) significantly increased the herbicidal efficacy under the simulated rainfall condition (Figure 2B). Table 1A shows that the effect of simulated rainfall on efficacy was significantly different among the rainfall treatments at 0 h, 1 h, 2 h, 3 h, and 4 h, and no rainfall. However, the effect of chitosan on paraquat efficacy was not significantly different among the chitosan concentrations (0.05, 0.1 and 0.15%) (Table 1B).

Table 1. Effect of simulated rainfall on herbicidal efficacy of a mixture of paraquat and chitosan against *Ageratum conyzoides* at different time intervals after mixture application.

Treatment	Average Paraquat Efficacy (%)
A: Rainfall interval after herbicide application	
0 h after herbicide application	77.86a
1 h after herbicide application	82.35b
2 h after herbicide application	87.59c
3 h after herbicide application	90.81c
4 h after herbicide application	100.00d
No rainfall	
B: Paraquat with chitosan	
Chitosan 0%	73.45a
Chitosan 0.05%	93.75b
Chitosan 0.1%	94.71b
Chitosan 0.15%	97.16b

Different letters show significant differences between average values in the same panel at the level of 5% according to Duncan's test.

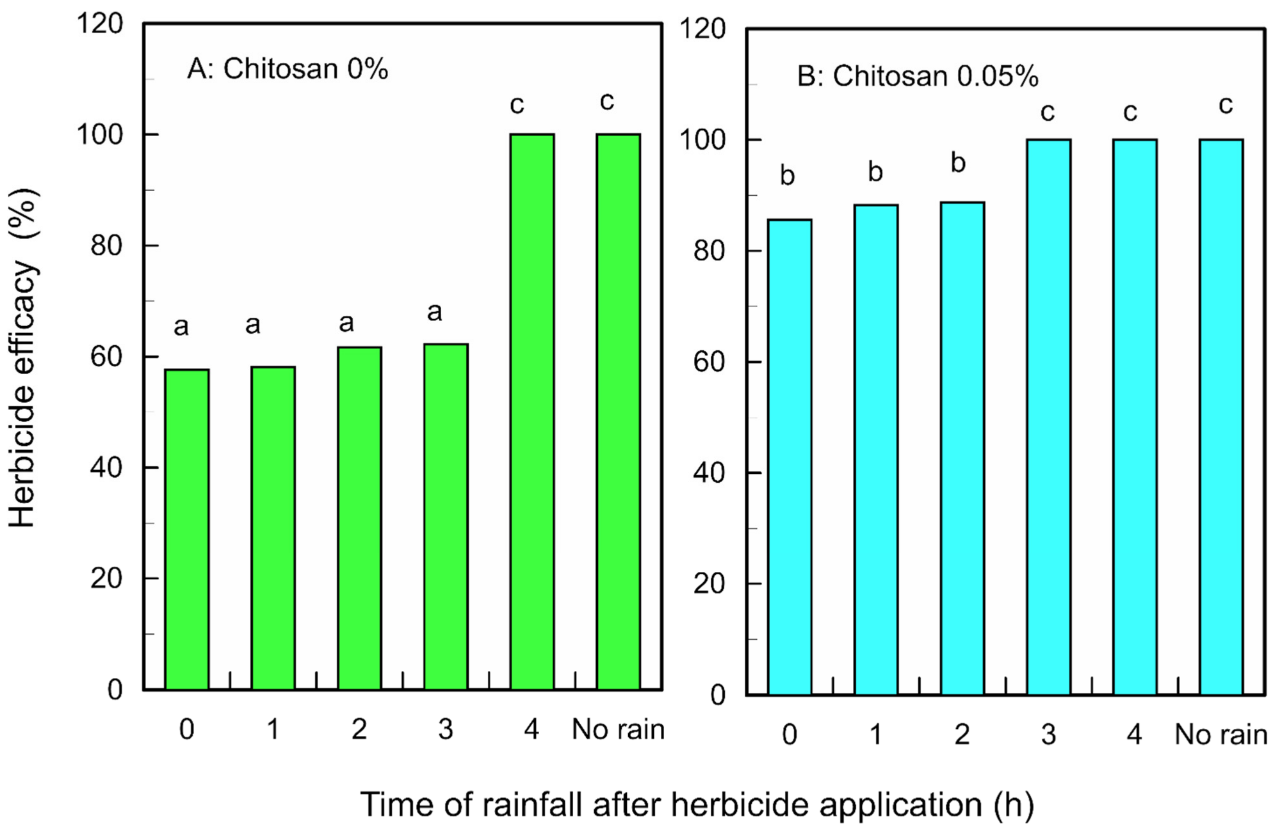

Figure 2. Effect of simulated rainfall at different time intervals after paraquat application on *Ageratum conyzoides*. (**A**): Chitosan 0%, (**B**): Chitosan 0.05%, Different letters show significant differences at the level of 5% according to Duncan's test.

3.2. *Paraquat Activity against Paspalum conjugatum*

Paraquat at g a.i./ha killed *P. conjugatum* (Figure 3A, no rain). Simulated rainfall suppressed the efficacy of paraquat within 3 h after the paraquat application (Figure 3A). Chitosan (0.05%) significantly increased the herbicidal efficacy under the simulated rainfall conditions (Figure 3B). Table 2 shows that the effect of simulated rainfall on efficacy was significantly different among the rainfall treatments, while the effect of chitosan on paraquat efficiency was not significantly different at different concentrations.

Table 2. Effect of simulated rainfall on herbicidal efficacy of a mixture of paraquat and chitosan against *Paspalum conjugatum* at different time intervals after mixture application.

Treatment	Average Paraquat Efficacy (%)
A: Rainfall interval after herbicide application	
0 h after herbicide application	65.95a
1 h after herbicide application	90.63b
2 h after herbicide application	93.47c
3 h after herbicide application	95.45c
4 h after herbicide application	97.52d
No rainfall	100.00d
B: Paraquat with chitosan	
Chitosan 0%	79.76a
Chitosan 0.05%	94.54b
Chitosan 0.1%	94.72b
Chitosan 0.15%	92.99b

Different letters show significant differences between average values in the same panel at the level of 5% according to Duncan's test.

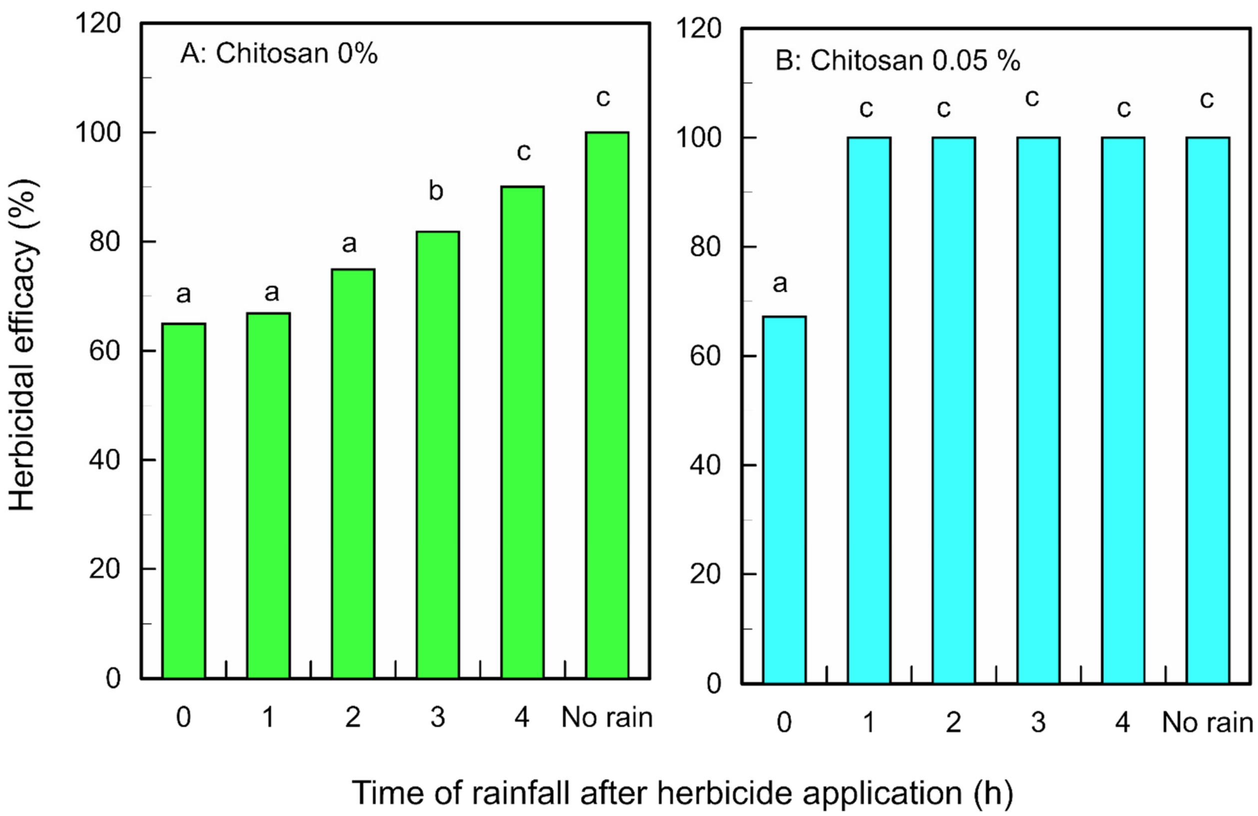

Figure 3. Effect of simulated rainfall at different time intervals after paraquat application on *Paspalum conjugatum*. (**A**): Chitosan 0%, (**B**): Chitosan 0.05%, Different letters show significant differences at the level of 5% according to Duncan's test.

3.3. Paraquat Activity against *Borreria alata*

Paraquat at 280 g a.i./ha killed *B. alata* (Table 3A). The effect of the simulated rainfall on herbicidal efficacy was significantly different among the rainfall treatments. Chitosan significantly increased the herbicide's efficacy under simulated rainfall conditions. However, paraquat mixtures with 0.1% and 0.15% chitosan were more effective than that with 0.05% chitosan (Table 3B). When rainfall was simulated 4 h after paraquat application, the herbicidal efficacy was 100%.

Table 3. Effect of simulated rainfall on herbicidal efficacy of a mixture of paraquat and chitosan against *Borreria alata* at different time intervals after mixture application.

Treatment	Average Paraquat Efficacy (%)
A: Rainfall interval after herbicide application	
0 h after herbicide application	62.46a
1 h after herbicide application	79.41b
2 h after herbicide application	88.24c
3 h after herbicide application	90.57c
4 h after herbicide application	100.00d
No rainfall	100.00d
B: Paraquat with chitosan	
Chitosan 0%	77.27a
Chitosan 0.05%	85.08b
Chitosan 0.1%	92.01c
Chitosan 0.15%	92.76c

Different letters show significant differences between average values in the same panel at the level of 5% according to Duncan's test.

3.4. *Paraquat Activity against Imperata cylindrica*

Paraquat at g a.i./ha killed *I. cylindrica* (Table 4A). Simulated rainfall reduced paraquat efficacy. Chitosan did not significantly increase herbicidal efficacy under simulated rainfall conditions (Table 4B). When simulated rainfall was applied 4 h after paraquat application, the efficacy was 91.85%, which was not significantly different from the "no rainfall" treatment.

Table 4. Effect of simulated rainfall on herbicidal efficacy of a mixture of paraquat and chitosan against *Imperata cylindrica* at different time intervals after mixture application.

Treatment	Average Paraquat Efficacy (%)
A: Rainfall interval after herbicide application	
0 h after herbicide application	63.39a
1 h after herbicide application	73.88a
2 h after herbicide application	83.03b
3 h after herbicide application	84.46b
4 h after herbicide application	91.85c
No rainfall	100.00c
B: Paraquat with chitosan	
Chitosan 0%	70.93a
Chitosan 0.05%	88.85a
Chitosan 0.1%	83.66a
Chitosan 0.15%	87.62a

Different letters show significant differences between average values in the same panel at the level of 5% according to Duncan's test.

4. Discussion

Paraquat at 280 g a.i./ha successfully killed broadleaf weed species *A. conyzoides* and *B. alata* and grass weed species *P. conjugatum* and *I. cylindrica* (Figures 2 and 3, Tables 1–4) that were found on a palm oil plantation in the Lampung area, North Sumatra, Indonesia. *A. conyzoides* belongs to the Asteraceae family, is native to tropical America, and has been naturalized in many tropical, subtropical and temperate countries as an invasive plant species. It is also a noxious weed in agricultural lands and forests and a host for many pathogens and nematodes [32]. *B. alata* belongs to the Rubioideae family, originated from the West Indies and tropical America and has naturalized in tropical and subtropical countries as an invasive plant species [33]. *P. conjugatum* belongs to Poaceae family, is native to tropical America, and has been naturalized widely in Southeast Asia, the Pacific Islands, Northern Africa and Australia. It is an aggressive weed in agricultural lands, grasslands and natural forests. The species establishes dense monocultural stands and inhibits the growth of other plant species. It was reported that some native forests have become extinct due to infestation by this weed species [34]. *I. cylindrica* belongs to *the* Poaceae family, is native to Asia, and has been naturalized in many tropical and subtropical countries. It occurs in a wide range of habitats, including forests, grasslands, agricultural lands and plantations. The species is listed among the top ten worst weeds in the world [35,36]. Paraquat is a non-selective herbicide for the management of all types of weeds [5,7]. The application of paraquat was reported to reduce the coverage and biomass of *A. conyzoides, B. alata, I. cylindrica* and *P. conjugatum* by up to 80% on oil palm plantations [37]. It was also reported that weeds in sugarcane plantations were reduced by 90% at 7 days after paraquat application [38].

The simulated rainfall treatments reduced paraquat efficacy against these weed species (Figures 2 and 3 and Tables 1–4). The rainfall treatments just after paraquat application (0 h) reduced the herbicide's efficacy against these weeds to 62.46–77.86% compared to that of the "no rainfall" control. Efficacy with rainfall simulated at 4 h after paraquat application was 100% for broadleaf weeds *A. conyzoides and B. alata* and 97.52% and 91.85%, respectively, for grass weed species *P. conjugatum* and *I. cylindrica* (Tables 1–4). However, the herbicidal efficacy on all weeds at 4 h after paraquat application was not significantly different from that of the control treatments (no rain). This observation suggests that a 4 h time interval after paraquat application is needed to ensure sufficient herbicidal efficacy under simulated rainfall conditions.

Agrochemicals on plant surfaces are exposed to biological and physical factors such as temperature, wind, UV radiation and biological degradation [39,40]. Those factors probably affect the efficacy of the agrochemicals. Rainfall and irrigation water also affect agrochemicals on the plant surface through dilution, redistribution and removal of the agrochemicals [30,31,41]. Thus, the time interval of rainfall after herbicide application is critical for post-emergence herbicides such as paraquat and glyphosate to be absorbed into plant tissues and work sufficiently as herbicides. In the present research, paraquat activity was reduced to 62.46–77.86 and 84.46–95.45%, respectively, when the rainfall occurred just after (0 h) and 4 h after the paraquat application (Tables 1–4). It was also reported that glyphosate activity was reduced to 50–80% when rainfall occurred within 4 h after the treatment [42–45]. Appropriate herbicide carriers may increase the absorption of herbicides by plant tissue and reduce the herbicide loss due to rainfall. As a result, the risk of environmental contamination by the herbicides could be decreased.

Chitosan (0.05%) significantly increased paraquat efficacy against *A. conyzoides, B. alata* and *P. conjugatum* under simulated rainfall conditions (Figures 2 and 3; Tables 1–3). The increases by chitosan were not significantly different among chitosan concentrations for *A. conyzoides* and *P. conjugatum,* while the effectiveness of chitosan 0.1% and 0.15% mixtures was greater than that of the chitosan 0.05% mixture for *B. alata.* These results suggest that 0.05–0.1% of chitosan may be sufficient to enhance paraquat performance as a carrier. However, chitosan did not increase paraquat efficacy against *I. cylindrica* under the simulated rainfall conditions (Table 4). *I. cylindrica* is stemless except for the flowering stalks. Its leaves are slender and linear-lanceolate, and its leaf sheaths are often tightly rolled. It accumulates silicates in the leaves [46,47]. Those morphological characteristics of *I. cylindrica* may have interfered with the enhancement of paraquat's herbicidal efficacy using chitosan under simulated rainfall conditions.

Chitosan is nontoxic to humans and able to form films, hydrogels, fiber and nanoparticles due to its deacetylated surfaces. Chitosan molecules have hydroxy and amine groups along their backbone, which allows them to bind to a variety of organic and inorganic compounds and to work as an excellent adsorption matrix [22,48]. Chitosan's structure may contribute to the sorption of active ingredients on the plant surface and enhance the penetration of active ingredients into plant cells through their cuticles and membranes, which may increase herbicidal efficacy under several severe conditions such as high and low temperatures, high wind and high UV radiation, and rainfall [49–51]. It was also reported that a complex of herbicide and chitosan maintained herbicidal activity for longer periods. The active ingredients with chitosan remained longer than free herbicides on the plant surface, thus enabling reduced herbicide loss [21,22]. Chitosan molecules were also reported to encapsulate herbicides. Encapsulation of the herbicides resulted in changes in diffusion and release of the herbicides from chitosan and herbicide complexes, and in sorption of herbicides with soil [21,22]. Therefore, chitosan may help reduce the contamination risk of herbicides in the environment.

It was also reported that paraquat-loaded chitosan was less toxic to mouse cell lines and *Allium cepa* L. cells. The herbicidal activity of paraquat with chitosan was preserved or enhanced against *Brassica* spp. and *Zea mays* L. [27,52]. Thus, complexes of paraquat and chitosan may reduce the toxicity of paraquat to animals and plant cells and increase or preserve paraquat efficacy. However, the herbicidal activity of paraquat and chitosan complexes had been determined with crop plant species, but not with weed plant species.

The present results indicate that a mixture of paraquat and chitosan increases the herbicidal efficacy against weed species *A. conyzoides, B. alata* and *P. conjugatum* under simulated rainfall conditions. On the other hand, the mixture did not increase the herbicidal efficacy against *I. cylindrica* under those conditions. The morphological characteristics of *I. cylindrica* may interfere with the enhancement of paraquat's herbicidal efficacy with chitosan under simulated rainfall conditions.

5. Conclusions

Simulated rainfall within 3 h after paraquat application decreased its herbicidal efficacy. A mixture of paraquat and chitosan significantly increased the herbicidal efficacy of paraquat against *A. conyzoides, B. alata* and *P. conjugatum* under simulated rainfall conditions. A chitosan concentration of 0.05–0.1% (w/v) may be sufficient to increase paraquat efficacy under these conditions. The chemical structure of chitosan may contribute to the penetration of paraquat into plant tissues through their cuticles and membranes. Chitosan is a degradable, nontoxic, easily available and low-cost material made from crustacean shells. The present results indicate that chitosan may work as a paraquat carrier and reduce herbicide loss due to rainfall. Consequently, the environmental contamination risk posed by paraquat could be decreased. This is the first article describing a mixture of chitosan and paraquat that enhanced herbicidal activity against three noxious weed species. Chitosan may also enhance the efficacy of other herbicides under unexpected rainfall conditions. However, further investigation will be necessary to evaluate the effects of chitosan mixed with other herbicides.

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