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Article

Influence of Adjuvants on the Surface Tension, Deposition and Effectiveness of Herbicides on Fleabane Plants

Influência de Adjuvantes na Tensão Superficial, Deposição e Eficiência de Herbicidas em Buva

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ABSTRACT - The use of herbicides is widespread in weed management, and adjuvants are added to the spray solution to improve the effectiveness of applications. The goal was to evaluate the influence of adjuvants added to the herbicides saflufenacil and glyphosate, isolated or in combination, and the effects on the surface tension, deposition and effectiveness in post-emergence applications to control *Conyza sumatrensis*. Experiments were conducted completely randomized experimental design to evaluate surface tension (TS), deposition and herbicide effectiveness. The treatments were glyphosate, glyphosate + saflufenacil and saflufenacil with or without the adjuvants Natur'al óleo®, Assist®, Aterbane®, Sillwet L-77 and Dash HC® (surface tension). For the experiments about mixture deposition and herbicide effectiveness, the factorial scheme 3 x 5 was adopted in the experiment performed in April, where factor A corresponded to the combination of the herbicieds glyphosate, saflufenacil and glyphosate + saflufenacil, and factor B was the addition of the adjuvants Natur'al óleo®, Assist®, Aterbane®, Sillwet L-77. For experiments conducted in November, the adjuvant Dash HC® was added, and the 3x6 factorial design was adopted. The adjuvants reduced the ST of the herbicide mixture, and Silwet L-77® was the most effective one. However, the ST reduction did not influence the mixture deposition on *C. sumatrensis* plants. The use of adjuvants did not result in an effective control for the applications with sole glyphosate.

Keywords: *Conyza sumatrensis*, glyphosate, saflufenacil, surfactants.

RESUMO - O uso de herbicidas é amplamente difundido no manejo de plantas daninhas, e os adjuvantes são acrescentados à calda de pulverização para melhorar a eficiência das aplicações. Assim, objetivou-se neste estudo avaliar a influência dos adjuvantes em adição aos herbicidas saflufenacil e glyphosate isolados ou em mistura, bem como os efeitos na tensão superficial, deposição e eficiência em aplicações em pós-emergência para o controle de ***Conyza sumatrensis****. Foram realizados experimentos em delineamento experimental inteiramente casualizado, para avaliar a tensão superficial (TS), deposição e eficiência dos herbicidas. Os tratamentos utilizados foram glyphosate, glyphosate + saflufenacil e saflufenacil, com ou sem os adjuvantes. Para os experimentos de deposição das caldas e eficácia dos herbicidas, adotou-se esquema fatorial 3 x 5 no experimento realizado em abril, em que o fator A correspondeu à combinação entre os herbicidas glyphosate, saflufenacil e glyphosate + saflufenacil, e o fator B, à adição dos adjuvantes Natur'al óleo®, Assist®, Aterbane® e Silwet L-77®. No experimento realizado em novembro, o adjuvante Dash HC® foi adicionado e adotou-se um esquema fatorial 3 x 6. Os adjuvantes reduziram a TS das caldas dos herbicidas,*

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sendo o Silwet L-77® o mais eficiente. Contudo a redução da TS não influenciou na deposição das caldas sobre as plantas de ***C. sumatrensis****. O uso de adjuvantes não resultou em controle eficiente para as aplicações apenas com glyphosate.*

Palavras-chave: *Conyza sumatrensis*, glyphosate, saflufenacil, surfatantes.

INTRODUCTION

Water is a universal solvent, and it is the most important vehicle in applications of agricultural pesticides. However, due to its high surface tension (72,6 mN m^{-1}), it presents low retention capacity when applied on targets with waxy and hydrophobic surfaces, such as the cuticle of plants (Kissman, 1997). When applying herbicides, it is necessary to use substances that mitigate this characteristic of the application mixture or that provide better spreading over the target.

Adding adjuvants to the spraying mixture may modify the physical-chemical characteristics to increase application effectiveness and target covering and it may help the absorption of the active ingredient (Mendonça et al., 2007). However, the effectiveness in applying herbicides does not only depend on the active ingredient quantity poured on the plant, but also on the size and density of drops, the losses to the soil and by drifting, the equipment, the spray volume, the spraying nozzles and the climate conditions (Souza et al., 2012), as well as on the evenness and distribution over the target surface (Terra et al., 2014).

Among the main herbicides used in the world agriculture, glyphosate stands out. The extensive use of this herbicide, mainly due to the wide adoption of transgenic cultures that are resistant to it, has caused a greater acceleration factor of the selection of resistant weeds. In this context, the different reports about glyphosate-resistant fleabane (*Conyza* spp.) species stand out (González-Torralva et al., 2012; Soares et al., 2012; Byker et al., 2013; Mellendorf et al., 2013; Moretti et al., 2013). Therefore, it is important to search for new ways to apply glyphosate, both by the association with other herbicides (Gandolfo et al., 2012) or by the addition of adjuvants to the spraying mixture, in order to improve the effectiveness of the applications (Iost and Raetano, 2010; Maciel et al., 2011).

Saflufenacil is an important option in association with glyphosate for the desiccation in areas with weeds that are difficult to control (Ashigh and Hall, 2010; Martins et al., 2012). Even considering the association of these herbicides, the association with adjuvants may improve the physical-chemical characteristics of the mixture and, consequently, the deposition on the target and the control over weeds (Carbonari et al., 2005; Maciel et al., 2011).

Therefore, this work had the goal to evaluate the surface tension of the mixtures containing saflufenacil and glyphosate, isolated or mixed with adjuvants, as well as the effects on the deposition and effectiveness of these herbicides applied in post-emergence to control *Conyza sumatrensis*.

MATERIAL AND METHODS

The experiments were conducted in the city of Botucatu/SP, in 2014. The study was divided in three steps: surface tension, deposition and effectiveness of the herbicides saflufenacil and glyphosate, isolated in a mixture with the addition of adjuvants.

Surface Tension (ST)

An experiment was conducted in laboratory, where it was possible to analyze the surface tension (ST) of the mixtures of the herbicides glyphosate (720 g a.e. ha^{-1}), saflufenacil (35 g a.i. ha^{-1}) and glyphosate + saflufenacil (720 g a.e. ha^{-1} + 35 g a.i. ha^{-1}), with or without the adjuvants described in Table 1. The concentrations used for each adjuvant were: 0.01; 0.02; 0.05; 0.1; 0.2; 0.5; 1 and 2% v/v. The highest concentrations were defined by the recommendation range described in the product instructions and, starting from them, lower concentrations were used in order to check the effectiveness of the adjuvants in influencing the ST.

Table 1 - Characteristics of the adjuvants added to the spraying mixtures

Surfactants				
Commercial product	Active ingredient	Conc. a.i. (g L^{-1})	Formulation	Class
Natur'l óleo®	Vegetal oil	930	Emulsifiable concentrate	Adhesive spreader
Assist®	Paraffinic hydrocarbons, saturated and unsaturated paraffinic and aromatic cycles coming from the distillation of petroleum	756	Emulsifiable concentrate	Adjuvant
Aterbane®	Alcohol-phenol condensate with etene oxide and organic sulphonates	466	Soluble concentrate	Adhesive spreader
Sillwet L–77	Polyether and silicone copolymer	77	Dispersible concentrate	Adhesive spreader
Dash HC®	Methyl esters, aromatic hydrocarbon, unsaturated fat acid and surfactant	933	Emulsifiable concentrate	Adjuvant

In order to determine the ST of the spraying mixtures, the gravimetric method was used, similarly to what was described by Mendonça et al. (1999). In order to create the drops, an ST 670 (Samtronic) infusion pump was used, with a 7 mL h^{-1} flow, to which a 5mL syringe containing samples of the application mixtures was connected. A capillary was connected to the syringe, whose edge was placed vertically on a precision scale (0.0001 g), so that the formed drops were weighed. In order to avoid losses by evaporation, the created drops were deposited in a beaker containing oil (vegetal), so that they remained submersed after coming away from the capillary. The system calibration was performed with distilled water, and the drops' weight was considered 76.2 mN m^{-1}. After weighing each treatment, the system washing was performed with distilled water until the drops' weight reached constant weight, in order to start the following treatment.

The used experimental design was completely randomized with four replications. For each replication, 10 drops from each treatment were weighed. The results were submitted to analysis of variance by F test and, when significant, the regressions were adjusted using the Mitscherlich model, modified according to Montório et al. (2005).

Mixture deposition on fleabane plants

Two experiments were conducted in a greenhouse in order to verify the deposition of the spraying mixtures on *Conyza sumatrensis* (fleabane). The experiments were conducted in April and November 2014. The seeds used in the experiments were harvested in areas with a history of glyphosate-resistant fleabane. For both experiments, seeds were harvested in different areas of the city of Botucatu/SP.

Fleabane was sown in a 188 cell Styrofoam tray, which were transplanted to planters containing 0.25 liters of soil, when they presented two to three leaves. Each planter containing a plant constituted a replication. At the time of treatment application, the plants from the experiment conducted in April were approximately 12 cm tall, whereas for the experiment conducted in November, the fleabane plants had a maximum height of 7 cm. The height of plants at the time of the application was defined according to studies conducted by Oliveira Neto (2010), who observed a close relation between the size of fleabane plants at the time of treatment application and the effectiveness of the herbicides.

The experimental designs used in the two experiments were completely randomized with four replications. In the first experiment, the factor scheme 3 x 5 was adopted, where factor A corresponded to the combination between the herbicides glyphosate (720 g a.e. ha^{-1}), saflufenacil (35 g a.i. ha^{-1}) and glyphosate + saflufenacil (720 g a.e. ha^{-1} + 35 g a.i. ha^{-1}), and factor B corresponded to the addition of the adjuvants (leaflet dose) Natur'l óleo® (1% v/v), Assist® (0.5% v/v), Aterbane® (0.25% v/v) and Silwet L-77 (0.1% v/v). In the second experiment, the adjuvant Dash HC® (0.5% v/v) was added to the treatments; therefore, a 3 x 6 factor scheme was adopted.

In order to spray the treatments, each fleabane plant replication was placed under each tip of the stationary sprayer, equipped with four Teejet XR11002-VS nozzles, with medium drops, spaced 0.5 m apart and placed at 0.5 m height from the plants. The used working pressure was 2.0 kgf cm^{-2}, with 3.6 km h^{-1} speed and 200 L ha^{-1} application rate. The conditions at the time of the application were: average temperature of 35 and 31 °C and mean relative humidity of 40 and 55%, respectively for April and November.

In the application mixture for the deposition test, a tracer (Bright Light Blue, FDC1) was added at the concentration of 1,500 mg L^{-1} (Palladini et al., 2005). After the application, all leaves from each plant were collected and washed three times with 50 mL of distilled water, in plastic bags that were shaken for 30 seconds. The solution from the three washings was mixed and it resulted into one composed sample, for the later quantification of the tracer. After washing, the leaf area was determined by a fixed LICOR meter (LI-3110).

Absorbance at the wave length of 630 nm was determined for all solutions in a Cintra 40 Dual Ray UV-Visible spectrophotometer. Absorbance data were transformed into µL of mixture cm^{-2} of leaf (Negrisoli et al., 2002).Data about the deposit over the leaves of fleabane plants were submitted to analysis of variance, and the comparison of the averages was made by Tukey's test ($p \leq 0.05$).

Herbicide effectiveness

Two experiments were conducted in a greenhouse, during the same period, using the same conditions and treatments from the experiments about the deposition of spraying mixtures, as well as the size of fleabane plants. After applying the treatments, visual control evaluations were performed on fleabane on day 7 and 28 after the application (DAA). In the visual control evaluations, a percentage grade scale was used, where 0 corresponds to no injury and 100 to the plant death (SBCPD, 1995).

Data about plant control were submitted to analysis of variance, and the comparison of the averages was made by Tukey's test ($p \leq 0.05$).

RESULTS AND DISCUSSION

Surface Tension (ST)

The regression analyses about the surface tension (ST) (mN m^{-1}) of the solutions with water and herbicides mixed with the adjuvants at different concentrations were conducted according to the Mitscherlich model (Figure 1). When compared to the herbicides without adjuvants, all treatments with the addition of adjuvants reduced the ST of the mixtures. The initial surface tension of the mixtures without the addition of adjuvants was reduced in the mixtures that contained glyphosate, when compared to the surface tension of water or isolated saflufenacil. It is important to highlight that the sole addition of glyphosate causes a reduction in the ST (Maciel et al., 2010). This may be related to the fact that glyphosate presents different surfactants in its formulation.

Silwet L-77® provided the lowest surface tension values (22.7 mN m^{-1}) in relation to the other adjuvants, for all herbicides and for water. In this context, some authors demonstrated the effectiveness of this organosilicone adjuvant to reduce the ST in aqueous solutions (Montório et al., 2005; Iost and Raetano, 2010; Oliveira, 2011).

The minimum surface tension observed for the other adjuvants was similar, except for Dash HC® mixed with glyphosate, saflufenacil and water (Table 2). Mendonça et al. (2007) and Maciel et al. (2010), when using the adjuvants Natur'l óleo® and Assist®, observed a reduction in the ST of the mixtures at different tested concentrations, with values close to the ones found in this work. On the other hand, Montório et al. (2005), when evaluating the adjuvant Aterbane®, found that the minimum ST was equal to 32.68 mN m^{-1}.

The adjuvants Aterbane®, Silwet L-77® and Dash HC® reached the minimum ST when used at lower concentrations than 1% of the concentration added to the mixture; however, for the

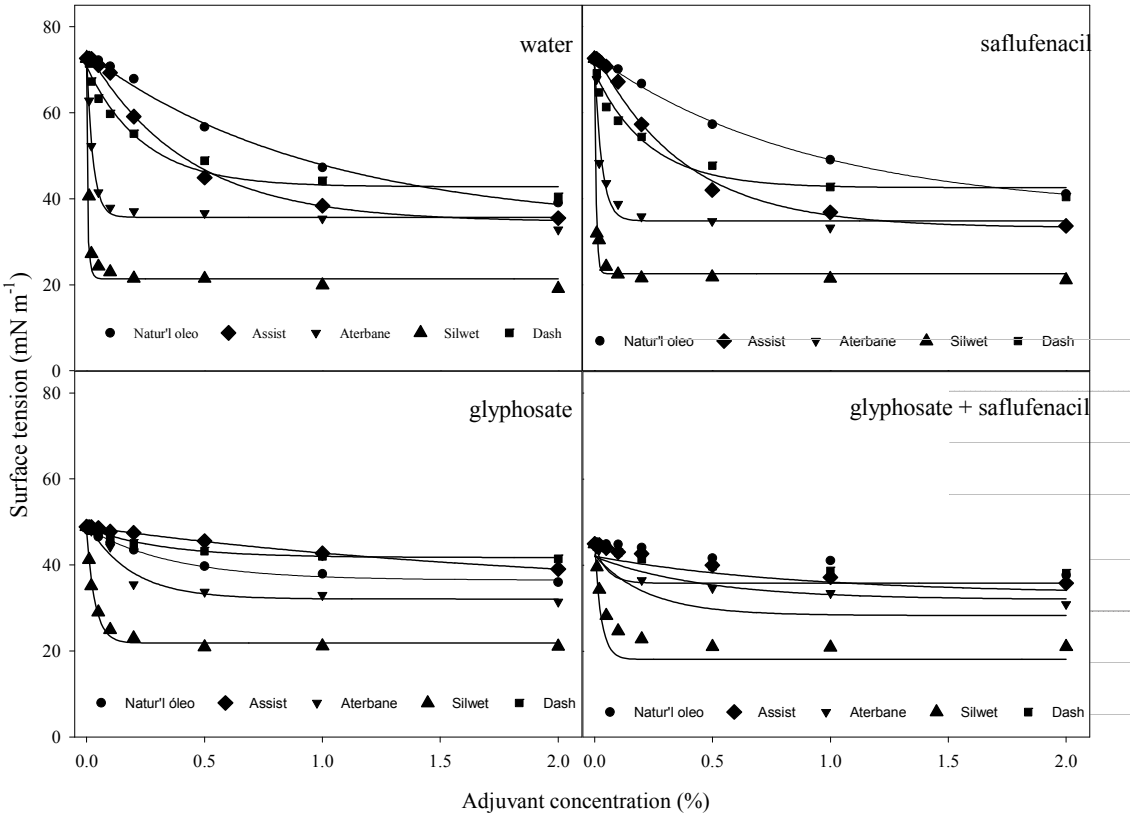

Figure 1 - Surface tension (mN m^{-1}) of adjuvants at different concentrations (%v/v), in herbicides and water.

Table 2 - Results of the analyses of variance and regression. Parameters of the obtained equations

Herbicide	Parameters of the Mitscherlich model	Surfactants				
		Natur'l óleo®	Assist®	Aterbane®	Silwet L-77®	Dash HC®
Glyphosate	A	12.1235	15.6983	17.6746	26.167	6.9524
	B	0.0235	-0.0004	-0.0495	0.0326	0.0285
	C	1.1807	0.2136	2.3351	12.301	1.356
	M.T.	36.7496	33.1748	31.1985	22.7061	41.9207
	F	403.82**	1524.85**	88.315**	253.60**	665.91**
	r^2	0.9926	0.998	0.9671	0.9844	0.9955
Glyphosate + saflufenacil	A	8.7928	9.9975	14.0438	26.877	9.168
	B	0.3245	0.2957	0.1847	0	0
	C	0.5061	0.9352	1.9355	15.2766	8.6987
	M.T.	36.1512	34.9465	30.9002	18.067	35.776
	F	16.85**	28.31**	37.42**	429.58**	21.96**
	r^2	0.8489	0.9042	0.9258	0.984	0.7583
Saflufenacil	A	36.1391	41.0697	37.792	50.0791	26.953
	B	-0.0135	-0.0415	0	0	0.1155
	C	0.475	1.1544	14.2076	62.5711	1.9035
	M.T.	36.4609	31.5303	34.808	22.5209	45.647
	F	1828.68**	383.80**	383.30**	390.28**	86.66**
	r^2	0.9984	0.9922	0.9528	0.9824	0.9665
Water	A	40.0803	39.8466	37.2909	51.2455	28.0013
	B	-0.0246	-0.0462	-0.0096	0	0.066
	C	0.4466	1.0355	16.0622	43.7162	1.819
	M.T.	32.5197	32.7534	35.3091	21.3545	44.5987
	F	523.57**	296.56**	287.29	109.73**	111.58**
	r^2	0.9943		0.9897	0.9482	0.9738

** Significant at 1% probability. M.T. = minimum tension.

minimum reduction of the ST of Natur'l óleo® and Assist®, a concentration above 1% was necessary. The higher the value of the parameter C in the Mitscherlich model equation, the lower the ST value obtained at a lower concentration. Higher values of the C parameter were observed for the adjuvants Silwet L-77®, Aterbane® and Dash HC®. Thus, as observed by Mendonça et al. (1999), the oils used as adjuvants did not present high values for the parameter C, that is, they are not as effective in reducing the ST at low concentrations as the adjuvants that do not contain oil in their formulation.

Mixture deposition

It was possible to observe different mixture deposition values on *Conyza sumatrensis* (fleabane) plants (Table 3). The lowest plants (7 cm) showed higher deposition, whereas the tallest plants (12 cm) presented low deposition, which may be explained by the greater biomass and lower deposition of the lowest leaves of plants.

Plants that were 7 cm tall showed a similar deposition for herbicides with or without adjuvants. O Silwet L-77® provided lower deposition in relation to the other adjuvants in the association with saflufenacil, which may have occurred due to the low surface tension that caused leaching of the mixture on the leaves. For 12 cm tall plants, there were no differences, regardless of the used treatment.

The results of this study demonstrate that the use of adjuvants does not always allow favorable conditions for the spraying deposition on plants. Again, according to Maciel et al. (2010), this happens mainly when the effects over drop size and the different anatomic compositions and, also, the composition of the epicuticular waxes of weeds and cultures. Carbonari et al. (2005), when adding the adjuvants Aterbane® and Silwet L-77® to an aqueous solution, observed significant differences between the treatments after the application; the maximum volume deposited on the leaves of bermuda grass (*Cynodon dactylon)* plants was 0.35 µL cm^{-2}, using the deposition evaluation found in this work.

Table 3 - Effects of different herbicides mixed with adjuvants over the deposition (µL cm^{-2}) on *Conyza sumatrensis* plants, applied in post-emergence

Treatment	7 cm height			12 cm height		
	glyphosate	glyphosate +saflufenacil	saflufenacil	Glyphosate	glyphosate +saflufenacil	saflufenacil
Without adjuvant	1.5 bA	1.7 abA	2.2 aAB	0.8 aA	1.1 aA	1.1 aA
Natur'l Óleo®	1.3 aA	1.3 aA	1.9 aAB	0.80 aA	0.8 aA	1.1 aA
Assist®	1.3 bA	1.6 bA	2.3 aA	0.90 aA	1.0 aA	1.1 aA
Aterbane®	1.5 aA	1.5 aA	1.9 aAB	1.0 aA	0.9 aA	1.1 aA
Silwet L-77®	1.3 aA	1.3 aA	1.4 aB	0.9 aA	1.0 aA	1.0 aA
Dash HC®	2.1 aA	2.0 aA	2.2 aAB	-	-	-
F herb* adj	0.91^{ns}			0.59^{ns}		
F herbicide	10.94*			5.26*		
F adjuvant	5.25*			0.90 ns		
VC (%)	22.87			20.28		

^{ns} Non-significant at 5% probability by Tukey's test; * Significant at 5% probability by F test. Averages followed by the same capital letter, in the column, and lowercase letter, on the line, do not differ among themselves.

Herbicide effectiveness

Both development stages of the fleabane plants were not controlled satisfactorily by glyphosate, even when mixed with adjuvants; however, on day 28 DAA all adjuvants in association only with glyphosate promoted control increments for 7 cm tall plants at the time of the application (Table 4).

Table 4 - Effectiveness (%) of different herbicides mixed with adjuvants on the control of*Conyza sumatrensis* plants, applied in post-emergence

Treatment	7 cm height					
	7 DAA			28 DAA		
	glyphosate	glyphosate +saflufenacil	saflufenacil	glyphosate	glyphosate +saflufenacil	saflufenacil
Without	7.0 bA	75.5 aA	86.0 aA	33.8 bB	100 aA	100 aA
Natur'l Óleo®	10.0 bA	95.5 aA	83.8 aA	36.3 bAB	100 aA	100 aA
Assist®	12.5 bA	97.8 aA	88.0 aA	36.8 bAB	100 aA	100 aA
Aterbane®	6.8 bA	86.8 aA	81.5 aA	37.0 bAB	100 aA	100 aA
Silwet L-77®	7.3 bA	82.8 aA	95.3 aA	36.8 bAB	100 aA	100 aA
Dash HC®	15.0 bA	88.0 aA	87.5 aA	40.3 bA	100 aA	100 aA
F herb* adj	0.92^{ns}			0.74^{ns}		
F herbicide	364.81*			4111.90*		
F adjuvant	1.38*			0.74^{ns}		
VC (%)	18.53			3.53		
	12 cm height					
Without	13.8 bA	42.5 aA	37.5 aB	30.0 bAB	97.3 aA	90.3 aA
Natur'l Óleo®	15.0 bA	52.5 aA	43.8 aAB	25.0 bB	97.5 aA	98.5 aA
Assist®	18.8 bA	56.7 aA	45.0 aAB	40.0 bA	97.8 aA	92.5 aA
Aterbane®	18.8 bA	53.8 aA	52.5 aA	36.3 bAB	100.0 aA	94.3 aA
Silwet L-77®	16.3 bA	51.3 aA	47.5 aAB	33.8 bAB	98.8 aA	89.5 aA
F herb* adj	0.61^{ns}			1.96^{ns}		
F herbicide	137.08*			711.119*		
F adjuvant	3.80*			1.23^{ns}		
VC (%)	18.85			8.13		

^{ns} Non-significant at 5% probability by Tukey's test; * Significant at 5% probability by F test. Averages followed by the same capital letter, in the column, and lowercase letter, on the line, do not differ among themselves.

For 7 cm tall plants, the herbicides saflufenacil and saflufenacil + glyphosate provided effective control. Control on day 7 DAA for saflufenacil, isolated or mixed with glyphosate, was high and it reached 100% on day 28 DAA, regardless of the evaluated adjuvants (Table 4). The lowest mixture quantities deposited over the leaves with the addition of Silwet L-77® on the shortest plants did not represent lower control; this may be related to a wider spreading of the herbicide over the leaf, especially for an herbicide that is poorly movable on plants (contact), such as saflufenacil.

As for 12 cm tall plants, the herbicides saflufenacil and saflufenacil + glyphosate presented low control levels on day 7 DAA and high levels on day 28 DAA. The adjuvants did not interfere in the control of fleabane plants with the application at a more advanced development stage. For 12 cm tall plants, it was possible to observe 100% control only with the association of glyphosate + saflufenacil with the addition of the adjuvant Aterbane® on day 28 DAA, whereas plants at the 7 cm height development stage presented 100% control on day 28 DAA for isolated saflufenacil and glyphosate + saflufenacil, with or without adjuvants. According to Oliveira Neto et al. (2010), the stage of *C. bonarienses* at the time of the application affects significantly control effectiveness.

The results of the application of saflufenacil were similar to the ones found by Dalazen et al. (2015), who observed up to 80% control on fleabane plants at the dose of 35 g a.i. ha^{-1} on day 7 DAA. According to Byker et al. (2013) and Mellendorf et al. (2015), the mixture of glyphosate and saflufenacil provided satisfactory control on *C. canadensis* plants. Saflufenacil presents physical-chemical properties that enable its mobility via phloem (Ashigh and Hall, 2010) and, consequently, there is a synergic relation in the combination with glyphosate (Dalazen et al., 2015).

The adjuvants were effective in reducing the surface tension (ST) of the herbicide mixtures, with the influence of their different concentrations. The mixtures with glyphosate and glyphosate + saflufenacil had lower ST reduction when compared to isolated saflufenacil and water. The

adjuvant Silwet L-77® was effective in reducing the ST, reaching the lowest minimum tensions regardless of the herbicide. The ST reduction did not influence in the deposition of the mixtures over *Conyza sumatrensis* (fleabane) plants. Therefore, the use of adjuvants did not result in an effective control in applications only with glyphosate.

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