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ENHANCEMENT OF BENTAZONE EFFICACY WITH NEWLY DEVELOPED ECOFRIENDLY ADJUVANTS

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ABSTRACT

Adjuvants have been developed to enhance the activity of pesticide and possibly could allow reduction of pesticide rates. This is a very important fact as there are many concerns associated with pesticides use, because of their potential to cause adverse effects to operators, crops and environment. Because of that there is continued government regulatory pressure for safer pesticide products and for reduction of pesticides application rate. Trend towards minimum use of pesticides lead to development of new, more effective adjuvants to enhance biological activity of pesticide formulations, either built-in formulation or added in tank mix just before application. Among others, crop oil concentrates (COC) and soluble concentrates (SL) are bioenhancing adjuvants which enhance the effectiveness of pesticides.

In our study we investigated how adjuvants with different compositions influenced bentazone efficacy. The first step was development of ecofriendly crop oil concentrates based on vegetable oils (sunflower oil, soybean oil and esterified rape seed oil) in combination with different surfactants. Then we compared the effects of the crop oil concentrates and the commercial adjuvant (Trend®90, soluble concentrate) during the application with bentazone on two different locations. The results after two year trials confirmed that all investigated adjuvants have beneficial effects on bentazone efficacy, but the effects of the developed crop oil concentrate with esterified rape seed oil was the most pronounced.

Key words: Ecofriendly adjuvants, crop oil concentrate, bentazone, efficacy.

INTRODUCTION

Adjuvants have been used in combination with pesticides in order to increased biological activity of active ingredients. An adjuvant is a substance which is not itself a pesticide, but which can enhances the effectiveness of the pesticide with which it is used or can improves physical properties of the spray solution. An adjuvant can be built-in pesticide formulations or applied separately to the spray tanks. Recently, due to a pressure on the pesticide industry for better performance of the products, there has been increased number of new adjuvants on the market (Knowles, 2006, 2008; Radivojević et al., 2011). Significant research is still being expended in the area of adjuvant and there is likely that further results from this work will be obtained. Adjuvants have been used with herbicides the most often, but now the motivation for rational plant protection leads to wider use of adjuvants also with insecticides and fungicides (Ryckaert, 2007).

The correct use of adjuvants can significantly increase the performance of pesticide products. It seems that the most important ways of adjuvants action are the improved retention, spreading, wetting and penetration of the pesticide on the target and reduction of fine droplets which counters the problems of the spray drift (Holloway et al., 2000; Green and Beestman, 2007). Pesticide spray drift is a major source of concern with respect to the environmental impact of agriculture on environment, particularly in the light of increasing stringent environmental standards. The most important effect of adjuvants is probably reduction of interfacial tension between spray drops and treated surface, which allows: a better covering of the cuticle and a better penetration through target surface. Solubilisation can play a major role in activating the transport of the active ingredient (Tadros, 2005).

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Adjuvants can be classified by the functions or the chemical classes to which they belong. However they are usually classified according to their functions rather than their chemical properties. A classification with respect to the application process describes adjuvants as “utility modifiers” (improvement of the formulation) or “activator or bioenhancing adjuvants” (improvement of the biological action) (Spanoghe, 2007). Bioenhancing adjuvants enhance the effectiveness of pesticides. Bioenhancing adjuvants are: surfactants (usually non-ionic or silicone compounds or their blend), crop oils, crop oil concentrates (COC, mixture of mineral or vegetable oil with blend of non-ionic surfactants) and inorganic salts. Utility adjuvants are used to improve application properties of a spray mix. They include a variety of types as: acidifiers (neutralize alkaline solutions, lower pH), buffering agents (stabilize the pH of spray solutions), anti-foaming agents, compatibility agents, drift control agents etc. Utility adjuvants allow a given product to be used under a wider range of conditions (Knowles, 2006).

It is well known that oils, both mineral and vegetable, are used extensively in pesticide formulation and in pesticide application as tank mix adjuvants. In the past the mineral oils dominated, but in time these oils gradually are being superseded by vegetable oils and their derivates. The use of vegetable oils and their esterified derivates is increasing, since they are more biodegradable and originate from renewable resources (Wang and Liu, 2007). Also, esterified oils are more and more attractive compared to the non esterified equivalent because they are less viscous. The second major adjuvants are surfactants, both nonionic and ionic, which are includes a wide range of chemicals such as polymers, inorganic salts etc.

Unfortunately, there is no universal adjuvant which will give enhanced effects with all pesticides. It could happen that biological efficacy with adjuvant may be even reduced or, in some cases, phytotoxicity problems to the crop may be increased (Ramsdale and Messersmith, 2002). Consequently, it is necessary to carry out field trials with adjuvants and the commercial pesticide products to avoid this problem.

The present study was directed at investigating of impact of different adjuvants on efficacy of bentazone. At the beginning of the study we developed three ecofriendly crop oil concentrates based on vegetable oils (sunflower oil, soybean and esterified rape seed oil) in combination with different surfactants. Common experimental approach in study of adjuvant is to compare the effects of an herbicide applied alone at one or a few doses and in the mixture with adjuvants, applying analysis of variance for the statistical assessment. In our study we compared the effects on the bentazone applied alone and in mixture with three developed crop oils concentrates and with commercial adjuvant Trend®90 (aqueous concentrate with the 90% isodecyl alcohol ethoxylate) during the application on two different locations during two years. The aim of this study was to find out if there is differences in beneficial effects of two different type of adjuvants formulations: (COC and soluble liquid, SL) on bentazone efficacy.

MATERIAL AND METHODS

The vegetable oils which were used for formulating crop oil concentrates were purchased from commercial sources (Dijamant, Zrenjanin, Uvita, Debeljaca, Oleon, Belgium) and used without further purification. Surfactants which were used were of commercial quality (Ajinomoto OmniChem, Belgium and Rhodia, Italy).

Crop oils concentrates ware obtained by mixing oil phases (sunflower oil, soybean oil and esterified rape seed oil) with surfactants. Magnetic stirrer (IKA, RH basic 2) was used for homogenisation (duration time 30 minutes, temperature 40 °C). The crop oil concentrates were prepared by mixing: soybean oil with 15% of surfactants (adjuvant A1), esterified rape seed oil with 10% of surfactants (adjuvant A2) and sunflower oil with 15% of surfactants (Adjuvant A3) (Gašić et al., 2012). After formulating, the accelerated storage tests (storage stability) were done (CIPAC method

MT 39 and 46). Before and after stability tests the same characteristics were checked according standard CIPAC methods: pH MT 75, density MT 3, persistent foam MT 47.2 and emulsion stability and re-emulsification MT 36.1 and compared (CIPAC, 1995).

Field trials were carried out in Serbia, on maize crops in two years (2011 and 2012), on two locations near Belgrade: Boljevci, which has a latitude of 44°42' North, a longitude of 20°14' East, an altitude of 77 m above sea level, and Glogonjski Rit, which has a latitude of 44°56' North, a longitude of 20°29' East, an altitude of 60 m above sea level.

The soil at Boljevci locality was silty clay loam with pH 7.8, 3.1% organic matter, 1.8% sand, 61.8% silt and clay 36.4%. The seeding of maize grains NS 6010 took place on 08 April 2011 and 04 May 2012. The soil at Glogonjski Rit locality was sandy clay loam with pH 7.65, 2.7% organic matter, 50.4% sand, 18.6% silt and 31.0% clay. The seeding of maize grains ZP 704 took place on 16 April 2011 and 26 April 2012.

The trial plots were laid out in randomised complete block design in four replications. The size of the main plot was 25 m^2 (6.25 × 4 m).

Developed crop oil concentrates were used with bentazone (commercial product Basagran, bentazone 480 g L^{-1}, BASF Ludwigshafen, Germany). The same herbicide was used with commercial adjuvant Trend®90 (DuPont International, Switzerland). Adjuvants (developed crop oil concentrates and Trend®90, soluble concentrate of isodecyl alcohol ethoxylate, 90%) were added to tank mixes (herbicide solutions) just prior application (0.1%). Herbicide bentazone was applied at lowest recommended rate in maize (1.44 kg a.i. ha^{-1}) for region Serbia and one control treatment (without herbicide application) was included.

Adjuvants with herbicide were applied when stage of maize was 3-5 leaves and stage of weeds was 2-6 leaves. All treatments were done with the Neptune 15, Kwazar® knapsack sprayer with Tee Jet XR 110/03 nozzles and applying 300 L ha^{-1} water. Visual observations on mortality of weed species, in randomly selected areas (1 m^2), were recorded 3 and 6 weeks after the treatment (WAT). Efficacy of treatments was determined on the basis of number of killed plants in the treated plots compared to the untreated plot.

Statistical evaluation: the obtained data were analysed separately for each trial using ANOVA and the means were separated by Duncan's multiple range test. In all analyses the level of significance was at least p=0.05.

RESULTS

The first step in our investigation was development of ecofriendly crop oil concentrates with three different vegetable oils and surfactants, which have good and stable physical characteristics. Before the field experiment started, the stability and physical properties of the developed crop oil concentrates had been checked and the results confirmed that they were stable enough to be used (Tables 1-3).

Table 1. Physical properties of fresh adjuvants on room temperature (20°C)

Adjuvants	A1	A2	A3
Density (g/cm^3)	0.929	0.891	0.929
pH value	5.61	5.10	5.26
Persistent foam (cm^3)	6	4	8
Stability of emulsion and re-emulsification (cm^3)	0.5 h 0/0	0.5 h 0/0	0.5 h 0/0
	1 h 0/0	1 h 0/0	1 h 0/0
	2 h 0/0	2 h 0/0	2 h 0/0
	24 h 0/0	24 h1/0	24 h 0/0
	REE 0/0	REE 0/0	REE 0/0

Table 2. Physical properties of the adjuvants after stability test (0°C, 7 days)

Adjuvants	A1	A2	A3
Density (g/cm^3)	0.933	0.932	0.934
pH value	5.03	5.23	4.94
Persistent foam (cm^3)	5	5	6
Stability of emulsion and re-emulsification (cm^3)	0.5 h 0/0	0.5 h 0/0	0.5 h 0/0
	1 h 0/0	1 h 0/0	1 h 0/0
	2 h 0/0	2 h 0/0	2 h 0/0
	24 h 1/0	24 h 2/0	24 h 2/0
	REE 0/0	REE 0/0	REE 0/0

Table 3. Physical properties of the adjuvants after stability test (54°C, 14 days)

Adjuvants	A1	A2	A3
Density (g/cm^3)	0.928	0.890	0.934
pH value	5.39	4.94	5.22
Persistent foam (cm^3)	6	5	7
Stability of emulsion and re-emulsification (cm^3)	0.5 h 0/0	0.5 h 0/0	0.5 h 0/0
	1 h 0/0	1 h 0/0	1 h 0/0
	2 h 0/0	2 h 0/0	2 h 0/0
	24 h 0/0	24 h 4/0	24 h 4/0
	REE 0/0	REE 0/0	REE 0/0

Meteorological data on two localities in 2011 and 2012 are presented in Table 4. Monthly precipitation data on two localities from the growing seasons indicate a large range in the precipitation and uneven distribution. These precipitation levels were accompanied by average daily temperature ranging from 12.5°C to 24.5°C, respectively.

Table 4. Total precipitation and average daily temperature at the study sites in 2011 and 2012

Months	Precipitation (mm)		Average daily temperature (°C)	
	2011	2012	2011	2012
Locality Glogonjski rit				
April	14.3	62.3	12.5	12.9
May	76.8	74.3	16.4	18.9
Jun	53.6	13.8	20.9	24.5
Locality Boljevci				
April	11.1	67.7	14.6	14.4
May	62.6	72.3	16.8	19.2
Jun	40.4	22.3	21.7	23.7

The presence of the following weed species *Abutilon theophrasti*, *Ambrosia artemisiifolia*, *Convolvulus arvensis*, *Helianthus annuus*, *Xanthium strumarium* were noticed on both locations. The results of bentazone efficacy alone and with adjuvants in maize crop are given in Table 5. Bentazone applied alone provided 74% control of *A. theophrasti*. Addition of Trend®90, A1, A2 or A3 adjuvants improved *A. teophrasti* control by 26% (from 74 to 100%). The best adjuvant was A2 which provided complete damage and mortality of this plant species at 3 and 6 WAT in experiments in both years.

Table 5. Efficacy of bentazone alone and with adjuvants in maize crop in 2011 and 2012

Treatments	Rate kg ha^{-1} (%)	Efficacy (%)				
		ABUTH	AMBAR	CONAR	HELAN	XANST
3 weeks after the treatments						
Bentazone	1.44	74 a*	76 a	33 a	62 a	99 a
Bentazone + Trend	1.44 + 0.1	89 b	79 a	39 ab	82 b	99 a
Bentazone + A1	1.44 + 0.1	96 cd	79 a	43 b	82 b	99 a
Bentazone + A2	1.44 + 0.1	100 d	91 b	43 b	96 d	99 a
Bentazone + A3	1.44 + 0.1	93 bc	80 a	33 a	88 c	99 a
6 weeks after the treatments						
Bentazone	1.44	84 a	80 ab	36 a	72 a	100 a
Bentazone + Trend	1.44 + 0.1	92 b	86 bc	41 ab	94 b	100 a
Bentazone + A1	1.44 + 0.1	92 b	89 ce	45 bc	94 b	100 a
Bentazone + A2	1.44 + 0.1	100 c	94 d	51 c	100 c	100 a
Bentazone + A3	1.44 + 0.1	97 bc	86 bc	41 ab	98 bc	100 a

ABUTH - *Abutilon theophrasti*, AMBAR - *Ambrosia artemisiifolia*, CONAR - *Convolvulus arvensis*, HELAN - *Helianthus annuus*, XANST - *Xanthium strumarium.*

*Means in the same column followed by the same letter do not differ ($p<0.05$) according to Duncan's multiple range test.

Bentazone applied alone provided control of *A. artemisiifolia* 76-80%. Efficacy control was similar when bentazone was applied with adjuvants Trend®90, A1 and A3. The best adjuvant was A2, which provided better efficacy then others adjuvants. The adjuvant A2 improved control of *A. artemisiifolia* to 91-94%.

Bentazone without adjuvant provided only 33-36% control of *C. arvensis* 3 and 6 WAT. Efficacy control increased to maximum 51% when bentazone was applied with adjuvants.

Bentazone applied alone provided 62% control of *H. annuus*, while addition of Trend®90, A1, A2 or A3 adjuvants improved *H. annuus* control by 38% (from 62 to 100%). The best adjuvant was A2 which provided better efficacy then others adjuvants. The adjuvant A2 improved control of *H. annuus* to 100% at 6 WAT.

Bentazone alone or with adjuvants control *X. strumarium* (99-100%) and provided complete damage and mortality of this plant species.

DISCUSSION

Generally, to improve biological efficacy, herbicides require use of adjuvants for foliage-applied treatments. Bentazone as selective contact herbicide, which is absorbed mainly by the foliage with very little translocation, requires, adjuvant help for better performance and usually its application is done altogether with adjuvant (Abouziena et al., 2009). Foliar uptake of pesticides is a complex process, depending on leaf surface characters of plants, physical chemicals properties of active ingredients, types of formulation, and environmental conditions (Wang, 2007). How each of these factors influence the uptake is only partially understood, but otherwise, it is well known that addition of an adjuvant increase herbicidal activity (Zabkiewicz, 2000; Kudsk and Mathiassen, 2007; Knowles, 2006) and modifies environmental fate (Weinterberg and Greenhalgh, 1984). Al-Khatib et al. (1995) reported that weed control with bentazone applied at rate of 0.56 kg ha^{-1} with any adjuvant was equal to weed control with bentazone applied alone at 1.12 kg ha^{-1}. Sometimes it happens that addition of an adjuvant doesn’t result in increased efficacy and that is why it is necessary to check the influence of adjuvant in field trials (Singh et al., 2002).

The major barrier to postemergence herbicides (as bentazone) absorption is the leaf cuticle of the weeds. Hydrophilic herbicides as bentazone enter the cuticle surface through diffusion, but the rate of diffusion is much lower than in lipophilic herbicides, due to their low solubility within the cuticle. The addition of adjuvants reduces the dynamic surface tension of spray droplets, which allows them to spread out and increase the contact area with the leaf surface, increase the spray retention by prolonging drying time and increase the penetration through the leaf cuticle. It is very important that the cuticle is hydrated and that water forms a hydrophilic component to the cuticle for diffusion of the water soluble pesticide. Bentazone as hydrophilic herbicide requires the solubilisation from the vegetable oil, but other more lipophilic soluble herbicides may penetrate the cuticle wax without oil (Tadros, 2005).

Our results suggest that *C. arvensis* is hard to control with bentazone. Bentazone without adjuvant had only 33-39% control of this plant species, while in combination with adjuvants its efficacy increased to maximum 52%. Similar result was reported with Bellinder et al. (2003) and Abouziena et al. (2009). Percent weed control below 80% is generally considered unacceptable (Nurse et al., 2008). Han and Wang (2002) reported that in tolerant plants bentazone can be quickly metabolised, while Anderson and Hall (1985) thought that leaf surface morphology was very important. According to results Clay and Oelke (1988) rice as a tolerant plant metabolised 98% of the bentazone one day after treatment, while *Sparganium eurycaprum* as a susceptible plant metabolised less than 2% of the bentazone five days after treatment.

Bentazone alone or with adjuvants provided complete damage and mortality of *X. strumarium*. These results suggest that bentazone has a highly herbicidal activity against *X. strumarium* and that this species was easily controlled with bentazone alone or with adjuvants.

All investigated adjuvants (Trend®90, A1, A2 or A3) added to bentazone increased control of *A. theophrasti*, *A. artemisiifolia* and *H. annuus*. Similar finding was reported by Abouziena et al. (2009) who reported that in greenhouse condition, bentazone at rate 1.68 kg ha^{-1} with adjuvants (ammonium sulphate, Induce, Kinetic) completely controlled *A. theophrasti*. They added that mixing adjuvant with bentazone generally enhanced *Solanum nigrum* control, but addition of adjuvant to bentazone for controlling *Morrenia odorata* did not cause any significant control. According to Idziak at al. (2013) efficacy of mesotrione increased greatly when applied with oil-type adjuvants. Knezevic at al. (2009) reported that adjuvant crop oil concentrate (COC) provided enhancement of saflufenacil efficacy across weeds.

In our investigation the best adjuvant was A2, which provided complete damage and mortality of *A. theophrasti* and *H. annuus,* while control of *A. artemisiifolia* was improved to 94%. The dates demonstrate that the performance of crop oil concentrates (in terms of bentazone efficacy) is almost equivalent to the registered adjuvant (Trend®90) in the situations for which use is proposed. Crop oil concentrates, like surfactants (Trend®90), improve coverage of plant surfaces. However, crop oils concentrates keep the leaf surface moist longer than water, allowing more time for the herbicide to penetrate, and thus, increasing the amount of herbicide that will enter the plant. The purpose of the nonionic surfactant in this mixture is to emulsify the oil in the spray solution and lower the surface tension of the spray solution. We believe that, because of that, addition of adjuvant A2 (the most effective combination of oil phase and surfactants) to spray mixer enhanced efficacy of bentazone to three weed species.

CONCLUSIONS

On the basis of results after two years investigations, it can be concluded that the developed ecofriendly crop oil concentrate with esterified rape seed oil (A2) had stronger beneficial effects on bentazone efficiency than soluble concentrate of surfactants (Trend®90). The crop oil concentrate enhanced efficacy of bentazone to weed species *H. annuus, A. theophrasti* and *A. artemisiifolia*. The main advantages in using crop oil concentrates is that both the oil and surfactant are expected to contribute to the biological activity and good effects can be achieved with relatively low surfactant concentration, which in the case of developed oil concentrates was only 10-15%, compared to Trend®90 where there are 90% of surfactants. It is worth to mention that the adjuvants formulated as COCs using vegetable oils lead to the use of safer and more environmentally friendly products with good biodegradability and low toxicity. Having in mind increasing pressures on product performance, adjuvants are becoming a way for optimisation and better use of present pesticide products. Further studies are needed to determine the most suitable bentazone rate with the crop oil concentrates that could be used to successfully manage the weeds.

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