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Nota/Note

Physical characteristics of insecticide spraying liquids with mineral oil and droplets formed on citrus leaves

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SUMMARY

The physical characteristics of a spray liquid are important in getting a good droplet formation and efficiency control over a target pest. These characteristics can be changed in various ways, the addition of mineral oil can be one of them. Thus, the aim of this study was to evaluate the physical characteristics of the surface tension of the diflubenzuron insecticide using different mineral oils in two concentrations and the interaction of droplets produced on the leaf surface of orange through the formed contact angle. Therefore, seven spraying liquids were prepared composed of diflubenzuron, often used in citrus for insect pest control, and three mineral oils (Argenfrut®, OPPA® and Nimbus®) in two concentrations (0.25 e 0.5% v/v). Pendant droplets formed from these mixtures were measured to examine their impact on surface tension. Droplets were applied to the surface of orange leaves and the contact angle formed were measured. The addiction of the mineral oil to diflubenzuron reduce the surface tension and contact angles of droplets on leaf surfaces, resulting in a large surface area covered. Among the evaluated mineral oils, OPPA® and Nimbus® showed greater reduction in surface tension and smaller droplets contact angles on the orange leaf. Therefore, the application of the diflubenzuron with OPPA® or Nimbus®, at concentrations of 0.25 and 0.50%, provide a better spreadability of the sprayed droplets.

Index terms: contact angle, surface tension, spreading.

Características físicas de calda inseticida com óleo mineral e gotas formadas sobre folhas de citros

RESUMO

As características físicas de um líquido pulverizado são importantes afim de obter boa formação de gotas e eficiência de controle sobre um determinado alvo. Essas características podem ser alteradas de diversas formas, a adição de óleo mineral pode ser uma delas. O objetivo desse trabalho foi avaliar as características físicas da tensão superficial do inseticida diflubenzuron utilizando diferentes óleos minerais em duas concentrações, e a interação das gotas produzidas na superfície foliar de laranja através do ângulo de contato formado. Portanto, foram preparadas sete caldas fitossanitárias compostas pelo inseticida diflubenzuron, comumente utilizado em citros para o controle de insetos praga e três óleos minerais (Argenfrut®, OPPA® e Nimbus®) em duas concentrações (0,25 e 0,5% v/v). Gotas pendentes formadas a partir dessas misturas foram medidas

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em sua tensão superficial. Aplicaram-se gotas sobre a superfície de folhas de laranja e foi medido o ângulo de contato formado pela gota. A adição de óleo mineral ao diflubenzuron reduziu a tensão superficial e ângulo de contato das gotas com a superfície foliar, resultando em uma maior cobertura. Entre os óleos minerais avaliados, OPPA® e Nimbus® apresentaram maior redução na tensão superficial e ângulos de contato menores formados com a folha de laranja. Portanto, a aplicação de diflubenzuron com OPPA® ou Nimbus®, nas concentrações de 0,25 e 0,50%, proporciona uma melhor capacidade de espalhamento das gotas pulverizadas.

Termos de indexação: ângulo de contato, tensão superficial, espalhamento.

INTRODUCTION

Brazilian citrus production is highly dependent on plant protection products due to the large amount of pests and diseases that occur in orchards. At that, farmers have adopted the chemical control (insecticides and acaricides) to reduce the population of the pests and decrease damages and harms, besides avoiding the transmission of phytopathogens (Yamamoto et al., 2009).

The importance of pests in the citrus culture leads farmers to perform successive applications in the areas and with high volumes of application, elevating the final production cost, which shows the need for basic studies involving the aspects of the application technology (Barbosa et al., 2013).

The diflubenzuron insecticide has been used to control *Phyllocoptruta oleivora* (Ashmead) (Acari: Eriophyidae), *Phyllocnistis citrella* Stainton (Lepidoptera: Gracillariidae) and *Diaphorina citri* Kuwayama (Hemiptera: Liviidae). The latter is the vector of huanglongbing (HLB, ex-greening), a disease that destroys citrus production. Diflubenzuron is a physiological insecticide/acaricide that belongs to the benzoylurea chemical group, acts through contact and intake and is formulated in concentrated suspension.

The high volumes used in insecticide application, up to the point of runoff of the leaf, are often used. This means of application can cause serious economic and environmental issues. According to Taylor (2011), the spray retention is controlled by a series of factors, among them: the dynamic surface tension of the solution sprayed, the surface properties of the leaf and the contact angle of the droplet in the leaf surface, and the type of adjuvant and volume of application.

Adjuvants are substances without phytosanitary properties added in a preparation to make the application easier, raise efficiency and reduce risks (Kissmann, 1998). The utilization of certain adjuvants can effectively improve the biological efficiency of insecticides. However, this improvement is not valid for all adjuvants – the product used and the biological target must be taken into account (Arrué et al., 2014). Adjuvants such as plant, mineral oils, or oil derivatives in the solution can raise the efficiency in the control of pests and diseases, since it protects the applied solution from unfavorable weather conditions, or improving the interaction between the solution and the target (Andrade Junior et al., 2010).

Besides, adjuvants can help reduce the volume of application, since it is known that the use of oils provide decrease of the maximum amount of liquid that the leaves can retain, contributing to a reduction of the solution volume used in sprays in the citrus production (Barbosa et al., 2013). However, the use of smaller solution volumes raises the autonomy and the operational capacity of sprayers (Cunha et al., 2005), and consequently reduces the cost of application, generating economy to the farmers.

One of the important factors that helped the retention of the solution in the target is the wetting, which is influenced by the surface tension. The surface tension of the droplets and its interaction with the target surface influence not only the wetting, but also the absorption process, what is fundamental for the effectiveness of the application (Cunha et al., 2017). The oils help the spreading and the absorption, reducing the degradation of active ingredients and the surface tension (Mendonça et al., 2007). On natural targets, the greatest wetting levels with water solutions were obtained through the smallest surface tensions and contact angles of the droplets (Iost & Raetano, 2010).

Thus, the aim of this study was to evaluate the physical characteristics of the surface tension of the diflubenzuron insecticide using different mineral oils in two concentrations and the interaction of droplets produced on the leaf surface of orange through the formed contact angle.

MATERIAL AND METHODS

Seven different spraying liquids were prepared. The compositions of these spraying liquids were the insecticide diflubenzuron (Micromite®) and three mineral oils (84.57 m/v - Argenfrut®; 90.00% m/v - OPPA®

and 42.80% m/v - Nimbus®) in two concentrations (0.5 e 0.25% v/v).

These different spraying liquids were analyzed on their physical characteristics when in contact with the adaxial surface of sweet orange of variety Valência [*Citrus sinensis* (L.) Osebeck cv. Valência] leaves and in contact with a comparatively smooth glass surface. Physiologically active citrus leaves were collected with the use of surgical gloves to avoid contact of skin oils with leaves.

Assessment of the results

The surface tension of the spraying liquids utilized in the experiment, as well as the contact angle by the applied droplets on the surface of citrus leaves and smooth glass, were assessed using a tensiometer equipment, Contact Angle System model OCA 15 EC/B, from Dataphysics enterprise. The tensiometer was equipped with a CCD high speed, high definition camera, which captures droplet formation with the aid of SCA20 software used for the automation of the equipment and handling of images obtained on a computer. For the surface tension analysis, pendant droplets were formed at the end of a needle (0.52 mm in external diameter) attached to a Hamilton® syringe (graduated until 5 µL of volume) which in turn was attached to the tensiometer.

For each spraying liquid, four pendant droplets were formed and analyzed by the software according to the Young-Laplace equation. Surface tension values expressed as mN.m-1 unit were then obtained. For the analysis of contact angle by droplets, the collected citrus leaves were cut into rectangles of about 5 cm^2. These were set in a press in such a way so their adaxial surfaces were facing upward, before droplets of each spraying liquid were deposited. Images were captured every second for 60 seconds. On the smooth surface of glass, the variable of contact angle was also determined in relation to the application of droplets. An automatic device applied to the tensiometer determined movements on the syringe plunger that dispensed droplets both on the citrus leaves and the glass surface, so as to allow for the analysis of the contact angle. Once the whole droplet volume was dispensed on the surfaces, the syringe was rapidly retracted from the camera focus so the contact angle measurement could begin.

For the contact angle analysis, droplets were dispensed in the fixed volume of 3 µL, while for surface tension analysis pendant droplets of 4 µL was used. These volumes were selected in the experiment to provide better quality droplet images by the software camera, without influencing the spraying liquid's characteristics. For all variables, values for the 5 seconds (5s), 30 seconds (30s) and 60 seconds (60s) were obtained and compared.

Experimental design

The analysis followed a randomized factorial design 7 × 3, representing 7 treatments (spraying liquids) in three different times (5s, 30 and 60s) with four replicates, for surface tension and contact angle variables, measured separately. The means of the variables were subjected to analysis of variance and compared using the multiple comparisons Tukey test to the level of 5% probability.

RESULTS AND DISCUSSION

Surface tension

Significant differences were found between the treatments ($F = 903.37$; $p < 0.0001$) and the interaction of factors ($F = 34.01$; $p < 0.0001$) evaluated for the surface tension values obtained in the tensiometer. Pending droplets from the six treatments, composed by the combination of diflubenzuron and mineral oils, presented a difference regarding the control treatment (diflubenzuron without oil). The surface tension was higher for diflubenzuron and smaller for the combination of diflubenzuron and Nimbus® in the two concentrations tested at five seconds (Table 1).

At 30s, the highest surface tension observed was for diflubenzuron, while the smaller values were observed for the combinations of diflubenzuron and Nimbus® and OPPA® oils in both concentrations. At 60s, the treatments presented the same behavior than at 30s (Table 1).

Comparing the surface tension values throughout the period evaluated, these were decreasing for all treatments. This surface tension variation throughout the 60s occurs due to the energy balance among solids, liquids and gases, tending to a balance of forces, and the use of adjuvants significantly affects this balance (Decaro Junior et al., 2015).

The surface tension refers to the existing forces in the interface of non-mixable liquids, stopping them from mixing with each other (Azevedo, 2001). Based on the results observed, it can be inferred that the addition of mineral oil to the Diflubenzuron insecticide reduces the connection force among molecules, reflecting in smaller surface tension values.

Table 1. Values in $mN.m^{-1}$ of droplets surface tension from the different spraying liquids at different moments of measurement

Spraying liquids	5s	30s	60s
Diflubenzuron + 0,5% Argenfrut®	67.79Ba[a]	52.72Bb	46.37Bc
Diflubenzuron + 0,25% Argenfrut®	63.96Ca	47.92Cb	40.86Cc
Diflubenzuron + 0,5% OPPA®	43.37Da	36.01Db	34.44Db
Diflubenzuron + 0,25% OPPA®	42.36Da	35.09Db	33.49Db
Diflubenzuron + 0,5% Nimbus®	36.91Ea	35.30Dab	33.83Db
Diflubenzuron + 0,25% Nimbus®	35.87Ea	34.10Dab	33.08Db
Diflubenzuron	72.10Aa	65.54Ab	61.75Ac
MSD[b]		3.09	
MSD[c]		2.43	
Média	51.77a	43.81b	40.55c
MSD		0.92	
CV		3.16	

[a]Means followed by the same lower case letter on the column and uppercase letter on the line does not differ by Tukey test (p>0.05). Minimum significant difference for columns[b] and lines[c].

Table 2. Degree values of contact angle formed by droplets applied on adaxial citrus leaves surface, using the different spraying liquids at different moments of measurement

Spraying liquids	5s	30s	60s
Diflubenzuron + 0,5% Argenfrut®	79.71ABa[a]	69.98ABb	66.41ABb
Diflubenzuron + 0,25% Argenfrut®	70.25BCa	63.39BCab	59.57BCb
Diflubenzuron + 0,5% OPPA®	60.34DEa	52.33Db	51.17Db
Diflubenzuron + 0,25% OPPA®	67.11CDa	55.10CDb	51.43CDb
Diflubenzuron + 0,5% Nimbus®	58.81DEa	51.06Dab	47.74Db
Diflubenzuron + 0,25% Nimbus®	55.69Ea	52.28Dab	44.72Db
Diflubenzuron	81.39Aa	76.13Aa	73.88Aa
MSD[b]		9.84	
MSD[c]		7.76	
Média	67.64a	60.04b	46.42c
MSD		2.93	
CV		7.45	

[a]Means followed by the same lower case letter on the column and uppercase letter on the line does not differ by Tukey test (p>0.05). Minimum significant difference for columns[b] and lines[c].

Foliar surface

Contact angle

Significant differences were found between the treatments (F = 59.16; p < 0.0001) and the evaluation times (F = 43.98; p < 0.0001). However, there was no interaction between the two factors (F = 0.61; p = 0.8224) for the contact angle values obtained regarding the citrus leaf. At 5s, diflubenzuron and diflubenzuron + Argenfrut at 0.5% had no difference and presented the highest values of contact angle formed with the leaf. The smallest values were obtained with the combination of diflubenzuron and Nimbus®, in both concentrations, and diflubenzuron and OPPA® in the larger concentration (Table 2).

At 30s and 60s, the treatments presented the same behavior as presented at 5s (Table 2). The contact angle values of each treatment decreased throughout the evaluation, presenting higher values for the first 5s, except for diflubenzuron without mineral oil, which was stable throughout the evaluation.

Droplets with smaller contact angles have their contact surface with the larger biological target, and consequently, higher coverage of this target (Queiroz et al., 2008).

According to Mendonça et al. (2007), the wetting area is correlated to the surface tension of the solution, to the type and to the dosage of the surfactant that composes the commercial product, in addition to the ultrastructure features (presence or absence of epicuticular wax) of the leaf surface.

Moita Neto (2006) observed that droplets with contact angle smaller than 90º formed with the surface can characterize this surface as hydrophilic, that is, the surface got wet by the liquid. Therefore, the droplet applied is more widespread over the surface, and it may even form an uniform film (Iost & Raetano, 2010). Iost & Raetano (2010), aiming to evaluate the effect of surfactants in water solutions over the dynamic surface tension and contact angle of the droplets in artificial and natural surfaces, checked that in natural surfaces the highest levels of wetting with water solutions were obtained through smaller surface tensions and contact angles of the droplets.

As observed in this experiment, oils with proportion of 90.00% (OPPA®) and 42.80% (Nimbus®) in their formulation were the ones which provided better physical features to the droplets. It is known that commercial mineral oils have non-phytotoxic oil and surfactants in their formula, both of which have their proportions indicated on the labels of the products. However, companies do not indicate the type of adjuvant used as emulsifier in the formulation of these oils (Queiroz et al., 2008). Since these emulsifiers also determine some physical and chemical features of the spray solution, such as the surface tension, we cannot infer that, in this case, the proportion of oil in the formulations was the only factor that determined the physical features of the droplets – they could also be influenced by the surfactants used in the formulations.

In summary, when adding mineral oil to the diflubenzuron solution, the surface tension decreases, the area covered by one droplet is larger, replacing a certain amount of smaller droplets that was formed by the solution without oil. Corroborating with the results from Decaro Junior et al. (2015), which observed that it would be necessary 40% less droplets from a profenofos solution with 12.50% of oil (863 mm^2 per droplet) to completely cover the same surface area of a coffee leaf when only water is applied (1.42 mm^2). Therefore, this ratio must be used to determine the application volume, because high volume applications commonly used in citrus culture could lead the coverage to the wetting level in the leaves. Barbosa et al. (2013), aiming to determine the retention capacity of the solution by citrus leaves, checked that, with the addition of mineral oil to the solution, 0.09 mg i.a. m^{-2} of leaf area would be retained from the acaricide. If plant oil is added, the acaricide retention would be 0.19 mg i.a. m^{-2} of the leaf. If the first amount is enough to control a given pest, it can be admitted that in the last case scenario there will be a superdosage happening. On the other hand, if 0.09 mg i.a. m^{-2} is considered enough, the solution volume used could be reduced, avoiding waste.

Xu et al. (2011) showed in a study that the use of adjuvants can significantly improve physical features of the sprayed solution and, consequently, raise the wet area in the surface of the target in question. These alterations of the physical features of the solution regarding the surface tension and contact angle of the droplet with the target result in economical and environmental benefits, since it allows the adoption of smaller application volumes, avoiding wastes (excessive volumes) and helping reduce environmental contamination.

CONCLUSION

Mineral oils mixed with diflubenzuron reduce the surface tension of the droplets and result in smaller contact angles of the droplets with the citrus leaves surface. The application of the diflubenzuron with OPPA® or Nimbus®, at concentrations of 0.25 and 0.5%, provide a better spreadability of the sprayed droplets.

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