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facts

Xanthan Gum and Triethyl Citrate
as green adjuvants
to improve spray applications in agriculture

Introduction

Production methods need to be highly efficient if they are to meet the ever increasing demand for agricultural goods for the food, feed and fibre industries. Therefore, pesticides and fertilisers are applied frequently along with adjuvants that support the performance of the active agent. Adhesives, surfactants, humectants, stabilisers and drift control agents (DCA) are often incorporated in spray applications to prevent a loss in efficacy at all stages of delivery. For example, wind-driven aerial displacement and evaporation can account for a loss of up to 50% in the total amount of spray the farmer applies to his fields (Pimentel and Burgess, 2012). In addition, drifting agrochemicals can damage susceptible plants on neighbouring fields and have a devastating impact on adjacent ecosystems. For this reason, ever stricter regulations on the use of agrochemical sprays are being implemented. These facts emphasise the importance of adopting both drift control and performance-enhancing measures to ensure efficient target coverage and high activity on the leaf.

Adjuvants in spray applications for drift control

With regard to spray drift, apart from meteorological conditions such as wind, temperature and relative humidity, droplet size is a crucial factor for risk management. On a warm day with a light breeze, a fine spray droplet measuring 70 microns is carried for roughly 10 metres after leaving the spray nozzle (Ozkan and Zhu, 2016). Under the same conditions, an even finer droplet measuring 50 microns will evaporate completely before covering a distance of 50 cm. Optimising droplet size is therefore highly important in agricultural sprays.

A variety of factors influence droplet size in sprays, such as the application equipment (especially nozzle design), operating parameters (spray pressure, driving speed) and the physiochemical characteristics of the spray liquid itself. To control the latter, synthetic or natural polymers are commonly applied as drift control agents (DCAs). These enhance the elongational viscosity of the liquid, thus preventing breakaway of very fine droplets. This shifts the volumetric mean diameter (VMD) to higher values and reduces the fraction of droplets below 150 microns, commonly defined as “driftable fines” (Lewis et al. 2016).

Long chain polyacrylamide, polyvinyl or poly(ethylene oxide) polymers are often used as a synthetic option. However, their limited mechanical stability is a major drawback. The recirculation system in the spray tank confers high shear rates, breaking down the polymers and rendering them inefficient during the spraying process (Lewis et al., 2016; Hilz et al., 2013). Furthermore, their limited biodegradability and the fact that they are produced using non-renewable resources are important environmental issues. The polysaccharide xanthan gum has been applied as a DCA, being a natural alternative derived from microbial fermentation of renewable materials. It offers high mechanical stability, complete biodegradability, stability over a range of physical and chemical conditions and high compatibility with chemical and biological active agents.

Adjuvants for improved performance on the leaf

Once the spray liquid has been delivered to the target surface successfully, its further properties become relevant. To reduce bouncing or rolling off the leaf, adjuvants that increase adhesion are commonly added – and this task can be fulfilled by xanthan gum. Wetting of the hydrophobic leaf surface is commonly improved by adding non-ionic surfactants, many of which are petrochemical in origin such as ethoxylates (Castro et al., 2013). As an efficient, green alternative, CITROFOL® AI may be applied. This brand name stands for triethyl citrate, an ester of citric acid, which has been investigated as an adjuvant in agriculture (Johnson et al., 2002).

Trial objectives

The combination of xanthan gum and CITROFOL® AI has the potential to overcome many challenges in the spray delivery of active agents – from the tank mix, through the nozzle and on to the plant surface. In our trials, we investigated the influence of these two bio-based adjuvants on relevant properties in agricultural spray, such as droplet size and range, wettability, adhesion and moisture retention.

Evaluation of spray deposition and droplet size distribution

In respect of the spray formation process, the pattern and deposition on the target site were checked by spraying water-sensitive yellow collector cards with solutions of xanthan gum and CITROFOL® AI in different concentrations and ratios. Due to the special coating of the cards, aqueous droplets leave dark blue stains on the yellow background, which allows for a straightforward visual evaluation of the spray coverage. The spray was applied by positioning an airbrush gun with a 0.55 mm nozzle, at a distance of 1 metre, perpendicular to the collector cards and spraying at a pressure of 2 bar for 5 seconds. The target coverage was determined by ImageJ software (Rueden et al., 2017). The volume throughput was measured gravimetrically, with the solution reservoir weighed before and after 30 seconds of spraying.

Droplet size distribution in the different spray compositions was measured by a PDPA (Phase Doppler Particle Analyser) laser-based system in cooperation with the Institute for Agricultural and Fisheries Research (ILVO, Merelbeke, Belgium). Using this approach, droplet size – an important parameter in drift control – can be determined precisely. The measurements were performed using a standard flat fan nozzle (TeeJet XR110 03) at a height of 50 cm, employing a pressure of 3 bar, at ambient temperature of 20°C and relative humidity of 65–70%.

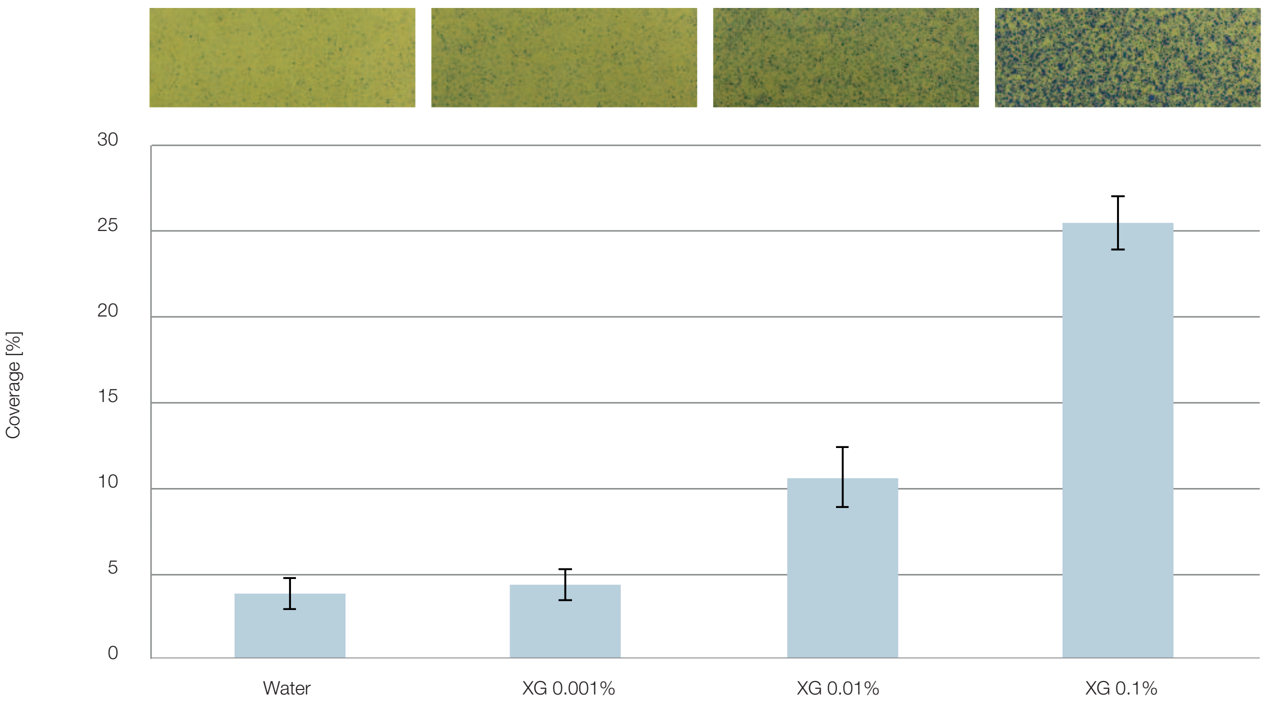
Evaluation of performance on the leaf

Following deposition on the leaf, a range of additional parameters influence the efficacy of the spray treatment and were thus investigated next. Enhanced wettability was demonstrated by measuring the contact angles of droplet silhouettes on a waxy model surface (Parafilm®), simulating the hydrophobic leaf surface. The adhesion of droplets to the same model surface was observed on a tiltable platform, determining the angle of inclination when the droplet rolled off (the "roll-off angle"). To estimate moisture maintenance, the end point of drying at 40°C was determined gravimetrically. Suspension stability was evaluated by determining gravimetrically the amount of model particles (zeolite 0–25 µm) in the supernatant of the different spray compositions.

Results: Spray coverage and drift control

Both xanthan gum and CITROFOL® AI had profound effects on the different parameters investigated. Looking at the target coverage when spraying pure water onto the collector cards, the total covered area was as low as 4% (figure 1). However, the addition of 0.01% (w/v) xanthan gum significantly changed this picture, resulting in a total coverage of 11%. Further increasing the amount of xanthan gum to 0.1% extended coverage to 25% – a remarkable fivefold improvement compared to the water spray.

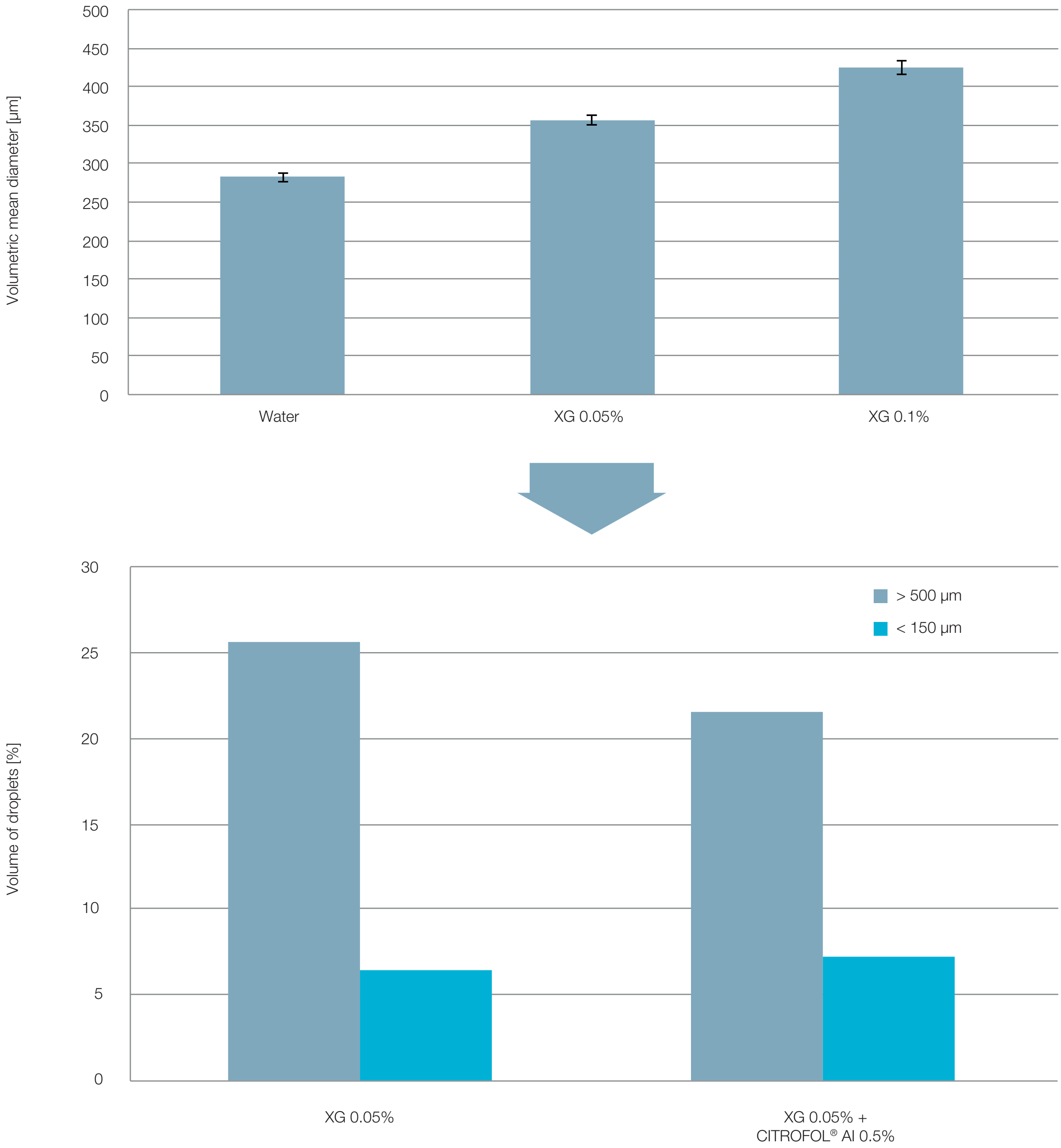
Figure 1: Increasing xanthan gum (XG) concentration in spray application enhances the mean coverage (n=3) of collector cards. Images of the collector cards are shown above the corresponding bars.



Measuring the throughput of the spray system revealed that approximately 10 mL of water were sprayed within 1 minute. With pressure and time unchanged, the addition of 0.1% xanthan gum led to an increase of sprayed volume to 14 mL. This 40% increase in spray liquid throughput can probably be ascribed to the fact that xanthan gum enhances the viscosity of the spray liquid, thus delaying the breakaway of droplets from the spray jet (Spanoghe et al., 2007). This also leads to the formation of coarser droplets, which are less prone to loss by evaporation on their way from the nozzle to the collector paper.

To take a closer look at the relationship between xanthan gum addition and droplet size, we employed a PDPA laser-based measuring system. The results obtained were in line with observations on the collector papers: the addition of xanthan gum shifted the droplet size range to higher values, producing on average coarser droplets. More precisely, increasing xanthan gum concentrations enhanced the VMD (volumetric mean diameter) of droplets, a common risk indicator for drifting, from 282 µm for pure water to 356 µm for xanthan gum 0.05% and 424 µm for xanthan gum 0.1% (figure 2). Depending on the operating conditions, standard polymeric DCAs enhance the VMD by between 11 and 119% (Spanoghe et al., 2007) – and xanthan gum can compete with these values. The volumetric fraction of driftable fines (< 150 microns) was reduced by 35% when using 0.05% xanthan gum instead of pure water, and by 50% when using 0.1% xanthan gum.

Figure 2: Volumetric mean diameter (VMD) in spray depending on xanthan gum (XG) concentration and corresponding fraction of oversized and driftable droplets with and without CITROFOL® AI



However, to get the full picture, the droplet size distribution needs to be considered in addition to the VMD. For drift control, the primary objective is to eliminate the fraction of droplets below 150 µm. While a limited fraction of oversized droplets over 500 µm might even have advantages, the majority of droplets should lie within a rather narrow range of 150–500 µm to achieve homogeneous coverage (table 1). This is where CITROFOL® AI comes into play: in combination with a threshold concentration of 0.05% xanthan gum, CITROFOL® AI maintained a low fraction of driftable droplets while at the same time lowering the amount of oversized droplets compared to xanthan gum alone. In other words, the addition of CITROFOL® AI reduced the droplet size spectrum, placing it nearer to the desirable range of 150–500 µm. CITROFOL® AI proved therefore a valuable partner in combination with xanthan gum, which by itself was responsible for a general upward shift in droplet size range.

Table 1: Suitable droplet sizes in agricultural sprays

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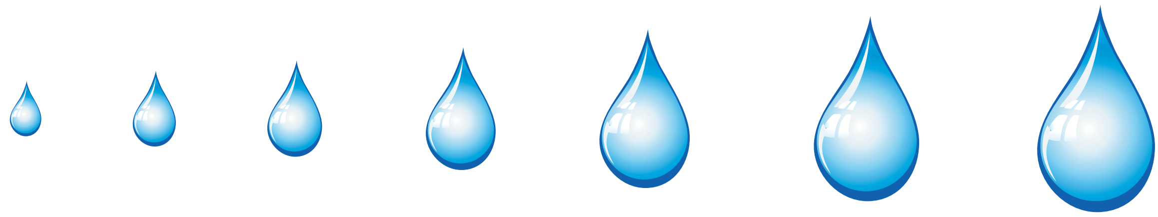
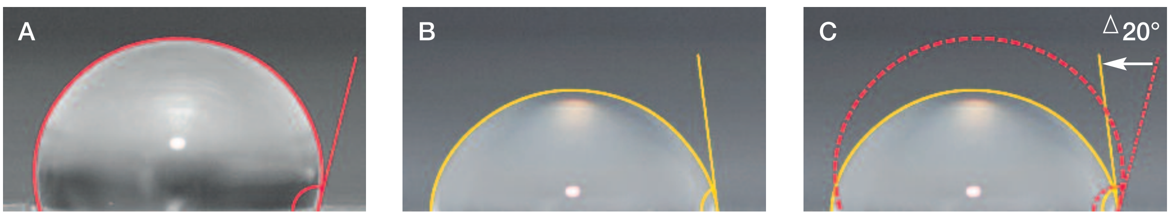


< 150 µm	50–500 µm	> 500 µm
⊕ Homogeneous coverage also on leaf lower side	⊕ Uniform coverage ⊕ Reduced loss by dripping off the plant ⊕ Low susceptibility to drift under normal conditions	⊕ Cuticle disruption upon impact: better uptake? ⊕ Slower evaporation: better uptake? ⊕ Highly concentrated spots: increased efficacy of insecticides
⊖ Highly susceptible to drift and evaporation		⊖ Less uniform coverage ⊖ Risk of bouncing or dripping off the leaf

Results: Wettability on the leaf

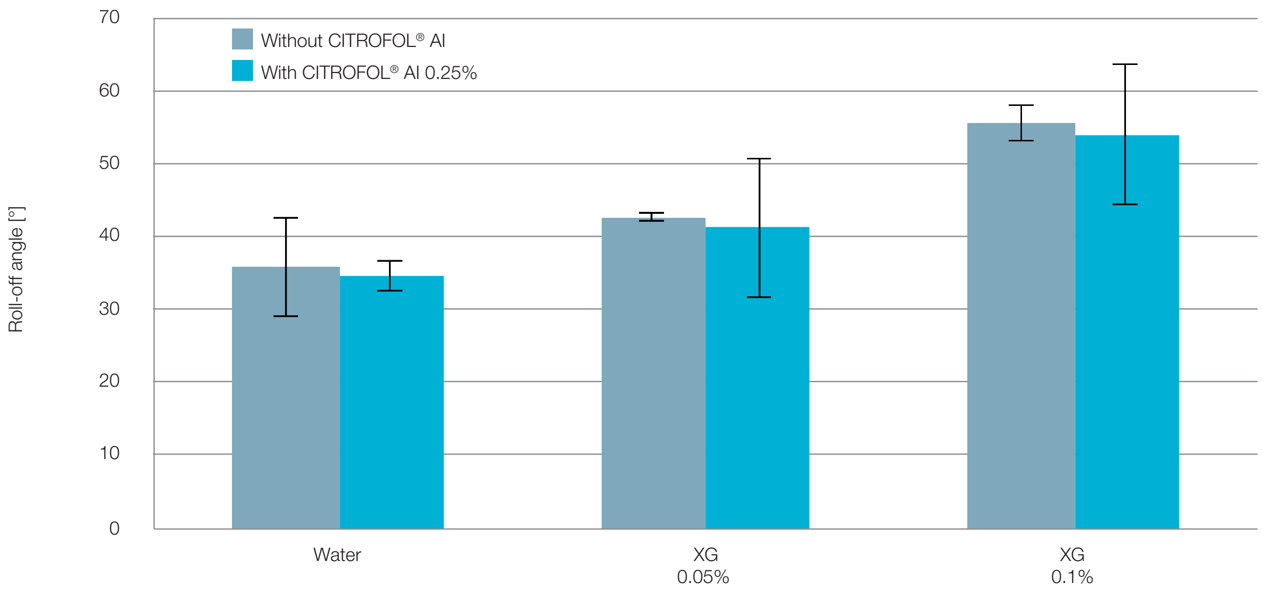
An important issue in agricultural spray application is the interaction of the formulation with the plant's leaf surface. Wetting agents and adhesives are often incorporated as adjuvants in order to ensure good spreadability on the hydrophobic leaf surface and to prevent dripping off. Trials showed that xanthan gum in combination with CITROFOL® AI can meet these requirements. The contact angle as an indicator for wettability was reduced from approximately 100° to 80° when adding CITROFOL® AI in concentrations as low as 0.25% (v/v), thus achieving a 20% improvement in wettability (figure 3).

Figure 3: Silhouette of droplets of XG 0.5% (A), XG 0.5% + CITROFOL® AI 0.25% (B) and a direct comparison of both (C). The contact angle is reduced from approximately 100° to 80° with the addition of CITROFOL® AI.



While this parameter was relatively independent of xanthan gum concentration, the adhesion of droplets was largely dependent on the amount of xanthan gum. Observing the movement of a drop along a tiltable surface, the roll-off angle was enhanced from 35° to 43° in the presence of 0.05% xanthan gum, and to 55° with 0.1% xanthan gum (figure 4). CITROFOL® AI had no effect on adhesion.

Figure 4: Roll-off angle of a droplet on a tiltable platform depending on xanthan gum (XG) concentration and the addition of CITROFOL® AI 0.25%



Results: Moisture retention

The penetration of active agents in the formulation may further be supported by the retention of moisture. When comparing the drying kinetics of pure water to an aqueous solution of xanthan gum and CITROFOL® AI, we observed that the latter samples dried much more slowly: the end point of drying was delayed by around 10% when adding CITROFOL® AI 0.25%, and by up to 15% when adding CITROFOL® AI 0.25% and xanthan gum 0.1%. Obviously, this moisture retention is also advantageous for drift control: slowing the evaporation of droplets during their passage through the air prevents losses before they even reach the plant surface.

Results: Stabilisation of suspension concentrate

Finally, an important aspect in agricultural formulations is their stability. The settling of particles can be an issue, especially when dealing with suspension concentrates, leading to blockage of the spraying equipment and inhomogeneous delivery of active agents to the plant. A high loading of suspended particles can be obtained when adding xanthan gum as a stabiliser, maintaining a homogeneous distribution of particles in the concentrate over extended periods of time.
For example, zeolite particles (size range 0–25 μm) were completely prevented from settling in a 0.5% solution of xanthan gum over one day.

Conclusion

Our trials confirmed the high potential of xanthan gum and CITROFOL® AI as adjuvants in agricultural sprays. Xanthan gum can prevent off-target drift by decreasing the fraction of driftable fines in sprays. It further improved the stability of suspension concentrates, the cling to leaves and moisture retention in concentrations as low as 0.05% (w/v). CITROFOL® AI can improve performance on the leaf by increasing wettability and slowing down evaporation when used in concentrations between 0.25 and 0.5% (v/v). Therefore, both materials constitute a promising alternative to synthetic adjuvants, meeting the growing demand for bio-based, biodegradable solutions for agriculture.

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