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REVIEW

Advances in surfactants for agrochemicals

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Abstract Pesticide efficacy is improved by surfactants. Increase in the foliar uptake is particularly useful for herbicides, growth regulators and defoliants, because less active compounds are needed, thus decreasing cost and pollution. Therefore, the choice of the adjuvant in an agrochemical formulation is crucial. The surfactants commonly used as adjuvants include anionic, non-ionic, amphoteric and cationic surfactants. This review analyses the role and properties of the new adjuvants for agriculture and the improvement of the ecotoxicity profile of the pesticide formulations in glyphosate formulation.

Keywords Surfactant formulation · Pesticide · Agriculture · Adjuvant · Glyphosate · Plant cell

Introduction

The world population is projected to continue increasing in the next century. Population growth is assumed to follow the United Nation medium projection, leading to about 10 billion people by 2050. A central question is how global food production may be increased to provide for the coming population expansion. It would be necessary to increase the current levels of food production more than proportional to population growth so as to provide most humans with an adequate diet (Kindall and Pimentel 1994).

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The agricultural breakthrough occurred during recent decades by the incorporation of new laboratory techniques, statistics, computer science and satellite information, and crop modified by genetic engineering produced a huge increase in yields per hectare of different crops. Finally, the fight against pests and weeds through pesticides is of paramount importance within the modern agricultural activity.

Agrochemical formulations require the use of a surface-active agent or surfactant, which is not only essential for its preparation and maintenance of long-term physical stability, but also essential for enhancing biological performance of the agrochemical, increasing the foliar uptake of herbicides, growth promoters and defoliants (Fig. 1).

The global pesticide production in 2000 amounted to over three million tons of active ingredients (Tilman et al. 2002). It is estimated that of the total amount of pesticides used for weed and pest control, only a very small part (<0.1 %) actually reaches the sites of action, with the larger proportion being lost via spray drift, off-target deposition, run-off, photodegradation and so on (Pimentel 1995).

Around 230,000 tonnes of surfactants is used annually in agrochemical products, with a formulation typically containing 1–10 % of one or more surfactants (Edser 2007). Surfactant, as a plasticizer, softens the crystalline waxes in cuticle and thus increases the mobility of the agrochemicals across the cuticular membrane (Schönherr et al. 2000).

The development of new surfactant-based system as bioactivator for actives is a key factor to improve the cost-effective performance increasing process efficiency, energy and raw material savings. Finally, sustainability should take into account the use of renewable resources and the improvement of eco-friendly product profile. This article is an abridged version of the chapter of Surfactants in Agriculture (Castro et al. 2013).

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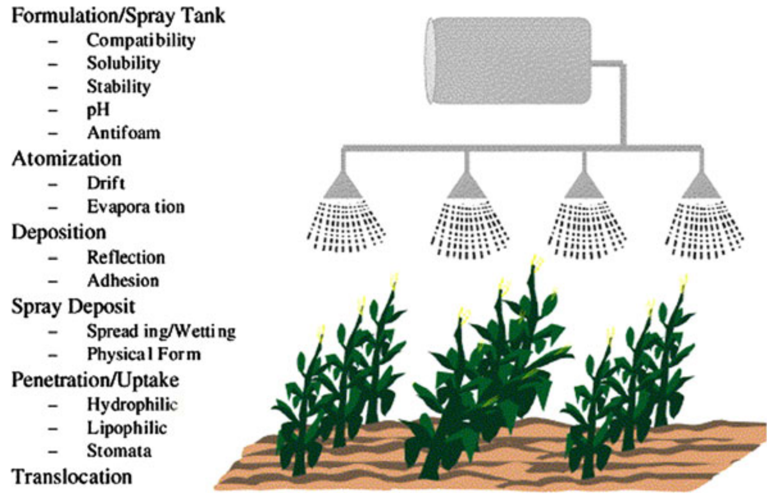


Fig. 1 Influence of formulation and adjuvants on herbicide performance. Reprint from Green and Beestman (2007)

Types of surfactants

Surface-active agents have a characteristic molecular structure consisting of a structural group that has a very little attraction for water, known as a hydrophobic group, together with a group that has strong attraction for water, called hydrophilic group. This is known as an amphiphilic structure. The hydrophobic group is usually a long-chain hydrocarbon, and the hydrophilic group is an ionic or highly polar group. According to the nature of the hydrophilic group, surfactants are classified as follows: anionic, cationic, nonionic and amphoteric (Fernández Cirelli et al. 2008).

Anionic surfactants

The hydrophilic groups of anionic surfactants consist in most cases of sulphonate, sulphate or carboxylate groups with either a sodium or a calcium as counterion (Table 1). Among them, linear alkylbenzene sulphonates (LAS) are produced in the largest quantities worldwide. These are mainly used in powdery and liquid laundry detergents and household cleaners. It is important to point out that calcium linear alkylbenzene sulphonate is employed as adjuvant in many agrochemical formulations.

Non-ionic surfactants

The hydrophilic behaviour of non-ionic surfactants is caused by polymerized glycol ether or glucose units (Table 1) (Fernández Cirelli et al. 2008). They are almost exclusively synthesized by the addition of ethylene oxide or propylene oxide to alkylphenols, fatty alcohols, fatty acids, fatty amines or fatty acid amides. Non-ionic surfactants found major applications as detergents, emulsifiers, wetting agents and dispersing agents. They are used in many sectors, including household, industrial and institutional cleaning products, textile processing, pulp and paper processing, emulsion polymerization, paints, coatings and agrochemicals. A large amount of them are employed as adjuvant in many agrochemical formulations.

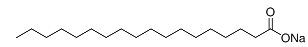
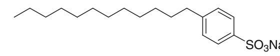
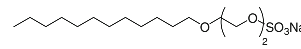
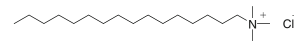
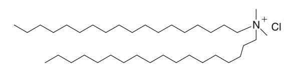
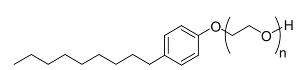
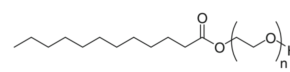
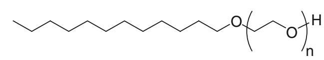
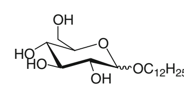
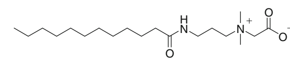
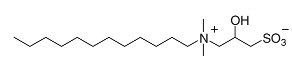
Cationic surfactants

Cationic surfactants contain quaternary ammonium ions as their hydrophilic parts (Table 1). This class of surfactants has gained importance because of its bacteriostatic properties. Therefore, cationic surfactants are applied as disinfectants and antiseptic components in personal care products and medicine. Because of their high adsorptivity to a wide variety of surfaces, they are used as antistatic agents, textile softeners, corrosion inhibitors and flotation agents.

Amphoteric surfactants

Amphoteric surfactants containing both cationic and anionic group in their structure sometimes are referred to as zwitterionic molecules (Table 1). They are soluble in water and show excellent compatibility with other surfactants, forming mixed micelles. The change in charge with pH of amphoteric surfactants affects wetting, detergency, foaming, etc. The properties of amphoteric surfactants resemble those of non-ionics very closely. Zwitterionic surfactants have excellent dermatological properties, they also exhibit low eye irritation and are frequently used in shampoos and other personal care products. Amphoteric surfactants are now starting to be used in agrochemical formulations.

Table 1 General classification and characteristic features of surfactants

Surfactants	Alkyl tail	Polar head	Example
Anionic	C_8–C_{20} linear or branched chain	–COOH	 Soap
	C_8–C_{15} alkylbenzene residues	$–SO_3Na$	 LAS
	C_8–C_{20} linear–chain ethoxylated	$–OSO_3Na$	 LES
Cationic	C_8–C_{18} linear chain	$–N(CH_3)_3Cl$	 CTAC
	C_8–C_{18} linear chain	$–N(CH_3)_2Cl$	 DODAC
Non-ionic	C_8–C_9 alkylphenol residues	$–(CH_2CH_2O)_n–OH$ n: 4–22	 APEO
	C_8–C_{20} linear or branched chain	$–COO(CH_2CH_2O)_n–OH$ n: 4–22	 FAEO
	C_8–C_{20} linear or branched chain	$–(CH_2CH_2O)_n–OH$ n: 2–22	 AEO
	C_8–C_{20} linear or branched chain	$–NH(CH_2CH_2O)_n–OH$ n: 2–22	
	C_8–C_{20} linear or branched chain	Glucose	 APG
Amphoteric	C_{10}–C_{16} amidopropylamine residue	$–N^+(CH_2)_2CH_2COO^-$	 (CAPB)
	C_8–C_{18} linear chain	$–N^+(CH_2)_2CH_2CH(OH)CH_2SO_3^-$	 (CAHS)

Efficiency parameters to increase the performance of agrochemicals

Cuticular uptake

One of the most important ways to improve the efficacy of pesticides and minimize their impact on off-target organisms is through increasing the penetration of active ingredients into plant foliage. Foliar uptake of pesticides is a complex process, depending on leaf surface characters of plants, physicochemical properties of the chemicals, types and concentration of the additives, and environmental conditions.

The fundamental mechanism of uptake has been considered, with most attention given to the epicuticular lipids and their role in modifying active ingredient diffusion through cuticles (Kirkwood 1999; Riederer and Markstädter 1996; Schönherr et al. 1999). However, there is a much simpler effect on the leaf surface that needs to be considered first. If a spray formulation contains adjuvants that cause droplet spread on a leaf surface (Fig. 2), this will in effect lower the mass of active per unit area without any change in concentration until the spray solution begins to evaporate. In any case, there will be a "solution residue" where the concentration of the active is many times more than in the starting spray solution (Zabkiewicz 2003).

Translocation

Adjuvants are known to facilitate cuticular "transport" (foliar uptake) but are not thought to play any significant part in further short- or long-distance translocation processes. However, in theory, if adjuvants could reach the cellular plasmalemma, then they could affect the initial stage of the sub-cuticular transport process (Fig. 3). The recent use of mass or molar relationships, instead of percentages, for xenobiotic uptake into plants from differing formulations, may be a means of elucidating some of the interactions among actives, adjuvants and plants (Forster et al. 2004).

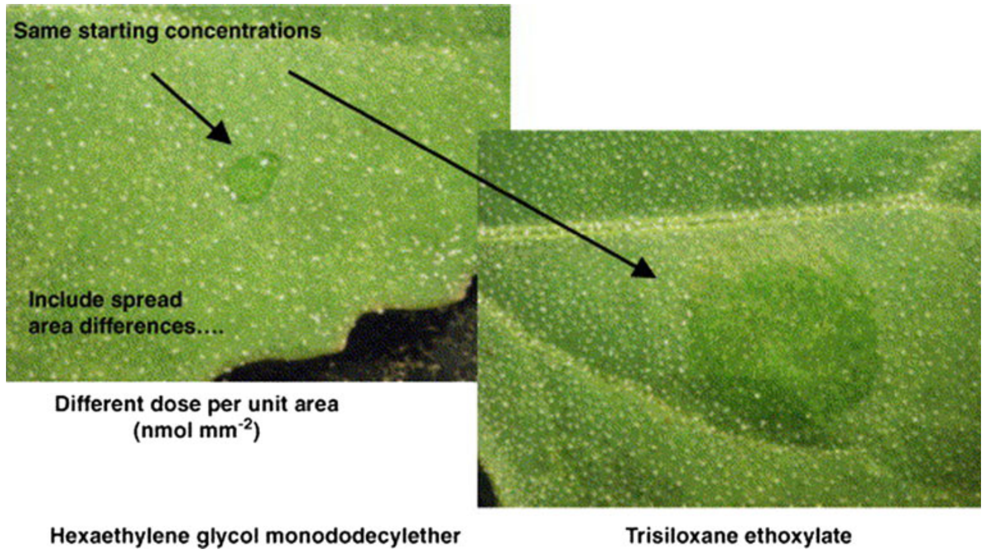


Fig. 2 Illustration of droplets' spread effects on *Chenopodium album* with different spray formulation. Reprint from (Zabkiewicz 2007)

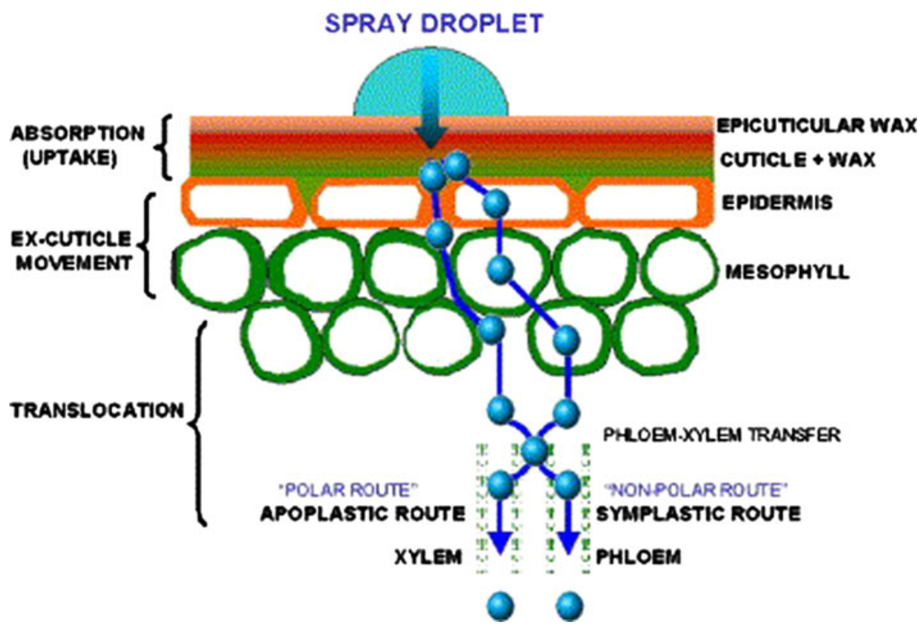


Fig. 3 Representation of different trans-cuticular pathways and subsequent apoplastic (polar) and symplastic (non-polar) pathways. Reprint from Zabkiewicz (2007)

Toxicity of adjuvants

Toxicity of wetting agents employed in the formulations of glyphosate will be analyzed in this section, because glyphosate is the most important pesticide worldwide, and the amount of wetting agent present in glyphosate formulation becomes as high as 150 g/lt.

Glyphosate, *N*-(phosphonomethyl) glycine (Fig. 4), the active ingredient of very well-known herbicide preparations, such as Roundup®, is a systemic and non-selective herbicide utilized for weed control, i.e. in agriculture, forestry, urban areas and even in aquaculture (Woodburn 2000; Williams et al. 2000).

The use of this non-selective and broad-spectrum herbicide increased dramatically after the introduction of genetically modified glyphosate-resistant crops in 1987 (Giesy et al. 2000). Although glyphosate is already one of the most used xenobiotics in modern agriculture, we should expect an increasing utilization of glyphosate largely due to the number of transgenic plants developed to be tolerant to this herbicide (May et al. 2002; Nadler-Hassar et al. 2004; Stephenson et al. 2004).

The main formulation of glyphosate is Roundup®, where glyphosate is present as an isopropylamine (IPA) salt, and its efficiency is enhanced by the addition of the surfactant polyoxyethylene amine (POEA) (Tsui and Chu 2003) in particular polyoxyethylene tallow amine (POETA).

Virtually, every pesticide product contains ingredients other than those identified as the "active" ingredient(s), i.e.

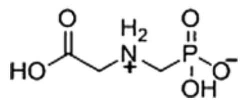


Fig. 4 Glyphosate structural formula

the one designed to provide the killing action. These ingredients are misleadingly called "inert". Commercial glyphosate formulations are more acutely toxic than pure glyphosate, since the amount of Roundup® required to kill rats is about 1/3 of the amount of glyphosate alone (Martinez and Brown 1991). Similar results have been obtained in cell division, thus indicating a synergy between glyphosate and Roundup® formulation products (Marc et al. 2002). On the other hand, mixture of glyphosate and PEOTA accelerated cell death via mitochondrial damage and induces apoptosis and necrosis (Kim et al. 2013). Mesnage et al. (2012) studied the potential toxicity on human cell of different glyphosate formulation. All the formulations evaluated were more toxic than glyphosate alone, the glyphosate formulated with polyoxyethylene tallowamine EO-15 being the most toxic against human cells inducing necrosis. There are in the literature important studies regarding the possible impact on environment and human health toxicity of glyphosate, particularly since there is a paucity of data regarding chronic exposure to sublethal doses during embryonic developments (Paganelli et al. 2010), but they are not included as they are out of the scope of this review.

Developing new plant protection formulations is a challenging task. The formulation of the active ingredient must assure a long shelf life stability at very high and low temperatures, even at high active ingredient concentration. At the same time, the active ingredient needs to be optimal bioavailable. Greenhouse tests to evaluate the biological performance are regularly done with small plants and spray chambers using nozzles and water amounts, which are not in accordance with practical field conditions.

Glyphosate formulation is the most active patent area by far in order to improve glyphosate performance. Many companies sell glyphosate, and the type and the amount of surfactant in glyphosate formulations vary greatly. Green and Beestman focused on new formulation and adjuvant technologies available to maximize performance and minimize safety and environmental impact of herbicides (Green and Beestman 2007). Even though governments have not approved many new chemicals for use with agrochemicals during the past decade, there is a rich record of patent applications and product introductions. Formulation technology is the principal mechanism agrochemical companies use to renew products when the initial patents covering the active expire. The adjuvant and formulation industry has done an impressive job, finding useful combinations and new utilities of currently approved chemicals.

Trends and perspectives in agrochemical formulations

The history of agricultural adjuvants dates back to eighteenth and nineteenth centuries when additives such as pitch, resins, flour, molasses and sugar were used with lime, sulphur, copper and arsenates to improve "sticking" and biological performance by modifying the physical and chemical characteristics of the applied mixture. Fundamentally, the goal of using adjuvants has stayed the same. Using substances that are inactive when used alone to improve the performance and application of an active ingredient by modifying the physical and chemical characteristics of the spray mixture is a fundamental part of all agrochemical research.

Despite the significance of agrochemicals' use for pest control, the environmental problems caused by the overuse of agrochemicals have brought scientists and publics much concern in recent years (Dayan et al. 2009). The reasons for this are (1) the high toxicity and non-biodegradability of agrochemicals and (2) the lack of scientific formulations. Thus, formulation scientists are now facing the challenge to explore novel green or environment-friendly agrochemical formulations to improve the biological efficacy and develop techniques that can be employed to reduce pesticide use while maintaining plant protection. The tremendous increase in crop yields associated with the "green" revolution has been possible in part by the discovery and utilization of chemicals for pest control. However, concerns over the potential impact of pesticides on human health and the environment has led to the introduction of new pesticide registration procedures, such as the Food Quality Protection Act in the United States. These new regulations have reduced the number of synthetic pesticides available in agriculture. Therefore, the current paradigm of relying almost exclusively on chemicals for pest control may need to be reconsidered. New pesticides, including natural product-based pesticides are being discovered and developed to replace the compounds lost due to the new registration requirements. Dayan et al. (2009) covered the historical use of natural products in agricultural practices, the impact of natural products on the development of new pesticides and the future prospects for natural product-based pest management.

New methodologies in agrochemical formulations

Microemulsions and nanoemulsions

Microemulsions are considered as thermodynamically stable colloidal dispersions that are optically transparent or translucent with drop size in the range of 100–200 nm (Prince 1977). Thus, microemulsion may be regarded as one-phase system (Lindman and Danielson 1981). As indicated above, the cloud point is one of the specific characteristics of the microemulsions. When the temperature of the microemulsion system is increased, the solubility of non-ionic surfactant decreases. The cloud point of microemulsion can be defined as the temperature at which the transparent microemulsion solution becomes cloudy, i.e. from one phase to two phases or three phases (Strey 1996).

It is common knowledge that by hydrating polyethylene oxide group (PEO) chain, non-ionic surfactant is dissolved in water medium, but it may dissociate with water as a result of dehydration when the temperature exceeds its cloud point. The cloud point increases with the increase in the amount of ethylene oxide groups in a chain, i.e. the higher the hydrophilicity of non-ionic surfactant, the higher the cloud point. The cloud point is also affected by the concentration of the surfactant solution and the electrolytes in the aqueous solution. In the later case, the cloud point is usually lower (Yoshihara et al. 1995; Saito and Shinoda 1967; Minanaperez et al. 1995; Tadros 1994). Chen et al. (2000) described two new types of pesticide microemulsions used for control *Liriomyza* spp., namely 16 wt% beta-cypermethrin (inside microemulsion xylene oil droplets) plus monosultap (dissolved in water medium) and 20 % abamectin (inside microemulsion xylene oil droplets) plus monosultap (in the water medium), were prepared. The effects of agrochemical concentration and various surfactants at various concentrations on the cloud points of microemulsions have been studied. The stability of microemulsions containing 5 wt% abamectin and 1 wt% beta-cypermethrin is also discussed. Similar to the cloud point of surfactant aqueous solution, at constant surfactant concentration the cloud point of the agrochemical microemulsions increases as the hydrophilicity of the surfactant increases. The cloud point of the formulated microemulsions depends on the characteristics of the agrochemical, the kinds and the amounts of the added surfactants and co-surfactants.

The results described earlier show that the values of the cloud point of microemulsions were dependent on the nature of agrochemical, the surfactants used and the concentration of surfactants. Surfactants with higher HLB value at same concentration produce more stable agrochemical microemulsions, i.e. with higher cloud point. The results show that the match between surfactant and oil phase or pesticide oil phase was the key to formulate stable microemulsions. However, the water quality showed almost no effect on the cloud point of the agrochemical microemulsions in the studies.

Meanwhile, microemulsions, which contain non-polar agrochemicals, usually have higher cloud points than those containing polar ones, especially electrolytic agrochemicals. As discussed, higher cloud points can be obtained with an increase in surfactant concentration, but it is more reasonable to use more co-surfactants rather than surfactants, because the former is much cheaper.

On the other hand, nanoemulsions have uniform and extremely small droplet sizes, typically in the range of 20–100 nm (Forgiarini et al. 2001). In addition, high kinetic stability, low viscosity and optical transparency make them very attractive systems for many industrial applications, for example in agrochemicals for pesticide delivery (Lee and Tadros 1982). Wang et al. (2007) investigated the potential applications of the system developed with water-insoluble pesticide, β-cypermethrin (β-CP), incorporated into the precursor microemulsion concentrate. The effect of this active pesticide on stabilities of the concentrate and the corresponding nanoemulsion was also investigated. The incorporation of β-CP in the concentrate showed no effect on the phase behaviour when present at less than 12 wt%. Compared with the commercial β-CP microemulsion, the excellent stability of sprayed solution diluted from the concentrate makes this system an ideal candidate as a water-insoluble pesticide delivery system. Thus, the application of the new methodology designing by spray formulations of β-CP may enable a reduction in the applied amounts, relative to those formulated as O/W microemulsions. These characteristics make the new methodology promising from both environmental and economical points of view.

Liposomes

Liposomes are structures made of lipid bilayers forming one or more concentric spheres, which entrap part of the solvent in which they freely float, into their interior. Their unique properties have triggered numerous applications in various fields of science and technology, from basic studies of membrane function to the use as carriers of very different substances. In agriculture, they can be used to improve the efficacy of different biocides and to deliver some essential nutrients (Lasic 1993). Herbicides, fungicides and pesticides are rapidly washed from the leaves of plants, and encapsulation in liposomes may prolong the action of these agents on plants and reduce the damage in soil cultures. Pons and Estelrich (1996) described the optimization of a cheap and easy method for preparing liposomes. Among the studied formulations, there are some with a high stability, and this property makes them very suitable to be used as an agrochemical product.

Nanomaterials

Materials with a particle size less than 100 nm in at least one dimension are generally classified as nanomaterials. The development of nanotechnology in conjunction with biotechnology has significantly expanded the application domain of nanomaterials in various fields. However, in the field of agriculture, the use of nanomaterials is relatively new and needs further exploration.

Khot et al. (2012) summarized the developments and application of novel nanomaterials in agriculture and described nanopesticides and its applications. Nanopesticides "involve either very small particles of pesticidal active ingredients or other small engineered structures with useful pesticidal properties" and can increase the dispersion and wettability of agricultural formulations (i.e. reduction in organic solvent runoff), and decrease unwanted pesticide movement. Nanomaterials and biocomposites exhibit useful properties such as stiffness, permeability, crystallinity, thermal stability, solubility and biodegradability needed for formulating nanopesticides. Nanopesticides also offer large specific surface area and hence increased affinity to the target. Nanoemulsions, nanoencapsulates, nanocontainers and nanocages are some of the nanopesticide delivery techniques that have been discussed recently for plant protection.

New surfactants and additives used in agrochemical formulations

There is an increasing regulatory and public pressure to decrease the amount of pesticides released into the environment. The current trends in the development of pesticide formulations are increased enormously to meet the needs of environmental safety, eliminate organic solvents, or to improve the activity and persistence of the active ingredient (Knowles 2008).

Alkyl polyglycosides

Alkyl polyglycosides or APGs are non-ionic surfactants with a hydrophilic saccharide instead of an ethylene oxide chain. The alkyl chain has 8–16 carbons. APGs are water soluble with excellent adjuvant properties. APGs are made from renewable raw materials and can be put into a highly concentrated liquid of dry formulations (Pompeo et al. 2005). They are called "green surfactants" because they are very safe to the environment.

Short-chain APGs show decent properties as wetting and penetrating agents and offer a high tolerance to saline solutions though they are non-ionic and do not exhibit a cloud point typical for alkoxylates (Hill et al. 1996). The importance of non-ionic APGs for glyphosate was first recognized by Syngenta as potentiators for glyphosate (Burval and Chan 1995).

Alkyl polyglycosides are superior surfactants with outstanding wetting properties and are used as adjuvants for pesticides as they improve the spreading and enhance the uptake of the pesticides (Garst 1997). Nonetheless, the effect of APGs on weed control of glyphosate cannot match industry standards. Advantageously, however, as compared to TAM-EO, APGs are generally classified as non-toxic and readily biodegradable. Several options were explored to take advantage of the benefits of APGs as high-performance wetting agents while optimizing the weed control.

A new class of non-ionic surfactants resulting from the direct ethoxylation of alkyl and/or alkenyl polyglycosides was designed as possible alternatives to TAM-EO (Behler and Clasen 2006). Their performance as adjuvants for glyphosate was assessed in greenhouse trials on two model plant species. The new derivatives were compared to TAM-EO and to straight APG. According to the greenhouse data, alkoxylated alkyl polyglycosides showed good weed control, almost reaching performance of TAM-EOs and surpassing efficiency of standard APG. Alkoxylated alkyl polyglycosides also exhibit a much better toxicological profile compared to TAM-EOs, reducing the risk to end-users.

Ethoxylated saccharose esters

In 2007, ethoxylated APGs were introduced. Due to their hydrophilic properties, they turned out to be suitable glyphosate potentiators and adjuvants (Abribat et al. 2007). However, their low lipophilicity makes them incompatible with oil-based formulations such as emulsifiable concentrate (EC) or concentrated oil-in-water emulsion (EW), and consequently, new lipophilic surfactants based on ethoxylated saccharose esters have been developed.

In a recent application, Mainx and Hofer (2009) described alkylene oxide adducts of oligosaccharides like saccharose. Their esterification leads to a new chemical class of label-free non-ionic surfactants. Selected representatives of this class of chemicals showed outstanding results in boosting the performance of crop protection products in greenhouse studies. Indeed, the protective property of azoxystrobin applied with these new ethoxylated saccharose esters was more effective than the industry standards, such as nonylphenol ethoxylated and isotridecyl alcohol 6 EO. In curative tests, the activity of the fungicide epoxiconazole was improved as well, although the effects were less pronounced.

Epoxiconazole was improved as well, although the effects were less pronounced, and even the activity of glyphosate was enhanced. Ethoxylated saccharose esters show a good toxicological and ecotoxicological profile. Their behaviour in pesticide formulations and tank mix solutions is excellent, so in total, they can be considered as a novel suitable class of adjuvants and surfactants for pesticide formulations.

The studies mentioned above showed that ethoxylated saccharose esters have an excellent potential as new adjuvants and emulsifiers in agrochemical compositions. Especially with fungicides at low concentrations, they show extraordinary results in improving the activity of the active ingredients, suggesting their suitability as both tank mix adjuvants and inserts for in-can formulations. Due to good compatibility with most new solvents, this new chemical class of surfactants can also be considered to become suitable components in all pesticide formulations either alone or in combination with other non-ionic or anionic surfactants.

Dimethylethanolamine-based esterquats

Esterquat chemicals are widely used in the commercial laundry market as fabric softeners. They have been used since 1970s as biodegradable alternatives to dihydrogenated tallow dimethyl ammonium chloride (DHTDMAC) chemistries. However, the use of esterquats in agrochemical formulations has not been thoroughly explored and would represent a biodegradable alternative chemistry (Zoller 2009). In addition, esterquats may offer reduced eye irritation or improved ecotoxicity profiles to an industry that is becoming ever more scrutinized for such formulation improvements.

Malec et al. (2009) explored the use of esterquats based on dimethylethanolamine (DMEA) in agricultural formulations. It was determined that DMEA-based esterquats can function as wetters or spreaders, but can also act as emulsifiers. The surface-active properties and aquatic toxicity of esterquats as surfactants will be explored as well. The esterquats have lower critical micelle concentrations, lower equilibrium surface tensions and faster wetting times than traditional agricultural surfactants.

Various formulations were explored including herbicides, insecticides and fungicides. These formulations included delivery systems such as soluble concentrates (SL) and emulsifiable concentrates (EC). The formulations were evaluated and in many cases provided performance properties that were equal to current standards for commercial products. Greenhouse trials were conducted evaluating the effectiveness of esterquats in glyphosate (*N*-(phosphonomethyl) glycine) formulations. It was found that esterquats were successful glyphosate adjuvants, utilizing lower surfactant use rates, while offering equal efficacy to commercial products. Additionally, glyphosate formulations using DMEA esterquats have lower eye irritation compared to other commercial standard glyphosate surfactants. The aquatic toxicity of DMEA esterquats was also studied, and the DMEA esterquats were found to be less toxic than TAM-EO.

The studies showed that DMEA esterquats may serve a valuable function in agrochemical formulations. They offer improved biodegradability, lower eye toxicity, improved wetting, spreading and penetration, and comparable aquatic toxicity to commercial surfactants already in use in agrochemicals.

Chitosan derivatives

Chitosan-based polymeric micelle, due to its outstanding biological properties and functions such as biodegradability, biocompatibility, insecticidal and antibacterial activity, has been widely researched or applied in the fields of agriculture, medicine, pharmaceuticals and functional food in the last decade (Chellat et al. 2000; Risbud and Bhonda 2000; Badawy et al. 2004; Hejazi and Amiji 2003; Kumar et al. 2004; Rabea et al. 2005). However, chitosan has no amphiphilicity, and it cannot form micelle and load drug directly. In recent years, chitosan-based micelle system has been developed by introducing hydrophobic and/or hydrophilic groups to the chitosan backbone (Zhang et al. 2008). Amphiphilic chitosan derivatives which grafted sulphuryl as hydrophilic moieties and octyl as hydrophobic moieties had been reported (Zhang et al. 2003, 2008).

Lao et al. (2010) described novel amphiphilic chitosan derivatives designed and synthesized by grafting octadecanol-1-glycidyl ether to amino groups and sulphate to hydroxyl groups (e.g. *N*-(octadecanol-1-glycidyl ether)-*O*-sulphate chitosan (NOSCS). Rotenone as a model drug was chosen and used to assess the potential loading capability of novel chitosan derivatives. The insecticide, rotenone, was loaded and formed about 116.4–216.0-nm nanoparticles, and its solubility in NOSCS micelles aqueous solution was increased largely. The highest concentration of rotenone was up to 26.0 mg/mL (NOSCS-1), which was about 13,000 times that of free rotenone in water (about 0.002 mg/mL).

Ammonium sulphate and sulphated glycerine as additives

The leaf cuticle and plasma membrane have been identified as barriers limiting glyphosate activity (Riechers et al. 1994; Denis and Delrot 1993). Neither glyphosate nor its different salts are effective in overcoming these barriers easily without appropriate surfactants (Buhler and Burnside 1983b; Jordan 1981). Cationic surfactants have been found to be more effective than non-ionic surfactants in increasing efficacy (Wyrill and Burnside 1976; Riechers et al. 1995). The addition of ammonium sulphate (AMS), an inorganic salt, to the glyphosate spray solution improved the efficacy of the herbicide (Blair 1975). Additionally, it has been found that salts dissolved in water used as the carrier for glyphosate may reduce its effectiveness, particularly calcium and magnesium salts. These salts have a positive charge and may associate with the negatively charged glyphosate molecule, replacing the isopropylamine or diammonium salts found in the formulated glyphosate product. AMS reduces the formation of calcium–glyphosate complexes on these leaves and therefore improves performance (Hartzler 2001). The inverse relationships between weed growth parameters and increasing concentration levels of AMS suggest that the ability of AMS to enhance glyphosate activity is to a large extent concentration dependent (Aladesanwa and Oladimeji 2005).

Glycerine and ammonium sulphate have both been popular additives in the long-held practice of adding chemical agents (adjuvants) to improve biological efficacy in crop protection sprays (Gednalske and Herzfeld 1994). Glycerine, a polyol of natural origins (triglycerides), is one of the principle building blocks of plant tissues. This biocompatibility as well as glycerine's humectancy is a strong contributor to its adjuvancy with additional benefit as a hydrotrope to homogenize water-based spray solutions (Heldt et al. 2000). Ammonium sulphate is a proven sequestrant of hard water cations as well as a nitrogen source, benefiting herbicides of diverse modes of action (Buhler and Burnside 1983a). The difficulties with ammonium sulphate solutions are their ionic strength and creating shelf-stable blends with surfactants (Gednalske and Herzfeld 1994).

Anderson presented the reaction product(s) resulting from sulphating glycerine shows strong adjuvant activity with herbicides (Anderson 2010). As with ammonium sulphate, the adjuvant activity of sulphated glycerine includes both sequestering cations commonly found in hard water and increased nitrogen for non-complexing herbicides. The field treatments including sulphated glycerine demonstrated statistically superior weed control when compared to un-sequestered reference samples. These "hard water" treatments including sulphated glycerine were statistically equivalent to control observed for glyphosate sprays prepared with de-ionized water. The increased efficacy of the herbicide glufosinate was demonstrated when using ammonium sulphate or sulphated glycerine as an adjuvant. Both of these biological observations were confirmed with rates of sulphated glycerine significantly lower than current label rates for ammonium sulphate.

Conclusion

Uptake of pesticides into plant foliage varies with plants and chemicals and can be greatly influenced by adjuvants and environmental conditions. Adjuvants usually have multiple functions in relation to pesticide efficacy. Increasing the foliar uptake of active ingredients is of particular importance for herbicides, growth regulators and defoliants. It is known that the penetration of pesticides into plant leaves is related to the physicochemical properties of the active ingredients, especially molecular size and lipophilicity. However, the uptake rate of a compound cannot be predicted by either of them or even by combination of them. For a specific chemical, uptake varies greatly with plant species, and there is no simple method at the moment to quickly evaluate the leaf surface permeability of a plant.

Environmental conditions have an important influence on herbicide efficacy. In particular, the effect of humidity on herbicide uptake has been attributed to changes in cuticle hydration and droplet drying. Herbicide uptaking slows or stops when herbicide droplets dry; it was suggested that humectants or wetting agents could enhance herbicide uptake by keeping droplets moist, maintaining the herbicide in solution and keeping it available for uptake.

Various adjuvants are being used to increase the penetration of pesticides into target plant foliage, but their effects vary with chemicals and plant species. The mechanisms of action of adjuvants in enhancing pesticide uptake remain unclear despite the effort made during the last three decades. Modern analytical and microscopic techniques provide powerful tools to deepen our understanding in this issue. However, a more multidisciplinary approach is urgently needed to elucidate the transcuticular diffusion behaviour of pesticides and the mode of action of adjuvants. A better understanding of the foliar uptake process should lead to a more rational use of pesticides and minimize their negative impact on the environment. Therefore, a systematic study on the complex interaction between active ingredients, surfactants and plants should lead to a more rational and cost-effective use of surfactants in weed control.

On the other hand, commercial glyphosate formulations are more acutely toxic than glyphosate, since the amount of Roundup® required to kill rats is about 1/3 of the amount of glyphosate alone. Similar results have been obtained in cell division, thus indicating a synergy between glyphosate and Roundup® formulation products. Although glyphosate is already one of the most used xenobiotics in modern agriculture, we should expect an increasing utilization of glyphosate largely due to the number of transgenic plants developed to be tolerant to this herbicide. Fatty amine ethoxylates or co-formulant called "inert ingredients" used in Roundup® are greatly responsible for the observed toxicity at the bioenergetic level. Quite unusual for a pesticide formulation is the co-formulant considered to be more toxic than the active ingredient. Glyphosate formulations with reduced labelling but with similar potency are therefore required in today's market.

The fact that the adjuvant could be more toxic than the active ingredient in one of the most active ingredients used pesticides together with the need that more effectiveness is required to reduce the environmental effect of xenobiotics has lead to the development of new adjuvants, e.g. more than 600 patents of glyphosate formulations have been published in the last 12 years.

It is important to point out that there is an increasing regulatory and public pressure to decrease the amount of pesticides released into the environment. The challenge is to maintain and safeguard their efficiency with effective adjuvants. The use of petrochemical-based surfactants like nonylphenol ethoxylates and fatty amine ethoxylates has declined significantly in the past decade, due to ecological and toxicological reasons. Hence, there is a continuing demand for alternatives based on a renewable source. Suppliers are developing new surfactants and new surfactants formulations based on natural products such as vegetable oils, lecithin, sugars, amino acid and others. Microemulsions, liposomes and nanoemulsions as emerging technologies in agrochemicals formulations have reduced the use of petrochemical solvents, e.g. xylene and improve the efficiency of biocides. The development of nanotechnology in conjunction with biotechnology has significantly expanded the application domain of nanomaterials in various fields. However, in the field of agriculture, the use of nanomaterials is relatively new and needs further exploration.

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