Design Of Eco-Friendly Compositions Herbicide/Amphiphilic Adjuvant Based On Optimized Structure - Activity Profile

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Research Article

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Abstract

To enhance the effectiveness of commercial herbicide clopyralid carbamate-containing surfactants have been explored as adjuvants. Based on systematic studies of the phytotoxic effect and wetting ability, functionality of surfactant series with different hydrophobicity was attested in terms of seed germination energy, seed germination, length of roots and seedlings of a number of monocotyledonous and dicotyledonous plants (sweet corn, meadow fescue, watercress, dandelion medicinal). In series of tested compounds, N-[2-(butylcarbamoyl)oxy)ethyl]-N,N-dimethylhexadecanammonium bromide (Ur-16 (Bu)) showed the best performance, which is supported by an optimal combination of indicators of physicochemical and biological activities, namely, high solubilizing ability in relation to clopyralid, providing facilitated transport of pesticide molecules into plant cells, with relatively low intrinsic phytotoxicity and high biodegradability. Vegetation experiments demonstrated that the addition of 0.1 %wt. Ur-16 (Bu) to the clopyralid solution leads to an increase in the effectiveness of herbicide action by almost 20%, when treating the crops of a weed plant dandelion medicinal. This result contributes to the optimization of functionality/human toxicity/biodegradability ratio, thereby reducing the side environmental effect.

1. Introduction

Technological progress takes the development of novel strategies and application of chemical additives facilitating their effectiveness, which is accompanied by negative ecological impacts. A variety of supplement compounds (improver, adjuvant, doping material, etc.) are environmental pollutants (Liu et al., 2022; Kermani et al., 2019), which forces researchers to face the problem of the limitation of non-target effect by increasing the efficacy, minimization of concentration, optimization of efficacy /toxicity/biodegradability profiles, selection of novel generations of additives answering the eco-friendly criterion.

The problem of weed infestation of crops is acute on a global scale, leading to a reduction in yield, quality of agricultural crops, and, ultimately, limiting the profitability of crop production. Weed plants actively compete with cultivated plants for available nutrients, carbon dioxide, water, space and insolation (Hemanth Kumar and Jagannath, 2021). Weeds are often a natural reservoir of microbial pathogens, in some cases act as hosts for insect pests (Hemanth Kumar and Jagannath, 2021; Trognitz et al., 2015), interfere with water management, crop cultivation and harvesting, contaminating crop yields and decreasing its quality (Zimdahl, 2007). According to (Oerke, 2006; Jabran et al., 2015; Devanathan et al., 2021), yield losses associated with the negative impact of the weed growth are priority and account for about 15-50% of all losses.

The main ways to control the spread and vital activity of weeds are preventive methods and control methods (Devanathan et al., 2021). Methods aimed at direct destruction of weeds using a special group of herbicide chemicals that kill plants or inhibit their growth are known as chemical; they are actively used and have proven themselves (Strehlow et al., 2019). The use of herbicides in modern agriculture is due to the high efficiency, low costs, speed of action and the period of aftereffect (Hemanth Kumar and Jagannath, 2021). However, this causes legitimate concern for farmers, public organizations and ordinary consumers. Among the main problems are 1) an exponential increase in the number of herbicide-resistant weeds, including species with multiple resistance (Beckie et al., 2019); 2) biological hazard to human and animal health when ingested with food and water; 3) environmental hazard to the environment as a result of their active migration in the ecosystem, accumulation and persistence (Jabran et al., 2015).

It is currently impossible to completely abandon the use of herbicides in agriculture. However, due to adjuvants, it is possible to significantly reduce the environmental risks associated with the use of agrochemicals, reducing their consumption doses, while maintaining and even increasing the effectiveness of the action. The functional classification of adjuvants is primarily based on the purpose for which they are used in the formulation: stabilization, removal, buffering, wetting, facilitating herbicide transport, adhesion and prevention of foaming, etc. (Kaczmarek et al., 2019; Kaczmarek et al., 2021; Marcinkowska et al., 2019; Castro et al., 2014; Foy, 2017) The use of pesticide adjuvants can also prevent the common phenomenon responsible for high losses in agricultural production, drift of sprayed solutions (Spanoghe et al., 2007; Mueller and Steckel, 2019).

Surfactants are often used as adjuvants (Mesnage et al., 2019; Sharma et al., 2018; Ramsey et al., 2005; Liu, 2004; Liu et al., 2016; Lin et al., 2016; Krogh et al., 2003). They improve the wetting of the surface of leaves and stems of plants, provide a longer retention and penetrating power of the herbicide. Nonionic surfactants, for example, ethoxylated alcohols, alkyl phenols, and trisiloxanes, have become widespread (Räsch et al., 2018; Baratella and Trinchera, 2018; Castro et al., 2014; Baratella et al., 2016). Cationic surfactants are used less frequently in herbicidal compositions (Castro et al., 2014; Parrish, 2015). Pesticide adjuvants have been described in the form of natural oils (Hao et al., 2019) or in the form of ionic liquids containing non-toxic ions (Sharpe et al., 2018; Kaczmarek et al., 2021).

Currently, there is no satisfactory semi-empirical or complex model that can quantitatively predict the effect of a particular surfactant on the properties and efficacy of herbicides. Therefore, the search for new adjuvants of different nature and structure, the optimization of the effective concentrations and characteristics, the establishment of the correlation between the structure of the surfactant and its effectiveness, the transition from *in vitro* experiments to vegetation and field experiments is a complex problem that requires a solution. In our previous work (Mirgorodskaya et al., 2020), it was shown that the presence of cationic surfactants containing a carbamate (urethane) fragment improves the wetting of various surfaces and facilitates the transport of the clopyralid herbicide into the plant. Undoubted advantages that allow expanding the study of these surfactants as adjuvants are their low aggregation threshold and high solubilization capacity, as well as moderate toxicity (Mirgorodskaya et al., 2018). The aim of this work was to improve liquid herbicidal compositions, enhance their physicochemical properties and operational characteristics using carbamate-containing surfactants of various structures. A systematic study of the phytotoxic effect of these compounds by varying the length of the hydrophobic tail and the alkyl substituent in the carbamate fragment (in the presence and absence of an agrochemical) was carried out. The most active compounds were evaluated for their biodegradability in natural conditions and were assessed for their effectiveness in herbicidal compositions in vegetation experiments. The selective, systemic, postemergence herbicide clopyralid, which belongs to the group of hormone-like herbicides or synthetic auxins was used as an agrochemical. Herbicides of this class are active mainly against dicotyledonous weeds in cereal crops (Todd et al., 2020). They can exhibit a toxic effect after adsorption by both roots and shoots; some of them may retain residual activity in the soil.

2. Experimental

2.1. Materials

For the study, herbicide clopyralid containing 99% of the main substance (Sigma Aldrich) was used. Commercial nonionic surfactant Tween 80 (Sigma Aldrich) was selected as adjuvant, as well as cationic surfactants containing a carbamate fragment:

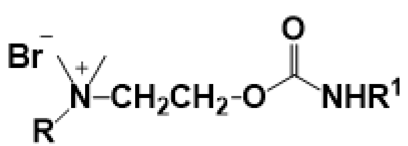
N-[2 -((butylcarbamoyl)oxy)ethyl]- N, N-dimethyldodecanammonium bromide, Ur-12 (Bu),

N-[2 -((butylcarbamoyl)oxy)ethyl]-N, N-dimethyltetradecanammonium bromide, Ur-14 (Bu),

N-[2 -((butylcarbamoyl)oxy)ethyl]-N, N-dimethylhexadecanammonium bromide, Ur-16 (Bu),

N-[2 -((butylcarbamoyl)oxy)ethyl]-N, N-dimethyloctadecanammonium bromide, Ur-18 (Bu),

N-[2 -((ethyl carbamoyl)oxy)ethyl] -N, N-dimethylhexadecanammonium bromide, Ur-16 (Et), which were synthesized as described in (Mirgorodskaya et al., 2018).



R = $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$, $C_{18}H_{37}$; R^1 = Et, Bu

The solutions were prepared using bidistilled water purified on a Direct-Q 5 UV water purification system (pH 6.8–7.0, χ = 2–3 $\mu S \cdot cm^{-1}$).

2.2. Phytotoxicity

Phytotoxicity was measured in laboratory experiments by testing parameters of seed germination, as well as biometric readings: the length of sprouts and roots. The test cultures were monocotyledonous plants corn (*Zea mays* L. Utrennyaya pesnya variety), meadow fescue (*Festuca pratensis* Huds Kazanskaya variety) and dicotyledonous plant watercress (*Lepidium sativum* L., Vitaminchik variety). Plant seeds (20 seeds) were sown in glass Petri dishes (R = 90 mm) on filter paper, to which 10 ml of either sterile distilled water (control) or 10 ml of solutions of laboratory synthesized carbamate-containing surfactants at concentrations of 0.1 and 0.2%wt. The experiment was carried out in 5 replicates and repeated 2 times.

Germination was done at 25°C, in the dark in the thermostat "TSvL-160" (Russia). Number of germinated seeds was counted after 72 h considered as the seed germination energy, after 168 hours – as seed germination. The length of the main root of plants was estimated at 3 days. After seven days, plants were harvested. Root and shoot lengths were recorded.

The experimental data were used to calculate percentage of inhibition and / or stimulation of measured parameters in relation to the untreated control (sterile distilled water), to allow comparison of effects of different surfactants on different plant species. Experimental data were analyzed with the STATISTICA version 10 (StatSoft. Inc (2011)), by the one-way ANOVA (analysis of variance) technique. The data processing methods were compared using the Least Significant Difference (LSD) test at the 0.05 probability level.

2.3. Herbicidal activity of clopyralid in combination with surfactants in laboratory experiments

The change in the herbicidal activity of the industrially used pesticide clopyralid was evaluated on the basis of similar measured parameters and under the same conditions as in section Phytotoxicity. As test plants, along with the previously listed cultivated plants, there were used a wild dicotyledonous plant – dandelion (*Taraxacum officinale* (L.) Webb ex F.H. Wigg.). Plant seeds were soaked for 2 hours in aqueous solutions of clopyralid (0.03%wt.) without the addition of surfactants and in their presence (Ur-16 and Tween 80 at a concentration of 0.1 and 0.2%wt.). Then the plant seeds were dried on filter paper and sown in 20 seeds in glass Petri dishes (R = 90 mm), to which 10 ml of sterile distilled water was added. The experiment was carried out in 5 replicates and repeated 2 times.

2.4. Contact angle of wetting

Determination of the contact angle of wetting was carried out by the standard method of a lying drop using the LK-1 goniometer. The volume of the investigated drop was 10 μL. Parafilm M, polypropylene, and a plant leaf (lettuce, cultivar Bistro) were used as a surface.

2.5. Herbicidal activity of clopyralid in combination with surfactants in vegetation experiments

The cultivated plant meadow fescue Kazanskaya variety and the wild plant dandelion were used as test plants in the vegetation experiments. In vessels (15x50x10 cm) there were placed nutrient soil for growing (Terre Vita Living Earth) 2.5 kg, which included high-moor peat of varying degrees of decomposition, purified river sand, perlite, complex mineral fertilizer, vermicompost. Then, 5 g of seeds were sown into the vessels in triplicate. The plants were grown in a climatic chamber Fitotron LiA-1 (Russia) under controlled conditions: 10 h night period/14 h day period, 10°C/20°C temperature regime, 10,000 lux luminosity, 60% humidity. After 21 days after seed sowing, foliar treatment of plants was carried out either with sterile distilled water (negative control), or clopyralid at a concentration of 0.03%wt., or clopyralid at a concentration of 0.03%wt. in combination with 0.1%wt. Ur-16 (Bu), or clopyralid at a concentration of 0.03%wt. in combination with 0.1%wt. Tween 80 (positive control) at the rate of 10 ml of solution per growing vessel. Then there was carried out a visual assessment of the plant condition. Seven days after treatment plants were harvested. The wet biomass of 100 plants was recorded and the average biomass of one plant was calculated.

2.6. *Biodegradability of the compounds in an aqueous medium*

The degree of biodegradation of surfactants was assessed by the Closed bottle test (OECD 301D, 1981) using the sewage sludge as a source of microorganisms. The concentration of dissolved oxygen, which changes during the biodegradation, was determined using WTW laboratory dissolved oxygen meter inoLab® Oxi 7310 (Germany). The experiment was carried out in aerated and deionized water, followed by the addition of mineral salts that provide nutrients for microorganisms and the tested surfactant at a concentration of 2 mg/L. The resulting solution was inoculated with a small number of microorganisms (5 ml of inoculum per 1 liter of prepared nutrient medium) and incubated in closed flasks in the dark at a constant temperature of 20.0 ± 1.0°C. A blank experiment was carried out under the same conditions without adding surfactants. The standard sodium acetate solution with inoculum was used as a reference system.

The degree of biodegradation was defined as the ratio of biological oxygen demand (BOD, mg/L) within 28 days to theoretical oxygen demand (TOD, mg /L):

$$\text{Degradation (\%)} = \frac{\mathrm{BOD} - \mathrm{BOD(blank)}}{\mathrm{TOD}} \times 100,$$

where BOD (blank) is the BOD of the biotic control (mg/L). TOD value is calculated using standard formulas (OECD 301D, 1981).

3. Results And Discussion

3*.1. Evaluation of the phytotoxicity of solution surfactants in relation to germination and initial growth of plants in laboratory experiments*

The indicators based on the plant response are widely used along with the determination of the chemical and physical properties of synthesized compounds to assess their interaction with biological objects (Shadrin et al., 2020). In some cases, only an assessment of changes in biological parameters makes it possible to establish the physiological activity of a substance, as well as to identify its critical concentrations in the environment. Phytotoxicity is the ability of chemicals (including surfactants) dissolved in water to inhibit seed germination and the growth of higher plants. The most common biological indicators for assessing the phytotoxicity of chemicals are seed germination, the length of roots and seedlings, and their biomass (Sun et al., 2020; Varjani et al., 2020). The main mechanisms for the formation of phytotoxicity of substances are physical (change of the permeability of the seed and seedling for water and air) (Shadrin et al., 2020), chemical (inhibition of the metabolism of plant cells) (Jiang et al., 2021), and biological (dysfunction of soil microbiocenosis) (Pour et al., 2020).

The mechanism of the phytotoxic action of different surfactants has not been sufficiently studied, however, information is available on their effect on seed germination, growth of roots and seedlings exemplified by natural saponins and some synthetic surfactants (Morán et al., 2001; Fernandes et al., 2020; Dane et al., 2012; Madsen et al., 2016).

In this work, the phytotoxicity of a number of carbamate-bearing (urethane) surfactants, differing in the length of the hydrophobic tail and containing a butyl or ethyl substituent in a head group, was evaluated. Since the metabolism can differ significantly depending on the class of flowering plants, for the assessment of phytotoxicity, the seeds of monocotyledonous and dicotyledonous plants – corn, meadow fescue, watercress were used. The data obtained are shown in Figs. 1-2, S 1-2.

It follows that a pronounced specificity of the surfactant toxic effect on various plant species occurs. In all parameters, the least sensitive of the tested plants was corn (monocotyledonous plant), the most sensitive is watercress (dicotyledonous plant). Similar data on the greater sensitivity of a dicotyledonous plant (cucumber variety Typhoon) compared to a monocotyledonous plant (wheat NS 40 S) was demonstrated for a series of surfactants with dodecyl alkyl chain and various aromatic (imidazolium, pyridinium, thiazolium) and aliphatic (guanidinium, ammonium, thiosemicarbazidium) polar heads (Tot et al., 2020). This is apparently due to the difference in the morphological and anatomical structure of the seeds of the tested plants, and also reflects the features of the physiological and biochemical characteristics of metabolism during germination. The differences in plant sensitivity depend on their genetic background.

The response to the introduction of carbamate-containing surfactants is not the same for the studied phytotoxicity parameters. Thus, a comparison of the effect of 0.1 %wt. surfactant solutions on corn seeds reveals the absence of their influence on the germination energy, whereas the seed germination, the length of roots and seedlings largely depend on the presence of surfactants: the depression of them ranges from 0 to 60% and from 20-50%, respectively. The effect of surfactants increases with an increase in their concentration in solution. In most cases, root length was inhibited to the greatest extent in the presence of surfactants in comparison with other studied parameters of plants. Similar data on different degrees of inhibition of root and shoot growth in the presence of surfactants were also noted in the work (Tot et al., 2020) using examples of other plants (cucumber, wheat). The authors make the assumption that the absorption of surfactant solutions by plants depends on the morphoanatomical characteristics of their parts.

The decisive role in the phytotoxicity of the studied carbamate-containing surfactants is due to their molecular structure. Based on all tested parameters, Ur-12 (Bu) had the greatest phytotoxic effect. Seed germination in a solution of Ur-12 (Bu) led to a significant decrease in the germination parameters in comparison with the control (sterile distilled water): by 90% or more in the case of watercress, by 60-80% in the case of meadow fescue and by 0-60% in the case of corn.

An increase in the length of the hydrophobic hydrocarbon tail led to a significant decrease in the phytotoxic effect. Thus, Ur-18 (Bu), like Ur-16 (Bu), at a concentration of 0.1 %wt. did not show an inhibitory effect on the germination energy of all studied plants, while the seed germination was 80% or more. The tests of Ur-18 (Bu) at a concentration of 0.2 %wt. not carried out due to its insufficient solubility in water.

In addition, an increase in phytotoxicity with a decrease in the length of the tail in the head group of surfactants was revealed: Ur-16 (Et) at both studied concentrations inhibited seed germination, root and seedling growth to a greater extent than Ur-16 (Bu). Unfortunately, the low water solubility of the carbamate surfactants obtained by us with a hexyl or octyl substituent in the head group did not allow them to be fully used for treating plants and did not make it possible to compare the phytotoxicity of a wider range of homologues.

As a mechanism of the phytotoxic action of the studied urethane surfactants, one can assume their ability to disrupt the integrity of the plant cell cytoplasmic membrane due to the phenomenon of hydrophobic / ionic adsorption at the cell membrane / water interface.

It is known that similar mechanisms of action on cell membranes also underlie the antimicrobial activity of surfactants. Due to the adsorption of positively charged surfactant molecules on the negatively charged surfaces of bacterial cells and their subsequent incorporation into the cell membrane, disordering of the lipid bilayer occurs, ion channels are formed, which leads to disruption of intracellular metabolism and damage to bacteria. An important role in the interaction of the surfactant and the membrane is played not only by the surfactant charge, but also by the correspondence between the length of its hydrophobic tail and the lipids that make up the basis of the cell membrane (Pinazo et al., 2016; Hae Cho et al., 2017; Wang et al., 2020). It should be noted that a large number of works have been devoted to the study of the mechanism of the antimicrobial action of surfactants, while the interaction of surfactants and plant cells has been studied much less. This is most likely due to the fact that surfactants will interact not only with the plant cell cytoplasmic membrane, but also with its cell wall. In addition to the negative effect on cell membranes, surfactants are capable of influencing physiological and biochemical processes inside plant cells. Thus, in the work (Tot et al., 2020) it was shown that under the influence of surfactants in wheat leaves the content of free proline changed. Proline contributes to an increase in plant immunity in stressful situations, improves the efficiency of photosynthesis, enhances the ability of seeds to germinate and increasing the content of chlorophyll in plants.

Thus, in decreasing phytotoxicity, the studied surfactants can be arranged in the following order: Ur-12 (Bu)> Ur-14 (Bu)> Ur-16 (Et) ≥ Ur-16 (Bu)> Ur-18 (Bu). That is, an increase in the length of the alkyl tail both in the carbamate fragment and in the quaternary nitrogen atom of the surfactant leads to a decrease in their negative effect on the growth rates of cultivated plants. Based on the data obtained, for further research as adjuvants of herbicidal compositions, there were made a choice in favor of surfactant Ur-16 (Bu), which is highly soluble in water and most indifferent to cultivated plants.

3.2. The wetting ability of aqueous solutions of carbamate-containing surfactants

Another factor to consider when choosing an adjuvant is the ability to effectively wet the leaf surface and facilitate penetration of the herbicide through the leaf cuticle. Surfactants promote good contact of the leaf surface with the herbicide solution by reducing the surface tension at the interface and reducing the contact angle of wetting. These characteristics depend both on the properties and concentration of the surfactant used and on the surface properties. So, when the solution spreads on the surface of the leaf, its structure will play an important role: hairiness and roughness of the surface, the presence of hydrophobic plant waxes on the outer tissue of the plant, the thickness of the cuticle, the number and location of stomata. However, the complexity of experiments on the study of leaf wettability is associated with the roughness of the leaf surface. In this regard, to characterize solutions of carbamate-containing surfactants, we determined the contact angle of wetting not only on the surface of a lettuce leaf fragment fixed in the holder of the device, but also on a polypropylene surface, as well as on glass covered with a layer of paraffin, imitating the waxy cuticle of the leaves.

The data obtained are illustrated in Fig. 3 and given in Table 1.

Table 1 Determination of the contact angle of wetting.

Surfactant	Angle, º (0.1 %wt. solution)			Angle, º (0.2 %wt. solution)		
	polypropylene	paraffin	leaf	polypropylene	paraffin	leaf
Water	77.86	79.86	60.023	77.86	79.86	60.03
Ur-12 (Bu)	50.89	69.76	57.41	43.55	50.73	39.67
Ur-14 (Bu)	49.89	52.04	56.11	40.56	47.17	42.17
Ur-16 (Bu)	34.87	59.74	48.38	31.98	44.37	37.01
Ur-16 (Et)	60.94	59.42	56.98	39.67	51.78	39.24
Ur-18 (Bu)	59.16	62.03	64.97	39.60	55.59	38.84
CTAB	46.29	65.15	57.51	43.30	58.77	41.64

The results describing changes in the contact angle of wetting on different surfaces correlated with each other. The surface of the plant leaf is characterized by the greatest wettability, paraffin has the lowest wettability. Regardless of the type of surface, the ability of the investigated surfactants to reduce the contact angle of wetting increased with increasing hydrophobicity of the compound and increased when going from 0.1% to 0.2 %wt. solutions. The exception was Ur-18 (Bu), which did not show a higher spreading ability than its low homologues. In all cases, carbamate-containing surfactants are more effective than cetyltrimethylammonium bromide (CTAB), a cationic surfactant traditionally used in colloid chemistry as a reference compound. At the same time, Ur-16 (Bu) showed the best properties. This makes it possible to expect that when used as an adjuvant in the herbicidal composition, this compound will ensure better contact of the plant. In addition, we have previously shown that Ur-16 (Bu) enhances the transport of the herbicide clopyralid into the plant, increases the effective concentration of the herbicide in it (Mirgorodskaya et al., 2020), which may be an important factor causing an increase in its efficacy. Taking into account the above, as well as data on the phytotoxicity of carbamate-containing surfactants in relation to cultivated plants, in further studies we focused on Ur-16 (Bu) as the most indicative and promising compound.

3.3. Evaluation of changes in the herbicidal activity of clopyralid in combination with surfactants during seed treatment in laboratory experiments

The next stage of the work included a study of the effect of Ur-16 (Bu) on the effectiveness of clopyralid. As a rule, the recommended effective concentration of clopyralid in working solutions when plant treatment is 0.03 %wt.; it is this content that was used in the experiments. Among the studied objects, along with the already studied cultivated plants, a weed plant - medicinal dandelion was added. There were compared the influence of the leader compound Ur-16 (Bu), selected from a number of carbamate-containing surfactants, and the nonionic surfactant Tween 80, which is often used as an adjuvant in agrochemicals because of its low toxicity and favorable colloidal properties, on the herbicidal action of clopyralid.

It was found that a solution of clopyralid at a concentration of 0.03 %wt. at the stage of germination and plant initial growth exhibited a selective herbicidal effect against dicotyledonous plants – dandelion and watercress, which is consistent with the known information regarding this compound. So, clopyralid is a selective herbicide that completely destroys malicious root-sprouting weeds (thistles, sow thistles), successfully suppresses ragweed, mountaineers, chamomile, dandelion and some other weeds, while it does not act on grass or strawberry leaves (Sharpe et al., 2018; Schütz et al., 1996) The results illustrating the effect of clopyralid in combination with surfactants on germination, germination and root growth are presented in Figs. 4,5,S3.

The clopyralid phytotoxicity in all the studied parameters increased when a surfactant was added to the solution for pre-sowing treatment of seeds. The germination energy decreased by 2.5-80%, germination – by 10-75%. The dicotyledonous plants dandelion and watercress also had the highest sensitivity to the compositions clopyralid-surfactants, the least – monocotyledonous maize and meadow fescue.

Clopyralid in combination with Ur-16 (Bu) had a greater phytotoxic effect compared to Tween 80: the depression of seedling and root length indices when using Ur-16 (Bu) was 21-92%, and Tween 80 – 4-82%. The phytotoxicity of the tested compositions increased with the concentration of surfactants in solution. However, a twofold increase in the surfactant dose in solution did not lead to a proportional increase in phytotoxicity.

From the set of indicators, it can be concluded that the dandelion (weed) showed the greatest sensitivity to the clopyralid-surfactant compositions, while the observed synergistic effect in the case of Ur-16 (Bu) is higher than that of Tween 80. The optimal dose of surfactants in the herbicidal composition is a concentration of 0.01 %wt. An increase in concentration of surfactants does not always entail a proportional increase in efficiency, while it leads to an increase in the cost of the composition, and also increases the risks of unwanted effects of surfactants on the environment.

3.4. Herbicidal activity of clopyralid in combination with surfactants during foliar treatments in vegetation experiments

Since clopyralid is a type of postemergence herbicide, foliar applications are typically used. To confirm the patterns identified in laboratory experiments, a model of field herbicide treatments of crops was created in a climatic chamber.

Visual inspection of dandelion plants treated with herbicide compositions within 4-6 hours after exposure revealed inhibition of vital activity and wilting of seedlings, which turned out to be significantly more pronounced when clopyralid was used in combination with the additive of Ur-16 (Bu). Further there was observed an increase in the manifestation of these signs (Fig S4). The wet biomass of one plant after seven days after treatment decreased in comparison with the control by 3.3-4.6 times (Table 2).

Meadow fescue showed no signs of inhibition in all processing options. Also, there were no significant differences in the raw biomass of one meadow fescue plant according to the experimental options.

Table 2 Raw plant biomass after seven days after foliar treatment with various compositions of clopyralid in combination with surfactants

Experimental version	Raw biomass of one plant, g	
	Meadow fescue	dandelion medicinal
Control	0.0562±0.009	0.0426±0.008
Clopyralid treatment 0.03 %wt.	0.0546±0.008	0.0130±0.004
Clopyralid treatment 0.03 %wt. + 0.1 %wt. Ur-16 (Bu)	0.0545±0.007	0.0093±0.004
Clopyralid treatment 0.03 %wt. + 0.1 %wt. Tween 80	0.0561±0.008	0.0124±0.005

The mechanism of cloiralid action is due to the imitation of the plant growth hormone auxin (Zhu et al., 2015). It is absorbed by the leaves, shoots and roots (in lesser degree), quickly moves via xylem and phloem (to a greater extent) and causes damage (Valenzuela-Valenzuela et al., 2001). In this regard, one of the main parameters that determine its transport into the leaves is the area of the leaf plate and the effective wetting of its surface with the herbicidal composition.

The translocation of herbicides into plants through the leaf plate is also determined by the epidermis. Thus, the structure and epidermis properties of the studied plants are very different: in meadow fescue, there is a cuticle and a waxy layer on the surface of the epidermis, and in dandelion, only a thin layer of the cuticle. It is known that the protective layer of various waxes and wax-like compounds worsens the wetting of the plant, severely restricts the intake of substances, including herbicides, into the plant cells (Mirgorodskaya et al., 2020). On the epidermis of dandelion leave veins, there are long unbranched multicellular multi-row hairs that can prevent the solution of active substances from draining off and increase the contact time; meadow fescue has no hairs on the epidermis (Musiał et al., 2013).

Also, meadow fescue has well-developed sclerenchyma, the cell walls are thickened (Raven et al., 1986; Zimmermann and Milburn, 1982) which makes it difficult for the molecules of substances to interact with the cytoplasmic membranes of plant cells.

The greatest phytotoxic effect was achieved when using clopyralid with the addition of 0.1 %wt. Ur-16 (Bu). Use of Tween 80, which is often used as an adjuvant in agrochemical formulations (Wang et al., 2020; Arand et al., 2018; Jibrin et al., 2021), did not lead to an increase in the herbicidal activity of clopyralid. The main factors affecting the increase in the phytotoxic effect of clopyralid in combination with Ur-16 (Bu) against dandelion seedlings, apparently, are an improvement in the interaction of the solution with the leaf surface, as well as an increase in the penetrating ability of clopyralid molecules into plant cells.

3.5. Evaluation of the biodegradability of carbamate-containing surfactants

The possibility of application of carbamate-containing surfactants as adjuvants raises questions related not only to its effectiveness, but also to its safety. It is known that cationic surfactants are more toxic than nonionic surfactants, have a reduced biodegradability and are able to be oxidized under aerobic conditions. The advantage of carbamate-containing surfactants over their trialkylammonium analogs may be the fact that they are significantly less toxic. Thus, the median lethal dose (LD_{50}) value for Ur-16 (Bu) is 82 mg/kg (mice, intraperitoneal administration), while the LD_{50} for CTAB is 24 mg/kg (Mirgorodskaya et al., 2018).

In addition, carbamate-containing surfactants, similar to compounds having an amide and ester fragment, under the action of enzymes of environmental microorganisms can undergo enzymatic hydrolysis with the release of carbon dioxide and the formation of readily biodegradable quaternary ammonium alcohols (Wang et al., 2019; Banno et al., 2010; Banno et al., 2009). The rate of oxidative decomposition of a carbamate-containing surfactant Ur-16 (Bu) was estimated by the closed bottle test using the sewage sludge as a source of microorganisms.

The degree of biodegradation was determined as the ratio of biological oxygen demand (BOD) within 28 days to theoretical oxygen demand (TOD). In the case of Ur-16 (Bu), the TOD calculated for complete oxidative degradation is 2.577 g/L (the calculation of this parameter is given in SI). For the reference system based on sodium acetate the TOD is 0.78 g/L. Average biodegradability values are presented as the dependence of this value on time (Fig.6). The data obtained for sodium acetate are in good agreement with the literature (Guziałowska-Tic and Tic, 2017). Average biodegradability values are presented as the dependence of average biodegradability value of Ur-16 (Bu) on time (Fig.6). It has been established that the level of biodegradation of Ur-16 (Bu) achieved 64% within 28 days, which makes it possible to classify this compoun as rapidly degradable substance, in accordance with the existing standards (Rombke and Moltmann, 1996; Žgajnar Gotvajn and Zagorc-Končan, 1999). This result is another compelling reason for recommending the use of Ur-16 (Bu) as an adjuvant in a herbicidal formulation.

4. Conclusion

Systematic studies of carbamate-containing surfactants with a variable length of the alkyl substituent at the quaternary nitrogen atom and in head group have shown that the main indicators of their phytotoxic effect on a number of monocotyledonous and dicotyledonous plants (seed germination energy, seed germination, length of roots and seedlings) decreased with an increase of hydrophobicity. Measurement of the contact angle for solutions of carbamate-containing surfactants made it possible to quantitatively characterize the efficiency of contact between the test systems and the plant surface. On the basis of the data obtained, it was found that Ur-16 (Bu) showed the best performance and can be used to enhance the activity of commercial herbicide clopyralid. By the closed bottle test using the sewage sludge as a source of microorganisms, it was shown that the level of biodegradation of Ur-16 (Bu) is as high as 64% within 28 days, which allowed us to classify it as a rapidly degradable substance. Vegetation experiments demonstrated that the addition of 0.1 %wt. Ur-16 (Bu) leads to an increase in the effectiveness of herbicidal composition by almost 20%, when treating crops of a weed plant dandelion medicinal with a solution of clopyralid. A high selectivity of the proposed herbicidal composition was revealed, i.e., significant inhibition of the growth of dicotyledonous plants (medicinal dandelion) occurred, with no effect observed on monocotyledons plants (meadow fescue). The data obtained indicate significant potential for the use of carbamate surfactants as adjuvants in herbicidal compositions, which make it possible to reduce the consumption rates of the herbicide, thereby reducing the unfavorable impact on the environment.

Declarations

CRediT authorship contribution statement

A.M. and N. Sh. – Conceptualization, Validation, Methodology, Writing - original draft, Writing - review & editing; R.K., A.R. and O.L. – Investigation, Visualization, Formal analysis; D.K. and D.T. - Investigation, Visualization; E.N.– Methodology, Validation; K.S. – Conceptualization, Methodology, Validation; K.P. – Conceptualization, Validation, Writing - review & editing; L.Z. – Supervision, Project administration. All authors read and approved the fnal manuscript.

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Consent to participate. Not applicable.

Consent for publication. Not applicable**.**

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Figures

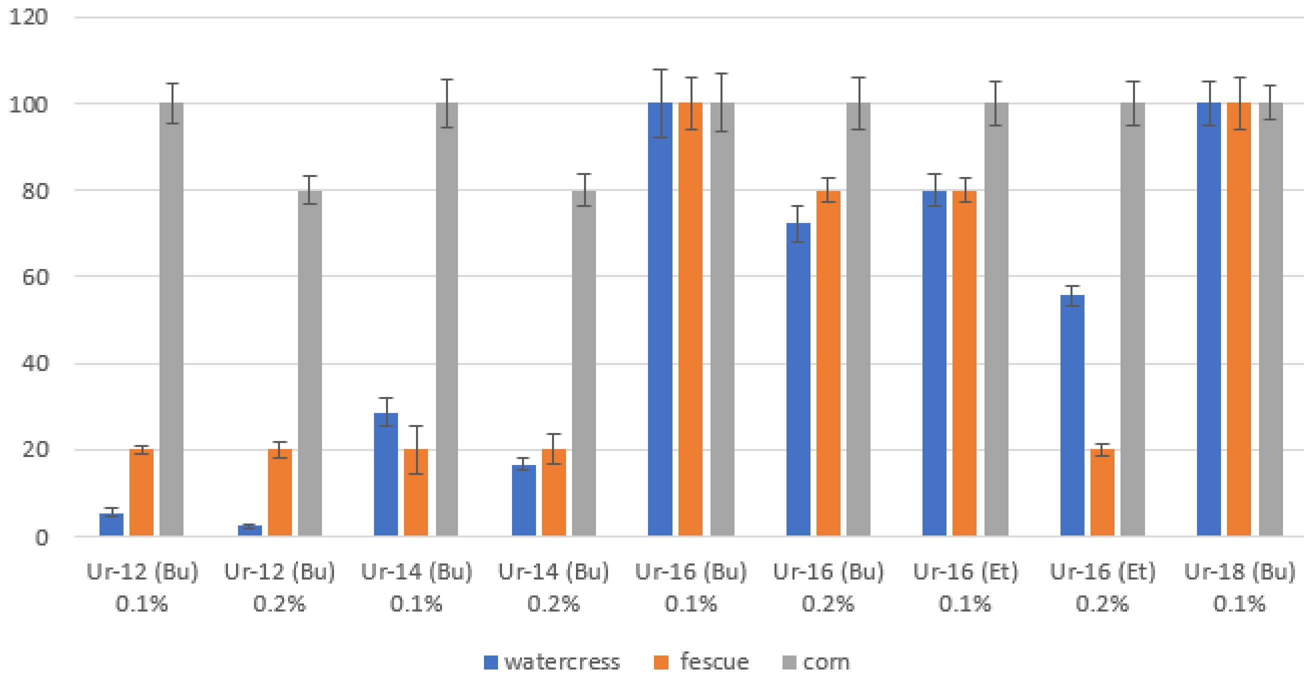

Figure 1

The germination energy in surfactant solutions in comparison with the control (sterile distilled water), %.

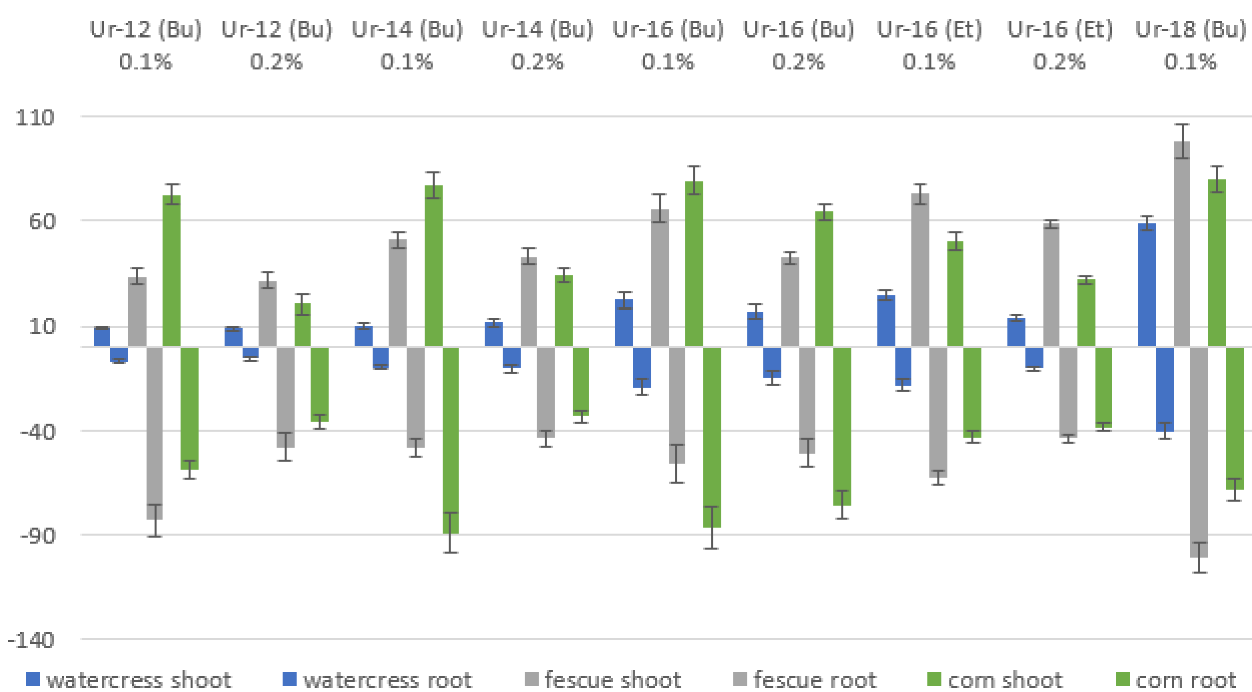

Figure 2

Seedling length / root length during germination of plant seeds in surfactant solutions for 7 days compared to control (sterile distilled water), %.

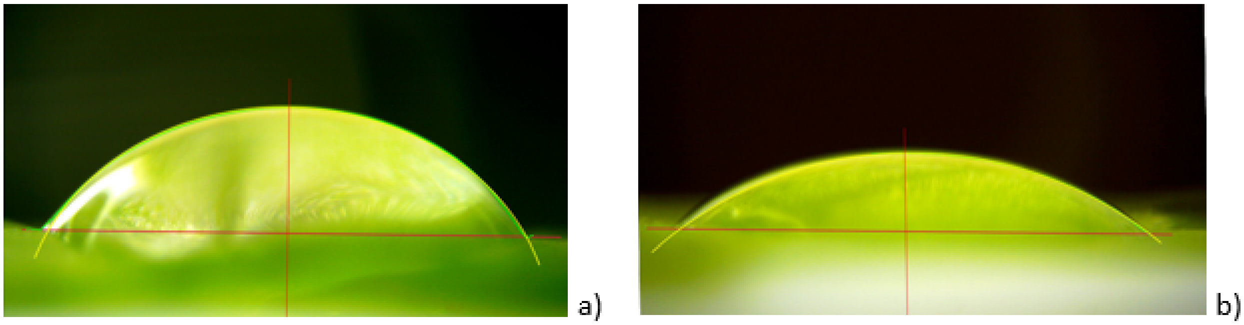

Figure 3

Wetting a leaf of lettuce with water (a) and 0.1% wt. solution of Ur-16 (Bu) (b).

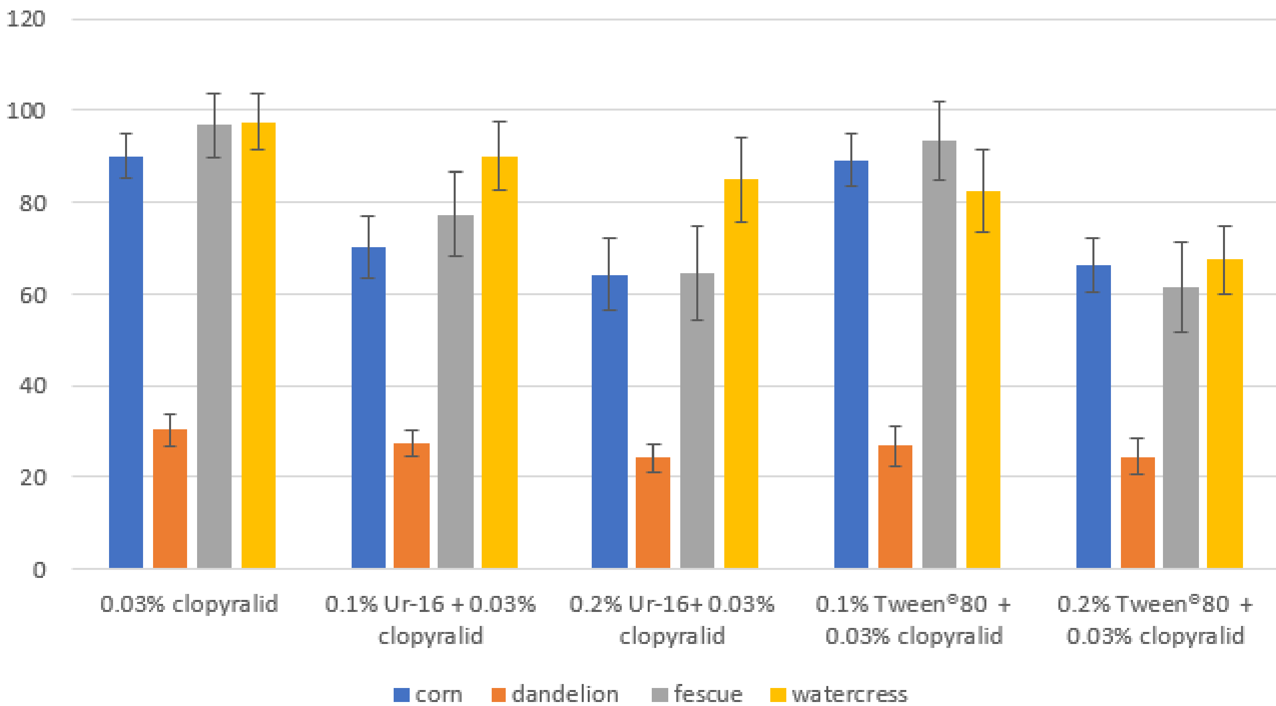

Figure 4

Seed germination during pre-sowing treatment with clopyralid solutions in combination with surfactants in comparison with control (sterile distilled water), %.

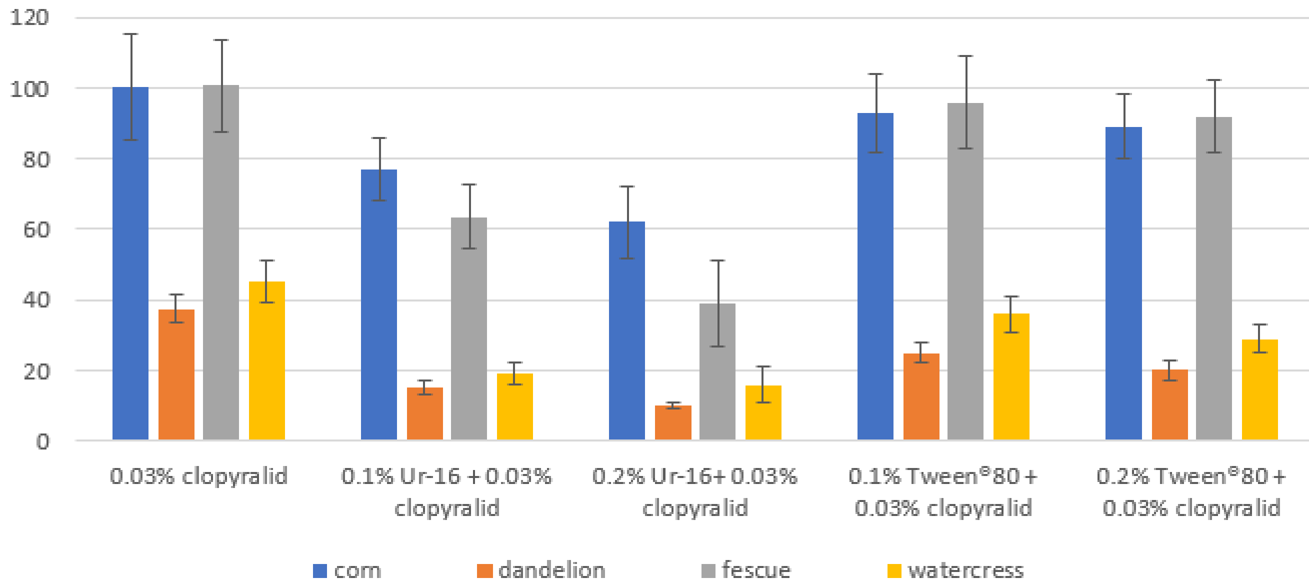

Figure 5

The length of seedlings during pre-sowing treatment with clopyralid solutions in combination with surfactants for 7 days compared to control (sterile water), %.

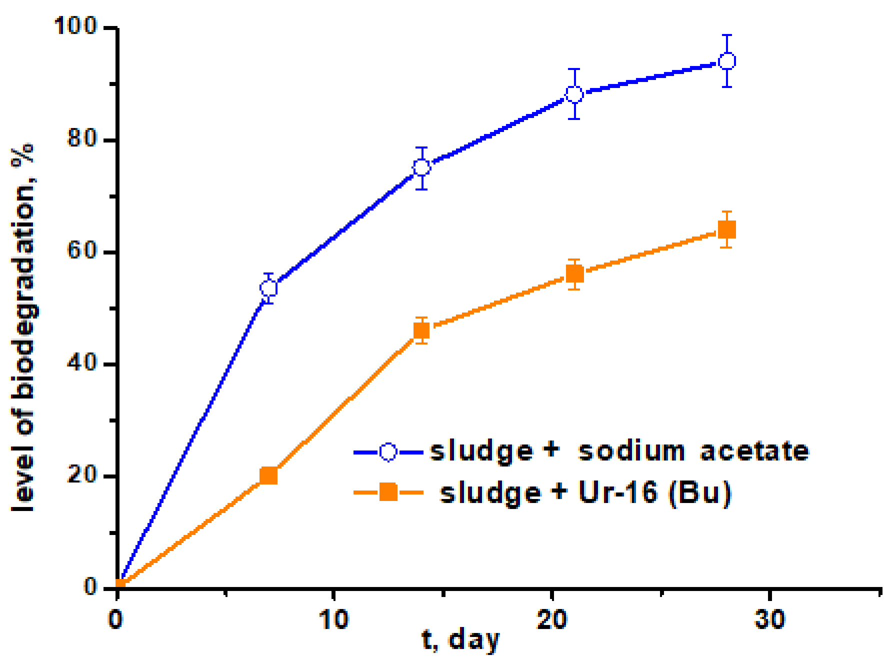

Figure 6

Biodegradation rate of Ur-16 (Bu) and sodium acetate in the closed bottle test.

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