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Assessment of ethylene glycol diacetate as an alternative carrier for use in agrochemical emulsifiable concentrate formulation

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ABSTRACT

The conventional emulsifiable concentrate (EC) formulation contains a large amount of aromatic solvents, which causes adverse effects to both the environment and human health due to the toxicity of the solvents. Here, we developed a 2.5% lambda-cyhalothrin EC formulation with ethylene glycol diacetate (EGDA) as the solvent, and the developed formulation serves as an environmental-friendly alternative to overcome the adverse effects of aromatic solvents. The physicochemical characterizations, wettability properties, phytotoxicity and bioassays of the EGDA-EC formulation were systematically investigated and compared with that of the EC formulation with xylene as the solvent. The results showed that both EC formulations had excellent emulsion properties and storage stabilities. Additionally, the EGDA-EC formulation possessed a higher flash point (96 °C), indicating safer production, storage and transport. The retentions of the EGDA-EC sample on leaves were 1.22–1.46-fold higher than that of the xylene-EC sample, and the EGDA-EC also exhibited lower surface tensions and contact angles, which would benefit decreasing drift-off and improving utilization. Furthermore, the bioassays demonstrated that the EGDA-EC formulation had lower acute toxicity to aquatic organisms and higher control efficacy to target insects compared with the xylene-EC formulation. Therefore, EGDA is a promising carrier for oil-soluble agrochemicals to improve their application performance and reduce their adverse effects.

1. Introduction

The emulsifiable concentrate (EC) formulation of pesticides is the most commonly used delivery system for increasing the yield and quality of crop production (Enserink et al., 2013). This formulation has the following main advantages: the convenient preparation process involving simple compositions, easy to handle with high efficacy, and possessing excellent thermodynamics and storage stability (Cao et al., 2013; Liu et al., 2009). However, conventional EC formulations usually contain large amounts of aromatic solvents, such as diesel, toluene and xylene, which are mainly derived from petroleum (Knowles, 2008). These solvents can cause soil, air and water pollution and be hazardous to human health because of their high toxicity and lack of biodegradation (Peng et al., 2017; An, 2004; Wiwattanapatapee et al., 2009; Regitano-D'Arce et al., 2017; Tobiszewski and Namieśnik 2015). They induce serious damage to off-target and beneficial species resulting from their drift and volatilization (Mackinnon and Duncan 2013), and can also generate terrible odors in the spraying process because of the high vapor pressure (Liu et al., 2017). Moreover, the overuse of aromatic solvents may consume a large amount of non-renewable limited petroleum resources, resulting in an insufficient supply of petroleum derivatives for transportation and industrial use (Perlatti et al., 2014). Furthermore, the repeated and excessive applications of conventional EC formulations further increase the treats to the environment, energy and human health. Therefore, it is crucial to develop an easily available and environmentally friendly solvent that can replace the current aromatic solvents in agrochemical formulations.

Some studies have attempted to develop a promising solvent with the desired properties, such as low toxicity, acceptable odor, low vapor pressure, good biocompatibility and satisfactory storage stability. For instance, vegetable oils, mineral oils, animal fats and biodiesel have been proposed as carriers or adjuvants in agrochemical formulations (Cao et al., 2013; Huang et al., 2011; Jiang, 2011; Chin et al., 2012a, 2012b). Nevertheless, vegetable and mineral oils may cause

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phytotoxicity on some crops when applied in high amounts (Bainard et al., 2006; Domenico et al., 2008). Biodiesel is mainly made from vegetable oils and animal fats (Chin et al., 2012a, 2012b), and these components usually contain large amounts of free fatty acids, water, odorants and other impurities, which would reduce the stability of the resulting formulation and shorten the shelf life of the product. In addition, some vegetable oils and animal fats are high viscosity or solid state at low temperature, and as a result they cannot be used directly as solvents or carriers. Overall, the immanent disadvantages of these proposed alternative solvents, such as phytotoxicity, low purity, high viscosity and poor stability, limit the potential application and development of solvent-rich formulations. Therefore, it is necessary to explore novel, practical and environmentally friendly alternatives for agrochemical formulations.

Ethylene glycol diacetate (EGDA) is a colorless and transparent organic solvent with low toxicity, which is widely applied in paints, coating, adhesives, cosmetics and the tobacco industries (Yang et al., 2015; Huang et al., 2016). The synthesis of EGDA is easy and direct and does not require complex equipment or technology (Yang et al., 2015), which ensures an abundant source and supply. In addition, the low vapor pressure of EGDA (0.036 kPa, 30 °C) can effectively suppress the volatilization and pungent odors during its preparation and application. EGDA also has excellent compatibility with organic solvents, such as alcohols and ether esters, which can be utilized as co-solvents in pesticide systems. Furthermore, compared to that of aromatic solvents, the storage and transportation of agricultural formulations with EGDA is safer due to a higher flash point (88 °C). Previous studies on EGDA mainly focused on optimizing the synthesis process and developing efficient catalysts. In particular, limited research has investigated its application, and its application as a solvent in the agricultural field has not been reported. Therefore, an in-depth investigation of EGDA will serve as a valuable reference and reduce the environmental risks associated with conventional aromatic solvents in agrochemical formulations.

Lambda-cyhalothrin is a halogenated pyrethroid with a broad insecticidal spectrum, high efficiency and rapid knockdown speed (Birolli et al., 2018; Colombo et al., 2013). It is easier to dissolve in organic solvents. EC is the dominant formulation of lambda-cyhalothrin, but the high utilization of aromatic solvents (ca. 80–90%) has resulted in serious problems to both the environment and humans. Therefore, the use of EGDA as a carrier in lambda-cyhalothrin EC formulations might be a potential solution to these problems.

In this study, we fabricated a 2.5% lambda-cyhalothrin EC formulation using EGDA as a substitute carrier to replace the conventional solvents. The storage stability, wettability, phytotoxicity, acute toxicity and bioactivity of the resulting formulations were systematically investigated. The unique characterization of such a solvent is that EGDA has low toxicity and vapor pressure, high flash point and high solubility with many pesticides, and these features are greatly suitable for agrochemicals. In addition, the substitution of conventional solvents with EGDA can reduce the depletion of petroleum-derived products in the agrochemical field and decrease the threats to public health by reducing environmental contamination.

2. Materials and methods

2.1. Materials

Lambda-cyhalothrin (purity 95%) was obtained from Yangnong Chemical Co., Ltd. (Jiangsu, China). EGDA (CAS: 111-55-7) was supplied by Guangzhou Yintian Chemical Co., Ltd. (Guangdong, China). The chemical structures of the EGDA and lambda-cyhalothrin were shown in Fig. S1 (Supplementary material). Calcium dodecyl benzene sulfonate (E-500), styryl phenol polyoxyethylene ether (E-602), phenylethyl phenol polyoxyethylene polyoxypropylene ether (E-1601), polyoxyethylene sorbitan monooleate (T-80), sorbitan monooleate (S-80), polyoxyethylene (20) castor oil ether (EL-20), alkylphenol polyoxyethylene ether (OP-10) and fatty alcohol-polyoxyethylene ether (AEO-5) were used as emulsifiers. All reagents were of analytical grade. Deionized water was used in all experiments.

2.2. Preparation of lambda-cyhalothrin EC

The 2.5% lambda-cyhalothrin EC formulation was prepared via the following process: 2.64 g of lambda-cyhalothrin was added to 88.3 g of an EGDA solution in an Erlenmeyer flask, and the mixture was stirred at room temperature until it was completely dissolved. Subsequently, the emulsifiers were added with continued stirring to form a homogeneous solution. Finally, the resulting samples were stored in a sealed state for subsequent research. In addition, the conventional lambda-cyhalothrin EC with xylene as the solvent was also prepared, and the compositions are listed in Table S1 (Supplementary material).

2.3. Determination of lambda-cyhalothrin concentration

The active ingredient (AI) of lambda-cyhalothrin in the EC formulation was determined using a high-performance liquid chromatography system (HPLC, Agilent 1200; Agilent Technologies; Santa Clara, CA) equipped with a UV detector and a C18 column (250 mm × 4.6 mm). The mobile phase was an acetonitrile/water mixture (85:15, v/v) at a flow rate of 1 mL/min. The injection volume was 20 μL. The UV detector was set at a wavelength of 240 nm, and the column temperature was maintained at 30 °C.

2.4. Emulsion stability tests

The emulsion stability tests were conducted according to the official CIPAC standard method (CIPAC MT36, 1995). In brief, 5 mL of the EC samples were diluted in 95 mL of deionized water in a 100-mL measuring cylinder. The cylinder was covered by a stopper, turned upside down ten times, and allowed to stand undisturbed. The amount of free oil or cream that separated out from the top or bottom of the emulsion was recorded at various intervals (0.5, 2 or 24 h). Note that the results at 24 h were required only when the results at 2 h were in doubt.

2.5. Storage stability tests

The storage stability was tested according to the official CIPAC standard method. Briefly, the two samples were separately packed in glass tubes and stored at 0 °C for 7 days (CIPAC MT39, 1995) and 54 °C for 14 days (CIPAC MT46, 1995). After storage, the AI concentration was determined to evaluate the degradation of lambda-cyhalothrin. The emulsion characteristics were measured to evaluate the physical stability of the samples. In addition, the density, pH value, viscosity and flash point of two samples after storage at ambient temperature for 200 days were also evaluated.

2.6. Wettability and retention performance tests

To identify the application properties of the developed EGDA-EC formulation, its surface tension, contact angle and retention were tested in detail and compared with the xylene-EC formulation. The two formulations were diluted to a series of concentrations (1, 5, 10, 25 and 50 mg/L) with deionized water throughout the tests.

The surface tensions were measured through the Wilhelmy plate (made of Pt–Ir alloy) method (Zwertvaegher et al., 2014) using an automatic surface tensiometer (BZY-1, Shanghai Hengping Instrument and Meter Factory, China) at room temperature. After one solution was measured, the plate was successively washed twice with deionized water and acetone and then burned in an alcohol flame. Each treatment was repeated three times.

The contact angles were measured using a static optical contact