



Chlorpyrifos-methyl solubilisation by humic acids used as bio-surfactants extracted from lignocelluloses and kitchen wastes



Barbara Scaglia ^a, Andrea Baglieri ^b, Fulvia Tambone ^a, Mara Gennari ^b, Fabrizio Adani ^{a,*}

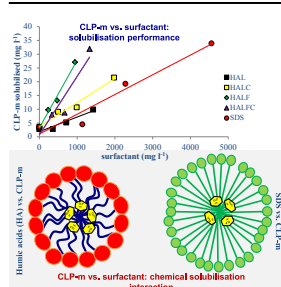
^a Gruppo Ricicla Labs – DiSAA – Università degli Studi di Milano, Via Celoria 2, Milano, Italy

^b Department of Agriculture, Food and Environment, Agricultural Chemistry Section, University of Catania, Via S. Sofia, 98, Catania, Italy

HIGHLIGHTS

- The insecticide Chlorpyrifos-methyl (CLP-m) accumulates in soil becoming toxic.
- CLP-m can be removed from soil by its solubilisation using synthetic surfactants.
- Humic acid (HA) from biomasses solubilized CLP-m as well as synthetic ones.
- HA from kitchen waste showed highest CLP-m solubilisation capability.
- HA alkyl-C fraction amount and composition affected CLP-m solubilisation.

GRAPHICAL ABSTRACT



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ABSTRACT

Chlorpyrifos-methyl (CLP-m) is a widely used organophosphate insecticide that can accumulate in soil and become toxic to humans. CLP-m can be removed from soil by its solubilisation using synthetic surfactants. However, synthetic surfactants can accumulate in soil causing contamination phenomena themselves. Bio-surfactants can be used as an alternative to synthetic ones, reducing costs and environmental issues.

In this work, humic acid (HA) extracted from raw biomasses, i.e. lignocelluloses (HA_L) and lignocelluloses plus kitchen food waste (HA_{LF}), corresponding composts (C) (HA_{LC} and HA_{LFC}) and leonardite (HAc), were tested in comparison with commercial surfactants, i.e. SDS, Tween 20 and DHAB, to solubilize CLP-m.

Results obtained indicated that only biomass-derived HA, composted biomass-derived HA, and SDS solubilized CLP-m: SDS = 0.006; HAL = 0.007; HALC = 0.009 g; HALF = 0.025; HALFC = 0.024 (g CLP-m g⁻¹ surfactant).

Lignocelluloses HAs (HA_L, HA_{LF}) solubilized CLP-m just as well as SDS while lignocellulosic plus kitchen food waste HA (HA_{LF}, HA_{LFC}) showed a three times higher CLP-m solubilisation capability. This difference was attributed to the higher concentration of alkyl-Carbon that creates strong links with CLP-m in the hydrophobic micelle-core of the surfactants.

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* Corresponding author.

E-mail address: fabrizio.adani@unimi.it (F. Adani).

1. Introduction

Chlorpyrifos-methyl (CLP-m) is a broad-spectrum organophosphate insecticide. Its use has increased a lot because it has replaced the usage of more highly toxic organophosphates (BCPC & The Royal Society of Chemistry, 1994; McConnel et al., 1997).

CLP-m use is restricted in the USA and EU (USEPA, 2002; Padovani and Capri, 2005) but it is widely employed in developing countries (i.e. India) (Eaton et al., 2008). The excessive use of CLP-m results in a progressive accumulation of this pollutant in the soil, leading to human intoxication phenomena either by direct contact or through the food chain (Gennari et al., 2009).

In order to reduce CLP-m contamination different technologies, such as phytoremediation, bioremediation and soil washing have been proposed (Cunningham and Berti, 1993; Pilon-Smits, 2005; Gennari et al., 2009). Soil washing consists in treating soil with water and/or surfactant solutions to extract soil pollutants. In water solution, surfactants are capable of trapping hydrophobic molecules inside the surfactant micelle-structure and removing them from the soil. Surfactants form micelles at a concentration defined as the critical micelle concentration (cmc) which varies according to the surfactant's chemical characteristics, pH and temperature (Terashima et al., 2004; Chilom et al., 2009).

The capabilities of cationic, anionic and non-ionic surfactants for CLP-m solubilisation were previously tested at lab scale, with the best results for the anionic molecule Sodium dodecyl sulphate (SDS) (Gennari et al., 2009). However, synthetic surfactants can accumulate in soil causing contamination phenomena themselves; moreover they are costly and not renewable (Kao and Prosser, 2001; Volkerling et al., 1998).

The use of natural surfactants (called biobased surfactants or natural surfactants) was recently proposed, since this practice is potentially more sustainable and environmentally friendly. Biobased surfactants are amphiphilic molecules characterized as organic molecules having both low (i.e. glycolipids, lipopeptides and phospholipids) and high (i.e. polymeric and particulate surfactant) molecular weight (Rosember and Ron, 1999). Biosurfactants can be extracted from biomasses (Salati et al., 2011) or produced by *ad hoc* cultivated microorganisms (Pacwa-Płociniczak et al., 2011). Cultivation of microorganisms has a high production cost which has limited biosurfactant development from this source (Rufino et al., 2014). On the other hand, several vegetable-based compounds showing surfactant properties (e.g. saponin), can be obtained at lower cost.

More recently, the possibility of obtaining biosurfactants from organic matter, i.e. humic acid (HA), has become interesting because of the high surfactant yield, low raw material cost and good surfactant performance (Salati et al., 2011).

Humic acid (HA) is defined as the alkali-soluble/acid-insoluble fraction of natural organic matter (soil, water, sediment and biomasses). HAs display amphiphilic characteristics so that in water they arrange themselves into micelle-like supramolecular structures (Salati et al., 2011).

From a chemical point of view, HAs are a complex mixture of low weight hydrophobic and hydrophilic molecules linked through both hydrophilic and hydrophobic bonds (Piccolo, 2002; Sutton and Sposito, 2005). HAs' composition depends on its origin: HAs from soil and sediment have high aromatic content (e.g., from lignin-derived molecules) and highly cross-linked lipid fractions (e.g. cutin and suberin from plants). Biomass HAs also contain raw or slightly degraded fractions such as carbohydrates, polysaccharides and fatty acids (Adani and Spagnol, 2008; Salati et al., 2011).

Chemical composition influences HA-surfactant properties (Conte et al., 2005; Salati et al., 2011): the hydrophilic/hydrophobic ratio (HI/HO) affects micellar structure, as does the presence of a

carboxylic fraction that gives polar or non-polar characteristics to the biosurfactant molecules (Quagliotto et al., 2006; Quadri et al., 2008). Again, the relative amounts of ionic vs. non-ionic hydrophilic fractions and/or of aromatic vs. alkyl hydrophobic fractions give different surfactant characteristics (Salati et al., 2011).

In previous studies, HAs were applied for soil washing to remove hydrophobic contaminants (Chin et al., 1997; Sakkas et al., 2002; Conte et al., 2005; Adani et al., 2010).

With a view to practical full-scale application, HA from biomasses is preferred rather than HA extracted from soil and sediment, because of the higher extraction yield. Moreover, the great variability in biomass sources offers a wide spectrum of HA-based surfactants having different characteristics which can be used for different applications (Salati et al., 2011).

The aim of this work is to test HAs extracted from various different sources to solubilize CLP-m and to assess their potential as substitutes for synthetic surfactants. A mechanistic understanding of the CLP-m solubilisation in the biosurfactant is proposed, as this knowledge can be useful for further studies in defining the optimal chemical characteristics of HA to solubilize CLP-m.

2. Materials and methods

2.1. Materials

Chlorpyrifos-methyl (CLP-m) (99% pure) was obtained from Riedel-de-Haen (Milan, Italy). Sodium dodecyl sulphate (anionic surfactant, SDS), Tween 20 (non-ionic surfactant), dihexadecyldimethylammonium bromide (cationic surfactant DHAB) and commercial humic substances from leonardite (HAc) (53680-technical) were purchased from Sigma-Aldrich (Milan, Italy).

2.2. Bio-based surfactant production

Two different biomass mixtures composed of lignocellulose waste (biomass L) and lignocelluloses plus kitchen food wastes (60:40 wet weight L_F) were composted at lab scale, obtaining the corresponding composts (L_C and L_{FC} respectively) (Quadri et al., 2008). Then bio-based surfactants (HA_L, HA_{LC}, HA_{LF}, HA_{LFC}) were extracted from the corresponding biomasses with aqueous 0.1 mol l⁻¹ NaOH and 0.1 mol l⁻¹ Na₄P₂O₇, using 1:50 w/v organic wastes/solution ratio, and successively precipitated at pH < 1.5.

2.3. Biobased surfactant characterisation

Micro-analytical data (C, H, N, S, and O contents) were obtained by using a C. Erba NA-2100 elemental analyser (Rodano, Milan, Italy) as reported by Quadri et al. (2008). CP MAS¹³C NMR spectra were acquired at 10 MHz on a Bruker AMX 600 spectrometer. The pulse repetition rate was set at 0.5 s and the contact time at 1 ms (Quadri et al., 2008).

Lipids were extracted from HA with hexane by using a Soxhlet apparatus. Fatty acids esterification, to obtain FAME, was achieved using 1 ml of BF₃/CH₃OH (1:4) and the solution was heated for 30 min at 60 °C; molecules were then separated using a capillary column ZB-WAX 30 * 0.25 mm * 0.25 μm (ID). The carrier gas was helium at a flow rate of 3 ml min⁻¹. One μl of sample was injected using CTC PAL into the GC injection port at 220 °C in splitless mode. The temperature program was set at 60 °C for 2 min, raised to 150 °C at a rate of 13 °C min⁻¹ then raised to 240 °C at 2 °C min⁻¹. The transfer line to the mass spectrometer was maintained at 250 °C. The mass spectra were obtained by electronic impact at 70 eV, and collecting data at an m/z range of 40–550. The FAME concentration was calculated quantitatively, by direct comparison with the external standard peak area (Supelco 37-Component mix, 47885-U).

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