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Extraction of model contaminants from solid surfaces by environmentally compatible microemulsions

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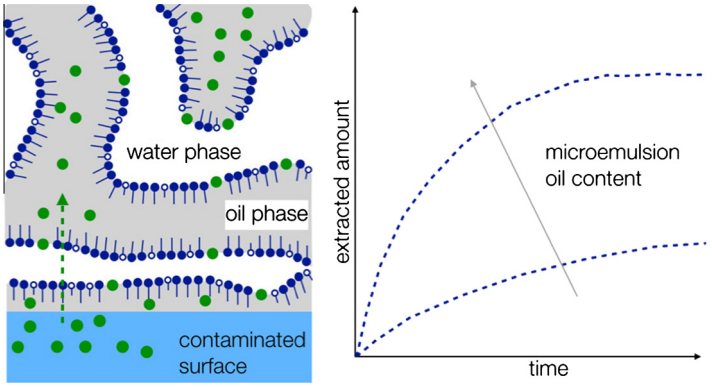
GRAPHICAL ABSTRACT



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ABSTRACT

In the present contribution, we evaluate the efficiency of eco-friendly microemulsions to decontaminate solid surfaces by monitoring the extraction of non-toxic simulants of sulfur mustard out of model surfaces. The extraction process of the non-toxic simulants has been monitored by means of spectroscopic and chromatographic techniques. The kinetics of the removal process was analyzed by different empirical models. Based on the analysis of the kinetics, we can assess the influence of the amounts of oil and water and the microemulsion structure on the extraction process.

1. Introduction

In view of a potential emergency caused by the accidental or intentional release of highly toxic substances, such as chemical warfare agents, pesticides, or toxic industrial compounds, it is required to develop and implement effective decontamination

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procedures. The effect of these toxic substances on the environment and the public health has to be mitigated and the initial conditions of the affected area have to be re-established [1,2]. The development of efficient decontamination media is challenging due to long persistence at solid surfaces of various chemical composition and surface morphology [3–5]. In this context, an universal and robust decontamination medium has to be able to (I) wet and eventually penetrate solid surfaces of different chemical nature and morphology (e.g. internal or external surfaces of technical equipment, wood, skin, concrete, among others), (II) remove and solubilize the toxic substances out of the solid surfaces and (III) ensure the in-situ degradation of the toxic substances to innocuous products (e.g., [6–8]). Furthermore, the decontamination medium should be environmentally compatible, non-toxic, biodegradable and stable under varying environmental conditions (temperature, humidity and pressure).

In view of this application, speed, residual content of the contaminant, and overall efficiency are crucial (e.g., [9,10]) and more important than for soil washing and remediation techniques based on surfactant solutions and microemulsions. Soil remediation includes micellar solubilization and mobilization of the trapped contaminant due to lowering the interfacial tension, e.g. [11,12]. For example, the desorption of organochlorine pesticides was promoted using empty and oil swollen micelles and optimized with respect to oil and surfactant type and concentration [13]. Microemulsions were also used to remediate chlorinated hydrocarbons [14]. The approach of using microemulsions for the conservation of cultural heritage needs to solve problems similar to decontamination, since sensitive target surfaces require a microemulsion formulation for a soft performance. For example, mild oil-in-water microemulsions have been used to remove hydrophobic material from hydrophilic surfaces of paintings [15,16].

To ensure environmental compatibility, the use of triglyceride oils in microemulsions designed for remediation was studied [17]. An interesting approach used rapeseed methyl ester and mixtures of anionic and non-ionic surfactants to form microemulsions, that have been proofed to extract polycyclic aromatic hydrocarbons from porous soil at low temperatures [18].

A versatile and robust decontamination medium should have a simple composition. To cover a wide range of external physical conditions the curvature of the amphiphilic interface and hence, the phase behavior, should not be tuned by temperature changes in a sufficiently wide range. Hence, sugar surfactant based microemulsions are promising media for the decontamination of the interfacial region of hydrophobically coated solid substrates. The sugar surfactant confers thermal stability in a wide temperature range to the microemulsions [19]. The stability and structure of the nanodomains are mainly determined by the properties of the surfactant interface between oil and water [20–23]. Knowledge about phase behavior and phase structures is also essential for the desired application. The polarity difference between the nanodomains favors wetting of and penetration into different kinds of solid surface [24,25]. This is an essential prerequisite for an efficient extraction out of the surface and solubilization inside the oil phase. The main advantage is the in-situ detoxification of the water-insoluble toxic compounds across the surfactant interface by means of active ingredients (enzymes, catalytic nanoparticles) hosted in the water phase. In this respect, it has been demonstrated that the enzyme diisopropyl fluorophosphatase (DFPase) efficiently detoxifies highly toxic G-type nerve agents inside the microemulsions [26–28].

The overall efficiency of the decontamination process is a complex interplay of these three processes (wetting, extraction and solubilization, in-situ detoxification). Detailed understanding of this interplay requires knowledge about the extraction kinetics at the solid substrate and the reaction kinetics inside the microemulsion in terms of rate constants. Moreover, based on rate constants, the influence of interfacial and structural properties of the microemulsion can be quantified. In the present article, we focus on the extraction process. In this study, the microemulsions are based on sugar surfactants and technical grade methyl oleate used as oil phase. These components are non-toxic, biodegradable and inexpensive [29,30]. Structural properties of the microemulsions as a function of their composition were characterized via SAXS, diffusion NMR spectroscopy and cryo-SEM.

We use three non-toxic lipophilic model contaminants in the extraction experiments. Sudan III dye is a lipophilic molecule that can easily be monitored by spectroscopic techniques. Methyl salicylate and 2-chloroethyl ethyl sulfide (CEES) are two lipophilic models for the highly toxic and water in-soluble sulfur mustard agent (see Table 1 in the supporting information). Often, empirical models are used to quantitatively analyze extraction or growth processes. Here, we applied four frequently used models to analyze the extraction kinetics. The models were compared with respect to the goodness of the fits. Thus, reliable kinetic parameters for the extraction by bicontinuous microemulsions at different oil-to-water ratios for three test molecules and detection methods were obtained.

2. Experimental section

2.1. Materials

The methyl oleate Synative ESMETI 05 (BASF, Germany), was used as oil phase. This oil is a synthetic equivalent of the main component of rapeseed methyl ester. The sugar surfactant Simulsol SL55 ($C_{12/13}G_{1.3}$) was provided by Seppic (Germany). Pentanol (99%), butyl methacrylate (99%), ethylene glycol dimethacrylate (99%), 2,2-dimethoxy-2-phenylacetophenone (99%), 3-(trichlorosilyl) propyl methacrylate (99%), 1-propanol (95%), 1,4-butanediol (90%) and 2-chloroethyl ethyl sulfide (CEES) were purchased from Sigma-Aldrich (Germany). All chemicals, except the surfactant were used as received. The surfactant stock solution was freeze dried to a residual water content of $\ll$1%. A three-stage Milli-Q Plus 185 (Millipore) purification system was used for water purification.

2.2. Composition and characterization of microemulsions

2.2.1. Composition

The quaternary microemulsions consist of water/MO/SL55/pentanol. The phase diagrams of this quaternary system were evaluated at constant oil to water ratio (α), while at constant α, the content of sugar surfactant (γ) and co-surfactant pentanol(δ) were varied.

$$\alpha = \frac{mass_{\text{oil}}}{mass_{\text{oil}} + mass_{\text{water}}} \tag{1}$$

$$\gamma = \frac{mass_{\text{surfactant}}}{mass_{\text{surfactant}} + mass_{\text{oil}} + mass_{\text{water}}} \tag{2}$$

$$\delta = \frac{mass_{\text{cosurfactant}}}{mass_{\text{cosurfactant}} + mass_{\text{surfactant}} + mass_{\text{oil}} + mass_{\text{water}}} \tag{3}$$

2.2.2. Cryo-SEM

Cryogenic scanning electron microscopy (cryo-SEM) allows to characterize and visualize the structural changes of the microemulsions caused by variation in their composition [31–33]. The structure of the bicontinuous microemulsion was examined by cryo-high resolution scanning electron microscopy