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Research paper

Investigation into the suitability of layered silicates as adsorption media for essential oils using FTIR and GC–MS

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ABSTRACT

This study assessed the suitability of layered silicate substrates as adsorption media for an essential oil (EO) blend with antimicrobial properties. It is anticipated that adsorption of the EO blend within the layered silicate will lead to controlled release of the blend. Three montmorillonites (Mt), a natural/synthetic hybrid Mt and two synthetic layered silicates were selected as potential adsorption materials. Gas chromatography (GC) was used to follow static adsorption of the EOs from heptane. The GC adsorption studies enabled the effect of adsorption on the individual molecular components of the oils to be determined, as well as providing a value for the overall level of adsorption of the EO. The Mts were found to degrade some of the important molecules in the EO and were therefore deemed to be unsuitable. The synthetic layered silicates provided the highest levels of adsorption, achieving up to 170 $mg \cdot g^{-1}$ without the degradation effects shown by the natural Mts.

1. Introduction

Essential oils (EOs) are natural volatile oils, which are responsible for many of the fragrances produced by plants. These oils can be easily obtained using a variety of different extraction techniques such as solvent extraction or distillation (El-Mougy, 2009). They are typically composed of simple molecules, based around repeating isoprene units, called terpenes (Williams, 1989). EOs have been used throughout history as simple remedies (Adams et al., 2011; Williams, 1989). Since the middle of the 20th century a wide range of uses for EOs have been investigated, including pest repellents, antidepressants, anti-inflammatories and antioxidants (El-Mougy, 2009; Lis-Balchin and Hart, 1997; Melo et al., 2011; Tumen et al., 2012; Yoon et al., 2009).

The most widely studied properties of EOs have been their effect on microorganisms, which have shown them to be effective at inhibiting the growth of, and in some cases killing, a wide range of bacteria, fungi and parasites (El-Mougy, 2009; Hammer et al., 1999; Inouye et al., 2006; Kunicka-Styczyńska et al., 2009; Porter and Wilkins, 1998; Rosato et al., 2007; Schelz et al., 2006). We were interested in the incorporation of EOs into polymers for the manufacture or coating of surfaces, in order to confer antimicrobial activity, which could be used to help combat healthcare associated infections. Due to the volatile nature of EOs, their direct incorporation into polymer materials was unlikely to prove beneficial, as they would bloom to the surface rapidly and be lost via evaporation. With studies showing that the antimicrobial activity of EOs exposed to air was significantly reduced after 60 min (Chao et al., 2005). In order to overcome this rapid loss of activity, controlled release of the EOs into the polymers would be required.

Research into the controlled release of EOs has focused mainly on encapsulation within organic media (Keawchaoon and Yoksan, 2011; Maji et al., 2007; Parris et al., 2005; Paula et al., 2011). It is possible that organic encapsulants could become damaged by the harsh conditions used in the production of many polymers, such as the high temperatures and shear involved in the processing of thermoplastics, or the solvents used in the preparation of paints. Any damage done to the encapsulant could result in the rapid loss of the EOs. It was proposed that adsorption of EOs onto an inorganic porous material could provide controlled release and protection against polymer processing conditions.

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The high surface area of montmorillonite (Mt) materials, which arises as a result of their layered structure, makes them an ideal adsorbent. The adsorption properties of Mt are well documented in the scientific literature, with many examples of adsorption of organic material; such as 2,4,6-trichloroanaline (Gianotti et al., 2008), and tetracycline (Parolo et al., 2012). The retention of clove oil within gelatine-egg white films has been shown to be improved via the addition of sepiolite, indicating adsorption of the oil onto silicate materials (Giménez et al., 2012). Adsorption of EOs onto Mt is a new area of study; a recent paper by Nguemtchouin et al. investigated the adsorption of *Ocimum gratissimum* EO onto Mt and organically modified Mt. They found that the insecticidal effect of the oil was retained after adsorption onto the Mt (Nguemtchouin et al., 2013).

The authors note that the papers reported above investigate the use of Mt as an adsorption media for EOs. However, they do not provide information as to the effect of adsorption on the oils or in depth analysis of the mass of adsorption achieved.

Allowing material to desorb off after adsorption would be a vital property for any material used in this study, as the antimicrobial EO blend would need to be available if it was to have any effect. Desorption of organic material from Mt has been less extensively studied than adsorption, there are however examples of controlled desorption being achieved using Mts (Sannino et al., 1999; Shin et al., 2005; Wang et al., 2005).

2. Experimental

2.1. Materials

Rockwood Additives Ltd. (Moorfield Road Widnes, Lancashire, WA8 3AA, UK) provided six porous minerals for use as adsorption substrates Fulcat® 400 (F400), Fulcat® 435 (F435), Fulcat® 800 (F800), Fulacolor® (Fcol), Laponite® RD (LRD) and Laponite® B (LB).

Fulcat® 400 was a raw bentonite clay, cation exchange capacity (CEC) of 90 meq 100 g^{-1} and Ca^{2+} interlayer cations.

Fulcat® 435 and Fulacolor® were acid leached bentonites with increased surface area, in comparison to Fulcat® 400, and H^+ interlayer cations.

Fulcat® 800 was an inorganic synthetically modified acid-leached bentonite, CEC of 128.8 meq 100 g^{-1} and a mixture of H^+ and Ca^{2+} interlayer cations.

Laponite RD was a synthetic layered silicate, CEC of 53.9 meq 100 g^{-1}, Na^+ interlayer cations and chemical formula $Na^+_{0.7}[(Si_8Mg_{5.5}Li_{0.3})O_{20}(OH_4)]^{0.7-}$.

Laponite B was a synthetic layered flurosilicate, CEC of 98.6 meq 100 g^{-1}, Na^+ interlayer cations and chemical formula $Na^{0.7+}[(Si_8Mg_{5.5}Li_{0.3})O_{20}(OH_{2.5})F_{1.5}]^{0.7-}$.

The substrates were dried at 120 °C for 48 h prior to all experimental and characterisation work, and stored in a desicator under nitrogen when not in use.

Geranium bourbon (*Pelargonium graveolens* L'Her.), rosewood (*Anibarosaeodora* var. *amazonica* Ducke, lavender English folgate (*Lavandula angustifolia* Mill.), origanum (*Origanum vulgare* L.), manuka (*Leptospermum scoparium*) Forster & Forster, grape seed oil (*Vitisvinifera* L.) were obtained from Essentially oils LTD (Chipping Norton, UK).

Heptane, for HPLC, ≥99% (Sigma-Aldrich, UK) was used as the EO solvent for all adsorption studies. Dodecane, ≥99% (Sigma-Aldrich, UK) was used as the internal standard (IS) for all gas chromatography adsorption studies.

2.2. Methods

2.2.1. Characterisation of substrates

FTIR spectra were acquired via Diffuse Reflectance Fourier Transform Infrared spectroscopy (DRIFTS) on a ThermoNicolet Nexus FT-IR spectrometer fitted with a Spectra-Tech DRIFTS cell. The spectra were collected by accumulating 164 scans at a resolution of 4 cm^{-1} in the range of 500–4000 cm^{-1}. Spectra of substrates recovered after adsorption of the EO were compared to spectra of the pure EOs and substrates prior to adsorption to confirm the presence of EO molecules after adsorption.

WAXS powder diffraction was undertaken using a Phillips PW 1730, fitted with a Cu-Kα tube Anode voltage and current were 50 kV and 40 mA, respectively. The conditions were as follows: start angle 1.5°, end angle 20°, step size 0.010°, counting time 1 s, and temperature 25 °C. Data was recorded and processed using Diffrac AT software.

Multi-point BET surface area determination was carried out on the substrates using a Tristar II 3020 BET analyser, and the data were processed and plotted using Tristar Confirm™ software. Samples were degassed by cooling under vacuum, then to heating 60 °C under vacuum overnight in preparation for analysis.

BET surface area was determined from a five point N_2 adsorption isotherm. The absolute pressures used were 50.0, 87.5, 125, 162.5 and 200.0 mm Hg.

To give a preliminary quantification of the number of Brønsted and Lewis acid sites of the substrates the pH of each substrate was measured. 15 g (1 g was used for Laponite® substrates due to gel formation at higher masses) of substrate was added to 45 mL of distilled water and stirred using a magnetic stirrer for 30 min. After 30 min the pH was measured using a pH probe calibrated at pH 2, 4, 7 and 10. The resulting pH was used to calculate the $[H^+]$, which was divided by the surface area of the substrate to provide a value for $[H^+]\cdot m^{-2}$.

2.2.2. Static adsorption studies from solution monitored using gas chromatography

Calibration curves for the key molecular components of the five major components of the EO were set up by running GC analysis of each oil at 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, and 0.4% (m/v) in heptane. The peak areas of each molecule were ratioed against the peak area of an internal standard and plotted against percentage (m/v) in order to obtain the calibration plot. The data points were fitted using linear regression analysis, and the regression equation was then used to calculate the percentage (m/v) of the molecule remaining in the solution after adsorption onto a substrate.

In a 100 ml bottle with a PTFE seal lid, the substrate to be analysed (5 g) was added to heptane (100 ml) spiked with dodecane (1.25%) as an internal standard (IS), and the chosen EO (1.25 g) was then added. A magnetic stirrer follower was placed in the heptane solution and the bottle was sealed. The mixture was stirred for 18 h at room temperature. After stirring, the substrate was filtered off from the supernatant liquor using Buchner filtration. The recovered substrate was then allowed to dry at room temperature to constant mass. The substrate was then analysed using DRIFTS. After filtration the supernatant liquor (25 ml) was centrifuged at 4000 rpm for 10 min using a Hermle Z200 A (relative centrifugal force, 1700 *g*), to deposit any fine particles remaining, and the resultant liquid was decanted into a small glass vial.

The supernatant liquor was analysed using an HP 5890 Series 2 GC in order to determine the concentration of molecular components after adsorption. By taking the ratio of the peak area of a particular component molecule to the peak area of the IS and inputting it into the relevant calibration equation it was possible to obtain the percentage (m/v) of the molecule in the supernatant liquor after adsorption. This value was then compared to the equivalent value for the molecule in a 1.25% (m/v) solution in order to determine the reduction due to adsorption. From the latter, the level of adsorption of that component onto the substrate was calculated.

Reported adsorption levels were the mean of three replicates. Student t-tests were performed to determine whether the differences in adsorption between the substrates were significant. Significance was assessed at 90% and 95% confidence levels, and the critical t values were 2.92 and 4.303 respectively.