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Encapsulation of essential oils in porous silica and MOFs for trichloroisocyanuric acid tablets used for water treatment in swimming pools

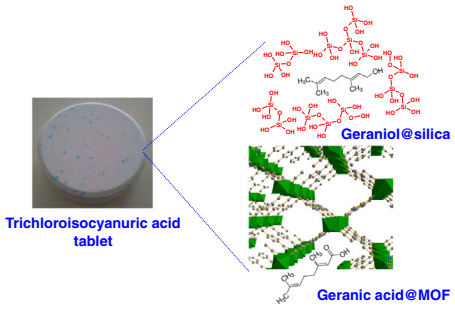
Lorena Paseta [a], Elena Simón-Gaudó [b], Francisco Gracia-Gorría [b], Joaquín Coronas [a,*]

[a] Chemical and Environmental Engineering Department and Instituto de Nanociencia de Aragón (INA), Universidad de Zaragoza, 50018 Zaragoza, Spain
[b] Ercros, S.A., R&D Department, Avenida Diagonal 595, 08014 Barcelona, Spain

HIGHLIGHTS

- Trichloroisocyanuric acid (TCCA) tablets for water treatment in swimming pools.
- Encapsulation of insect repellents in silica and MOFs MIL-53(Al) and MIL-88A(Al).
- Repellents were geranic acid, citronellic acid, geraniol and IR3535®.
- Inclusion in TCCA tablets of encapsulated insect repellents.
- TCCA with encapsulated repellents produced stable multifunctional tablets.

GRAPHICAL ABSTRACT



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ABSTRACT

Trichloroisocyanuric acid (TCCA) tablets are used for water treatment in swimming pools. This is a safe way of releasing hypochlorous acid with disinfectant, algaecide and bactericide functions. This work investigates the inclusion in such tablets of insect repellents (geranic acid, citronellic acid, geraniol and IR3535®) with a simultaneous perfume function. A simple mixture of TCCA with the repellents is not possible due to the incompatibility between both components. A strategy of encapsulation in silica and MOFs MIL-53(Al) and MIL-88A(Al) has been developed. The subsequent formulation of TCCA with the encapsulated repellents avoided the compatibility problems and produced marketable stable multifunctional (water treatment–insect repellency–perfume) tablets for water treatment.

1. Introduction

Porous solids can act as hosts and encapsulate active materials (guests) by entrapping them within their porosity. The most commonly used materials for encapsulation are silicas (both non-ordered and ordered) [1], zeolites [2] and MOFs (metal-organic frameworks) [3]. Amorphous silicas are cheap, compatible with many systems, and present high pore volume, usually with low specific interaction with target guests. Zeolites may develop more specific interactions with guests than silicas and provide higher energy confinement (e.g. stronger adsorption sites). However, they are limited by their prototypical microporosity. Meanwhile, MOFs offer many new opportunities due to their chemical variety, structural flexibility and wide range of porosity [4].

The advantage of encapsulation is that it is a way of conveying the properties of the target guests into convenient hosts. Among other beneficial effects, encapsulation can enhance the thermal

* Corresponding author. Tel.: +34 976 762471; fax: +34 976 761879.
E-mail address: coronas@unizar.es (J. Coronas).

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stability of the encapsulated substance [5], chemically protect substances from oxidation in the case of foods [6], control the release of medication into the body to maximize its efficacy [7], improve the compatibility of poorly water-soluble drugs for proper absorption in the body [8], heterogenize homogeneous catalysts such as metal complexes for handling as common solid catalysts [9], and convert non-conductive solids into conductive materials [10].

Even if certain substances like caffeine have been used as model compounds for evaluation [11], encapsulation in porous materials applies not only to a wide range of fields as mentioned above but also to different types of chemical substances. These range from metal complexes [12], vitamins [13], dyes [14] and pheromones [2] in zeolites to biocides in silica [15], and drugs in MOFs [16]. In this work, we focus on the encapsulation of insect repellents with a simultaneous perfume function (i.e. geranic acid, citronellic acid, geraniol and IR3535®, see Fig. 1a) in amorphous silica, zeolites and MOFs with the purpose of producing a marketable multifunctional tablet for water treatment in swimming pools. These tablets, with disinfectant, algaecide and bactericide functions, usually incorporate trichloroisocyanuric acid (TCCA, $C_3Cl_3N_3O_3$) which can react in water releasing hypochlorous acid (HClO), see Fig. 1b. This is an interesting example in which the encapsulation in nanoporous materials helps the fabrication of a marketable product (TCCA tablets formulated with insect repellents). Due to the small amount of nanoporous material needed in the formulation, the cost increase in the final product would be low. The emphasis of the research carried out was on minimizing, through the encapsulation technique, the Cl_2 outgassing of the tablets that the direct presence of non-encapsulated repellents produced. In addition, the perfume function of the repellents would neutralize the acrid smell due to the possible presence of Cl_2 during tablets handling. Finally, besides use as a disinfectant, TCCA has found applications as a chlorination [17] and oxidant [18] agent and as a mild homogeneous catalyst [19] in organic chemistry.

2. Experimental section

2.1. Silica encapsulation

500 mg of the liquid insect repellent (geranic acid, Alfa Aesar, ⩾90%; citronellic acid, Alfa Aesar, 94%; geraniol, Sigma Aldrich, 98%, and IR3535®, Merck) together with 2.5 mL of ethanol (Scharlau, 99.9%) was placed in a 8 mL vial and stirred until dissolution. This solution was then poured over 500 mg of previously dried silica (overnight at 100 °C) in a Petri dish. Both were mixed with the help of a spatula until obtaining a homogeneous mixture that was dried at room temperature to remove ethanol. Commercial amorphous silica IBERSIL® A-400 was generously provided by the IQE S.A. company.

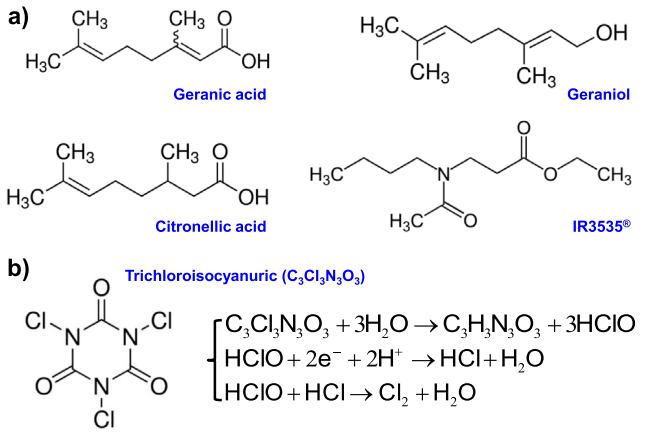

Fig. 1. (a) Formulae of selected insect repellents: geranic acid, 3,7-dimethyl-2,6-octadienoic acid; citronellic acid, 3,7-dimethyl-6-octenoic acid; geraniol, (trans)-3,7-Dimethyl-2,6-octadien-1-ol; and IR3535®: 3-(N-n-butyl-N-acetyl)aminopropionic acid ethyl ester. (b) Formula of trichloroisocyanuric acid (TCCA) and its reactions in water to produce first cyanuric acid and hypochlorous acid and then Cl_2 upon oxidation of HClO to give Cl_2.

2.2. Synthesis of MOFs

In a typical synthesis of MIL-53(Al) [20], 5.2 g (13.9 mmol) of aluminum nitrate nonahydrate (Sigma Aldrich, ⩾98%) and 1.12 g (6.7 mmol) of terephthalic acid (Sigma Aldrich, 98%) were dissolved in 20 mL of distilled water and placed in a Teflon-lined steel autoclave for 3 days at 220 °C. The product obtained was recovered by centrifugation at 10,000 rpm during 10 min, washed once with ethanol by centrifugation under the same conditions and dried overnight at 65 °C. The solid was activated by calcination at 380 °C for 24 h (see thermogravimetric analyses (TGA) in Fig. S1).

To obtain MIL-88A(Al) [21], two different solutions were prepared. First, 2.98 g (7.94 mmol) of aluminum nitrate nonahydrate (Sigma Aldrich, ⩾98%) was dissolved in 10 mL of distilled water in a spherical flask. Second, 0.92 g (7.94 mmol) of fumaric acid (Acros Organics, ⩾99) was dissolved in a mixture of 4.8 mL of NaOH solution (0.1 g/mL) and 10.2 mL of distilled water. The second solution was then added to the first and stirred at 60 °C during 10 min. The suspension obtained was centrifuged at 10,000 rpm for 10 min, washed once with ethanol centrifuging under the same conditions as described above and dried overnight at room temperature. No activation process was needed, in agreement with TGA in Fig. S1.

2.3. Encapsulation in MIL-53(Al) and MIL-88A(Al)

The encapsulation was carried out as follows: 100 mg of the activated MOF was placed in a 8 mL vial and 1 mL of pure insect repellent was added. The contents of the vial were stirred at 60 °C during different periods of time (1, 2, 4 and 7 days in the case of MIL-53(Al) and 3 days in that of MIL-88A(Al)). The solid was collected and washed with ethanol 3 times by centrifugation as described above and dried overnight at room temperature. This encapsulation is commonly described as conventional or multistep encapsulation (MSE).

2.4. In situ or one step encapsulation (OSE) in MIL-88A(Al)

The procedure followed has two differences with respect to the synthesis of the MOF itself. One is the addition to the reactive medium of a solution corresponding to 1 mg of the insect repellent in 1 mL of ethanol; the other refers to the synthesis time which is 1 h instead of 10 min.

2.5. Citronellic acid release

Release experiments were carried out at 30 °C with three different samples: citronellic acid@silica, citronellic acid@MIL-53(Al) and citronellic acid@MIL-88A(Al). The corresponding sample (50 mg) was suspended in a beaker with 500 mL of distilled water. Periodically, a 3 mL aliquot was taken and analyzed with a UV–vis spectrophotometer (V-670 Jasco UV–vis spectrophotometer) at the wavelength of maximum citronellic acid absorption (200 nm). The concentration of citronellic acid was calculated from a calibration curve prepared with several citronellic acid–water solutions in the 0–0.06 g/L concentration range. Before each release experiment, a blank measurement was made with distilled water under the same conditions as mentioned above.