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

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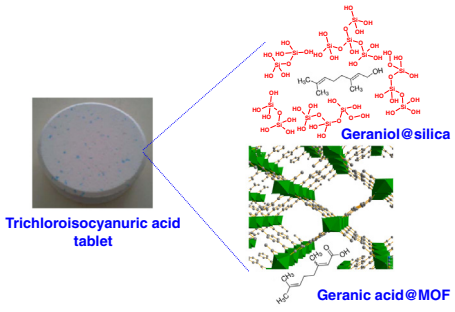
HIGHLIGHTS

- 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

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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.

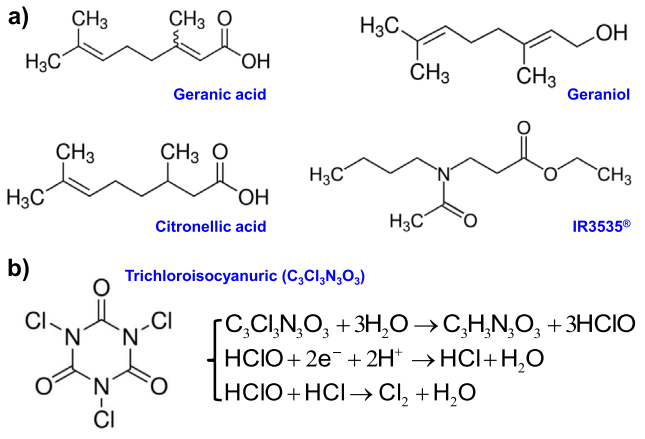

Fig. 1. (a) Formulae of selected insect repellents: geranic acid, 3,7-dimethyl-2,6-octadienoic acid; citronellic acid, 3,7-dimethyl-6-octenoic acid; geraniol, (trans)-3,7-Dimethyl-2,6-octadien-1-ol; and IR3535®: 3-(N-n-butyl-N-acetyl)aminopropionic acid ethyl ester. (b) Formula of trichloroisocyanuric 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.

2.6. Tablet preparation

The tablet preparation process comprises the following steps: (a) TCCA and additive blending; (b) feeding the molds with the mixture of step a; (c) compressing the molds of step b by means of a hydraulic press, and (d) ejecting the tablet from the mold. The tablets were 12.5 mm thick with a diameter of 60 mm and a weight of 200 g.

2.7. Cl_2 outgassing

TCCA was mixed with the different additives at 0.2 wt% loading. A given mixture (100 g) was placed in a 500 mL ground Erlenmeyer flask. This was capped with a suitable stopper, fixed to the flask with a clamp. The flask was placed in an oven at 60 ± 2 °C for 15 h, after which it was removed and allowed to cool down for 1 h.

Aided by a vacuum pump, the gas contained in the Erlenmeyer flask was bubbled through three consecutive wash bottles: the first and the third empty for safety reasons and the second containing 70 mL of 10 wt% KI and 30 mL of 10 wt% H_2SO_4. This operation lasted 5 min, enough time to reduce the pressure to below 100 mmHg. The wash bottles were then disconnected from the Erlenmeyer flask and the second bottle content was decanted, together with its washing water, to another 500 mL Erlenmeyer flask. The released iodine was titrated with 0.05 M $Na_2S_2O_3$ until the disappearance of the yellow color. The result was expressed in grams of Cl_2 released. This procedure was also carried out with the tablets.

2.8. Characterization

Powder X-ray diffraction (XRD) was performed at room temperature in a D-Max Rigaku diffractometer with a copper anode and a graphite monochromator so as to select Cu–Kα_1 radiation (λ = 1.540 Å). Data were collected in the 2θ range = 2.5–40°, and the scanning rate used was 0.03 °/s.

Powder samples were characterized by attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR). The spectra were recorded in the 4000–600 cm^{-1} wavenumber range with an accuracy of 4 cm^{-1}, and the equipment used was a BrukerVertex 70 FTIR spectrometer equipped with a deuterated triglycine sulfate detector and a Golden Gate diamond ATR accessory.

Thermogravimetric analyses (TGA) were carried out using Mettler Toledo TGA/SDTA 851e equipment. The samples were put in 70 μL alumina pans and heated up to 700 °C with a heating rate of 10 °C/min under a N_2 atmosphere.

3. Results and discussion

3.1. First screening of host materials

Some decomposition of the acid occurs during the storage of the TCCA tablets, producing Cl_2, see the three reactions in Fig. 1b. Since HClO behaves as a strong oxidant (E° = 1.63 V), the second reaction produces HCl which in turn reacts with HClO giving rise to Cl_2. There is a threshold of 15 mg Cl_2 (produced at 60 °C for 15 h) that determines whether a procedure of handling or modification is or is not appropriate. This criterion, not a normalized one, is based on the experience that company Ercros has developed dealing with TCCA tablets. Table 1 shows the results of the initial screening carried out regarding the possible compatibility between TCCA and the encapsulating materials. Upon measuring the Cl_2 outgassing, this revealed that certain MOFs were not desirable materials. In addition, ZSM-5 and HKUST-1 were also discarded due to their low porosity and/or relatively high outgassing values. Even though it is difficult to give a general explanation of the behavior of the solids, the fact that MOFs have certain metals in their composition (Zn, Zr, Fe) may promote the decomposition of TCCA. In any event, the materials chosen for the study of encapsulation and tablet formulation were the MOFs MIL-53(Al) and MIL-88A(Al) prepared here, and commercial amorphous silica.

Table 1
Outgassing screening results corresponding to the mixture of 200 mg of porous material with 100 g of TCCA; BET specific surface areas of porous materials from N_2 adsorption; the value for MIL-53(Al) was obtained from Ar adsorption, while that for MIL-88A(Fe) was not available.

Porous material	Type	Outgassing [mg Cl_2]	S_{BET} [m^2/g]
TCCA (alone)	–	1.4	–
MIL-53(Al)	MOF	1.1	1140 ± 39
MIL-88A(Al)	MOF	2.8	939 ± 15
IBERSIL® A-400 from IQESIL Co.	Amorphous silica	4.4	168 ± 1
HKUST-1	MOF	8.7	1925 ± 37
ZSM-5 from Zeolyst International	Zeolite	9.7	367 ± 7
UiO-66(Zr)	MOF	35	1059 ± 20
MIL-88A(Fe)	MOF	49	–
ZIF-8	MOF	51	1924 ± 17

3.2. Impregnation of silica with insect repellents

Commercial amorphous silica IBERSIL® A-400 has a BET area of 182 ± 1 m^2/g, a pore volume of 0.62 cm^3/g and an average pore size of about 14 nm. This means that this material does not produce a strong physical confinement in agreement with the temperature of weight loss similar to that of the pure additive, as can be seen in Fig. 2 when comparing the TGA curves of the pure additive IR3535® (A) and IR3535®@silica (B). However, the impregnation of silica with the four repellents dissolved in ethanol (their solubility in water was very low) for proper mixing allowed the production of homogeneous powder materials with 122–142 g of additive per 100 g of dry solid (silica), as determined by TGA (see Table 2), once the alcohol was evaporated. The homogeneous dispersion was observed with the naked eye. If ethanol was not used, the impregnation of silica with repellents, at least in the working proportions, would not happen homogeneously throughout the porous material due to the highly viscous slurry obtained. Fig. 2 depicts as an example the TGA curves corresponding to the encapsulation of IR3535® in the different materials. The other TGA curves used to produce the data in Tables 2–4 are analogous.

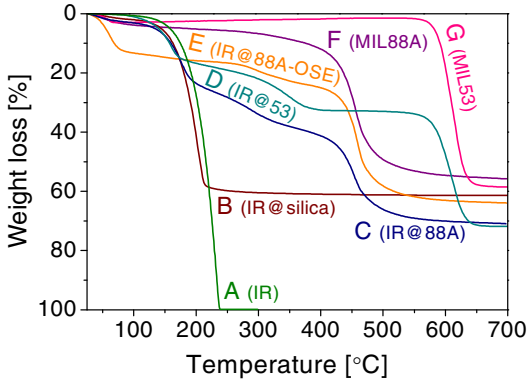

Fig. 2. TGA curves of pure IR3535® (A, IR), IR3535®@silica (B, IR@silica), IR3535®@MIL-88A(Al) (C, IR@88A), IR3535®@MIL-53(Al) (D, IR@53), IR3535®@MIL-88A(Al) (OSE) (E, IR@88A-OSE) and activated MIL-88A(Al) (F, MIL88A) and MIL-53(Al) (G, MIL53).

Table 2
Impregnation of IBERSIL® A-400 at room temperature with the different insect repellent additives. Loadings of repellents as determined by TGA.

Additive	(g additive/g dry solid)·100
Geranic acid	126
Citronellic acid	132
Geraniol	122
IR3535®	142

Table 3
Encapsulation of insect repellent additives in MIL-53(Al) by multi-step encapsulation (MSE) at 60 °C. Loading of repellents as determined by TGA.

Additive	(g additive/g dry solid)·100			
	1 day	2 days	4 days	7 days
Geranic acid	18.4	23.7	24.5	30.3
Citronellic acid	16.3	15.8	16.4	20.0
Geraniol	16.2	19.1	21.0	23.9
IR3535®	17.9	18.2	19.0	20.4

Table 4
Encapsulation of insect repellent additive in MIL-88A(Al) by multi-step encapsulation (MSE) for 3 days and one-step encapsulation (OSE) for 1 h at 60 °C. Loading of repellents as determined by TGA.

Additive	(g additive/g dry solid)·100	
	MSE	OSE
Geranic acid	11.0	14.6
Citronellic acid	9.5	12.0
Geraniol	9.3	11.5
IR3535®	20.7	21.1

The advantage of the impregnation/encapsulation in amorphous silica is not related to controlled release (something unthinkable with a material having pores at least 20 times greater than the molecular sizes of the repellents) but to the fact that it allowed a homogeneous dispersion with TCCA without altering significantly its Cl_2 outgassing, as will be shown below.

3.3. Encapsulation of repellents in MOFs MIL-53(Al) and MIL-88A(Al)

As mentioned above, zeolites were initially discarded from this research. In addition, it has been demonstrated that, due to their flexibility, MOFs can encapsulate molecules larger than their corresponding pore sizes, as is the case of caffeine in ZIF-8 [22]. However, here we have focused on the carboxylate type MOFs MIL-53 (Al) and MIL-88(Al), since their possible decomposition in water would release biocompatible moieties [23]. MIL-53(Al) and MIL-88(Al) were synthesized from terephthalic and fumaric acids as organic linkers. Both MOF structures have great flexibility and pore sizes of 0.86 and 0.6 nm, respectively [24], together with specific surface areas of 1100 m^2/g (BET) [25] and 1140 m^2/g (Langmuir) [21].

To encapsulate the additives, the MOFs were equilibrated for some time at 60 °C with the pure additives, i.e. no solvent was used. Besides its simplicity, this methodology increased the driving force for encapsulation and was in part necessary due to the low solubility in water of the repellent additives in question. The use of an alternative solvent to water would have produced some inefficient competitive adsorption. Table 3 (and Fig. S2) shows the results obtained. For the four repellents the encapsulation increased with time under contact, reaching values probably close to saturation after 4–7 days. In any event, the adsorption amounts in the 20.0–30.3 g of additive per 100 g of dry solid (MOF) achieved after 7 days for any of the additives were considered enough for the purpose of this research. Furthermore, unlike the encapsulation in silica, the corresponding TGAs (Fig. 2) exhibit some thermal stabilization which is due to the stronger host–guest interaction that occurs with MOFs.

FTIR characterization was used to assess the chemical prevalence of the different repellents upon encapsulation. Fig. 3 shows the characterization of geranic acid as an example. The FTIR spectra of the rest of the materials can be seen in Figs. S3–S5. In the case of geranic acid, the absorbances at 2920 and 2970 cm^{-1}, related to C—H stretching, and at 1690 and 1635 cm^{-1}, respectively assigned to C=O and C=C stretching, are evidence of the unchanged presence of this acid in the solids.

To encapsulate an organic compound into a MOF there are two possible methodologies [11]. One corresponds to the conventional or multi-step encapsulation (MSE), whose results have been described in the previous paragraph. The alternative is one-step encapsulation (OSE), also called in situ encapsulation, which consists of building the MOF around the guest-molecule to be encapsulated. OSE may be preferable to conventional MSE which requires: (1) synthesis of the MOF host, (2) subsequent activation of the host, and (3) the encapsulation itself. Table 4 compares MSE and OSE of the additives in MIL-88A(Al). In general, there are no substantial differences between the methodologies in terms of the amount encapsulated. OSE is favored over MSE due to its simplicity. In previous studies with caffeine, the OSE methodology produced saturation of the material with the guest molecule, i.e. the highest encapsulation value was achieved with MSE [22]. This suggests that the capacity of encapsulation of MIL-88A is below that of MIL-53, as is shown by a comparison of Tables 3 and 4, and more clearly in Fig. S6. This result is also consistent with the above-mentioned differences in pore sizes, favoring MIL-53 (0.86 nm) over MIL-88A (0.6 nm).

In addition, Hansen solubility parameters (HSP) [26,27] were used to gain insight into the repellent-MOF interaction [11]. HSP account for the possible chemical interaction without considering limitations due to guest molecular dimensions and MOF pore sizes [11]. The corresponding HSP parameters (δ_D, δ_P and δ_H for dispersion or London interaction, polar interaction and hydrogen bonds, respectively) are given in Table 5. They allow the calculation of the parameter *Ra* with the following equation [27]:

$$Ra^2 = 4(\delta_{D1} - \delta_{D2})^2 + (\delta_{P1} - \delta_{P2})^2 + (\delta_{H1} - \delta_{H2})^2 \quad (1)$$

In our case parameters δ_{D1}, δ_{P1} and δ_{H1} and δ_{D2}, δ_{P2} and δ_{H2} correspond to guest (repellent) and MOF ligand (since HSP for MIL-53 and MIL-88A are not available [11]), respectively. The smaller the

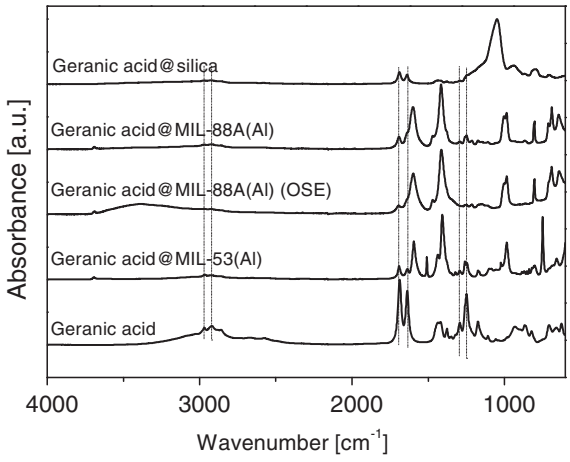

Fig. 3. FTIR spectra of pure geranic acid, geranic acid@MIL-53(Al), geranic acid@MIL-88A(Al) (OSE), geranic acid@MIL-88A(Al) and geranic acid@silica.

Table 5
Ra values calculated from Hansen solubility parameters (HSP) for repellents and ligands terephthalic acid (MIL-53(Al)) and fumaric acid (MIL-88A(Al)). HSP values were obtained using Y-MB technique with the commercial package Hansen solubility parameters in practice [26].

	HSP [MPa$^{0.5}$]			*Ra* [MPa$^{0.5}$]	
	δD	δP	δH	Terephthalic acid (MIL-53)	Fumaric acid (MIL-88A)
Geranic acid	17.2	4.35	8.80	7.5	15.7
Citronellic acid	16.7	4.12	8.62	8.4	16.1
Geraniol	16.9	4.16	7.61	8.6	16.9
IR3535	16.9	8.11	5.74	9.5	16.9
Terephthalic acid	20.0	7.20	12.8		
Fumaric acid	18.2	10.8	23.0		

Ra value the better the repellent-MOF compatibility. In consequence, the *Ra* values in Table 5 support a higher encapsulation from the point of view of chemical interaction in MIL-53 (*Ra* 7.5–9.5 for the four studied repellents) than in MIL-88A (*Ra* 15.7–16.9), in line with the previous discussion related to MOF pore size. Namely, both chemical interaction and porosity favor MIL-53 over MIL-88A.

Figs. 4 and 5 show the X-ray diffractograms corresponding to encapsulation in both MOFs MIL-53(Al) and MIL-88A(Al) using the MSE and OSE methodologies. Diffractograms of MIL-53 are not susceptible to obvious analysis due to the flexibility of the structure, which was distorted and altered after the encapsulation in all cases. Recently, it has been observed that the NH_2-MIL-53(Fe) structure is converted into NH_2-MIL-88B(Fe) when encapsulating caffeine [5]. In any event, the diffractograms in Fig. 4 are proof of a crystalline order and of an open structure (since the diffraction peaks remain at low angles comparable to those of the activated material) in the MIL-53(Al) based materials encapsulating the insect repellents. In the case of MIL-88A(Al) based materials (Fig. 5), the diffraction patterns are similar for the different materials. This may be due to two reasons: (i) the different flexibility of the structure (described also as one that can exhibit the breathing phenomenon [28]), and (ii) the weaker host–guest interaction consistent with the lower encapsulation achieved with MIL-88A(Al) for all the repellents (Tables 3 and 4).

As proof of controlled release, citronellic acid@silica, citronellic acid@MIL-53(Al) and citronellic acid@MIL-88A(Al) were suspended in water for several hours and their evolution followed by UV-vis. Fig. 6 shows how the normalized release reached its

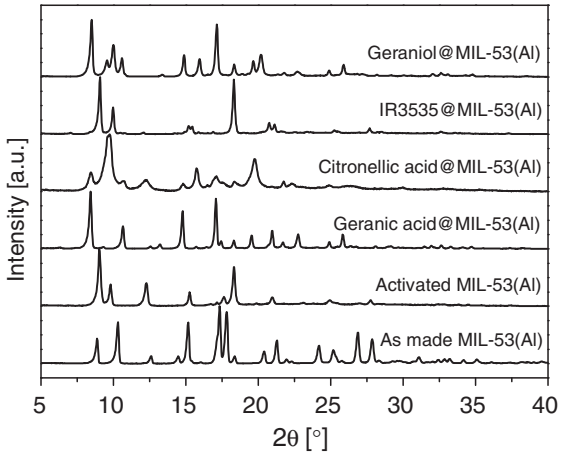

Fig. 4. X-ray diffractograms of MIL-53(Al) based materials.

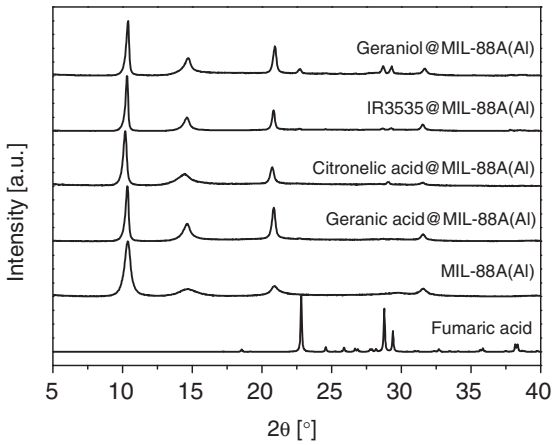

Fig. 5. X-ray diffractograms of MIL-88A(Al) based materials.

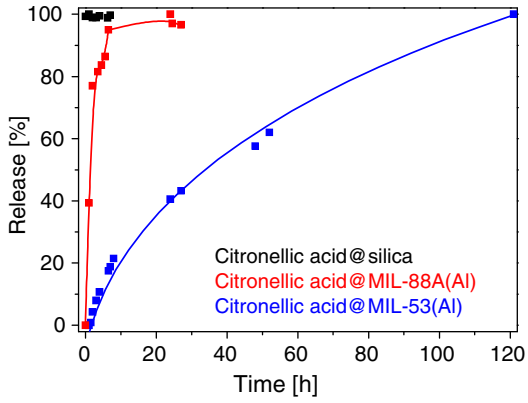

Fig. 6. Release of citronellic acid at 30 °C from citronellic acid@silica, citronellic acid@MIL-53(Al) and citronellic acid@MIL-88A(Al) obtained after encapsulation by impregnation (silica) and MSE for 2 (MIL-53(Al)) and 3 (MIL-88A(Al)) days.

maximum value instantaneously in case of silica, in agreement with its large porosity. Steady state was reached at about 20 h in case of MIL-88A. In both cases it was not possible to recover any solid at the end of the release experiment, indicating that both matrices (silica and MIL-88A(Al)) were practically dissolved and the additive release was complete. However, in case of MIL-53 (Al), steady state was not reached even at about 120 h, corresponding to about 15% of the total loading, as estimated by TGA from the solid recovered at the end of the experiment release. On the one hand, this suggests a step release for MIL-53(Al), which would appear at much higher times than that corresponding to the TCCA tablet dissolution (see below), as previously observed in the encapsulation of caffeine in this kind of material [5]. On the other, the water stability of MIL-53(Al) seems to be superior to that of MIL-88A(Al), which was totally hydrolyzed in the tested conditions contributing to the release. This agrees with the high resistance to hydrolysis that MIL-53(Al) has shown at room temperature, particularly in neutral and acidic media [29,30]: water reflux transformed MIL-53(Al) surface into γ-AlO(OH) [29], while in basic aqueous solution at 100 °C it underwent some structure transformation [30].

Interestingly, TCCA tablet dissolution produces at 8.5 g/h (i.e. it takes about 24 h for a conventional 200 g tablet). Considering TCCA tablet dissolution and additive release as serial processes, this means that the former process would not significantly interfere in the slow release materials (those obtained from MIL-53(Al), which in fact could be used as additive reservoirs). In case of fast

release materials (those obtained from silica and MIL-88A(Al)), the dissolution of the tablet would slow the release of the additive.

3.4. Cl_2 outgassing of modified tablets

The outgassing of TCCA alone (1.4 mg Cl_2, see Table 6) is like a blank experiment. Thus, any substance mixed with TCCA gave rise to an increase in the generation of Cl_2. However, the selected samples in Table 5 with encapsulated additives were clearly below the above-mentioned threshold of 15 mg Cl_2. When the pure additives were combined with TCCA in the form of a tablet (note that the mass of additive per unit mass of TCCA was always the same whether encapsulated or not), the generation of Cl_2 was always far above the threshold. The high porosity of silica would make a delayed release such as that observed for the MOF impossible. Nevertheless, the impregnation of silica with the additives allows a homogeneous formulation of the additives with TCCA, because the mixture of a relatively viscous substance with a solid is replaced by the easier blending of two solids.

In consequence, the encapsulation of the additives in either silica or MOF (MIL-53(Al) was chosen for these tests because of its higher encapsulation capacity) is a strategy able to: (i) make the additives compatible with TCCA; (ii) produce a homogeneous formulation of additive + TCCA; and (iii) provide additional functions (repellent, perfume) to the TCCA tablet.

4. Conclusions

The encapsulation of insect repellents with a simultaneous perfume function (geranic acid, citronellic acid, geraniol and IR3535®) in silica and the MOFs MIL-53(Al) and MIL-88A(Al) allows, from the point of view of Cl_2 outgassing, a stable formulation of such additives with trichloroisocyanuric acid (TCCA).

The FTIR characterization carried out demonstrates that the additives remain unchanged upon their encapsulation. The impregnation/encapsulation with silica has the only advantage of allowing a homogeneous dispersion with TCCA without significantly altering its Cl_2 outgassing. However, encapsulation in MOFs would bring to the final tablet the function of controlled release. As in other examples of encapsulation in MOFs, the presence of the additive in intimate contact with the porous structure produces modifications in the corresponding thermogravimetric curves (both MIL-53(Al) and MIL-88A(Al)) and X-ray diffraction patterns (MIL-53(Al)). Repellents are more efficiently encapsulated in MIL-53(Al) than in MIL-88A(Al) due to pore size and chemical compatibility (estimated using Hansen solubility parameters) issues.

In any event, the encapsulation of the additives in either silica or MOF (MIL-53(Al) gives rise to composite materials with a high loading of additive. Furthermore, this encapsulation makes the additives compatible with TCCA, allowing a homogeneous mixture. Consequently, besides having a low Cl_2 outgassing, the modified TCCA tablets (with only 0.2 wt% additive loading) may provide additional functions (for example, insect repellent or perfume) to the TCCA beyond the disinfectant, algaecide and bactericide functions.

Table 6
Outgassing screening results corresponding to TCCA tablets of 100 g containing 200 mg of additive (the equivalent amount when encapsulated).

Sample	Outgassing [mg Cl_2]
TCCA (alone)	1.4
TCCA + IR3535®@MIL-53 (MSE)	5.3
TCCA + geranic acid@MIL-53 (OSE)	7.0
TCCA + IR3535®@MIL-53 (OSE)	7.6
TCCA + citronellic acid@silica (impregnation)	12
TCCA + geranic acid	29
TCCA + IR3535®	58

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2016.02.001.

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