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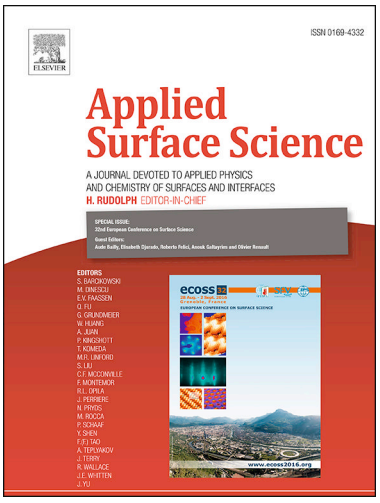

Full Length Article

Incorporation of the zosteric sodium salt in silica nanocapsules: synthesis and characterization of new fillers for antifouling coatings

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Incorporation of the zosteric sodium salt in silica nanocapsules: synthesis and characterization of new fillers for antifouling coatings

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Abstract

In the last decade many commercial biocides were gradually banned for toxicity. This work reports, for the first time, the synthesis and characterization of silica nanocontainers loaded with a natural product antifoulant (NPA), the zosteric sodium salt which is a non-commercial and environmentally friendly product with natural origin. The synthesis approach is a single step dynamic self-assembly with tetraethoxysilane (TEOS) as silica precursor. Unlike conventional mesoporous silica nanoparticles, the structure of these silica nanocontainers provides loading capacity and allows prolonged release of biocide species. The obtained nanocapsules have been characterized morphologically by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The encapsulation was checked by FTIR ATR spectroscopy and thermogravimetric analyses. **The results of the release studies show the great potential of the here presented newly developed nanofillers in all applications where a controlled release of non-toxic and environmentally friendly biocides is required.**

KEYWORDS: Zosteric sodium salt, environmentally friendly biocide, encapsulation of biocides, silica nanoparticles, TEOS

HIGHLIGHTS

- Design of a new system to reduce the amount of biocide in antifouling coatings
- A single step self-assembly method to encapsulate environmentally friendly biocide
- Successful encapsulation of the zosteric sodium salt in silica nanocapsules

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1.Introduction

Biofouling has frequently been reported for any kind of material from stone surfaces such as building facades, historical monuments and outdoor artworks to metallic surface, such as ship-hull or industrial platform**. Those surfaces are inevitably exposed to the weather that contributes to create a suitable combination of factors necessary for the algal growth (e.g. dampness, warmth and light) [1].**

Biofouling involves many living organisms (bacteria, fungi, algae, cyanobacteria, mosses, ferns and higher plants), **with the formation of complex systems (biofilms) [2]. To overcome biofouling, two different strategies can be used: i) acting on the bioreceptivity of the substrates; ii) applying antifouling agents on the substrates. The first approach provides the application of products that weaken the link between the cells of the microorganisms and the exposed surface. The most promising material is titanium dioxide (TiO_2). Under ultraviolet (UV) exposure, TiO_2 becomes superhydrophilic and creates a film on treated surfaces that changes the bioreceptivity of the substrates. One of the most controversial aspect of TiO_2 coatings when applied on stones is their durability. Recent investigation on the latter - in the specific case of TiO_2 nanotreatments on architectural stones - shows in fact a very limited time efficiency of the superhydrophilic and hydrophilic treatment that thus becomes quite short-life because of the quick degradation of the coatings [3].**

According to the second approach, antifouling agents can be traditionally applied in various forms (spray, compresses soaking, brushing, etc.) or added to coating formulations applied to protect substrates against biological colonization. Generally, when the biocides are added into the coating formulations, the antifouling action usually becomes quite short-lived, because of the premature release or the degradation of the active substance. Most biocides are small molecules and hence subject to fast self-diffusion in the coating matrix. As a consequence, this simple approach requires the use of very high concentrations of the biocide in order to maintain the antifouling function for a long time [4]. The use of excessive amounts of biocide may pollute the environment and, if the biocide is incompatible with the used matrix, it may also induce a macroscopic phase separation in the coating film [5]. The encapsulation/entrapment of biocides in nanocapsules to control the release of bioactive species is a good approach to reduce the amount of biocide and to obtain a satisfactory long-action antifouling coating increase.

Many early antifouling substances consisting of organo-mercury, lead and dichloro-diphenyltrichloroethane (DDT) posed severe environmental and human health risks [6-9]. Considerable studies were made to implement and evaluate alternative antifoulants with better environmental compatibility [10]. The European directive 98/8/CE highlights the important contributions offered by the natural product antifoulants (NPAs) as non- or less toxic alternatives to traditional biocides [11]. Among the NPAs the zosteric acid (ZA), or p-(sulfoxy) cinnamic acid (figure 1), is proposed as an alternative biocide suitable for preventive or integrative anti-biofilm approaches. The zosteric acid was first extracted from the *Zostera marina*. Marine plants are constantly exposed to harmful attacks by bacteria, spores or fungi building biofilms on the plant surfaces [12-13]. In order to protect itself the seagrass *Zostera marina* produces and continuously releases the water-soluble zosteric acid. The antifouling capability of the zosteric acid and its sodium salt was attributed to the sulfate group present in these compounds [14]. These antifoulants bind the attachment sites on cell surfaces at non-toxic concentrations inhibiting the adhesion of the microorganism interfering with key-steps orchestrating biofilm formation [15-16].

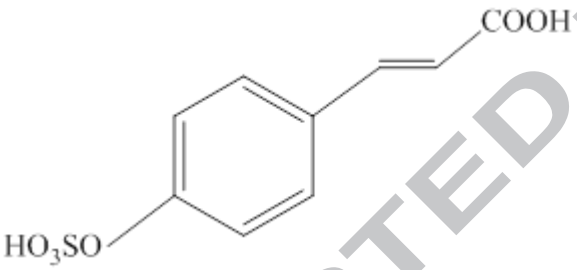


Figure 1. Structure formula of the zosteric acid (p-(sulfo-oxy) cinnamic acid).

At present, the possibility to realize the entrapment of NPAs in coatings formulations or their encapsulation to control the release have not been sufficiently addressed. **In this work we focused on the encapsulation of zosteric sodium salt to create an innovative filler with controlled-release properties for antifouling coatings. We decided to test the not commercial zosteric sodium salt, derivative of the zosteric acid, in accordance to the pro-ecological trends and EU regulations. We compared the results of zosteric sodium salt encapsulation with the encapsulation of sodium benzoate (BS), a commercial biocide used in many areas from cultural heritage to food preservatives**. These compounds were encapsulated in silica nanocapsules through a single step dynamic self-assembly synthesis approach [17].

2. Experimental procedure

2.1. Materials

The active compounds used for encapsulation were sodium benzoate (BS) (Aldrich) and the zosteric sodium salt (ZS). ZS was synthesized from *trans*-4-hydroxycinnamic and the sulphur trioxide pyridine complex. Methyl zosteric ester (EZS) was synthesized according to the literature [16]. For the preparation of the capsules, cetyltrimethylammonium bromide (CTAB, Aldrich), ammonia solution (NH_{3aq}, Anala®), tetraethoxysilane (TEOS, Aldrich) and diethyl ether (Et_2O, Aldrich) were used. All the chemicals were analytic grade and were used without further purification.

2.2. Encapsulation of the zosteric sodium salt in silica nanoparticles

The synthesis of the silica nanocapsules was adapted from the procedure by Chen et al. [17] (Chen et al. 2008). Denionized water (35 ml) and CTAB (0.25 g) were stirred at 55 °C for 15 minutes. Following the complete dissolution of CTAB, 0.25 ml of ammonia solution (25-28 %) were added into the mixture under continued stirring and heating. Afterward, a ZS solution in methanol (5 ml, 1.3 % in wt) dissolved in 25 ml of diethyl ether was added to the aqueous solution under constant stirring. After 30 minutes, when the oil-in-water (O/W) emulsion was stabilized, 1.25 ml of TEOS was dripped slowly to the emulsion. The reaction was left at room temperature for 24h under constant stirring. The resulting precipitates were filtered under vacuum, repeatedly washed (in deionized water) and dried at room temperature. The encapsulation of BS was performed in the same way. A small portion of these materials were calcined at 550 °C for 5h in order to remove CTAB and other organic components, on which the amount of the loaded biocide was determined.

2.3. Silica nanoparticles characterization

The **morphology** and dimensions of the nanoparticles were studied via scanning and transmission electron microscopy using a EG-ESEM FEI Quanta 200 F instrument equipped with a field emission gun, operating both in high and low (120 Pa) vacuum conditions and using a JEOL JEM 3010 operating at 300 KV, respectively. All the samples were sputtered with graphite before observations. **Particle size distribution was determined using the "ImageJ" software for image processing** [18]. FTIR experiments were carried out on a Nicolet Nexus 750 equipped with the ATR system. Thermogravimetric analysis (TG/DTA) was carried out under air atmosphere, with a heating rate of 5°C min^{-1} from room temperature up to 800 °C, using the NETZSCH STA 449 TG/DTA analyzer.

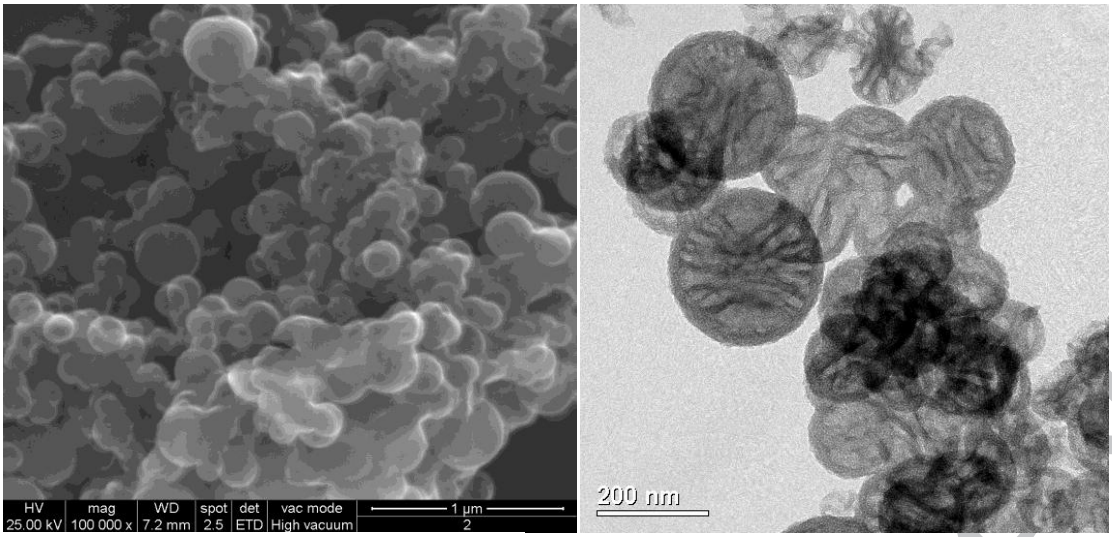
2.4. Release studies of the biocides

The release of the biocides was monitored by UV-Vis spectrophotometry (Unicam UV500) in the range of 200-650 nm by dispersing 15 mg of silica nanocapsules loaded with zosteric sodium salt and with sodium benzoate in 5 ml of ethanol separately. The suspensions were slowly stirred (93 rpm) at room temperature. A 3 ml sample of the mixture was collected with a syringe and analysed by UV-Vis spectrophotometry at given time intervals, being no filtering process performed because of the clarity of the suspensions. After measurement the extracted mixture was added back to the initial ethanol mixture. The correlation coefficient of the calibration curves obtained with 5 standards was higher than 0.99. The aliquots collected to quantify light emission were also used to quantify the amount of the biocide released in solution.

3. Results and discussion

In this research it was used a single step method to obtain the silica nanocontainers. This encapsulation procedure used TEOS condensation at the oil-in-water miniemulsion interface. Diethyl ether has the important role of porogen, cosolvent and template with CTAB for silica shell formation [19]. To successfully encapsulate the hydrophilic zosteric sodium salt some adjustments were performed and here reported for the first time. First, an organic solvent in which ZS was soluble and miscible with the organic phase of the miniemulsion was selected. According to the literature, the solubility of zosteric acid in methanol was found to be 1.3% [20] and methanol was used to solubilise the sodium salt in order to hinder its complete dissolution in the water phase of the O/W miniemulsion during the nanocapsule formation and hardening. Sodium benzoate was analogously encapsulated using the same amount of biocide.

In order to analyse the morphology of the synthesized nanoparticles, SEM and TEM analyses were performed. Typical SEM and TEM **images** of the empty silica nanocapsules (NC) are shown in figure 2 a and b. Clearly, they consist of spherical particles with a regular shape. TEM micrographs show that shells of these nanocapsules have a thickness of ca 11 nm and have a porous structure with clearly distinguished pleats. According to previous studies, the spherical nanoparticles have a hollow nature, as revealed by the contrast between the dark edge and the pale centre [17].



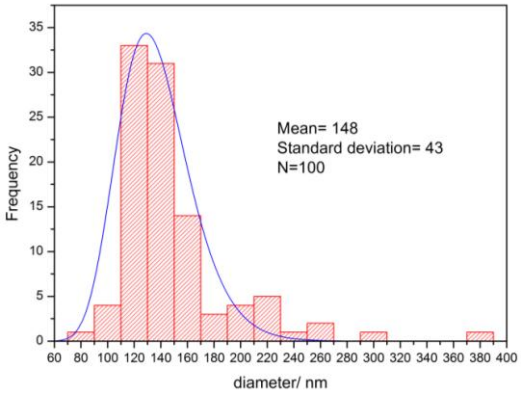


Figure 2. (a) SEM and (b) TEM micrographs of the empty silica nanocapsules (NC) and **(c) histograms with size distribution determined with ImageJ.**

Comparing the empty nanocapsules (NC) with the nanocapsules loaded with the different biocides, it is possible to verify that the encapsulation did not promote any changes in shape, but in size only. **NC have a size distribution centered at 148 nm with a standard deviation of 43 nm for 100 measurements, as reported in Figure 2c. Containers loaded with ZS seem to be larger than the empty ones (Figure 3 a and b), resulting in a size distribution centered at 563 with a standard deviation of 25 for 100 measurements (Figure 3 c).**

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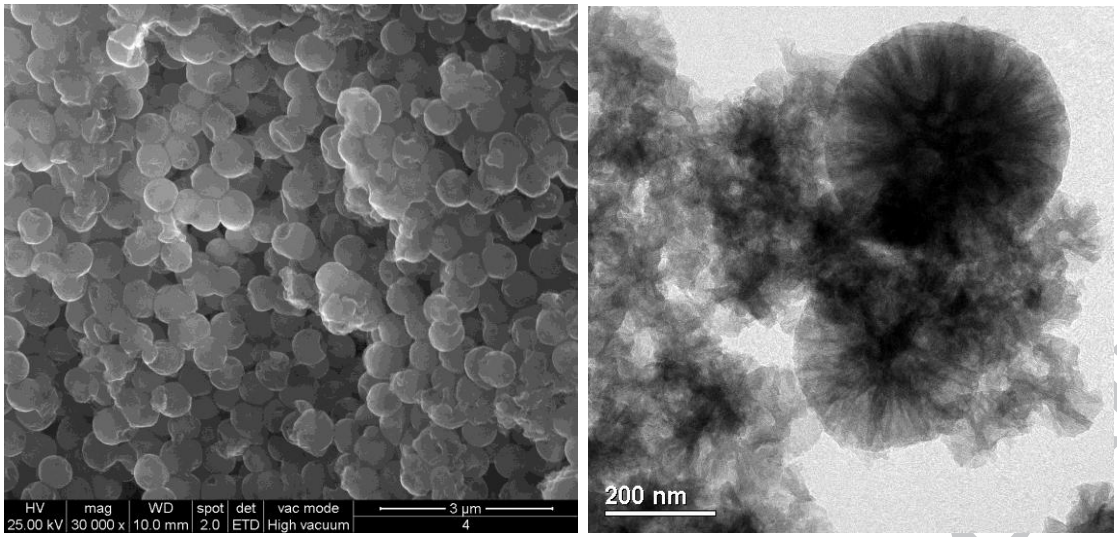

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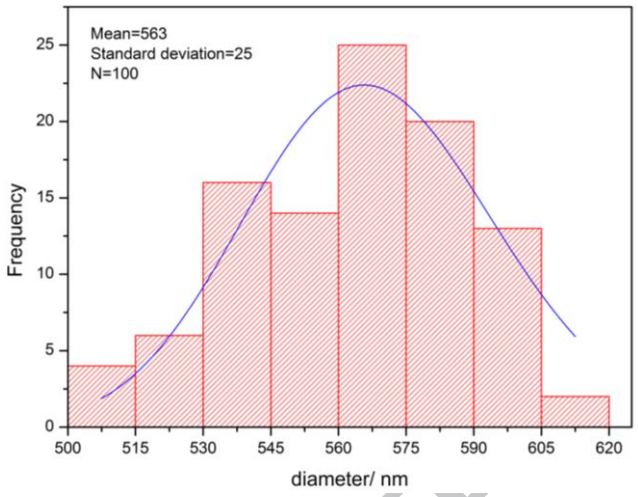

149 **Figure 3.** (a) SEM and **(b) TEM** micrographs of the silica nanocapsules loaded with the zosteric sodium salt
150 (NC-ZS) **and (c) histograms with size distribution determined with ImageJ.**

151 **Instead, when the encapsulation of BS was performed, no significant variation in the size distribution**
152 **of empty capsules was observed (Figure 4 a and b). The NC-BS have a size distribution centered at**
153 **164 nm with a standard deviation of 16 nm for 70 measurements (Figure 4 c).** Due to the organic
154 residual, the nanoparticles of both samples appear agglomerated (figure 2-4).

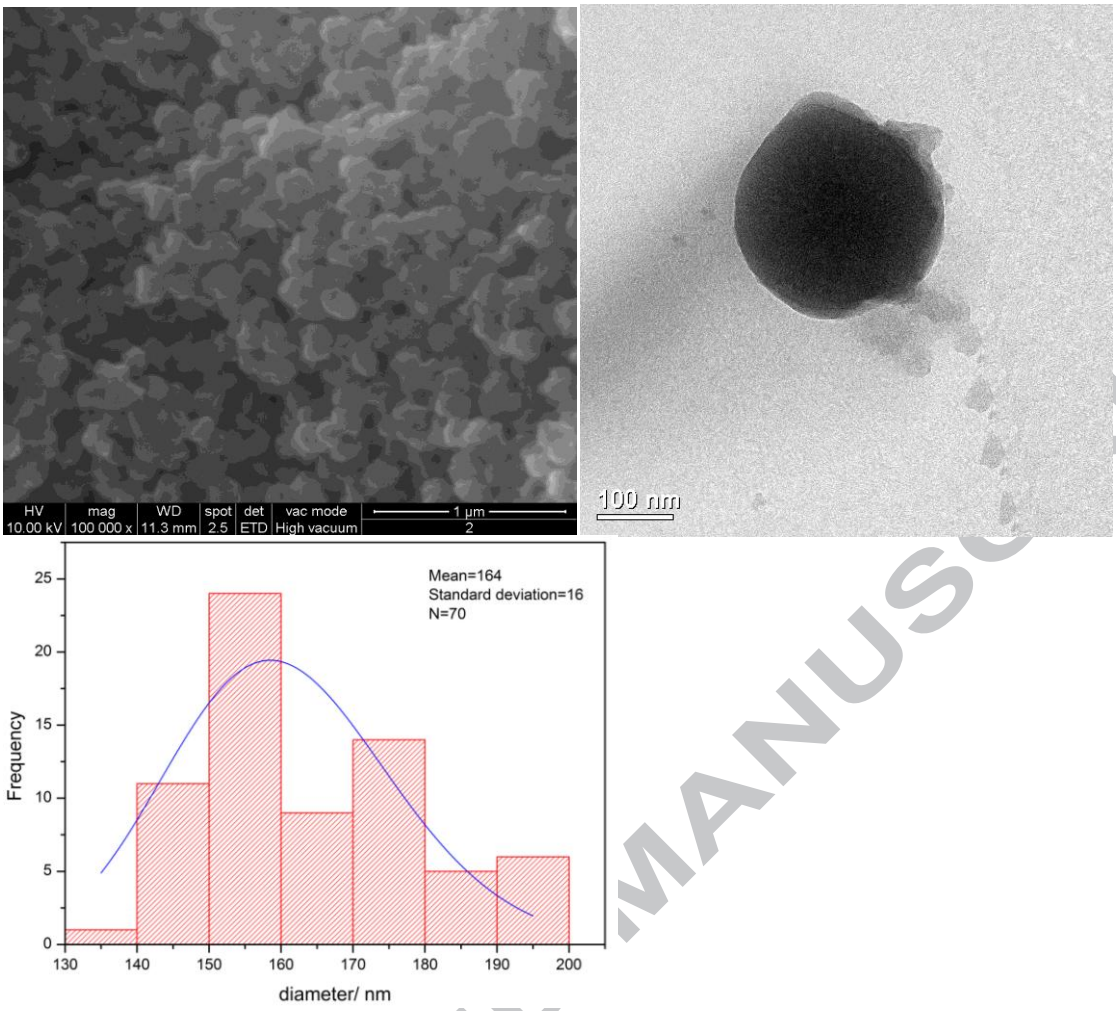

Figure 4. (a) SEM and **(b) TEM** micrographs of the nanocontainers with BS (NC-BS) **and (c) histograms with size distribution determined with ImageJ.**

FTIR analyses were performed in order to confirm the presence of the biocides in the nanocontainers. The FTIR spectrum of the empty silica nanoparticles (figure 5) shows the typical absorbance bands associated with amorphous silica, in particular the 470 cm^{-1} bending peak, the 800 cm^{-1} and 1040 cm^{-1} stretching peaks of the Si-O-Si group [21]. In this spectrum several characteristic bands associated with CTAB can be observed: $\nu_{as}(CH_3)$ and $\nu_{sym}(CH_3)$ at 2943 and 2870 cm^{-1}, $\delta(CH_2)$ mode at 1462 and 1472 cm^{-1} and the δ_{sym} ($N–CH_3$) and ν(C–N) at 1396 and 912 cm^{-1}, respectively [22]. In the case of the nanoparticles loaded with the zosteric sodium salt (NC-ZS) (figure 5), the presence of ZS is confirmed by the bands observed at 1645 cm^{-1}, which are associated with the stretching mode of C=O [23]. The enlarged band centered at 1028 cm^{-1} due to the ν(Si-O-Si) has a shoulder at 1220 cm^{-1}, which is associated with ν_{as}(S=O) signal, relative to the sulfate group present in the zosteric sodium salt . In the case of the nanoparticles loaded with sodium benzoate (NC-BS) (figure 5), the encapsulation of BS is confirmed by the bands at 1601 cm^{-1} and 1406 cm^{-1}, which are associated with the ν_{as} and ν_{sym} (COO-), respectively [24].

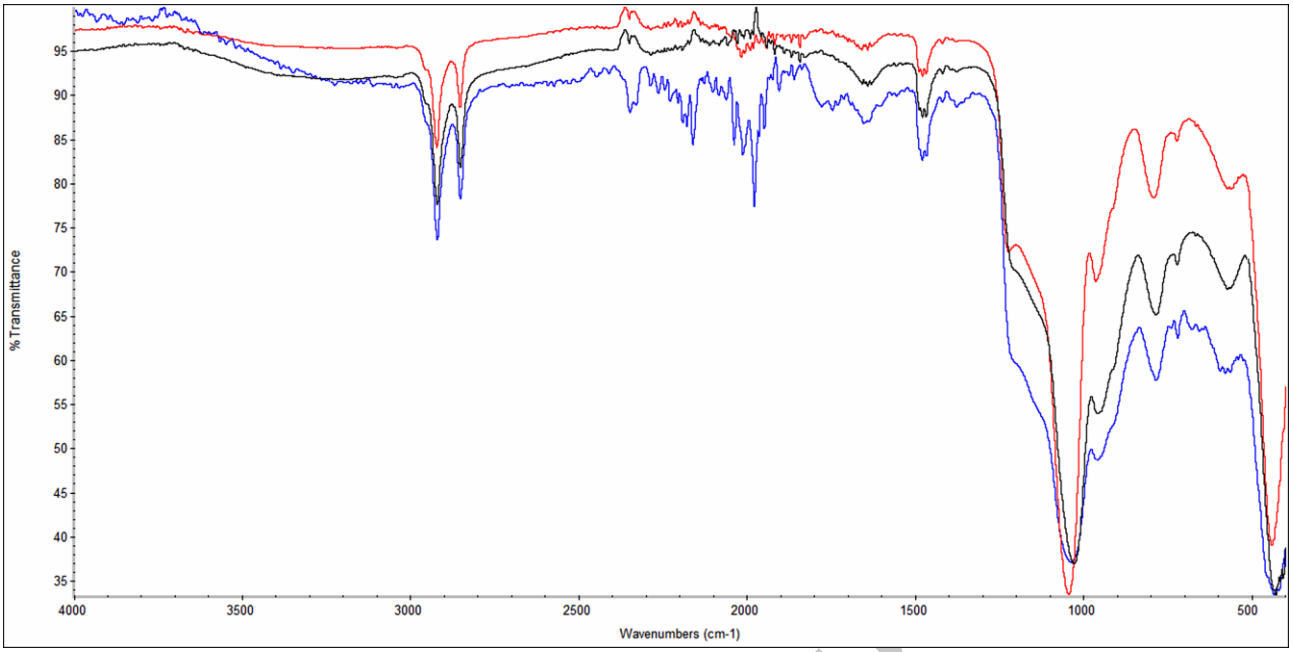

Figure 5. FTIR spectrum of NC-BS (blue line), NC-ZS (black line), NC (red line).

To verify the thermal stability of the silica nanocontainers and to quantify the amount of the encapsulated biocides, thermogravimetric tests were carried out. In agreement with the literature the calcined empty silica nanocontainers do not show significant variation with temperature.

Comparing the not calcined silica nanoparticles (NC) with the calcined ones (NC-A), the total weight loss is 31%. This value is relative to the degradation of non-hydrolysed/condensed TEOS and to the removal of the organic fraction comprising the cationic surfactant CTAB [25]. The curves corresponding to the capsules with ZS and BS show a similar profile to that of the empty capsules, except in the range between 200 and 300 °C, **as evidenced by the derivatives of thermogravimetric curves (Figure 6 b)**. In this range a weight lost is more pronounced and is attributed to desorption of the biocides degrading in this range of temperature (figure 6) [26-27].

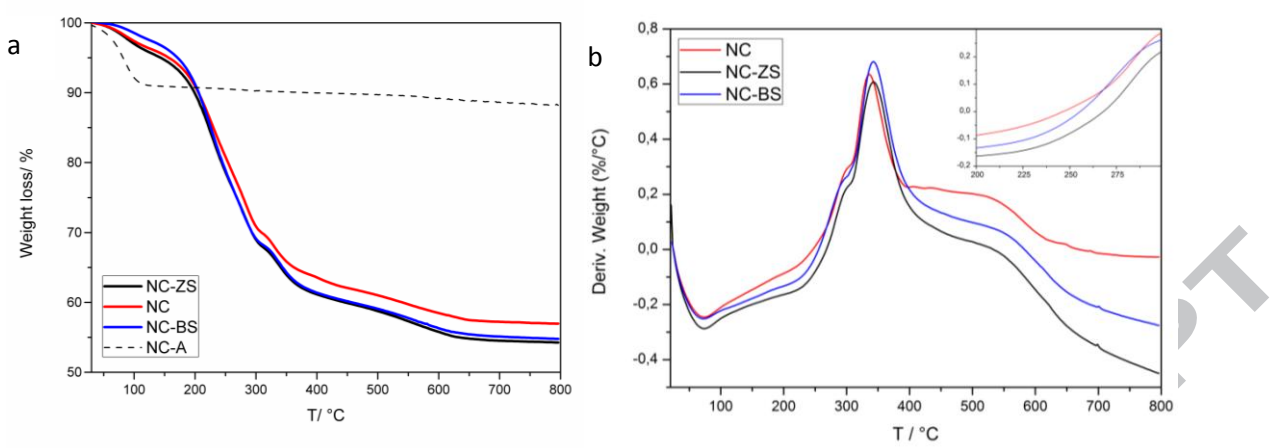

Figure 6. (a) Thermogravimetric curves and (b) their derivatives of the calcined empty nanocapsules (NC-A), the not calcined ones – (NC) and those encapsulating ZS (NC-ZS) and BS (NC-BS). **The insert in figure 6 b shows the enlarged area between 200 and 300 °C.**

It is interesting to use the difference of mass loss between the loaded and empty capsules to estimate the amount of biocide loading, 3.2% in the case of NC-ZS and 2.6% for NC-BS.

Analogously to a previous work [19], the controlled release of ZS and BS from the silica nanoconteiners dispersed in ethanol was examined by means of UV-Vis spectrophotometry at different times. The release process was monitored by following the absorption change of the ethanol media in the range of 200-650 nm after removal of the silica nanoparticles. A kinetic release curve (**shown in** figure 7) was plotted by using the absorption of the peak at ca. 267 nm for ZS and at 223 nm for BS. **The releasing process of ZS initially proceeded fast (figure 7a), then gradually slowed and levelled off after 22 h; actually nearly 52% of ZS as estimated via the following equation [17]:**

(1) Cumulative release (%)= Ab_{st}/ Abs_{max} x 100

(where Abs_{max} is the absorbance of the peak at ca. 267 nm at 26h after which the peak intensity no longer changed; Ab_{st} is the absorbance of the same peak recorded at time t) was released into ethanol in 1h. In the case of BS, the process does not level off after 50 h and after 1h the 34% of BS (estimated from eq 1. at ca 223 nm at 50 h) was released into ethanol. According to the literature data, these release results indicated that the encapsulation and controlled release of the organic molecule has been realized. Once the nanocapsules are dispersed in ethanol, a fraction of the biocide is released until equilibrium between biocide in the nanocapsule and in the ethanol phase is reached. The differences in the release

profiles of biocides are probably due to their different solubility in ethanol. Furthermore, it is possible that during the synthesis ZS and BS are encapsulated in different region of the nanoparticles (core *vs* shell). As particles were repeatedly washed prior to the characterisation procedure, either ZS or BS are definitely in the core of the particles or in the porous silica shell.

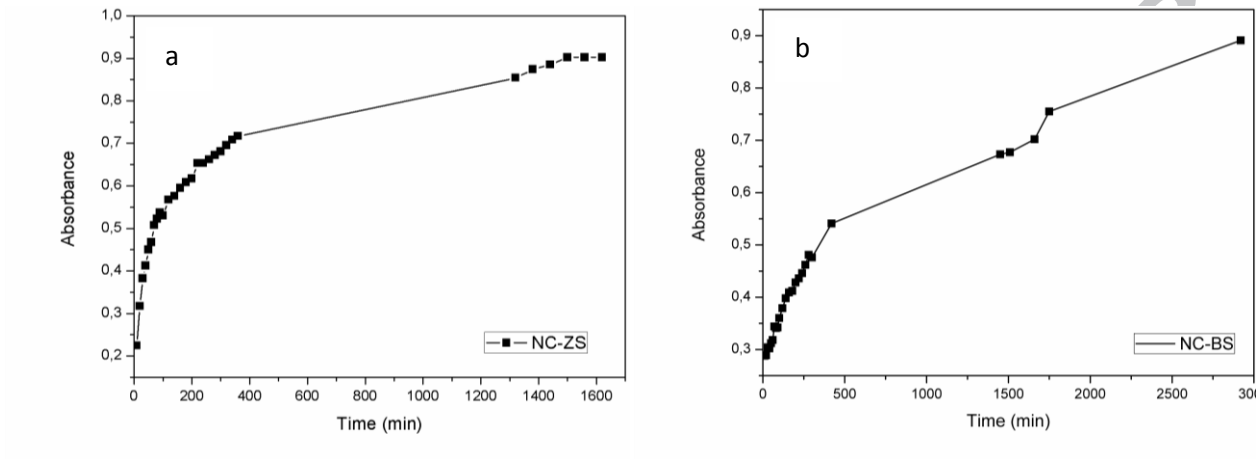

Figure 7. Release profiles of the nanocapsules loaded with ZS (a) and BS (b).

To verify that the release proceeded by diffusion of guest molecules into ethanol through the shells of nanocapsules, we decided to study the release of another sample, in which methyl zosteric ester (EZS) [28] was physically adsorbed on silica. However, when this sample was dispersed in ethanol to perform the release studies, the cumulative release of EZS was 97%, after 1h. This result shows that BS and ZS encapsulated by one-step miniemulsion process were mostly allocated in the core or in the shell structure of nanoparticles providing a good prolonged release.

4. Conclusion

The present paper reported, for the first time, the encapsulation of the zosteric sodium salt in silica nanocapsules combining two innovative research lines: the use of environmentally friendly antibiofouling agent and the one-step encapsulation method. The known biocide effect of the zosteric sodium salt makes the developed nanomaterial a promising engineering system with application in antifouling coating on an outdoor surface. The synthesized nanomaterials were thermally stable with a regular and spherical shape. The size of the obtained materials were influenced by the molecular size of the biocides. The loading content of ZS and BS were found to be 3.2 and 2.6 wt%, respectively.

The preliminary release studies in ethanol showed that the release of ZS was relatively gradual but after 22 hours it was levelled off, while the releasing process of BS was still on after 50 hours.

The nanocontainers synthesized in this work were designed to be one component of a more complex antifouling coating system, namely supercoating so that it will be interesting to evaluate the effectiveness of free zosteric sodium salt free as well as encapsulated in silica nanocontainers in water-based and solvent-based coatings.

Acknowledgments

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Graphical Abstract