Omeg@Silica: In-Silica Stabilization of Sustainable Fish Oil

Claudia Lino,[a] Mario Pagliaro,[a] Rosaria Ciriminna*[a]

Abstract: Fish oil rich in docosahexaenoic acid (DHA) and eicosapentaenoic acid (EPA), vitamin D_3 and natural astaxanthin sustainably extracted from anchovy fillet leftovers using biobased limonene only, can be conveniently stabilized by adsorption on periodic mesoporous silicas. The simplicity of the process, the high load of entrapped fish oil, and the biocompatible nature of silica support numerous forthcoming applications of this new class of "Omeg@Silica" materials.

Keywords: Omeg@Silica; periodic mesoporous silica; omega-3; anchovy; fish oil

1. Introduction

Inuit populations living in Greenland in the early 1970s eating only whale, seal and fish meat presenting virtually no cardiovascular disease (and no diabetes mellitus) were found to have high levels of two omega-3 long chain polyunsaturated fatty acids, DHA and EPA, in their plasma and platelet lipids [1]. Following this discovery and a large number of subsequent biochemical and clinical studies [2], fish oil rich in EPA and DHA omega-3 lipids has become the active ingredient in a variety of nutraceuticals and dietary supplements with multiple health benefits, starting from reducing cardiovascular risk and tissue inflammation [3].

To increase intake of omega-3 lipids, whose recommended daily intake is not met by the population of most economically developed countries, marine oil rich in EPA and DHA are added also to "fortified" milk powders (including infant formulas) [4] and to animal feed for example to produce omega-3 enriched eggs [5].

One of the main deficiencies in diets common to industrially developed countries is the insufficient consumption of EPA and DHA, which has led to the introduction of a new index (EPA+DHA in red blood cells) directly responsive to changes in EPA+DHA intake [6]. Increasing the amount of EPA+DHA essential fatty acids in the body requires to either increase consumption of fish and seafood in the diet or omega-3 supplementation.

Increasing global awareness of this diet deficiency has led to a global and increasing demand of fish oil which, in its turn, is threatening marine wildlife by enhancing overfishing [7]. Accordingly, shifting the production of fish oil, the main ingredient of omega-3 dietary supplements, from fish to fish processing waste produced in huge yearly amounts by the fish processing industry is an urgent global need [8].

In this context, we recently reported a new circular approach to the production of high quality fish oil involving the solid-liquid extraction of anchovy fillet leftovers using citrus-derived *d*-limonene as green biosolvent [9]. The terpene, which is also an antioxidant [10], protects PUFAs in the fish oil from otherwise quick catalytic oxidation due to free radicals formed in the presence of air's oxygen [11], both during the fish oil extraction at room temperature and during solvent recovery by evaporation under reduced pressure (3 mbar) at 90 °C [9].

In general, fish oil in food supplement capsules first undergoes chemical refining and transformation into ethyl esters and then is added with natural or synthetic antioxidants prior to encapsulation in soft gelatin capsules [8]. In other applications, a number of microencapsulation techniques are used by industry to microencapsulate and protect fish oil from peroxidation [12].

To the best of our knowledge, the only fish oil microencapsulation process involving silica was reported by Australia's scholars in 2018 [13]. Spray drying a fish oil submicroemulsion stabilised by food-grade hydrophilic silica particles (Aerosil 300), the team showed that microencapsulation in silica indeed protects the omega-3 lipids from oxidation regardless of the harsh fabrication conditions (inlet temperature, 140 °C and high pressure) employed to spray dry the functionalized silica particles.

Now, we report the outcomes of encapsulating the newly extracted fish oil obtained from anchovy filleting industrial waste in periodic mesoporous silica particles. Both biocompatible MCM-41 silica and organically modified mesoporous silica materials were used as adsorbent for this new fish oil rich not only in EPA and DHA [9] but also in vitamin D_3 [14] and natural astaxanthin.

The outcomes of the material synthesis and structural investigation reported in this study suggest that this this new class of materials called "Omeg@Silica" has the potential to expand the biological applications of omega-3 lipids, from better fortified foods, through controlled release in the gastrointenstinal tract.

2. Results and Discussion

Experimental

Fish oil extraction

Fish oil was extracted from anchovy filleting industrial waste kindly donated by an industry based in Sicily (Agostino Recca Conserve Alimentari) using *d*-limonene as green biosolvent according to the solid-liquid extraction and solvent recovery processes previously described [9].

[a]   Dr. C. Lino, Dr. M. Pagliaro, Dr. R. Ciriminna
        Istituto per lo Studio dei Materiali Nanostrutturati, CNR
        via U. La Malfa 153
        90146 Palermo (Italy)
        E-mail: rosaria.ciriminna@cnr.it

Material Synthesis

MCM-41 was synthesized by the template-assisted sol-gel process using a published synthetic protocol [15]. In detail, 1 g of hexadecyltrimethylammonium bromide (CTAB ≥99% pure, Aldrich) and 280 mg of sodium hydroxide (Analyticals, Carlo Erba) were dissolved in 480 mL of deionized water. An aliquot (5.4 mL) of tetraethylorthosilicate (TEOS ≥99% pure, Aldrich) was added dropwise to the solution. The resulting mixture was kept under continuous mechanical stirring (400 rpm) at 80 °C for 2 h.

The solid precipitate was recovered by filtration, washed with abundant deionized water and methanol (99.8% pure, Aldrich) and dried at 60°C for 48 h. The residual surfactant entrapped in the silicate was removed via calcination at 550°C for 6 h.

Functionalization of MCM-41 silica with 3-amino-propyl groups was achieved by a published post-grafting method [16]. In detail, an aliquot (600 mg) of the as-synthesized MCM-41 was refluxed in 15 mL toluene (≥99.5% pure, Fluka Chemika) added with 152 μL of 3-amino-propyltrimethoxysilane (APTMS, 0,42 mmol, 97% pure, Alfa Aesar).

The solution was kept under stirring for 6 h after which it was decanted. The solid product thereby obtained was washed three times with 15 mL of isopropanol (99% pure, J.K. Baker, Fisher Scientific), and dried at 40°C for 3 h.

Loading of the Materials with Fish Oil

The fatty acid composition of anchovy discard fish oil was assessed following the standard method involving trans-esterification of the oil triglycerides and CG-MS analysis of the respective fatty acid methyl esters using a ThermoScientific Trace 1310/ISQ LT single quadrupole GC/MS spectrometer [9]. The marine oil extracted was once again found to be rich in omega-3 eicosapentaenoic acid (EPA) and docosahexenoic acid (DHA, Table 1).

Table 1. EPA and DHA in fish oil extracted from anchovy waste

Polyunsaturated Fatty Acid (in lipid numbers)	Abundance
EPA (20:5, *n*-3)	5.4%
DHA (22:6, *n*-3)	12.4%

Loading of the MCM-41 and of the MCM-41 organically functionalized with 3-amino-propyl groups (FMCM-41) was carried out by direct adsorption of the oil by adding dropwise the oil to the material kept in a glass flask under agitation. For example, addition of a first 60 μL aliquot of fish oil to FMCM-41 (100 mg), was followed by additions of 20 μL aliquots. After 8 min, addition of oil was terminated and the material left under agitation for 24 h.

In detail, MCM41 was loaded up to 50% w/w fish oil (MCM-41_50%) (Figure 1), while FMCM41 could be loaded up to 40% w/w (FMCM-41_40%).

Characterization

The materials were characterized by FT-IR spectroscopy (Bruker, ALPHA model), scanning electron microscopy (SEM) and thermogravimetric analysis (Mettler Toledo TGA/DSC). Surface area and porosity were determined from cryogenic nitrogen adsorption-desorption analysis using a Micromeritics ASAP 2020 Plus 1.03 porosimeter.
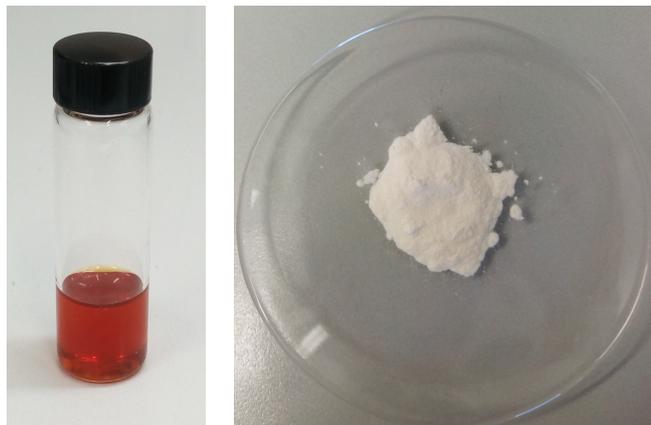

Figure 1. Oil extracted from anchovy filleting waste (*left*), Omeg@Silica comprised of MCM-41 loaded with 50% w/w fish oil (*right*).

The SEM analyses were conducted with a SEM Zeiss EVO MA10 microscope. Particle size, polydispersity index (PDI) and zeta-potential were measured with a Zetasizer Nano ZS (Malvern Instrument, United Kingdom) using Dynamic Light Scattering (DLS) after dispersing material samples in distilled water.

3. Results and Discussion

The inner porosity of MCM-41 silica is able to encapsulate more oil (50 wt%) than amino-silica FMCM-41 (40 wt%). Figure 2 readily shows the reason. Both materials show type IV N_2 adsorption-desorption isotherms whose hysteresis loop of moderate steepness is associated with capillary condensation taking place in narrow slit-like mesopores [17].

Table 2. Textural properties of MCM-41 and FMCM-41.

Material	Specific surface area (m^2/g)	Specific pore volume (cm^3/g)	Average pore diameter (nm)
MCM-41	825	0.6	2.9
FMCM-41	440	0.3	2.5

However, Table 2 shows the significant decrease of both specific surface area (SSA), specific pore volume (SPV) and average pore diameter of MCM-41 upon grafting the internal pore wall of surface with the amino-propyl group.

Once loaded with 50 wt% of sustainably sourced anchovy fish oil, the surface area of MCM-41 decreases to 16 m^2/g (entry 1 in Table 3). Increasing the load of fish oil adsorbed by the aminopropyl-functionalized silica from 10 to 40 wt%, the SSA and the SPV go, respectively, from 166 m^2/g to 16 m^2/g and

from 0.1 cm^3/g to 0.02 cm^3/g (entries 2 and 5 in Table 3) providing evidence of the adsorption of the fish oil triglyceride molecules via entrapment in the inner porosity of the silicas.

Table 3. Textural properties of Omeg@Silicas comprised of MCM-41 and FMCM-41 loaded with different amount of sustainably extracted fish oil revealed by N$_2$ cryogenic absorption.

| Entry	Material	Specific surface area (m^2/g)	Specific pore volume (cm^3/g)	Average pore diameter (nm)
1	MCM-41_50%	16	0.02	6.1
2	FMCM-41_10%	166	0.1	3.3
3	FMCM-41_20%	49	0.08	6
4	FMCM-41_30%	24	0.06	8.5
5	FMCM-41_40%	16	0.02	5.3
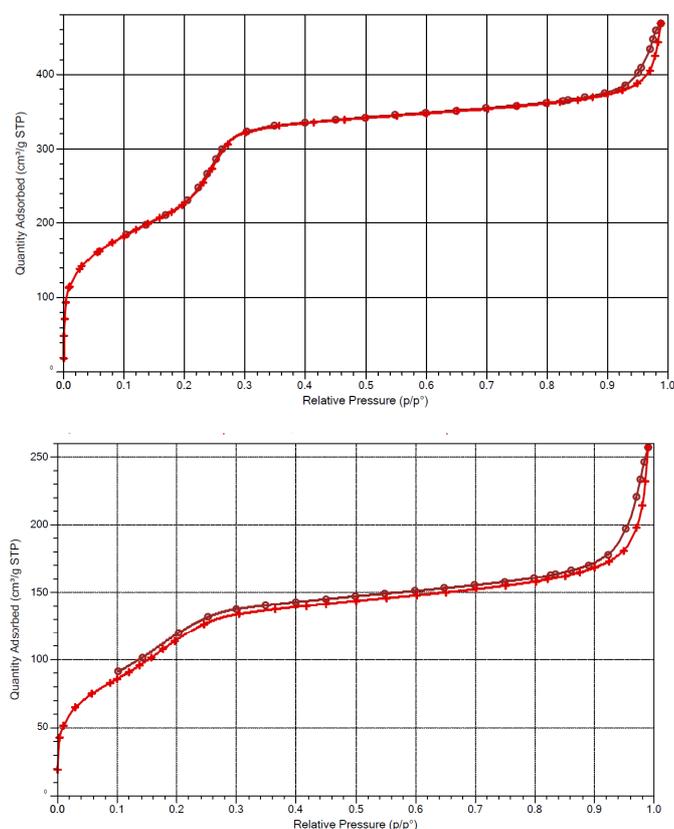
Figure 2. N$_2$ adsorbtion-desorption isotherms of MCM-41 (*top*), and FMCM-41 (*bottom*).

The amount of amino-propyl-trimethoxysilane grafted on the MCM-41 silica surface is derived from the thermogravimetric analysis (TGA) of both MCM-41 and FMCM-41 displayed in Figure 3 along with the derivative thermogravimetry (DTG) curve.
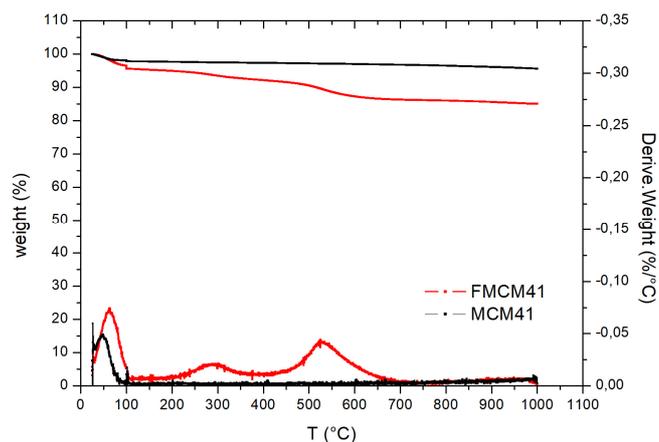

Figure 3. TGA and DTG curves of MCM-41 (black) and FMCM-41 (red).

Three weight losses are observed in the TGA curve of FMCM-41. The first, close to 100 °C (-4.4%), is due to evaporation of water adsorbed at the surface of hydrophilic silica. The second, at about 300 °C (-4.3%), originates from the desorption of physically adsorbed APTMS [18]. The third, above 430 °C (-6.2%), is due to thermal decomposition of the -(CH$_2$)$_3$NH$_2$ groups chemically bound ("grafted") to the silica structure, with the C–Si bond starting to break up at 450-510 °C [18].

Following Wang and co-workers [19], the mole number of APTMS grafted on the silica surface was determined from the weight loss ΔW (%) at 430 °C, n_A (mol) amount = m_{430}/M_{NH} where m_{430} (g) is the weight loss of the sample at 430 °C (0.9513 mg), and M_{NH} (g/mol) is the molecular weight of -(CH$_2$)$_3$NH$_2$ group (58 g/mol). The APTMS content (mmol/g$_{silica}$) is given by n_A divided by the silica mass (m_{SiO2}) determined by subtracting the mass brought by grafted APTMS from the residual weight at 300 °C (m_{300}). In the present case, the calculated amount of amino-propyl groups of 1.07 mmol/g, namely 76% of the theoretical value (1.4 mmol/g), pointing to the fact that MCM-41 functionalization via post-grafting method was successful.

The TGA was used to assess also the thermal stability of the silicas loaded with 50 wt% and 40 wt% anchovy fish oil carrying out the TGA measurements one month after storing the materials at room temperature under conventional atmosphere.

The overlapping curves in Figure 4 clearly show that both MCM-41 loaded with 50 wt% oil and its amino-propyl-functionalized counterpart doped with 40 wt% fish oil show excellent thermal stability over time.
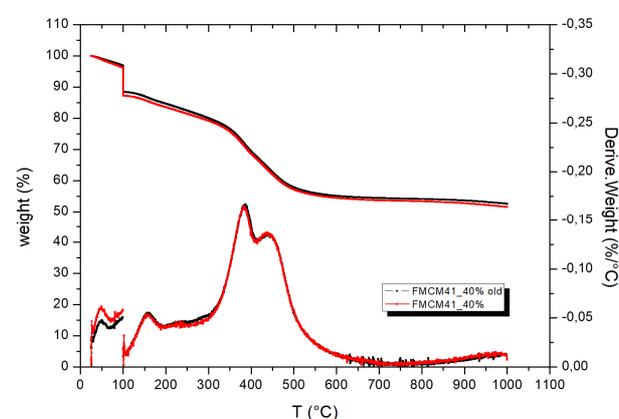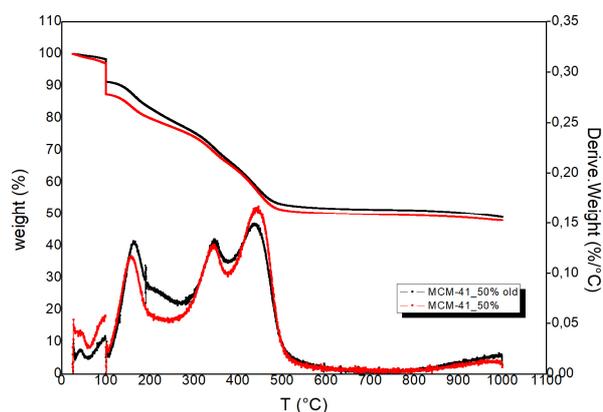
Figure 4. TGA and DTG curves of Omeg@Silicas MCM-41_50% (*top*), and FMCM-41_40% (*bottom*).

Evidence of successful encapsulation of fish oil was obtained also from comparing the FTIR spectrum of MCM-41 with that of the same material functionalized with 50 wt% anchovy fish oil. The black curve in Figure 5 is typical of sol-gel silica with the main infrared bands νOH at 3200–3300 cm^{-1}, ν_{as} Si-O-Si at 1080 cm^{-1}, νSi-OH at 950 cm^{-1} and ν_s Si-O-Si at 800 cm^{-1}, and ρ Si-O-Si at 460 cm^{-1} [20].

The red curve in Figure 5 displaying the IR spectrum of MCM-41 loaded with 50 wt% fish oil clearly shows peaks in the fingerprint region (800–1500 cm^{-1}), especially in the 1050–950 cm^{-1} region, which has been ascribed to =C–H out-of-plane bending [21].

Remarkably, the C=O carbonyl band at 1720–1746 cm^{-1} normally significant in omega-3 lipids is absent, which points to likely coordination of the carbonyl's oxygen with the numerous Si-OH groups at the surface of the sol-gel cages.
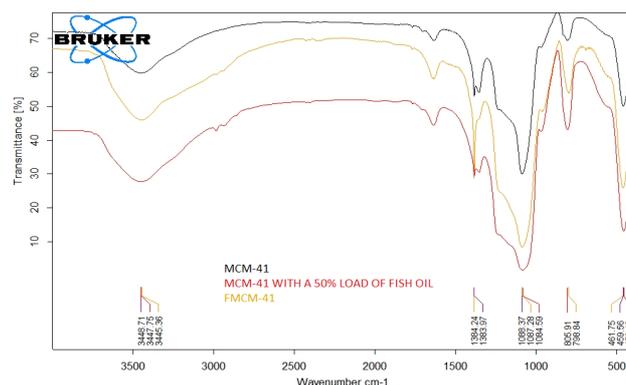

Figure 5. FT-IR spectra of MCM-41, Omeg@Silica MCM-41_50% and FMCM-41.

The SEM microphotographs (Figure 6) show that filling the inner porosity of MCM-41 with 50 wt% fish oil changes the outer surface morphology of the spherical SiO$_2$ submicroparticles into a smoother, more compact agglomerate of amorphous particles.
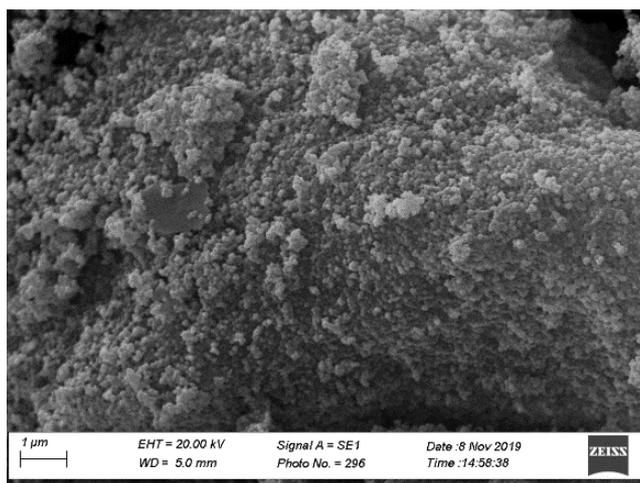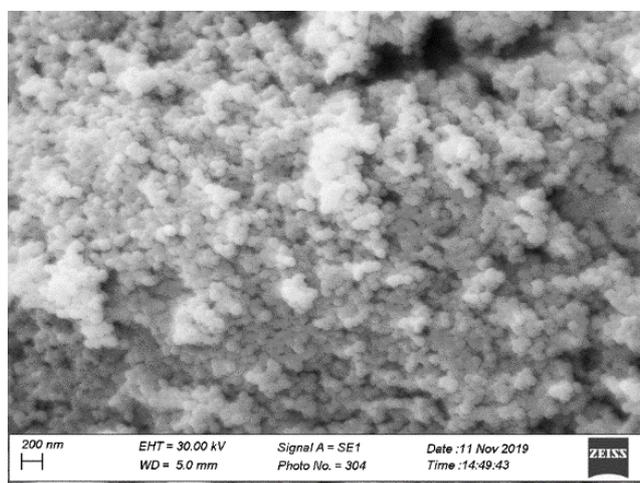

Figure 6. SEM microphotographs of MCM-41 silica (*top*), and Omeg@Silica MCM-41_50% (*bottom*).

Finally, the zeta potential of MCM-41 and FMCM-41 Omeg@Silicas doped, respectively, with 50 wt% and with 40 wt% fish oil indicate (entries 2 and 7 in Table 4) pronounced stability of the aqueous suspensions of the materials.

Table 4. Zeta potential, Z-Ave and PDI of MCM-41 and FMCM-41 and Omeg@Silicas loaded with different amounts of anchovy fish oil

Entry	Material (1 mg/mL)	Zeta potential (mV)	Z-Ave (nm)	PDI
1	MCM-41	-33,4	217	0.3
2	MCM-41_50%	-37.6	269	0.3
	Material (0.5 mg/mL)			
3	FMCM-41	-14.9	297	0.4
4	FMCM-41_10%	-8.67	1915	0.4
5	FMCM-41_20%	-23.7	1777	0.4
6	FMCM-41_30%	-29.4	1100	0.5
7	FMCM-41_40%	-40.4	522	0.5

We briefly remind that the zeta potential -- the electric potential at the shear layer formed in the double layer of the surface of a particle immersed in a liquid -- allows to evaluate the electrostatic stability of particles suspended in water. Particles in suspension having a large positive (>30 mV) or negative (<-30 mV) value of the zeta potential repel each other: aggregation is prevented and the dispersion remains electrostatically stable.

Showing evidence of the silica nature of the suspended particles [22], all suspensions have negative zeta-potential. The 40.4 mV absolute value of zeta-potential of the amino-propyl-silica doped with 40 wt% anchovy fish oil points to its pronounced stability. On the other hand, the absolute values for suspensions of the same organically modified silica empty or doped with 10, 20 and 30 wt% fish oil indicate lack of stability towards aggregation.

In brief, functionalization with fish oil of both pure silica or organically modified silica is beneficial for the electrostatic stability of microparticles suspensions in water provided that high amounts of fish oil are loaded within the silica inner porosity.

The outcomes of DLS measurements indicate (Figure 7) that the population of particles is represented by well dispersed submicroparticles distributed around 269 nm for the MCM-41_50% Omeg@Silica and around 522 nm for the FMCM-41_40% Omeg@Silica.

The materials respectively have a polydispersity index (PDI) value lower (0.3) or equal to 0.5, which is an important characteristic in drug ("payload") delivery applications [23]. The Z-average size (measure of the average size of the particle size distribution resulting by DLS) indicates a moderate increase from 217 to 269 nm for MCM-41 silica going from empty to filled with 50 wt% fish oil, and almost doubling in size for FMCM-41 aminopropylsilica particles going from empty to doped with the maximum 40 wt% load (from 297 to 522 nm).
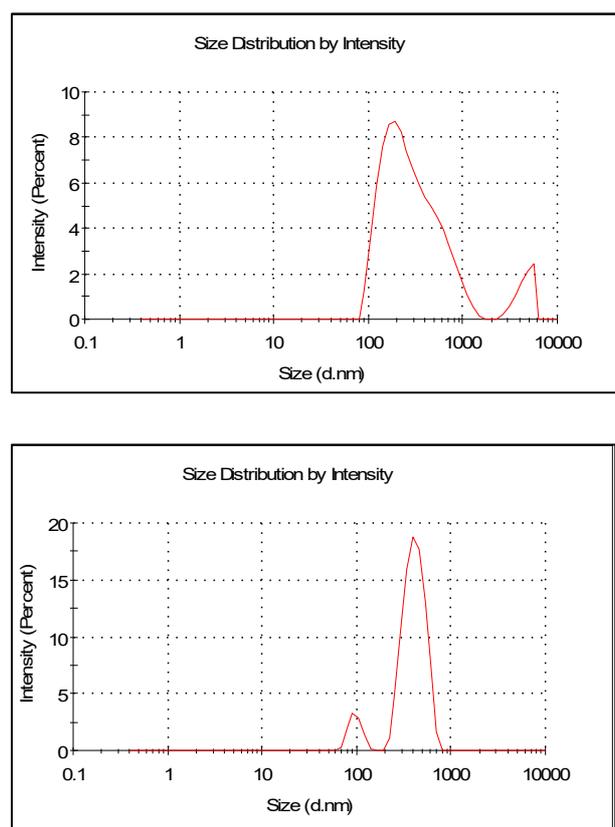

Figure 7. Particle size distribution of Omeg@Silica MCM-41_50% (*top*), and Omeg@Silica FMCM-41_40% (*bottom*).

3. Conclusions

The huge demand of omega-3 lipids, whose main ingredient used by the nutraceutical and dietary supplement industries is fish oil, is accelerating depletion of several marine species [7], including anchovies: one of the most fished species across the world.

Sourcing fish oil from fish processing waste is an urgent and global societal, economic and environmental need [8]. In a series of papers opened by the discovery of the extraction process using biobased limonene [9], we have jointly shown how fish oil sourced from anchovy or shrimp [24] industrial waste has exceptional nutraceutical value [14], and that the method is technically and economically viable [25].

Expanding the uses of valued fish oil via microencapsulation and stabilization is of great practical relevance. In this study, we show how micrencapsulation of sustainably sourced fish oil is readily and easily achieved by adsorption over periodic mesoporous silicas.

Both mesoporous MCM-41 silica and FMCM-41 amino-propyl-silica submicroparticles are excellent biocompatible supports for adsorption and delivery of fish oil rich in omega-3, vitamin D_3 and natural astaxanthin sustainably sourced from anchovy filleting industrial waste [9].

The entrapment process is simple and takes place at room temperature and pressure with no need for microencapsulation devices. It is enough to add the newly extracted fish oil the as-synthesized materials kept under agitation at room temperature to rapidly obtain silicate powders incorporating a high load of marine oil.

Quick and effective oil entrapment of the oil is due to the huge specific surface area and pore volume of both silicas whose ordered hexagonal pores act as "chemical sponges", adsorbing and concentrating the lipid, vitamin D_3 and astaxanthin molecules at their inner surface.

The outcome is a white and free flowing powdered material series dubbed herein "Omeg@Silica".

In general, periodic mesoporous silicas are biocompatible and suitable for the targeted release of bioactive molecules in the gastrointestinal tract [26], even though mesoporous silica comprising the MCM-41 structure is rapidly degraded under *in vitro* digestion conditions, while organically functionalized silica with 3-amino-propyl groups is generally more stable [27].

Due both to larger interfacial surface area of silica-entrapped fish oil triglyceride molecules and to the interfacial effect of the silica cages guiding access of the external reactants (including enzymes) to the entrapped species [28], once entrapped in mesoporous silicas omega-3 triglycerides were found to be even more bioaccessible to lipase (40% faster lypolisis kinetics ascribed to the lipase molecules adsorbed to the silica surface in their active, open-lid conformation [29]) in comparison to crude fish oil [13].

All this suggests that Omeg@Silica materials of facile preparation and handling are suitable for multiple forthcoming practical applications, ranging from fortified foods to controlled release and delivery of omega-3 lipids protected from oxidation and biological degradation.

Acknowledgements

Author Information

Corresponding Authors

*E-mail: rosaria.ciriminna@cnr.it

ORCID

Rosaria Ciriminna: 0000-0001-6596-1572

Claudia Lino: 0000-0002-8724-7772

Mario Pagliaro: 0000-0002-5096-329X

Notes

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Valued fish oil? Encapsulate it in silica!
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C. Lino, M. Pagliaro, R. Ciriminna

Anchovy filleting industrial waste → Fish oil rich in Omega-3 and vitamin D_3 → Omeg@Silica