



Research Paper

From old to new inorganic materials for advanced applications: The paradigmatic example of the sepiolite clay mineral

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ABSTRACT

This review article focuses on sepiolite fibrous clay mineral, which has been selected here as an example of an ancient inorganic natural material that is currently receiving much attention as excellent candidate for advanced materials and applications. Sepiolite clay is an abundant hydrated magnesium silicate whose crystal structure determines the presence of nanoporous cavities as well as large surface and rheological properties of great interest for the further design of functional materials. The present work introduces and discusses the relationship between aspects of this clay, in terms of its structural and morphological organization, and its physicochemical characteristics from which emerging applications arise. One of the sections is devoted to describe current industrial applications of commercially available sepiolite-based materials. As sepiolite can be considered a nanomaterial by itself, approaches including its controlled chemical and physical modifications intended to develop new advanced inorganic and hybrid nanostructured materials provided with pre-designed functionalities. Among them, polymer nanocomposites that include bionanocomposites and carbon-sepiolite nanomaterials, materials for adsorption of pollutants, functionalization with magnetic nanoparticles, active phase of sensors and DNA support for gene transfer are some of the examples that we refer to in the present review article.

1. Introduction: sepiolite from past to present. Towards advanced applications

Clays are very abundant silicate raw materials present in the Earth's crust as one of the fundamental constituents of soil, being even present in ocean sediments and atmospheric aerosols (Ito and Wagai, 2017). Given their affordability, they have been used since the dawn of humanity in pottery, ceramics, building materials, paper coating, cosmetics, medicine, decoration and artistic objects, among other applications. These uses were fundamentally based on their structural features and colloidal behavior, which determine current industrial production and uses of clay minerals even in daily life activities (Murray, 1999; Sposito et al., 1999; Bergaya and Lagaly, 2013; Faustini et al., 2018). Interestingly, since long time ago clays and clay minerals have been suitably modified by applying different physical or chemical procedures to obtain more and more upgrading materials.

The most common examples of clay minerals refer to aluminum and magnesium silicates with a 2D structural arrangement showing lamellar morphology (typically kaolinite, montmorillonite, vermiculite and other

layered clay minerals). However, other important members of clay silicates present related structural arrangements but showing different morphologies and textural characteristics. This is, for instance, the case of 1D clay minerals appearing as nanotubular silicates, such as halloysite and imogolite, and fibrous silicates, such as palygorskite and sepiolite. The great interest towards these one-dimensional clay minerals focusing the development of functional materials has been recently introduced as a Special Issue in the *Frontiers in Chemistry* journal edited by Wang et al. (2021).

According to Suárez and García-Romero, sepiolite and palygorskite could be considered as the final members of a continuous polysomatic series of this group of natural fibrous silicates (Suárez and García-Romero, 2011, 2013). Sepiolite is a microcrystalline hydrated magnesium silicate with $\text{Si}_{12}\text{O}_{30}\text{Mg}_8(\text{OH},\text{F})_4(\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}$ as unit-cell formula (Brauner and Preisinger, 1956; Santaren et al., 1990), showing a microfibrillar morphology and interesting surface properties (Ruiz-Hitzky, 2001) that makes this silicate very attractive for applications in many diverse fields (Alvarez, 1984; Galán, 1996; Alvarez et al., 2011; Tian et al., 2019a).

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To our best knowledge the sepiolite term was first introduced by Glocker (1847) using the names of *sepiolithus* and *sepiolith* (the last one is the current name of sepiolite in German) referring to the mineral called at that moment as *meerschaum* (“sea foam”, in German) (Glocker, 1847), term that was apparently introduced by Abraham Gottlob Werner in 1788 (Wikipedia, Sepiolite). Interestingly, it can be observed that the composition of this mineral as analyzed 175 years ago is relatively close to that obtained recently (García-Romero and Suárez, 2010), with the proportions of the main components (SiO_2 , MgO and H_2O), being very close to the theoretical ones with values calculated from the ideal formulae.

Sepiolite is provided with a unique structural arrangement (see below for details on its crystal structure) which, for short, consists of alternating T-O-T Mg-silicate blocks, as in the lamellar talc structure with cavities (*structural tunnels*) aligned with the c^* axis (Sposito et al., 1999; Ruiz-Hitzky, 2001). These cavities constitute pores of nanometric dimensions, which together with larger pores associated with imperfections in crystal growth as well as the fibrous morphology, give this silicate a high specific surface area and total porosity (typically in the order of $300 \text{ m}^2/\text{g}$ and $0.4 \text{ cm}^3/\text{g}$, respectively).

The presence of these nanopores or nanocavities in fibrous clays was exploited several centuries ago in Central America to develop very stable organo-inorganic pigments known as Maya Blue. As described below, the molecular indigo dye was entrapped into the palygorskite nanopores protecting it from the environmental degradation. Another ancient use of fibrous clays is the hand-made smoke pipes by carving nodules of sepiolite (named then as *meerschaum*) from Eskisehir deposits in Turkey. This clay mineral was considered an excellent material to provide a “fresh, dry and tasty smoke” (sic). Apart this initial and peculiar application of sepiolite, some of these old pipes can be considered today as true artworks (Fig. 1) (Lacambalam, 2014).

Sepiolite-based tobacco pipes were manufactured by carving practices using raw natural clay blocks, since the consolidation and shaping of sepiolite by means of conventional thermal treatments produced ceramic materials (*fired clays*) with significant shrinkage problems, limiting their use for this application. However, at the Buen Retiro Royal Porcelain Factory in Madrid, a convenient procedure was found to be able to manufacture ceramics based on sepiolite avoiding these problems. This factory, popularly known as “la China”, produced porcelain of exceptional quality, although only limited to the short period of time between 1802 and 1808, in which kaolin, typically used for the manufacture of porcelain, was replaced by a *proximity clay* such as the sepiolite from Vallecas, then a little town near Madrid. The formula to make the Buen Retiro porcelain was closely guarded as a state secret by the Spanish Crown in the reigns of Carlos III and Carlos IV, being the only one able to compete in Europe at that time with various famous

manufacturers (e.g. Sèvres and Meissen in France and Germany, respectively) (Olaya, 2001). Of these sepiolite-based porcelains, only a few remains have been preserved to date, due to their very limited production. The Buen Retiro factory was sadly destroyed by Napoleon’s soldiers in 1808 and its ruins were later burned by order of the Duke of Wellington in 1812. It is still not clear if it was with the aim of avoiding foreign competition (Ouellet-Plamondon et al., 2015; MDO, 2017). The chemical and mineralogical analyses of a selection of samples of tableware, tiles and sculptural fragments found in 1996 in an archaeological excavation near the place where the factory was built, confirmed the production of a new hard-paste porcelain where sepiolite was used as a substitute of kaolin (Pascual et al., 2011). It has been recently described the preparation of ceramics with a total porosity of ca. 50% and acceptable mechanical properties using sepiolite from Henan province in China blended with polyvinylalcohol that began to sinter at 1000°C (Tian et al., 2019b).

In addition to these ancient applications and others recently reported by Galán and Aparicio (2015), several decades ago Robertson described sepiolite as an extraordinarily versatile raw material having a wide variety of uses, largely due to its outstanding adsorption capacity and rheological properties (Fig. 2).

Nowadays it is well known that sepiolite is an industrial mineral widely traded throughout the world that is used in its natural state or modified by the application of physical methods, including thermal activation and mechanical defibrillation processes, as well as by chemical methods, such as acid and cation exchange treatments and by assembly to diverse organic components including polymers. In this way, sepiolite was, and still is, widely used in fields as diverse as industry, agriculture, health and environment dealing with interest in uses related to catalysis, polymer nanocomposites, pesticide and agrochemicals-controlled delivery, cosmetics, pharmacy and biomedicine, animal feed, waste and water treatments, among other applications (Álvarez, 1984; Galán, 1996; Álvarez et al., 2011; Ruiz-Hitzky et al., 2013a; Tian et al., 2019a).

As it is well known, to develop the so-called “advanced materials” it is generally required the application of high technology, including nanotechnology. Currently, diverse research groups belonging to academia and industry are devoting deep efforts in R&D activities to create new advanced functional materials derived from sepiolite. In this context, this review article contributes to report and discuss on the approaches of nanoscience and nanotechnology in the transformation of this raw and versatile clay mineral in high-quality sepiolite products for many specific uses (Ruiz-Hitzky et al., 2011a; Ruiz-Hitzky et al., 2013a; Aranda and Ruiz-Hitzky, 2018; Tian et al., 2019a). Throughout this contribution, emphasizing on our own experience on the topic, it is showed that the unique structural and textural characteristics of sepiolite allow controlled and precise modifications using diverse chemical and physical tools.

2. Origin and physicochemical characteristics of sepiolite

2.1. The origin of sepiolite

The presence of sepiolite around the world has been mainly associated with the genesis of this silicate in lacustrine or perimarine saline and alkaline environments (Akbulut and Kadir, 2003; Sanz-Montero et al., 2008; Jones and Conko, 2011; Karakaya et al., 2011). One of the world’s largest and well-developed deposits of sepiolite is located in the Miocene Madrid sediments belonging to the Tagus Basin in Spain, where this clay mineral often appears associated with dolomite, Mg-smectites, and palygorskite among other minor components such as feldspar and quartz (Sanz-Montero et al., 2008). It is remarkable that sepiolite could be present as monomineralic rocks in these sediments with layers up to 6 m thick (Fig. 3a). Other important commercial sepiolite deposits are in Anatolia, Turkey, the most known from the Eskisehir Province where sepiolite occurs predominantly in Lower Pliocene gypsum-bearing clays



Fig. 1. Ancient artistic objects made in sepiolite. On the left: “Vintage Carved Meerschaum Estate Tobacco Pipe” (Reproduced from (Haupt, 2015), photo by Joe Haupt, CC BY-SA 2.0). On the right: Porcelain tray manufactured with sepiolite at the Royal Porcelain Factory of Buen Retiro (Museo Cerralbo, 2023) (Cerralbo Museum, Madrid, Spain. Access number 1678, photo by Ángel Martínez Levas).

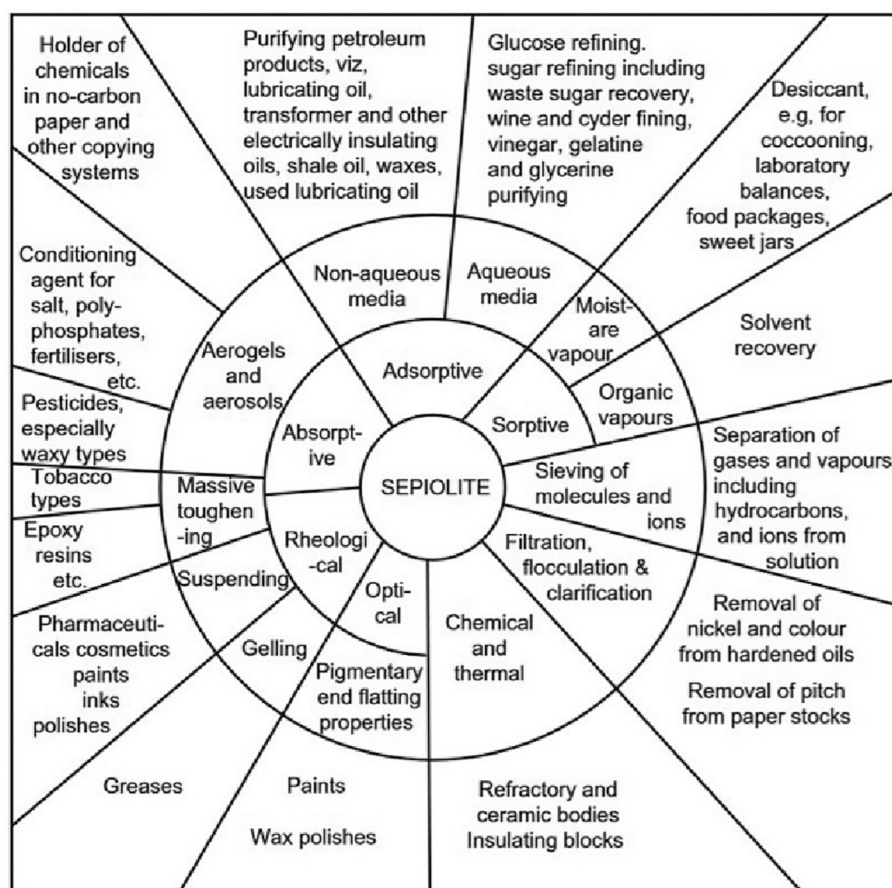


Fig. 2. Scheme illustrating some old applications received by sepiolite as reported 65 years ago by Robertson (Robertson, 1957) (Reproduced with permission from Elsevier (Álvarez et al., 2011)).

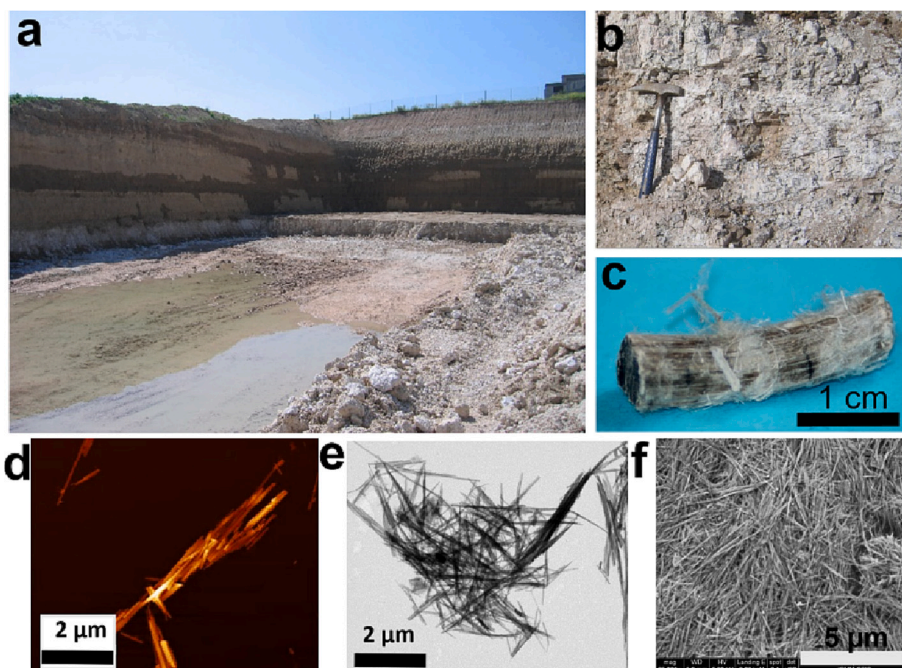


Fig. 3. a) Deposit of sepiolite located in the Tagus Basin (Toledo-Madrid region, Spain), where the mineral is distinguished in the lower white stripe, which has been partially removed for exploitation (Photo by Santiago Leguey & José Casas). b) Detail of the sepiolite layer showing some extracted rocks (Photo by Santiago Leguey & José Casas). c) Morphological aspect of macroscopic fibers of sepiolite from Ampandrandava, Madagascar (Photo by Cristina Ruiz-García). d-f) Morphology of sepiolite (disaggregated by ultrasonication) from Tagus Basin observed by Atomic Force Microscopy (AFM) (Photo by Olivier Pietrement), Transmission Electron Microscopy (TEM) and Field Emission Scanning Microscopy (FE-SEM), respectively.

and in dolomite (Akbulut and Kadir, 2003).

The proposed formation mechanism of *sepiolite* has been primarily based on transformations of precursor phases by dissolution–precipitation (Sanz-Montero et al., 2008; Jones and Conko, 2011), but more recently it has been associated with biomineralization processes from cellulose fibers produced by microorganisms (Leguey et al., 2014). Diverse similitudes between this type of organic fibers and fibrous sepiolite have been established supporting the proposed genesis of this clay mineral. In this way, the organization of fibers and ribbons developed by the biopolymer in lattices can be directly related to the texture of sepiolite, which presents the coexistence of two types of fiber associations acting as support for the organic-mineralization: short and straight fibers (<2 μm length) intertwined in compact bundles and long curved fibers (>10 μm length), forming thin tissues that mimic cellulose and other exopolymers produced by bacteria, as acetobacter and cyanobacteria. This similarity is extended to the nanometric scale as Leguey and collaborators pointed out regarding the dimensions of the cellobiose unit cell, which are comparable to those of the sepiolite tunnels, i.e., between 1.0 and 1.8 nm in the b direction of the crystal (Leguey et al., 2014).

2.2. Morphological & structural features of sepiolite

As above indicated, sepiolite is a hydrated magnesium silicate belonging to the clay minerals family with fibrous-like morphology, crystallizing in the form of needles or ribbons from about 1–10 μm in length and approximately 0.01 μm in width for clays from sedimentary origin (Galán and Aparicio, 2015). The sepiolite exploited for commercial purposes coming from this type of deposits have an average particle length shorter than 5 μm , typically in the range of 1 to 2 μm , although in very rare cases (e.g., sepiolite from Ampandandava, Madagascar) they appear as macroscopic fibers of several centimeters in length (Fig. 3c).

The crystal structure of sepiolite proposed by Brauner and Preisinger (1956) deduced from X-ray diffraction data, indicated an orthorhombic symmetry of *Pnan* space group and cell parameters: $a = 13.4$ Å, $b = 26.8$ Å and $c = 5.28$ Å. In this model, the number of octahedral cations varies from 6.95 to 8.11 for eight octahedral positions and the ^{VI}Mg from 4.96 to 8.1. The structure of sepiolite is integrated by T-O-T blocks of $[\text{SiO}_4]$

(T) and $[\text{MgO}_6]$ (O) sheets. This octahedral sheet becomes discontinuous due to an inverted tetrahedral arrangement leading to the formation of structural cavities of nanometric dimensions, which are characteristic of the fibrous clay minerals (Preisinger, 1957; Ruiz-Hitzky, 2001) (Fig. 4a). This inversion is regularly produced every six units of the tetrahedron layers (Preisinger, 1957; Ruiz-Hitzky, 2001). The formed cavities, with cross-section dimensions of 1.06×0.37 nm², act as tunnels elongated along the fiber direction (c^* axis). Tunnels and channels (i.e., the tunnels acceding to the external surface of the fibers) are usually filled with two types of water molecules: *coordinated* water molecules, which are bound to the Mg^{2+} ions located at the edges of the octahedral sheets, and *zeolitic* water, which is associated with the coordinated water through hydrogen bonding. These last water molecules could be eliminated by heating ($T > 100$ °C), vacuum exposure favoring the access of small polar molecules to interior of the mineral through the structural tunnels (Suárez and García-Romero, 2011).

In addition to the nanocavities defined by the structural tunnels, high resolution transmission electron microscopy (HR-TEM) studies of ultrafine cross-sections of sepiolite fibers indicate the presence of additional nanometric cavities of variable size (Rautureau and Tchoubar, 1976; Krekeler and Guggenheim, 2008; García-Romero and Suárez, 2014). In fact, sepiolite appears as a bundle of single crystals, and these nanocavities can be attributed to crystal growth defects that are longitudinally extended in the direction of the fiber (c^* axis). These common defects have been named by Krekeler and Guggenheim (2008) as “open channels defects”. This arrangement can also be visualized by admitting that the microfibers that make up a bundle of fibers are not perfectly compacted and therefore some of them are laterally aggregated with each other, leaving empty spaces between the fibers. We propose here to name these voids as *interfibrillar space* in accordance with the space between layers in lamellar clay minerals (interlayer space) (Fig. 5). Previously, Shuali et al. (2011) stated that porosity of sepiolite has two contributions: the external porosity resulting from the inter-fibers/bundles spaces and the structural porosity determined by the intracrystalline tunnels. Suárez and García-Romero (2012) have experimentally extended the concept of microporosity and mesoporosity associated with the interfibrillar space, supported by electron microscopy and textural analysis applied to a large number of sepiolite samples of diverse origin. The existence of this type of nanocavities is

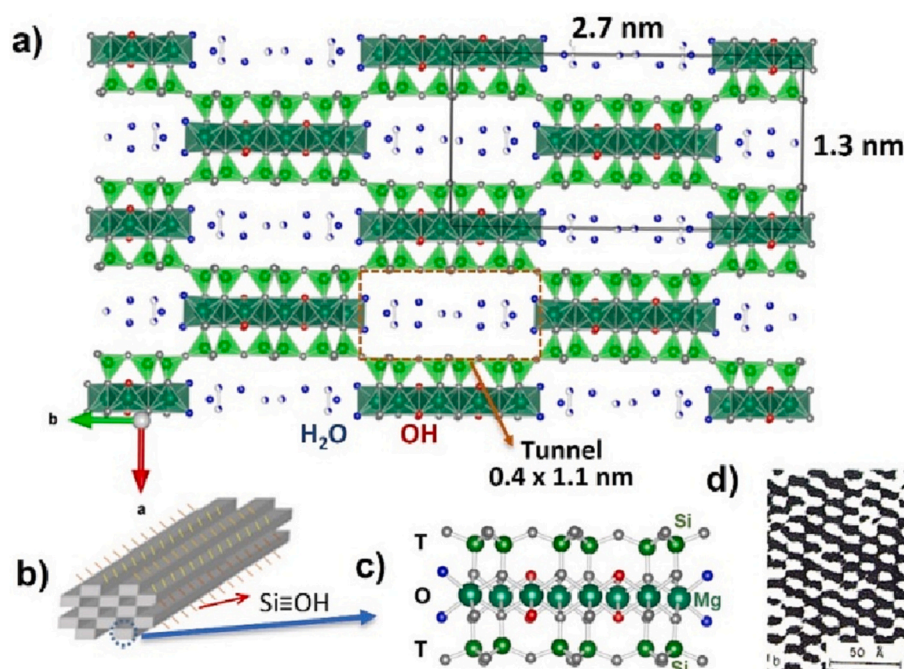


Fig. 4. a) Crystal structure of sepiolite based on Brauner and Preisinger (1956) using VESTA software (Momma and Izumi, 2011). b) Idealized model of an elemental sepiolite fiber showing the arrangement and distribution of the nanodimensional tunnels and silicate blocks and as well as the channels located at the external surface, with indication of the presence of silanol groups. c) Tetrahedral-Octahedral-Tetrahedral (T-O-T) elemental blocks whose staggered alternation defines the structural tunnels. d) visualization of the alternance of the elemental blocks and tunnels by HR-TEM (Image adapted from (Rautureau and Mifsud, 1977), reproduced with permission).

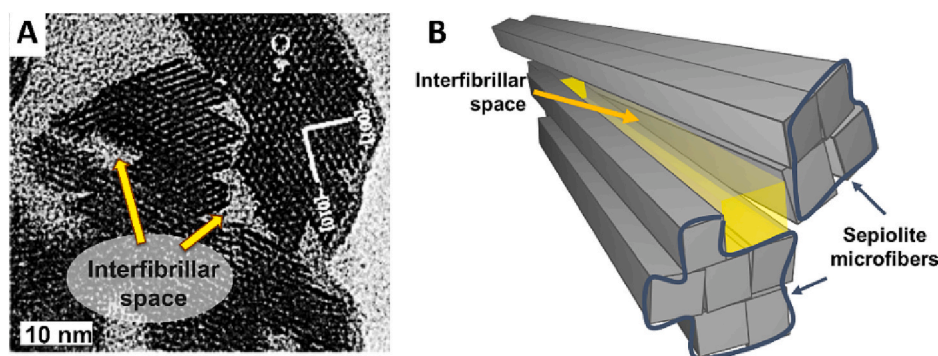


Fig. 5. a) HR-TEM image of the cross-section of a sepiolite fiber showing the presence of structural tunnels and interfibrillar spaces between elemental fibers (modified image, reprinted from (Krekeler and Guggenheim, 2008) with permission from Elsevier); b) Schematic representation of the arrangements of microfibrillar components of a sepiolite bundle.

supported by the corresponding N_2 adsorption isotherms, STEM bright-field microscopy, and X-Ray microtomography allowing the evaluation of the porosity ascribed to micro- and meso-pores in untreated blocks of natural sepiolite (Ruiz-Hitzky, *in preparation*). Actually, these intracrystalline regions corresponds to micropores of a few nanometres wide allowing molecular accessibility within unmodified sepiolite samples. Therefore, the interfibrillar spaces of sepiolite can be considered as nanoscale molecular reservoirs (*nanocounters*) allowing the access of molecules and polymers of several nm dynamic volume.

The discontinuity of the silica sheets in the sepiolite structure leads to the presence of surface silanol groups ($\equiv\text{Si-OH}$), which are regularly disposed on the edges of the channels located at the external surface of the sepiolite (Ruiz-Hitzky, 2001; Alves et al., 2020), as it is indicated in Fig. 4b. These silanol groups allow hydrogen bonding interactions between the silicate surface and many diverse inorganic and organic species (including polymers), the grafting reactions with functional organosilanes and other reagents, or the interaction with metal oxide nanoparticles, leading to functionalized sepiolite materials (Ruiz-Hitzky and Van Meerbeek, 2006; Ruiz-Hitzky et al., 2011a; Shuali et al., 2011; Aranda and Ruiz-Hitzky, 2018).

Isomorphous substitutions of Si^{4+} by Al^{3+} in the tetrahedral layer and/or Mg^{2+} for Al^{3+} or other trivalent cations in the octahedral layer, determine the formation of negatively charged sites in the sepiolite structure, which are compensated by exchangeable cations. The cation exchange capacity (CEC) of sepiolite is low compared with smectite clays, ranging typical values around $7 \cdot 10^{-4}$ – $13 \cdot 10^{-4}$ eq/g (Christidis, 2013), in the order of $1 \cdot 10^{-4}$ – $2 \cdot 10^{-4}$ eq/g depending on the origin the fibrous silicate. Therefore, the negatively charged surface can also offer chemical bonding through ionic interactions that lead to assembly of sepiolite with inorganic and organic cations, which together with the presence of silanol groups represents an important approach for the preparation of functional materials derived from this silicate.

In summary, taking into account the abovementioned structural characteristics of sepiolite, its interaction with very diverse types of compounds through Si-OH groups and hydroxyls belonging to the coordinated water molecules can topologically take place: i) at the external surfaces involving the structural channels according to the exterior of the mineral (Ruiz-Hitzky, 2001), and ii) inside the nanocavities i.e. the structural tunnels and the interfibrillar space, which are capable of acting as molecular sieves (Barrer et al., 1954) and nanocounters allowing the intracrystalline penetration of small adsorbates such as ions or neutral molecules, and exceptionally some linear polymers (Ruiz-Hitzky, 2001).

3. The Maya Blue concept: ancient nanotechnology applied to palygorskite and sepiolite fibrous clays

According to Gettens (Gettens, 1962; Fan et al., 2014), a peculiar

blue pigment was discovered in 1931 by the mineralogist Herbert Eugene Merwin as a component of Maya wall paintings in Yucatán, Mexico. Later on, this pigment of enigmatic nature at that time, received the name of “Maya Blue” by Gettens and Stout in 1942 (Gettens and Stout, 1942). Maya Blue is a pigment that today is characterized as an organic-inorganic nanohybrid material formed by the assembly of palygorskite and indigo, a natural dye from *Indigofera tinctoria* (Gettens, 1962; Van Olphen, 1966; Gómez-Romero and Sanchez, 2005; Sánchez del Río et al., 2006; Doménech et al., 2009; Sánchez del Río et al., 2011; Arnold et al., 2012).

This pigment represents an ancient approach to take advantage from the nanopores associated with the structural tunnels of fibrous clays with the aim to stabilize organic molecules inside them. As here discussed, it signifies a useful and modern nanotechnological tool to develop advanced functional materials using these silicates (*vide infra*).

The Maya Blue pigment was developed several centuries ago in Central America primarily from VII to XVI century CE (Giustetto and Wahyudi, 2011). Its elaboration and use were exported after the XVI century, to Spain including the colonial Cuba (here under the name of Havana Blue) (Tagle et al., 1989; Sánchez del Río et al., 2011). Crystal refinements have confirmed the formation of the Maya Blue complexes in both palygorskite and sepiolite clay minerals by the insertion in their structural tunnels of the indigotine molecule, presents in the indigo natural dye as represented in Fig. 6 (Chiari et al., 2003). The intracrystalline access to those tunnels assures the protection against external agents giving rise to very stable blue pigments. These processes are favored by the partial loss of zeolitic water molecules that are filling the fibrous clay tunnels, under heating above 100 °C. Studies by the archaeologist Arnold and co-workers (Arnold et al., 2008) showed traces

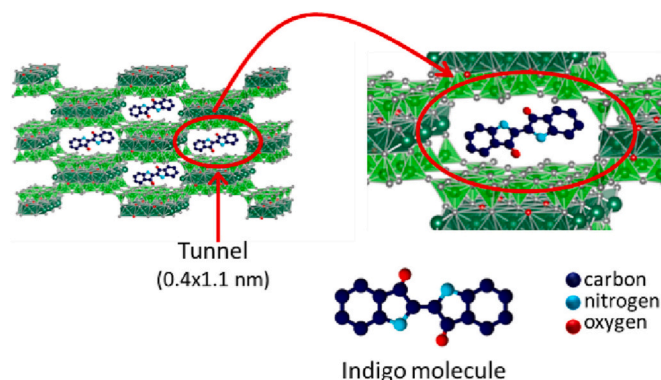


Fig. 6. Schematic representation of the sepiolite crystalline structure and the indigo molecule inserted in their tunnels. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of a resin incense called copal, that melts around 150 °C. It has been proposed that when heated, the copal fused the indigo and palygorskite together, producing the Maya Blue pigment. Similar tests replacing these host silicates with other clay minerals, such as montmorillonite, do not produce comparable clay-based pigments (Chiari et al., 2003).

The Maya Blue pigment has extraordinary stability as it resists against heating at temperatures close to 250 °C, treatments with organic solvents, acids and alkalis, and exposure to the action of microorganisms. In this way, the original Maya Blue was first applied to ancient decoration on fired clays (Fig. 7) and temple murals, as well as in drawing manuscripts. The blue pigment was also sadly used as part of the ritual of the cruel religious sacrifices practiced by the ancient Mayans (Arnold et al., 2008).

The Mayan pigments reveal the presence of indigotine extracted from indigo, as well as other related dyes showing diverse colors such as yellow or green (Buti et al., 2018). Using non-destructive analytical techniques, the nature of diverse pigments have been investigated in the painted figures appearing at the Codex Fejérváry-Mayer, a pre-Hispanic manuscript from Central Mexico, also called Codex Tezcatlipoca, (Fig. 8). Apart from palygorskite, other components as for instance the oxidized yellow form of indigo (dehydroindigo), isatin and indirubin as minority components accompanying indigotine in such formulations, have been observed in some of the figures of the aforementioned Codex, explaining the peculiar greenish-blue tone of the pigment in agreement with investigations by Doménech et al. (Doménech-Carbó et al., 2012; Doménech-Carbó et al., 2013).

Nowadays, Maya Blue concept can be considered as an attractive model to apply nanotechnological approaches for the encapsulation and preservation of molecular and polymeric species within sepiolite and palygorskite structural tunnels. Many works based on this concept have recently been published, showing the substitution of the indigo dye encapsulated in palygorskite, by many other dyes that can finally leads a whole colour palette. Thus, inspired by Maya Blue, stable synthetic analogue pigments have been prepared using diverse molecular dyes leading to a variety of colors that have received in some cases the specific names as for instance “Maya Red”, “Maya Violet” or “Maya Purple” (Giustetto and Wahyudi, 2011; Fan et al., 2014; Zhang et al., 2015; Chen et al., 2019). The procedures for the preparation of these analogues, using either palygorskite or sepiolite, are based on diverse approaches such as by direct adsorption of dyes from aqueous solutions (for soluble dyes), thermal treatment of grinded mixtures of the clay and the dye in solid state (Zhang et al., 2015), dye adsorption from aqueous solutions in previously vacuum treated at 180 °C clay (Chen et al., 2019), and more recently, using molecular dyes in organic solvents (Rahman et al., 2022). Summarizing, the procedures intend to induce the removal of the zeolitic water molecules filling the structural tunnels, facilitating then the inclusion of molecular dyes provided of appropriate dimensions.

After the initial uses of the original Maya Blue, advanced



Fig. 7. Crocodile-shaped rattle pottery using Maya Blue pigment for surface decoration (Maya culture; 8th century; The Michael C. Rockefeller Memorial Collection, Metropolitan Museum of Art, MET (The Metropolitan Museum of Art), photo by Eduardo Ruiz-Hitzky). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

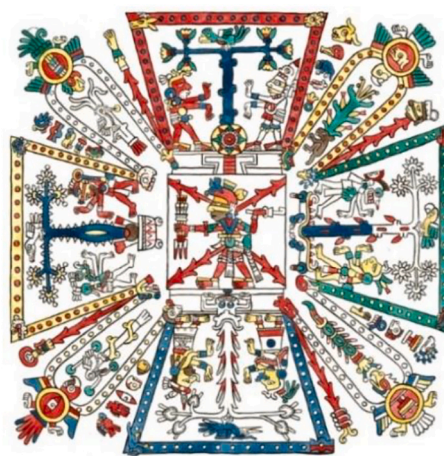


Fig. 8. Example of image appearing in painted manuscripts such as the Codex Fejérváry-Mayer at the National Museums Liverpool, containing Maya Blue pigment and analogues. (image corresponding to “Detail of Codex Fejervary-Mayer, also known as Codex Pochteca”, drawn by Lacambalam (Reproduced from (Lacambalam, 2014), CC BY-SA 4.0). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

applications based on a similar concept have been developed more recently. In this way, persistent mass coloration of polymer matrices in polymer–clay nanocomposites can be introduced in a very stable manner using Maya Blue based on the indigo dye/sepiolite pigment (Volle et al., 2011). The water insoluble indigo and lawsone natural dyes (hanna) have been loaded in sepiolite through solutions in organic solvents, by the immobilization of the molecular dyes into the clay tunnels according to Rahman et al. (Rahman et al., 2022). Interestingly, the resulting hybrid materials can be efficiently used to dye hair in very diverse colors, even unusual colors such as blue and yellow, which are retained after six consecutive shampooing. In our opinion, this feature paves the way for future applications of these materials for the coloring of various natural fibers.

The development of synthetic Maya Blue analogues may receive new uses of the resulting hybrid materials. For instance, synthetic molecular dyes such as methylene blue and methylene red adsorbed on sepiolite from diluted solutions or by solid-state interactions, led to Maya Blue-like pigments for durable coloring of geopolymers (Ouellet-Plamondon et al., 2015). The idea of supporting molecular dyes on nanoporous fibrous clays taking advantage of their stability can be extrapolated to other types of both dyes and silicates, as it is the case reported by Ogawa and co-workers about the immobilization of anthocyanin in the interlamellar space of saponite and montmorillonite layered clay minerals, resulting bionanohybrids in which anthocyanine molecules were efficiently confined. These materials may be capable to change their colour in acidic/ basic environments, offering potential application as active phase of colorimetric sensors (Ogawa et al., 2017).

Summarizing this section, the Maya Blue concept represents a good connection between nanotechnology developed several centuries ago and fibrous clay minerals which is conferred by the nanodimensions of the structural cavities. As discussed below, an important effort is being currently devoted to the development of advanced materials derived from sepiolite by means of nanoarchitectonics tools.

4. Surface and rheological properties: the basis of the main industrial applications

Based on their physicochemical properties, sepiolite and palygorskite have been widely used in many diverse traditional applications as adsorbents, catalysts and catalyst supports, filler of polymers, etc. The set of structural blocks and channels in which sepiolite is organized,

entails a large specific surface area and pore volume (ca. 300 m²/g and 0.4 cm³/g, respectively), leading to an elevated adsorption capacity in this type of clay mineral. The presence of silanol groups (Si-OH) at the external surface of the silicate, makes these hydroxyls as active centers for interaction with diverse polar species, often acting through hydrogen bonding mechanisms. Likewise, properties of pores associated with crystal imperfections as well as the presence of structural tunnels acting as microporous cavities, also represent an important contribution to the adsorption capacity of sepiolite. In this way, gases and vapors such as nitrogen, argon, CO₂ and water, and small polar molecules such as ammonia or methanol, and even medium size compounds such as pyridine or methylene blue, can be accessible to these intracrystalline cavities replacing water molecules in the interior of the tunnels (Ruiz-Hitzky, 2001). On the other hand, as above indicated, in a similar way than occurs in many other clay minerals, the sepiolite surface is negatively charged, by the isomorphical substitution of Mg²⁺ for Al³⁺ in its octahedral sheets, allowing the adsorption of positively charged species through ion-bonding mechanism (vide supra).

Due to these surface properties, the first large-volume application of sepiolite has been its use as a powerful absorbent applied for the control of toxic and dangerous spills, the inertization and stabilization of waste, the support for different bioactive chemical compounds such as drugs, insecticides and herbicides, and adsorbent products for humidity control among other applications (Ruiz-Hitzky et al., 2007).

In addition to the characteristic textural properties, the rheological behavior of sepiolite, as well as palygorskite, are determinant for many of their current applications as additives leading to viscous fluids showing thixotropic behavior. Both fibrous clays are strongly hydrophilic that easily disperse in water, or even in other polar solvents, giving rise to homogeneous and stable suspensions that improve and enlarge their applicability. Viscous and stable dispersions are reached by application of mechanical shear or by addition of chemical dispersants (Alves et al., 2020; Ruiz-Hitzky et al., 2021). The stability and homogeneity of the fibrous clay dispersions are directly related to the morphology of the sepiolite whose elemental fibers appear in nature forming aggregates that in turn are grouped forming bundles. (Suárez and García-Romero, 2012). During the dispersion of these bundles in water, the sepiolite microfibers create a colloidal network leading to stable gels provided of high viscosity properties.

The treatments to disaggregate the silicate fibers are mainly based on mechanical treatments assuring high shearing on the clay sample in the presence of water. By applying these processes, TOLSA company was pioneer to produce and commercialize sepiolite of rheological grade (e. g. Pangel-S9®) (Alvarez Berenguer et al., 1985). Recently, alternative methods have been reported using sonomechanical treatments instead the classical mechanical shearing, because of the ultrasonic irradiation generates cavitation of bubbles that act as micro-jets to efficiently disaggregate the fibers (Ruiz-García et al., 2014; Mamvura et al., 2018). Additionally, the disaggregation of the fibers is also accompanied by changes on their textural properties, modifying the porosity and increasing the specific surface area of sepiolite. However, it must be taken into account that the energy applied during these processes must be controlled to avoid damage of the fibers, since an intense mechanical treatment could result in the amorphization of the sepiolite silicate with the consequent loss of porosity in detriment of its application as adsorbent material (Cornejo and Hermosin, 1988).

The capacity of the sepiolite to be de-agglomerated and to produce gels with interesting rheological properties has been extensively investigated to stabilize nanocomponents of different composition such as carbon nanomaterials, metal nanoparticles, biopolymers, etc. (Ruiz-Hitzky et al., 2011a; Fernandes and Ruiz-Hitzky, 2014; Ruiz-Hitzky et al., 2016; González del Campo et al., 2018; Ruiz-García et al., 2018; Lo Dico et al., 2019; González del Campo et al., 2020; Lisuzzo et al., 2020; Ruiz-Hitzky et al., 2021). The colloids formed by sepiolite in water help to disperse additional components, allowing to stabilize nanomaterials from very different nature, as for instance hydrophobic carbons, such as

multiwall carbon nanotubes (MWCNT) or graphite nanoplatelets (GNP), in aqueous phase (Fernandes and Ruiz-Hitzky, 2014; Ruiz-Hitzky et al., 2016). The formation of these stable colloids is an interesting way to prepare functional nanocomposite materials showing selected suitable properties.

5. Industrial applications of sepiolite

As above indicated, the inherent physical and chemical properties of the fibrous clay minerals are the basis to apply suitable transformations of sepiolite and palygorskite for very diverse industrial applications. According to Alvarez et al. (Álvarez et al., 2011) six different generations of sepiolite treatments have been developed leading to a wide variety of applications as illustrated in Fig. 9.

The first processes generation corresponds to conventional drying, crushing, grinding and sieving processes leading to sepiolite granular products showing variable particle size, e.g. 15/30, 30/60 and 60/90 mesh, and medium to fine grades ranging from 100 to 325 mesh (Álvarez et al., 2011). These products were longtime and nowadays used in typical applications as industrial adsorbents due to the elevated specific surface area and porosity, rigidity of the porous structure, and chemical inertness of sepiolite. In this way, sepiolite allows the formation of the so-called “dry liquids” or “powdered liquids”, by adsorption of liquid products on the porous solid maintaining their activity but facilitating its manipulation and preventing pollution and accidents (Prisma rubber additives, 2023). An example related it is the use of sepiolite as phytosanitary carriers, in some cases associating controlled release properties. Another type of application within the 1st generation processes is the use of sepiolite as an additive in feed for animals presented as pellets or granular products able to agglomerate the feed ingredients, as well as to absorb the existing moisture, increasing homogeneity and reducing potential fungus contaminations (Álvarez et al., 2011). An important additional feature is the ability of sepiolite to act as mycotoxin sequestering agent that fixes mycotoxins present in feeds reducing their intestinal adsorption and therefore protecting the animals' health (Wicklein et al., 2010; Li et al., 2020).

The micronization processes belonging to the 2nd generation produce disaggregation of sepiolite bundles following *dry or wet* micronization procedures using, in the first case, jet mills to break the fiber bundles down into micron-size particles or, in the second case, in concentrated water dispersions by applying high mechanical shearing (Alves et al., 2020). Pansil® and Pangel® are respectively the trademarks of commercial dry- and wet-micronized products fabricated by the TOLSA S.A. company. More recently have been reported ultrasound-assisted treatments of raw sepiolite in water dispersions as an alternative strategy for disaggregation of silicate fibers in sepiolite bundles (Ruiz-Hitzky et al., 2021). The micronized materials are mainly used for polymer fillers (e.g., in rubber) and water-based rheological additives in paints and coatings, modified asphalt for roads, controlled viscosity in animal feeds, as well as mortars, plasters and concrete for diverse building applications.

The hydrophilic character of sepiolite surface due to its coverage by silanol groups and water molecules inherent to the sepiolite surface could be chemically changed into an organophilic surface resulting in organo-sepiolite hybrid materials. These materials can be synthesized by treatments with surfactant agents leading for instance to Pangel B® commercial products from TOLSA, and in minor extent due to its elevated cost, by grafting reactions using alkoxysilanes reacting with the silanol surface groups (Ruiz-Hitzky and Van Meerbeek, 2006). This is related with the 3rd generation processes, producing on this way sepiolite-based organophilic thixotropic additives for application in diverse organic-solvent systems such as solvent-based paints, greases, solvent-based inks and adhesives as well as polymer fillers such as epoxy resins and plastisols (Álvarez et al., 2011). The possibility to accommodate the surface polarity of sepiolite allows the application of the resulting organic derivatives in the development of polymer-sepiolite

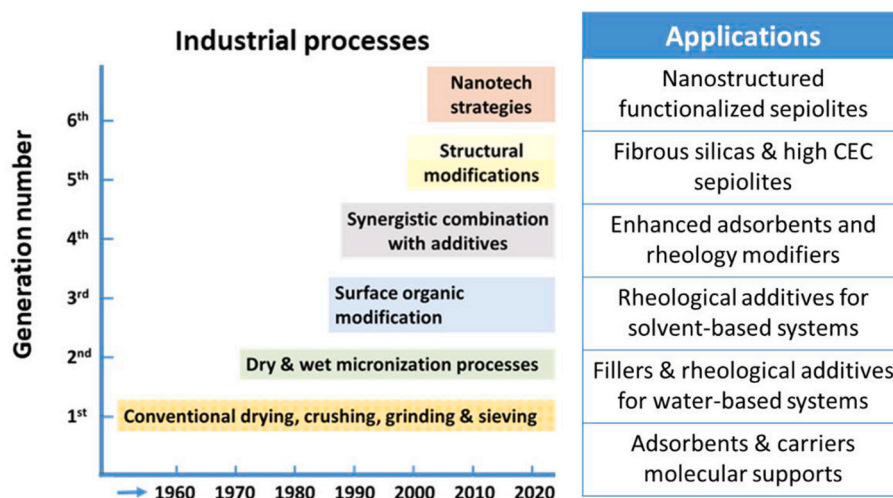


Fig. 9. Evolution of sepiolite applications vs. development of industrial processes included within the 6 consecutive generations proposed by Alvarez et al. (Álvarez et al., 2011).

nanocomposites.

The 4th generation products are industrially prepared by the synergistic combination of diverse additives such as polysaccharides, e.g., cellulose ethers and other additives to prepare enhanced adsorbent materials as well as rheology modifier products. These products are used in construction purposes as for instance to improve the workability of mortars. Concerning the 5th generation products, the results from deeper chemical modifications leading to e.g. special fillers and carriers for catalysts based on fibrous silica derived from sepiolite. Aluminum-exchanged sepiolite by hydrothermal processes in alkaline medium developed by TOLSA S.A. is an example of resulting sepiolite-based materials showing elevated cation exchange capacity and high surface acidity, useful in applications as for example fluid catalytic cracking (FCC) processes (Álvarez et al., 2011).

Finally, the most recent generation of products, preconized by Alvarez and co-workers as the 6th generation, refers to the application of the nanoarchitectonic concepts (Ariga, 2020). The most salient example concerns the incorporation of sepiolite nanofibers to polymers, as it is the case for instance of the materials used as nanofillers in biopolymers, thermoplastics and thermosets showing improvements in the mechanical and thermal properties, reduced flammability and enhancing barrier properties compared with the pristine polymers. In fact, this ultimate generation of commercial products represents the most recent approaches towards more and more advanced applications based on the assembly of diverse nanoparticles to sepiolite in order to prepare functionalized nanomaterials as discussed in the next Section (vide infra). Regarding the safety of sepiolite widely used at domestic and industrial level, it would be considered that apparently it does not represent significant health problems for its exploitation and commercialization. In fact, no real epidemiological problems have been never observed in the populations near those clay deposits and in the surrounding soils. In addition, according to the International Agency for Research on Cancer dependent on the WHO, sepiolite can be considered barely toxic, being classified as “inadequate evidence” of toxicity and carcinogenicity (International Agency for Research on Cancer, 1997). Concerning the potential carcinogenicity associated with fibers of commercially available sepiolite, it should be considered that the length of this clay mineral is typically in the range of 1 to 2 μm (Galán and Aparicio, 2015). This may be one of the reasons for the health safety of this clay, despite the elongated shape of the particles. In fact, elongated particles with a length of <5 μm are not even considered a fiber by the World Health Organization (WHO) from a healthcare point of view. WHO consider fibers as those particles with a length >5 μm , a diameter <3 μm and a length to diameter ratio >3:1 (World Health Organization, 1997).

Recent results by Castro-Smirnov and others, confirmed the scarce toxicity of sepiolite from gene transfer studies in mammals, including human cells. Therefore, the safety of sepiolite allows its use in fields such as animal feed, pharmacy, being now proposed its use in biomedicine (Castro-Smirnov et al., 2017; Ragu et al., 2020; Brooks et al., 2022).

6. Advanced materials based on sepiolite: the nanotech approach

The rise of sepiolite-based advanced materials in both, Academia and Industry, results from the convergence of their physicochemical properties with the characteristic approaches offered by nanotechnology. Nowadays, there is an increasing number of publications, clearly establishing the link between Nanotechnology and sepiolite focusing on the preparation of advanced materials. Thus, an exponential increase in the number of publications (typically observed in the recent emerging fields of Science and Technology) have appeared in the last years. For instance, in the period from 2001 up to 2021, a total of 741 articles were published according to the results of Web of Science searching by “(sepiolite* AND nano*) AND mater*” (Clarivate, 2023). These results, mainly deal with the following topics: materials science, chemistry, engineering, physics, polymer science, crystallography, environmental sciences & ecology, mineralogy, energy & fuels, and spectroscopy. The previous section dedicated to the Maya Blue pigment illustrates an example to develop advanced materials through the application of Nanotechnology on sepiolite (vide supra). In addition, as the mined sepiolite from most of its deposits is presented as micrometric fibers in length but nanometric in thickness, it can therefore be considered as a nanomaterial. On the other hand, the interactions between its external surface and many other diverse components usually take place at the nanometric scale, so the resulting compounds can be considered undoubtedly as nanoarchitectural or nanostructured materials, and as well the nanocomposites derived from this silicate.

Table 1 groups examples of these resulting nanostructured materials, with a brief indication about their preparation procedures, as well as their physicochemical properties and potential applications, which have been mainly reviewed by Aranda and Ruiz-Hitzky (2018).

Among the many diverse examples in Table 1 we have selected the case of the nanostructured carbon and sepiolite nanostructured materials to explain them deeply. Nanostructured carbon-sepiolite materials have been prepared either by in situ generation of graphene-like compounds or by the direct assembly with carbon nanoparticles to obtain conducting hybrid materials. Graphene-like compounds have been generated taking advantage of the sepiolite porosity entrapping carbon

Table 1

Representative examples of nanostructured materials derived from sepiolite highlighting preparation procedures, properties and potential applications.

Sepiolite-based nanostructured materials	Preparation procedure	Properties/ Potential applications	Reference
Graphene-like/sepiolite nanocomposites	Adsorption of biopolymers as precursors followed of thermal treatment in absence of oxygen	<ul style="list-style-type: none"> - Good electronic conductivity, maintaining the sepiolite properties - Electrochemical components (sensors, batteries...) - Hydrogen adsorption and heterogeneous catalysis 	(Fernández-Saavedra et al., 2004; Gómez-Avilés et al., 2010; Ruiz-Hitzky et al., 2011b; Ruiz-García et al., 2013)
Carbon-nanotubes & graphene nanoplatelets /sepiolite nanocomposites	Assisted assembling of sepiolite and carbon NP in aqueous media	<ul style="list-style-type: none"> - Electronic conductivity. Very stable and high viscosity dispersions - Heterogeneous catalysis - Reinforcement and functionalization of polymers - Combined with polymers for food packaging 	(Fernandes and Ruiz-Hitzky, 2014; Ruiz-Hitzky et al., 2016; Ruiz-García et al., 2018; Lo Dico et al., 2019; Barra et al., 2020)
Silica & alumina-sepiolite nanocomposites	Surface coverage from Si- and Al-alkoxides (sol-gel) of organo-sepiolites	<ul style="list-style-type: none"> - Glass microfibers-like easy to functionalize - Reinforcement of epoxy and other polymers - Heterogeneous catalysis 	(Belver et al., 2013; Gómez-Avilés et al., 2013)
Na-silicates/sepiolite nanostructured materials	Synergistic action of silicate as inorganic adhesive, sodium fluorosilicate as curing agent	<ul style="list-style-type: none"> - Porous structure showing high compressive strength and low bulk density. - Inorganic heat insulation panels for saving energy 	(Wang et al., 2014)
TiO ₂ or ZnO NP/sepiolite	Sol-gel of Ti-alkoxides in the presence of sepiolite modified by surfactants	<ul style="list-style-type: none"> - High specific surface photoactive systems - Photodecomposition of organic pollutants in water 	(Aranda et al., 2008; Pérez-Carvajal et al., 2016; Akkari et al., 2018; Ruiz-Hitzky et al., 2019)
Magnetic Fe ₃ O ₄ NP/sepiolite	Infiltration of magnetite-based ferrofluids	<ul style="list-style-type: none"> - Superparamagnetic behavior maintaining the sepiolite properties - Removal of organic pollutants and radionuclides from water - Magnetic polymer-sepiolite nanocomposites. Panels for microwave shielding (antiradar systems) 	(González-Alfaro et al., 2011; Darder et al., 2014; Akkari et al., 2017)
LDH-sepiolite heterostructures	Growth of layered double hydroxides grafted on the external surface of sepiolite	<ul style="list-style-type: none"> - Simultaneous anionic and cationic exchange ability from both sepiolite and LDH - Adsorption /heterogeneous catalysis of pollutants 	(Gómez-Avilés et al., 2016; Charradi et al., 2019)
Zeolites-sepiolite heterostructures	Growth of nanosized zeolites on the external surface of sepiolite	<ul style="list-style-type: none"> - Synergistic properties of zeolites and sepiolite - Ion-exchangers, adsorbents of pollutants and heterogeneous catalysis 	(Gómez-Avilés et al., 2014)
Biopolymers-sepiolite nanocomposites (bio-nanocomposites)	Assembly of polysaccharides, proteins, lipids and nucleic acids to sepiolite	<ul style="list-style-type: none"> - Capability to conform as powders, thin films or monolith with cellular texture. - Biodegradable, biocompatible, fire retardancy, bioactivity, etc. - Films of nanopaper based on sepiolite-nanocellulose composites - Active phase of sensors, thermal and acoustic insulating materials, support of enzymes, adjuvant of vaccines - Controlled drug and gene delivery systems 	(Darder et al., 2006; Ruiz-Hitzky et al., 2008; Ruiz-Hitzky et al., 2010; Ruiz-Hitzky et al., 2013b; Castro-Smirnov et al., 2016; González del Campo et al., 2018)

precursors such as sucrose, caramel and other polymers prior a thermal treatment at temperatures above 500 °C in absence of oxygen (Ruiz-García et al., 2014). On the other hand, multiwalled carbon nanotubes and graphene nanoplatelets have been assembled to sepiolite fibers by means of sonomechanical treatments of their mixtures with rheological grade sepiolite aqueous suspensions (e.g., Pangel S9), which act as an effective suspending agent (Fernandes and Ruiz-Hitzky, 2014; Ruiz-Hitzky et al., 2016). The resulting carbon-sepiolite nanostructured materials present interesting physicochemical properties with synergies associated with each of their components. Here, for example, the important electrical conductivity of these nanostructured materials stands out without affecting too much the presence of an electrical insulator such as sepiolite showing great interest for various applications, such as electrochemical and food packaging applications (Fernández-Saavedra et al., 2004; Gómez-Avilés et al., 2010; Ruiz-Hitzky et al., 2011b; Lo Dico et al., 2019; Barra et al., 2020). Furthermore, these nanostructured materials have demonstrated their important role as catalysts in environmental remediation (Ruiz-García et al., 2018), in H₂ storage (Ruiz-García et al., 2013), and in improving the mechanical properties of diverse biopolymers (Ruiz-Hitzky et al., 2016).

7. Conclusions and future perspectives

Sepiolite as well as palygorskite, are fibrous or needle-like clay minerals known since ancient times but only recently have been thoroughly investigated and are now receiving important applications in many different fields. The particularities of sepiolite in terms of its physicochemical characteristics, referring mainly to its structure and morphology and, consequently, to its textural characteristics and rheological behavior, are directly related to the current wide industrial applications, many of them related with its outstanding adsorption capacity. The ability of fibrous clays for molecular sequestration in narrow but long structural tunnels of nanometric dimensions as well as in narrow cavities defined by their interfibrillar spaces, opens the way for the encapsulation of diverse type of species, such as small molecules, carbon nanomaterials, metal and organic cations, and metal and metal oxide nanoparticles.

The elevated specific surface area and porosity together with the ability of sepiolite microfibers to generate stable and viscous gels are the basis for its widespread use in a large number of commercial products associated with a growing market. See, for example, the case of highly traded sepiolite-based materials such as cat litter and the rheology modifier products for new generation of paints and additives for

building materials.

A more recent generation of sepiolite-based products are nano-architected materials that broaden current and future applications. In this context, supported carbon and metal nanoparticles or bioactive species assembled to the sepiolite surface are examples of derived materials for new applications in sensing devices, selective catalysis, drug carriers and DNA transfection, or even immunization towards viruses. Potential uses for cancer treatment based on sepiolite-biohybrid materials are at the present time under investigation. Also, the incorporation of sepiolite nanofibers conveniently functionalized by diverse nanoscale approaches efficiently act as nanofillers in polymers (biopolymers, thermoplastics, thermosets, etc.), improving mechanical and thermal properties, reducing flammability, and enhancing barrier properties compared to pristine polymers. In fact, this latest generation of commercial products represents the most recent approaches towards increasingly advanced applications and marks the future of sepiolite-derived nanomaterials that will most likely be the subject of new developments in the coming times.

Author contributions

A.I.R., C.R.-G. and E.R.-H.: equally participated in conceptualización, writing—original draft preparation, writing—review, editing and supervision. All authors have read and agreed to the published version of the manuscript.

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Declaration of Competing Interest

All authors declare that they have no conflicts of interest.

Data availability

No data was used for the research described in the article.

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