



ORDERED MESOPOROUS ORGANOSILICA ADSORBENTS FOR INORGANIC POLLUTANTS REMOVAL FROM WATER

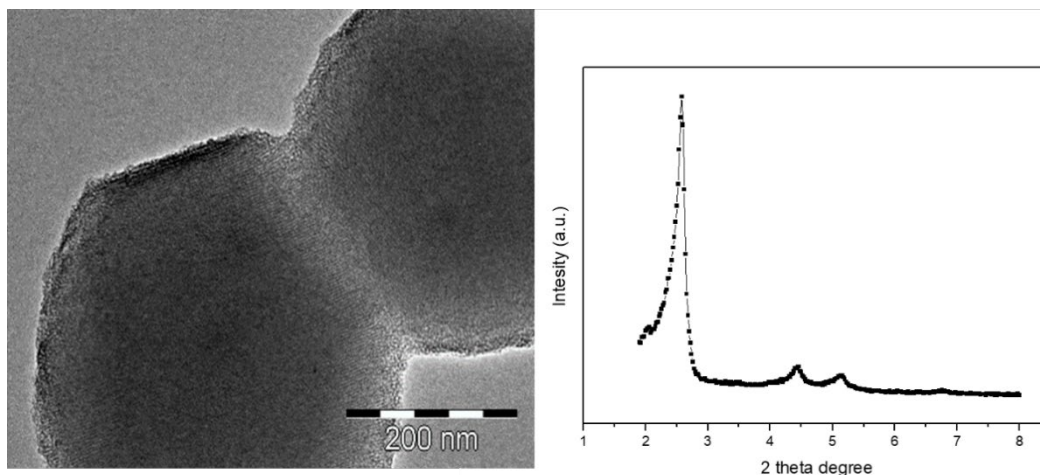
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Graphical abstract



TEM image and powder X-ray diffraction profiles at low angles of an MCM-41-NH₂

Resumen

Este manuscrito hace un repaso de las contribuciones más importantes sobre el uso de las sílices mesoporosas ordenadas (SMO) modificadas aplicadas a la remoción de contaminantes inorgánicos de matrices acuosas. En primer lugar, se discute brevemente sobre los diferentes caminos para sintetizar este tipo de materiales mesoporosos nanoestructurados, mencionando también las características estructurales y químicas principales que se obtienen al utilizar cada uno de ellos. Se hace énfasis en los reportes sobre la aplicación de las SMO como adsorbentes para la remediación ambiental, aunque también se mencionan brevemente otros campos donde se utilizan este tipo de sistemas sólidos nanoestructurados. Finalmente se discute en profundidad sobre la síntesis y aplicación de la SMO denominada MCM-41, su modificación con diferentes grupos orgánicos y su desempeño en la remoción de cromo hexavalente de soluciones acuosas de

variada composición química. De esta SMO en particular se discute cómo afectan sobre su desempeño como adsorbente el tamaño de partícula y la cantidad y distribución de grupos orgánicos anclados dentro de la red de mesoporos. Finalmente se mencionan algunas estrategias actualmente en estudio que buscan aumentar la estabilidad de la MCM-41 de manera de conseguir un adsorbente efectivo y de larga vida útil.

Abstract

This article reviews the most important contributions on the use of organically modified ordered mesoporous silicas (OMS) for removal of inorganic pollutants from aqueous matrices. First, we briefly discuss the different preparation methods to synthesize this type of nanostructured mesoporous hybrid materials, mentioning the main structural and chemical features than can be obtained. Emphasis is placed on the application of OMS as adsorbents for environmental remediation purposes, although other fields where this type of nanostructured solid systems are used are also briefly mentioned. Finally, a depth discussion on the synthesis and application of the OMS called MCM-41, its modification with different organic groups, and its performance in the removal of hexavalent chromium from aqueous solutions of varied chemical composition is presented. The MCM-41 mesophase is taken as an example to discuss how the particle size and the amount and distribution of organic groups anchored within the mesoporous network affect the performance of these kind of materials as adsorbents. Finally, some possible strategies that seek to improve the stability of the MCM-41 based sorbents for its use in a wide range of operational conditions are mentioned.

Palabras Clave: *Silices mesoporosas ordenadas, adsorbentes, remediación, contaminación, cromo.*

Keywords: *Ordered mesoporous silica, sorbents, remediation, pollutants, chromium.*

1. Introduction

The availability of potable water is a key factor for human health and development. However, fresh water systems are being modified by several anthropogenic activities, which generate and discharge a wide variety of effluents into lakes, rivers, lagoons and soils containing organic and inorganic pollutants. Therefore, the treatment of aqueous effluents to ensure the conservation, recovery (if needed) and sustainable use of terrestrial and inland fresh water is mandatory for our survival as a species.

Inorganic compounds are related to several industrial processes, agricultural practice, as well as mining activities, and their existence in natural water courses is one of the most serious environmental problems today. Alloys and steel manufacturing, metal finishing, electroplating, leather tanning process, pigments synthesis and dyeing, use of fertilizers and pesticides,

extraction of precious metals, all these processes give rise to aqueous effluents with varying concentrations of a wide variety of inorganic-based compounds. Currently, several methods are being used to treat these effluents looking for minimizing the negative impact to the surrounding aqueous environment: chemical extraction, precipitation, reverse osmosis, remediation by electrodeposition, bioleaching process, ion exchange, cross flow ultrafiltration^{1,2}. Nonetheless, these methods have their own restrictions such as low efficiency, low selectivity towards specific target, high operational costs and production of large quantities of toxic slurry. In this way, adsorption-based technologies emerge as the most effective, economic and selective method for water treatment and preservation. Besides, it can be applied in remote areas on the small scale without electricity requirements. Adsorption is defined by IUPAC as an increase in the concentration of a dissolved substance at the interface of a condensed and a liquid phase due to the operation of surface forces. Therefore, the surface, i.e. the adsorbent, is the key in these processes. As a consequence, in the last years considerable efforts are being devoted to the development of new adsorbents³. The ultimate purpose of these studies is to develop an adsorbent, the ideal one, which fulfilling all optimal features: very high adsorption capacity, perfect selectivity, long-term durability, good mechanical stability, fast uptake processes, easy regeneration consistent with a negligible loss of adsorption capacity on multiple adsorption-desorption cycles, low cost and low toxicity to living species.

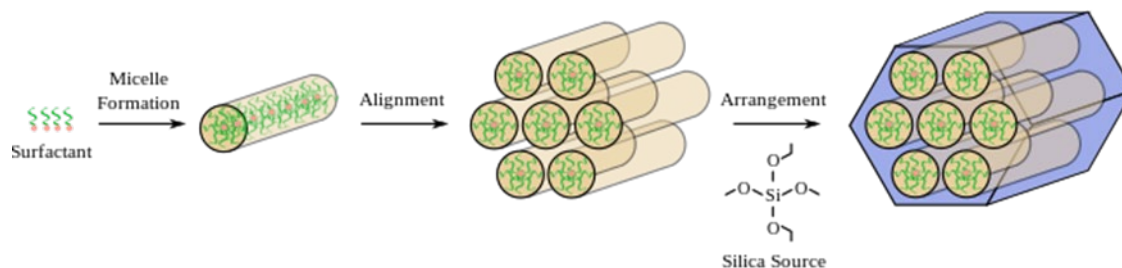
In this review, we will discuss the most relevant advances in the development of ordered mesoporous silicas and its application as sorbents to remove inorganic pollutants from water matrices, analysing to what extent these solids are close to the ideal adsorbent. Different preparation methods to synthesize this type of nanostructured mesoporous solid phases are mentioned, highlighting the main features that can be obtained. Special attention is focused in the case of hexavalent chromium removal from water matrices using MCM-41 functionalized with different agents.

2. Preparation and characterization methods of ordered mesoporous silicas

Ordered mesoporous silicas (OMS) are solids structures with a periodic and regular arrangement of well-defined pores, whose walls are constituted by an amorphous inorganic skeleton of SiO₂. The pore diameters can be regulated between 2 and 30 nm with a very narrow pore size distribution. The most known and studied mesophases belonging to this group are the hexagonal MCM-41 and cubic MCM-48 (MCM: Mobil Composition of Matter), the hexagonal SBA-15 and cubic SBA-16 (SBA: Santa Barbara Amorphous) ^{4, 5}. They can be synthesized by the sol-gel route using different silica sources, although the most commonly used is based on alkoxysilanes (e.g. tetraethoxysilane –TEOS–), and a template agent. In a general way, the synthesis can be described as a polymerization reaction, where a monomer containing a silicon atom polymerizes around of structure generated by the template agent. The final mesophase obtained depend markedly of the careful control of the synthesis parameters. Thus, choosing different template agents, by controlling the pH of the synthesis media, and by using or not, co-solvents or additives, mesophases with different pore arrangements, pore diameters, particle sizes, morphologies and topologies can be obtained ⁴⁻⁶.

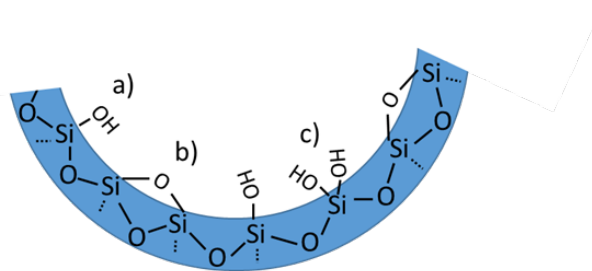
A typical synthesis procedure of the hexagonal MCM-41 mesophase, with a pore diameter of \approx 3.0 nm, is represented in Scheme 1. This synthesis is carried out by mixing an aqueous ammonia solution containing the template agent named hexadecyltrimethyl-ammonium bromide (CTMA-Br) with TEOS as silica source. The final obtained solid phase was an MCM-41 structure without specific particle morphology ⁴. However, using an ethanolic solution of ammonia instead of an aqueous solution, Grün and co-workers were able to prepare submicron sized mesoporous silica spheres (particles sizes of around 500 nm) ⁷. This last procedure is in fact a modification of the well-known Stöber process used for the synthesis of non-porous silica spheres ⁸. Besides, by changing the number of carbon atoms of the template agent that produces the micelles, as it can see in Scheme 1, the same hexagonal pore ordering can be obtained, but with different pore

diameters values, e.g.: 1.8 and 2.0 nm using templates agents with 8 and 10 carbon atoms respectively ^{4,9}.



Scheme 1. Sol-gel synthesis pathway of a hexagonal ordered mesoporous silica (surfactant extraction by solvent treatment or calcination is done later, as the last step).

On the other hand, modifying the ratio TEOS/CTMA-Br, the MCM-48 cubic mesophase is obtained instead of the hexagonal structure ¹⁰. If a hydrothermal post-synthesis treatment is incorporated before the surfactant removal, an increasing of the pore diameter and the pore walls thickness via an increase of the crosslinking within the silicate framework occurs ¹¹. Other possible change in the synthesis route consists in the introduction into the reaction media of a second template agent, which has different affinity for silica. This last modification produces the generation of a layer that surrounds the particles, limiting thus their growth to sizes as small as 20 nm ¹². Besides, different particles morphologies (spheres, shell-like, rugby-like, hexagonal) can be achieved throughout the incorporation, in the synthesis media, of co-solvents and/or a second template agent such as Pluronic F127, ethanol, methanol, ethylene glycol, etc ^{7, 13}. A characteristic feature of all OMS materials is its very high specific surface area, independently of the synthesis pathway chosen and the final mesophase.



Scheme 2. Schematic view of possible groups on the inner surface of an OMS: (a) Si-OH: free silanol, (b) Si-O-Si: siloxane bridge (c) HO-Si-OH: geminal silanol.

In this way, after surfactant removal, values as high as 1500 m² per gram of solid can be obtained^{4,5,7,13,14}. In terms of chemical surface composition of the as-synthesized OMS, different type of silicon atoms can be found: free silanols, geminal silanols and siloxane bridges. These last are produced as a result of two free neighbouring silanols condensation¹⁵. The Scheme 2 depicts a typical surface of an OMS as-synthesized. Finally, the synthesis is completed after removal of the template agent. This can be done either by calcination or by solvent extraction. The use of one or other method will lead to the same pores arrangement but different chemical surface composition. In a general way, the calcination produces a more hydrophobic pore's surface with a minor Si-OH content due to the appearance of more quantities of siloxane bridges¹⁶. While the solvent extraction procedure -in which a hydrochloric acid or ethanol solution under reflux is generally used- generates pores with high silanols density. About this, Wang and co-workers reported that the silanol density was increased from 3.4 Si-OH/nm² for a calcined SBA-15 to 8.5 Si-OH/nm² for the same solid but where the template was removed by solvent extraction¹⁷.

Due to the chemical reactivity of OMS is essentially governed by their surface properties and composition, their careful characterization is a fundamental issue. A deep surface understanding can be carried out using a set of techniques. X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), ²⁹Si and ¹H nuclear magnetic resonance (NMR) and infrared

spectroscopy (IR) give useful information about the surface composition, denoting the potential applications of the synthesized OMS^{14, 15}.

In Figure 1, a typical X-ray diffraction (XRD) pattern of the ordered hexagonal MCM-41 mesophase and its transmission electronic microscopy image (TEM), are depicted. This sample was synthesized using the procedure described by Cai and co-workers¹⁸. The solid is composed by faceted particles ($\approx 1 \mu\text{m}$ of size), with linear and parallel channels inside them, with diameter in the mesopore range ($\approx 2.8 \text{ nm}$). The XRD pattern has an intense peak at $2\theta = 2.6^\circ$ and two broad and less intense peaks between $2\theta = 4 - 6^\circ$. This diffractogram is characteristic of the hexagonal ordered mesoporous arrangement of the MCM-41 structure.

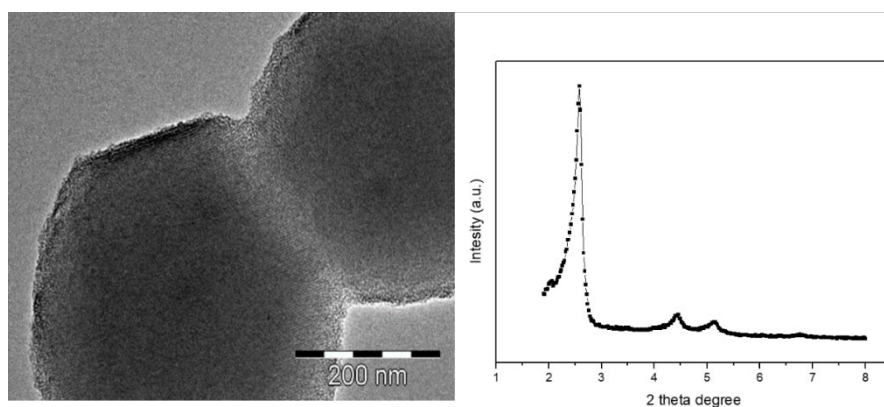


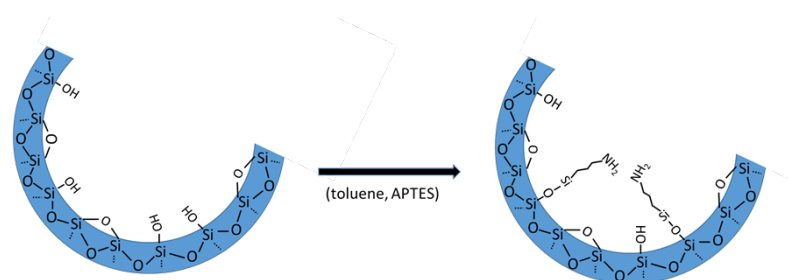
Figure 1. TEM image and powder XRD profiles at low angles of an MCM-41-NH₂ sample.

All the aforementioned demonstrate the enormous possibilities of OMS nanostructures synthesis, with a wide range of chemical and structural properties. Due to that, this kind of materials have been applied in many fields such as catalysis¹⁹, drug delivery²⁰, bones regeneration²¹, separations²², optoelectronics and sensing²³.

3. Preparation of OMS-based sorbents: surface modification by organics groups incorporation

As it was already mentioned, the surface chemistry of as-synthesized OMS is governed by the presence of silanol species. The acidity of silanol groups, $\text{pK}_a \approx 3-4$, offers the possibility to

attach by a post-synthesis treatment a wide variety of organic functions over the OMS surface²⁴. The final composite material consist in an organic-inorganic hybrid ordered mesoporous silica which combines in a single solid phase both, the properties of a rigid ordered three-dimensional silica network and the particular chemical reactivity of the organic functionalizing agent²³⁻²⁴. A typical functionalization reaction takes place between an organoalkoxysilane with silanols onto the OMS surface (Scheme 3).



Scheme 3. Post-synthesis reaction between OMS surface silanols with 3-aminopropyltrimetoxysilane (APTES). Notice that not all silanols are replaced by aminopropyl groups.

Such grafting is often made in an organic solvent (e.g. toluene, hexane) in which alkoxysilanes or chlorosilanes are soluble. The most common anchored terminal groups are NH_2 , COOH , SH and SO_3H ^{9, 17, 20}. Exists a second way to synthetize hybrid organic-inorganic OMS materials, this is named co-condensation or direct method. In this one the organic function, *i.e.* the selected organosilane, is introduced in the synthesis mixture jointly with the TEOS. This step is followed by the hydrothermal synthesis and, finally, the chemical removal of the surfactant is performed (in this method only solvent extraction can be used). The organic functions are distributed homogeneously by this way, unlike the post-synthesis surface modification, avoiding any pores blockage. However, two main disadvantages appear with this synthesis procedure: (a) the formation of the periodic mesoporous structure is often disturbed by the presence of the organosilane in the synthesis mixture, giving rise to solids with low chemical and thermal stability and (b) a fraction of the organic functions are unexposed to the surrounding because they remain inside the pore walls, so they cannot interact with other species²⁵.

The first examples of adsorbents based on hybrid mesoporous silica have been disclosed in 1997^{26, 27}. The most important finding of these works was to demonstrate that the ability of the functionalized adsorbents to bind mercury ions to each active site (thiol ligand) in the material is directly related with the homogeneity and the large framework structural of these type of solids. This advantage was observed in the OMS mesostructures but not when non-ordered silica gel-based adsorbents functionalized with the same thiol ligands were used. This result was attributed to pores blocking effects when the grafting is performed in these disordered porous frameworks. Although disordered silicas, such as silica gel, can exhibit surface areas and average pore diameters comparable to OMS, their broad pore size distributions leads to a significant blockage after functionalization treatment^{26, 27}. Thus, high sorption rates in OMS, such as MCM-41, MCM-48, SBA-15 and SBA-16, can be attributed exclusively to the uniform porous structure made of regular and linear mesochannels with monodisperse sizes, where diffusional hindrance is avoided or minimized. The absence of diffusional impediments can be quantified by the Thiele modulus (h) applied to a diffusional/adsorption process²⁸. For example, for an MCM-41-NH₂ composed by spherical particles (mean particle diameter of 480 nm) with average pore size of 2.5 nm and specific surface area equal to 834 m²/g, a Thiele modulus value of $h^2 = 10^{-7}$ was obtained, expressing that the intraparticle diffusion rate exceeds the adsorption rate by about seven orders of magnitude²⁸.

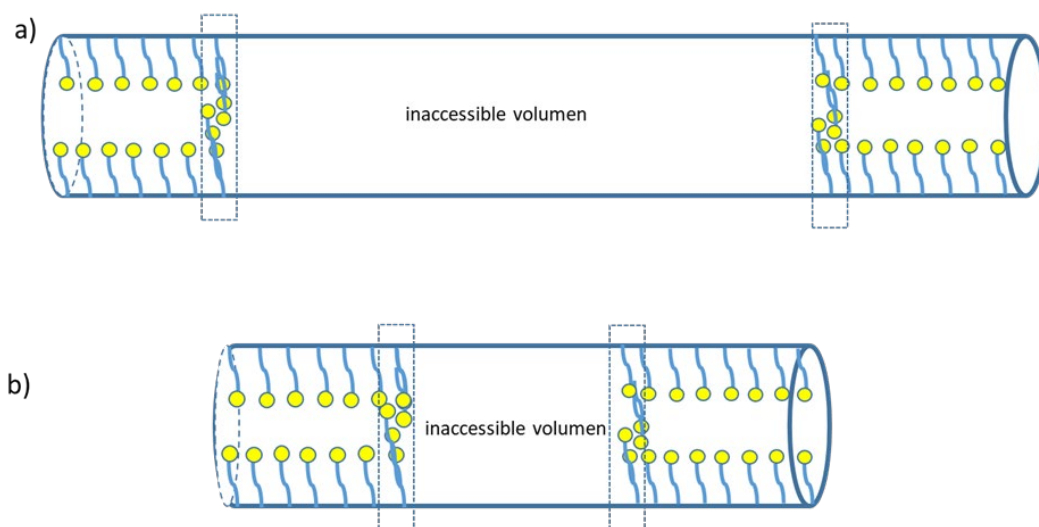
After those pioneering works, huge amounts of reports appeared deepening the studies on hybrid OMS-based sorbents, with new synthesis pathways looking for the improvement on pollutant removal performance. All the reported data indicate high separation capacities for these adsorbents jointly with the possibility of regeneration and reuse with low or medium sorption capacity loss. Most of these works investigate the OMS performance as sorbents in batch assays. Instead, very few of them use continuous flow systems. The effects of different operating conditions such as temperature, adsorbent loading, initial ion concentrations, pH and presence of competitive ions have been described. Saad *et al.* demonstrated that phosphate removal was

maximized at pH = 5 and it was almost unaffected by the presence of competitive ions when an ammonium-functionalized MCM-48 was used as sorbent²⁹.

It is already widely demonstrated that pH of the aqueous solution to be treated is a key point to keep in mind when OMS-based sorbents are used, due to the dependence of the OMS surface chemical composition with the pH, especially after organic groups incorporation. For example, the surface of an MCM-41-NH₂ when the working pH is fixed at 2 is composed mainly of ammonium (–NH₃⁺) and silanols (Si–OH) entities, leading to the preferential adsorption of anions on the positively charged sites on the adsorbent surface³⁰. At a pH value of 7, the MCM-41-NH₂ presents a more complex pore surface composition. Silanols are partially deprotonated creating silanol/silanolate entities which provide negative charges. Meanwhile, with a pK_a of ≈ 9–10 (depending the organic tail formulae), the N-containing groups are as ammonium and amino. Therefore, the surface at neutral pH presents negative, neutral and positive sites^{30,31}.

The concentration and speciation of the anchored organics groups at the OMS surface is other parameter that affects the performance of this hybrid sorbents. For example, Gartmann *et al.* demonstrated, using MCM-41 and APTES, that increasing the amount of water in the silane solution leads to a non-uniform distribution of the grafted amino groups onto the MCM-41 surface³². In the same way, increasing the mass ratio silane/OMS during the functionalization step, the probability of a fast clogging pores -which induces a dramatic fall in the specific surface area and low organic groups loading- is increased. Both phenomena will generate an adsorbent with low removal capacity. By reducing the size of the particles to be functionalized, it is possible to achieve greater load of organic groups, avoiding or minimizing the pores blockage due to clustering of silanes molecules³³. We have demonstrated this using two different MCM-41 systems, one of them with an average particle diameter of 500 nm and the other one with 1000 nm. A decreasing in the specific surface area from 1032 to 727 m²/g, after APTES post-synthesis functionalization, was registered for the small MCM-41 particles, while a change from 1055 to 517 m²/g in was observed for the biggest ones³³. Scheme 4 represents and clarifies this concept

showing how an early blockage of pores give rise to a hybrid OMS sorbent with low surface area and low organic groups loading per gram of sample.



Scheme 4. Pores blockage representation due to postsynthesis surface treatment with a silane agent. a) and b) represent two cylindrical pores with the same diameter but different length, the largest (a) give rise to an inaccessible area bigger than the shortest (b).

Therefore, being able to control both the load and the distribution of the chemical functions anchored onto the surface is a crucial issue that should be addressed in the OMS-based sorbents development.

4. Study case: hexavalent chromium elimination using modified MCM-41-based materials.

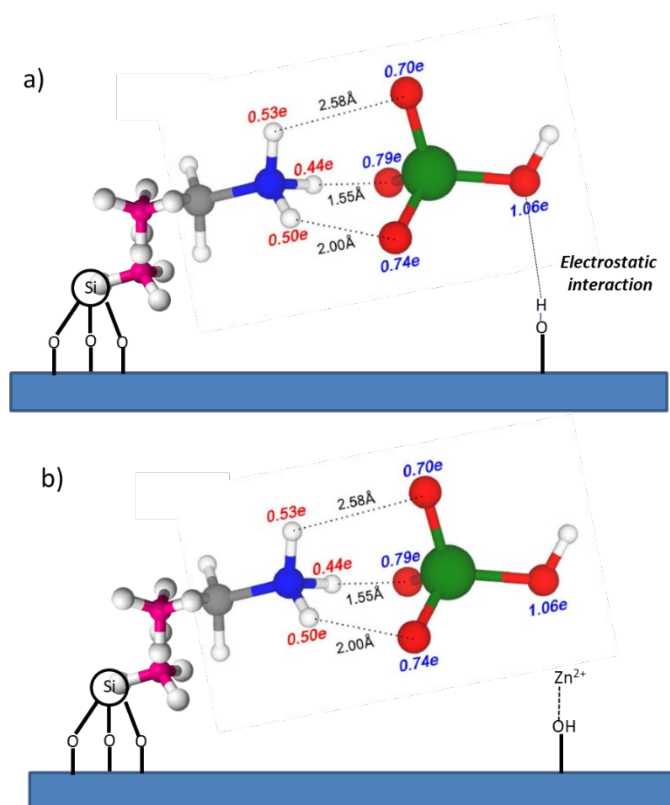
Chromium is at the top-priority list of toxic inorganic pollutants defined by the US Environmental Protection Agency due to its mutagenic and carcinogenic properties against biological species^{30, 33}. Many industrial activities are associated with hazardous liquid wastes with high contents of chromium compounds: alloys and steel manufacturing, metal finishing, cement production, leather tanning and pigments synthesis and dyeing, among others^{30, 33}. Chromium in water matrices, discharged from industries, is commonly trivalent (Cr(III)) or

hexavalent (Cr(VI)). However, the hexavalent specie is many times more toxic than the trivalent one because it is highly water soluble and carcinogenic^{30, 33}. Therefore, in order to minimize industrial sludges, strategies for remediation of aqueous effluents with high levels of Cr(VI) involving a mechanism of adsorption and reduction to the less toxic trivalent state, present a clear advantage versus those that only achieve separation of Cr(VI) without chemical transformation.

Most of the works describing concomitant adsorption-reduction of hexavalent chromium deal with bio-sorbents or carbon-based systems^{34, 35}. Bio-sorbents, especially those with high contents of amino groups, are able to promote this mixed mechanism to eliminate Cr(VI) from water³⁴. Surprisingly, in the field of hybrid OMS-based sorbent there are very few articles reporting Cr(VI) reduction. Walcarius *et al.* reported the synthesis of a bi-functionalized MCM-41 containing thiol and sulfonic acid moieties (MCM-41-SH/SO₃H). The final hybrid material was applied to the removal of Cr(VI). The obtained results can be explained as a sorption-reduction mechanism involving reduction of Cr(VI) by thiol groups and immobilization of Cr(III) onto sulfonic acid moieties³⁶. Besides, the generated Cr(III) species remained adsorbed in the material in a proportion that reached about of 35% of the total Cr(III) produced. On the other hand, metallic iron nanoparticles were immobilized on OMS surface to reduce Cr(VI). This composite material has proved higher removal capacity than the unsupported Fe⁰ nanoparticles, showing again the advantages of introducing OMS structures as adsorbents³⁷.

Recently, we have demonstrated that MCM-41-NH₂ sorbents have high efficiency for aqueous Cr(VI) elimination at pH = 2²⁸. Besides, the selectivity towards to chromium oxyanions could be modulated by changing the pH of the aqueous solution to be treated, adsorbing (or desorbing) preferentially chromium compounds instead of other ions, such as Zn²⁺³⁰. An important finding was that the final Cr(VI) concentration decreases dramatically after batch assays in acidic conditions throughout a combined adsorption-reduction process. The chromium sorption by MCM-41-NH₂ can be described as follows: the adsorption of hexavalent

chromium starts with the electrostatic interaction between HCrO_4^- and the positive ammonium surface species. After, a partial reduction to Cr(III) occurs³³. The Cr(III) is partially retained on the surface of the sample, as it was also described by Walcarius³⁶. Besides, about of 50% of Cr(III) is kept on the MCM-41-NH₂ surface. The experimental adsorption data were well fitted using the Langmuir model, obtaining a total chromium elimination capacity (q_m) of 86.4 mg per gram of MCM-41-NH₂. However, when zinc was introduced into the water matrix, the reduction capacity was totally suppressed and q_m fall to 30.3 mg per gram of amino-MCM-41^{30, 33}. Taking into account that cations such as Zn(II) in aqueous solution interact preferentially with the silanol surface species, this result would indicate that the combined mechanism of adsorption-reduction of hexavalent chromium would be related to the existence of free surface silanols and aminopropyl groups simultaneously. The Scheme 5 shows the interaction between chromium and the MCM-41-NH₂ surface, with and without zinc, using the results of first principles calculations reported by Choi *et al.*³⁸. When protonated amino functions have a neighbour free silanol, the adsorbed HCrO_4^- can interact with this entity at the same time (Scheme 5-a). Thus, the silanol group would produce an electrostatic attraction on the oxygen atom of -OH that belongs to HCrO_4^- . Therefore, the bond between Cr and OH is weakened and the Cr(VI) reduction could occur. On the contrary, if cations are present in the water solution they block the silanols sites, and the interaction HCrO_4^- -HO-Si does not occur (Scheme 5-b). The availability of free silanols to interact with Cr species adsorbed on ammonium functionalities and the occurrence of the reduction step can be understand considering the well-known mechanism of Jones Oxidation Reaction (JOR)³⁹.



Scheme 5. Cr (VI) is adsorbed on protonated primary amine by hydrogen bonding. If a free silanol neighbour group is present a second interaction can occur giving rise to the mixed sorption-reduction mechanism (a). If there are not free silanols or if they are blocked by other species, the second interaction is not possible and only Cr(VI) sorption is observed (b).

5. Summary and Outlook.

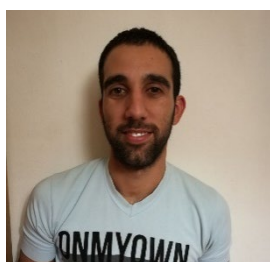
In this brief review we have described diverse synthesis methods and structural characteristics of ordered mesoporous silica (OMS). Besides, we have mentioned applications in different fields, focusing in their use as sorbent of hexavalent chromium from water. In order to get the highest capacity and selectivity of adsorption, OMS must be functionalized with very diverse type of organic groups. The resulting organic-inorganic OMS hybrids have high removal capacities and selectivities towards to Cr, Cu, Zn, As, P, Hg, etc. in aqueous matrices. Although important advances in the "tailored" structural design of these adsorbents have been made, a lot of disadvantages have yet to be overcome. For example, OMS more "robust", able to be unalterable to many adsorption-desorption cycles are necessary. In the same way, these organic-inorganic

OMS hybrids must be resistant to the leaching of the functionalizing agent during these cycles. Bearing in mind that the ordered mesochannels structure is essential with the aim to use the solid as sorbent and that an OMS is strongest when its wall has more thickness, the functionalization of nanospheres of the SBA family could allow to achieve these goals. Finally, there is an operative system different from batch reactors that has practically not been studied and that can have a marked influence on the performance and economy of the process. This is the use of a continuous flow adsorption reactor. Therefore, the exploration of this type of systems is extremely important in the immediate future.

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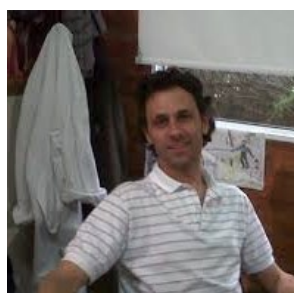


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