



# Synthesis of silica materials containing cyclodextrin and their applications in wastewater treatment

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## Abstract

Cyclodextrin-functionalized silica networks are advanced adsorbents for environmental applications. Silica-based adsorbents are low-cost and robust inorganic solids having large surface areas, high porosity, and excellent mechanical, physical, and chemical properties. They also possess wide possibilities of functionalization due to the silanol reactivity. Cyclodextrins are natural molecules obtained from the enzymatic degradation of starch. They belong to the family of cage molecules having a hydrophobic cavity that can encapsulate other molecules. Cyclodextrin-functionalized silicas offer generally improved access to the binding sites because cyclodextrins are located on the external surface of the material. However, an uneven distribution of cyclodextrin molecules is often observed, and these materials have low cyclodextrin loading, which can limit adsorption capacities. Nonetheless, for cyclodextrin-silica hybrid systems prepared through sol–gel or self-assembly process, cyclodextrin molecules are located within the framework of nanoporous silicas and, as a consequence, high cyclodextrin loadings, robust structures and higher surface area are observed. The application of cyclodextrin-based silica materials in solving environmental pollution problems has recently received a lot of attention due to their combined physical and chemical properties, resulting in strong binding affinities toward target chemical substances such as metal ions, dyes, pesticides, and drugs. This review reports the use of cyclodextrin-silica hybrid systems and cyclodextrin-functionalized silica used as adsorbents for the removal of inorganic and organic pollutants from aqueous solutions in solid-phase extraction and adsorption-oriented processes.

**Keywords** Silica · Cyclodextrin · Materials · Pollutants · Adsorption · Filtration

## Introduction

This article is an abridged version of the chapter published by Morin-Crini et al. (2018) in the series Environmental Chemistry for a Sustainable World.

Among the numerous techniques for pollutant removal of filtration/separation, liquid–solid adsorption using conventional adsorbents is the procedure of choice and gives the best results as it can be used to remove different types of pollutants (Crini and Badot 2010). What is the best adsorbent? There is no direct answer to this question because each solid material has advantages and drawbacks (Wase and Forster 1997). However, there is no doubt that activated carbons are one of the oldest and most widely used adsorbents in industry because systems using carbons are technologically

simple, efficient, and also economically feasible although the initial cost of the carbon can be high (Morin-Crini and Crini 2012). Other conventional adsorbents can be also used, and the list includes commercial ion-exchange resins and inorganic-based materials such as activated aluminas, silica, zeolites, and molecular sieves.

Among these inorganic-based materials, silica beads are good adsorbents due to their high adsorption capabilities because of their large surface areas and high porosity with highly uniform pore distribution and tunable pore size, excellent physical and chemical properties such as water stability, thermal and mechanical stability. Silica is also non-toxic and a low-cost inorganic material with extraordinarily wide possibilities of functionalization due to the silanol reactivity. Indeed, the presence of silanol groups on the surface makes silica a better solid for the immobilization of a wide range of inorganic and organic ligands. Numerous three-dimensional network structures can be obtained such as amorphous silica, fumed silica, silica gels, and mesoporous silica.

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Among them, literature data clearly indicate that well-prepared mesoporous materials show excellent pollutant adsorption capabilities compared to their amorphous counterparts. In general, these materials can be prepared by the hydrolysis of alkoxy silane precursor (tetraethoxysilane, e.g.) in the presence of suitable surfactant, the template, and catalyst, to form condensed polymerized networks of siloxanes (Beck et al. 1992; Kresge et al. 1992, 1995; Davis 2002; Vunain et al. 2016). The sol–gel chemistry leads to the synthesis of ordered mesoporous silicas, for example the well-known mobile crystalline materials such as MCM-41 or SBA-15, with large surface area, high porosity, and high amount of silanol groups.

Mesoporous silica can be further modified by immobilization of various functional groups at the particle surface as well as at the pore wall surface to form organic–inorganic hybrid materials (Samiey et al. 2014). The modification provides new opportunities for fine-tuning the chemical, physical, and mechanical properties of these novel materials. The modified materials are used not only in electrochemical detection, electronic devices, controlled drug delivery, and catalysis but also in separation technology.

Indeed, the application of silica beads containing cyclodextrin molecules as adsorbents in solving environmental problems such as pollutant removal or filtration from water, wastewater, and atmosphere, for example indoor air and gas treatment, has recently received a lot of attention (Gibson 2014; Morin-Crini et al. 2015). The past decade has seen an explosive interest in ordered mesoporous silica-based materials. Their unique physical and chemical properties make them more superior and useful in various fields than conventional carbons. In these compounds, the high mechanical properties and physical strength of inorganic substrates, the silica beads, are combined with advantages of a complexing substrate, the cyclodextrin, resulting in strong binding affinities toward target pollutants and relatively high pollutant adsorption capacities (Morin-Crini and Crini 2012).

The main objectives of this review are to provide a summary of the recent information concerning the innovative synthesis of silica containing cyclodextrin and to describe the developments in the use of these materials for the

removal of pollutants by reviewing some selected studies reported in the literature.

## Incorporation of cyclodextrin molecules into silica-based materials

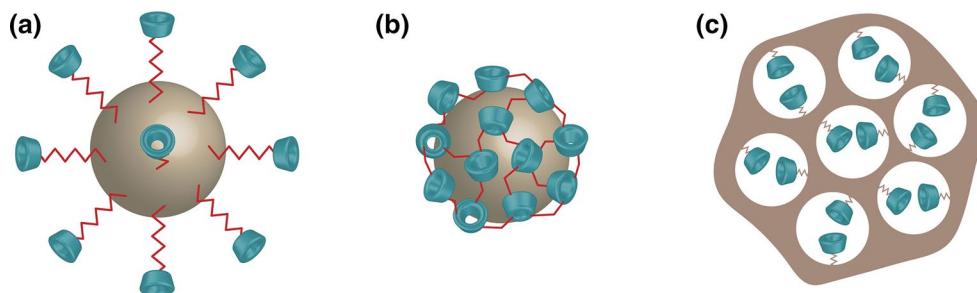
In the literature, there have been numerous studies on the preparation, characterization, properties, and applications of cyclodextrin-based silica materials in separation technology (Crini and Morcellet 2002; Morin-Crini et al. 2015). Here, we propose to classify these adsorbents into two main classes: cyclodextrin-functionalized silicas prepared through grafting or coating reactions and cyclodextrin-silica hybrid systems prepared through sol–gel or self-assembly process.

Figure 1 shows three schematic representations of silica networks containing cyclodextrin molecules: (a) grafted matrices, (b) coated materials, and (c) nanoporous frameworks. The first approach involves the grafting or coating of cyclodextrin moieties onto silica gel by using generally cross-linking reactions (Crini and Morcellet 2002). Cyclodextrin-grafted or cyclodextrin-coated silicas offer improved access to the binding sites because the moieties are located on the external surface of the material, and the structure has improved thermal, mechanical, and chemical stability owing to the robustness of the bead. However, the disadvantage of this synthetic approach is often uneven distribution of cyclodextrin molecules. In addition, it is known that these materials have low cyclodextrin loading which can limit adsorption capacities. In the second approach, the cyclodextrin molecules are located within the framework of nanoporous silicas (Bibby and Mercier 2003). These materials possess both high cyclodextrin group loadings and robust structures.

## Cyclodextrin-silica hybrid systems

Recent advances in the development of innovative functionalized materials such as organic–inorganic hybrid systems are having a major impact on analytical and environmental chemistry, catalysis, and biorefinery production (Walcarius and Mercier 2010; Rahmat et al. 2010; Al

**Fig. 1** Schematic representations of three silica networks containing cyclodextrin molecules: **a** cyclodextrin-functionalized silicas prepared through grafting, **b** cyclodextrin-functionalized silicas prepared through coating, and **c** incorporation of cyclodextrins into nanoporous frameworks



Othman 2012; Han and Zhang 2012; Samiey et al. 2014). Numerous fields are concerned such as water analysis for metal detection, pollutant removal from liquid or gas phases, adsorbents for solid-phase extraction, electrochemical detection of metals, and also chemical processes using immobilized catalysts.

The organic–inorganic hybrid systems have been obtained through the coupling of inorganic and organic components by template synthesis. The main methods include sol–gel process, self-assembly process, assembling or dispersion of nanobuilding blocks or interpenetrating networks (hierarchical structures). The incorporation of functionalities onto material pore surfaces or into the frameworks can be achieved by post-synthesis grafting or co-condensation method (Vartuli et al. 2008; Samiey et al. 2014). Organic–inorganic hybrid systems are classes of materials whose structure includes both organic and inorganic units that interact with each other at the molecular level. The inorganic part provides mechanical strength, and the organic part shows functional activities. These materials are divided into two classes, class I and class II, on the basis of interaction between organic and inorganic components. In class I, organic and inorganic are embedded and there are weak interactions, such as hydrogen bonding, van der Waals,  $\pi$ – $\pi$ , or electrostatic interactions between them, and in class II, the two components are bonded together through strong covalent bonds such as coordinative bonds.

At the beginning of the 1990s, the formation of mesostructured silica using surfactants as templates (Myers 1992) was reported by researchers from the Mobil Oil Corporation and by Kuroda's group (Yanagisawa et al. 1990a, b; Hench and West 1990; Beck et al. 1992, 1994; Inagaki et al. 1993, 1996a, b; Chen et al. 1993; Kresge et al. 1992, 1995). These materials found potential applications such as heterogeneous catalysis, electrochemical chemistry, host–guest chemistry, and separation processes (Walcarius 2001; Pan et al. 2009). This new route of synthesis immediately attracted attention in the material science community.

Numerous works based on mesoporous silica and other oxides such as alumina were published (Patarin et al. 2002; Sanchez et al. 2005; Simsek et al. 2012; Yamamoto and Kuroda 2016). At the same period, a novel generation of mesoporous hybrid silicas containing organic groups on the surfaces of ordered mesoporous silicas was developed by grafting or anchoring of organic guests onto the mesopore channel surface or by the direct incorporation of organic groups through co-condensation of organotrialkoxysilanes with tetraalkoxysilanes (Al Othman and Apblett 2009). As documented in a comprehensive review by Samiey et al. (2014), sol–gel chemistry is a versatile tool for the synthesis of ordered organic–inorganic hybrid materials with advanced properties that are often difficult to achieve either from totally inorganic or from totally organic materials.

Usually, this process involves the hydrolysis and condensation of a tetraalkoxysilane ( $\text{Si}(\text{OR})_4$  with  $\text{R} = \text{Me}$  or  $\text{Et}$ ) in the presence of a supramolecular template such as surfactant or more recently water-soluble polymer. The silica framework can be formed around preformed liquid crystal mesophases but, in many cases, the organized architectures are obtained via a self-assembly cooperative process taking place in situ between the templates and the silica network precursors. The organic template is then removed by calcination or solvent extraction to give the resulting mesoporous open structure. Both ionic (cationic form such as long-chain quaternary ammonium) or nonionic (neutral amine, water-soluble copolymers) surfactants can be used to produce ordered mesoporous silicas by the sol–gel process.

Mesoporous silicate M41S (Mobil Oil Corporation), a well-known family of nanostructured mesoporous materials, is synthesized using tetraethylorthosilane  $\text{Si}(\text{OC}_2\text{H}_5)_4$ , known as TEOS, as a silica source in the presence of long-chain alkyltrimethylammonium halide surfactants (Valtchev et al. 2009). MCM-41 having a hierarchical structure is undoubtedly the best known and most widely studied of this family of materials. MCM is an abbreviation of Mobil Crystalline Materials. Most common materials are based on 2D and 3D structures but lamellar and less-ordered mesostructures, for example wormlike, can be also obtained. The other members are the cubic MCM-48 and lamellar MCM-50 forms. Other types of ordered mesoporous silicas are MSU-2, SBA-15 and SBA-16, FSM-16, and HMS. MSU, SBA, FSM, and HMS are abbreviations of Michigan State University, Santa Barbara Amorphous, Folded Sheets Mechanism, and Hexagonal Mesoporous Silica, respectively (Zhao et al. 1996; Rahmat et al. 2010).

Compared to their non-ordered homologues, these mesostructured porous solids also offer other significant advantages: (1) exceptionally good accessibility to active centers due to highly ordered nanochannels of uniform pore size; (2) very high number of functional groups that can be attached to the (mostly internal) surface of mesoporous silica, as a consequence of very large surface areas; (3) fast mass transport rates inside the porous structure due to the regular spatial arrangement of mesopore channels of monodisperse dimensions; and (4) good mechanical and hydrothermal stabilities. This last point is controversial because these properties are strongly dependent on mesostructure types and post-synthesis treatments. All these attractive features make such innovative materials of interest for the adsorptive removal of pollutants from waters.

Mercier's group previously reported cyclodextrin-silica hybrid systems with uniform framework mesoporosity as a new class of efficient materials (Huq et al. 2001) for adsorption and separation of water-soluble aromatic molecules (Bibby and Mercier 2003), phenols, or pesticides such as dichlorodiphenyldichloroethylene and

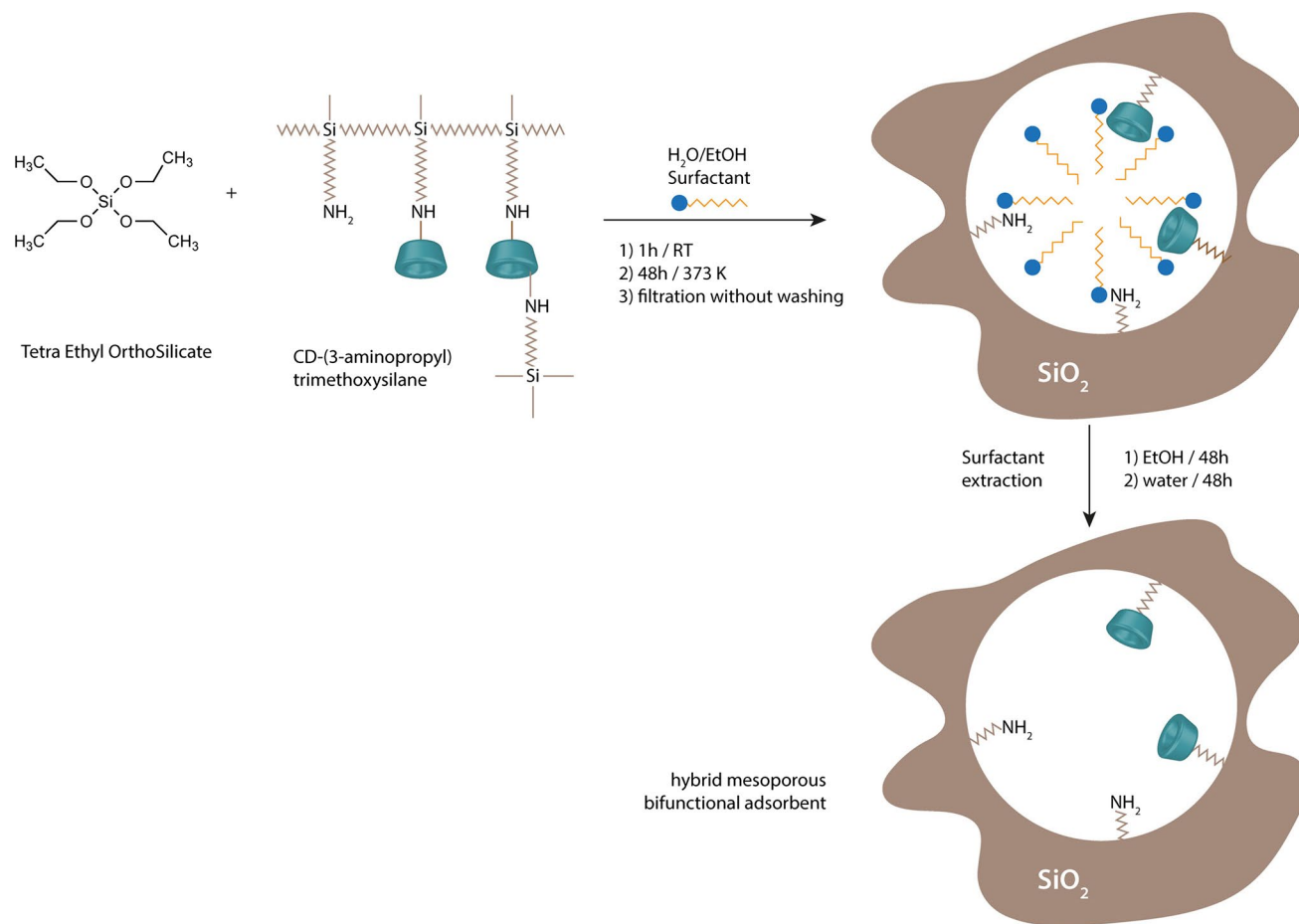
dichlorodiphenyltrichloroethane (Sawicki and Mercier 2006). This group utilized the concept of surfactant-directed mesostructured oxide assembly to produce cyclodextrin-silica hybrid materials with well-defined nanometer-scale porosity. The materials were prepared using an entirely aqueous/ethanolic one-step procedure involving incorporation of ethoxysilane precursors (silylated cyclodextrin) in the presence of structure-directing surfactants solutions including alkylamine agents such as dodecylamine and pore-expanding additives such as trimethylbenzene.

The Mercier's group studies highlighted the importance of molecular-scale engineering of target-specific materials in which optimal adsorptivity was not necessarily obtained by maximizing the number of binding sites, but rather by controlling their placement and orientation within the structure of mesosilica. Indeed, only adsorbents containing low to intermediate amounts of cyclodextrin molecules (2–4% with respect to total Si in sample) were found to have optimal affinity toward the pesticides target (Sawicki and Mercier 2006). Materials produced with cyclodextrin loadings higher than 8% had poor performance. This can be explained by the

destruction of the periodic mesoporous structure with high cyclodextrin amount. Two interesting results were reported by Walcarius and Mercier (2010): (1) The location of cyclodextrin moieties within the structure of a siliceous framework may reduce the materials' susceptibility to chemical and biological degradation; (2) cyclodextrin-silica hybrid materials exhibited higher adsorption properties toward pollutants after multiple uses, indicating high chemical and mechanical stability. Mercier's group concluded that the incorporation of cyclodextrin molecules into mesostructured silica was an innovative and promising tool for environmental protection.

Using similar synthetic procedure (Fig. 2), Bacquet's group also reported mesoporous silicas containing both cyclodextrin and amino groups for *p*-nitrophenol removal from aqueous solutions (Willai et al. 2008; Degoutin and Bacquet 2013). However, their results revealed an adsorption capacity of only 61  $\mu\text{mol/g}$ , far inferior to what was reported by Mercier's group (Bibby and Mercier 2003).

Others researchers also reported that samples with high cyclodextrin molecules loading (up to 6%) were generally

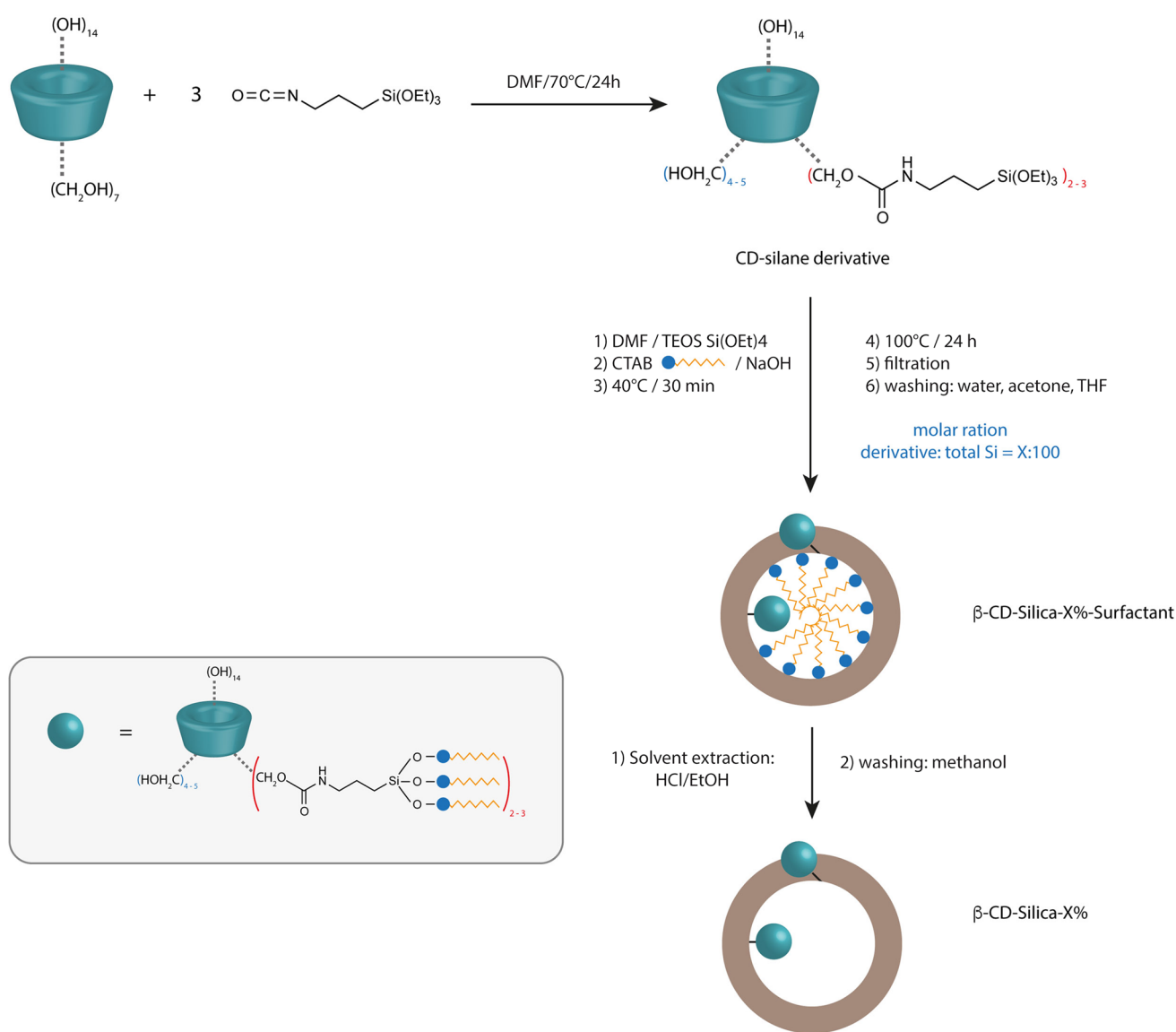


**Fig. 2** Preparation of templated hybrid mesoporous bifunctional organo-silica proposed by Degoutin and Bacquet (2013)

much less effective than those with lower cyclodextrin content (Liu et al. 2004; Gibson 2014; Mahmud and Wilson 2016). Liu et al. (2004) proposed a new mesoporous organo-silica material (cyclodextrin-silica-4%) containing microporous cyclodextrin prepared by the copolymerization of a silylated cyclodextrin monomer with tetraethylorthosilane in the presence of cetyltrimethylammonium bromide template (Fig. 3). Surfactant extraction resulted in an adsorbent containing covalently bound microporous cyclodextrin moieties capable of adsorbing efficiently humic acid from water. Nitrogen adsorption experiments showed that cyclodextrin-silica-4% material had a BET surface area of 460 m<sup>2</sup>/g and an average mesopore diameter of 2.52 nm. Small-angle powder X-ray diffraction pattern of cyclodextrin-silica-4% material revealed the lack of highly ordered

mesoporous structure. Solid-state C-13 and Si-29 nuclear magnetic resonance studies provided evidence for the presence of covalently attached cyclodextrins in the mesoporous material. Adsorption experiments showed that new material removed up to 99% of humic acid from an aqueous solution containing 50 ppm of humic acid at a solution-to-solid ratio of 100 mL/g. The authors claimed that the new mesoporous cyclodextrins-containing organo-silica material was potentially useful both in environmental remediation and in chromatographic separation.

Gibson (2014) published an interesting tutorial review on the removal of organic pollutants from the aqueous phase by mesoporous silica. After a discussion about mesosilica formation and silica surface modification, the review focused on the use of mesosilica for the removal of organic compounds



**Fig. 3** Synthesis of mesoporous organo-silica material containing microporous cyclodextrin molecules. Adapted from Liu et al. (2004)

such as dyes and phenols and emerging contaminants, for example pharmaceutical, from aqueous solutions. High extraction capacities could be obtained, although results were cyclodextrin loading dependent. Indeed, extraction capacities were significantly more important with increased cyclodextrin loading (between 2 and 8%) into mesosilica but materials produced with cyclodextrin loadings higher than 8% had poor performance. Gibson (2014) concluded that mesoporous cyclodextrin-silica nanocomposites were efficient adsorbents. However, cyclodextrin loading, accessibility, molecular size, and structure were crucial factors when assessing extraction performance of cyclodextrin-loaded mesosilica.

Wilson's group reported two comprehensive studies on the synthesis and characterization of surface-modified mesoporous silica materials with cyclodextrin molecules and their adsorption properties toward two types of gas phase (nitrogen and methyl chloride) and *p*-nitrophenol in aqueous solution (Wilson and Mahmud 2015; Mahmud and Wilson 2016). This group synthesized silica containing microporous cavities provided by surface-bound cyclodextrin by co-condensation of a cyclodextrin-functionalized triethoxysilane with tetraethylorthosilane using alkylamine-based surfactants such as dodecylamine, tetradecylamine, and hexadecylamine as structure-directing agents. The materials had an ordered silica mesostructure framework that depended on the type of surfactant template and the level of loading of cyclodextrin. The MALDI-TOF mass spectrometry characterization and adsorption data provided corroborating support that cyclodextrin molecules were incorporated within and onto the surface of the silica framework. Small-angle X-ray diffraction and nitrogen adsorption also provided evidence of ordered silica mesostructured frameworks. C-13 solid cross-polarization magic angle spinning nuclear magnetic resonance data were interesting to show the presence of residual pore expander such as 1,3,5-trimethylbenzene in the material. Mahmud and Wilson (2016) demonstrated that the use of a pore expander for the synthesis of such composites may result in entrapped impurities during the formation of the silica framework, in contrast to the results published by Huq et al. (2001). The authors supposed that 1,3,5-trimethylbenzene containing aromatic group was entrapped in the silica network during the condensation process. Small-angle X-ray diffraction data showed that greater loading of cyclodextrin was accompanied by a concomitant decrease in the tetraethylorthosilane content, resulting in a reduction in the stability of the silica framework, in agreement with the loss of long-range ordering. Thermogravimetric analysis results confirmed that cyclodextrin was covalently bound to the silica network. For materials with similar cyclodextrin loading, the textural properties (surface area and pore volume) doubled as the surfactant changed from C12 (dodecylamine) to C16 (hexadecylamine). The textural properties decreased

with cyclodextrin loading (2–6%). The surface area also decreased by *ca.* 1.5-fold as the cyclodextrin loading varied from 2 to 6%. The adsorption capacity of gas phase with polar and apolar species ( $\text{CH}_3\text{Cl}$  and  $\text{N}_2$ ) varied along with the adsorption properties in aqueous solution toward *p*-nitrophenol according to the CD loading (2–6%) and surfactant template employed. Indeed, incremental variations in the uptake of gas-phase adsorbates and *p*-nitrophenol from an aqueous solution were observed, according to the composition of materials (Wilson and Mahmud 2015). The adsorption capacity of *p*-nitrophenol increased from 61 to 84% as the cyclodextrin loading increased from 2 to 6% and as the alkyl chain length of the surfactant template varied from C12 to C16. The adsorption properties of materials with  $\text{CH}_3\text{Cl}$  in the gas phase and for *p*-nitrophenol in aqueous solution adopted a multilayer adsorption profile, as described by the BET isotherm model. Their results revealed the structural contribution of surface modification and framework incorporation of cyclodextrin with mesoporous silica framework materials. Mahmud and Wilson (2016) concluded that the general concept 'more cyclodextrin, more adsorption' may not necessarily apply due to changes in the mechanical stability of the framework, potential steric effects due to loading of the cyclodextrin moiety in mesopore channels (that reduce the accessibility of pollutants), and limitations on the surface immobilization of cyclodextrin for the synthetic conditions.

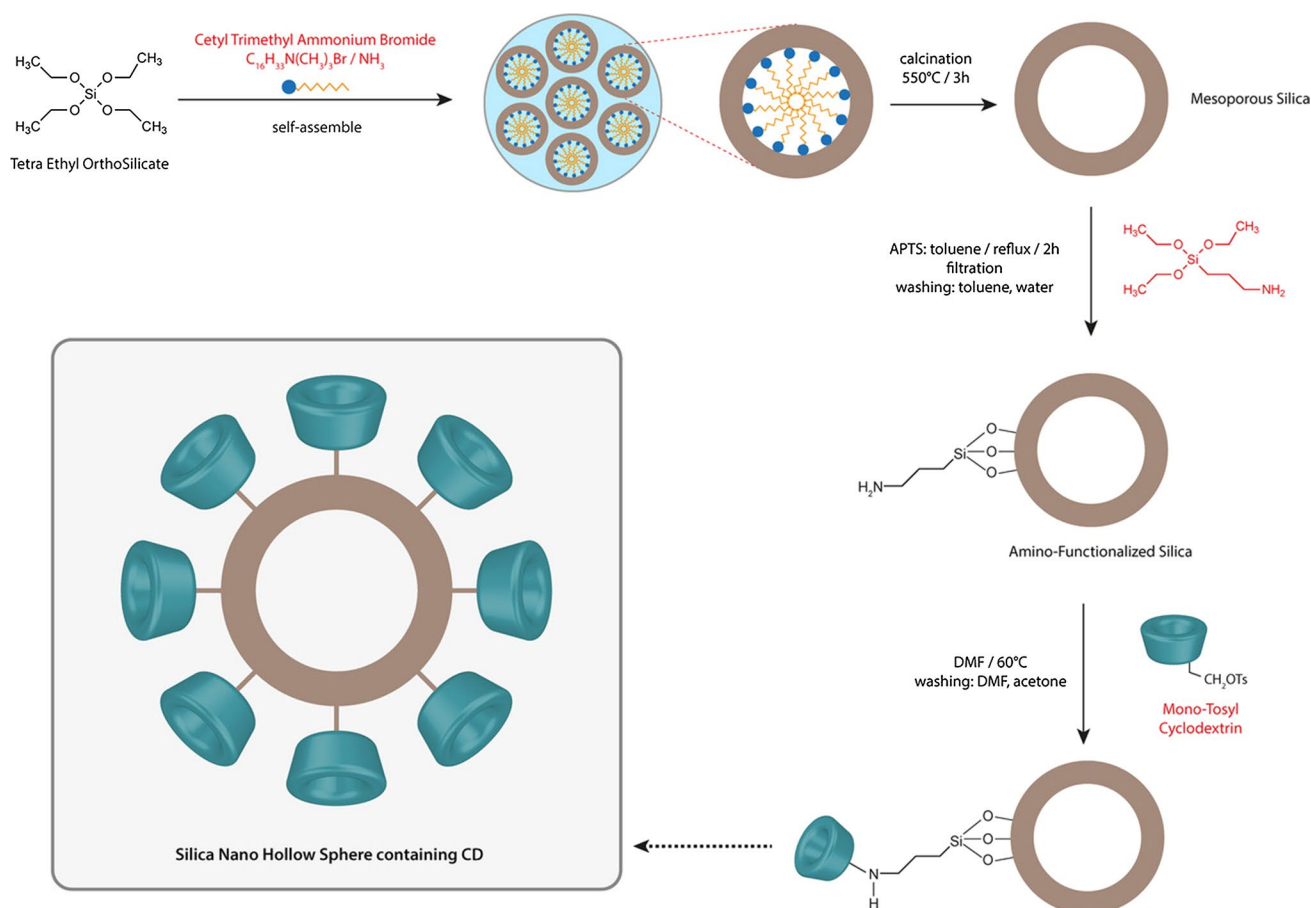
The main drawbacks in the synthesis of cyclodextrin-containing silicas are the use of aggressive and toxic solvents and activating agents in multistep procedures of organic reactions at elevated temperatures. These conditions may affect the structure of final product. New approaches for ordered cyclodextrin-containing silicas synthesis under mild conditions were proposed by Trofymchuk et al. (2016). MCM-41 materials with hexagonally ordered mesoporous structure were prepared by post-synthesis grafting and by co-condensation methods. Cyclodextrin molecules activated by a *N,N'*-carbonyldiimidazole were employed for post-synthesis treatment of 3-aminopropyl-modified MCM-41 support (3-aminopropyltriethoxysilane was used as silica source) as well as for sol-gel synthesis with cyclodextrin-containing organosilane and tetraethylorthosilane, as silica source, participation in the presence of surfactant cetyltrimethylammonium bromide. The successful incorporation of cyclic oligosaccharide moieties in silica surface layer was verified by means of Fourier transform infrared spectroscopy and elemental analysis. In spite of commensurable loading of cyclodextrin groups attained by both proposed approaches (up to  $0.028 \mu\text{mol}/\text{m}^2$ ), it was found that co-condensation procedure provided uniform distribution of cyclodextrin functionalities in silica framework, whereas post-synthesis grafting resulted in modification of external surface of silica surface. Adsorption of benzene from aqueous solutions onto

the surface of cyclodextrin-containing materials prepared by co-condensation method was studied as the function of time and equilibrium concentration. Calculated maximum adsorption capacity for benzene was 111 mg/g. Adsorption experiments showed that ordered cyclodextrin-containing silicas could be promising for the trace amount removal of aromatics from water.

Ebadi and Rafati (2015) prepared new silica mesoporous nanoparticles functionalized by cyclodextrin molecules for methylene blue removal from aqueous solution. Modified nano-hollow sphere silica was proposed by sol–gel method using amino-functionalized silica and mono-tosyl-cyclodextrin derivatives (Fig. 4). Nanoparticles showed regular sphere particles with radius less than 100 nm, with a surface area of 754 m<sup>2</sup>/g (from BET data). Fourier transform infrared data indicated both the grafting and cross-linking of cyclodextrin molecules onto nanoparticles. Adsorption behaviors of methylene blue onto nanoparticles were studied from equilibrium and kinetic viewpoints. High adsorption capacities were obtained with a maximum adsorption capacity of 99.22 mg/g at pH 10.5. The results were, however, strongly pH dependent. The equilibrium data could be well

described by several isotherms but Toth isotherm model was designed for investigation of heterogeneous adsorption systems. Host–guest interactions between cyclodextrin and organic molecules had a great contribution to dye adsorption. These nanoparticles could be applied in the elimination, enrichment, and detection of some environmental pollutants. The authors concluded that the new nanoparticles could be a potential material for in situ remediation of contaminated surface and groundwater.

Results on drug complexation by mesoporous silicas containing cyclodextrin were reported by Pasqua et al. (2013). Ordered silica SBA-15 was hybridized using two different synthetic procedures to produce a covalent bond with cyclodextrin molecules as a drug delivery device for progesterone. In the first approach, SBA-15 silica ( $S_{\text{BET}} = 766 \text{ m}^2/\text{g}$ ) was first let to react with 3-glycidypropyltrimethoxysilane to produce an epoxide ring functional group on mesoporous silica. The latter was then reacted under basic conditions with mono-6-deoxy-6-mercapto-cyclodextrin, prepared in its turn in two steps from cyclodextrin through mono-tosylation followed by thiolation with thiourea. In the second approach, silica suitably functionalized with a terminal



**Fig. 4** Modification of silica nano-hollow sphere containing cyclodextrin molecules. Adapted from Ebadi and Rafati (2015)

thiol group, obtained by the reaction of SBA-15 silica with 3-mercaptopropyltrimethoxy-silane, was reacted with monotosyl-cyclodextrin (Fig. 5). The obtained materials (denoted SC1 and SC2) were characterized by X-ray diffraction, nitrogen adsorption, scanning electron microscopy, and C-13 cross-polarization magic angle spinning nuclear magnetic resonance. The BET surface area obtained was 150 m<sup>2</sup>/g and 190 m<sup>2</sup>/g for SC1 and SC2, respectively. Nuclear magnetic resonance solid-state spectroscopy permitted a complete characterization for both materials. Scanning electron microscopy observations did not evidence substantial variations in morphological properties. Progesterone was loaded on both the materials producing complete filling of mesopores and cyclodextrin cavities. Its release was studied at different pH values. The results showed that only one of the two progesterone-loaded delivery devices (SC2) was, however, able to retain the drug in the system during the first period at acid pH (2 h) and release it after pH increase. A possible explanation for the immediate release from SC1 was the increase of solubility in acidic solution of progesterone adsorbed on the external surface and included in the hybrid material.

## Cyclodextrin-functionalized silica materials

Liu et al. (2016b) proposed a novel and low-cost cyclodextrin-functionalized silica gel prepared with grafting cyclodextrin to silica gel containing salicylamide as adsorbent for UO<sub>2</sub><sup>2+</sup> removal (Fig. 6). Salicylamide (*o*-hydroxybenzamide) is known as drug for its analgesic and antipyretic properties but also as organic ligand for metal chelation. At the following conditions: pH 4.5, equilibrium time 60 min, and initial UO<sub>2</sub><sup>2+</sup> concentration 25 mg/L, the equilibrium adsorption capacity was found to be 6.45 mg/g. Adsorption performances were strongly pH dependent. Modeling indicated that Langmuir and Freundlich models were suitable to describe the adsorption process. Thermodynamic data also indicated that the process was endothermic, spontaneous and dominated by entropy rather than by enthalpy change. The new material also adsorbed UO<sub>2</sub><sup>2+</sup> in aqueous solution in the presence of interfering ions such as Na<sup>+</sup>, Fe<sup>3+</sup>, Cu<sup>2+</sup>, Mg<sup>2+</sup>, La<sup>3+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>, and Hg<sup>2+</sup>. Apparently, the performance of the adsorbent was not appreciably deteriorated after repeated use and regeneration for five cycles. This new and efficient adsorbent for uranium (VI) was considered as low-cost since raw materials were cheap and commercially available, and the synthetic procedure was easy.

De Carvalho et al. (2014) proposed a cyclodextrin-functionalized silica adsorbent for the removal of methylene blue in aqueous media. Modification of the silica surface using cyclodextrin (~44%) was performed in one-step by refluxing using citric acid as a linking agent (Fig. 7). The authors

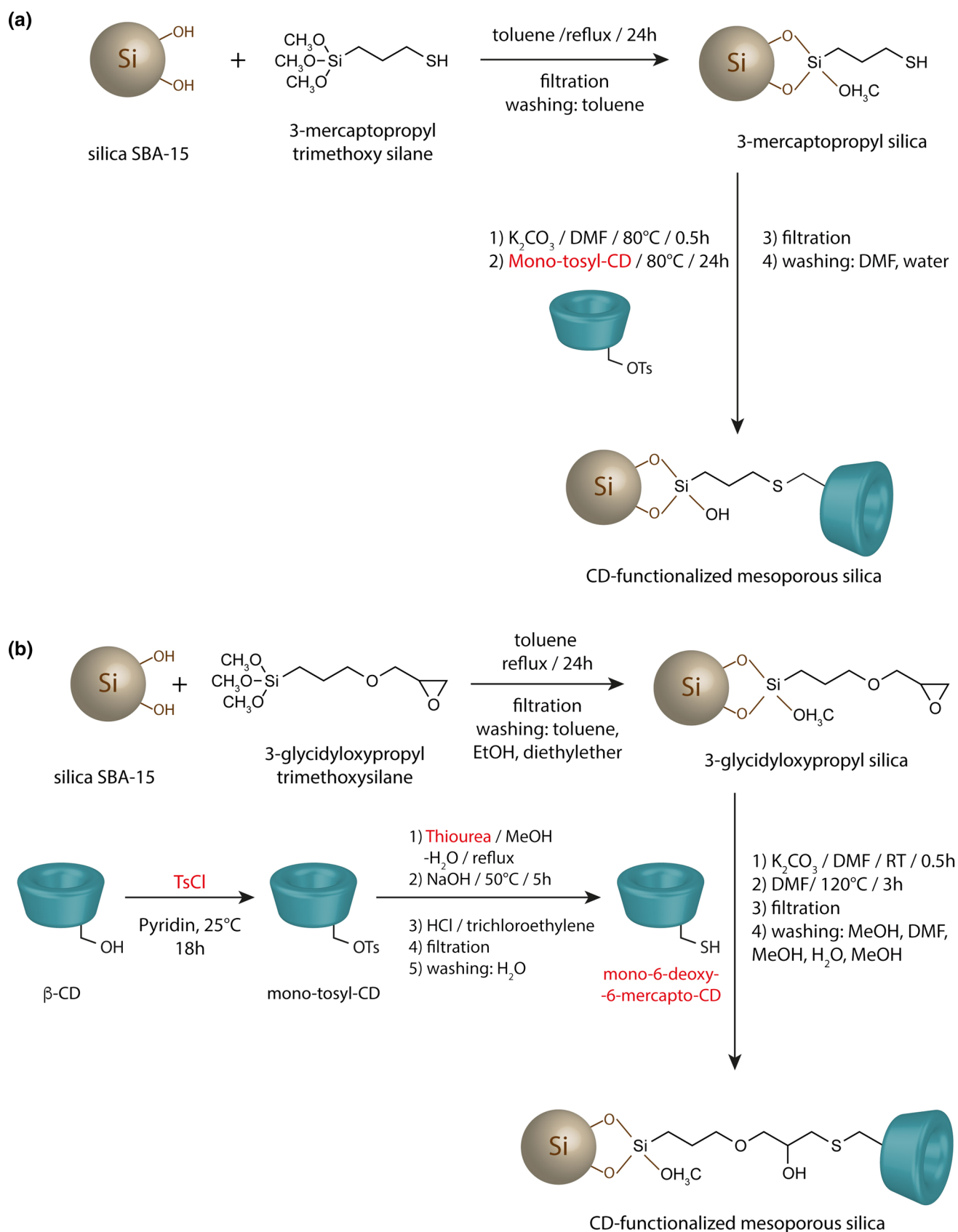
showed that two mechanisms might occur in solution during the synthesis, as shown in Fig. 7.

The maximum capacity of the nano-adsorbent for adsorption of the dye was 212 mg/g, and the best adsorption was achieved at pH values higher than 3.5. This value was in agreement with adsorption performances obtained employing commercial activated charcoal. The correlation coefficients obtained using the Langmuir isotherm enabled elucidation of the adsorption mechanism. Thermodynamic data also showed that the mechanism was spontaneous and temperature dependent (adsorption decreased with increasing temperature), with adsorption following the pseudo-second-order kinetic model and being fastest during the early stages, with equilibrium achieved after around 3 h. Advantages of these new materials include not only good adsorption properties but also ease of preparation and relatively low cost. The authors claimed that cyclodextrin-silica adsorbents can be used for the removal of dyes from aqueous media and could therefore substitute for other more expensive adsorbents.

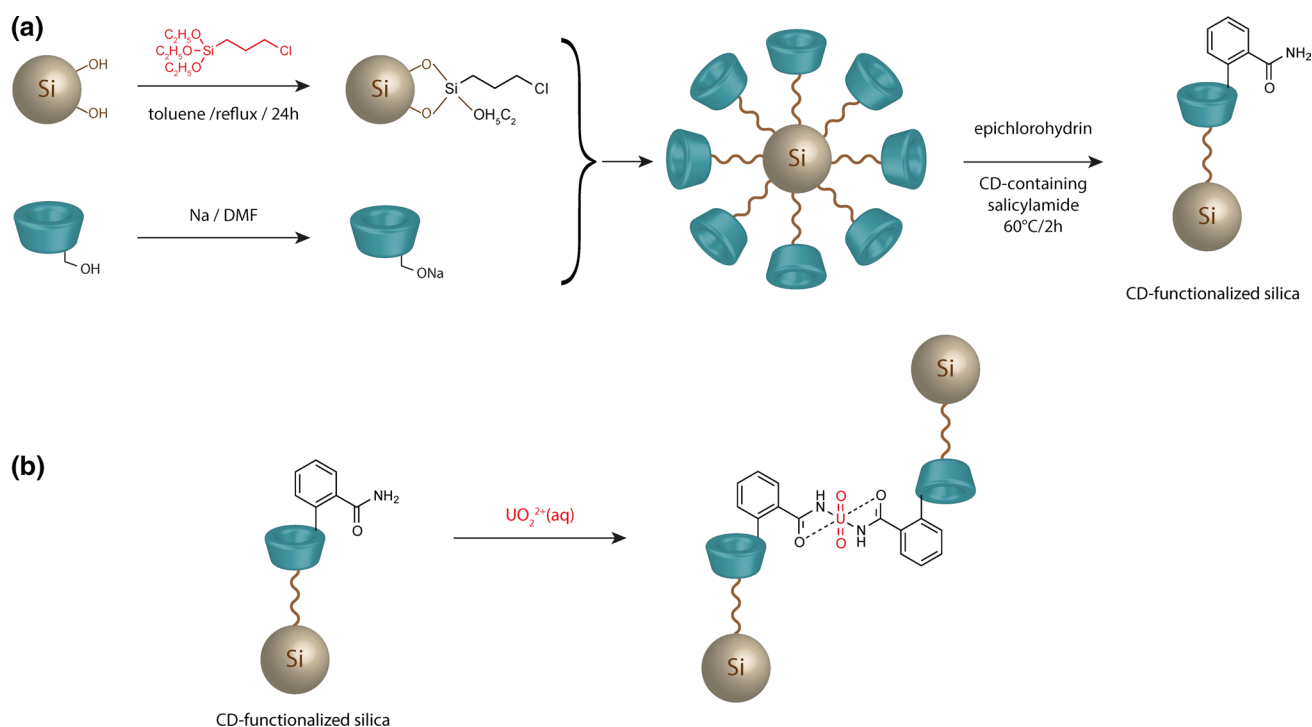
Belyakova's group proposed new functional organosilicas for adsorption of toxic metals such as mercury (II), cadmium (II) and zinc (II) from aqueous solution (Belyakova et al. 2014; Belyakova and Lyashenko 2014; Shvets and Belyakova 2015). The materials were synthesized using a nanoporous amorphous highly disperse silica with the following characteristics: specific surface area 133 m<sup>2</sup>/g, particle size 0.3–0.5 μm, concentration of silanol groups 0.4 mmol/g, adsorption pore volume 0.8 cm<sup>3</sup>/g, and mean pore diameter 46 nm. For chemical functionalization, the authors used aminopropylsilica preliminary obtained by the electrophilic substitution of aminopropyl radicals for the proton of silanol groups and the grafting reaction with three cyclodextrin derivatives (mono-tosyl, bromoacetyl, and thiosemicarbazidoacetyl functional derivatives) to introduce in the material secondary alcohol, bromoacetyl, and thiosemicarbazidoacetyl functional groups of the wide edge of cyclodextrin molecules. In all cases, the chemical modification of the surface of the silica by cyclodextrin molecules led to a decrease in the surface area (by 26–32%), adsorption volume (25–48%), and diameter of pores (37–63%). Nevertheless, cyclodextrin-silicas remained highly disperse materials with nanosized pores. Adsorption data demonstrated that cyclodextrin-silicas were found to have high affinity to mercury (II), cadmium (II), and zinc (II) cations, indicating strong interactions between the chemical groups grafted in the cyclodextrin molecules and metal cations.

This research group also investigated the impact of hardness salts modeling soft and hard waters on adsorption of trace amounts of cadmium (II) by cyclodextrin-silicas, which differed by chemical nature of adsorption centers (Belyakova et al. 2014; Shvets and Belyakova 2015). The driving force of cadmium (II) adsorption on the surface of





**Fig. 5** Synthetic strategies proposed by Pasqua et al. (2013) to prepare cyclodextrin-functionalized mesoporous silica



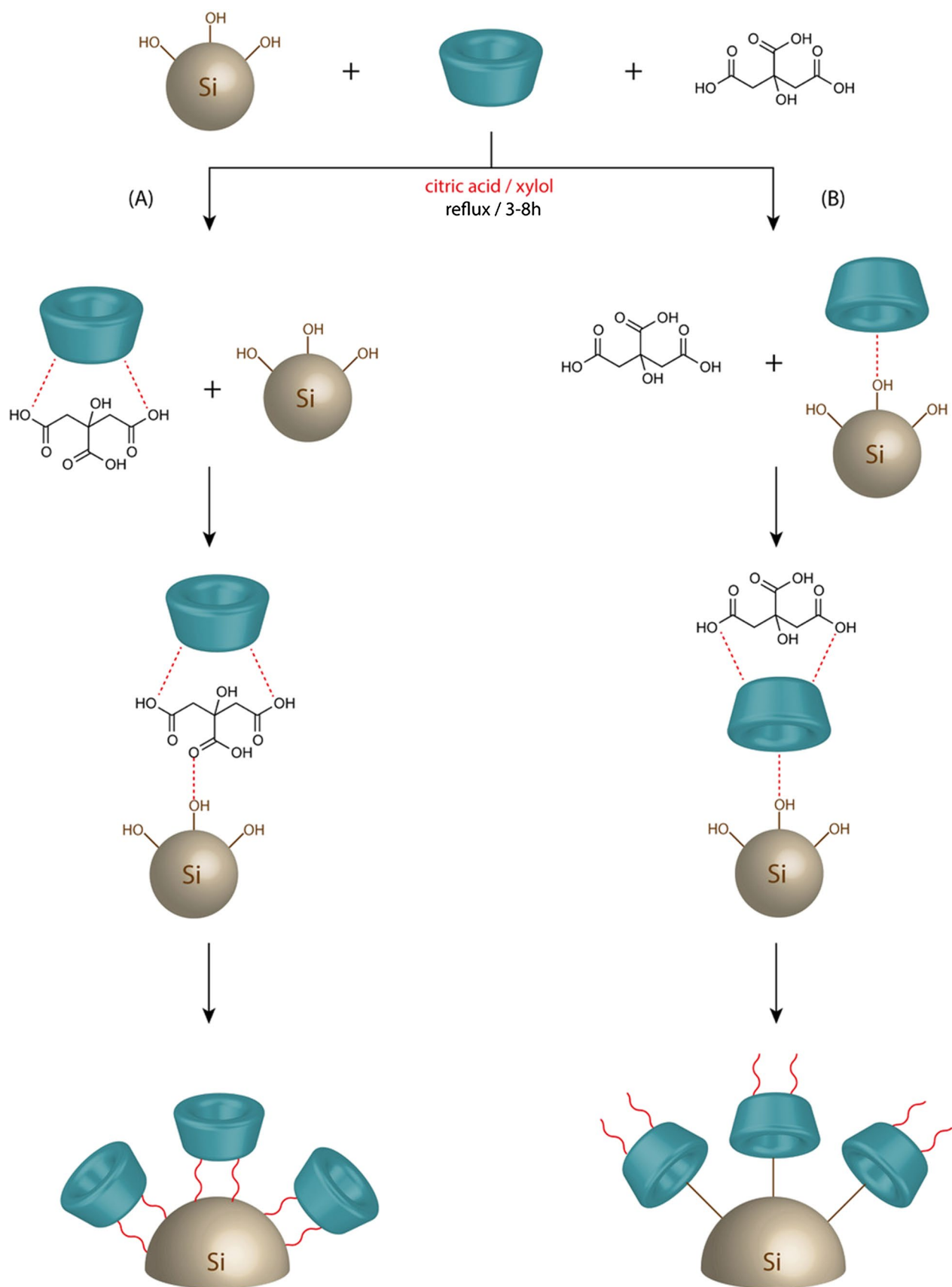
**Fig. 6** **a** Synthesis of cyclodextrin-functionalized silica gel and **b** its application for adsorption of uranium(VI). Adapted from Liu et al. (2016b)

functional cyclodextrin-containing silica was the formation of inclusion complexes cyclodextrin–nitrate–anion. The results demonstrated high affinity of nanoporous organosilica to cadmium (II) in its adsorption from multicomponent solutions with rapid kinetics (equilibrium was reached in 30 min). The adsorption of trace amounts of cadmium (II) from multicomponent solutions did not decrease, but even increased in the presence of hardness salts, simulating soft and hard water. Equilibrium adsorption of cations from aqueous nitrate solutions within a broad interval of concentrations has been described by means of the Langmuir and Freundlich models and was interpreted in terms of the theory of hard and soft acids and Pearson bases. The formation of supramolecular structures on the surface of synthesized organosilicas as a result of cadmium (II) adsorption has been proved.

Shen's group (Han et al. 2016; Shen et al. 2014a, b, 2015a, b) proposed a new cyclodextrin-grafted silica gel, denoted CD@Si, for *p*-nitrophenol removal. Cyclodextrin was grafted onto the surface of silica using (3-chloropropyl)-trimethoxysilane and ethylenediamine as linking groups. Fourier transform infrared, X-ray photoelectron, and nuclear magnetic resonance data demonstrated the successful graft of cyclodextrin molecules on silica surface (Shen et al. 2015a). From thermogravimetric analysis data, the amount of cyclodextrin grafted was estimated about 20% (w/w). Scanning electron microscopy analysis indicated that the morphologies of the different materials, i.e., activated gel,

silica-grafted (3-chloropropyl)-trimethoxysilane and CD@Si, were uniform in both shape and size, and the graft of (3-chloropropyl)-trimethoxysilane and cyclodextrin molecules did not affect the morphology of silica gel. Adsorption data indicated that (1) the adsorption of *p*-nitrophenol onto CD@Si was a very fast process: The equilibrium can be reached in 5 s with a maximum adsorption capacity of 41.5 mg/g at pH > 8.5, much faster than many reported adsorbents based on cyclodextrin; (2) the adsorption process followed the pseudo-second-order and Freundlich models; (3) thermodynamic data indicated that the process was spontaneous and exothermic but temperature-dependent (adsorption was more favorable in lower temperature); and (4) CD@Si can be recycled and reused at least five runs with acceptable adsorption capacity, showing the chemical stability of the material. A systematic study of the adsorption mechanism using spectroscopic data showed that the two main interactions were inclusion complex formation and hydrogen bond interactions (Morin-Crini et al. 2018). In another recent work, the authors provide a new strategy to increase the adsorption rate of CD@Si adsorbents using different experimental conditions during synthetic procedure (Shen et al. 2015b). The authors claimed that these new cyclodextrin-grafted silica gels were promising for pollutant removal not only due to their efficiency but also from an economic point of view (Han et al. 2016).

Bhattarai et al. (2014) developed silica-coated cyclodextrin polymeric adsorbents for the removal of



**Fig. 7** Functionalization of silica gel with cyclodextrin molecules using citric acid as a bonding agent. Adapted from de Carvalho et al. (2014)

several emerging pollutants such as steroid hormones (17- $\beta$ -estradiol), bisphenol A, and perfluorooctanoic acid. Three different approaches were used to functionalize cyclodextrin onto silica (40  $\times$  100 mesh size). In the first approach, cyclodextrin molecules can be polymerized onto surface silica by a reaction between the hydroxyl groups with a coupling agent such as epichlorohydrin or hexamethylene diisocyanate. In the second, cyclodextrin was supported on silica with copolymers glycidoxypropyltrimethoxysilane and 3-aminopropyltriethoxysilane. In the third approach, cyclodextrin was coated on silica with both cross-linking agents and copolymers. Fourteen different adsorbents were synthesized under different experimental conditions, for example solvent, temperature, and reactant concentration. Adsorption results showed that the material prepared by using hexamethylene diisocyanate as cross-linking agent with DMSO as solvent was the best in terms of performance for the removal of 17- $\beta$ -estradiol, perfluorooctanoic acid, and bisphenol A with more than 90% abatement in all cases. This material had thermal stability of up to 300 °C. This adsorbent was also resynthesized in seven batches, and its performance was reproducible for the removal of ten steroid hormones at 1.5 g/L adsorbent dosage. It showed very good regeneration potential for four successive adsorption–regeneration cycles to remove steroid hormones and perfluorooctanoic acid without significant loss in its performances. The new adsorbent showed higher adsorption capacity ( $38.8 \pm 5.6 \mu\text{g/g}$ ) for 17- $\beta$ -estradiol when compared with that of commercially available activated carbon ( $23.6 \pm 6.3 \mu\text{g/g}$ ). Furthermore, the cyclodextrin loading on pollutant removal was studied which showed that the adsorbate removal increased with increase in loading of cyclodextrin on the substrate (a loading of 0.23 g/g was recommended). The results suggested the main role of the cyclodextrin molecules in the adsorption process (physisorption was negligible since the BET surface area of the materials was less than 1 m<sup>2</sup>/g) and also possible numerous inter-molecular hydrogen bond interactions between the cyclodextrin host molecules and the guest pollutants.

A highly effective cleanup adsorbent was developed by Liu et al. (2016a) for eliminating matrix interferences, especially main organochlorine pesticide residues during the determination of highly chlorinated polychlorinated biphenyls in seafood. The multifunctional adsorbent was prepared by grafting carboxymethyl cyclodextrin on the surface of amino-functionalized mesoporous nanoparticles. The amino group-functionalized mesoporous SiO<sub>2</sub> can remove most of the matrix interference in samples. Moreover, carboxymethyl cyclodextrin had stronger host–guest complexation with 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl) ethane, 2,2-bis(*p*-chlorophenyl)-1,1-dichloro-ethylene, and 1,1-dichloro-2,2-bis(*p*-chlorophenyl) ethane. However, it showed weaker adsorption ability toward highly chlorinated polychlorinated biphenyls due to a steric hindrance effect. A

gas chromatography–mass spectrometry method coupled with the multifunctional adsorbent as a cleanup adsorbent for dispersive solid-phase extraction was developed for the analysis of several highly chlorinated polychlorinated biphenyls in seafood samples. The results indicated that the multifunctional adsorbent as a purification material could easily and effectively remove matrix interferences in seafood samples within a short time. The recoveries for polychlorinated biphenyls were in the range of 88.4–103.2%, with relative standard deviations varying between 1.3 and 5.7%.

## Conclusion

The field of silica containing cyclodextrin molecules has been studied for about 25 years but is still an area attracting a lot of attention. These kinds of materials often present the best properties of each of its components in a synergic way and have high performances of physical, chemical, and mechanical properties. Cyclodextrin-silica material such as cyclodextrin-silica hybrid systems prepared through sol–gel or self-assembly process and cyclodextrin-functionalized silicas prepared through grafting or cross-linking reactions are regarded as effective adsorbents for pollutant removal. Indeed, from a point of view of their efficiency, there is no doubt that these materials exhibited interesting adsorption capacities toward pollutants and will find industrial environmental applications. However, it is important to note that research mainly focused on the performances of these innovative materials, while their economic aspect is neglected. An important question is the following: Could mesosilica adsorbents compete with conventional activated carbon in price, durability, and efficiency?

In addition, although extensive work has been done, future research needs to look into some of the following aspects: use of eco-friendly procedures, demonstration of the possibilities on an industrial scale, with polycontaminated real effluents, removal of emerging pollutants from water such as pharmaceuticals products. Other questions concern their long-term stability and effective reusability after regeneration, and adsorption mechanisms. It is therefore necessary to continue to search for and select the most promising types of cyclodextrin-silica materials. Finally, the works reviewed in this paper indicated that adsorption onto these new materials is becoming a promising alternative to replace conventional materials although the mechanisms involved are not fully understood.

## References

- Al Othman ZA (2012) A review: fundamental aspects of silicate mesoporous materials. *Materials* 5:2874–2902. <https://doi.org/10.3390/ma5122874>
- Al Othman ZA, Apblett AW (2009) Synthesis and characterization of a hexagonal mesoporous silica grafted with

- 3-glycidoxypropyltrimethoxy-silane. *Mater Lett* 6:2331–2334. <https://doi.org/10.1016/j.matlet.2009.07.067>
- Beck JS, Vartuli JC, Roth WJ, Leonowicz ME, Kresge CT, Schmitt KD, Chu CTW, Olson DH, Sheppard EW, McCullen SB, Higgins JB, Schlenker JL (1992) A new family of mesoporous molecular-sieves prepared with liquid-crystal templates. *J Am Chem Soc* 114:10834–10843. <https://doi.org/10.1021/ja00053a020>
- Beck JS, Vartuli JC, Kennedy GJ, Kresge CT, Roth WJ, Schramm SE (1994) Molecular or supramolecular templating—defining the role of surfactant chemistry in the formation of microporous and mesoporous molecular-sieves. *Chem Mat* 6:1816–1821. <https://doi.org/10.1021/cm00046a040>
- Belyakova LA, Lyashenko DY (2014) Nanoporous functional organosilicas for sorption of toxic ions. *Russ J Phys Chem A* 88:489–493. <https://doi.org/10.1134/S0036024414030030>
- Belyakova LA, Lyashenko DY, Shvets AN (2014) Sorption of Cd(II) from multicomponent nitrate solutions by functional organosilicas. *J Water Chem Technol* 36:56–61. <https://doi.org/10.3103/S1063455X14020027>
- Bhattarai B, Muruganandham M, Suri RPS (2014) Development of high efficiency silica coated beta-cyclodextrin polymeric adsorbent for the removal of emerging contaminants of concern from water. *J Hazard Mat* 273:146–154. <https://doi.org/10.1016/j.jhazmat.2014.03.044>
- Bibby A, Mercier L (2003) Adsorption and separation of water-soluble aromatic molecules by cyclodextrin-functionalized mesoporous silica. *Green Chem* 5:15–19. <https://doi.org/10.1039/B209251B>
- Chen CY, Burkett SL, Li HX, Davis ME (1993) Studies on mesoporous materials. II. Synthesis mechanism of MCM-41. *Microporous Mat* 2:27–34. [https://doi.org/10.1016/0927-6513\(94\)00077-9](https://doi.org/10.1016/0927-6513(94)00077-9)
- Crini G, Badot PM (2010) Sorption processes and pollution. PUF, Besançon
- Crini G, Morcellet M (2002) Synthesis and applications of adsorbents containing cyclodextrins. *J Sep Sci* 25:789–813. [https://doi.org/10.1002/1615-9314\(20020901\)25:13%3c789:AID-JSSC789%3e3.0.CO;2-J](https://doi.org/10.1002/1615-9314(20020901)25:13%3c789:AID-JSSC789%3e3.0.CO;2-J)
- Davis ME (2002) Ordered porous materials for emerging applications. *Nature* 417:813–821. <https://doi.org/10.1038/nature00785>
- de Carvalho LB, Carvalho TG, Magriotis ZM, Ramalho TD, Pinto LDA (2014) Cyclodextrin/silica hybrid adsorbent for removal of methylene blue in aqueous media. *J Incl Phenom Macrocycl Chem* 78:77–87. <https://doi.org/10.1007/s10847-012-0272-z>
- Degoutin S, Bacquet M (2013) Novel porous organosilica containing amino and beta-cyclodextrin groups. *J Porous Mat* 20:663–671. <https://doi.org/10.1007/s10934-012-9640-8>
- Ebadi A, Rafati AA (2015) Preparation of silica mesoporous nanoparticles functionalized with beta-cyclodextrin and its application for methylene blue removal. *J Mol Liq* 209:239–245. <https://doi.org/10.1016/j.molliq.2015.06.009>
- Gibson LT (2014) Mesosilica materials and organic pollutant adsorption: Part B—removal from aqueous solution. *Chem Soc Rev* 43:5173–5182. <https://doi.org/10.1039/c3cs60095e>
- Han Y, Zhang D (2012) Ordered mesoporous silica materials with complicated structures. *Curr Opin Chem Eng* 1:129–137. <https://doi.org/10.1016/j.coche.2011.11.001>
- Han YQ, Zhou WJ, Shen HM, Liu QP, Yu WY, Ji HB, She YB (2016) Progress in the immobilization of beta-cyclodextrin and their application in adsorption of Environmental Pollutants. *Chin J Org Chem* 36:248–257
- Hench LL, West JK (1990) The sol–gel process. *Chem Rev* 90:33–72. <https://doi.org/10.1021/cr00099a003>
- Huq R, Mercier L, Kooyman PJ (2001) Incorporation of cyclodextrin into mesostructured silica. *Chem Mat* 13:4512–4519. <https://doi.org/10.1021/cm010171i>
- Inagaki S, Fukushima Y, Kuroda K (1993) Synthesis of highly ordered mesoporous materials from a layered polysilicate. *J Chem Soc Chem Commun* 8:680–682. <https://doi.org/10.1039/C39930000680>
- Inagaki S, Koiwai A, Suzuki N, Fukushima Y, Kuroda K (1996a) Syntheses of highly ordered mesoporous materials, FSM-16, derived from kanemite. *Bull Chem Soc Jpn* 69:1449–1457
- Inagaki S, Fukushima Y, Kuroda K, Kuroda K (1996b) Adsorption isotherm of water vapor and its large hysteresis on highly ordered mesoporous silica. *J Colloid Int Sci* 180:623–624. <https://doi.org/10.1006/jcis.1996.0345>
- Kresge CT, Leonowicz ME, Roth WJ, Vartuli JC, Beck JS (1992) Ordered mesoporous molecular-sieves synthesized by a liquid-crystal template mechanism. *Nature* 359:710–712. <https://doi.org/10.1038/359710a0>
- Kresge CT, Vartuli Roth WJ, Leonowicz ME, Beck JS, Schmitt KD, Chu CTW, Olson DH, Sheppard EW, McCullen SB, Higgins JB, Schlenker JL (1995) M41S: a new family of mesoporous molecular-sieves prepared with liquid-crystal templates. *Sci Technol Catal Book Ser* 92:11–19
- Liu CQ, Naismith N, Economy J (2004) Advanced mesoporous organosilica material containing microporous beta-cyclodextrins for the removal of humic acid from water. *J Chromatogr A* 1036:113–118
- Liu HB, Zhang JB, Gan N, Chen YJ, Huang J, Cao YT, Li TH, Lan HZ (2016a) Application of a multifunctional magnetic mesoporous material for seafood sample clean-up prior to the determination of highly chlorinated polychlorinated biphenyls. *RSC Adv* 6:183–189
- Liu HJ, Jing PF, Liu XY, Du KJ, Sun YK (2016b) Synthesis of beta-cyclodextrin functionalized silica gel and its application for adsorption of uranium(VI). *J Radioanal Nuclear Chem* 310:263–270
- Mahmud ST, Wilson LD (2016) Synthesis and characterization of surface-modified mesoporous silica materials with beta-cyclodextrin. *Cogent Chem* 2:1132984. <https://doi.org/10.1080/23312009.2015.1132984>
- Morin-Crini N, Crini G (2012) Review of current physical and chemical technologies for the decontamination of industrial wastewater. *Int J Chem Eng* 5:143–186
- Morin-Crini N, Fourmentin S, Crini G (2015) Cyclodextrines. Presses Universitaires de Franche-Comté, Besançon, p 370
- Morin-Crini N, Fourmentin M, Fourmentin S, Torri G, Crini G (2018) Silica materials containing cyclodextrin for pollutant removal. In: Fourmentin S, Crini G, Lichtfouse E (eds) *Environmental chemistry for a sustainable world*, vol 2. Chapter 6. Springer, Berlin, pp 1–56. [https://doi.org/10.1007/978-3-319-76162-6\\_6](https://doi.org/10.1007/978-3-319-76162-6_6)
- Myers D (1992) *Surfactant science and technology*. VCH, New-York
- Pan BJ, Pan BC, Zhang MW, Lv L, Zhang QX, Zheng SR (2009) Development of polymeric and polymer-based hybrid adsorbents for pollutant removal from waters. *Chem Eng J* 151:19–29
- Pasqua L, Veltri L, Gabriele B, Testa F, Salerno G (2013) Progesterone inclusion into cyclodextrin-functionalized mesoporous silica. *J Porous Mat* 20:917–925
- Patarin J, Lebeau B, Zana R (2002) Recent advances in the formation mechanisms of organized mesoporous materials. *Curr Opin Colloid Int Sci* 7:107–115
- Rahmat N, Abdullah AZ, Mohamed AR (2010) A review: mesoporous Santa Barbara amorphous-15, types, synthesis and its application towards biorefinery production. *Am J Appl Sci* 7:1579–1586
- Samiey B, Cheng CH, Wu JG (2014) Organic–inorganic hybrid polymers as adsorbent for removal of heavy metal ions from solutions: a review. *Materials* 7:673–726. <https://doi.org/10.3390/ma7020673>
- Sanchez C, Julian B, Belleville P, Popall M (2005) Applications of silica-based organic–inorganic hybrid materials. *J Chem Mater* 15:3559–3592. <https://doi.org/10.1039/B509097K>

- Sawicki R, Mercier L (2006) Evaluation of mesoporous cyclodextrin-silica nanocomposites for the removal of pesticides from aqueous media. *Environ Sci Technol* 40:1978–1983
- Shen HM, Ji HB, Wu HK, Shi HX (2014a) Recent advances in the immobilization of beta-cyclodextrin and their application. *Chin J Org Chem* 34:1549–1572
- Shen HM, Wu HK, Ji HB, Shi HX (2014b) Progress in the construction of beta-cyclodextrin-Fe<sub>3</sub>O<sub>4</sub> supramolecular systems and their application. *Chin J Org Chem* 34:630–646
- Shen HM, Zhu GY, Yu WB, Wu HK, Ji HB, Shi HX, She YB, Zheng YF (2015a) Fast adsorption of *p*-nitrophenol from aqueous solution using beta-cyclodextrin grafted silica gel. *Appl Surf Sci* 356:1155–1167
- Shen HM, Zhu GY, Yu WB, Wu HK, Ji HB, Shi HX, Zheng YF, She YB (2015b) Surface immobilization of beta-cyclodextrin on hybrid silica and its fast adsorption performance of *p*-nitrophenol from the aqueous phase. *RSC Adv* 5:84410–84422. <https://doi.org/10.1039/C5RA15592D>
- Shvets O, Belyakova L (2015) Synthesis, characterization and sorption properties of silica modified with some derivatives of beta-cyclodextrin. *J Hazard Mat* 283:643–656. <https://doi.org/10.1016/j.jhazmat.2014.10.012>
- Simsek EB, Duranoglu D, Beker U (2012) Heavy metal adsorption by magnetic hybrid-sorbent: an experimental and theoretical approach. *Sep Sci Technol* 47:1334–1340
- Trofymchuk IM, Roik N, Belyakova L (2016) Sol-gel synthesis of ordered beta-cyclodextrin-containing silicas. *Nanoscale Res Lett* 11:1–12. <https://doi.org/10.1186/s11671-016-1380-2>
- Valtchev V, Mintova S, Tsapatsis M (2009) Ordered porous solids—recent advances and prospects. Elsevier, Amsterdam, p 800
- Vartuli JC, Roth WJ, Degnan TF (2008) Mesoporous materials (M41S): From discovery to application. In: Scharwz JA, Contescu CI, Putyera K (eds) Dekker encyclopedia of nanoscience and nanotechnology. Taylor and Francis, New-York, pp 1797–1811
- Vunain E, Mishra AK, Mamba BB (2016) Dendrimers, mesoporous silicas and chitosan-based nanosorbents for the removal of heavy-metal ions: a review. *Int J Biol Macromol* 86:570–586. <https://doi.org/10.1016/j.ijbiomac.2016.02.005>
- Walcarius A (2001) Electrochemical applications of silica-based organic-inorganic hybrid nanocomposites. *Mater Chem* 13:3351–3372. <https://doi.org/10.1021/cm0110167>
- Walcarius A, Mercier L (2010) Mesoporous organosilica adsorbents: nanoengineered materials for removal of organic and inorganic pollutants. *J Mater Chem* 20:4478–4511. <https://doi.org/10.1039/B924316J>
- Wase J, Forster C (1997) Biosorbents for metal ions. Taylor & Francis, Bristol
- Willai S, Bacquet M, Morcellet M (2008) Organosilica mesoporous materials with double functionality: amino groups and β-cyclodextrin synthesis and properties. In: Ganachaud F (ed) Silicon based polymers. Springer, Berlin, pp 213–221
- Wilson LD, Mahmud ST (2015) The adsorption properties of surface-modified mesoporous silica materials with beta-cyclodextrin. *Int J Technol* 6:533–545. <https://doi.org/10.14716/ijtech.v6i4.2036>
- Yamamoto E, Kuroda K (2016) Colloidal mesoporous silica nanoparticles. *Bull Chem Soc Jpn* 89:501–539
- Yanagisawa T, Shimizu T, Kuroda K (1990a) The preparation of alkyltrimethylammonium-kanemite complexes and their conversion to microporous materials. *Bull Chem Soc Japan* 63:988–992
- Yanagisawa T, Shimizu T, Kuroda K, Kato C (1990b) Trimethylsilyl derivatives of alkyltrimethylammonium-kanemite complexes and their conversion to microporous SiO<sub>2</sub> materials. *Bull Chem Soc Jpn* 63:1535–1537
- Zhao XS, Lu GQ, Millar GJ (1996) Advances in mesoporous molecular sieve MCM-41. *Ind Eng Chem Res* 35:2075–2090. <https://doi.org/10.1021/ie950702a>

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