Chapter 6
Silica Materials Containing Cyclodextrin for Pollutant Removal

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Contents

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Abstract This chapter reviews the use of cyclodextrin-silica hybrid systems and cyclodextrin-functionalized silica used as adsorbents or filters for the removal of inorganic and organic pollutants from aqueous solutions in solid-phase extraction and adsorption-oriented processes. Actually, there is a need to develop efficient processes for the synthesis and application of multifunctional silica-based materials for pollutant removal by adsorption or filtration, and for sample purification and concentration using solid-phase extraction.

On one hand, of silica-based adsorbents are low-cost, robust inorganic solids having large surface areas, high porosity, and excellent mechanical, physical and chemical properties, and wide possibilities of functionalization due to silanol reactivity. On the other hand, cyclodextrins are natural molecules obtained from the enzymatic degradation of starch. They belong to the family of cage molecules due to their structure which is composed of a hydrophobic cavity that can encapsulate other molecules. Cyclodextrin-functionalized silicas usually display improved access to the binding sites because the moieties are located on the external surface of the material. In cyclodextrin-silica hybrid systems prepared through sol-gel or self-assembly process, cyclodextrin molecules are located within the framework of nanoporous silicas. Here, both high cyclodextrin loadings, robust structures and higher surface area are observed. Cyclodextrin-based silica materials have strong binding affinities for chemical substances such as metal ions, dyes, pesticides, and drugs.

Abbreviations

AAm	Acrylamide
APTES	3-aminopropyltriethoxysilane
BET	Brunauer-Emmett-Teller
BPA	Bisphenol A
CD	Cyclodextrin
CPMAS	Cross-polarization magic angle spinning
CTAB	Cetyltrimethylammonium bromide
EDS	Energy-dispersive X-ray spectroscopy
EPI	Epichlorohydrin
FSM	Folded sheets mechanism
FT-IR	Fourier transform infrared
GPTS	Glycidoxypropyl trimethoxysilane
HMDI	Hexamethylene diisocyanate
HMS	Hexagonal mesoporous silica
MCM	Mobil crystalline materials
MCT-CD	Monochlorotriazinyl-cyclodextrin
MS	Mass spectrometry
MSU	Michigan State University

NMR	Nuclear magnetic resonance
PAAM	Polyacrylamide
PAH	Polycyclic aromatic hydrocarbons
PCB	Polychlorobiphenyls
SBA	Santa Barbara amorphous
SDS	Sodium dodecylsulfate
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TEOS	Tetraethylorthosilane
TGA	Thermogravimetric analysis
Triton X-45	A nonionic surfactant
VOC	Volatile organic compounds
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

6.1   Introduction

Amongst 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 (Volesky and Holan 1995; McKay 1996; Yang 2003; Crini and Badot 2010). As adsorption is a surface phenomenon, any porous solid having a large surface area may be an adsorbent. In general, the selection of an adsorbent in a suitable adsorption process is based on the following criteria: low-cost and readily available, granular type with a good particle size distribution, a well-developed structure, porous material with a large total surface area, presence of surface charge due to functional groups considered as adsorption sites, high physical strength in solution, suitable mechanical properties, efficient for a large range of pollutants, a long life, and able to be regenerated if required (Crini 2005; Crini and Badot 2010). For an excellent adsorbent to remove a large amount of pollutant in a short period of time, it should also possess short adsorption equilibrium times, fast adsorption rates, high capacity, and selectivity.

What is the best adsorbent? There is no direct answer to this question because each solid material has advantages and drawbacks (Volesky 1990; McKay 1996; 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 both 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.

Amongst 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. Their versatility is also another interesting aspect: for instance, there are several types of contacting systems available for industrial applications such as batch methods, fixed-bed type processes or fluidized beds.

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 (Bergna 1994; Cooney 1999; Mocanu et al. 2001; Berggren et al. 2005; Morin-Crini and Crini 2012).

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 alkoxysilane precursor (tetraethoxysilane for example) 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; Sohmiya et al. 2015; Vunain et al. 2016). The sol-gel chemistry leads to the synthesis of ordered mesoporous silicas, e.g. 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 (Goyal et al. 2011; 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.

The application of silica beads containing cyclodextrin (CD) molecules as adsorbents in solving environmental problems such as pollutant removal or filtration from water, wastewater, and atmosphere, e.g. indoor air and gas treatment, has recently received a lot of attention (Sharma and Sanghi 2012; Gibson 2014). In particular, 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, is 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; Sharma and Sanghi 2012).

The main objectives of this chapter 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.

## 6.2 Cyclodextrins and Silicas, Raw Materials to Produce Innovative Complexing Networks

The most characteristic feature of cyclodextrins, natural substances obtained from starch, is their ability to form inclusion compounds with various molecules, ions and polymers. This remarkable property combined with their relatively low-cost and non-toxic character to humans have led to their use in pharmaceuticals, cosmetics, as food additives, as well as in the complexation of pollutants. Numerous books and chapters books can be consulted (Bender and Komiyama 1978; Szejtli 1982, 1988, 1998; Atwood et al. 1984; Duchêne 1987, 1991; Cram 1988; Frömming and Szejtli 1994; Robyt 1998; Dodziuk 2006; Bilensoy 2011; Crini 2014; Morin-Crini et al. 2015). Cyclodextrin molecules themselves, however, are highly water-soluble, and must therefore be processed into solid forms or grafted on solid supports (such as silica) before they can be implemented into usable separation technology (Mocanu et al. 2001; Crini and Morcellet 2002; Landy et al. 2012; Guo and Wilson 2013; Sharma 2015).

As already mentioned, silica-based materials are robust inorganic solids displaying both high specific surface area (200–1500 m^2/g) and a three-dimensional structure made of highly open spaces interconnected to each other via SiO$_4$ tetrahedra, giving rise to highly porous structures, up to 1 cm^3/g or even more (Bergna 1994). Most of them can be manufactured quite easily at room temperature by sol-gel processing for example, involving hydrolysis of silicon alkoxide precursors such as tetramethoxysilane or tetraethoxysilane, and catalytic polycondensation to produce a macromolecular network of siloxane bonds. Accurate tuning of the experimental parameters affecting the production steps, i.e. polymerization, gelation, aging, drying and heating steps, allows control over the microstructure of the final materials. Porosity control can be achieved by the surfactant template route, giving rise to novel ordered mesoporous materials that possess large uniform pore sizes (1.5–10 nm), highly ordered nanochannels, large surface areas (>1000 m^2/g), and tunable liquid crystal-like structures. The chemical reactivity of silicas is essentially governed by their surface properties, especially via the weakly acid silanol groups (Bergna 1994). Originally used mainly in chromatography, silica-based materials are actually used in numerous industrial applications including catalysis, pharmacy, medicine, dentistry, cosmetology, paper, paints, coatings, and also in environment (Descalzo et al. 2006; Pagliaro 2009).

6.3   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. There are several synthetic procedures and numerous materials have been characterized and proposed as adsorbents. Here, we propose to classify these adsorbents in two main class: cyclodextrin-functionalized silicas prepared through grafting or coating reactions and cyclodextrin-silica hybrid systems prepared through sol-gel or self-assembly process. Fig. 6.1 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.
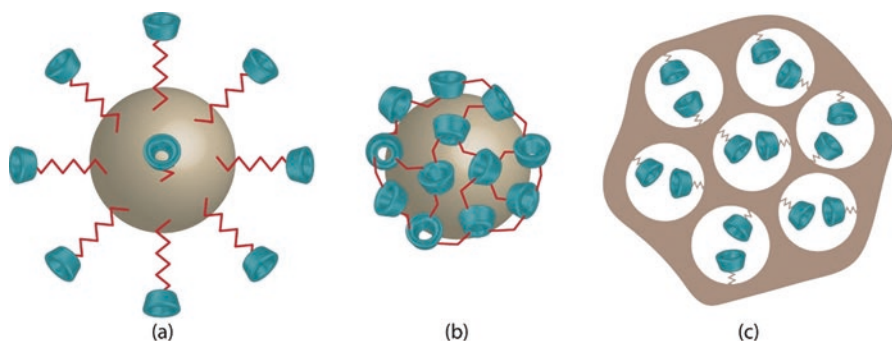
Fig. 6.1 Schematic representations of three silica networks containing cyclodextrin molecules: (**a**) cyclodextrin-functionalized silicas prepared through grafting, (**b**) cyclodextrin-functionalized silicas prepared through coating and (**c**) incorporation of cyclodextrins into nanoporous frameworks

6.4 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 (Descalzo et al. 2006; Walcarius and Mercier 2010; Rahmat et al. 2010; Al Othman 2012; Han and Zhang 2012; Samiey et al. 2014; Lee and Park 2015; Dinker and Kulkarni 2015). 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 nano-building 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 (Hoffman et al. 2006; 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, π–π 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 (Hench and West 1990; Yanagisawa et al. 1990a, b; Beck et al. 1992, 1994; Kresge et al. 1992, 1995; Chen et al. 1993; Inagaki et al. 1993, 1996a, b; Fukushima et al. 1995; Wen and Wilkes 1996; Lim et al. 1998; Lim and Stein 1999; Ciesla and Schüth 1999; Ying et al. 1999; Polarz et al. 2001). 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 others oxides such as alumina were published (Ying et al. 1999; 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 (Wen and Wilkes 1996; Ogoshi and Chujo 2005; Hoffman et al. 2006; Al Othman and Apblett 2009). As documented in a recent comprehensive review (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. The previous reviews of Hench and West (1990), Wen and Wilkes (1996), Hoffman et al. (2006), Vartuli et al. (2008), and Walcarius and Mercier (2010) can be also consulted.

Usually, this process involves the hydrolysis and condensation of a tetraalkoxysilane ($Si(OR)_4$ with R = Me or 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 non-ionic (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 synthetized using tetraethylorthosilane $Si(OC_2H_5)_4$, 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, e.g. 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).

The interaction between the inorganic precursor and the template is a key factor in the control of the mesostructured materials. Ordered silica-based mesoporous materials are solids displaying a periodic and regular arrangement of well-defined and controllable mesopores with size ranging between 2–10 nm, and amorphous inorganic framework structures. They are highly porous (pore volume > 0.7 mL/g), having high specific surface areas up to 1500 m^2/g, and they share characteristics of both silica gels and molecular sieve zeolites, showing however larger pore sizes.

Compared to their non-ordered homologues, these mesostructured porous solids also offer other significant advantages: (i) exceptionally good accessibility to active centers due to highly ordered nanochannels of uniform pore size; (ii) 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; (iii) fast mass transport rates inside the porous structure due to the regular spatial arrangement of mesopore channels of monodisperse dimensions; and (iv) good mechanical and hydrothermal stabilities. This last point is controversial because these properties strongly dependent on mesostructure types and post-synthesis treatments. All these
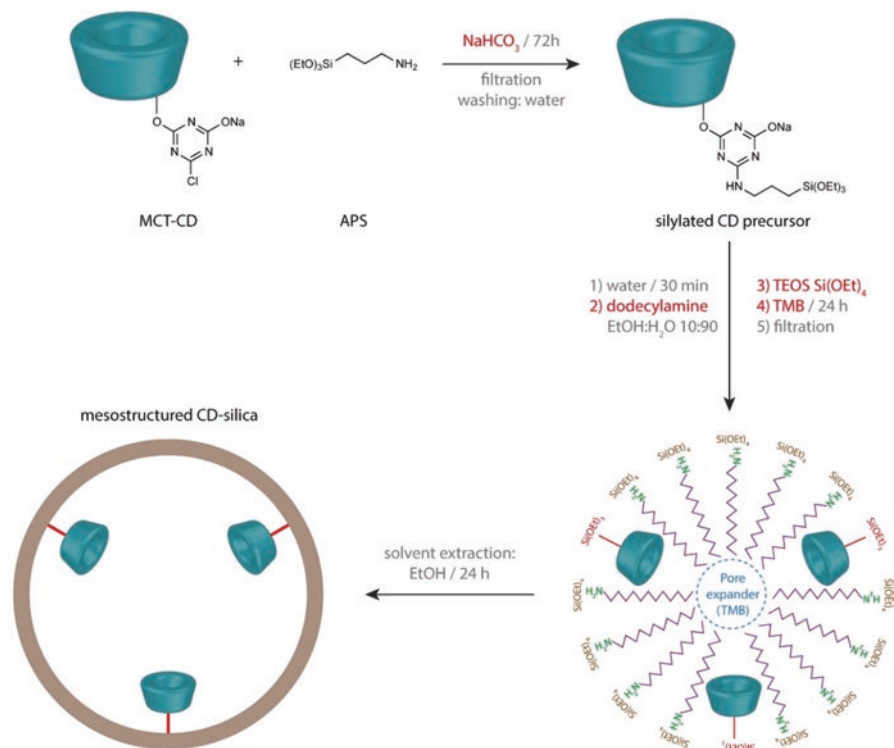
Fig. 6.2 Incorporation of cyclodextrin molecules into mesostructured silica (adapted from Huq et al. 2001)

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.

A silylated-cyclodextrin derivative was first prepared by reaction between monochlorotriazinyl-cyclodextrin (MCT-CD) and 3-aminopropyltriethoxysilane (APS or APTES). The second step was the co-polymerization of this derivative with tetraethylorthosilane in the presence of a structure-directing template. Fig. 6.2 shows the

synthetic procedure proposed by Huq et al. (2001). In preliminary experiments, the incorporation of cyclodextrin molecules inside mesoporous silica frameworks was attempted using two methods: by the grafting of the cyclodextrin into the channels of preformed mesoporous silica hosts and by the direct synthesis of cyclodextrin-containing mesoporous materials by a one-step process. While the grafting procedure failed to incorporate cyclodextrin inside the pore channels of mesoporous silica substrates, the direct synthesis approach yielded materials whose physical and chemical characteristics as determined by numerous techniques such as X-ray diffraction XRD, nitrogen adsorption analysis, transmission electron microscopy (TEM), and elemental analysis were indicative of the presence of cyclodextrin inside the pore channels of the materials. Materials with cyclodextrin loadings up to 0.39 mmol/g and uniform pore channels with diameters in the range of 38–42 Å were prepared by this method. Preliminary adsorption experiments using aqueous monocontaminated solutions showed that the materials were promising in environmental applications.

Indeed, in another work, Mercier's results demonstrated that the materials could selectively separate organic molecules by using the shape- and function-specific inclusion properties of receptor binding sites (Bibby and Mercier 2003). The materials exhibited high adsorption capacities due to inclusion complex formation: up to 0.33 mmol/g for *p*-nitrophenol. These adsorption capacities were superior to those achieved with pure silica materials. This can be also attributed to their higher surface areas, good accessibility to active centers, which increase selectivity, and higher mass transport rates inside the porous structure. Mercier' group also found that materials with higher cyclodextrin loadings generally possessed greater performances for aromatic pollutants. However, the authors demonstrated that adsorption capacity varied not only as a function of the amount of cyclodextrin molecules in the material but also as a function of the complexation thermodynamics of the pollutants with cyclodextrin. Thus, *p*-nitrophenol was found to have the highest adsorption capacity compared to the other pollutants (phenol, *m*-nitrophenol, *p*-chlorophenol and *p*-nitroaniline). In another study (Sawicki and Mercier 2006), the same materials were used for the removal of 14 pesticides from aqueous solutions (initial concentrations in the range 0.06–0.27 μg/L). The results showed that the complete uptake of all pesticides was observed when 250 mg of material were used for adsorption. The cyclodextrin receptor sites in the materials were very effective toward the binding of pesticide molecules to the adsorbents. Fig. 6.3 depicts bidentate complexation of cyclodextrin receptors with *p,p'*-dichlorodiphenyl-based pesticide within a cyclodextrin-silica hybrid system pore channel proposed by the authors.

The Mercier's group studies also 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

Fig. 6.3 Depiction of bidentate complexation of cyclodextrin receptors with a *p,p'*-dichlorodiphenyl-based pesticides within a cyclodextrin-silica hybrid system pore channel (adapted from Sawicki and Mercier 2006)
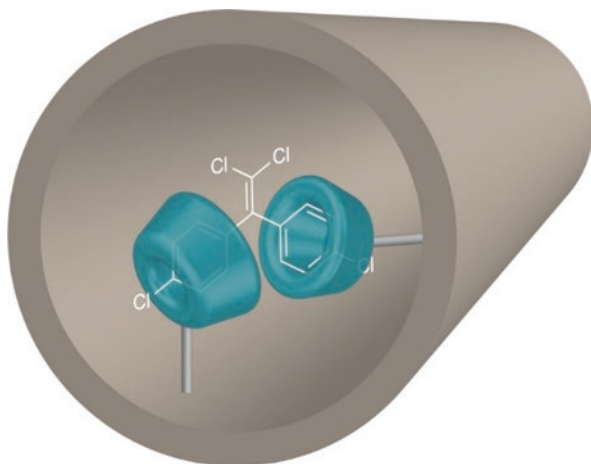

cyclodextrin loadings higher than 8% had poor performance. This can be explained by the destruction of the periodic mesoporous structure with high cyclodextrin amount. Two interesting results were reported by Walcarius and Mercier (2010): (i) the location of cyclodextrin moieties within the structure of a siliceous framework may reduce the materials' susceptibility to chemical and biological degradation; (ii) 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, 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 μmol/g, far inferior to what was reported by Mercier's group (Bibby and Mercier 2003). The synthetic procedure is schematized in Fig. 6.4. The strategy was based on a classical direct co-condensation between the components via a sol-gel pathway but templated by three different surfactants, namely an anionic template (sodium dodecylsulfate SDS), a cationic one (cetyltrimethylammonium bromide CTAB) or a neutral surfactant (Triton X-45, a nonionic polyethylene oxide containing an aromatic part). Each of them presents difference on the pore size and the repartition of the chemical groups. However, in the three cases, the use of the surfactant gave materials with smaller pores. Adsorption mechanism was interpreted by the presence of two main interactions between *p*-nitrophenol and the porous organo-silica depending on the surfactant used: hydrogen bonds and inclusion complex with Triton X-45, ionic interactions and inclusion complex with SDS and CTAB. No significant differences were observed for the three bifunctional materials.
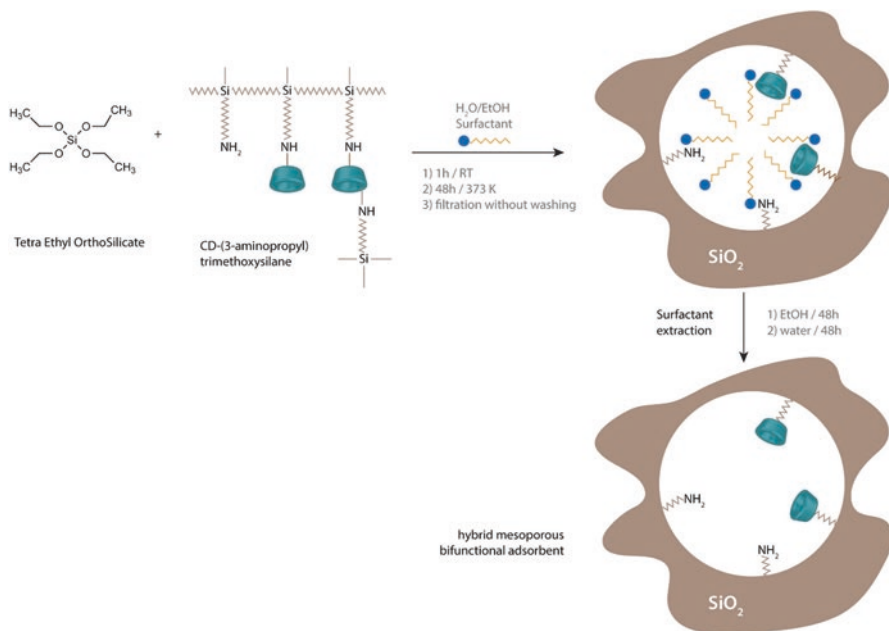
Fig. 6.4 Preparation of templated hybrid mesoporous bifunctional organo-silica proposed by Degoutin and Bacquet (2013)

Others researchers also reported that samples with high cyclodextrin molecules loading (up to 6%) were generally 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 co-polymerization of a silylated cyclodextrin monomer with tetraethylorthosilane in the presence of cetyltrimethylammonium bromide template. Fig. 6.5 depicts the synthesis procedure. Surfactant extraction resulted in an adsorbent containing covalently bound microporous cyclodextrin moieties capable to adsorb efficiently humic acid from water. Nitrogen adsorption experiments showed that cyclodextrin-silica-4% material had a BET surface area of 460 m^2/g and an average mesopore diameter of 2.52 nm. Small-angle powder XRD pattern of cyclodextrin-silica-4% material revealed the lack of highly ordered mesoporous structure. Solid-state C-13 and Si-29 nuclear magnetic resonance (NMR) 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 chromatographic separation.
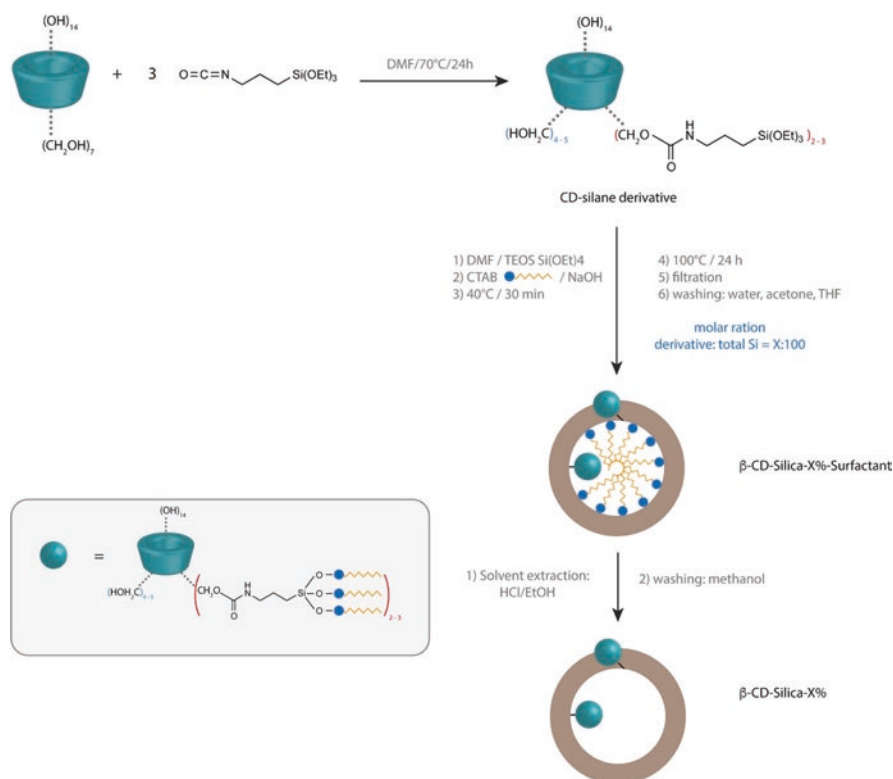
Fig. 6.5 Synthesis of mesoporous organo-silica material containing microporous cyclodextrin molecules (adapted from Liu et al. 2004)

Gibson (2014) recently published an interesting tutorial review on the removal of organic pollutants from the aqueous phase by mesoporous silica. After a discussion about mesosilica formation (MCM-41 and SBA-15) and silica surface modification, the review focused on the use of mesosilica for the removal of organic compounds such as dyes and phenols, and emerging contaminants, e.g. 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 2–8%) 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 incorporation of cyclodextrin within the mesoporous framework was supported by spectroscopic techniques such as Fourier transform infrared (FT-IR) spectroscopy, Raman, mass spectrometry (MS) and NMR, and thermogravimetric analysis (TGA) data (Mahmud and Wilson 2016). The MALDI-TOF MS characterization and adsorption data provided corroborating support that cyclodextrin molecules were incorporated within and onto the surface of the silica framework. Small-angle XRD and nitrogen adsorption also provided evidence of ordered silica mesostructured frameworks. C-13 solid cross-polarization magic angle spinning (CPMAS) NMR 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 of 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. TGA 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 to 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 (CH_3Cl and 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 CH_3Cl in the gas phase and for *p*-nitrophenol in aqueous solution adopted a multi-layer 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.

Alahmadi et al. (2014) studied the covalent attachment of cyclodextrin on MCM-41 through two different reactions using toluene diisocyanate as linker. The FT-IR spectra and TGA analysis demonstrated that the cyclodextrin molecules were covalently attached to the mesoporous silica while the preservation of the MCM-41 channel system was checked by XRD and nitrogen adsorption analysis. These materials were used to evaluate the adsorption properties of organotin compounds such as tributyltin, triphenyltin and dibutyltin. The results showed that mesoporous silica MCM-41 functionalized with cyclodextrin, using toluene diisocyanate, was a more highly effective adsorbent for organotin compounds especially for triphenyltin, compared to mesoporous silica MCM-41 functionalized with cyclodextrin using 3-chloropropyltriethoxysilane and toluene diisocyanate as linkers.

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 CTAB. The successful incorporation of cyclic oligosaccharide moieties in silica surface layer was verified by means of FT-IR spectroscopy and elemental analysis. Obtained cyclodextrin-containing materials were characterized by XRD, TEM, and low-temperature adsorption-desorption of nitrogen. In spite of commensurable loading of cyclodextrin groups attained by both proposed approaches (up to 0.028 μmol/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. Langmuir and Freundlich models were used to evaluate adsorption processes and parameters. 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.

Kawamura et al. (2015) prepared novel organic-inorganic hybrid nanoparticles with a bisphenol A (BPA)-responsive hydrogel layer on the surface of SiO$_2$ nanoparticles via surface-initiated atom transfer radical polymerization of acrylamide (AAm), acryloyl-modified cyclodextrin and N,N'-methylenebisacrylamide. The resulting CD-PAAm/SiO$_2$ nanoparticles underwent a change in size in response to
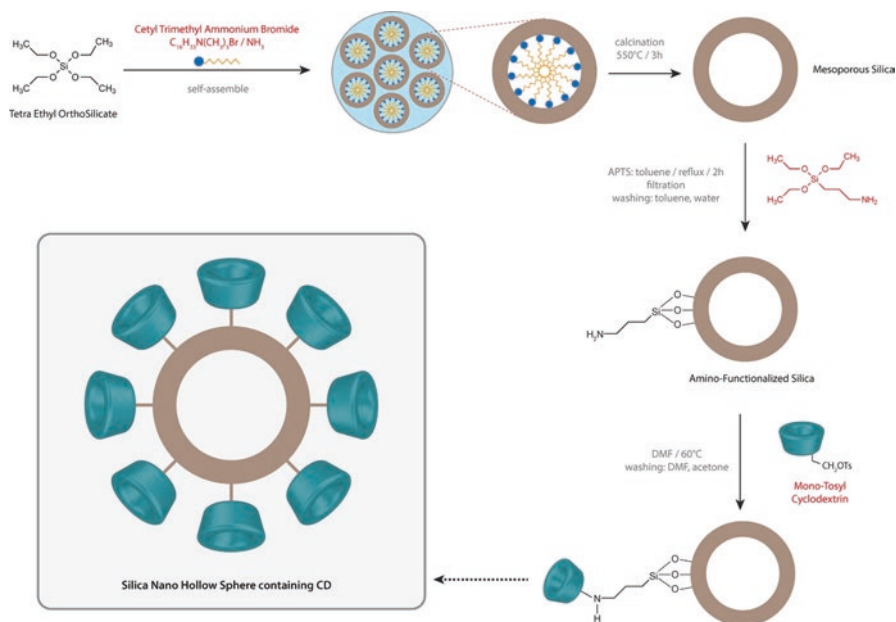
Fig. 6.6 Modification of silica nano-hollow sphere containing cyclodextrin molecules (adapted from Ebadi and Rafati 2015)

BPA. The BPA-responsive shrinkage of the CD-PAAm/SiO$_2$ nanoparticles was caused by an increase in the crosslinking density of the CD-PAAm hydrogel layer, which resulted from the formation of CD-BPA-CD complexes acting as dynamic crosslinks. The authors concluded that the smart functions of BPA-responsive hybrid nanoparticles could provide useful tools for constructing molecular sensors and adsorption materials.

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 were proposed by sol-gel method using amino-functionalized silica and mono-tosyl-cyclodextrin derivatives according the procedure described in Fig. 6.6. Structure of nanoparticles was identified by scanning electron microscopy (SEM) images and FT-IR spectroscopy. Nanoparticles showed regular sphere particles with radius less than 100 nm, with a surface area of 754 m^2/g (from BET data). FT-IR data also indicated both the grafting and crosslinking of cyclodextrin molecules onto nanoparticles. Adsorption behaviors of methylene blue onto nanoparticles were studied from equilibrium and kinetic viewpoints. Experimental data showed that 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 ground water.

Mesoporous silicas containing cyclodextrin were also useful for pollutants present in air samples and for drug complexation. Mauri-Aucejo et al. (2012, 2015, 2016) published a series of works on the determination of phenolic compounds, polycyclic aromatic hydrocarbons (PAH) and volatile organic compounds (VOC) in air and in water samples by using cyclodextrin-silica hybrid composites. The preparation of these materials was very easy and inexpensive. Proposed samplers compared with other conventional solid phases present the advantages of a wider range of operative conditions for VOC desorption (Mauri-Aucejo et al. 2012). Samplers were tested based on results for the determination of BTEX, i.e. benzene, toluene, ethylbenzene, *o-*, *m-* and *p-*xylene, in air. Operational parameters were optimized and quantitative recovery was obtained using a solid phase from 2-hydroxypropyl-beta- cyclodextrin and acetonitrile as the extraction solvent. The recoveries obtained were $89 \pm 4\%$ for benzene, $90 \pm 6\%$ for toluene, $91 \pm 2\%$ for ethylbenzene, and $87.0 \pm 0.9\%$, $88 \pm 4\%$, $88 \pm 4\%$ for *o-*, *m-* and *p-*xylene, respectively. Moreover, results indicated a good reproducibility with a coefficient of variation below 6% and no significant difference between the reproducibility intra-synthesis and inter-synthesis. The proposed procedure has been applied to the determination of BTEX in several contaminated air samples and compared with results provided by a reference method. The authors also showed that cyclodextrin-silica composite samplers were particularly suitable for the sampling of phenol, cresol isomers, eugenol, guaiacol, 4-ethylguaiacol, and *p-*ethylphenol in air samples. The proposed method constituted an alternative to other methods due to low-cost and higher recoveries.

In another work (Mauri-Aucejo et al. 2015), the method has been applied to the assessment of exposure in different areas of a farm and regarding the quantification of these compounds in the vapors generated by burning incense sticks and an essential oil marketed as air fresheners. The acquired results were comparable with those provided from a reference method for a 95% of confidence level. The possible use of these samplers for other toxic compounds such as phthalates was also evaluated by qualitative analysis of extracts from incense sticks and essential oil samples. In a recent work (Mauri-Aucejo et al. 2016), the authors used the materials as adsorbent in solid-phase extraction combined with high-performance liquid chromatography to determine PAH in water samples. The experimental results indicated that the material exhibited high adsorption capacities toward PAH. Under optimum conditions, the quantification limits of the method were in the range of 0.09–2.4 μg/L and fine linear correlations between peak height and concentration were found around 1.3–70 μg/L. The method had good repeatability and reproducibility, with coefficients of variation under 8%. Due to the concentration results, this material might represent an alternative for trace analysis of PAH in water trough solid phase extraction.

Results on drug complexation by mesoporous silicas containing cyclodextrin were reported by Pasqua et al. (2013). Ordered silicas 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_{BET} = 766 m^2/g) was first let to react with 3-glycidoxypropyltrimethoxysilane (GPTS) 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, a silica suitably functionalized with a terminal thiol group, obtained by the reaction of SBA-15 silica with 3-mercaptopropyltrimethoxy-silane, was reacted with mono-tosyl-cyclodextrin (Fig. 6.7). The obtained materials (denoted SC1 and SC2) were characterized by XRD, nitrogen adsorption, SEM and C-13 CP/MAS NMR. The BET surface area obtained were 150 m^2/g and 190 m^2/g for SC1 and SC2, respectively. NMR solid state spectroscopy permitted a complete characterization for both materials. SEM 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 device (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.
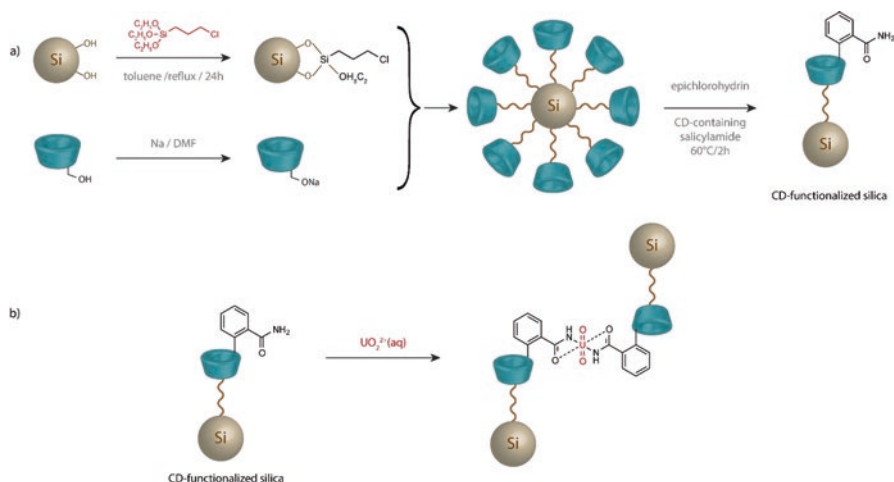
6.5   Cyclodextrin-Functionalized Silica Materials

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_2^{2+} removal (Fig. 6.8). 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_2^{2+} concentration 25 mg/L, the equilibrium adsorption capacity was found to be 6.45 mg/g. Adsorption performances were strongly pH-dependent. Modelling 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 enthalpy change. The new material also adsorbed UO_2^{2+} in aqueous solution in presence of interfering ions such as Na^+, Fe^{3+}, Cu^{2+}, Mg^{2+}, La^{3+}, Mn^{2+}, Zn^{2+}, Pb^{2+} and Hg^{2+}. 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.
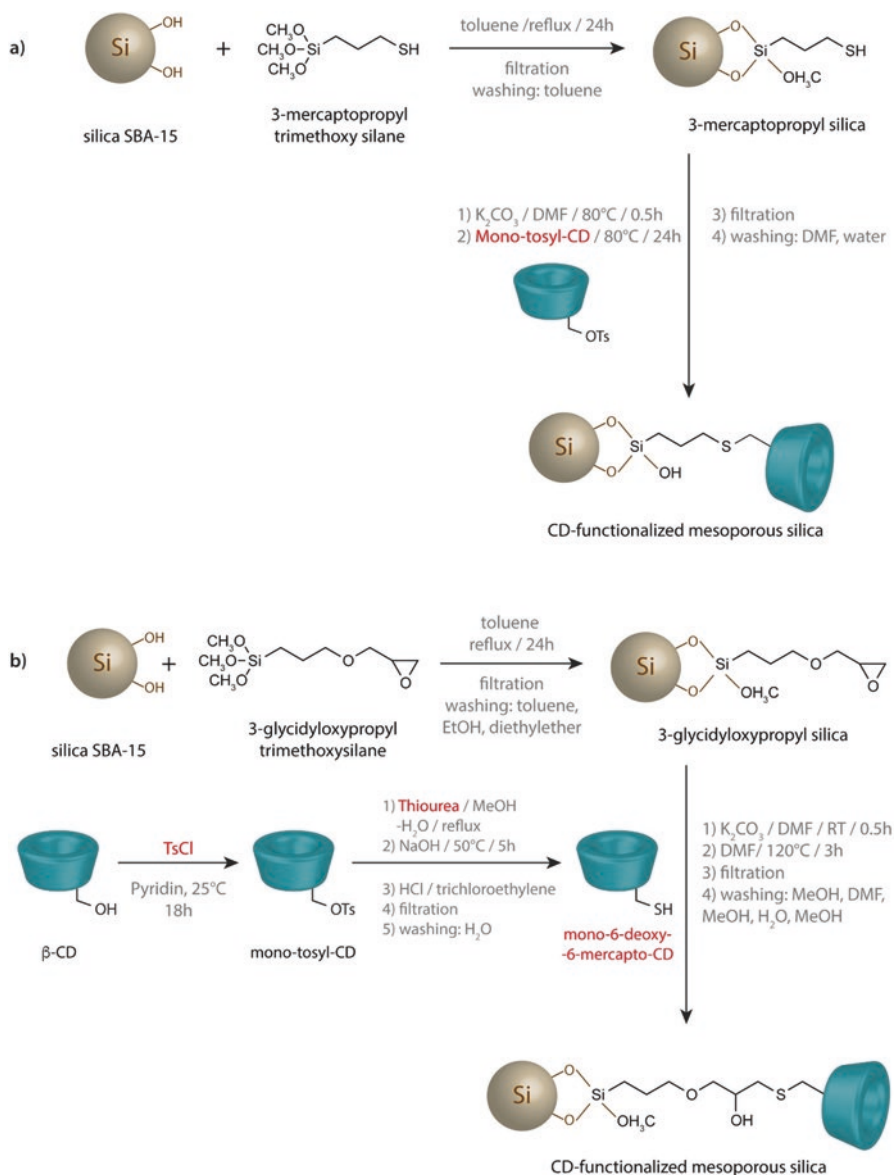
Fig. 6.7 Synthetic strategies proposed by Pasqua et al. (2013) to prepare cyclodextrin-functionalized mesoporous silica
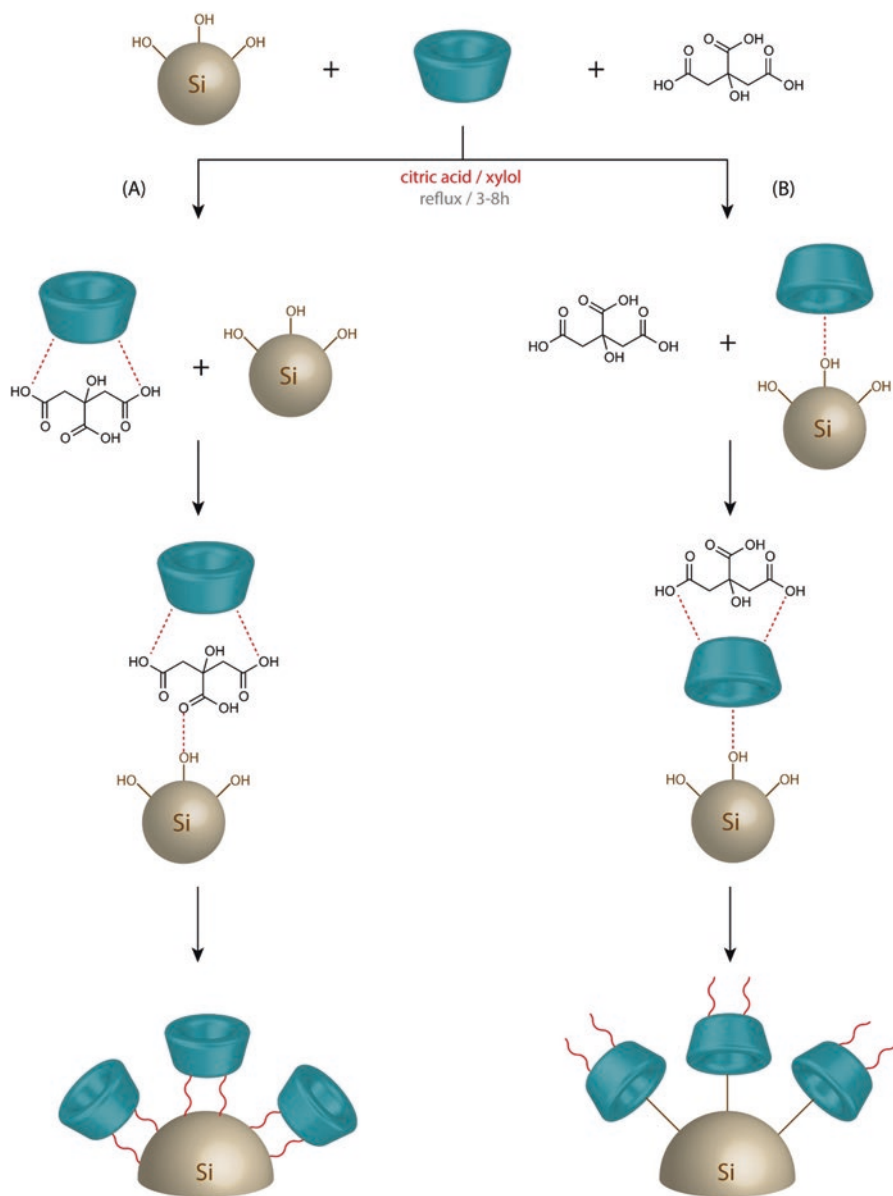
De Carvalho et al. (2014) proposed a cyclodextrin-functionalized silica adsorbent for the removal of methylene blue in aqueous media. Modification of the silica surface using cyclodextrin (~44%) was performed in one-step by refluxing using citric acid as a linking agent (Fig. 6.9). The material obtained was characterized

Fig. 6.8 (a) Synthesis of cyclodextrin functionalized silica gel and (b) its application for adsorption of uranium(VI) (adapted from Liu et al. 2016b)

using SEM, FT-IR spectroscopy, XRD and TGA. Based on these data, the authors showed that two mechanisms might occur in solution during the synthesis, as shown in Fig. 6.9. In the first route (A), an intermediary was formed between the linking agent and the cyclodextrin molecules which became both more active and capable of being functionalized to the surface of the silica. In a second route (B), the cyclodextrin molecules might be modified with groups from citric acid and became covalently linked to the surface of the silica without the direct intervention of the linking agent. However, it was difficult to choose between these two mechanisms and more studies should be conducted to improve knowledge of the functionalization mechanism. The authors reported interesting adsorption capacities. Indeed, 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 removal of dyes from aqueous media, and could therefore substitute 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

Fig. 6.9 Functionalization of silica gel with cyclodextrin molecules using citric acid as a bonding agent (adapted from de Carvalho et al. 2014)

disperse silica with the following characteristics: specific surface area 133 m²/g, particle size 0.3–0.5 mm, concentration of silanol groups 0.4 mmol/g, adsorption pore volume 0.8 cm³/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. The material obtained by grafting of mono-tosyl-cyclodextrin was denoted CD-1-SiO$_2$, the one obtained with bromoacetyl-cyclodextrin, CD-2-SiO$_2$ and the one obtained with thiosemicarbazidoacetyl-cyclodextrin, CD-3-SiO$_2$. They were characterized by elemental analysis, adsorption/desorption of nitrogen, potentiometric titration, SEM, TGA and FT-IR spectroscopy. In all cases, the chemical modification of the surface of the silica by cyclodextrin molecules leaded 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. Cyclodextrin content were similar in the three types of materials: 0.02, 0.01 and 0.1 mmol/g for CD-1-SiO$_2$, CD-2-SiO$_2$ and CD-3-SiO$_2$, respectively. 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 was confirmed by a detailed FT-IR analysis (Belyakova and Lyashenko 2014). The authors clearly indicated that only the side functional groups of the grafted cyclodextrin were the real adsorption sites for metal removal. The adsorption ability of cyclodextrin-silicas with respect to mercury(II) and cadmium(II) increased in the series CD-1-SiO$_2$ < CD-2-SiO$_2$ < CD-3-SiO$_2$. For zinc (II), the series was CD-1-SiO$_2$ < CD-3-SiO$_2$ < CD-2-SiO$_2$. The maximum monolayer capacities for mercury(II) were: 34 ± 2, 12.6 ± 0.6 and 22 ± 1 mg/g for CD-1-SiO$_2$, CD-2-SiO$_2$, and CD-3-SiO$_2$, respectively. These results were consistent with the chemical and elemental analysis data for supramolecular compounds formed on the surface of nanoporous CD-silicas. The data were also in agreement with Pearson's theory. The softness of the side functional groups of the wide edge of cyclodextrin increased in the series secondary alcohol < bromoacetyl < thiosemicarbazidoacetyl groups. Belyakova and Lyashenko (2014) concluded that supramolecular surface structures formed whose chemical composition depended on the nature of the adsorbed cations and the functional substituents in the grafted cyclodextrin molecules. 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 functional cyclodextrin-containing silica was the formation of inclusion complexes cyclodextrin-nitrate-anion. The results demonstrated high affinity of nanoporous organo-silica 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 multi-component 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. It has been proved the formation of supramolecular structures on the surface of synthesized organosilicas as a result of cadmium (II) adsorption.

Shen's group (Shen et al. 2014a, b; Shen et al. 2015a, b; Han et al. 2016) 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 according to the procedure described in Fig. 6.10 (Shen et al. 2015a). The obtained CD@Si adsorbent was characterized through FT-IR spectroscopy, X-ray photoelectron spectroscopy (XPS), contact angle measurement, TGA, solid-state C-13 NMR, SEM, and XRD analyses. FT-IR spectroscopy, XPS and NMR data demonstrated the successful graft of cyclodextrin molecules on silica surface. From TGA data, the amount of cyclodextrin grafted was estimated about 20% (w/w). SEM 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 (i) 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 CD; (ii) the adsorption process followed the pseudo-second-order and Freundlich models; (iii) thermodynamic data indicated that the process was spontaneous and exothermic but temperature-dependent (adsorption was more favorable in lower temperature); and (iv) 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 as illustrated in Fig. 6.10. 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 several emerging pollutants such as steroid hormones (17-β-estradiol), bisphenol A and perfluorooctanoic acid. Three different approaches were used to functionalize cyclodextrin onto silica (40x100 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 (EPI) or hexamethylene diisocyanate (HMDI). In the second method, cyclodextrin were supported on silica with copolymers glycidoxypropyltrimethoxysilane (GPTS) and 3-aminopropyltriethoxysilane (APTES). In the third approach, cyclodextrin were coated on silica with both cross-linking agents (EPI or HMDI) and copolymers (GPTS or APTES). Fourteen different adsorbents were synthesized under different experimental conditions, e.g. solvent, temperature, and reactant concentration. All the adsorbents were characterized using FT-IR, TEM and TGA techniques, and
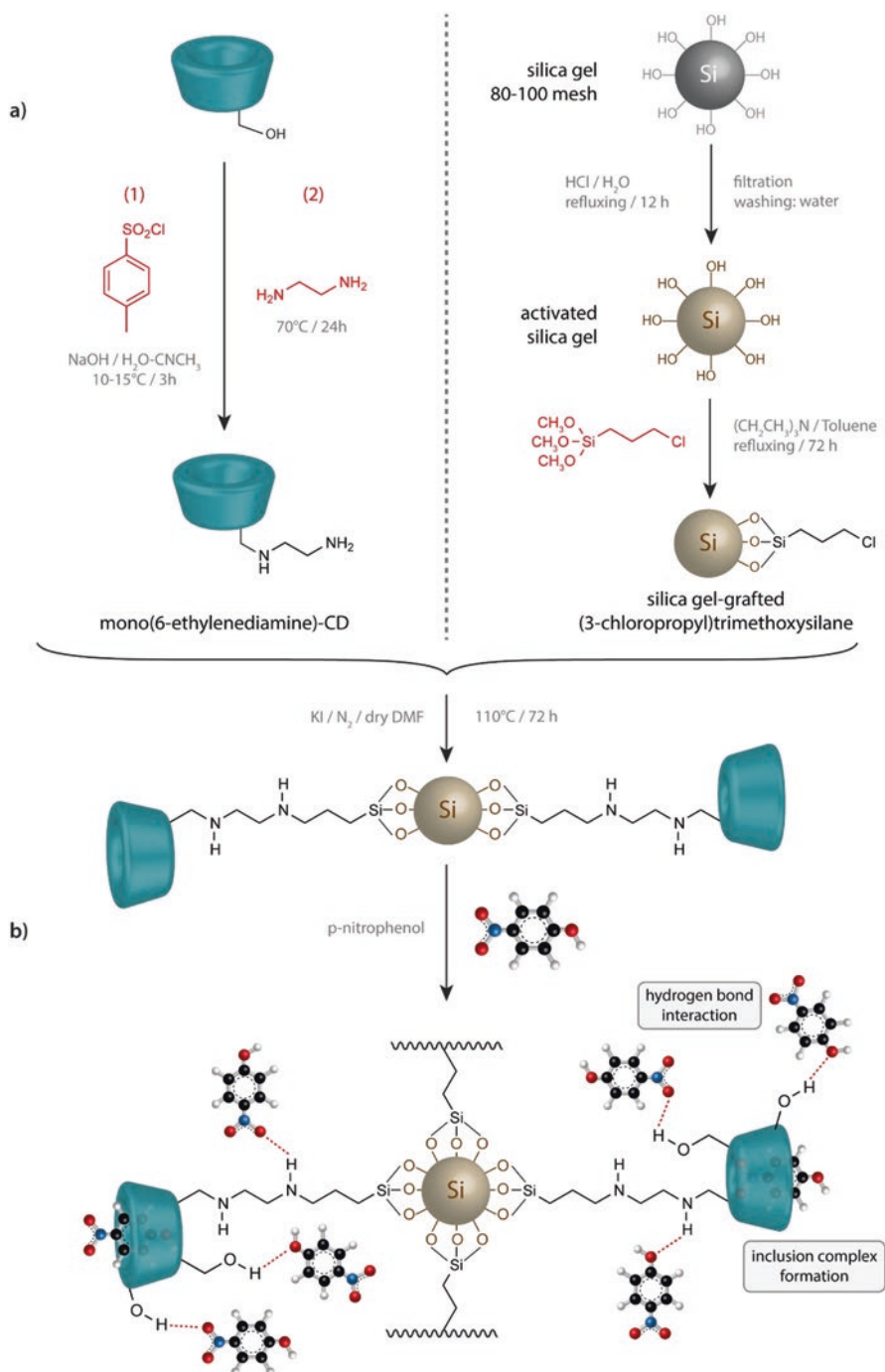
Fig. 6.10 (a) Preparation of cyclodextrin-grafted silica according to Shen et al. (2015a) and (b) adsorption mechanism proposed for *p*-nitrophenol removal from aqueous solution

nitrogen adsorption analysis. Adsorption results showed that the material prepared by using HMDI as crosslinking agent with DMSO as solvent was the best in term of performance for the removal of 17-β-estradiol, perfluorooctanoic acid, and bisphenol A with more than 90% abatement in all case. 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 ± 5.6 µg/g) for 17-β-estradiol when compared with that of commercially available activated carbon (23.6 ± 6.3 µ/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 were less than 1 m^2/g), and also possible numerous inter-molecular hydrogen bond interactions between the cyclodextrin host molecules and the guest pollutants.

3,5-dimethylphenylcarbamoylated cyclodextrin bonded silica gel was used as adsorbent in solid-phase extraction to selectively enrich forchlorfenuron and thidiazuron, a plant growth regulators used on kiwi fruits and grapes for example, followed by determination with surface-enhanced Raman spectroscopy (Chen et al. 2016). This new adsorbent exhibited high adsorption capacities, 40 and 30 µg/g for chlorfenuron and thidiazuron, respectively, and showed excellent selectivity.

A highly effective clean-up 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$_2$ can remove most of 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 clean-up 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%.

6.6 Other Materials

Matias et al. (2015) proposed porous silica-based aerogels/xerogels containing cyclodextrin with different degrees of hydrophobicity/hydrophilicity as adsorbents for phenolic compounds removal. The materials were synthesized by using a combination of methyltrimethoxysilane (MTMS) and tetramethylorthosilicate precursors in different proportions, in order to provide a variable number of methyl and hydroxyl groups in the aerogels structure, and by cyclodextrin functionalization of the aerogels to introduce possible inclusion complex formation. The sol-gel synthesis followed a one-step NH_4OH-catalyzed procedure and the drying of the gels was accomplished by supercritical fluid drying/extraction with CO_2, to obtain aerogels, and evaporative drying, to produce xerogels. The characterization of materials showed that silica-based aerogels/xerogels containing cyclodextrin had high surface area (800 m^2/g) and tailored levels of hydrophobicity/hydrophilicity. The aerogels with intermediate and high contact angles showed higher adsorption capacities, with favorable isotherms, for the phenolic compounds, such as phenol, *p*-cresol and *p*-chlorophenol, with higher hydrophobicity, which showed the important role of hydrophobic interactions in the adsorption process. The best results were obtained for the aerogel functionalized with cyclodextrin when adsorbing the *p*-chlorophenol (adsorption capacity 117.8 mg/g), proving the positive effect of the presence of the cyclodextrin hydrophobic cavity in the adsorption of this highly hydrophobic pollutant.

Chen et al. (2014) synthetized cyclodextrin-modified cellulose nanocrystals (CNC)@Fe_3O_4@SiO_2 superparamagnetic nanorods for the removal of two model drugs (procaine hydrochloride and imipramine hydrochloride). Cellulose nanocrystals and silica served as supporting template and coating materials, respectively. The silica shell was previously functionalized with primary amine and then reacted with mono-chlorotriazine-cyclodextrin derivative. Cellulose nanocrystals are attracting increasing interest due to their abundance, uniform nanorod shape, good mechanical strength, liquid crystalline character, high specific surface area, biocompatibility, biodegradability, and sustainability. Cellulose nanocrystals can be produced at an industrial scale by acid hydrolysis of pulp fibers. During the synthetic process proposed by the authors, sustainable natural materials and low-cost chemicals were used, and mild reaction conditions were adopted. TEM and SEM images indicated good dispersion of Fe_3O_4 nanoparticles with uniform silica coating on Cellulose nanocrystals. The thickness of the silica coating was controlled by manipulating the amounts of precursor solution used. TGA data confirmed that the silica coating significantly enhanced the thermal stability of cellulose nanocrystals. The onset decomposition temperature of CNC@Fe_3O_4@SiO_2 hybrids increased by 60 °C compared to pure cellulose nanocrystals. XRD, energy-dispersive X-ray spectroscopy (EDS), and FT-IR analyses confirmed the structure of CNC@Fe_3O_4@SiO_2 and the successful grafting of CD. The CNC@Fe_3O_4@SiO_2@CD hybrids displayed good adsorption toward the two pharmaceutical compounds. The adsorption capacities were determined to be 13 ± 0.09 mg/g and 14.8 ± 0.16 mg/g for procaine

hydrochloride and imipramine hydrochloride, respectively. Compared with conventional membrane separations that generally suffer from fouling, poor permeate quality and low flux enhancement, the magnetic separation proposed by the authors demonstrated several advantages including simple cleanup, good magnetic properties, effective adsorption characteristic toward two model drugs with fast kinetics, and easy recovery of materials. The authors concluded that the procedure reported can be extended to prepare other inorganic-organic nanocomposites using cellulose nanocrystals as the template material.

Superparamagnetic Fe_3O_4 core could be rapidly separated from matrix to simplify time-consuming washing extraction as reported by Wang et al. (2015). These authors proposed core-shell superparamagnetic Fe_3O_4@CD composites for host-guest adsorption of polychlorinated biphenyls (PCB). Their protocol involved the synthesis of Fe_3O_4 particles through a solvothermal reaction and the covering of a silica layer bonded cyclodextrin over Fe_3O_4 via a sol-gel process to produce core-shell Fe_3O_4@CD composites. Cyclodextrin molecules were linked covalently to Fe_3O_4 nanoparticles to generate the binding sites, enhancing the stability of Fe_3O_4 nanoparticles in water. The adsorption capacity of composites to PCB28 and PCB52 in aqueous solutions was investigated. To estimate the theoretical binding site number of Fe_3O_4@CD, the obtained binding data were replotted according to Scatchard equation. The host-guest interaction between cyclodextrin and PCB were further examined with density functional theory calculations. It provided theoretical evidence of cyclodextrin as host molecule had a higher binding amount towards PCB-28 than PCB-52 on the basis of their optimized geometries and calculated complexation energies. The authors concluded that the new nanomaterial was an ideal candidate for various applications, including the recognition and removal of environmentally deleterious substances.

Although cholesterol plays significant biochemical function in the human body, excess of it leads to various disorders, and thus, its control/separation is important in medical science and food industries. However, efficient and selective separation of cholesterol is challenging because cholesterol often exists in microheterogeneous or insoluble forms in remote organ and exists with other substances. Sinha et al. (2015) have described a colloidal magnetic mesoporous silica-based approach for efficient separation of cholesterol in different forms. Magnetic mesoporous silica was functionalized with cyclodextrin for selective binding with cholesterol via host-guest interaction. The colloidal form of magnetic mesoporous silica offered effective interaction with cholesterol of any form, and magnetic property of magnetic mesoporous silica offered easier separation of bound cholesterol. Functionalized material was efficient in separating cholesterol crystals, water-insoluble cholesterol, and the microheterogeneous form of cholesterol from milk or a cellular environment. The authors concluded that the new material could be used to remove cholesterol from a complex environment and extended for large-scale cholesterol separation from food.

Ennist et al. (2014) synthesized novel dendronized silica substrates that adsorbed targeted analytes. First- and second- generation poly(arylether) dendrons were appended to silica surfaces. Using Cu(I) mediated cycloaddition click chemistry,

cyclodextrin was tethered to the dendronized surfaces and to a nondendronized surface for comparison purposes. This synthesis strategy afforded a modular, versatile method for surface functionalization in which the density of functional groups could be readily varied by changing the generation of dendron used. The surfaces have been characterized and studied using XPS and vibrational sum frequency spectroscopy. Fluorescence spectroscopy was used to study the surfaces' ability to retain coumarin 152 (C152). These studies indicated that the cyclodextrin-functionalized surfaces not only adsorbed C152 but also retained it through multiple aqueous washes. Furthermore, these observations were quantified and showed that substrates functionalized with first-generation dendrons had a more than 6 times greater capacity to adsorb C152 than slides functionalized with monomeric cyclodextrin. The first-generation dendrons also had 2 times greater the capacity than the larger generation dendrons. This result was explained by describing a dendron that had an increased number of cyclodextrin monomers but, when covalently bound to silica, had a footprint too large to optimize the number of accessible monomers. Overall, both dendronized surfaces demonstrated an increased capacity to adsorb targeted analytes over the slides functionalized with monomeric cyclodextrin. Their study provided a methodology for characterizing and evaluating the properties of novel, highly functional surfaces.

6.7 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. The recent state-of-the-art in their synthesis is reviewed in this chapter, based on a substantial number of relevant references published recently. Of course, this is an ambitious project since a direct comparison of data obtained using different materials is difficult to make. Nevertheless, as demonstrated in this chapter, 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 is mainly focused on the performances of these innovative materials, while their economic aspect is neglected. Cost is an important parameter for comparing adsorbents. An important question is the following: could mesosilica adsorbents compete with conventional activated carbon (that are produced on a significantly larger scale) in price, durability and efficiency? To date, there is no systematic and comparative study. Mesosilica is not yet produced on an industrial scale. In addition, starting materials such as alkoxides as the silica source are relatively expensive and the

product made from them can only find use in applications such as catalysis or CO_2 capture where price is not a major issue. Recently, the use of inexpensive inorganic silicates (water glass) has been proposed in the synthesis of mesostructured materials (Han and Zhang 2012; Al Othman 2012).

In addition, although extensive work has been done, future research needs to look into some of the following aspects. Numerous progresses have been realized on the control of the structure and at the same time control of the size and the size distribution of the particles, and the cyclodextrin content of different materials. The chemical procedures involving multistep reactions are also well-known. However, several issues related to the synthesis using eco-friendly procedures are still poorly investigated. Adsorption processes are basically at the stage of laboratory-scale study in spite of unquestionable progresses. Much work is necessary to demonstrate the possibilities on an industrial scale. The experimental conditions should be chosen to simulate real effluents on the basis of thermodynamics and reaction kinetics studies. Indeed, a major challenge is the design of mesosilica in a form compatible with treatment of large volumes of polycontamined real effluents. The use of these materials is still underdeveloped in real-world environmental remediation applications. For example, only a few reports have focused on their use for the 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. Significant decreases in crystallinity, average pore diameter and pore volume can be observed when the materials were used in alkaline conditions. So, it is necessary to continue to search for and select the most promising types of cyclodextrin-silica materials. Finally, the works reviewed in this chapter indicated that adsorption onto these new materials is becoming a promising alternative to replace conventional materials although the mechanisms involved are not fully understood.

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