



**Mesosilica Materials and Organic Pollutant Adsorption: Part
B Removal From Aqueous Solution**

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Mesoporous Materials and Organic Pollutant Adsorption: Part B Removal From Aqueous Solution.

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Abstract

This tutorial review will focus on the removal of organic pollutants from the aqueous phase by mesoporous silica. After a brief discussion about mesoporous silica formation (MCM-41 and SBA-15) and silica surface modification, the review will focus on the use of mesoporous silica for the removal of (i) organic compounds, (ii) organic dyes, or (iii) pharmaceuticals from aqueous solutions.

1. A brief summary of MCM-41 and SBA-15 production

Ordered mesoporous silicates are a class of materials that share the amorphous characteristics of gels and the ordered porosity of crystalline materials such as zeolites. These periodic materials consist of extended inorganic or inorganic-organic hybrid arrays with exceptional long-range order, highly tunable textural and surface properties and controlled pore size and geometry. Their robust structure and long channels (see Figure 1) make them attractive materials as adsorbent platforms allowing diffusion of gases or liquids along the mesochannels providing good opportunities for adsorbent-adsorbate interactions.

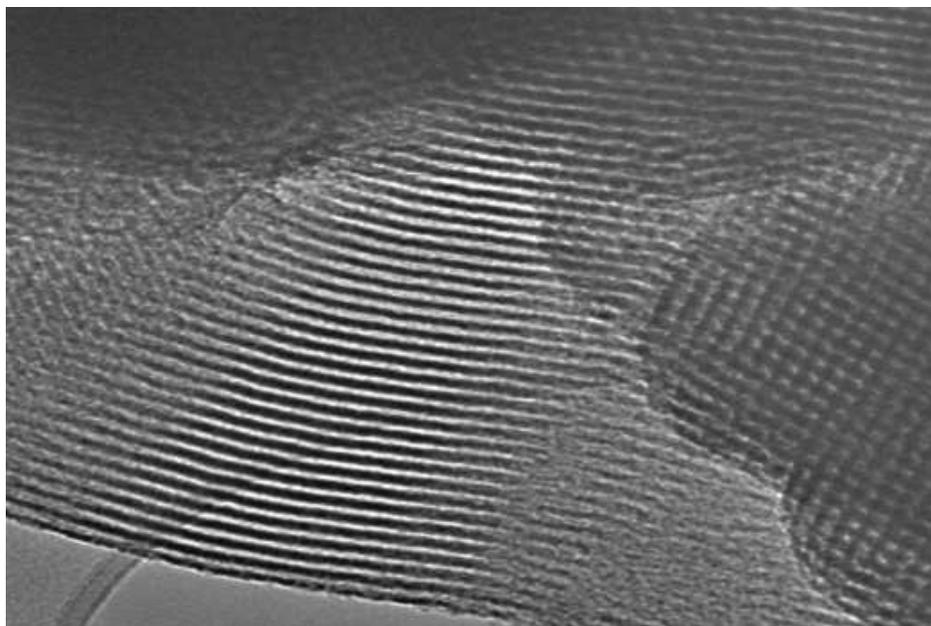


Figure 1: Transmission Electron Micrograph of calcined SBA-15 highlighting the long mesoporous channels.

Mesosilica manufacture combines silica sol-gel chemistry and the use of molecular surfactant assemblies as framework templates. Several types of silica precursors can be used to synthesis mesoporous silica materials; the most common types are alkoxides, especially tetramethyl orthosilicate (TMOS) or tetraethyl orthosilicate (TEOS) however other alkoxides with longer alkyl chains can also be used. Sodium silicate is an alternative, cheaper, silica precursor that can be used individually or in combination with an alkoxide. TEOS is the most studied precursor in the sol-gel process presumably due to its low reactivity towards hydrolysis making it possible to follow and control the reaction more easily. It can hydrolyse or condense under acidic or basic conditions as outlined in Figures 2 and 3. When added to molecular templates that contains hydrophobic and hydrophilic sections the silica self-assembles around the template producing ordered channels. Cetyltrimethyl ammonium bromide (CTAB) is one of the most common cationic surfactants used to produce MCM-41; whereas a non-ionic triblock copolymer (Pluronic-type surfactant or triblock copolymer P123) is the surfactant template of choice for SBA-15 manufacture (see Figure 4).

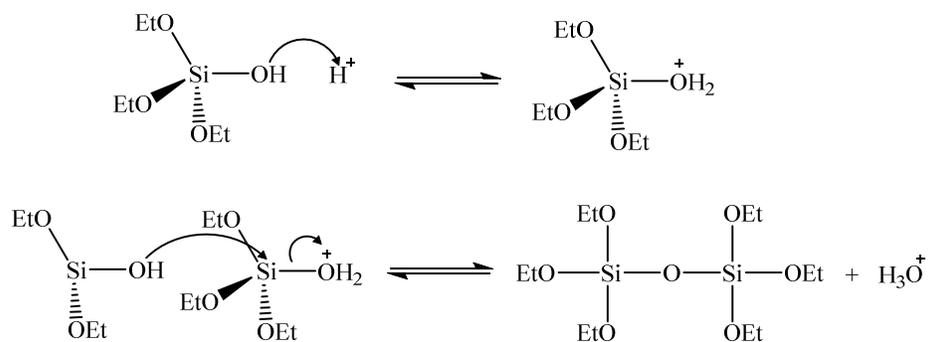


Figure 2: Hydrolysis and condensation of silica under acidic conditions.

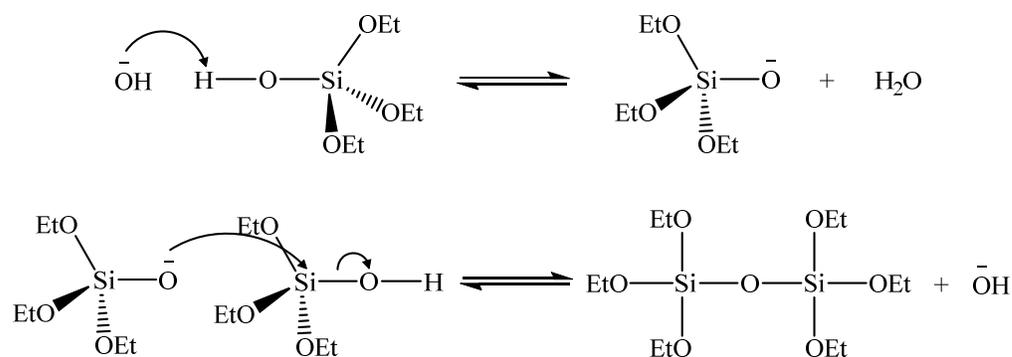


Figure 3: Hydrolysis and condensation of silica under alkaline conditions.

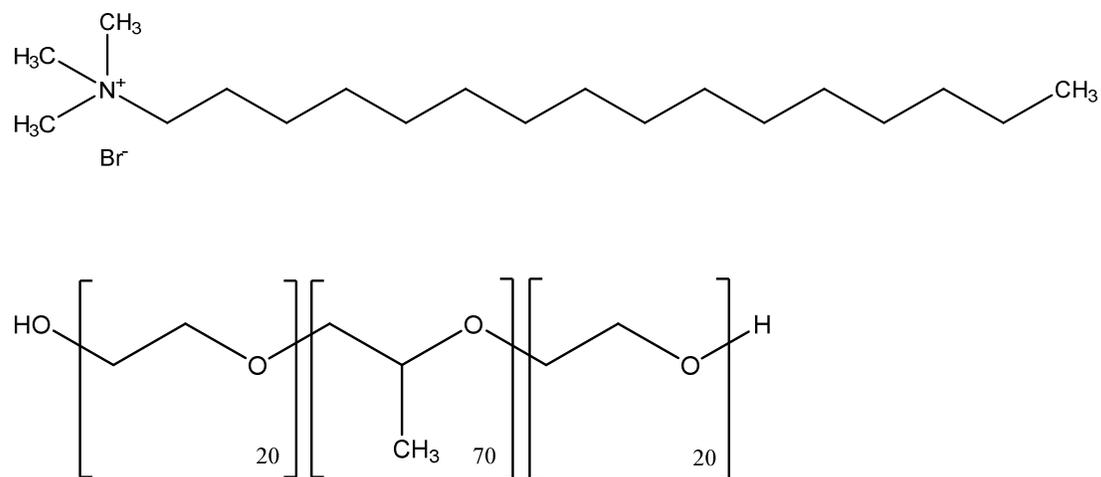


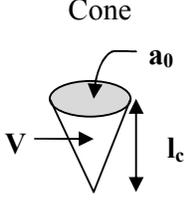
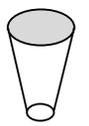
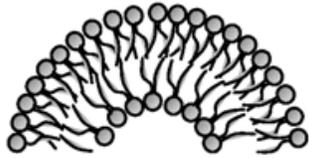
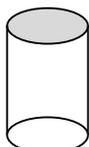
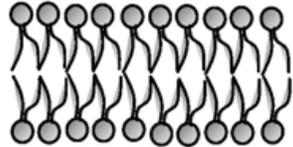
Figure 4: Typical templates used include CTAB (top structure) and P123 (bottom structure).

The final structure of the silica framework is dictated by a variety of factors including the type and concentration of the surfactant used in the templating processes. When added to water, the aggregate shape of a surfactant depends not only on the given concentration but also on the nature of the surfactant itself such as the size, shape and charge of the surfactant molecule. According to a concept introduced by Israelachvili *et. al*¹, predications can be made about the arrangement of different surfactant aggregates just above the critical micellar concentration and thus their corresponding mesophase structures. This concept is known as the packing parameter g ;

$$g = \frac{V}{a_0 l_c}$$

where V is the total volume of the hydrophobic chains plus any co-surfactant organic molecules between the chains, a_0 is the effective head group area and l_c is the critical length of the hydrophobic tail. If the packing parameter is below $1/3$, only spherical micelles exist in the solution. If the surfactant concentration is sufficiently high the spherical micelles will organise into arrays, creating mesostructures with cubic ordering as found in SBA-15. If the packing parameter, g , is between $1/3$ and $1/2$ cylindrical micelles are produced which assemble into ordered hexagonal mesostructures which, on addition of TEOS, leads to the synthesis of MCM-41. Table 1 lists typical g values, demonstrating their use in predicting the structure of the micelle aggregates and therefore the geometry of the final mesophase. When the surfactant molecules remain within the silica framework the term ‘as-synthesised’ materials is used. However, when the synthesis procedure is complete and the material has reached a sufficient degree of condensation, the templating molecules are no longer needed and can be removed to open the porous structure by calcination, solvent extraction or microwave digestion.

Table 1: Expected aggregate characteristics and mesophase structures in relation to surfactant packing parameter, g .

g	Shape of Cross Section	General Surfactant Type	Expected Aggregate Structure	Expected Mesostructure
$<1/3$	Cone 	Single Chain with large head group	Spherical micelles 	Cubic (Pm3n) e.g. SBA-1
$1/3 - 1/2$	Truncated Cone 	Single Chain with small head group	Large cylindrical micelles 	Hexagonal e.g. MCM-41, FSM-16
$1/2 - 1$	Truncated Cone 	Double chain with large head group and flexible chains	Vesicles and flexible bilayers 	Cubic (Ia3d) e.g. MCM-48
1	Cylinder 	Double chain with small head groups or rigid chains	Planar bilayers 	Lamellar e.g. MCM-50

2. Surface Functionalisation

In stark contrast to the use of calcined mesosilica materials for the successful removal of gaseous organic compounds, in aqueous solution calcined mesosilica has very low affinities for the removal of hydrophobic compounds from water because the high silanol density on the silica surface has a preferential attraction for water molecules. Various strategies are therefore used to increase removal performance by increasing the hydrophobicity of the adsorbents. This can be done by the addition of alkyl groups to the surface, and/or pore walls,

of the silica and two methods commonly used to derivatise silanol groups include the post-synthesis grafting (PSG) process or the co-condensation route.

2.1 The PSG process.

The process of grafting, involves modification of the inner surfaces of pre-fabricated mesoporous silica structures with organic groups. This process has three principle objectives: to change the pore wall polarity and adsorption properties using organic groups, to eliminate unreacted silanol groups (passivation) or to introduce specific organic functionality. Common organosilane species used as reactants for the grafting process are chloroorganosilanes ClSiR_3 , alkoxyorganosilanes $(\text{R}'\text{O})_3\text{SiR}$ and silazanes $\text{HN}(\text{SiR}_3)_2$. Among them chloroorganosilanes are hard to control and give rise to unwanted polymerisation reactions, so the other two species are preferentially used. In principle, functionalisation with a wide range of organic groups can be achieved by variation of the organic residue R. A schematic illustration of the PSG process is shown in Figure 5.

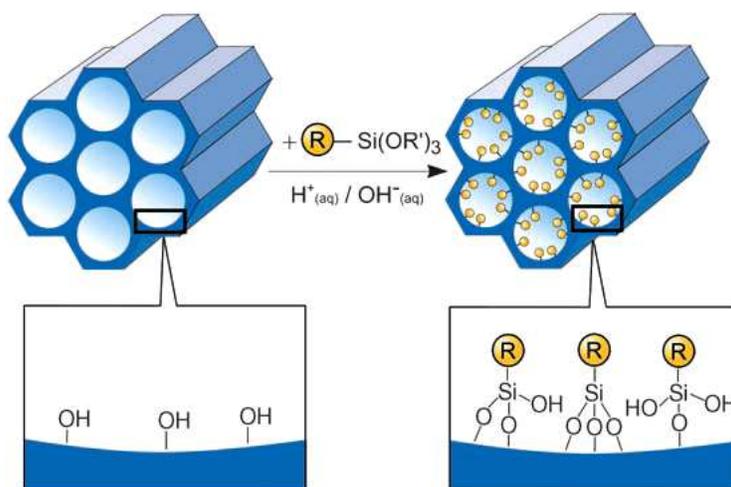


Figure 5: Functionalisation of mesoporous silicates by grafting².

An advantage of the PSG process is that it works on a pre-existent structure, thereby usually retaining the mesostructure of the starting phase and lowering the risk of creating a pore-less material. Nevertheless, depending on the size of the organic molecule and the degree of occupation on the pore walls, the grafting process is accompanied by a reduction in the porosity of the organic-inorganic hybrid material. Additionally the materials obtained by this method can exhibit non homogenous distribution of the organic groups within the pores and a lower degree of occupation.

2.2 Co-condensation method for surface functionalisation

Co-condensation is a direct synthesis method where tetraalkoxysilanes $(RO)_4Si$, e.g. TEOS or TMOS, condenses with terminal trialkoxyorganosilanes $(R'O)_3SiR$ in the presence of a surfactant. Since the organic functionalities (R) are usually hydrophobic they tend to intercalate into the hydrophobic region of the surfactant micelles, causing the incorporated functionalities to modify the pore walls (see Figure 6); therefore pore blockage and shrinkage are not as much of an issue as they are with the PSG process, and the organic units are generally more homogeneously distributed. Additionally co-condensation allows easy control of the final mesoporous silica morphology. Despite these merits, the co-condensation methods also have limitations. First, the addition of organosilanes can dramatically change the characteristic of the reaction solution potentially changing the mesostructure of the final product leading to a disordered or non-porous material; the situation worsening with an increase in organosilane concentration.

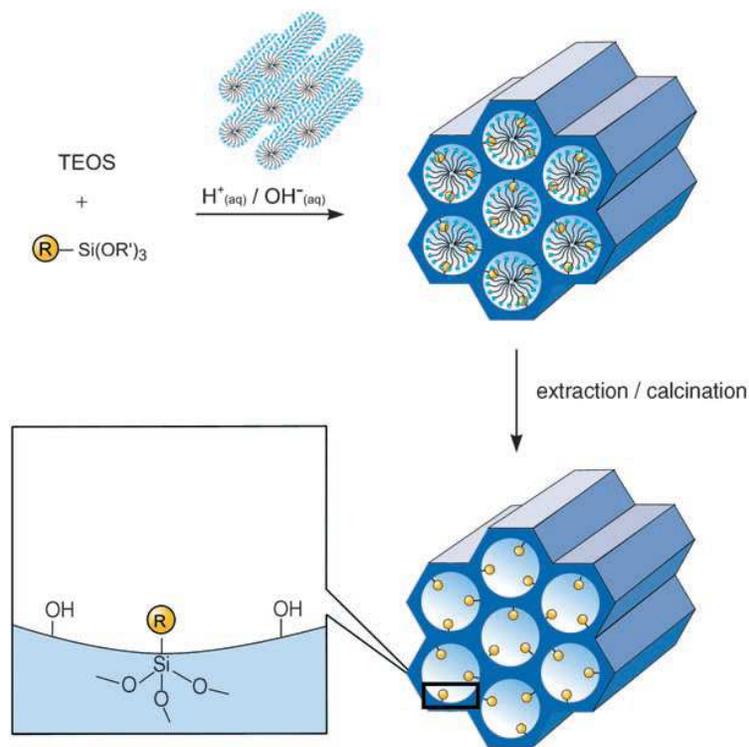


Figure 6: Co-condensation between organoalkoxysilanes and tetraalkoxysilanes to synthesise hybrid inorganic-organic mesoporous silicates².

3. Use of mesosilica materials for the removal of organics from aqueous solution

Since tighter legislative control over the presence of organic pollutants in water supplies, numerous methods have been deployed to sequester pollutants such as phenolic compounds (including alkylphenolic species which are biodegraded products of oestrogen), chlorinated phenolic compounds, polycyclic aromatic hydrocarbons and pesticides. Even at low concentration many organic pollutants can prevent the use, or reuse, of water and removal of these components remains high on political and research agendas. Current mitigation methods are numerous and include the use of photochemical pollutant destruction using ozone, hydrogen peroxide or manganese oxide or by sequestering pollutants onto an adsorbent surface. Various carbon or polymer-based sorbents are used for environmental

remediation however not without their limitations; for example microporous materials are better suited to gaseous adsorption and are less well suited to extraction of organic molecules from aqueous solution as it is more difficult for the target molecules to access the pores. Carbon materials have shown great promise as adsorbents for aqueous solution however they are not selective and regeneration is difficult and costly. For these reasons various research groups have studied mesoporous silica as adsorbents for organic pollutants from aqueous solution in spite of their increased cost; particularly when they can be tuned to target specific molecules, be economically regenerated and reused with high capacity.

As noted above, in contrast to the area of gaseous VOC adsorption, calcined mesosilica has a low affinity for the removal of hydrophobic compounds from water because the high silanol density has a preferential attraction for water molecules. Therefore the surface of the material has to be suitably modified to permit its efficient use in aqueous media. Various strategies have therefore been used to increase the hydrophobicity of mesosilica by using (i) as-synthesised mesosilica, (ii) alkyl-grafted calcined mesosilica (iii) cyclodextrin incorporated mesosilica (iv) mesosilica with aluminium groups (v) as-synthesised SBA-15 or (vi) as-synthesised mesosilica with encapsulated magnetic nanoparticles. Each will be discussed in more detail below.

3.1 Surfactant loaded (as-synthesised) MCM-41

Calcined MCM-41 is not a useful adsorbent in aqueous solution because the unreacted silanol groups will hydrogen-bond with water molecules. Therefore attempts have been made to use as-synthesised MCM-41 (where the silica framework retains the template) to provide pockets of hydrophobic sites where the organic molecules will preferentially diffuse (see Figure 7).

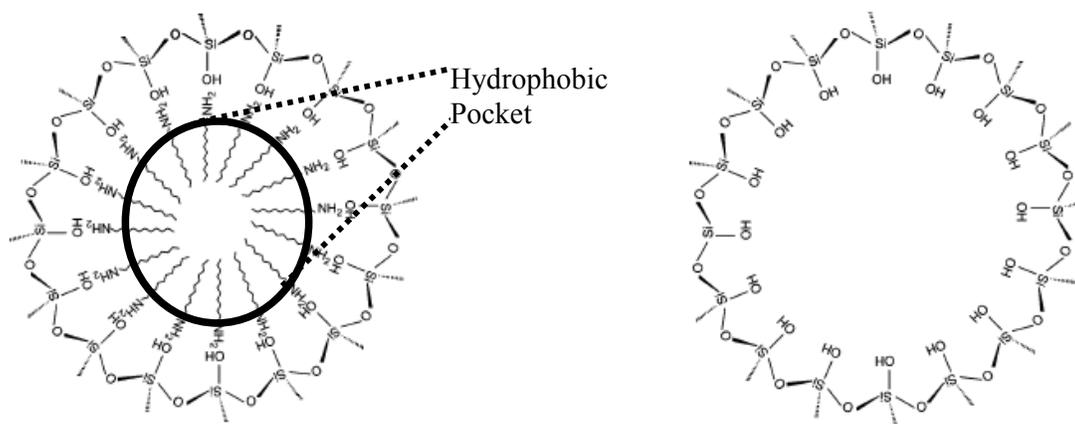


Figure 7: As-synthesised MCM-41 (LHS) and Calcined MCM-41 (RHS)

The first reported results which examined C_{12} , C_{14} or C_{16} templated MCM-41 adsorbents for organic pollutant removal from water assessed the potential to extract 3-chlorophenol³. The capacity values achieved (of 0.91, 1.2 or 1.35 mmol g⁻¹) correlated with increasing alkyl tail length of the surfactant. Different microcalorimetry adsorption enthalpies were measured during adsorption indicating different molecular adsorption sites; it was therefore proposed that after solubilisation in the micelle the surfactant-analyte aggregates were positioned at either the polar head or between the alkyl chains. Extraction of trichloroacetic acid (TCA) was also shown to be effective with surfactant loaded mesosilica, moreover higher adsorbate-adsorbent interactions were measured for materials containing higher surfactant concentrations (up to 30 % w/w)⁴. Rather than diffusing into the hydrophobic pocket of the micelle, here it was postulated that TCA anions were retained by the cationic surfactant head group. Evidence of increased adsorption of chlorinated species by as-synthesised MCM-41 (compared to calcined MCM-41) was reported again in 2000⁵ with the efficient removal of trichloroethylene and tetrachloroethylene by as-synthesised adsorbents. Moreover the materials were reported to be stable even after immersion in water for over 124 d without any significant loss of surfactant (< 1 %). Reports of increased performance of as-synthesised

MCM-41, MCM-48 or mesosilica continued to grow with target molecules increasing to cover the extraction of benzene, toluene and phenol⁶, phenol, aniline, *o*-cresol and 1-naphthol⁷, phenol and *o*-chlorophenol⁸, 2,4,6 trinitrophenol⁹, furfural¹⁰ and toluene¹¹. In each case the as-synthesised mesosilica materials outperformed calcined materials and the increased efficiencies reported were attributed to the increased hydrophobicity of the adsorbent (increasing with the surfactant alkyl chain length) or, in the case of acidic molecules, the H-bonding and electrostatic attraction of the anionic adsorbate to the protonated head group of CTA⁺.

As-synthesised mesosilica containing C₁₂, C₁₄, C₁₆ or C₁₈ surfactant templates were also shown to have increased performance with increased hydrophobicity of the target molecule¹². The adsorption performance increased for the molecules: phenol < methylphenol < catechol, salicylic acid, 2,3-dimethylphenol, *p*-ethylphenol, benzoic acid and 2-naphthol. Further, the influence of the nature of the surfactant loaded into the mesosilica was also studied by comparison of materials incorporated with CTAB (the templating agent with a long hydrophobic tail) or cetylpyridinium bromide (CPB), a templating agent with a ring headgroup¹³. Solutions containing chloroacetic acids, or nonionic species (toluene, naphthalene and methyl orange) were studied. The chloroacetic acids had adsorption capacity values in the order mono < di < tri for the CTAB template, which was more effective than the CPB prepared adsorbent, supporting the hypothesis of electrostatic interaction between the ionic analyte and CTA⁺. Adsorption capacity values for the nonionic species were larger for CPB prepared adsorbents and this increase in efficiency was attributed to pi-pi interactions between the surfactant head group with the aromatic adsorbates.

3.2 Assessment of alkyl-grafted mesosilica for pollutant removal.

Surface modification of silanol groups by the PSG process has also been assessed as a way of increasing mesosilica hydrophobicity (see Figure 8 as an example).

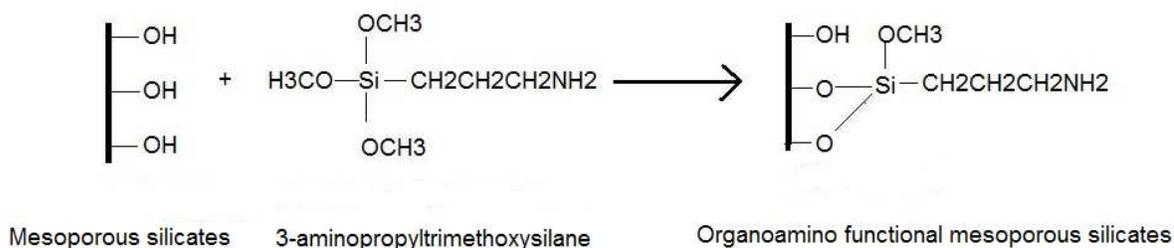


Figure 8: Surface modification of mesosilica to increase surface hydrophobicity.

Most literature studies reported on the success of grafted mesosilica adsorbents, compared to non-grafted mesosilica, and in each case increased adsorption capacities were reported for the former with capacity values typically ranging between 0.4 – 2.5 mmol g⁻¹. Target compounds have included nonylphenol¹⁴, alkyl phenol and alkyl anilines¹⁵, 2-chloro-4-methoxyphenol¹⁶, *N,N*-diethyl-*m*-toluamide¹⁷, 2-chlorophenol and 2,4,6-trichlorophenol¹⁸, tannic acid¹⁹ haloacetonitriles²⁰. Interestingly, unlike the as-synthesised materials, adsorption capacity values did not necessarily increase with increased alkyl chain length; demonstrating the need to carefully tune surface hydrophobicity for optimum extraction. For example, when used to extract 2-chloro-4-methoxyphenol¹⁶, extraction performance increased in the order hexyl > phenyl > propyl > silica > hexadecyl, with a maximum adsorption capacity value of 0.4 mmol g⁻¹. On the other hand, the ability to tune the surface of the mesosilica can lead to advantages; the possibility of specific surface groups selectively targeting and removing organic pollutants. For example, nonylphenol was selectively removed (94 %) using alkyl-

modified mesosilica despite being in the presence of phenol; whereas activated carbon was shown to remove > 90 % phenol from solution¹⁴.

3.3 Cyclodextrin-incorporated mesosilica

Similar to the use of micelles in the as-synthesised materials, cyclodextrin (CD) molecules with hydrophobic cavities (hydrophobic pores and hydrophilic surfaces) have also been incorporated into mesosilica to increase its hydrophobicity (see Figure 9).

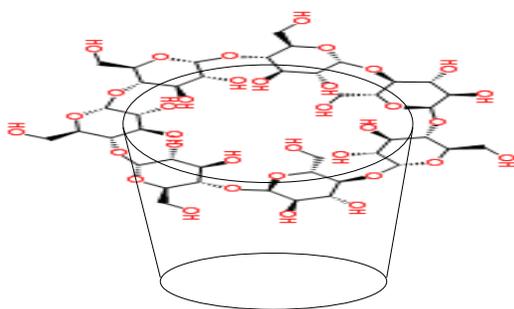


Figure 9: Schematic illustration of a cyclodextrin cavity.

Different masses of cyclodextrin (CD) have assessed for extraction of *p*-nitrophenol²¹, a range of phenolic and chlorphenolic species²², humic acid²³, and hexachlorocyclohexane and DDT²⁴. Some authors^{21, 22} reported an increase in extraction capacities with increased CD loading and most reports compared performance to unmodified mesosilica, where little-no extraction of organic analytes from aqueous solution were typically reported. Adsorption capacities varied depending on the CD loading (2 – 8 %) suggesting a 1:1 complexation between the analyte and the CD cavity with rapid uptake of analyte which compared favourably to CD loaded polymers²². Note, however, that materials produced with CD loadings higher than 8 % must be used with caution as most authors reported a significant decreases in performance as the CD loading increased above this value. For example,

extraction efficiency of humic acid decreased from 99 to 33 % when CD loadings were altered from 4 to 10 %²³. This might, in part, be explained by destruction of the periodic mesoporous structure; a study of CD-mesosilica with pesticides reported retention of periodic mesoporous structure up to 8 % CD whilst at concentrations above this framework destruction occurred producing amorphous material²⁴. Moreover depending on the target molecule mesosilica with lower CD loadings might be preferential. For example a 4 % CD loaded mesosilica was reported to have highest extraction efficiencies for hexachlorocyclohexane, and have outstanding performance for the globally persistent pollutant DDT²⁴. In general CD-loading, accessibility, molecular size and structure were shown to be important factors when assessing extraction performance of CD-loaded mesosilica.

3.4 Mesosilica functionalised, or incorporated, with aluminium.

Studies have also focused on removal of organic pollutants from water using Al-mesosilica. In the earliest reported work²⁵, successful removal was achieved for cyanuric acid (1,3,5-triazinane-2,4,6-trione) and *p*-chlorophenol onto Al-MCM-41. The performance of the material was shown to depend strongly on the Si:Al ratio of the final material. For example MCM-41 prepared with a Si:Al ratio of 30:1 was most effective in the removal of citric acid (0.7 mmol g⁻¹) when compared to materials produced with ratios of 51 – 97:1²⁶; indeed the material outperformed activated charcoal or H-β zeolite. It is important to note however that the Si:Al ratio of the final adsorbent needs to be optimised for each application; 30:1 is not necessarily the ideal ratio for all organic pollutants. When used to extract polycyclic aromatic hydrocarbons, for example, highest interactions were observed for naphthalene (0.83 mmol g⁻¹), anthracene (1.71 mmol g⁻¹) and pyrene (1.84 mmol g⁻¹), with a Al-mesosilica with a Si:Al ratio of 10:1²⁷. X-ray photoelectron spectroscopy was used to examine structural framework changes after incorporation of Al. It was shown that a higher

number of octahedral Al species were measured in the 10:1 sample compared to the 30:1 sample and as the octahedral sites were proposed as the adsorptive positions increased removal of PAHs was observed with the 10:1 sample. Increased Al-acidic sites on MCM-41 or MCM-48 were also shown to improve extraction of nitrosamines from tobacco-extract solution when compared to corresponding unmodified silica²⁸; here a 10:1 ratio was preferred as higher Al loadings led to materials with decreased surface area and pore volume. Finally, calcined 3-D cubic mesosilica monoliths have been prepared with various Si:Al ratios (19:1 to 1:1) and assessed for removal of aniline, *p*-chloroaniline, *o*-aminophenol or *p*-nitroaniline²⁹. In batch extraction the 1:1 monolith demonstrated best performance with maximum adsorption capacities of 0.34, 0.26, 0.21 or 0.19 mmol g⁻¹, respectively.

3.5 Use of SBA-15 mesosilica

In contrast to the published literature for volatile organic compound removal from air, SBA-15 features far less than MCM-41 when applied to the removal of organic pollutants from aqueous solution as evidenced by the first application noted by the author of this review, which appeared as recently as 2006³⁰. Presumably SBA-15 has received far less attention because (i) its micropores would become blocked by alkyl groups or templates (SBA-15 is microporous and mesoporous) and (ii) there is restricted access to the mesopores via microporous channels. In this first published report SBA-15 was functionalised with pyridine prior to removal of acid dyes. Six years later SBA-15 was assessed for the removal of mono-, di- or trichlorophenol³¹. Adsorption capacity at equilibrium was significantly higher for trichlorophenol compared to the di- or mono- counterparts with all capacities decreasing with increased temperature (as adsorption is an exothermic process). To enhance the capacity of SBA-15 for removal of organic pollutants from water at low concentration, 'designer' silica surfaces have been proposed by Zhang³². SBA-15 was functionalised with a two-agent

combination of diamine-phenyl, diamine-cetyl or phenyl-cetyl groups for the targeted removal of eosin, 4-nonylphenol or di-n-butyl phthalate, respectively. Specifically, eosin was removed with 99.95 % efficiency even when present at low concentration. With its negatively charged groups and aromatic system, eosin was attracted to amine-phenyl-SBA-15 by electrostatic interactions and pi-stacking. Mixed amine- and phenyl- functionalised SBA-15 did not achieve the same adsorption capacity thus validating the theory that cooperative adsorption of functional groups in close proximity enhanced adsorption. Moreover, the maximum capacity of eosin at 0.59 mmol g^{-1} was significantly higher than any other reported value of which activated carbon previously demonstrated highest capacity at 0.36 mmol g^{-1} .

3.6 Mesosilica with encapsulated magnetic nanoparticles

An interesting and perhaps emerging area of research involves the preparation of magnetic particles combined with mesoporous materials for the selective removal of organic species from water. The magnetic nanoparticles have been dispersed in the silica mesopores, grafted onto the surface or used as a core upon which silica is grown to produce microspheres. In particular removal of 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT) by as-synthesised mesosilica with Fe_3O_4 was examined³³. The adsorbent was shown to be a fast and highly efficient material for DDT removal (despite being calcined prior to use) and additionally the magnetic properties of the microsphere core were used to permit ease of separation of the DDT-loaded microspheres from the aqueous solution. A similar magnetic microsphere (Fe_3O_4) with a thiol-functionalised mesoporous shell was used to extract chloro- and nitrophenolic compounds from water³⁴. Here the mesoporous shell had the surfactant incorporated and as such the as-synthesised material was used. Adsorption performance was pH specific with highest extraction of 2,4-dinitrophenol and 4-methyl-2,6-dinitrophenol at pH 3 - 4, whereas chlorophenol, 2,4-dichlorophenol and *p*-nitrophenol were more efficiently removed

from solutions with pH values of 4 - 7. Ionisation of the CTAB surfactant producing CTA^+ was thought to be the main driving force of interaction with the phenolate anions; at low pH the phenolic compounds did not dissociate and so adsorption was reduced considerably. Extraction at higher pH also decreased due to competitive interaction between OH^- on the surface of the silica and the phenolate anions. Interestingly this was one of the few papers where field applications were examined by extraction of analytes in the presence of organic matter such as urea, benzoic acid, aniline, L-alanine and imidacloprid; extraction of 4-methyl-2,4-dinitrophenol reduced by approximately 10 %. Real samples of waste, river and sea water containing 48, 43 or 40 mg dm^{-3} of dinitrophenol reduced to 10, 11 or 20 mg dm^{-3} after addition of the sorbent. A potential significant environmental application advantage was demonstrated by exploiting the magnetic nanoparticle property which was used to permit easy removal of the sorbent after application.

4 Use of mesosilica to remove organic dyes from aqueous solution.

Approximately 3.5×10^6 kg of dye components are thought to be discharged into aqueous streams each year. The colour produced is aesthetically objectionable and may inhibit light penetration reducing photosynthetic activity but more importantly, as the majority of dyes and their degradation products may be toxic and carcinogenic to mammals, mitigation of dyes from water systems is of global environmental concern. A variety of methods have been used to remove dyes from water streams including filtration, photodegradation, sonication and flocculation, however many of these treatments are not efficient or they produce secondary pollutants which may equally be harmful to human health. Although traditional adsorbent methods include the use of supports such as peat, pith, wood and activated carbon, mesosilica material emerged as potential adsorbents in 2003 due to their high surface area, high pore volumes, well characterised pore structures and ease of regeneration. Recognising

that dye components can be neutral, acidic or basic, most applications use unmodified, aminated- or acidified mesosilica, respectively. In general it is found that as the adsorbent-adsorbate interaction is dominated by electrostatic interactions, the process is strongly dependent upon solution pH and that adsorption efficacy decreases with increasing pH for anionic (acid) dyes while it increases for cationic (basic) dyes.

Basic dyes which contain cationic groups have increased interaction with silica materials at higher pH values where the silica surface is negatively charged. For example the isoelectric point of MCM-41 is at pH 4.0 and above this pH the silica surface will have a net negative charge interacting with cationic groups on the dye molecule by electrostatic interaction. Similarly acid dyes will have increased interaction with silica below pH 2-4 as the silica surface possesses a net positive charge and can therefore attract anionic groups by electrostatic interaction. The solution pH will also have an influence over the form of the dye depending on the pKa value of the dye. If the dye is not ionic and is neutral it can still be adsorbed onto the surface of the silica by H-bonding and van der Waals interactions. Moreover the surface charge of the silica can be altered by the addition of carboxylate or sulfonated groups (to further increase the negative charge and attractiveness to basic dyes) or aminated to provide positively charged active sites for acid dyes.

4.1 Basic/cationic dye removal

Basic dyes such as methylene blue^{35, 36}, Basic Green 5 and Basic Violet 10³⁷, Crystal Violet and Rhodamine B³⁸, which all contain cationic sites, have been removed by unmodified and carboxylic acid functionalised MCM-41. Capacity values ranged from 0.17 – 1.04 mmol g⁻¹ and since the retention of dyes involved ionic interactions, regeneration of the sorbent was possible by washing the loaded sorbent with water acidified to pH 2. At this low pH the silica surface was positively charged repelling the cationic groups of the basic dye. However,

although the dyes were removed quickly from water (within 5 min) if the adsorbent was not removed from the water the dyes were released back into solution 150 h after the initial adsorption³⁶. It was proposed^{36,37}, that this lack of adsorbent performance was, in part, due to pore destruction and it was recommended that neither MCM-41 nor MCM-48 were good sorbents for removal of basic dyes from aqueous solution. Interestingly, in contrast MCM-50, which was shown to have a similar adsorption capacity for methylene blue as MCM-41 and MCM-48, retained the dye almost completely (94 %) 400 h after extraction. The lamellar form of the silica framework appearing to retain the dye more strongly, however no explanation was given to support this observation. The results published by Lee³⁸ gave, for the first time, kinetic data for the dye adsorbate-adsorbent interaction and an intraparticle diffusion model was proposed. Here, 3 diffusion steps explaining the adsorbent-adsorbate interaction were attributed to (i) migration of adsorbate through the external boundary layer film of liquid surrounding the sorbent, (ii) solute movement from the surface into the pore and/or surface diffusion and (iii) adsorption. The rate determining step was shown to be controlled by the second step in the kinetic model i.e., the kinetics are limited by the diffusion of the dye molecule into the pore. indicating that the dyes adsorb by surface adsorption and intraparticle (pore) diffusion, with external mass transfer controlling the rate determining adsorption process (see Figure 10).

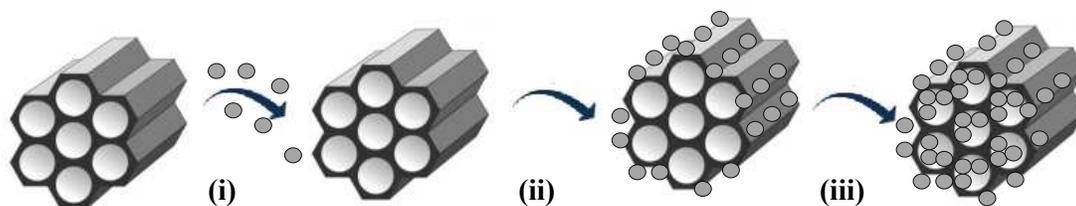


Figure 10: a Schematic illustration of dye adsorption onto MCM-41 by the intraparticle diffusion model where diffusion process include (i) external mass transfer of dye molecule to silica surface, (ii) solvent movement into the pores and (iii) adsorption

4.2 Acidic/anionic dye removal

Anionic dyes possess negative sulfonated functional groups and therefore have best interaction with mesosilica materials at low pH when the silica surface possess positive charge or with amine- or pyridine-functionalised silica. Among the most studied anionic dyes Acid Blue 25³⁵, gave an adsorption capacity value of 0.6 mmol g⁻¹ onto amine-MCM-41 which was reported as an exceptional result as this dye cannot be removed from water using traditional carbon-based sorbents. Pyridine functionalised SBA-15 was examined for the removal of dyes Alizarin Red S, Brilliant Red X-3B and Reactive Yellow X-RG³⁰. Solution pH was controlled to 3.5 permitting protonation of the pyridine molecule which increased the attraction between the cationic adsorption sites and the negatively charged sulfonate groups on the acidic dyes. Although Alizarin Red S and Brilliant Red X-3B followed the Langmuir adsorption isotherm model, suggesting monolayer coverage of molecules on homogeneously distributed active site, Reactive Yellow X-RG had a better fit with the Freundlich isotherm model suggesting multilayer adsorption of the molecule through H-bonding interactions. To assess the field utility of amine-MCM-41 for the removal of Reactive Red RB and Reactive Yellow GR (both dyes contain a number of sulfonated groups) the extraction was examined in the presence of dodecylbenzene sulfonate (DBS), which is a surfactant commonly present in textile effluent streams³⁹. In general, at low dye-surfactant concentrations, adsorption of the negatively charged dyes were effective however above the critical dye-surfactant aggregate concentration the neutral aggregate formed could not be removed by the cationic silica surface. This study highlights the need to assess sorbent performance in 'field' conditions otherwise the results of simulated studies will be futile. CD molecules have also been combined with amine mesosilica to provide an adsorbent platform for Remazol Red 3BS, (an azo dye with 5 sulfonate groups)⁴⁰. The presence of the cyclodextrin ring increased

the adsorption capacity value from 0.14 to 0.28 mmol g⁻¹. Moreover the cyclodextrin-mesoporous silica material was regenerated by washing it with sodium dodecyl sulfate without significant loss of adsorption capability. Since the diameter of the dye molecule exceeded that of the cyclodextrin cavity the adsorbent-adsorbate interaction was thought to be via surface electrostatic interactions. It was therefore proposed that cyclodextrin-HMS adsorbent is an ideal adsorbent for acid dyeing processes where the solution pH will be optimal for adsorption without the need for solution pre-treatment. Similar to that of anionic dyes, a study of adsorbate-adsorbent interactions between Methyl Orange, Orange IV, Reactive Brilliant Red X-3B and Acid Fuchsin with amine functionalised MCM-41⁴¹ also supported the intraparticle diffusion kinetic model.

The slope of this step was also shown to correlate with the size of the dye, with longer kinetics (slower diffusion) being observed for molecules of larger size. This paper also considered the effect of interferents and it was shown that although nitrate and chloride suppressed capacity values by approximately 15 %, the presence of polyvalent ions, carbonate and phosphate, caused a much larger and more significant suppression on the adsorption capacity of all dyes. Although not widely studied in the published literature the effect of interferent ions should not be underestimated and need to be studied otherwise the results of laboratory studies cannot be translated to real environmental or industrial applications.

5 Extraction of pharmaceutical products from aqueous solution

Only recently has attention been given to the presence of pharmaceutical products in aqueous systems. Current drinking water treatments have low efficiencies for removal of pharmaceuticals with average extraction rates of 50 %. The potential long term effects of

such products are not yet known however it is widely agreed that better extraction methods need to be developed to better protect human health. One of the first reported studies using SBA-15 as an adsorbent to examine the removal of carbamazepine, clofibric acid, diclofenac, ibuprofen and ketoprofen was published in 2009⁴². Laboratory simulated studies used solutions of the pharmaceutical targets in aqueous solution at 10 mg dm^{-3} . Adsorption kinetic results indicated equilibrium had been reached in a period of a few min which compared favourably to activated carbons which typically have equilibrium times of 4 h. Each analyte was extracted to different extents with ibuprofen having the strongest affinity whereas clofibric acid had the lowest affinity. There was a direct correlation between adsorbent-adsorbate affinity and the pKa value of the target with highest affinities being observed for pharmaceutical compounds with the highest pKa value. As the mass of SBA-15 added to a solution was increased the removal efficiencies increased linearly up to maximum removal efficiencies of 62, 67, 84, 95 and 91 % for clofibric acid, diclofenac, carbamazepine, ibuprofen and ketoprofen, respectively, although to reach such high values of extraction solution pH had to be altered depending on the target with little adsorption of any product at solution $\text{pH} > 7$. This is once again explained by the surface chemistry of the mesosilica which has a net positive charge at pH values < 4 and a net negative charge at pH values > 4 . When solution pH is greater than the pKa of the target compound the acidic pharmaceuticals are negatively charged and so are repulsed by the net negative charge on the silica surface. Therefore highest removal rates for carbamazepine, diclofenac, ibuprofen and ketoprofen were measured at a solution pH of 3. The strong correlation between solution pH and adsorption performance suggests a hydrophilic interaction via hydrogen bonding. This strong interaction mechanism influences desorption (and thus sorbent regeneration) which was shown to be as low as 20 - 40 % at pH 7, which would limit the regeneration capacity of SBA-15 for these products. More recently, mesoporous silica nanoparticles were used to

remove telmisartan after sorbent surface modification with aminopropyl groups⁴³. However the paper focussed more on the drug loading capacity of the material rather than extraction efficiencies which could relate to an environmental application. Nonetheless the drug loading capacity was shown to be related to the total pore volume and pore diameter of the material as opposed to the surface area. Amine functionalised mesoporous periodic silica materials were also used to examine extraction of nicotine from water or simulated human blood plasma⁴⁴. After adsorption of the target the surface area of all adsorbents were, as expected, reduced significantly. Less expected was the influence on pore size which increased when added to the simulated body fluid due to the formation of nicotine salt in the body of the pore. Although nicotine was successfully removed from solution in batch solutions (both water and body fluids) the sorbent efficiencies suffered from competitive water adsorption. Finally amine functionalised MCM-41 and SBA-15 were used successfully to remove cisplatin⁴⁵. Without grafting adsorption efficiencies reduced to 9.1 % wt at room temperature or 14.8 % wt at 50 °C.

4. Conclusions and Discussions

Since the earliest assessment of mesosilica focused on VOC isotherms and TPD experiments, studies of adsorption performance have expanded into removal of organic pollutants, dyes and, more recently, pharmaceutical products from aqueous solution. Calcined mesosilica demonstrates low extraction efficiencies for most organic molecules present in aqueous solution and thus the hydrophobicity of the material must be increased to permit partitioning of the organic molecule into the modified adsorbent. To induce hydrophobicity as-synthesised materials have been used to provide micelle pockets within the mesosilica framework. All the results reported supported the theory as-synthesised mesosilica materials consistently outperformed calcined materials when used to extract a wide range (chlorinated,

phenolic, aromatic, ionic) of organic pollutants from water. Moreover, extraction efficiencies were shown to increase with increased surfactant alkyl chain length or the target pollutant's hydrophobicity. Although the exact mechanisms of interaction were not clear it was postulated that surfactant-pollutant aggregates formed at polar head groups and/or lodged within the alkyl tails of the hydrophobic miscelle pocket. Hydrophobicity has also been introduced by the presence of alkyl groups on the surface of the mesosilica (incorporated by the PSG or co-condensation process). Once again better extraction performance was achieved compared to the calcined silica counterparts, however unlike the as-synthesised materials, extraction performance did not necessarily increase with an increase in the grafted alkyl chain length. Here further considerations of pore blocking, reduced surface area and pore volume must be deliberated and the surface of the material needs to be carefully tuned to provide best extraction results. Analogous to the as-synthesised materials, CD complexes have also been used to provide hydrophobic cavities for organic pollutant extraction. The CD loading was shown to be crucially important with most studies using CD loadings at 8 % or lower. Otherwise, it was postulated that the incorporation of higher CD concentrations resulted in disruption of the silica framework leading to an amorphous material which provided little-no extraction capabilities. Incorporation of octahedral Al-adsorptive sites has also been shown to promote extraction of organic pollutants. The importance of the Si:Al ratio in the final product needs to be optimised for each application with published reports citing best performance for materials with a 30:1, 10:1 or 1:1 ratio. Despite the small number of publications featured at the time of writing, the potential use of magnetic mesoporous microspheres for removal of organic pollutant is appealing. After removal of the pollutants into micelles in the silica framework the absorbant-adsorbate aggregates can be easily removed by magnets which act upon the magnetic Fe_3O_4 core. Finally, only a few reports have focused on the use of mesosilica for the removal of pharmaceutical products from water

with varied success. Significantly however, these studies focused on 'real' applications and assessed the effect of interferences and dynamic flow which is a marked improvement on previous work.

There are general limitations to the use of mesosilica in aqueous solutions as prolonged exposure to alkaline solution has been observed to cause a loss of pore shape uniformity as well as a significant decrease in pore size. In particular significant decreases in crystallinity, average pore diameter and pore volume can be observed. Moreover, the longer the silica is in the alkaline solution the bigger the impact on the material; similarly with increased temperatures. The poor stability of the material experienced in alkaline solution and at higher temperature would restrict the material's lifetime. Perhaps one of the biggest hurdles to overcome is that most literature studies (> 95 %) examine the potential use of mesosilica as an environmental remediation solution in simulated experiments (ie., in the laboratory and not in the field). This prevents an ability to estimate the future utility of mesosilica in commercial and industrial application as most studies are idealised and do not examine potential interferences that would be found in the field, adsorbent regeneration or even how the materials will be used. For example, presumably if used in the water industry the preferred method of application would be to flow the contaminated water through sorbent beds containing the appropriate functionalised mesosilica material. However such 'dynamic' mode, or flowing studies, are not common in the laboratory and most researchers still examine capacity based on batch experiments where a small amount (50 – 100 mg) of adsorbent is stirred in a beaker with a small amount of solution containing the target analyte. Whether the sorbent's calculated capacities are applicable in dynamic mode have yet to be explored. More crucial perhaps is that mesosilica is not yet produced on an industrial scale. Until chemical engineering studies focus on manufacture and scale up procedures the

materials may not be able to compete with current commercially available materials that are produced on a significantly larger scale.

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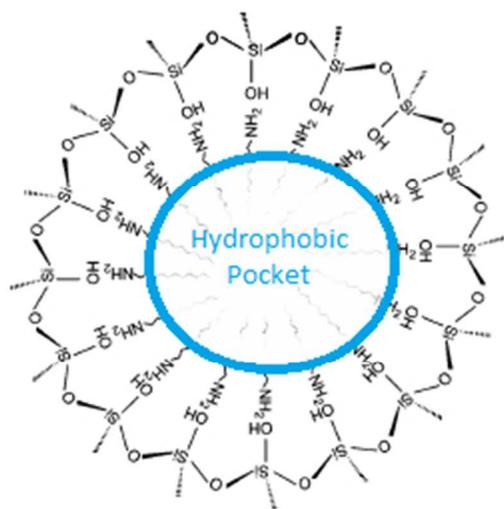
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Mesosilica Materials and Organic Pollutant Adsorption: Part B Removal From Aqueous Solution.

Learning Objectives:

1. Recognise the importance of increasing mesosilica hydrophobicity, when used to extract organics from aqueous solution, by incorporation of surfactants or by post-synthesis grafting.
2. Know how to chemically modify the surface of mesosilica to target specific pollutants from aqueous solution.
3. Be able to use reported adsorption data (adsorption capacity values and isotherm data) to better understand adsorbent-adsorbate interactions.
4. Identify potential research applications in developing areas such as the extraction of pharmaceutical products from riverwater or the use of magnetic mesoparticles to aid pollutant removal.
5. Be aware of the necessity of phenomenological/field experiments to test the efficacy of mesosilica adsorbents, for use in complex matrices or in the presence of interferents, prior to environmental or industrial application.