



## Silica-based mesoporous materials; emerging designer adsorbents for aqueous pollutants removal and water treatment



Paul N.E. Diagboya\*, Ezekiel D. Dikio

Department of Chemistry, Vaal University of Technology, Vanderbijlpark, Gauteng, South Africa

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### ABSTRACT

This is a review of recent literature on pristine and specifically functionalized mesoporous silica-based materials or ‘designer silicates’ used as adsorbents for aqueous pollutants removal and water treatment. Ordered mesoporous silicates, their synthesis, surfactants removal, and preparation of the designer silicates were briefly introduced before discussing their applications in the removal of inorganic and organic pollutants. Designer silicates, such as the nitrogen/thiol-containing, the magnetics, and the composites, are highlighted with their various applications for the removal of toxic metal cations, anionic species, dyes, pesticides, industrial organics, pharmaceuticals and other emerging pollutants. These applications were briefly discussed indicating salient features and using illustrating figures where possible.

### 1. Introduction

Pollution of water sources by organic and inorganic chemical toxins is a priority concern worldwide. The magnitude of this concern is enormous, and remediation of contaminated water sources is seemingly intractable because of the diverse nature of pollution sources [1–9]. Most current water treatment technologies are either expensive or lack the effectiveness for complete toxins removal; hence, the search for more efficient technologies is a continuing process.

Several techniques have been employed for pollutants removal from water, such as filtration, chemical precipitation, ion exchange, reverse osmosis, electrochemical treatment, membrane technology, evaporation recovery, photocatalysis, solvent extraction, and adsorption. However, most of these are limited by techno-economic and environmental considerations [2–4,10–17]. Advances in materials science have triggered large interests in specifically-designed adsorbents for water treatments. The concept of a synergistic combination of two or more molecules into a larger one has become a very successful approach in materials science for achieving highly efficient and specific goals in materials' property, such as adding new structural and functional properties superior to those of the individual pure components [1,2,8,14,18–24]. This kind of focus has resulted in the discovery of a plethora of designer adsorbents such as the mesoporous silica-based adsorbents [2,14,18,19,23].

Ordered mesoporous silica is eliciting a growing interest in water treatment chemistry due to its various remarkable properties. These properties include high specific surface area, large pore-size, chemical

inertness, an abundant repertory of surface functional groups that can be tailored for excellent selectivity towards specific pollutant, good thermal stability and low cost of manufacture [18,25]. Highly porous adsorbents, which are of particular demand in aqueous separations involving large molecules, can be synthesized from ordered mesoporous silica in other to include a wide variety of functionally active chemical components by exploiting the structure-directing functions of electrostatic, hydrogen-bonding, and van-der-Waals interactions associated with amphiphilic molecules [26–28]. Since mesoporous silica meet most of the criteria for selection of adsorbents such as high specific surface area, large pore-size, chemical inertness and easy addition of abundant repertory of surface functional groups, pristine and functionalized silica [26–28] have been successfully synthesized and studied for adsorption of both organic and inorganic aqueous pollutants [29–34]. Many recent references demonstrate the versatility of ordered mesoporous silica-based adsorbents.

The objectives here are to focus on the advances in ordered mesoporous silica-based adsorbents used for aqueous inorganic and organic pollutants removal. Brief highlights of the types, synthesis routes and modifications/functionalization of the ordered mesoporous silica-based adsorbents are given. This is followed by an overview of several studies involved with the application of ordered mesoporous silica-based adsorbents in the specific adsorption of inorganic and organic pollutants from aqueous solutions. In summary, the review highlights the recent reports (mainly from 2009 to 2017) on the use of ordered mesoporous silica-based adsorbents for the removal of inorganic and organic pollutants from aqueous solutions, and presents a brief description of these

\* Corresponding author.

E-mail address: [pauldn2@yahoo.com](mailto:pauldn2@yahoo.com) (P.N.E. Diagboya).

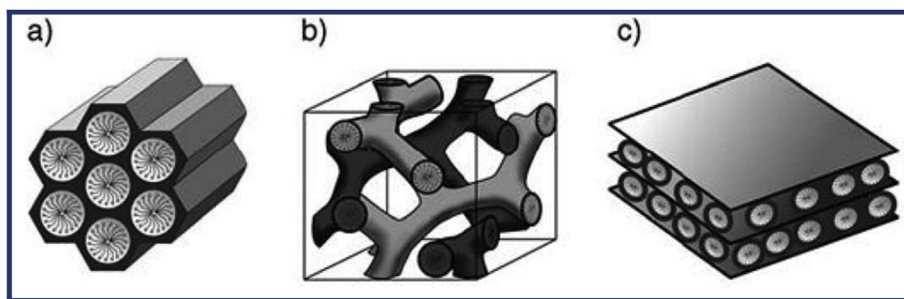


Fig. 1. Morphologies of (a) MCM-41, (b) MCM-48, (c) MCM-50. Reproduced from Ref. [39] with permission from The Royal Society of Chemistry.

adsorbents, advantages, and limitations; and reports on regeneration methods where available. To give insight into the adsorbents effectiveness, reported adsorption capacities are noted.

## 2. Ordered mesoporous silicates

This class of mesoporous materials consists of extensive inorganic or inorganic–organic hybrid arrays with the exceptional long-range order, highly tunable textural and surface properties and controlled pore size and geometry [35]. These properties, in addition to their usually large surface areas, make them excellent adsorbent materials providing higher possibilities for adsorbent–adsorbate interactions. It is worthy to state here that silica framework is not crystalline but amorphous; it is the mesopores that are arranged periodically within the structure. Mesoporous silicates include the Mobile Composition of Matter (MCM) family (such as the MCM-41, MCM-48, and MCM-50; Fig. 1), the Santa Barbara Amorphous (SBA) family (such as the SBA-1, SBA-2, SBA-6, SBA-8, SBA-11, SBA-12, SBA-15, and SBA-16), KIT-5 and KIT-6 [36–38]. The MCM, like most silicates, are classified according to the order of the pores: hexagonal, cubic or mesolamellar phases for the MCM-41, MCM-48, and MCM-50, respectively.

### 2.1. Synthesis of ordered mesoporous silicates

Mesoporous silicates can be synthesized under varying range of pH conditions (from strongly acidic to highly basic – Fig. 2a) and temperatures (from below room temperature to  $\approx 150$  °C) using different templates or surfactants (cationic, anionic, neutral, zwitterionic, etc.) [36]. Under appropriate synthesis condition, the silicate's surface area, pore size, and volume can be controlled from the mesopore dimensions to macropore. Typically, mesoporous silica synthesis comprises the addition of a silicate source to the surface of ordered surfactant micelles in an aqueous solution to produce the ‘as-synthesized’ mesoporous silica. The discovery of template-assisted mesoporous silica synthesis using surfactants has led to the synthesis of mesoporous silica with high surface areas, tunable pore sizes, large pore volumes and a plethora of different kinds of functionalization [36,40]. Mesoporous silica materials are synthesized under conditions where surfactant–silica assembly occurs simultaneously with condensation of the inorganic species to produce the composites (Fig. 2b). The dimensions and morphologies of the resulting materials are dependent on the sol–gel chemistry conditions such as temperature, water content, pH, characteristics of surfactants or copolymers, and the concentrations and the sources of silica used. Hence, it is possible to design the silica size, mesostructure, and morphology by controlling of these parameters [41]. Ideally, mesoporous silica to be applied as an adsorbent for aqueous pollutant removal should possess large surface area, large pore size, and pore volume. These external and internal properties provide large surfaces for independent functionalization, as well as allow for a small amount of the adsorbent to have contact with a large volume of the aqueous solution and consequently a significant amount of the pollutant, resulting in possibly high removal efficiency.

Usually, a single surfactant (such as the Pluronic-type surfactant; poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide)-Pluronic P123 (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>) or Pluronic F127, (EO<sub>106</sub>PO<sub>60</sub>EO<sub>106</sub>), and cetyltrimethylammonium bromide (CTMAB)) is used as the organic structure directing agent or template for the synthesis of surfactant-templated silica materials [18,41–44]. However, binary surfactants of different molecular weights has been used resulting in the formation of dual-mesoporous silica materials [41].

### 2.2. Post-synthesis removal of surfactants

To access the pores within the ‘as-synthesized’ mesoporous silica composites, it is necessary to remove the surfactants used in the self-assembly. Mesoporous silica synthesized via the surfactant-templated sol–gel reaction is carefully packed and shrink significantly and irreversibly when directly dried from solution thus losing its characteristics [41]. Thus, it is necessary to be cautious of template removal methods. Calcination is mostly used for the removal of surfactant from within the pores [45–49] though in some cases solvent extraction is preferred to calcination [18,42,50] and microwave digestion using UV [51]. The typical calcination temperature range is 550–800 °C in flowing air or nitrogen, while the optimized solvent extraction process is carried out by refluxing for 24 h using a high ratio ethanol to water mixture. Without high-temperature calcination, the extent of the silane modification can be relatively high, thus making the surface properties to be easily adjusted.

### 2.3. Functionalization

Though remarkable properties of ordered mesoporous silicates are highlighted for water treatment purposes, these properties are sometimes not accessible. A major challenge with mesoporous silicate upon template removal is its hydrophilicity due to the high surface silanol density (Fig. 3), consequently resulting in low adsorption for aqueous pollutants especially the hydrophobic ones. Functionalization, or attachment of highly active groups to the surface of the silicate material, has become a highly successful method of accessing these remarkable properties of ordered mesoporous silicates for water treatment purposes. This has resulted in a plethora of functional designer silicates with high efficiency and excellent selectivity towards specific aqueous pollutants.

Typically, an organic functionality can be introduced post-synthesis by grafting or chemical attachment onto the silanol groups in the mesoporous silica or by co-condensation during the template-directed synthesis of the mesoporous material. The chemical attachment of organic functionalities onto the silanol groups changes the silica wall polarity and introduces the desired functionality which enhances the surface adsorption properties (Fig. 3). One advantage of post-synthesis chemical attachment is that the mesoporous structure is usually retained, though this depends on the size and loading of organic functionality added, as these could result in pore blockage. Post-synthesis functionalization of the silicate surface may be achieved by the

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