



## Removal of Heavy Metal Ions From Water Bodies Using Mesoporous Silicates: A Silica Based Novel Hybrid Material

**Sandhya Sayantini Mohanty**

Centurion University of Technology and Management, Paralakhemundi, Gajapati, Odisha

**Nilakantha Dash**

Department of Chemistry, Panchayat College, Dharmagarh, Kalahandi, Odisha

**S.P. Nanda**

Centurion University of Technology and Management, Paralakhemundi, Gajapati, Odisha

**R. K. Dey**

Center for Applied Chemistry, Central University, Ranchi, Jharkhand

ABSTRACT

Heavy metals (Cadmium, Nickel, Lead and Chromium) which are natural components of the Earth's crust are usually associated with toxicity. Exposure to heavy metals, even at trace level, is known to be a risk for human beings. The presence of zinc, cadmium, nickel and others metals in the aqueous environment has a potentially damaging effect on human physiology and other biological systems when the acceptable levels are exceeded. Heavy metals cannot be degraded or destroyed. Heavy metal toxicity could result, for instance, from drinking-water contamination (e.g. lead pipes), increased ambient air concentrations near sources of emission, or ingestion via the food chain. The increased use of heavy metals in industry has resulted in increased availability of metallic substances in natural water sources. Many technologies like adsorption, precipitation, membrane filtration, and ion-exchange have been used to remove metal pollutants from water. However, adsorption has proven to be economical and efficient for removing heavy metals, organic pollutants and dyes from polluted waters. Several adsorbents such as activated carbon, silica, and graphene can be used in the purification of water. Activated carbon has shown to be an efficient adsorbent for the removal of a wide variety of organic and inorganic contaminants present in the aquatic environment. Because of its high surface areas is widely used in the treatment of wastewaters. The effectiveness of Mesoporous silicates in cleaning up polluted water is due to its well developed porosity structure as well as the presence of a wide spectrum of surface functional groups. This makes it capable of distributing pollutants on its large internal surface, making them accessible to reactants.

### KEYWORDS

Heavy metals, Mesoporous silicates, Water bodies

### INTRODUCTION

A heavy metal is a member of a loosely defined subset that exhibit metallic properties. It mainly includes the transition metals, some metalloids, lanthanides and actinides. Many different definitions have been proposed some based on density, some on atomic number or atomic weight and some on chemical properties or toxicity [11,12]. There are 35 metals that concern us because of occupational or residential exposure; from these 23 are the 'heavy elements' or heavy metals. These are Sb, As, Bi, Cd, Cu, Co, Ce, Ga, Au, Fe, Pb, Mn, Hg, Ni, Pu, Ag, Te, Th, Sn, Ur, V and Zn. Some amounts of these elements are common in our environment and diet and are actually necessary for good health but large amounts of any of them cause acute and chronic toxicity. The specific gravity of water is 1 at 40 °C (39F), simply it is stated that specific gravity is a measure of density of a given amount of a solid substance when it is compared to an equal amount of water [1,13]. But some well known toxic metallic elements with a specific gravity that is 5 or more times that of water As – 5.7, Cd – 8.65, Fe – 7.9, Pb – 11.34, and Hg – 13.54 [4,8,9,21,22].

With rapid development of industries such as metal plating facilities, tanneries, batteries, paper industries, pesticides and heavy metals waste waters are directly or indirectly discharged in to the environment increasingly, especially in developing countries. Toxic heavy metals are not biodegradable and tend to accumulate in living organism and many heavy metal ions are known to be toxic or carcinogenic [6,7]. Heavy metals are the environmental priority pollutants and are becoming one

of the most serious environmental problems. So these toxic heavy metals should be removed from the waste water to protect the people and the environment. In general irritable health concern related to heavy metal might be mainly divided in to two types, i.e. heavy metal poisoning caused by excessive extrinsic exposure and genetic disorder [14,15,17,18]. This special issue is well organized to explain the biological significance of several heavy metals and their toxicity and also described the influence of several immune response and metabolism and several related cascades.

Human activities have increased the concentrations of heavy metals in the environment. Health risks of heavy metals include reduced growth and development, cancer organ damage, nervous system damage, and extreme cause death. The pollutants that enter the inshore waters and estuaries create serious problems causing extensive damage to the life and activities of the living aquatic organisms and even to mass mortality [10,16,19]. Heavy metal contamination may have devastating effects on the ecological balance of the recipient environment and a diversity of aquatic organisms [2,3,5]. Water defects and contamination of existing water supplies threaten to be critical environmental issues today for agricultural, domestic and industrial uses [23].

### Adsorbents for Heavy metal Removal

Living organisms require varying amount of heavy metals, Iron, Cobalt, Copper, Manganese, molybdenum and zinc are required by humans. Excessive levels can be damaging to the organism. Water contamination with heavy metal is a very

important problem in the current world [24]. Concerning the heavy metal contamination problem, various water and waste water treatment techniques, such as chemical oxidation, reduction, precipitation, coagulation, flotation, ion-exchange, membrane filtration, microbial degradation and solvent extraction have been developed [25,26,27&28]. However the application of these methods is sometimes restricted because of technical or economic constraints. Their major disadvantages are incomplete metal removal, high operating cost and generation of toxic sludge or other waste products.

The application of adsorption, a more efficient effective and economical technology has therefore received increased attention from both academia and industry in recent years. Adsorption is a process that occurs when a gas or liquid solute (adsorbate) accumulates on the surface of a solid or more rarely in a liquid (adsorbent) to form a molecular or atomic film. The process of adsorption involves separation of a substance from liquid phase accompanied by its accumulation or concentration at the surface of another. A solid surface in contact with a solution has the tendency to accumulate a surface layer of solute molecules, and because of the imbalance of forces, an adsorption takes place. The rate of adsorption is defined as the rate at which substances are transferred from the liquid phase to the solid phase. Most of the colourants are hydrophobic in nature and they can be easily adsorbed on the suspended matter from aqueous media. The major advantages of adsorption are no sludge formation, simplicity in operation and cost effectiveness [26].

Analysis of metal ions at trace levels poses a unique problem to analysts, because it involves the rigorous requirements of versatility, specificity, sensitivity and accuracy in the analysis. A wide variety of analytical techniques has been developed to determine concentrations of trace metals in various samples. However the results may be erroneous because the metal ions may be present in these samples together with other elements at low levels. The most widely used method for the separation and preconcentration of metal ions with suitable complexing agent is solid phase extraction (SPE). SPE is considered to be a powerful tool for the separation and enrichment of various inorganic as well as organic analytes. The basic principle of SPE is the transfer of the analyte from the aqueous phase to the active sites of the solid phase. The various advantages of this techniques are stability and reusability of the solid phase, high preconcentration factors, ease of separation and enrichment under dynamic conditions no need for toxic and costly organic solvents, minimum costs due to low consumption of reagents etc. Current trends in preconcentration focus on the development of faster, safer and more environment friendly extraction techniques. The techniques generally employed in analytical chemistry are liquid-liquid extraction [29-33], coprecipitation [34-37], ion-exchange resins [38-41], electrothermal deposition [42-43] and solid-phase extraction [44-54]. Solid phase extraction continues to be the leading technique for the extraction of pollutants in aquatic systems; recent developments in this field are mainly related to the use of new sorbents. Solid phase extraction (SPE) has emerged as a powerful tool for separation/enrichment of inorganics, organics and biomolecules. The basic principle of SPE is the transfer of analytes from aqueous phase to active sites of adjacent solid phase. Recently, solid-phase extraction technique for preconcentration of heavy metal ions has become very popular, compared with traditional solvent extraction techniques and has almost replaced liquid-liquid extraction techniques because of several advantages:

- (1) The fast, simple and direct sample application in very small size (micro liter volume) without any sample loss.
- (2) Higher preconcentration factor.
- (3) The ability of combination with different modern analytical techniques.
- (4) Time and cost saving.

(5) There is no need of organic solvents which are inflammable, toxic and even some of them carcinogenic.

(6) Absence of emulsion.

(7) Rapid phase separation.

(8) Stability and re-usability of solid phase.

(9) To isolate analytes from large volumes of sample with minimal or zero evaporation losses.

The choice of solid-phase extractant is a decisive factor that affects the analytical sensitivity and selectivity [55]. The main requirement with respect to substances to be used as solid-phase extractants are as follows:

- (1) Possibility of extracting a large number of elements over a wide pH range.
- (2) High surface area and high purity.
- (3) Good sorption properties including porosity, durability and uniform pore distribution.
- (4) Selectivity for specific analytes.
- (5) Fast quantitative sorption and elution.
- (6) Regenerability and accessibility.

The substances such as ion-exchange resins [56], chelating resins[55-60], modified silica [61-77], alumina[78], activated carbon[78-83], zeolite [84], chitosan[85] and polyurethane foam[86-91] have been used as solid phase extractant. Ion-exchange resins even though frequently used for preconcentration of metal ions, but have the disadvantage of low sensitivity and selectivity, while chelating sorbents have greater selectivity than ion-exchangers. Slow kinetics, irreversible adsorption of organics, sensitivity toward many chemical environment, loss of mechanical stability in modular operation and swelling are the main disadvantages exhibited by polymeric resins. These problems suggest the use of inorganic supports in place of polymeric resin. Some of the advantages of inorganic supports are:- (1) No Swelling (2) Rapid sorption (3) Good mechanical stability (4) Good selectivity A chelating sorbent essentially consists of two compounds, the chelate forming functional group and polymeric matrix support. Different polymeric materials used for chelating group immobilization can be ordered as follows:-

Inorganic: - Silica gel, Alumina, Kieselgur, Controlled pore glass.

Support Natural: - Cellulose, Dextran, Activated carbon

Organic Synthetic: -Polymeric resins, Fibrous materials, Foamed plastics

Among the natural organic matrices, is the most extensively used support for grafting of suitable functional groups because of its easy availability, low price and high mechanical strength. Thus, cellulose sorbents with bonded groups of iminodiacetic acid, 8-hydroxyquinoline, mercapto groups, aminoalkyl groups, pyridyl-azoresorcinol have been frequently used. In the same way, chelating sorbents with functional groups immobilized by covalent bonds on silica gel, have been synthesized by chemical transformation of the matrix. Even though the inorganic supports have high mechanical strength, thermal and chemical stability, chelating sorbents based on inorganic matrix have a poor degree of functionalization, reliability, and low sorption capacity. The disadvantages of chelating sorbents with grafted functional groups determined by synthesis difficulty, such as: low reversibility of sorption-desorption processes and unsatisfactory kinetic features [92].

a. Immobilization of organofunctional groups on silica gel support, offers pronounced advantages over other organic/inorganic supports as listed below.

b. Immobilization on the silica results in the great variety of silylating agents allowing pendant functional groups in the inorganic framework.

c. Attachment is easier on silica surface than on organic polymeric supports which have a high number of cross-linking bonds, requiring hours to reach equilibrium for surface activation.

d. Silica Gel is the first commercially available high specific surface area substrate with constant composition, enabling easy analysis and interpretation of results.

e. Silica Gel has high mass exchange characteristics, no swelling and great thermal resistance.

Attention has been focused on various natural supports which are able to pollutants from contaminated water at low cost. Cost is actually an important parameter for comparing the adsorbent materials. According to [93], a sorbent can be considered low cost if it requires little procession is abundant in nature or is a byproduct or waste material from another industry.

### Silica Based Adsorbent

The use of natural siliceous sorbents such as silica beads, glasses alunite, perlite and dolomite for waste water treatment is increasing because of their abundance, availability and low price. Their porous texture, high surface area and mechanical stability also make them attractive as sorbents for decontamination applications. Activated silica and silica based adsorbents have been proved as efficient adsorbents for the removal of all categories of dyes [92-97] made an exclusive study on the silica nano-sheets derived from vermiculite via acid leaching process and they proved that silica nano sheets are efficient adsorbents for the removal of cationic dye from aqueous solution. However due to their low resistance towards alkaline solutions, their usage is limited to media of pH less than 8.

Three pathways are available for the synthesis of porous hybrid materials based on organosilica units (1) the subsequent modification of the pore surface of a purely inorganic silica material "grafting" (2) the simultaneous condensation of corresponding silica and organosilica precursors "Condensation" (3) the incorporation of organic groups as bridging components directly and specifically in to the pore walls by the use of bisilylated single source organosilica precursors production of periodic mesoporous organosilicas (PMO)". The synthesis of organic-inorganic hybrid materials by hydrolysis and condensation reactions of bridged organo silica precursors of the type  $(R'O)_3Si-R-Si(O R')_3$  has been known for a long time from sol-gel chemistry [98]. In contrast to the organically functionalized silica phases contrast to the organically silica phases, which are obtained by postsynthetic or direct synthesis, the organic units in this case are incorporated in the three-dimensional network structure of the silica matrix through two covalent bonds and thus distributed totally homogeneously in the pore walls. These materials, which are obtained as porous aero- and xerogels, can have large inner surface areas of up to  $1800\text{m}^2\text{g}^{-1}$  as well as high thermal stability but generally exhibit completely disordered pore systems with a relatively wide distribution of pore radii [99]. PMO materials are considered as highly promising candidates for a series of technical applications, for example, in the areas of catalysts, adsorption, chromatography, nanoelectronics or the preparation of active compound release system.

Silica gel is a granular porous form of silica and is made synthetically from sodium silicate or silicon tetrachloride or substituted chlorosilane/orthosilicate solution. Stober et al have reported the synthesis of spherical silica particles from tetraethoxysilane using  $\text{NH}_3$  as catalyst. Silica gel is commonly used

as rigid matrix for ligand immobilization. The chemical modification of silica gel surfaces with donor atoms such as N, S, O and P is primarily aimed at improving the adsorption and exchange properties of the silica gel along with incorporation of the particular selective characteristics in to the modified silica gel phases towards certain metal ions.

The immobilization of chelating materials containing donor atoms on the silica gel surface can occur via chemical bond formation between organic modifiers like amino or chloro modified silica gel phases or through simple physical adsorption processes. This process often incorporates selectivity in the synthesized materials [100]

Metal quantification at low concentration levels comprises one of the most considered targets in analytical chemistry. Sample pretreatment methods, such as separation and/or preconcentration prior to the determination of metal ions have developed rapidly due to the increasing need for accurate and precise measurements at extremely low levels of ions in diverse matrices.

### Mesoporous silicates

The synthesis, characterization, and application of novel porous materials have been strongly encouraged due to their wide range of applications in adsorption, separation, catalysis, and sensors. The design, synthesis, and modification of porous materials are in some aspects more challenging than the synthesis of dense materials. Therefore, new strategies and techniques are continuously being developed for the synthesis and structure tailoring of mesoporous materials. Ordered mesoporous materials, based on MCM-41 (Mobile Crystalline Material), are silicates obtained by hydrothermal synthesis and a liquid templating mechanism [101-106]. Such materials exhibit remarkable features such as pores with well-defined sizes and uniform shapes that are ordered to some degree over micrometer length scales to yield arrays of non-intersecting hexagonal channels. The latter structures are readily identifiable by transmission electron microscopy (TEM) images and X-ray powder diffraction (XRD) patterns (Figure 1). These materials possess high surface areas of about  $1000\text{m}^2\text{g}^{-1}$  as revealed from surface area measurements. Mesoporous materials based on MCM-41 show excellent thermal, hydrothermal, and hydrolytic stabilities [107-111]. The walls of the channels are amorphous  $\text{SiO}_2$ , and the porosity can be as high as 80% of their total volume [102,103,107]. These materials can be synthesized using anionic, cationic, or neutral surfactants or non-surfactant template pathways. The diameter of the channels (pores) can be controlled by changing the length of the template molecule. Moreover, changing the silica sources [e.g., fused silica, colloidal silica, tetraethylorthosilicate (TEOS)], surfactants [e.g., hexadecylamine (HDA), and cetyltrimethylammonium bromide (CTAB)], auxiliary compounds [e.g., 1,3,5-trimethylbenzene (TMB)], or reaction conditions (solvent, temperature, aging time, reactant mole ratio, and the pH of the medium) leads to the production of new mesoporous systems. At the same time, these changes also affect the thermal, hydrothermal, and mechanical stabilities of the materials [101-103,107]. Functionalization of the surface of these mesoporous materials with organic or inorganic functional groups leads to new physical and chemical properties [110]. These modified materials can be used in a variety of applications such as catalysis, adsorption, and separation as chromatographic column packing [112-114]. The materials have been characterized using several characterization techniques including X-ray powder diffraction (X), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), elemental analysis (EA), thermogravimetric analysis (TGA), solid-state  $^{29}\text{Si}$  and  $^{13}\text{C}$  nuclear magnetic resonance spectroscopy (NMR), and surface area analysis including pore size, pore volume, and pore size distribution (PSD) measurements. In addition, the as-synthesized materials have been subjected to derivatization reactions in order to modify their surface with functional groups of interest. Their adsorption efficiency and selectivity have been determined along with their

applications for separation of heavy and transition metal ions, radioactive materials, and organic compounds. This review provides an introduction to the fundamental aspects of silicate mesoporous materials. It includes an overview and a concise historical introduction, a brief initiation to surfactant science, a broad introduction to sol-gel science, a general review of modification methods for MCM-41, and a summary of some applications of these materials. This review also includes introductions to the application of these modified materials for the adsorption and separation of toxic materials. The adsorption capacity, selectivity, and separation efficiency are reported, and the effect of pH of the media, temperature, and time on the adsorption and separation is also covered. In addition, the competition effect of some metal ions of alkali and alkaline earth metals such as sodium (Na), potassium (K), magnesium (Mg), and calcium (Ca) with respect to the adsorption and separation of heavy metal ions and radioactive materials is reported. Various techniques were used in order to determine the adsorption and separation efficiency such as ultraviolet-visible spectroscopy (UV-Vis), inductively coupled plasma atomic emission spectroscopy (ICP), and atomic absorption spectroscopy (AAS).

### Developments of Porous Materials

Zeolites and porous silicas take their place among the important porous materials for their wide applications in separation and catalysis. Zeolites are members of a large family of crystalline aluminosilicates. They were first discovered in 1756 by the Swedish scientist Cronstedt when an unidentified silicate mineral was subjected to heat; these strange minerals were found to bubble and froth, releasing bursts of steam. In the nineteenth century, zeolite minerals began to be well documented although there was a lack of general scientific interest. The term molecular sieve was derived from McBain in 1932 when he found that chabazite, a mineral, had a property of selective adsorption of molecules smaller than 5 Å in diameter [115]. In other words, molecular sieves retain the particles that fit within the channels and let the larger ones pass through. The term molecular sieves is used to describe a class of materials that exhibit selective sorption properties (i.e., that are able to separate a class of mixtures on the basis of molecular size and shape). However, Barrer and coworkers [116] studied the sorptive properties of chabazite and other porous minerals and reported that nitrogen and oxygen could be separated using a zeolite that had been treated to provide the necessary shape selectivity for discrimination between the molecular dimensions. Later, synthetic zeolites began to be used in large amounts for the production of pure oxygen from air. Between 1949 and 1954, Breck and coworkers [117] were able to synthesize a number of new zeolites (types A, X, and Y) which were produced in large scale to be used for the separation and purification of small molecules. Since then, the nomenclature of this kind of porous material has become universal. The success of synthesizing crystalline aluminosilicates, in particular the emergence of the new family of aluminophosphates [118] and silicoaluminophosphates [119], made the concept of zeolites and molecular sieves more complicated.

The small pore entrances (diameters) in zeolites (e.g., 0.4 nm in zeolite A) were attractive for commercial applications because they provided the opportunity for selective adsorption based on small differences in the size of gaseous molecules. In addition, these materials caught the attention of scientists who were interested in catalysis. At the beginning, the oil industry was reluctant to accept the idea, since it was thought that these materials had pores too small to be of interest for cracking activity (break down of long hydrocarbon molecules into gasoline and other useful products). The zeolite marketing prospects were improved when Breck and coworkers showed rare earth-containing zeolites had the ability to handle cracking activity [117]. There has been, however, a continually growing interest in expanding the pore sizes of zeotype materials from the micropore region to mesopore region in response to the increasing demands of both industrial and fundamental studies. Examples are the separation of heavy metal ions, the separation and selective adsorption of large or-

ganic molecules from waste water, the formation of a supra-molecular assembly of molecular arrays, the encapsulation of metal complexes in the frameworks, and the introduction of nanometer particles into zeolites and molecular sieves for electronic and optical applications [120–122]. Therefore, to meet these demands, numerous experiments to create zeotype materials with pore diameters larger than those of the traditional zeolites were carried out. Since it was thought that most of the organic templates used to synthesize zeolites affect the gel chemistry by filling the voids in the growing porous solid, many of these attempts used larger templates. It was not until 1982 that success was achieved by changing the synthesis gel compositions when the first so-called ultra large pore molecular sieve, which contains 14-membered rings, was discovered [118]. Indeed, this not only broke the deadlock of the traditional viewpoint that zeolite molecular sieves could not be constructed with more than 12-membered rings, but also stimulated further investigations into other ultra large pore molecular sieves, such as VPI-5 with an 18-tetrahedral ring opening, cloverite, and JDF-20 [123–125]. While these zeolites attracted much attention and were of scientific importance, they have not found any significant applications because of their inherently poor stability, weak acidity, or small pore size (0.8–1.3 nm). As a consequence, they seem to be inferior compared to pillared layered clays.

Yanagisawa et al. described in the early 1990s the synthesis of mesoporous materials that have characteristics similar to that of MCM-41 [126]. Their preparation method is based on the intercalation of long-chain (typically C-16) alkyltrimethylammonium cations, into the layered silicate kanemite, followed by calcination to remove the organic species, which is later called surfactant, yielding a mesoporous material. The silicate layers condensed to form a three dimensional structure with nanoscale pores. <sup>29</sup>Si solid-state NMR spectroscopy indicated that a large number of the incompletely condensed silica site Si(OSi)<sub>3</sub>(OH) (Q3) species were converted to the completely condensed silica site Si(OSi)<sub>4</sub> (Q4) species during the intercalation and calcination processes. The X-ray powder diffraction gave only an uninformative peak centered at extremely low angles. Unfortunately, there were no further characterization data available which lead to disregard of the results of Yanagisawa *et al.* in 1992, researchers at Mobil Corporation discovered the M41S family of silicate/aluminosilicate mesoporous molecular sieves with exceptionally large uniform pore structures [127] and later they were produced at Mobil Corporation Laboratories [128]. The discovery resulted in a worldwide resurgence in this area [101–103,107]. The synthesis of this family of mesoporous materials is based on the combination of two major sciences, sol-gel science and surfactant (templating) science. The template agent used is no longer a single, solvated organic molecule or metal ion, but rather a self-assembled surfactant molecular array as suggested initially [107–109,111]. Three different mesophases in this family have been identified, i.e., lamellar (MCM-50), hexagonal (MCM-41), and cubic (MCM-48) phases [129]. The hexagonal mesophase, denoted as MCM-41, possesses highly regular arrays of uniform-sized channels whose diameters are in the range of 15–100Å depending on the templates used, the addition of auxiliary organic compounds, and the reaction parameters [107–111]. The pores of this novel material are nearly as regular as zeolites, however, they are considerably larger than those present in crystalline materials such as zeolites, thus offering new opportunities for applications in catalysis, chemical separation, adsorption media, and advanced composite materials [111,128,129]. MCM-41 has been investigated extensively because the other members in this family are either thermally unstable or difficult to obtain [130]. In 1998, prominent research produced another type of hexagonal array of pores namely Santa Barbara Amorphous no 15 (SBA-15). SBA-15 showed larger pore size from 4.6 to 30 nm and discovery of this type of material was a research gambit in the field of mesoporous material development [131]. This SBA-15 mesoporous material has not only shown larger pores, but also thermal, mechanical and chemical resistance properties and that makes it a preferable choice for use as a catalyst. The



formation of ordered hexagonal SBA-15 with uniform pores up to 30 nm was synthesized using amphiphilic triblock copolymers in strong acidic media was reported in the literature [132–134]. A detailed review on types, synthesis, and applications towards Biorefinery Production of this SBA 15 mesoporous material has already been published in the literature [135].

Hybrid organic inorganic silica nanoparticles are a special class of synthetically modified mesoporous materials. The composition of these nanostructured materials are silicon oxide (SiO<sub>2</sub>) with abundant silanol groups (Si-OH) on the external surface and the internal of the pores [Fig.1]. Ordered mesoporous silicate has unique properties, including good monodispersity, with extremely high surface areas (>1000 m<sup>2</sup>/g) due to a narrow pore size distribution and well defined pore networks, large pore volume (1.5 cm<sup>3</sup>/g), controlled pore size (2.0-45.0 nm) by the size of the surfactant template, high mechanical and thermal stability (up to 1000°C) and longer hydrothermal treatment times under boiling water and steam, hence providing a confined space for controlled intrapore inclusion chemistry as hosts. Therefore, the mesoporous silicates nanoparticles have recently received much attention for their practical applications in catalysis, adsorption, sensing, lasers, optical and electronic devices. These hybrid materials were synthesized using surfactant/block copolymer as a template in sol-gel chemistry [136].

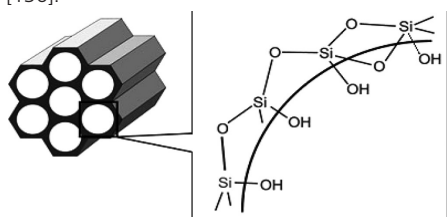


Fig-1: SiO<sub>2</sub> mesoporous silicates with abundant silanol group (Si-OH)

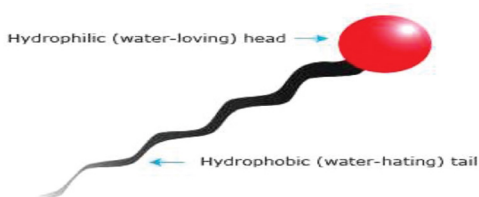


Fig. 2: Structure of the surfactant

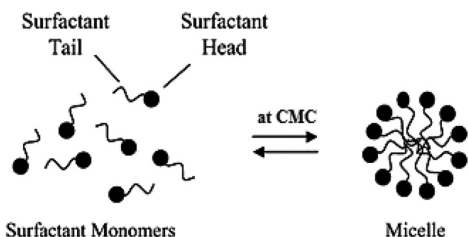


Fig. 3: Surfactant classification according to the charge of head group

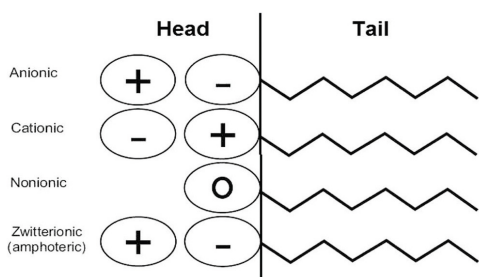


Fig. 4: Aggregation of surfactant to form of micelle

**Surfactant**

Surfactants are surface active agents. At low concentrations, they usually reduce the surface or interfacial energies when adsorbed onto a surface or interface [137]. They have an amphiphathic structure with a lyophilic (hydrophilic) head group and a lyophobic (hydrophobic) tail (Fig.2). Surfactants are classified as an ionic (negatively charged head group), cationic (positively charged head group), non-ionic (no charge on the head group) and zwitterionic or amphoteric (both positive and negative charges on the head group) as illustrated in (Fig.3-4) [138]. In solution the surfactants tend to aggregate to form micelles, when the concentration of the surfactant is equal to the critical micelle concentration (CMC). The formation of micelles is governed by molecular interactions (e.g. Vanderwaals forces, hydrogen bonding and electrostatic forces) and hydrophobic interactions [139]. The major aggregates formed are spherical (normal) micelles, cylindrical (rod-like) micelles, hexagonal, cubic and lamellar (bi-layer) structures, based on the concentration and shape of surfactant [140]. An increase in surfactant concentration above the CMC causes the individual micellar structures to pack together into different.

**Silanol**

It is a functional group in silicon chemistry with the connectivity Si-O-H (Fig.5). It is related to the hydroxy functional group (C-O-H) found in all alcohols. Silanols are often invoked as intermediates in organosilicon chemistry and silicate mineralogy [141].

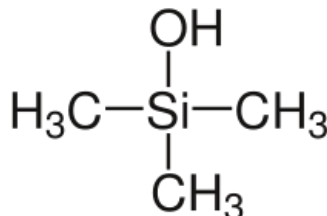


Fig.5: Structure of Trimethylsilanol

**From alkoxysilanes**

The first isolated example of a silanol was Et<sub>3</sub>SiOH, reported in 1871 by Albert Ladenburg. He prepared the "silicol" by hydrolysis of Et<sub>3</sub>SiOEt (Et = C<sub>2</sub>H<sub>5</sub>) [142].

**From silyl halides**

Silanols are generally synthesized by hydrolysis of halosilanes, alkoxysilanes, or aminosilanes. Chlorosilanes are the most common reactants:



The hydrolysis of fluorosilanes requires more forcing reagents, i.e. alkali. The alkoxysilanes (silyl ethers) of the type R<sub>3</sub>Si (OR') are slow to hydrolyze. Compared to the silyl ethers, silyl acetates are faster to hydrolyze, with the advantage that the released acetic acid is less aggressive. For this reason silyl acetates are sometimes recommended for applications [143].

**From silyl hydrides**

An alternative route involves oxidation of hydrosilanes. A wide range of oxidants have been employed including air, peracids, dioxiranes, and potassium permanganate (for hindered silanes). In the presence of metal catalysts, silanes undergo hydrolysis [143]:



**Structure and examples**

The Si-O bond distance is typically about 1.65 Å. [143] in the solid state, silanols engage in hydrogen-bonding [144].

Most silanols have only one OH group, e.g. trimethylsilanol. Also known are some silanediols, e.g., diphenylsilanediol. For sterically bulky substituents, even silanetriols have been prepared [143].

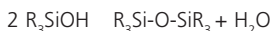
## Reactions

### Acidity

Silanols are more acidic than the corresponding alcohols. This trend contrasts with the fact that Si is far less electronegative than carbon (1.90 vs 2.55, respectively). For  $\text{Et}_3\text{SiOH}$ , the  $\text{p}K_a$  is estimated at 13.6 vs. 19 for *tert*-butyl alcohol. The  $\text{p}K_a$  of  $(3\text{-ClC}_6\text{H}_4)_2\text{Si}(\text{CH}_3)_2\text{OH}$  is 11. Because of their greater acidity, silanols can be fully deprotonated in aqueous solution, especially the arylsilanols. The conjugate base is called a siloxide or a silanoate. Despite the disparity in acidity, the basicities of the two series are similar [143].

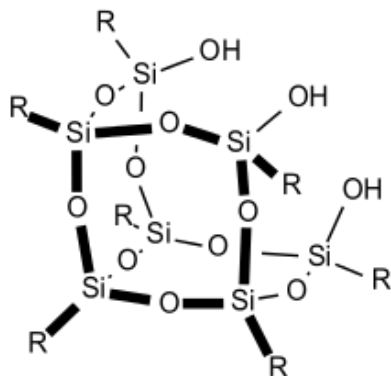
### Condensation and the sol-gel process

Silanols condense to give siloxanes:



The conversions of silyl halides, acetates, and ethers to siloxanes proceed via silanols. The sol-gel process, which entails the conversion of, for example,  $\text{Si}(\text{OEt})_4$  into hydrated  $\text{SiO}_2$ , proceeds via silanol intermediates.

Silanols exist not only as chemical compounds, but are pervasive on the surface of silica and related silicates (Fig.6). Their presence is responsible for the absorption properties of silica gel [145]. In chromatography, derivitization of accessible silanol groups in a bonded stationary phase with trimethylsilyl groups is referred to as endcapping.



**Fig.6: Trisilanol intermediate in the formation of a cubic silsesquioxane.**

Literally, silanol refers to a single compound with the formula  $\text{H}_3\text{SiOH}$  (Chemical Abstracts number 14475-38-8). The family  $\text{SiH}_{4-n}(\text{OH})_n$  ( $n = 1, 2, 3, 4$ ) are highly unstable and are mainly of interest to theoretical chemists. The perhydroxylated silanol, sometimes called orthosilicic acid, is often discussed in vague terms, but has not been well characterized.

### Application of These Materials in Environmental Pollution Control Processes

Contamination of water streams by transition metals, heavy metals, and radioactive compounds (e.g., nickel, copper, lead, mercury, cadmium, uranium, and thorium) remains a concern in the field of environmental remediation. These materials enter the environment through a variety of avenues that include: mining, nuclear power plants, and industrial processing plants. Furthermore, some natural waters contain naturally high concentration levels of metals [146]. The presence of even low concentrations (ppb) of some heavy metals or radioactive substrates in natural water systems can have a harmful effect on both wildlife and humans. However, at these low concentrations of metal ions the sample often requires pre-concentration before analysis can be undertaken. Adsorption onto solid substrates (e.g., activated carbons, zeolites, aluminas, and silicas) provides one of the most effective means for adsorption, separation and removal of trace pollutants (heavy metal ions, radioactive compounds, etc.) from aqueous streams [146,147]. A wide variety of novel materials can be prepared by the chemical modification of ordered mesoporous materials, since

numerous organic and inorganic functionalities can be used for this purpose. In addition to their use in chromatographic separations, these materials have been increasingly used as heterogeneous catalysts in liquid phase organic reactions. It is their characteristics, such as viability and environmental safety, which makes them alternatives to traditional absorbent materials such as activated charcoal and zeolites. Their use as efficient materials for the selective adsorption and separation, and high capacity uptake of trace metals from aqueous systems is due to their unique characteristics such as high surface area, large pore size, and presence of reactive groups on the surfaces [146-148]. Many of the more recent advances have been focused on the use of modified silicas for clean technology. One area of research in which modified silicas are used for clean technology applications, other than catalysis, is in the adsorption, separation, removal, and analysis of trace components in aqueous systems. A wide variety of analytical techniques have been developed to separate and determine trace metal concentrations in natural water [146]. Several methods have been employed in the adsorption and separation of metal ions from aqueous solutions, such as activated charcoal, zeolites, clays, solvent extraction using a chelating agent [146] and the use of polymeric resins [147]. These methods suffer from a number of drawbacks. The use of activated charcoal, zeolites and clays showed low loading capacities and relatively small metal ion binding constants [148]. However, the use of chelating reagents (i.e., iminodiacetate resin) is time consuming, whereas organic resins possess low surface area and low mechanical stabilities, and the time taken for the metal ion to be complexed, can be of the order of hours. Conventional methods such as precipitation are unfavorable especially when dealing with large volumes of matter which contain heavy metal ions in low concentration. Typically these ions are precipitated as hydrated metal oxides or hydroxides or sulfides using calcium oxide. Precipitation is accompanied by flocculation or coagulation, and one major problem is the formation of large amounts of sediments containing heavy metal ions. In addition, these methods are often unselective towards the metal being analyzed, with interference from alkaline earth metals being particularly problematic [149]. In recent years, the use of modified mesoporous silica in the pre-concentration and separation of trace metal ions has been investigated [150]. Modified silica gels offer the advantages of high surface areas and increased chemical and mechanical stability. Nitrogen-containing organic groups have been shown selectively to bind to first row transition metals from solution [150]. Thus, Marshall and Mottola [149] prepared an immobilized quinolin-8-ol complex for the pre-concentration and separation of copper (II) ions. By varying the pH of the solution, a variety of transition metal (II) ions could be extracted selectively, even in the presence of alkali and alkaline earth metal ions. This makes the material useful for separation and analysis of trace metals in natural waters where alkaline earth metals are to be expected. There are factors that affect the adsorption and selectivity such as the pH and ionic strength of the water medium, the concentration ratio of the metal ion to the adsorbent, and the agitation time [151]. However, the unitary silica framework of siliceous MCM-41 limits its practical application, especially in catalysis owing to the lack of active sites. Therefore, great efforts have been focused on surface modification to expand the area of applications and many elements have been doped into the wall of MCM-41 including Al, Fe, Zn, Ti, V, Cu, Ni, W, and Mn [152-156]. Many researches have been focused on manganese oxides, owing to their ion-changing, molecular adsorption, catalytic, and magnetic properties and use as catalysts for environmental treatment of water. The detailed application of mesoporous materials as host-guest chemistry, environmental technology, adsorption, chemical sensors and electrode catalysis or adsorption is broadly reported in the published paper [157].

### CONCLUSION

Increased utilization of mechanically stable synthetic matrices particularly silica gel as a solid support and its surface modification either by impregnation of organic ligands directly or covalent grafting through spacer unit for extractive concentra-

tion of trace elements are highlighted in the present article. Experimental evidences for existence of surface silanol and its chemical nature have explored the idea of silica surface modification. Recent methods of development in functionalized silica synthesis by attachment of various ligands or organic reagents to the silica surface and techniques of characterization of the modified surface have been reported. Analytical applications of various modified silica surfaces, in particular, adsorption of trace elements taking separation and pre concentration into account from complex synthetic mixture as well as natural water is presented.

#### ACKNOWLEDGEMENT

The authors are thankful to Department of Chemistry, Central University, Ranchi, Jharkhand for providing necessary facilities for carrying out the experimental work. Finally we are thankful to Gayatri Nahak for helping in computer work without which preparation of the manuscript would not have been possible.

#### REFERENCE:

- Ippolito JA, Barbarick KA, Redente EF. Co-application effects of water treatment residuals and biosolids on two range grasses. *J. Environ. Qual* 1999;28:1644-1650.
- Baby J, Raj JS, Biby ET, Sankarganesh P, Jeevitha MV, Ajisha SU, Rajan SS. Toxic effect of heavy metals on aquatic environment. *Int. J. Biol. Chem. Sci* 2010;4(4): 939-952.
- Farombi EO, Adelowo OA, Ajimoko YR. Biomarkers of oxidative stress and heavy metal levels as indicators of environmental pollution in African Cat fish (*Clarias gariepinus*) from Nigeriaogun River. *Int. J. Environ. Res. Public Health* 2007;4(2): 158-165
- Clarkson TW. Human toxicology of mercury. *J. Trace. Elem. Exp. Med.*, 1998;11(2-3): 303-317.
- Yi Y, Yang Z, Zhang S. Ecological risk assessment of heavy metals in sediment and human health risk assessment of heavy metals in fishes in the middle and lower reaches of the Yangtze River basin. *Environ. Pollut* 2011;159:2575-2585.
- Sun YB, Zhou QX, Xie XK, Liu R. Spatial, sources and risk assessment of heavy metal contamination of urban soils in typical regions of Shenyang, China. *Journal of Hazardous Materials* 2010;174:455-462.
- Anas Ghadouani, Liah Coggins X. Science, technology and policy for Water Pollution Control at the Watershed Scale: Current issues and future challenges *Physics and Chemistry of the Earth* 2011;36:335-341
- Wang Q, Cissoko N, Zhou M, Xu X. Effects and mechanism of humic acid on chromium (VI) removal by zero-valent iron (Fe0) nanoparticle. *J. Phys. Chem. Earth* 2011; 36: 442-446.
- Moore MR. A commentary on the impacts of metals and metalloids in the environment upon the metabolism of drugs and chemicals. *Toxicol Lett* 2004;148:153-158.
- Inoue KI, Satoh M. *Metallothionein as a Therapeutic Molecular Target against Human Diseases*. *Curr Pharm Biotechnol* 2013 Apr 12.
- Mishra A, Shukla SK. *Heavy metal toxicity: A blind evil*. *J. Forensic Res* 2014;5:2.
- Zhu, LK. Plant salt tolerance. Heavy Metal Pollution is More Common than You Think. *Conservation Currents, Northern Virginia Soil and Water Conservation District*. *Trends in Plant Science*, 2005;6(2):66-71.
- Husam Malassa, Mutaz Al-Qutob, Mahmoud Al-Khatib, Fuad Al-Rimawi. Determination of Different Trace Heavy Metals in Ground Water of South West Bank/Palestine by ICP/MS. *Journal of Environmental Protection* 2013;4:818-827.
- Momodu MA, Anyakora CA. Heavy Metal Contamination of Ground Water: The Surulere Case Study," *Research Journal Environmental and Earth Sciences* 2010;2(1):39-43.
- Ghanem M, Samhan N. Groundwater Pollution Assessment in Tulkarem Area, Palestine. *Journal of Earth Sciences and Geotechnical Engineering* 2012;2(4):1-16.
- Dupler D. Heavy Metal Poisoning, In: J. L. Longe, Ed., *Gale Encyclopedia of Alternative Medicine*, Gale Group, Farmington Hills 2001;2054-2057.
- Chen Ye, Siyue Li, Yulong Zhan, Xunzhang Tong, Quanfa Zhang. Assessing heavy metal pollution in the water level fluctuationzone of China's Three Gorges Reservoir using geo chemical and soil microbial approaches. *Environ Monit Assess* 2013;185:231-240.
- Szczewski P, Siepak J, Niedzielski P, Sobczyk T. Research on Heavy Metals in Poland. *Polish J. of Environ. Stud* 2009;18:5:755-768.
- Dianne Baldwin R, William Marshall J. *Heavy Metal Poisoning and its Laboratory Investigation Ann Clin Biochem* 1999;36:267-300.
- Ahmad, AL, Ooi, BS. A study on acid reclamation and copper recovery using low pressure nano filtration membrane. *Chem. Eng. J.* 2010;56:257-263.
- Ajibi LC, Chouba L. Biosorption of Cu2p and Zn2p from aqueous solutions by dried marine green macroalga *Chaetomorpha linum*. *J. Environ. Manage* 2009;90:3485-3489.
- Barakat MA, Schmidt E. Polymer-enhanced ultrafiltration process for heavy metals removal from industrial waste water. *Desalination* 2010;256:90-93.
- Mohd Muzamil Bhat, Kamini Narain, Syed Zulfiqar Ahmad Andrabi, Shukla RN, Yunus M. Assessment of Heavy Metal Pollution in Urban Pond Ecosystems. *Universal Journal of Environmental Research and Technology* 2012;2(4):225-232.
- Fenglian Fu, Qi Wang. Removal of heavy metal ions from wastewaters: A review. *Journal of Environmental Management* 2011;92:407-418.
- Feng D, Aldrich C, Tan H. Treatment of acid mine water by use of heavy metal precipitation and ion exchange. *Miner. Eng* 2000;13:623-642.
- Demirbas E, Kobya, M, Sulak MT. Adsorption kinetics of a basic dye from aqueous solution on to apricot stone activated carbon. *Bioresour Technol* 2008;99(13):5368-5373.
- Suzuki RM, Andrade AD, Sousa JC, Rollemberg MC. Preparation and characterization of activated carbon from rice bran. *Bioresour Technol* 2007;98(10):1985-1991.
- Kurniawan TA, Chan GYS, Lo WH, Babel S. Physico Chemical treatment techniques for waste water laden with heavy metals. *Chemical Engineering Journal* 2006;118(1-2):83-98.
- Khuhawar MY, Lanjwani SN. Indirect Determination of Mefenamic Acid by Atomic Absorption Spectrometry. *J. Chem. Soc. Pak.* 2001;23(3):157-162.
- S.Tautkus, L. Steponeniene, R. Kazlauskas, J.Serb. Determination of iron in natural and mineral waters by flame atomic absorption spectrometry. *Chem. Soc* 2004;69:393.
- Tautkus S. Extractive Preconcentration and Determination of Nickel in Water and Wastewater Samples by Atomic Absorption Spectrometry. *Chem. Anal* 2004;49:271.
- Anthemidis AN, Zachariadis GA, Farastelis CG, Stratis JA. On-line liquid - liquid extraction system using a new phase separator for flame atomic absorption spectrometric determination of ultra - trace cadmium in natural waters. *Talanta* 2004;62(3):437-443.
- Fang G, Liu Y, Meng S, Guo Y, Spectrophotometric determination of lead in vegetables with dibromo - p - methyl -carboxysulfonazo. *Talanta* 2002;57(6):1155-1160.
- Krishna PG, Gladis JM, Rambabu U, Rao TP, Naidu GRK. Preconcentrative separation of chromium (VI) species from chromium (III) by coprecipitation of its ethyl xanthate complex on to naphthalene. *Talanta* 2004;63(3):541-546.
- Cavaco SA, Fernandes S, Quina MM, Ferreira LM. Removal of chromium from electroplating industry effluents by ion exchange resins. *J. Hazard. Mater* 2007;144:634-638.
- Gode F, Pehlivan E. Removal of chromium (III) from aqueous solutions using Lewatit S 100: the effect of pH, time, metal concentration and temperature. *J. Hazard. Mater* 2006;136:330-337.
- Minami T, Atsumi K, Ueda J. Determination of Cobalt and Nickel by Graphite - Furnace Atomic Absorption Spectrometry after coprecipitation with scandium hydroxide. *Anal. Sci* 2003;19(2):313-315.
- Anezaki K, Chen XZ, Ogasawara T, Nukatsuka I., Ohzeki K., Determination of Cadmium and Lead in tap water by Graphite Furnace Absorption Spectrometry after preconcentration on a finely divided ion exchange resin as the pyrrolidinedithiocarbamate complexes. *Anal. Sci* 1998;14(3):523-527.
- Shayesteh D, Mostafa T, Ali Mohammad Haji Shabani, ZahraAmani B. Determination of Lead and Cadmium in Different Samples by Flow Injection Atomic Absorption Spectrometry Incorporating a Microcolumn of Immobilized Ammonium Pyrrolidine Dithiocarbamate on Microcrystalline Naphthalene. *Croatia Chemica Acta CCACAA* 2007;80(1):17-23.
- Lemos VA, Santos JS, De Carvalho MB, Baliza PV, Yamaki RT. Amberlite XAD-2 functionalized with Nitroso R Salt: synthesis and application in an on-line system for preconcentration of cobalt. *Anal. Chim. Acta* 2003;494:87-95.
- Lemos VA, Silva DG, Carvalho AL, Santana DA, Novaes GS, Passos AS. Synthesis of Amberlite XAD-2-PC resin for preconcentration and determination of trace elements in food samples by flame atomic absorption spectrometry. *Microchem. J* 2006;84:14-21.
- Jain VK, Sait SS, Shrivastav P, Agrawal YK. Application of chelate forming resin Amberlite XAD-2-o-vanillinthiosemicarbazone to the separation and preconcentration of copper(II), zinc(II) and lead(II). *Talanta* 1997;45:397-404.
- He HB, Ma GZ, Zhang WL, Shen HX. Determination of Europium (III) by graphite furnace atomic absorption spectrometry with preconcentration by 2-Thenoyl Trifluoroacetone Phenanthroline modified electrode. *Chin. J. Anal. Chem* 2001;29:1125.
- Stafilov T, Zenzelovska D, Pavlovska G, Cundeva K. Determination of trace elements in dolomite and gypsum by atomic absorption spectrometry: over-

- coming the matrix interference by flotation separation. *Spectrochimica Acta, Part B* 2002;57:907-917.
45. Soylak M, Elci L, Dogan M. Determination of trace amounts of cobalt in natural water samples as 4-(2-thiazolylazo) resorcinol complex after adsorptive preconcentration. *Anal. Lett* 1997;30:623-630.
  46. Narin I, Soylak M, Kayakirilmaz K, Elci L, Dogan M. Preparation of a chelating resin by immobilizing 1-(2-pyridylazo) 2-naphthol on Amberlite XAD-16 and its application of solid phase extraction of Ni(II), Cd(II), Co(II), Cu(II), Pb(II), and Cr(III) in natural water samples. *Anal. Lett* 2003;36:641.
  47. Ghiasvand AR, Shadabi S, Mohagheghzadeh E, Hashemi P. Homogeneous liquid-liquid extraction method for the selective separation and preconcentration of ultra trace molybdenum. *Talanta* 2005;66:912-916.
  48. Yu JC, Chan SM, Chen ZL. Preconcentration using diethylenetriamine-tetraacetic acid - functionalized polysiloxane (DETAP) for determination of molybdenum (VI) in seawater by ICP - OES. *Anal. Bioanal. Chem* 2003; 375:139-144.
  49. Dogutan M, Filik H, Apak R. Preconcentration of manganese (II) from natural and sea water on a palmitoyl quinolin-8-ol functionalized XAD copolymer resin and spectrophotometric determination with the formaldoïn reagent. *Anal.Chim. Acta* 2003;485:205.
  50. Okumura M, Anate T, Fujinaga K, Seike Y. A simple and rapid in situ preconcentration method using solid-phase extraction for the determination of dissolved manganese in brackish lake water samples. *Anal. Sci* 2002;18:1093-1097.
  51. Bag H, Turker AR, Tunceli A, Lale M. Determination of Fe(II) and Fe(III) in water by flame atomic absorption spectrophotometry after their separation with *Aspergillus niger* immobilized zednon sepiolite. *Anal. Sci* 2001;17:901-904.
  52. Ersoz A, Say R, Denizli A. Ni(II) ion-imprinted solid-phase extraction and preconcentration in aqueous solutions by packed-bed columns. *Anal. Chim. Acta* 2004; 525:281-287.
  53. Starvin AM, Rao TP, Hazard J. Removal and recovery of mercury(II) from hazardous wastes using 1-(2-thiazolylazo)-2-naphthol functionalized activated carbon as solid phase extractant. *Mater* 2004;113:77.
  54. Muthuraman G, Teng TT, Leh CP. Extraction and recovery of methylene blue from industrial wastewater using benzoic acid as an extractant. *J. Hazard. Mater* 2009; 15;163(1):363-9.
  55. Nickson RA, Hill SJ, Worsfold PJ. Analytical perspective. Solid phase techniques for the preconcentration of trace metals from natural waters. *Anal. Proc. Sep* 1995;32:387-395.
  56. Lemos VA, Santos JS, De Carvalho MB, Baliza PX, Yamaki RT. Amberlite XAD-2 functionalized with nitroso R salt :synthesis and application in an on-line system for preconcentration of cobalt. *Anal. Chim. Acta* 2003;494:87-95.
  57. Guo Y, Din B, Liu Y, Chang X, Meng S, Liu J. Solid phase spectrophotometric determination of nickel in water and vegetable samples at sub-mg level with O-Carboxylphenyl Diazoaminoazobenzene loaded XAD-4. *Talanta* 2004; 64(1):160-166.
  58. Phol P, Prusisz B. Pre-concentration of Cd ,Co ,Cu , Ni and Zn using different offline ion exchange procedures followed by the inductively coupled plasma atomic emission spectrometric detection. *Anal. Chim. Acta* 2004;508:83.
  59. Scindia YM, Pandey AK, Reddy AVR, Manohar SB. Selective preconcentration and determination of chromium (VI) using a flat sheet polymer inclusion sorbent : potential application for Cr (VI) determination in real samples. *Anal. Chem* 2002;74:4204-4212.
  60. Sengupta B, Das J. Preconcentration of trace amounts of mercury(II) in water on picolinic acid amide-containing resin. *Anal. Chim. Acta* 1989;219:339-343.
  61. Walcarius A, Etienne M, Delacote C. Uptake of inorganic Hg(II) by organically modified silicates :influence of pH and chloride concentration on the binding pathways and electrochemical monitoring of the processes. *Anal. Chim. Acta* 2004;508:87-98.
  62. Singh AK, Venkataramani B. 8-Hydroxyquinoline anchored to silica gel via new moderate size linker: synthesis and applications as a metal ion collector for their flame atomic absorption spectrometric determination. *Talanta* 2003;60:1141.
  63. Mahmoud ME, Gohai GA. Review of various techniques for preconcentration of metal ions. *Talanta* 2000;51:77.
  64. Mahmoud ME, Osman MM, Amer ME. Selective pre-concentration and solid phase extraction of mercury (II) from natural water by silica gel - loaded dithione phases. *Anal. Chim. Acta* 2000;415:33-40.
  65. Filha VLSA, Espinola JGF, DaFonseca MG, DeOliveira SF, Arakaki T, Airoidi C. New thiol adsorbent grafted on silica gel: synthesis, characterization and employment for heavy metal adsorptions. *J. Environ. Monit* 2003;5:366-370.
  66. Dey RK, Jha U, Singh AC, Samal S, Ray AR. Extraction of metal ions using chemically modified silica gel covalently bonded with 4,4'-diaminodiphenylether and 4,4'-diaminodiphenylsulfone-salicylaldehyde Schiff bases. *Anal. Sci* 2006;22:1105-1110.
  67. Prado AGS, Airoidi C. Adsorption, preconcentration and separation of cations on silica gel modified with the herbicide 2,4-dichlorophenoxyacetic acid. *Anal. Chim. Acta* 2001; 432:201-211.
  68. Hassanien MM, Sherbini KSA. Synthesis and characterisation of morin-functionalised silica gel for the enrichment of some precious metal ions. *Talanta*, 2006;68:1550-1559.
  69. He Q, Chang X, Zhang H, Jiang N, Hu Z, Zhai Y. Review of various techniques for preconcentration of metal ions. *Chem. Anal* 2006;51:715.
  70. Matoso E, Kubota LT, Cadore S. Use of silica gel chemically modified with zirconium phosphate for preconcentration and determination of lead and copper by flame atomic absorption spectrometry. *Talanta* 2003;60:1105-1111.
  71. Sadeghi S, Sheikhzadeh E. Solid phase extraction using silica gel functionalized with Sulfasalazine for preconcentration of Uranium(VI) ions from water sump. *Microchim. Acta* 2008;163:313-320.
  72. Javid A, Heravi MM, Bamoharrami FF. Review of various techniques for preconcentration of metal ions. *J.Chem* 2011;8:910.
  73. Hassanien MH, Sherbini KSA. Synthesis and characterization of Morin-functionalized silica gel for the enrichment of some precious metal ions. *Talanta*, 2006;68:1550-1559.
  74. Akl MAA, Kenawy IMM, Lasheen RR. Organically modified silica gel and flame atomic absorption spectrometry: employment for separation and preconcentration of nine trace heavy metals for their determination in natural aqueous systems. *Micro chim. J.* 2004;78:143-156.
  75. Chen XM, Yamamoto C, Okamoto Y. Influence of vinyl monomers and temperature on immobilization of cellulose 3,5-dimethylphenylcarbamate onto silica gel as chiral stationary phases for high-performance liquid chromatography. *J. Chromatogr. A* 2006;1104:62-68.
  76. Merdivan M, Seyhan S, Gok C. Use of benzoylthiourea immobilized on silica gel for separation and preconcentration of Uranium(VI). *Micro chim. Acta* 2006;154:109-114.
  77. Barbette F, Rascaou F, Chollet H, Babouhot JL, Denat F, Guillard R. Extraction of uranyl ions from aqueous solutions using silica-gel-bound macrocycles for alpha contaminated waste water treatment. *Anal Chim Acta* 2004;502:179-187.
  78. Xie ZH, Xie FZ, Guo LQ, Lin XC. Thioacetamide chemically immobilized on silica gel as a solid phase extractant for the extraction and preconcentration of copper(II), lead(II), and cadmium(II). *J. Sep. Sci* 2005;28:462-470.
  79. Tokalioglu S, Oymak T, Kartal S. Determination of Palladium in various samples by atomic absorption spectrometry after preconcentration with dimethylglyoxime on silica gel. *Anal. Chim. Acta* 2004;511:255-260.
  80. Trojanowicz M, Pyrzynska K. Determination of trace amounts of cobalt by flow injection with spectrophotometric detection. *Anal. Chim. Acta* 1994;287:247.
  81. Narin M., Soylak L., Elci, Dogan M. Determination of trace metal ions by AAS in natural water samples after preconcentration of pyrocatechol violet complexes on an activated carbon column. *Talanta* 2000;52:1041-1046.
  82. Takara EA, Cabello SDP, Ceruti S, Gasquez JA, Martinez LD. On-line preconcentration/determination of copper in parenteral solutions using activated carbon by inductively coupled plasma optical emission spectrometry. *J. Pharm. Biomed. Anal* 2005;39:735-739.
  83. Lee SH, Choi HS. Determination of copper after preconcentration as its 1-nitroso-2-naphthol complex onto activated carbon. *Bull Korean Chem Soc* 2003;24(1):1705-1707.
  84. Akl MAA, Kenawy IM, Lasheen RR. Silica gel modified with N-(3-propyl)-O-phenylenediamine: functionalization, metal sorption equilibrium studies and application to metal enrichment prior to determination by flame atomic absorption spectrometry. *Anal. Sci* 2005;21:923-31.
  85. Jafari A, Maghimi A. Selective pre-concentration and solid phase extraction of mercury(II) from natural water by alumina loaded bis (2-hydroxyphenyl-amino) glyoxime phases. *Orient. J. Chem* 2007;23:129.
  86. Sheta AS, Falatah AM, Al-Sewaillem MS, Khaled EM, Sallam ASH. Sorption Characteristics of Zinc and Iron by Natural Zeolite and Bentonite. *Micropor. Mesopor. Mater* 2003;61:127-136.
  87. Chang YC, Chen DH. Preparation and adsorption properties of monodisperse chitosan-bound Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles for removal of Cu(II) ions. *J. Colloid. Inter. Sci* 2005;283:446-451.
  88. Chang YC, Chang SW, Chen DH. Magnetic chitosan nanoparticles: studies on chitosan binding and adsorption of Co(II) ions. *React. Funct. Polym* 2006;66:335-341.
  89. Sabarudin A, Oshima M, Takayanagi T, Hakim L, Oshita K, Gao YH, Motomizu S. Functionalization of chitosan with 3,4-dihydroxybenzoic acid for the adsorption/collection of uranium in water samples and its determination by inductively coupled plasma-mass spectrometry. *Anal. Chim. Acta* 2007;581:214-220.



90. Phol P, Prusisz B. Review of various techniques for preconcentration of metal ions. *Anal. Chim. Acta* 2004;508:83-90.
91. Moawed EA. Separation and preconcentration of trace amounts of cadmium (II) and mercury (II) ions on rosaniline-grafted polyurethane foam. *Acta Chromatographica* 2004; 378(2):470-478.
92. Bermudez VZ, Carlos LD, Alcacer L. Sol-Gel Derived Urea Cross-Linked Organically Modified Silicates. 1. Room Temperature Mid-Infrared Spectra. *Chem. Mater* 1999;11:569-580.
93. Bailey SE, Olin TJ, Bricka RM, Adrian DD. A review of potentially low cost sorbents for heavy metals. *Water Research*.1999;33:2469-2479.
94. Vieira LF, Lemos MJ, Reis MJ, Botelho do Rego AM. UV-Vis absorption, luminescence and X-ray photoelectron spectroscopic studies of rhodamine dyes adsorbed on to different pore size silicas. *Langmuir* 2000;16:5673-5680.
95. Ho KY, Mckay G, Yeung KL. Selective adsorbents from ordered mesoporous silica. *Langmuir* , 2003;19:3019-3024.
96. Prado AGS, Miranda BS, Guilherme GVM. Interaction of Indigo carmine dye with silica modified with humic acids at solid / liquid interface. *Surf Sci* 2003;542:276-282.
97. Yan Z, Li GT, Mu L, Tao SY. Pyridine – functionalized mesoporous silica as an efficient adsorbent for the removal of acid dye stuffs, *J Mater .Chem* 2006;16:1717-1725.
98. Shea KJ, Loy DA. Bridged polysilsesquioxanes molecular engineered hybrid organic-inorganic materials. *Chem . Mater* 2001;13:3306 -3319.
99. Asefa T, MacLachlan MJ, Coombs N, Ozin GA. Periodic mesoporous organo-silicas with organic groups inside the channel walls. *Nature* 1999;402:867-871.
100. Sharma RK, Mittal S, Koel M. Extraction of Mo(VI) using Silica modified-with2,6-diacetylpyridine-diacetylpyridinediacetylpyridine-monosalicyloylhydrazone monosalicyloylhydrazone monosa. *Crit . Rev. Anal. Chem* 2003;33:183-197.
101. Kresge, CT, Leonowicz ME, Roth WJ, Vartuli JC, Beck JS. Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. *Nature* 1992;359:710-712.
102. Monnier A, Schüth F, Huo Q, Kumar D, Margolese D, Maxwell RS, Stucky GD, Krishnamurty M, Petroff P, Firoozzi A, Janicke M, Chmelka B.F. Cooperative formation of inorganic-organic interfaces in the synthesis of silicate mesostructures. *Science* 1993;261:1299-1303.
103. Karakassides MA, Bourlinos A, Petridis D, Coche-Guerente L, Labbe P. Synthesis and characterization of copper containing mesoporous silicas. *J. Mater. Chem* 2000;10:403-408.
104. Naik SP, Chiang AST, Thompson RW. Synthesis of zeolitic mesoporous materials by dry gel conversion under controlled humidity. *J. Phys. Chem B* 2003;107:7006-7014.
105. Trewyn BG; Slowing II, Giri S, Chen HT, Lin VS-Y. Synthesis and functionalization of a mesoporous silica nanoparticle based on the sol-gel process and applications in controlled release. *Acc. Chem. Res* 2007;40:846-853.
106. Parida KM, Dash SS. Manganese containing MCM-41: Synthesis, characterization and catalytic activity in the oxidation of ethylbenzene. *J. Mol. Catal. A* 2009;306:54-61.
107. Beck JS, Vartuli JC, Roth WJ, Leonowicz ME, Kresge CT, Schmitt KD, Chu CTW, Olson DH, Sheppard EW, McCullen SB, Higgins JB, Schlenkert JL. A new family of mesoporous molecular sieves prepared with liquid crystal templates. *J. Am. Chem. Soc* 1992;114:10834-10843.
108. Yang XY, Zhang SB, Qiu ZM, Tian G, Feng YF, Xiao FS. Stable ordered mesoporous silica materials templated by high-temperature stable surfactant micelle in alkaline media. *J. Phys. Chem B* 2004;108:4696-4700.
109. Jiang T, Shen W, Tang Y, Zhao Q, Li M, Yin H. Stability and characterization of mesoporous molecular sieve using natural clay as a raw material obtained by microwave irradiation. *Appl. Surf. Sci* 2008;254:4797-4805.
110. AlOthman ZA, Apblett AW. Metal ion adsorption using polyamine-functionalized mesoporous materials prepared from bromopropyl-functionalized mesoporous silica. *J. Hazard. Mater* 2010;182:581-590.
111. Song K, Guan J, Wang Z, Xu C, Kan Q. Post-treatment of mesoporous material with high temperature for synthesis super-microporous materials with enhanced hydrothermal stability. *Appl. Surf. Sci* 2009;255:5843-5846.
112. AlOthman ZA, Apblett AW. Preparation of mesoporous silica with grafted chelating agents for uptake of metal ions. *Chem. Eng. J* 2009;155:916-924.
113. AlOthman ZA, Apblett AW. Synthesis of mesoporous silica grafted with 3-glycidoxypropyltrimethoxy-silane. *Mater. Lett* 2009;6:2331-2334.
114. AlOthman ZA, Apblett AW. Synthesis and characterization of a hexagonal mesoporous silica with enhanced thermal and hydrothermal stabilities. *Appl. Surf. Sci* 2010;256:3573-3580.
115. McBain JW. *The Sorption of Gases and Vapors by Solids*; Routledge and Sons: London, UK, 1932;169.
116. Barrer RM, Brook DW. Molecular diffusion in chabazite, mordenite, and levynite. *Trans. Faraday Soc* 1953;49:1049-1059.
117. Breck DW, Eversole WG, Milton RM. New synthetic crystalline zeolites. *J. Am. Chem. Soc* 1956;78:2338-2339.
118. Wilson ST, Lok BM, Messina CA, Cannan TR, Flanigen EM. Aluminophosphate molecular sieves: A new class of microporous crystalline inorganic solids. *J. Am. Chem. Soc* 1982;104:1146-1147.
119. Lok BM, Messina CA, Lyle Patton R, Gajek RT, Cannan TR, Flanigen EM. Silicoaluminophosphate molecular sieves: Another new class of microporous crystalline inorganic solids. *J. Am. Chem. Soc* 1984;106:6092-6093.
120. Davis ME, Lobo RF. Zeolite and molecular sieve synthesis. *Chem. Mater* 1992;4:756-768.
121. Mitchell PCH. Zeolite-encapsulated metal complexes: Biomimetic catalysts. *Chem. Ind* 1991;6:308-311.
122. Ozin GA. Nanochemistry: Synthesis in diminishing dimensions. *Adv. Mater.* 1992;10:612-649.
123. Davis ME, Saldarriaga C, Montes C, Garces J, Crowder C. A molecular sieve with eighteen-membered rings. *Nature* 1988;331:698-702.
124. Estermann M, Mccusker LB, Baerlocher Ch, Merrouche A, Kessler H. A synthetic gallophosphate molecular sieve with a 20-tetrahedral-atom pore opening. *Nature* 1991;352:320-323.
125. Jones RH, Thomas JM, Chen J, Xu R, Huo Q, Li S, Ma Z, Chip-pindale AM. Structure of an unusual aluminium phosphate (Al-5P6O24H2-2N(C2H5)3H+2H2O) JDF-20 with large elliptical apertures. *J. Solid State Chem* 1993;102:204-208.
126. Yanagisawa T, Schimizu T, Kiroda K, Kato C. The preparation of alkyltrimethylammonium-kanemite complexes and their conversion to mesoporous materials. *Bull. Chem. Soc. Jpn* 1990;63:988-992.
127. Beck JS, Calabro DC, McCullen SB, Peltine BP, Schmitt KD, Vartuli JC. Method for Functionalizing Synthetic Mesoporous Crystalline Material. U.S. Patent 1992;2:069-722.
128. Chen J, Xia N, Zhou T, Tan S, Jiang F. Mesoporous carbon spheres: Synthesis, characterization and supercapacitance. *Int. J. Electrochem. Sci* 2009;4:1063-1073.
129. Vartuli JC, Roth WJ, Degnan TF. Mesoporous materials (M41S): From discovery to application. In *Dekker Encyclopedia of Nanoscience and Nanotechnology*; Schwarz, JA, Contescu, CI, Putyera, K, Eds; Taylor and Francis: New York, NY, USA 2008;1797-1811.
130. Vartuli JC, Schmitt KD, Kresge CT, Roth WJ, Leonowicz ME, McCullen SB, Hellring SD, Beck JS, Schlenker JL, Olson DH, Sheppard EW. Effects of surfactant/silica molar ratios on the formation of mesoporous molecular sieves: Inorganic mimicry of surfactant liquid-crystal phases and mechanistic implications. *Chem. Mater* 1994;6:2317-2326.
131. Zhao D, Huo Q, Feng J, Chmelka BF, Stucky GD. Nonionic triblock and star diblock copolymer and oligomeric surfactant syntheses of highly ordered, hydrothermally stable, mesoporous silica structures. *J. Am. Chem. Soc* 1998;120:6024-6036.
132. Zhao DJ, Sun QL, Stucky GD. Morphological control of highly ordered mesoporous silica SBA-15. *Chem. Mater* 2000;12:275-279.
133. Colilla M, Balas F, Manzano M, Vallet-Regi M. Novel method to enlarge the surface area of SBA-15. *Chem. Mater* 2007;19:3099-3101.
134. Puputti J, Jin H, Rosenholm J, Jiang H, Lindén M. The use of an impure inorganic precursor for the synthesis of highly siliceous mesoporous materials under acidic conditions. *Microporous Mesoporous Mater* 2009;126:272-275.
135. Rahmat N, Abdullah AZ, Mohamed AR. A review: Mesoporous Santa Barbara Amorphous-15, types, synthesis and its applications towards biorefinery production. *Am. J. Appl. Sci* 2010;7:1579-1586.
136. Lu GQ and Zhao XS. *Nanoporous materials an overview*, The Nanomaterials Centre, The University of Queensland, Brisbane 4072, Australia 1992.
137. Rosen MJ. *Surfactants and Interfacial Phenomena*. 3rd ed. New Jersey: John Wiley and Sons, Inc 2004;46-49 and 121-148.
138. Riegels JA. *Handbook of Industrial Chemistry*. KluwerAcademic Publishers 2003;353:851-854.
139. Berthod A, Coque CG. *Micellar Liquid Chromatography*, Chromatographic Science Series, Marcel Dekker, Inc., New York, NY 2000;83:19-23.
140. Fennema OR, Karel M, Sanderson GW, Tannenbaum SR, Walstra P, Whitaker J R. *Food emulsions*. 3rd ed. (pp. 166). New York: Marcel Dekker Inc. geometric structures called liquid crystal phases. Liquid crystals possess molecules arranged in solid crystal form but have the fluid movement of a liquid (Hyde and Schroder, 2003) 1997.
141. Vadapalli C, Ramamoorthy B, Selvarajan N. Recent Developments in the Synthesis and Structure of Organosilanol. *Chem. Rev* 2004;104:5847-5910.
142. Ladenburg A. On the silicoheptyl series, from *Deut. Chem. Ges. Ber., iv*, 901 as summarized in "Organic chemistry" *J. Chem. Soc* 1872;25:133-156.
143. Paul Lickiss D. The Synthesis and Structure of Organosilanol, *Advances in Inorganic Chemistry* 1995;42:147-262.

144. Beckmann J, Dakternieks D, Duthie A, Larchin ML, Tiekink ERT. Tert-butoxysilanol as model compounds for labile key intermediates of the sol-gel process: crystal and molecular structures of (t-BuO)<sub>3</sub>SiOH and HO[(t-BuO)-2SiO]<sub>2</sub>H, *Appl. Organomet. Chem* 2003;17:52–62.
145. Nawrocki J. The silanol group and its role in liquid chromatography, *Journal of Chromatography A* 1997;779:29–72.
146. Salmawy MSEL, Nakahiro Y, Wakamatsu T. The role of silanol group in flotation separation of quartz from feldspar using non ionic surfactants , 18th IMPC, pp.845-849, The Australian Institute of Mining and Metallurgical Engineering, Sydney, Australia 1993.
147. Rubin AJ *Aqueous-Environmental Chemistry of Metals*; Ann Arbor Science Publishers: Ann Arbor, MI, USA 1974.
148. Krenkel PA. *Heavy Metals in the Aquatic Environment*; Pergamon Press: Oxford, UK 1975.
149. Mercier L, Pinnavaia TJ. Heavy metal ion adsorbents formed by the grafting of a thiol functionality to mesoporous silica molecular sieves: Factors affecting Hg(II) uptake. *Environ. Sci. Technol* 1998;32:2749–2754.
150. Marshall MA, Mottola HA. Performance studies under flow conditions of silica-immobilized 8-quinolinol and its application as a preconcentration tool in flow injection/atomic absorption determinations. *Anal. Chem* 1985;57:729–733.
151. Dias F, Newton L. Adsorption of copper(II) and cobalt(II) complexes on a silica gel surface chemically modified with 3-amino-1,2,4-triazole. *Colloids Surf. A* 1998;144:219–227.
152. Bresson C, Menu MJ, Dartiguenave M, Dartiguenave YNS. Ligands for preconcentration or elimination of heavy metals. Synthesis and characterization of aminoethanethiols and aminoethanethiol-modified silica gel. *J. Chem. Res* 1998;490:1919–1932.
153. Jiang TS, Zhao Q, Chen KM, Tang YJ, Yu LB, Yin HB. Synthesis and characterization of Co (Ni or Cu)-MCM-41 mesoporous molecular sieves with different amount of metal obtained by using microwave irradiation method. *Appl. Surf. Sci* 2008;254:2575–2580.
154. Nilsen MH, Antonakou E, Bouzga A, Lappas A, Mathisen K, Stocker M. Investigation of the effect of metal sites in Me-Al-MCM-41 (Me = Fe, Cu or Zn) on the catalytic behavior during the pyrolysis of wooden based biomass. *Microporous Mesoporous Mater* 2007;105:189–203.
155. Zhang A, Li Z, Li Z, Shen Y, Zhu Y. Effects of different Ti-doping methods on the structure of pure-silica MCM-41 mesoporous materials. *Appl. Surf. Sci* 2008;254:6298–6304.
156. Chaliha S, Bhattacharyya KG. Wet oxidative method for removal of 2,4,6-trichlorophenol in water using Fe(III), Co(II), Ni(II) supported MCM41 catalysts. *J. Hazard. Mater* 2008;150:728–736.
157. Davis ME. Ordered porous materials for emerging applications *Nature* 2002;417:813–821.