Review Article

Sensing Heavy Metals Using Mesoporous-Based Optical Chemical Sensors

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Heavy metal pollution is one of the more serious environmental problems; therefore, there is a constant demand for the development of new analytical tools for its monitoring. An optical chemical sensor represents a good alternative to classical instrumental methods. The mesoporous materials used in optical chemical sensors' fabrications have properties such as high porosity, exceptional adsorption capacity, tuneable 3D shape, geometry, and morphology, which enable improved limit of detection, response time, and selectivity properties of optical sensors. In this review, we firstly present the properties of mesoporous materials, provide a brief description of sensing mechanisms, and briefly discuss the importance of continuous monitoring. Recent advances in those mesoporous silica-based optical sensors used for heavy metal detection have been reported and their advantages and limitations also discussed. This review covers publications that have appeared since 2008.

1. Introduction

The monitoring of heavy metals within the environment, drinking water, food, and biological fluids has become essential due to the raising of environmental awareness and increasingly stringent regulations for pollution control. Heavy metals, by definition, are metals with densities of $>5 \text{ g cm}^{-3}$. They are released into the environment mainly by industrial activities. In small quantities, certain heavy metals such as iron, copper, manganese, and zinc are nutritionally essential for a healthier life. However, heavy metals such as Hg, As, Pb, and Cd are highly toxic and carcinogenic, even at the trace level [1, 2]. The toxicity and bioaccumulative properties of most heavy metals make its control a top-priority environmental task. Table 1 summarises the standards and guidelines for heavy metals in drinking water set by the World Health Organization (WHO), U.S. Environmental Protection Agency (EPA), and European Union (EU) legislation [3–5].

Standard methods for heavy metal determination cover a wide range of laboratory-based techniques such as atomic

absorption spectroscopy (AAS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), inductively coupled plasma-mass spectrometry (ICP-MS), and X-ray fluorescence spectroscopy (XFS) [6–12]. Although these methods are sensitive and selective they require time-intensive sampled pretreatment and expensive analytical instrumentation, as well as highly qualified staff. On the other hand, optical chemical sensors (OCSs) have great potential for detecting multiple heavy metals on-site. OCSs are a group of chemical sensors in which electromagnetic (EM) radiation is used to generate an analytical signal in a transduction element. The interaction of this radiation with the sample causes the change of a particular optical parameter that can be related to the concentration of the analyte [13, 14]. OCSs usually rely on the principle of an immobilised indicator (organic dye) that changes its optical properties (absorption, transmission, emission, lifetime, etc.) on binding the analyte [15–17]. When designing an OCS with the desired sensor characteristics, it is not only the selection of a suitable indicator, solid support (matrix), and immobilisation technique that is important but also the morphology and suitable functionalisation of

TABLE 1: Standards and guidelines for heavy metals in drinking water set by WHO, EPA, and EU legislation [3–5].

Metal	WHO (mg/L)	EPA (mg/L)	EU (mg/L)
Hg	0.006	0.002	0.001
Cu	2	1.3	2
Zn	—	5	—
Pb	0.010	0.015	0.01
Cr	0.05	0.1	0.05

such materials [18]. Over the years, different optical chemical sensors have been introduced based on silica mesoporous materials for the determination of mercury [19–34], copper [35–38], zinc [39–42], and other heavy metal ions [43–48].

The purpose of the presented review was to provide a general overview on the latest studies relating to mesoporous silica-based optical chemical sensors for heavy metals' determination. The papers in question mainly focused on the receptor part of the OCS and not on the development of the whole sensor system including the transducer and signal processing unit. The syntheses, properties, and other applications of mesoporous materials are already described in detail elsewhere [49–54].

2. Mesoporous Material

Over the past decade, mesoporous materials due to their highly porous natures combined with low absorption and emission within the visible spectra have been shown to be excellent candidates for OCSs. Mesoporous materials are a class of nanostructures with well-defined mesoscale (2–50 nm diameters) pores, surface areas up to 1000 m²/g, and large pore volumes (~1.0 mL/g). In general, these ordered mesostructured materials are formed from solution by the coassembly and cross-linking of network-forming inorganic species (typically oxides) in the presence of structure-directing agents (SDAs) [55]. The SDAs are typically surfactants or block copolymers that self-organise into mesoscale (2–50 nm) structures, according to the solution's composition and the used processing conditions [56]. Mesoporous inorganic materials can have various mesophase structures, for example: 2D-hexagonal (space group *p6mm*), biscontinuous cubic (space groups *Ia-3d*, *Pn-3m*, and *Im-3m*), cage-type cubic (space groups *Pm-3n*, *Fm-3m*, *Im-3m*, *Fd-3m*, etc.), cage-type hexagonal (space group *P6₃/mmc*), lamellar (L, space group *p2*), and others (space groups *P4₂/mnm*, *P4₁/mmm*, *c2mm*, *Pmmm*, etc.), Table 2 [52, 53, 57]. The structures of the mesoporous materials are highly dependent on the geometries of the surfactants, including the sizes and charging of the head groups, the length and saturation of the hydrophobic tail, and its molecular shape.

From amongst several families of mesoporous silica materials (MPS) already developed and used in sensor applications, it is worth mentioning the more typical MCM [19, 32, 33, 36, 39, 42, 58–65], SBA [21–28, 34, 35, 45, 48, 58, 60, 66], HOM [20, 36, 43–46, 67], HMS [29, 38].

TABLE 2: List of some typical mesoporous silica materials and their mesophase structures.

Mesophase structure	Space group	Material or researcher	Ref.
2D-hexagonal	<i>p6mm</i>	MCM-41	[32, 33, 36, 39, 42, 58–63]
		SBA-15	[22–28, 35, 45, 48, 58, 60]
		HOM-2	[43]
3D-biscontinuous cubic	<i>Ia3d</i>	MCM-48	[63]
		KIT-6	[91]
		FDU-5	[92]
	<i>Pn3m</i>	HOM-5	[93–95]
		HOM-7	[96]
	<i>Im3m</i>	AMS-10	[97]
3D-cage-type cubic	<i>Pm3n</i>	SBA-16	[98]
		SBA-1	[99–101]
		SBA-6	[100, 101]
	<i>Fm3m</i>	HOM-9	[20, 46]
		SBA-2	[99]
		SBA-12	[98]
	<i>Im3m</i>	HOM-10	[46]
		FDU-12	[102]
		KIT-5	[103]
	<i>Fd3m</i>	FDU-1	[104]
		SBA-16	[98]
		FDU-2	[105]
3D-cage-type hexagonal	<i>P6₃/mmc</i>	AMS-8	[106]
		HOM-11	[36, 44]
		SBA-2	[99]
		SBA-12	[98]
Lamellar		SBA-7	[98]
		HOM-3	[93, 94]
		MCM-50	[107, 108]

The structures of the more studied mesoporous materials for sensor applications are presented in Figure 1.

The use of MPS as a solid support for the fabrications of OCSs has many advantages. MPS materials allow covalent immobilisation either (a) by covalently anchoring the active sensor dye during synthesis and low-temperature removal of the structure-directing agent or (b) by the grafting of indicator dyes via postsynthetic functionalisation making them even more desirable in sensor applications, since leaching is minimised in this way. The sensor properties can be significantly altered by the method chosen for indicator immobilisation [17, 46, 68]. In general, high concentrations of dye molecules often lead to significant fluorescent self-quenching resulting from intermolecular collisions, since all the molecules are completely free within the solution [68].

FIGURE 1: Structures of mesoporous materials. (a) 2D-hexagonal (space group $p6mm$); (b) biscontinuous cubic (space groups $Ia-3d$); (c) cage-type cubic (space groups $Pm3n$).

Moreover, it is known that the packaging of dye molecules within a solid base will also cause self-quenching. MPS materials have abundant pore channels and surface silanol groups; therefore, dye molecules can be highly dispersed throughout the pore channels of MPSs and fixed at different locations of the pore's surface by reaction with silanol groups, which means that the mobility and rotation of the dye is restricted to a fixed area. Therefore the dye molecules are densely located in MPSs, and the generally observed self-quenching in the dye solution with high concentration can be reduced considerably [37, 40]. It has been reported that the fluorescence of the dye inside the MPS particles does not quench, although its concentration is ≈ 230 times higher than the maximum nonquenching concentration of the free dye in the solution [68–70]. The high concentrations of the dye immobilised in MPS improves the signal-to-noise ratio and can also affect the sensor's sensitivity and detection limit (LOD). Furthermore, the ability to control the pore size, tailor the composition of the inorganic framework and internal pore-surface or channel, can affect or improve the sensor's selectivity [26, 44, 71], since limited accessibility can help to shield the dyes from interferences. Moreover, it has also been shown that the 3D shapes and geometries of mesopores have a significant effect on LOD and response time (t_R) (3D compared to 2D). This can be related to the fact that 3D morphologies and cage functionalities are expected to transport analyte efficiently using much more direct and easier diffusion to network sites [46, 47]. An additional benefit of mesoporous materials is also that they can be prepared in various morphological forms such as thin-films, nanoparticles, and monoliths. The exceptional adsorption capacities of mesoporous materials may serve as in-situ preconcentrators for analyte, thus improving the LOD of a MPS-based sensor [20, 36, 44, 47].

The interesting fields of usage regarding MPS materials for optical sensing have been reviewed a few times over recent years. In 2008, Melde et al. [72] reviewed how mesoporous silicas had been applied to sensing optical and electrochemical changes in relative humidity, changes in pH, metal cations, toxic industrial compounds, volatile organic compounds,

small molecular ions, nitroenergetic compounds, and biologically relevant molecules. A tutorial review published by Han et al. in 2009 [73] reported on the development of silica-based organic/inorganic hybrid nanomaterials for use within biological and environmental applications, in which the chromogenic and fluorogenic probes can selectively detect and separate specific anions and neutral organic guests, as well as toxic metal ions. Recently, Jung et al. [74] reviewed the preparing of a variety of silica nanotubes by self-assembled organogels and the recent development of silica-based organic-inorganic hybrid nanomaterials for use as chemosensors for environmental studies, as well as within biological applications. Tran-Thi et al. [75] noticed that sol-gel porous materials with tailored nanostructured cavities were being increasingly used with regard to their potential as sensitive matrices or layers of chemical sensors for the determination of gaseous and ionic analytes.

3. Sensing Mechanisms

The more commonly applied methods for the optical sensing of heavy metals using mesoporous materials are those based on light absorption or light emission. Absorption or colorimetric sensing is accomplished using an indicator that changes its colour upon binding the analyte; this change is not only spectroscopically determined but can also be observed visibly [14, 76]. In light-emission methods, the analyte concentration is determined by the change in the emission properties of a luminophore after being excited by a defined electromagnetic wavelength. Fluorescence typically occurs from aromatic molecules due to the rigid conjugated structure and the high rigid density of π electrons [77]. Compared to the absorption-based methods, molecular emissions (fluorescence, phosphorescence, and, generally speaking, luminescence) are particularly important because of their extreme sensitivities and good specificities. The sensitivity of the luminescence method is about 1000 times greater than that of most spectrophotometric methods. In addition, lower LOD for the desired analytes can be achieved [76–80].

Measuring the emission intensity is also the most popular because the instrumentation needed is very simple and cheap. Nevertheless, measuring light-emission intensity has some disadvantages compared to emission lifetime measurements, in which the sample is excited only by a pulse of EM rather than via continuous illumination, which is the case with intensity-based methods. The precisions and accuracies of luminescence intensity-based schemes are greatly affected by fluctuations in the light-source's intensity, detector sensitivity, inner filter effects, indicator concentration (bleaching and leaching), sample turbidity, and sensing layer thickness. One method of reducing the problems associated with intensity detection principles is the use of ratiometric measurements. This technique employs dual emission or dual excitation indicators or mixtures of two luminophores, exhibiting separated spectral areas with different behaviour. For example, the ratio of two fluorescent peaks is used instead of the absolute intensity of one peak. The sensors therefore typically contain a reference dye; the advantage of this approach is that factors such as excitation source fluctuations and sensor concentration will not affect the ratio between the fluorescence intensities of the indicator and reference dye [81–83].

When a fluorescent indicator is used for sensing heavy metals, the complexation of the metal ions with the indicator results in either enhanced fluorescence (chelation-enhanced fluorescence—CHEF) or in decreased fluorescence (chelation-enhanced quenching—CHEQ). These mechanisms usually involve electron transfer (ET) and charge transfer (CT). Accordingly, these categories include photoinduced electron transfer (PET) and photoinduced charge transfer (PCT), also called intramolecular charge transfer. The PET mechanism is the more widely accepted and belongs to the group of turn-on fluorescent sensors, which fluoresce only in the presence of analytes. Sensors based on the PET mechanism often use a rational combination of a triple component system, namely, the “fluorophore-spacer-ionophore” format [84]. The receptor contains a high-energy nonbonding electron pair (e.g., nitrogen or sulphur atoms), which can transfer an electron to an excited fluorophore group and result in fluorescence quenching. However, when the electron pair is coordinated by a metal ion, the electron transfer will be prevented and the fluorescence is switched on [85, 86]. The principle is shown in Figure 2. PET type fluorescent response does not cause any spectroscopic shifts in the emission band regarding the complexation of the metal ions [86].

The PCT mechanism involves the transfer of an electron between the donor and acceptor functionalities in order to promote fluorescence [86, 87]. All the indicators have integrated ionophore and fluorophore, as opposed to the PET indicators that have the electron donor moiety separated by spacer from the fluorophore. For this reason, with PCT indicators, the complexation of the metal ions give rise to alterations in electron-energy levels causing fluorescence turn-off or turn-on and a variation in emission and absorption wavelengths (Figure 3), depending on the type of fluorophore, metal ion, and complexation mode [86]. More detailed descriptions of sensing mechanisms are described elsewhere [86–88].

Basically, the turn-on or increasing of fluorescence emissions is a better approach than quenching because in real samples there are many species that can in fact quench the fluorophore emission besides the analyte (e.g., oxygen and other heavy metals). In case an insufficient selective indicator is applied, the sensing mechanism based on fluorescence quenching can be prone to several interferences.

4. Continuous Monitoring

The concentrations of trace metals within natural waters vary considerably as functions over time, depending on the discharger sources, seasons, types of urban activities, and so forth. The monitoring of dissolved heavy metals such as copper, lead, and cadmium over four-day periods within coastal waters showed that potentially most toxic forms of metals may vary in concentrations over a time scale of less than one hour [89]. These data confirm the poor ecological relevance of the average conventional sampling protocol and the need for continuous monitoring.

Conventionally, ions have been determined by making use of so-called indicator dyes that undergo a binding reaction with ions. The ion-binding reactions with indicators are reversible in principle [90]. In practice, however, most complexation reactions with heavy metals are irreversible. The indicator is essentially saturated with metal ions and any further increase in metal ion concentration produces little if any change in the observed signal. The decomplexation procedure is used for sensor regeneration/reusage, which needs the appropriate stripping agent. EDTA and ClO^- stripping agents are used mostly. In the best case the reuse cycle can be repeated up to 6 times.

5. Specific Sensors for Heavy Metals' Ions

The determination of toxic heavy metal cations by mesoporous material sensors/probes is usually based on the incorporation of appropriate dye molecules within selected mesoporous materials, where either absorbance or fluorescence is used as an optical detection method. Since 2008, researchers have mostly developed mesoporous materials for sensing mercury (Hg^{2+}) and copper (Cu^{2+}). Materials for sensing other cations have also been proposed (zinc, lead, cobalt, chromium, etc.).

5.1. Mercury Sensing. The determination of mercury ions has been a subject of investigation by different research groups (Table 3). Most of the sensing materials use fluorescence as a detection principle, whilst only a few use absorption. In regard to Hg^{2+} sensing material, SBA-15 is mostly used [21–28]. Other mesoporous materials such as UVM-7 [19], HOM-9 [20], Au-HMS [28] core-shell MPS nanoparticles [30, 31], and MCM-41 [32, 33] have also been studied. The more often used is covalent bonding of the indicator dye to the mesoporous material but immobilisation via H-bonds [23] or ionic bonds [20] is also possible.

In 2008, Ros-Liz et al. [19] reported on the fabrication of dual-function hybrid material for the simultaneous

FIGURE 2: Principle of heavy metal recognition by fluorescent PET sensors.

FIGURE 3: Principle of heavy metal recognition by fluorescent PCT sensors.

determination and removal (adsorbent) of Hg^{2+} ions within acetonitrile/water (1 : 1) solutions. A mesoporous 3D material such as UVM-7 was used as an inorganic support. The sensing principle is based on a chemodosimeter approach. In this case, a chromofluorogenic squaraine dye is first “switched-off” (colorless and nonfluorescent) by reacting to $-\text{SH}$ groups

attached to a silica framework. The addition of sensing material to the solution containing Hg^{2+} ions results in a rapid and dramatic colour change of the solution from colourless to deep blue (new absorption band at 642 nm), due to the dye released when Hg^{2+} reacts with $-\text{SH}$ groups in sensing materials. After a two-minute reaction, the solid is collected

TABLE 3: Sensors for Hg^{2+} determination.

Indicator dye	Material	Detection principle	Working range (M)	LOD (M)	t_R (s)	Ref.
Squaraine	UVM-7	Absorption (turn-on)	4.9×10^{-7} – 4.9×10^{-4}	4.9×10^{-7}	120	[19]
TPPS	HOM-9	Absorption (colour change)	5.9×10^{-9} – 1.7×10^{-5}	5.9×10^{-9}	60	[20]
Acyclic dye	SBA-15	Absorption (colour change)	1 – 10×10^{-6}	1×10^{-6}	~10	[21]
R6G	SBA-15	Fluorescence enhancement	4.9×10^{-9} – 4.5×10^{-7}	4.9×10^{-9}	Not given	[22]
R6G	SBA-15	Fluorescence enhancement	4.9×10^{-9} – 6.5×10^{-8}	4.9×10^{-9}	Not given	[23]
R6G	SBA-15	Fluorescence enhancement	1×10^{-8} – 4×10^{-8}	1×10^{-8}	Not given	[24]
Pyrene	SBA-15	Fluorescence enhancement	8.5×10^{-7} – 2×10^{-5}	8.5×10^{-7}	Few seconds	[25]
Ethynylpyrene	SBA-15	Fluorescence enhancement	0.2×10^{-8} – 3×10^{-5}	2×10^{-8}	Not given	[26]
DS	SBA-15	Fluorescence quenching	10^{-6} – 10^{-3}	10^{-6}	Not given	[27]
RhB	SBA-15	Fluorescence (turn-on)	Not given	1.5×10^{-8}	Not given	[28]
RhB	Au-HMS	Fluorescence (turn-on)	7×10^{-8} – 7.5×10^{-6}	7×10^{-8}	100	[29]
Pyrene	Core-shell MPS NPs	Fluorescence enhancement	1.7×10^{-8} – 9×10^{-5}	1.7×10^{-8}	Not given	[30]
Pyrene	Core-shell MPS NPs	Fluorescence enhancement	8.5×10^{-7} – 9×10^{-5}	8.5×10^{-7}	14	[31]
Azo dye	MCM-41 NPs	Absorption (colour change)	Not given	9.97×10^{-6}	Not given	[32]
Eu(PTA)	MCM-41	Fluorescence quenching	1 – 12×10^{-6}	1×10^{-6}	Not given	[33]

by filtration and the absorbance of the resulting solution measured. Inorganic support can be partially regenerated by sample washing with concentrated HCl, which quantitatively removes the loaded mercury, and the material can therefore be used for several cycles. The apparent LOD of the probe is 4.9×10^{-7} M (0.1 ppm). Interestingly, the authors did not try to reduce the LOD by measuring the fluorescence. In addition, the leaching of the dye from the inorganic support raises the question of such a system regarding its practical application. A different approach was used by El-Safty et al. [20], where solid mesoporous cubic *Pm3n* discs were used for the simultaneous naked-eye detection and removal of mercury ions within aquatic samples. This method was based on a design of disc-like (HOM-9) sensors by the immobilisation of two different organic groups, however, the first an organic moiety for changing the silica surface polarity and the second a tetraphenylporphine tetrasulphonic acid (TPPS) probe for Hg^{2+} ions that showed prominent colour-change when in contact with the analyte. The sensing assay exhibited a t_R of 1 min and LOD of 5.9×10^{-9} M at pH 9. The reversibility of the disc-like sensor allowed for the retention of its functionality (sensitivity and fast t_R) after multiple regeneration/reuse cycles using ClO_4^- as the decomplexation agent. After multiple regeneration/reuse cycles (≥ 6) there was a kinetic hindrance, as the t_R was prolonged to 2 min but the sensitivity stayed at up to 92% and the disc was fully reversible. In 2008, and 2010 Kim et al. [21, 34] synthesised a Hg^{2+} sensitive acyclic dye which was immobilised on the surface of MPS. The sensing material was a light yellow solid and resulted in a colour change from light yellow to red within 10 s in the presence of Hg^{2+} . The removal of Hg^{2+} (regeneration) was carried out by the addition of EDTA. A linear response was observed within the concentration range 1 – 10×10^{-6} M with an LOD of $\sim 1 \times 10^{-6}$ M [15]. The mesoporous silica-immobilised acyclic dye recognised the Hg^{2+} with a high degree of selectivity from amongst other metal ions within the aqueous solution.

Inorganic-organic hybrid fluorescence-based SBA-15 mesoporous materials have been reported over past years (Table 3). In 2008, Zhou et al. [22] reported a fluorescent sensor, R6-SBA-15, for the determination of Hg^{2+} within acetonitrile/water (7 : 3) solution by the covalent bonding of an organic fluorescent molecule Rhodamine 6G (R6G) within the channel of mesoporous silica. In 2010, they published another article [23] involving the same indicator dye for Hg^{2+} determination within dimethylformamide/water (1 : 1) solution that was assembled into SBA-15 (RBSN/SBA-15) through intermolecular hydrogen bonding, instead of covalent bonding [22]. Both SBA-15-based sensors resulted in a slight pink powder that could quantitatively determine Hg^{2+} at the 10^{-9} M (ppb) level. However, it would be interesting to know and compare the t_R of the two described R6G-based sensors, since the dyes were immobilised by two different approaches. Namely, it was shown that covalent-bonding can significantly prolong the t_R of the sensor [17]. Moreover, from the practical point of view it would be advisable to perform the measurements in water. Wu et al. [24] fabricated a Rhodamine- (R6G-) based SBA-15 sensor that can be used to detect Hg^{2+} ions in water. However, the sensor's LOD (1×10^{-8} M) compared to previously developed sensors [22, 23] was poorer. Fluorescent detection of Hg^{2+} ions was also proposed using pyrene-based fluorescent dye [25, 26] and the dansylamine derivate (DS) [27], being covalently grafted onto SBA-15. All the sensors showed good sensitivities and selectivities for Hg^{2+} . Dong et al. [28] have prepared a Rhodamine group modified SBA-15 nanocomposite for the determination of Hg^{2+} ions in MeCN- H_2O solution (9 : 1 v/v).

Recently, Zhang et al. [29] prepared a worm-like pore-structured mesoporous silica-based (HMS) sensor (Au-HMS-sensor). In this case, gold was used as a connector to prepare Au-HMS and determination was possible through Rhodamine B derivate, covalently grafted on Au-HMS. This sensor exhibited “turn-on” fluorescence enhancement and

showed good selectivity for Hg^{2+} over other metal ions. LOD of 7×10^{-8} M concentration was reached within 100 s. The Au-HMS-sensor was successively regenerated by treatment with tetrapropylammonium hydroxide solution.

A different approach for detecting Hg^{2+} was used by Guo et al. [30] and Zhang et al. [31], who developed core-shell mesostructured silica as solid support, functionalised with pyrene. The LODs for both sensors were 1.7×10^{-8} M [30] and 8.5×10^{-7} M [31], respectively, whereas the linear working concentration range was between 10^{-8} and 10^{-4} M in both cases. In comparison with the covalently grafted pyrene-SBA-15 sensor [25] the LOD of the core-shell-based system is 50 times lower [30].

MCM-41 mesoporous materials have also been used for preparation of the Hg^{2+} sensor [32, 34]. However, compared to other mesoporous materials, it seems that MCM-41 is not the best material for the fabrication of Hg^{2+} sensors, since both of the two sensors have rather high LODs.

In view of water legislation, the LODs of the majority of the mentioned sensors are still far from the “ $0.05 \mu\text{g/L}$ (2.5×10^{-10} M)” target [109]. The sensors developed by Zhou et al. [22] and Song et al. [23] have the lowest LODs and can detect the maximum allowed contaminant level of $1 \mu\text{g/L}$ (4.98×10^{-9} M) set by EU legislation for drinking water [5]. Only a few papers [26, 30] have shown the practical applicabilities of the proposed sensors by evaluating them using real samples. Most of them lack water compatibility and need to be used in organic or aqueous organic solvents. Nevertheless, most Hg^{2+} sensors have demonstrated high selectivity towards other competing metal cations, showing that mesoporous structures may exhibit high selectivity potential, which is also an important sensor characteristic. Furthermore, the response time is also an important sensor characteristic, which has been overlooked by many authors.

5.2. Copper Sensing. Copper(II) ions have been the subject of continuous control, as copper is commonly used throughout industry and is therefore a widespread pollutant. However, it is also an essential trace element that plays important roles in a variety of fundamental physiological processes within living organisms [110]. Two sensors are based on fluorescence quenching [35, 37] and two are based on colour change (absorption) [36, 38].

In 2010, Meng et al. [35] reported on an inorganic-organic silica material, prepared by covalent immobilisation of the 1,8-naphthylthlimide-based receptor (P2) within the channels of mesoporous silica material SBA-15 (SBA-P2). SBA-P2 exhibited a Cu^{2+} specific fluorescence-quenching response in ethanol/water (3:7) solution with an LOD of 1.6×10^{-9} M. The sensor was highly selective towards Cu^{2+} ions over the interfering ionic species. Furthermore, the SBA-P2 material was applied for the fluorescence imaging of zebrafish organisms and the subsequent addition of Cu^{2+} ions resulted in SBA-P2 emission quenching. Presumably, being the first report on detecting Cu^{2+} ions in vivo using a functionalised nanomaterial, these results suggest that MPS is potentially

useful for studying the toxicity or bioactivity of Cu^{2+} within living organisms. However, experiments regarding regeneration and t_R should be done additionally in order to further characterise the sensor characteristics. Recently, El-Safty et al. [36] constructed a Cu(II) ion sensor based on immobilised dithizone (DZ) in 2D hexagonal MCM-41 and 3D cubic *Fd3m* HOM-11 mesoporous silica microscopic monoliths. The reflectance spectra of this sensor exhibited a blue shift as a result of the binding of Cu^{2+} ions with the DZ. 3D shape and the geometries of the mesoporous materials significantly affected the ion diffusion and affinity of the metal-ligand binding, thus affecting the sensor's characteristics. The sensors exhibited specific behaviour by permitting Cu(II) ion-selective determination in the model wastewater, despite the presence of active component species. The LODs were 3.1×10^{-8} M and 12.5×10^{-8} M for 3D cubic *Fd3m* HOM-11 and 2D-hexagonal MCM-41, respectively. The t_R of HOM-11 (3D) was 20 s shorter compared to MCM-41 (2D).

On the other hand, Lu et al. [37] used monodispersed mesoporous silica nanospheres modified by anthracene derivative (SGAAn) and fabricated a fluorescent sensor for the determination of Cu^{2+} metal ions in ethanol/water (3:7) solution. Determination of Cu^{2+} ions was possible through fluorescent quenching of the modified spheres in a few seconds within a concentration range from 5×10^{-8} to 10^{-4} M of Cu^{2+} , with the LOD being 2×10^{-8} M. The recovery of the sensor was repeatedly studied over 4 cycles by the use of EDTA as the recovery agent. Liu et al. [38] designed an absorption-based sensor for Cu^{2+} by using an indicator 4-(2-pyridylazo) rescinol (PAR) immobilised on functionalised hexagonal mesoporous silica (HMS). Determination of Cu^{2+} ions was possible under strong acidic conditions (pH 12) through colour change from yellow to red of the modified spheres in 60 seconds within a concentration range from 6.3×10^{-7} M to 6.3×10^{-6} M of Cu^{2+} , with LOD being 1.3×10^{-8} M. With the addition of EDTA as a regenerating agent, the sensor is reusable and can be used up to 6 times. The authors also showed a potential for developing sensors for other ions, such as Fe^{3+} , Cd^{2+} , Ni^{2+} , Zn^{2+} , Pb^{2+} , Co^{2+} , and Hg^{2+} , using this sensor design.

All of the reported sensors (Table 4) satisfied the quality of the Cu^{2+} parameter for water intended for human consumption (2 mg/L or 3.1×10^{-5} M) as set by the EU directive [5], WHO [3], and EPA [4].

5.3. Sensing of Other Heavy Metal Ions. Table 4 summarises the recently developed mesoporous silica-based sensors used for heavy metal cation sensing, including Zn^{2+} , Pb^{2+} , Co^{2+} , Bi^{3+} , Cr^{3+} , and Cr^{6+} .

The determination of Zn^{2+} ions is possible using ordered MPS material MCM-41 functionalised with quinoline derivative N-(quinolin-8-yl)-2-[3-(triethoxysilyl)propylamino]acetamide (QTEPA) [39]. This reported system selectively detects Zn^{2+} ions with LOD of 0.1×10^{-6} M and a working range of $0.01\text{--}30 \times 10^{-6}$ M. The presence of other metal ions did not affect the selectivity, even at high concentrations of Na^+ , K^+ , Ca^{2+} , and Mg^{2+} along with Zn^{2+} ions

TABLE 4: Properties of OCSs for selected heavy metal ions.

Analyte	Indicator dye	Material	Detection principle	Working range (M)	LOD (M)	t_R	Ref.
Cu ²⁺	P2	SBA-15	Fluorescence quenching	1.6×10^{-9} – 1.1×10^{-8}	1.6×10^{-9}	Not given	[35]
Cu ²⁺	DZ	HOM-11	Absorption (colour change)	1.57×10^{-8} – 7.86×10^{-6}	3.1×10^{-8}	60 s	[36]
		MCM-41		7.86×10^{-8} – 7.86×10^{-6}	12.5×10^{-8}	80 s	
Cu ²⁺	SGAAn	Type not defined	Fluorescence quenching	5×10^{-8} – 10^{-4}	2×10^{-8}	4–5 s	[37]
Cu ²⁺	PAR	HMS	Absorption (colour change)	6.3×10^{-7} – 6.3×10^{-6}	1.3×10^{-8}	60 s	[38]
Zn ²⁺	QTEPA	MCM-41	Fluorescence enhancement	0.1×10^{-6} – 30×10^{-6}	0.1×10^{-6}	Not given	[39]
Zn ²⁺	8-AQ	Type not defined	Fluorescence enhancement	5×10^{-8} – 2×10^{-5}	2×10^{-8}	Not given	[40]
Zn ²⁺	SSD	Type not defined	Fluorescence enhancement	Not given	70×10^{-9}	Not given	[41]
Zn ²⁺	8-HQ	MCM-41	Fluorescence enhancement	Not given	1.2×10^{-6}	30 s	[42]
Cd ²⁺					1.9×10^{-9}	30 s	
Co ²⁺	Azo dye	HOM-2	Absorption (colour change)	1.7×10^{-8} – 17×10^{-6}	$\sim 15 \times 10^{-9}$	15 min	[43]
Bi ³⁺	DZ	HOM-11 (3.2 nm pore size)	Absorption (colour change)	2.3×10^{-9} – 9.6×10^{-6}	6.5×10^{-10}	20 s	[44]
		MCM-41		2.39×10^{-8} – 9.6×10^{-6}	8.1×10^{-9}	40 s	
Cr ³⁺	R6G	SBA-15	Fluorescence enhancement	1×10^{-6} – 6×10^{-6}	1×10^{-6}	Not given	[45]
Cr ⁶⁺	DPC			13.3×10^{-10} – 3.8×10^{-6}	8.1×10^{-10}	60 s	
Pd ²⁺	TPPS	HOM-10	Absorption (colour change)	9.4×10^{-9} – 9.4×10^{-6}	2.3×10^{-9}	80 s	[46]
Co ²⁺	PR			8.4×10^{-9} – 1.7×10^{-5}	2×10^{-9}	45 s	
Pb ²⁺	DZ			2.4×10^{-10} – 4.8×10^{-6}	2.7×10^{-11}	60 s	
Pb ²⁺	DTAR	HOM-13	Absorption (colour change)	4.8×10^{-8} – 4.83×10^{-7}	13×10^{-9}	12.5–17.5 min	[46]
		HOM-9		2.4×10^{-8} – 7.2×10^{-7}	9×10^{-9}	5–7 min	
Pb ²⁺	PMBA	SBA-15	Fluorescence quenching	2×10^{-6} – 50×10^{-6}	0.5×10^{-9}	Immediate response	[48]

in solution. On the other hand, transition metals, from iron to copper, competed with the binding sites, even though there was an overall increase in fluorescence intensity with Zn²⁺ binding. Core-shell mesoporous silica nanospheres encapsulated with Rhodamine 101 into the solid core and 8-aminoquinoline derivatives (AQ) into the mesoporous shell were used as Zn²⁺ ratiometric fluorescent sensor [40]. The fluorescence intensity of 8-AQ dramatically increased after the addition of Zn²⁺ ions. Concentrations as low as 5×10^{-8} M could be detected in ethanol-water solution (30%). Recently, Shahid et al. [41] reported on the development of a fluorescent-based Zn²⁺ sensor using MPS beads on which the fluorescent bis chromophoric dye containing naphthalimide and anthracene moieties (SSD) was covalently immobilised. The complexation between the fluorescent silica beads and Zn²⁺ ions (50×10^{-6} M) caused a ~6-fold increase in fluorescence intensity, accompanied by a 13 nm blue shift of the emission maxima. The sensor was selective for Zn²⁺ in the presence of other metal ion interactions and had a LOD of 70×10^{-9} M. The regeneration of the sensor was carried out using EDTA. Tan et al. [42] developed an imprinted mesoporous silica (MCM-41)-based fluorescence sensing arrays for metal ions (Zn²⁺ and Cd²⁺). A fluorescent functional monomer containing an 8-hydroxyquinoline (8-HQ) moiety in combination with a one-pot cocondensation method was employed for preparing the sensor array. The LODs for Zn²⁺ and Cd²⁺ were 1.2×10^{-6} M and 1.9×10^{-6} M, respectively, and were achieved within 30 s. Nevertheless,

both imprinted materials were, to some extent, cross-responsive towards nontemplate metal ions such as Mg²⁺, Ca²⁺, and Mg³⁺ and optimisation of the method is needed.

The absorption monitoring of Co²⁺ ions can be performed by the use of sensing materials designed by the direct physical adsorption of 8-(4-*n*-dodecyl-phenylazo)2,4-quinolinediol (azo dye) with long hydrophobic tails, onto hexagonal MPS monoliths (HOM-2) [43]. This sensor has a LOD of 15×10^{-9} M concentration of Co²⁺ ions, achieved within minutes and a working range of between 0.017 – 17×10^{-6} M. The sensor can be used up to 6 times with insignificant loss of sensing efficiency, although a slight decrease in sensing activity (t_R) can be observed. The selectivity studies revealed no interferences from heavy metal ions such as Al³⁺, Bi³⁺, Cr⁶⁺, La³⁺, Ir³⁺, Sn²⁺, and Sb³⁺. However, interference was observed from Cu²⁺, Ni²⁺, Hg²⁺, and Zn²⁺ ions that can be eliminated by using 0.2×10^{-3} M thiosulphate and thiocyanide. No leaching of the indicator dye from MPS was observed over a long period of time (≥ 4 months), with only slight changes in the absorption spectra.

El-Safty et al. [44] designed absorption-based sensors for the determination of Bi³⁺ ions by immobilising diphenylthiocarbazone (DZ) dye into a solid support without previously modifying the pore-surface. Different MPS monoliths were evaluated for solid support, such as 2D hexagonal-(MCM-41) and 3D cubic *Fd3m* (HOM-11). Additionally, the 3D structures were prepared of various pore sizes (2.3 nm, 2.8 nm, and 3.2 nm). The LOD of the MPS-immobilised dye

was ~1100-fold (MCM-41) or ~14000-fold (HOM-11, 3.2 nm pore-size) lower compared to the free dye, which indicated that the mesoporous matrix efficiently preconcentrates the analyte. The LODs were 81×10^{-10} M and 6.5×10^{-10} M for the 2D hexagonal and 3D cubic (3.2 nm pore-size) based sensors, respectively. The t_R of the 3D cubic-based sensor was about 15–20 s shorter than in the case of the 2D-hexagonal monolith. This study revealed that the pore-size of the 3D cubic mesoporous sensor affected the sensor's characteristics. Bigger pores provided lower LOD and shorter t_R . Although the DZ dye was physically entrapped within mesopores, no leaching was detected of the dye from the matrix. The sensors were highly selective towards other interfering compounds and could be reused 3 times.

Monitoring all forms of chromium (e.g., Cr^{3+} and Cr^{6+}) is necessary as they have toxic properties of high levels and are harmful to human health [111]. In 2011, Meng et al. [45] presented a multifunctional material that covalently linked the fluorescent dye Rhodamine 6G (R6G-TETA) and a mesoporous material (SBA-15), thus enabling fluorescent response and high adsorptivity for Cr^{3+} in water. The LOD of this method was 1×10^{-6} M and the working range was between 1×10^{-6} and 6×10^{-6} M. The functional nanomaterials' features provided good selectivity towards Cr^{3+} over the competitive cations. The sensor was also used *in vivo* and showed a potential for monitoring Cr^{3+} within living cells and organisms. Furthermore, a “building-block” approach for the immobilisation of indicator dye was used for the development of an optical sensor for Cr^{6+} ions determination [46, 67]. This approach is based on firstly modifying the polarities of the silica surface matrices with surfactant and then adsorption of the indicator dyes onto the solid support without the common use of silane- or thiol-coupling agents. In regard to the fabrication of DPC-based optical sensors using the building-block approach, several 3D mesoporous silica monoliths (3D HOM), such as cylindrical cubic *Fm3m* (HOM-10), cubic *Pm3n* with worm-like pore (HOM-13), and cage cubic *Pm3n* (HOM-9) materials, were used as solid supports. This study showed that pore ordering and the geometries of mesoporous materials affect the sensor's LOD and t_R but do not affect the sensor's selectivity. The LODs were 8.1×10^{-10} M, 13.2×10^{-10} M, and 80×10^{-9} M for HOM-10 and HOM-9 and HOM-13-based sensors, respectively; they were achieved within 60 s in the cases of HOM-10, HOM-9, and within 750 s in the case of the HOM-13-based sensor. The regeneration of the sensors was carried out by the addition of stripping agents (EDTA , ClO_4^- , CH_3COO^- , and $\text{C}_2\text{O}_4^{2-}$) that enabled its reuse over more than 6 cycles.

El-Safty and co-workers [47] reported on an absorption-based Pb^{2+} nanosensor using 3D monoliths (wormhole and ordered mesostructures—HOM-type) as solid supports for the immobilisation of indicator dye 4-*n*-dodecyl-6-(2-thiazolylazo)-resorcinol (DTAR). Ordered (HOM-9) and wormhole (HOM-13) cubic *Pm3n* cage monoliths were fabricated via an instant direct-templating method using microemulsion systems by the addition of nonionic surfactants. The sensing characteristics are strongly defined by 3D pore geometry and the shapes of the monoliths,

thus influencing the t_R ($5 \leq t_R \leq 7$ min for HOM-9 and $t_R > 15$ –20 min for HOM-13), as well as working ranges of (0.048 – 0.483×10^{-6} M for HOM-13 and 0.024 – 0.724×10^{-6} M for HOM-9). The prepared sensors exhibited good selectivity for Pb^{2+} and showed good efficiency after several regeneration cycles. Furthermore, there was no detected leaching of DTAR, although the dye was physisorbed into solid support. Wang et al. [48] prepared a series of hybrid fluorescent sensors by direct covalent-coupling of bis-schiff-based $\text{N,N}'$ -(1,4-phenylenedimethylidene)bis-1,4-benzenediamine (PMBA) on the inner surface of MPS (SBA-15), functionalised with chlorine groups. The fluorescent sensor exhibited high selectivity and sensitivity towards Pb^{2+} ions with a LOD of 0.55×10^{-9} M (0.1 ppb) and a working range of 2 – 50×10^{-6} M. However, there is no information on the sensor t_R . The DZ-HOM-10 sensor [46] had the lowest LOD compared to DTAR-HOM-9 [47] and PMBA-SBA-15 for the determination Pb^{2+} . All of them had LODs below the target value for Pb^{2+} set by the water directive 2008/32/EC [109] (3.4×10^{-8} M or $7.2 \mu\text{g/L}$).

6. Conclusions

Many published articles demonstrate that mesoporous materials are a good alternative to other solid supports (classical sol-gel materials, polymers) in OCS designs. Since mesoporous materials exhibit tuneable size- and shape-dependent chemical and physical properties, they have found applications for sensing various kinds of analytes.

In summary, the more frequently ordered SBA-15, MCM-41, and HOM mesoporous silica structures have been presented for sensing various heavy metal ions. Rare published studies on applying disordered worm-like materials have also been introduced. The sensors are mostly in the form of particles, rather than thin films. The majority of the published papers were devoted to the determination of mercury, which is one of the most toxic environmental contaminants. Besides the more explored SBA-15 material, MCM-41, and HOM were also reported as solid supports for sensing heavy metals, with SBA-15 being the preferable material of choice for mercury determination. It has been shown that 3D materials such as HOM are more suitable in terms of sensor sensitivity, response time and LOD as solid support, than 2D materials (SBA-15 and MCM-41).

The immobilisation of an indicator into MPS is usually carried out by covalent bonding. Interestingly, when physical entrapment of the organic dye was applied for sensing species in liquids, no indicator leaching was detected and therefore good results were observed in terms of stability.

In most cases, the MPS-based sensors showed good selectivity for the respective analytes. Furthermore, the improved adsorption properties of the heavy metals helped to lower the LOD. In spite of the fact that fluorescence is usually regarded as a more sensitive technique than spectrophotometry, it was also shown that LODs with MPS-based sensors are comparable for absorption and fluorescence-based systems.

The chemical and biological species in real-world samples such as river water, wastewater, and cells, have severe interferences on the sensing signal. Therefore, to show the practical implementation of the developed sensors, the sensors should be tested in real-world samples. However, most of the work only demonstrated a proof-of-concept for sensors that could detect heavy metals in buffer solutions, organic/water solutions, or artificial matrices. Only a few papers had reported the testing of real-world samples and only one paper had reported the sensors' validation data. There was no report on the development of cadmium and nickel MPS-based sensors, although cadmium and nickel are listed as target priority heavy metals by the Water Framework directive (2000/60/EC, 2006/11/EC, and 2008/105/EC). The on-line monitoring of heavy metals remains a significant challenge.

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