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ABSTRACT

Heavy-metal pollution is a foremost concern, as excessive heavy metals produce environmental contamination, and the accumulative effects of heavy metals pose a major hazard to human health. There is an urgent need for a fast, sensitive and effective method for detecting heavy metal cations in the environment. In recent years, using Quartz Crystal Microbalance (QCM) technique, significant progress was achieved in quantitative analysis by providing a new approach for determination of chemical content analysis. The objective aim of this review is to assess the research development of QCM applications in detection of heavy metal cations in natural water (or aqueous solution) and reflect the challenges and forthcoming point of view for QCM-based sensors for heavy-metal ions. A brief outline about the basic measurement methodologies and analytical techniques is given. To illustrate applications of the QCM techniques, the influence of the structural transformation resulting from polymer, macrocyclic 'calixarenes' and nanostructural coating on sensation will be discussed. Lastly, we summarise fields of applications and future forecast for the utilisation of functionalised QCM surface as a chemical sensor to study the interaction of heavy metal ions with calixarenes.

1. Overview of the problem

Many developments in industry have brought to a plenty of new products and services. These advancements cause not only producing useful technology but also more usage of chemicals. The ecological contamination is responsible for destruction of environmental systems, increase in sicknesses and diseases in humans, plants and animals. Three major types of ecological contamination are the follows: atmospheric [1,2]; water [3,4] and soil pollutions [5,6]. The atmospheric and water contamination can lead to huge disasters in short time [7–11]. Many processes involve chemicals, which are harmful to the human health and the environment when they're released. Heavy metal ions are toxins due to their harmful impact to human health even at very low concentrations. They can be released easily into the environment (water, air, soil) via human activities and processing of natural resources. Thus, early detection of the heavy metal ions is vital task in order to protect the environment and avoid pollution.

The detection of heavy metal ions remains a huge problem due to measuring these ions at very low concentration, as well as to the need of complex sampling procedures and application of costly apparatus. Conventional methods for heavy metal ion measurements include the inductively coupled plasma/atomic emission spectrometry (ICP-AES), inductively coupled plasma/mass spectrometry (ICP-MS) and atomic absorption spectroscopy (AAS) just to mention some of them.

These analytical techniques (ICP-MS, ICP-AES, AAS or AFS) are highly sensitive and can selectively determine the concentrations of the different metal ions. On the other hand, their disadvantages are; the necessity of tedious sample preparation and pre-concentration procedures, the need of specialists for measurement and evaluation, and the instruments are expensive.

2. Introduction to determination techniques of heavy metals in water

There exist numerous methods for heavy metal ions detection in water environment and assessing their trace concentrations. The methods can be classified as follows:

2.1. Analytical detection techniques

Several types of analytical methods have found applications in detecting and analysing heavy metal ions in water [12]. Conventional analytical methods for heavy metals detection have advantageous characteristics such as: precise, sensitive, versatile (suited for a large group of elements) and their excellent limit of detection. On the other hand, they suffer from numerous disadvantages such as: expensive instruments, challenging sample pretreatment and complex analytical processing, which are inappropriate for monitoring uses. Various sorts of analytical techniques will be briefly exemplified:

2.1.1. Atomic absorption spectroscopy

Atomic absorption spectroscopy (AAS) is extensively used technique for heavy metal ions trace determination in all samples varieties. It is used for one single element per analysis determination [13]. Cold vapour-atomic fluorescence spectroscopy (CV-AFS) and cold-vapour AAS (CV-AAS) are also used.

2.1.2. Inductively coupled plasma spectrometry

Inductively coupled plasma spectrometry (ICP) a multi-element analysis technique. It can be subdivided into two techniques: i.e. inductively coupled plasma-optical emission spectroscopy (ICP-OES) [14], and inductively coupled plasma-mass spectrometry (ICP-MS) [15].

2.1.3. Laser induced breakdown spectroscopy

Laser induced breakdown spectroscopy (LIBS) is a multipurpose technique as it accomplishes fast analysis of heavy metals in water and provides monitoring as well. The elements in water are identified by their unique spectral signatures [16].

2.1.4. X-ray fluorescence

X-ray fluorescence (XRF) is an elemental analysis technique which uses primary excitation source, provided by X-rays tubes, which cause sample elements to emit X-ray photons of

a characteristic wavelength and detectors are used to detect and analyse the secondary radiation (X-ray photons) [17].

2.1.5. Neutron activation analysis

Neutron activation analysis (NAA) is an extremely sensitive technique for determining different heavy metals concentrations put together on sensitivities, where concentration of the elements is determined by reviewing the spectra of the radioactive sample emissions [18].

2.1.6. Ion chromatography

Ion chromatography (IC) is a simple technique for the concurrent analysis and quantification of heavy metals ions in the solution. It is an HPLC technique in which ion exchange resins are applied for simultaneous determination of many ionic species in aqueous solutions on ppm and ppb scale. IC proves advantageous over the spectroscopic methods for cation analysis [19].

2.1.7. UV-VIS spectrometry

UV-VIS spectrometry (UV-VIS) is founded on the concept of molecular absorption and proved useful in the determination of anions and cations concentrations at low scale, that's challenging to evaluate by the utilisation of AAS. The advantages of this method are: easy to use, simplicity, speedy and economical measurements of heavy metal ions in low to high concentrations [20].

2.2. Electrical methods for heavy metals ions detection

The principal electrochemical techniques used in the field of heavy metals detection are: potentiometric, voltammetric and AC electrochemical impedance spectroscopy methods [21]. Electrochemical analysis has many characteristics, such as high sensitivity, high accuracy, wide measuring range, simple device, economic, user-friendly, reliable and suitable for in-field applications. However, those methods have a disadvantage of having typically poor selectivity.

2.2.1. Potentiometric technique [22]

It is a classical technique in which information about the composition of the sample is provided through the potential appearing between two electrodes. Ion-selective electrodes (ISEs) provide rapid selective potentiometric techniques for the determination of the major cations (metal samples). Detection limit is in the nanomolar range (or even lower).

2.2.2. Voltammetric technique

It is a method in which information about the composition of electrolytic solutions is provided by measuring the current as a function of applied potential. Stripping analysis is one of the most sensitive voltammetric method, which makes possible to determine a very small concentration of analyte (subnanograms).

Limits of detection in the picomolar range. These techniques are recognised as powerful techniques and versatile because in contrast to conventional analytical techniques, the

electrochemical methods are much cheaper, quicker and simpler for carrying out heavy metals detection [23].

2.2.2.1. Cyclic voltammetry. Cyclic voltammetry (CV) method controls the potential of the electrode to scan one or more times with a triangular waveform at different rates over time to follow the dynamics and record all the corresponding changes in the electrical signals. The scanning potential range needs to cover reduction and oxidation reactions alternately occurring on the electrode, and so a current–potential curve is recorded accordingly. In addition to the Hg electrode, platinum, gold, glassy carbon (GC), carbon fibre microelectrodes, and chemically modified electrodes can also be used with this method. The CV method has been widely used since it can provide much information about the dynamics and mechanisms of reactions [24].

2.2.2.2. Anodic stripping voltammetry (ASV). ASV is a voltammetric method for the quantitative determination of specific ionic species. In recent years, the influence of ASV has increased by its incorporation with various technologies and its application to detect trace metals. ASV is an attractive analytical technique due to the next advantages where ASV has: an ultrahigh sensitivity (the determination ranges from $10 – 6$ mol L^{-1} to 10^{-11} mol L^{-1}, with a detection limit of 10^{-10}–10^{-12} mol L^{-1}; an extensive choices of applications [25].

Presently, in excess of 30 elements in the periodic table that can be detected by ASV while about 20 elements can be detected by cathodic stripping voltammetry (CSV).

The best advantage of this technique is that it can instantaneously determine the concentration of several elements at ppb or even ppt levels and without the need for preceding separation. Besides, ASV only involves regular apparatus, such as a potentiometer, electrodes and conventional 3-electrodes electrolytic cell, which are simple structure wise and economically affordable for applications in many fields [25].

2.2.2.3. Square wave anodic stripping voltammetry (SWASV). SWASV can be understood literally as applying a pre-concentration voltage for enriching the metal ions in solution around the working electrode before applying a scan signal [26]. The size of an ac differential signal induced by the square wave signal can be measured and thus gets a diagram of the electrode scanning potential and AC signal (square wave voltammogram). Differential pulse anodic stripping voltammetry (DPASV) was introduced to abolish the shortcomings of SWV [26].

2.2.3. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is regarded as a powerful and versatile technique due to being: inexpensive, quicker and simpler for applying in detection [27]. EIS is a non-destructive method applied for detecting and determining specified species concentrations as a consequence of variations of electrical impedance at the sensor-analyte interface. Its limits of detection in the picomolar range.

2.3. Electrochemiluminescence techniques

Electrochemiluminescence techniques (ECL)These techniques are often used to detect a specific metal ion in some solution based on fluorescence detection that is rather highly sensitive (ppb-ppt), simple and inexpensive [28].

2.4. Piezoelectric biosensors

Piezoelectric biosensors are devices in which the bio-recognition element is integrated with a piezoelectric material used as a transducer. Among many types of natural and synthetic materials that exhibit a piezoelectric effect, quartz crystals are most commonly used [29] because of their availability, as well as high temperature resistance and chemical stability in aqueous solution.

Biosensors based on immobilised enzymes are also used, and they show several advantages compared to free enzymes [30]: low depletion of immobilised enzymes, reduced interferences in differential mode, does not require preincubation, fast analysis, sometimes reactivation of the enzyme activity is not necessary. The problem with biosensors based on enzymatic inhibition is that only a few enzymes are sensitive to heavy metals.

Table 1 shows some advantages and disadvantages of different methods for the heavy metals detection and determination.

Researchers have considered many other new ways to detect heavy metal ions in aqueous environment by exploring the possibility of utilisation of sensors (especially chemical sensors). The so called 'lab-on-chip' technique uses sensors as a tool that can save time and cost besides having great potential in high throughput detection of multiple heavy metals ion on-site. Sensors are classified based on different signal transduction mechanisms, including chemical, electrochemical, optical and gravimetrical sensors. In general, the advantages of chemical sensors include the possibility to perform real-time continuous measurements and these are relatively inexpensive apparats. Electrochemical sensors can overcome the limitations of other methods and to improve the portability, besides getting a rapid response [31,32]. The sensitivities of these techniques can be enhanced by the application of polymers, nanostructures or macrocyclic molecules, like calixarenes, as detecting element.

Recently, the nanomaterials application has been widely explored in the heavy metal ions pollution management, in that context, Wu et al. gave an overview on the synthesis and modification of new nanostructures including metal-organic frameworks [33]. However, those materials present the advantage of having large surface area, and high sorption capacities, but on the other hand, using a lot of chemicals during the nanomaterials synthesis, make their application in the heavy metal ions remediation restricted [33]. Nanomaterials were not only used to manage the heavy metal ions pollution in aqueous media, but also, they were applied in the radionuclides (RNs) elimination from waste water. In this framework, Wang et al., described many applications of graphene oxide (GO) nanostructures as radionuclide adsorbents, and the sorption mechanisms between (GO) and (RNs) were emphasised. Though (GO) by their turn, can be considered as environmental pollutants, so the understanding of their properties is a goal of particular importance before further environmental application [34].

In another work, Wang et al., reviewed different low-temperature plasma processes aiming to synthesise, functionalise, furthermore to modify the properties of (GO), for environmental application (Heavy metal ions elimination, organic pollutants removal... etc.). Hopefully, the plasma treatment is ecological and time saving [35].

Xie et al., reviewed the different applied approaches for the elimination of Uranium from liquid media, by means of biomass materials (organic polymers, inorganic materials...etc.).

Table 1. Some advantages and disadvantages of different methods for the heavy metals detection.

Method	Advantages	Disadvantages	Ref.
ASS	• Cheapness • Comparatively easy and simple to manipulate the machine • Sensitivity such that many elements can be determined at ppm level or even less • High precision and accuracy obtained by the calibration curves • Absorption signal considerably free from inter-element interferences	• Limited application as only about 70 elements excluding earth metals have been detected by this method. • Cannot yet detect non-metals	13
XRF	• Non-destructive analytical technique; • Relatively simple spectra line void of many interference; • Speed and convenience of the procedure which permits multi-element analyses to be completed in few minutes and • High accuracy with precision.	• Analysis of relatively large spot of sample (typically >1g) • Difficulty in quantifying elements lighter than sodium • Difficulty in distinguishing variations among isotopes of an element or ions of the same elements in different valence state • difficulty in achieving high sensitivity of weak peak when strong one is present and high cost of instrument	17
ICP-MS	• Very reliable, with overnight or unattended operation possible • Fast; it can scan the mass spectrum from 3 to 250 in just a few seconds • Capable of moving from mass to mass with a high degree of precision • It has high sensitivity, being able to detect trace quantities of many metals at levels well below part per billion (ppb)	• The inability to resolve target isotopes easily from molecular interferences • High background noise on the detector caused by the ion optics of the quadrupole mass analyser, higher noise levels could result in degraded or reduced detection limits • Relatively slow analysis speed • Mass drift	14, 15
LIBS	• Costs are low • Can analyse large number of samples in short span of time • Capable of doing multi elemental analysis simultaneously • All states of matter (solid, liquid and gases) can be analysedAble to analyse extremely hard materials • Minimal sample preparation is required which reduces worker exposure to hazardous radioactive or toxic substances • Requires small amount (μgm) of sample • Element detection limit can be achieved in the range of ppm/ppb.	• Difficult to obtain suitable standards for LIBS analysis because of matrix effect • Detection limits for solids are generally not good • Dissolved gases and bubbles produced by prior laser pulses can lead to un-focusing of the laser beam • Due to these inherent problems, LIBS analysis of liquids has not been widely successful	16
NAA	• Excellent sensitivity and accuracy especially in respect of some trace elements • Multi-element character, i.e. it enables the simultaneous determination of many elements without chemical separation	• Number of suitable activation nuclear reactors is declining in many countries due to the shutdown of many research reactors, • Expensive equipment, • Analysis require special laboratories and highly qualified personnel • Requiring handling and disposal protocols for low-level to medium-level radioactive irradiated samples	18
IC	• Applicable for the analysis of cations and anions, but mostly used for detecting anions, because there are better methods for the detection of cations • Provides accurate quantitative analyses	• Only ion concentrations can be determined • Complete salt-phases are determined by deduction, which is only possible for simple systems	19

(Continued)

Table 1. (Continued).

Method	Advantages	Disadvantages	Ref.
UV-VIS	• Wide-ranging area of applicability • High sensitivity (low LOD), • High selectivity • Simple and rapid automatic method	• Time-demanding sample preparation and measuring procedure • Interferences by other coloured substances in the sample	20
Electrochemical techniques			
CV	• Speedy analysis • Higher selectivity and fair sensitivity • low coast • automated • Miniaturised equipment with low energy requirements • Easy operation and the ability of analysing element speciation	• Sensitivity, selectivity and detection limits don't fulfil today's requirements • Background noise control	21 22–24
ASV	• High sensitivity and diversity: the most sensitive electroanalytical technique • Suitable for the determination at trace levels of many metals • Lower detection limit • Low cost • Extremely pertinent	• Toxicity of some electrodes • Difficulties in the determination of metals with dissolution potentials that are more positive than that of WE • Metals insolubility (like As in mercury) • Formation of intermetallic compounds in amalgams • Low cathodic potential limit (in solid electrodes) • Multiple peaks • Large background contributions	25
SWASV	• Speedy measurements where the entire scan can be performed on a single mercury drop in about 10 se • Time saving • Reduces the amount of mercury used per scan by a factor of 100 in some instances • Used in conjunction with a pre-reduction step • The limits of detection can reach up to 1–10 ppb • Low limits of detection	• rely on the in-situ preparation of the working electrode where the analyte ions and the working ions are introduced into the solution simultaneously and the deposition of both at the working electrode are done at the same time. • Complicated interferences and complex matrices can result in enormous gaps between real conditions and lab measurements • Presence of natural organic compounds in samples and the interference caused by other ions, which have negative impacts on the stripping procedure, and thus increase the electrolyte background to high levels and interfere with detection of the target ions	26
EIS	• Detection of ions at the ppb level without using a reference electrode • Requires no reference electrode, thus reducing the instrument and maintenance costs	• Inability to distinguish between different ions • Software required to determine the real impedance of the sample, and using that information to determine concentration in parts per million	27
ECL	• Electronic excitation requires comparatively simple and inexpensive instrumentation. • Electrochemiluminescent reactions are quite rare: when used for labelling, because of the smaller likelihood of interference. • Often confined to the surface of the electrode or its close vicinity: can be exploited, for example, in developing methods for homogeneous immunoassay.	• The frequent fouling of the electrodes: can sometimes be prevented by regular electrochemical cleaning of the electrodes.	28

(Continued)

Table 1. (Continued).

Method	Advantages	Disadvantages	Ref.
Piezoelectric biosensors			
QCM	• Piezoelectric transducer is available in any desired shape	• The transducer is used for dynamic measurement only	29, 30
	• Has rugged construction	• It has high temperature sensitivity	29,30
	• Small in size	• Some crystals are water soluble and dissolve in high humid environment	
	• Good frequency response		
	• Negligible phase shift		
	• High sensitivity		
	• High mobility		

Furthermore, the adsorption mechanisms occurring between various adsorbents and Uranium, were also highlighted [36].

Since calixarene represents versatile molecules with superior sensing properties, it has been intensively investigated and reported for sensing applications. Therefore, the focus of this review is to summarise the recent developments in calixarene chemistry related to the detection of heavy metal ions. The progress in the field of monitoring of heavy metal ions through sensitive, selective, reproducible, less time consuming, and reliable detection techniques, such as QCM, involving the use of appropriate calix[n]arene as sensing materials, will be highlighted. Other sensing materials, as polymers and nanostructures, will also be discussed.

3. Piezoelectric transducers

Quartz has piezoelectric properties. Piezoelectric effect, also known as direct piezoelectric effect, refers to a change in electric polarisation that is produced in certain non-conductive materials when they are subjected to mechanical compression, and vice versa. An important feature to note about this phenomenon is that the process is reversible. The inverse piezoelectric effect refers to a deformation of these materials that results from the application of an electric field. The deformation could lead to either tensile or compressive strains and stresses in the material depending upon the direction of the electric field, the preferred direction of polarisation in the material, and how the material is connected to other adjacent structures.

A piezoelectric sensor can transform one form of energy to another while piezoelectric actuator works in reverse mode of piezoelectric sensor. In other words, in the case of a piezoelectric sensor, when force is applied to stretch or bend it, an electric potential is generated; to the contrary, when an electric potential is applied on a piezoelectric actuator, it is deformed i.e. stretched or bended (vibrate). This vibration takes place at the nominal resonance frequency of the piezo-materials. So a piezoelectric transducer consists of quartz crystal, which is prepared from silicon and oxygen arranged in crystalline structure (SiO_2). Due to its outstanding frequency response, it is normally used as an essential part of the QCM, where mass variations can be detected by resonance frequency changes. The advantages of the piezoelectric transducer are: The high frequency response, it's self-generating, the simplicity of use, the flexibility (made in any desired shape and form), and the large dielectric constant. On the other hand, the disadvantages of this transducer are the follows: It is not suitable for measurement in static condition, it needs high impedance cable for electrical interface because the device operates with small electric charge, the output may vary according to the temperature variation depending on the crystal cut, and the output is largely affected by relative humidity variations, which demands coating the crystal with materials like polymers, macrocycles or nanostructures. This is the principle of piezoelectric sensors; the focus will be placed on different QCM techniques.

3.1. Quartz crystal microbalance

A QCM is a timing apparatus that determines a mass change per unit area by measuring the change in frequency of a quartz crystal resonator (QCR). The resonance is altered by the accumulation or subtraction of a small mass due to many criteria such as: oxide growth-decay; film deposition on the surface of the acoustic resonator. The QCM can be

applied under different conditions; under vacuum, in gas sensors and lately in liquid environments. It is beneficial for monitoring the rate of thin film deposition systems under vacuum. By operating in liquid, it is extremely effective at determining the affinity of molecules to functionalised surfaces through recognition layers. Frequency measurements are accomplished to high accuracy; therefore, increasing the mass sensitivity down to a nanogram level per unit area.

Oscillations of the quartz crystal can be induced by applying alternating current between the electrodes of a properly cut crystal. The operation principle of a QCM sensor is that a physical dimension (mass), transmuted into a force, acts on the sensing element.

A typical arrangement for the QCM measuring system contains: an oscillation source, frequency sensing equipment through a microdot feed-through, water cooling tubes, the retaining unit, and input/output devices. The frequency of oscillation of the quartz crystal is partially dependent on the thickness of the crystal. During normal operation, all the other influencing variables remain constant; as mass is deposited on the crystal surface, the thickness increases; consequently, the frequency of oscillation decreases. When Sauerbrey equation assumptions, rigid and very thin layers, are fulfilled, the frequency variation can be quantified and correlated accurately by the linear relationship between frequency and mass change:

$$\Delta m = -C_f.(1/n).\Delta F \tag{1}$$

where n = overtones = 1, 3, 5, 7, 9, 11,13, C_f [ng.cm^{-2}.Hz^{-1}] is called the mass sensitivity constant mass sensitivity (a function of the resonance frequency, shear modulus and density of quartz, respectively; and Δm and ΔF are the changes of mass and frequency, respectively. For a 5 MHz AT-cut QCR, $C_f = -17.7$ ng. cm^{-2}. Hz^{-1}, the Film thickness can be calculated by:

$$\delta = (\Delta m/\rho.A) \tag{2}$$

where δ is the film thickness and ρ is the density and A is the area (cm^{-2}).

Micro-gravimetrical measurements are the typical sensing application of QCR, by applying the Sauerbrey equation. But, when the film thickness increases, viscoelastic effects come into play. Investigations of viscosity, layer viscoelastic properties, are of great significance too.

The electrochemical version of QCM (EQCM) is a device where electrochemical experiments can be performed by coupling the QCM with a potentiostat (to control both potential and current of the surface). Only one side of the QCR, which functions both as a part of the QCM oscillator circuit and as the working electrode in the electrochemical cell, are made in contact with the electrolyte. Frequently, the EQCM is applied simultaneously to quasi-steady state methods, as in the case of slow scan cyclic voltammetry (SSCV), where scan rates less than 0.1 mV. S^{-1}. In this technique mass variations during electrolysis can be obtained from $\Delta f(\Delta m/A)$ vs. potential curves. On the other hand, depiction of $\Delta f(\Delta m/A)$ vs. charge density allows, by use of Faraday's law of electrolysis, the calculation of the number of Faraday exchanged per mole of electro-active species [37]. Simultaneously, the current density can be measured as a function of potential as well.

Additionally, to measuring the frequency, the dissipation is often measured to support analysis. The dissipation (D) is a parameter quantifying the signal damping in the system, and is related to the viscoelastic properties of the layer. The behaviour of the dissipation

energy (ΔD) and crystal frequency (ΔF) curves over time, can indicate the adsorption activities of different species ions on the modified surface. This valuable information allows to monitor the species (metal) ion interaction and complexing process with the coated surface. One advantage of this QCM-D method is the high frequency and dissipation resolution in liquids (in the order of $\pm$ 0.1 Hz and 1×10^{-7}, respectively) [38]. Combination with simulation software, permits experimental data modelling to extract meaningful physical parameters such as mass, thickness, density, viscosity, or storage modulus in order to characterise the formed complex layers [39].

Another version of the QCM-D mode of operation is the QCM-I, where the 'I' stands for impedance. The measuring principle is based on impedance analysis of the QCR. Resonant frequency and the bandwidth, which is the full width at half maximum (FWHM), of the resonant conductance curve are obtained. FWHM is a direct correlation with the quality factor (Q), which is by definition the inverse of the well-known dissipation energy (D) [40].

Several research works demonstrated that modified QCM resonators are valuable for sensors applications in general [41] and in detection of heavy metals in particular [42]. Nevertheless, general restrictions due to the viscoelastic nature of the applied sensing films, modified systems were developed namely the quartz crystal microbalance with dissipation mode (QCM-D) [38,43] and with impedance measurements (QCM-I) [40].

At the present time, the challenges in the applications of QCM (EQCM, QCM-D, QCM-I) in the sensor fields are more chemical than instrumental. As already deliberated, the response of these devices is nonspecific (nonselective). Therefore, the interfacial chemistry needs to be adjusted to provide more specific and reproducible measurements. Further advancement for the reproducible immobilisations of the desired chemical agents into thin films on the sensor-detecting surface must be developed.

4. QCM crystal surface immobilisation

The process of applying a thin film to a surface is known as thin-film deposition, which indicates any technique for depositing a thin film onto a substrate. Most deposition methods can regulate the layer thickness within a few tens of manometers. Furthermore, several types of immobilisation techniques for layer deposition will be highlighted.

4.1. Film immobilisation

In the recent years, nanostructured materials have received much consideration through developing innovative designs applied in different sensing approaches (definitely electrochemical and biosensors) [44,45]. A noteworthy argument, in addition to the applicability of nanomaterials as the sensor recognition elements, is to use manipulation procedures for their construction [46]. There are four basic methods of immobilisation: physical adsorption, chemical adsorption, self-assembling molecular layers (SAMs), and modification with Langmuir-Blodgett film (LB) method.

4.1.1. Physical adsorption
Physical adsorption is a simple and quick process for manufacturing sensors (for instance enzymatic biosensors). It goes through the reduction of the nanoparticles with a negatively charged ligand. The ensuing layer transfers a negative charge onto the colloidal particle

surface. Even though this method has the advantage of quickness and simplicity, unfavourable orientations and reduced functionality are possible [47].

4.1.2. Chemical adsorption

Chemical adsorption includes direct covalent binding between the materials to be applied and the sensor surface. Chemisorption is accomplished via covalent interaction between the active groups and the gold surface [48,49].

4.1.3. Self-assembly

In the course of Self-assembly (SA) process, a layer with well-organised structure is formed on the solid surface without any external direction. Similar complex processes can be observed in the nature. The building blocks of the ordered layers, which could be atoms, molecules, nano- and mesoscopic structures, are kept together with week interactions (like Van der Waals force, hydrogen bonds, π- π interaction), or by metallic, covalent and ionic bonding.

4.1.4. Langmuir-Blodgett film

The Langmuir-Blodgett (LB) method is based on the transfer of insoluble Langmuir monolayers from the liquid-air interfaces to the solid supports. (The term 'Langmuir film' is normally reserved for a floating monolayer at the air-water interface [50]. The LB technique is one of the most favourable techniques for deposition of nanolayer films as it ensures the following conditions [51].

- The precise control of the monolayer structure, thickness,
- The homogeneous deposition of the monolayer over large areas and
- The possibility to make multilayer structures with varying layer composition.

A further benefit of the LB method is that monolayers can be deposited on practically any kind of solid substrate.

4.2. Techniques for thicker layer deposition

Coating a material, commonly termed as a substrate, is application of a layer to its surface, which intention could be functional and/or decorative. The coating itself may be completely or partially covering the substrate.

The most common procedures applied for layer deposition are:

- spin-coating
- drop-coating
- spray- coating
- inkjet printing and
- Layer-By-Layer technology (LBL).

4.2.1. Spin-coating

Spin-coating, mainly applied at laboratory scale: after deposition of small amount of solution into the centre of the solid substrate starts the spinning at high speed; the advantage is the homogeneity of the layer.

4.2.2. Drop-coating

The application of a thin cover onto a sample surface by depositing consecutive drops of a solution on its surface, and allowing the solvent to evaporate. With the drop method it is hard to get uniform thickness and additionally it is very complicated to control the processes. As a result, the thickness of the boundary layer of the drops can significantly exceed the thickness layer in the centre of the drop. This method has the disadvantages: non-reproducibility and non-uniform films. Beside it is applicable in cases of small samples and the process is time consuming depending on the solvents evaporation rate.

4.2.3. Spray coating

In this method, the coating solution is transported into an aerosol (pressure-driven, nozzle-based atomizer). The solvent viscosity should be reduced. The droplets driven by the carrier gas settle on the solid surface by gravitation forces or by electrostatic field.

4.2.4. Inkjet printing

This method, applicable at industrial scale, is an encouraging tool for electronic sensing due to its cost effectiveness. In this situation, thin droplets are deposited onto the solid surface from a printer head.

4.2.5. Layer-by-layer technology

Layer-by-layer technology (LbL) is a powerful technique for preparation of nanostructured, multi-layered nanocomposites with well-ordered structures at molecular level. LbL method mainly is established by the alternative adsorption of molecular layers of opposite charges when a solid surface is dipped, by turns, into solutions of anionic and cationic electrolytes. The method is practically simple; the nanolayers are applicable as biosensors or as biological materials which could be immobilised on the nanolayer surface by electrostatic interactions [52,53]. As an example, the polyaniline films are often functionalised as chemical sensors [54] and biosensors [55], due to their chemical stability, simplistic synthesis and low cost.

Vieira showed that a water solution/dispersion of polyaniline, prepared by interfacial polymerisation, can be used for preparation of LbL-modified electrode surface for pH sensing [56].

5. Surface coating materials

Many coating materials have been used for molecular recognition, heavy metal detection including small organic molecules, macrocycles, polymers, DNA, aptamer, proteins, bacteria, nanomaterials and nanostructures as sensors, aiming at significant improvement in the sensing performance [57]. In the next paragraphs, the emphasis will be on calixarenes as coating materials used for molecular recognition. But other sensing agents as polymers and nanostructures will also be deliberated.

5.1. Calixarenes as sensing agents

Calix[n]arenes are an important type of macrocyclic receptors due to their adaptable cavity dimensions, which can play a significant role in the detection and early warning of heavy metals in environmental water. The cyclic assembly of calixarenes is analogous to

cyclodextrin (CD) [58–60] and crown ethers [61,62]. Calix[n]arenes (n = 4,6,8, etc.) have advantages as a macrocyclic receptor because of their different conformational isomeric form. Thus, their ability to control the rigidity and flexibility can be used to separate guest ions easily, which may display different affinities towards heavy metals ions. In other words, we can define calix[n]arenes (n = 4–20) as phenolic[1]n-metacyclophanes obtained by acid- or base-catalysed condensation of formaldehyde and p-substituted phenols. They possess a distinct hydrophilic lower rim to encompass a hollow cavity with dimensions that can be varied by changing the number of the phenolic units (n) present and a hydrophobic upper rim as shown in (Figure 1) [63].

The diversity of calix[n]arenes is principally linked to their conformational isomerism due to constrained rotation of the Ar-CH2-Ar bonds, or complete molecular rotation through the annulus. In the case of a calix[4]arene, the molecular rotation through the annulus is suppressed if the upper-rim alkoxy groups are bulky enough to restrict this flipping motion. With the progress of synthetic methodologies, a lot of procedures have been presented for obtaining cone, partial-cone, 1,3-alternate and 1,2-alternate conformations of calix[4]arene derivatives, shown in Figure 2. Those advances can offer helpful capabilities for molecular and ionic detection and recognition [63].
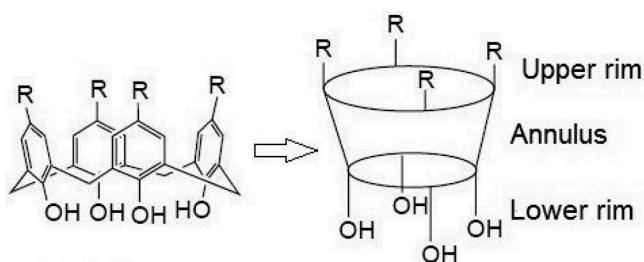

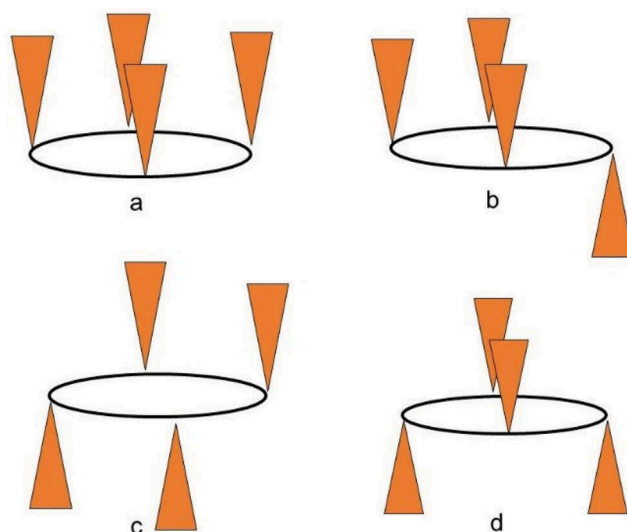Figure 1. Cone conformation of a typical calix[4]arene.

Figure 2. Different conformations of lower- and upper-rim substituted calix[4]arenes: a. Cone, b. Partial cone, c. 1,2 alternate, d. 1,3 alternate.

Calixarenes in general have poor solubility and low toxicity, high melting points, high chemical and thermal stability, and their structure can be modified. These attributes make them attractive materials for separation and sensing applications, especially for heavy metal ions [63].

5.1.1. Properties of calixarenes

The calixarene molecules have special structure with a 'basket' that can trap molecules or ions, i.e. these molecules can host guest molecules. They can adsorb heavy metal ions [64]. These macrocyclic molecules can also adsorb gases (methane acetylene, carbon dioxide, etc.). The flexibility of the upper rim's functional groups is responsible for the gas uptake [65].

To improve the properties of the calixarenes, they can be modified both at the narrow, on the wide or on both rims. They can be characterised by different physical parameters. It is interesting that the melting point of the calixarenes is unusual high; this is influenced by the substituents as well as by the position of the substituents. The solubility of calixarenes is very low; generally, they are very insoluble in water and in different organic solvents. The solubility can be influenced by the built-in substituents. If it is important to increase the water solubility, generally the involvement of carboxyl groups will increase it (not only under neutral, but in alkali and acidic conditions) [66].

According to the infrared spectroscopic characterisation of calixarenes the stretching vibration of the OH groups is at very low frequency; at cyclic tetramers: 3150 cm^{-1}, at cyclic pentamers at 3300 cm^{-1}. This is due to the very strong intermolecular hydrogen bonding. There are not significant differences in the fingerprint region of the infrared spectra in the range of 1500 and 900 cm^{-1}. On the other hand, in the region of 500–900 cm-1 the molecular differences cause variations in the spectra. When the calixarenes are characterised by their UV spectra, it is important that the ratio of intensities between 280 and 288 nm depends on the ring size of the cyclooligomers.

The temperature dependent 1H NMR studies show that at higher than room temperature the CH$_2$ hydrogens appear as a sharp singlet and below the room temperature a well reserved pair of doublets appears, which is due to the conformational inversion. The time scale of the NMR measurement also influences the spectra; at low time scale the CH$_2$ hydrogens are chemically shifted and coupled, at rapid time scale the CH$_2$ hydrogens are in averaged environment. It is interesting that the conformation of calixarenes is less symmetric in solution than in solid state.

Special calixarens can solve as selective components of stationary phase in capillary gas chromatography. It is also interesting that the calixarenes undergo on photochemical cycloisomerisation (photocyclisation/rearrangement). This reaction needs the presence of free OH groups. Interesting observation was that some calixarene derivatives can mimic enzymatic reactions of metallo enzymes. When they can bind transition metal ions, their conformation alters and so they mimic the funnel of an enzyme [67].

In liquid phase, and at room temperature, the ^{1}H NMR technique makes it possible to differentiate between the four conformations of the p-tert-butylcalix[4]arene as an example, by the corresponding signals of the methylenic bridges, the hydroxyl functions or the tert-butyl groups (Figure 3). Furthermore, Jaime [68] showed that by using the ^{13}C NMR technique, one can see that the chemical shift of the methylenic bridges is different (For two conformations), and it's due to the phenols orientation (Figure 4).
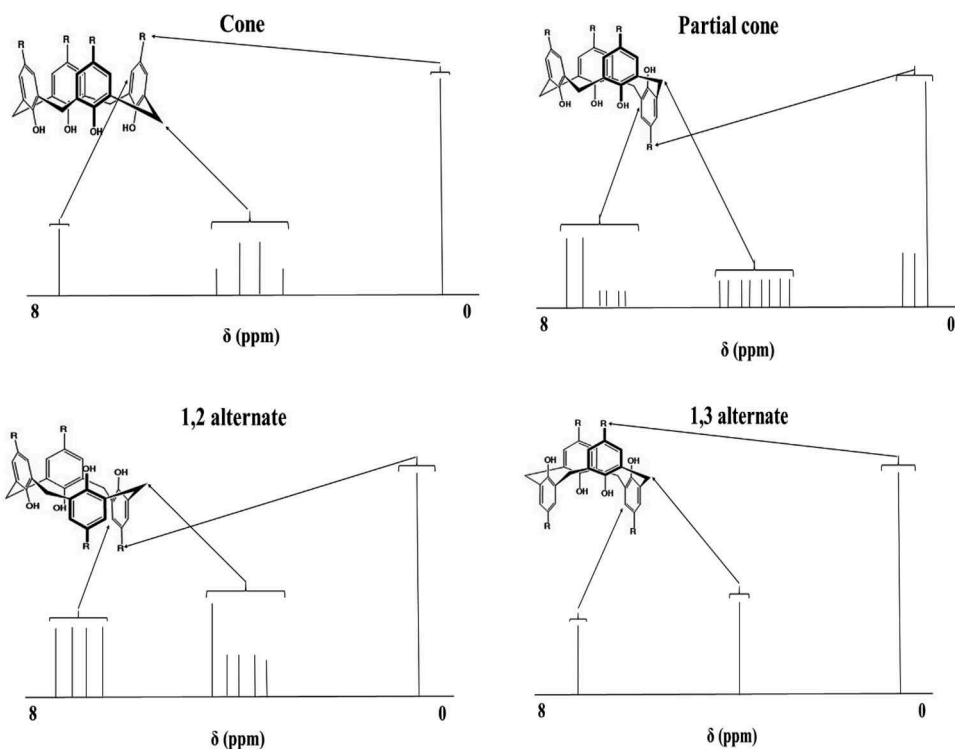
Figure 3. ^{1}H NMR spectra for each p-tert-butylcalix[4]arene's conformation (R = tert-butyl).
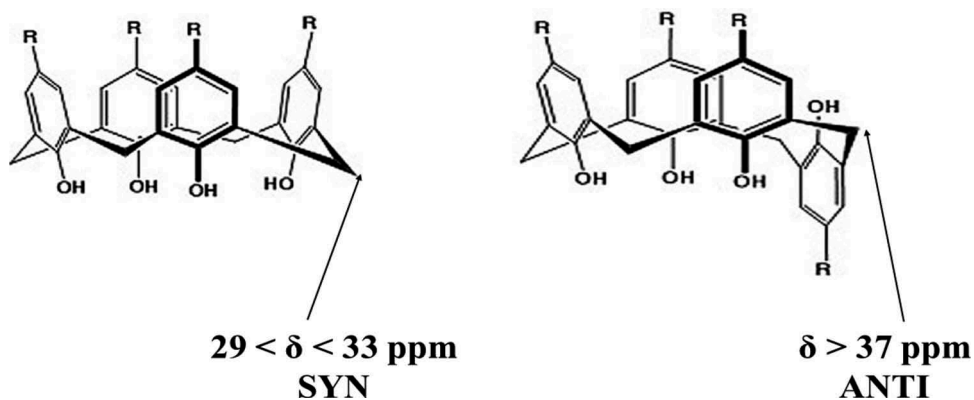
Figure 4. ^{13}C NMR chemical shifts of the calix[4]arene's methylenic bridge carbon atom. (R = tert-butyl).

Consequently, when the two phenols are oriented in the same direction (SYN), the Ar-CH$_2$-Ar chemical shift is between 29–33 ppm, while when the orientation is opposite (ANTI), the chemical shift is greater than 37 ppm.

In solid state, and when the calixarene hydroxyl groups are not substituted, all calix[4] arenes adopt the cone conformation, for the reason of the intramolecular hydrogen bonds establishment. The unmodified calix[4]arenes are difficult to handle in solution, due to their low solubility in most organic solvents. They have almost no complexing

properties towards metals, but they are capable of complexing metal cations after ionisation of one or more hydroxyl groups, and the modification of calixarenes makes it possible to improve the complexing and extracting properties, also to increase the selectivity towards metal ions.

Generally, the calix[4]arene macrocycles can be functionalised in four positions (Figure 5): Lower rim; Upper rim; Methylene bridges level; and, in the phenols meta position.

The change in the chemical nature of the bridges connecting the phenolic units makes it possible to increase the number of coordination sites, but also to modify the cavity size. Considering a normal calix[4]arene, only the phenols oxygen's participate in the metal ions coordination. But, by changing the methylenic bridges with sulphur atoms (tetrathiacalix[4]arene) (Figure 6) [69], the number of coordination sites increases leading to the possibility of chelates formation with sulphur atoms.

In addition, the C-S bond in tetrathiacalix[4]arene is longer than the C-C bond in calix[4]arene, furthermore the size of the tetrathiacalix[4]arene cavity is larger (Figure 7).

The replacement of methylenic bridges by sulphur atoms modifies certain properties of the calixarenes. Sone et al showed, by NMR and IR studies, that the progressive replacement of methylene bridges decreases the intramolecular hydrogen bonds strength; this is due to the bond length between the phenol's ortho position carbon and the sulphur bridge (C-S bond), which is longer compared to the (C-C bond) of a normal calixarene (Figure 7) [70]. Accordingly, the fact of replacing methylenic bridges with sulphur atoms is increasing the calixarene cavity's diameter by 0.6 Å. Besides, increasing the distance between the hydroxyl groups in the case of thiacalixarene causes a reduction of 2 Kcal. mol^{-1} in the free activation energy ΔG associated to the rotation leading to the conformational interconversion (Table 2), this was estimated by spectroscopic data [71].

5.1.2. Calixarenes as complexing, extracting and coordinating agents

Calix[n]arenes are advantageous complexing agents for metal ions, anions and neutral organic molecules [72–76]. Calixarene can take either cone or basket type structures creating cavities, which can encapsulate ions or small molecules [53,77]. The shape and size of calixarene void can be easily altered by simple chemical reactions to accommodate specific molecule.
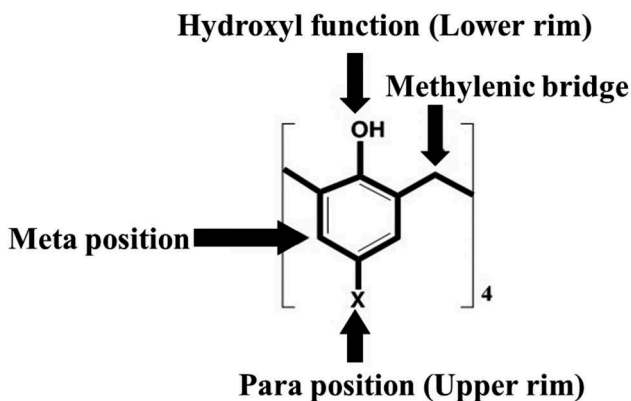
Figure 5. The calix[4]arene's functionalisation sites.
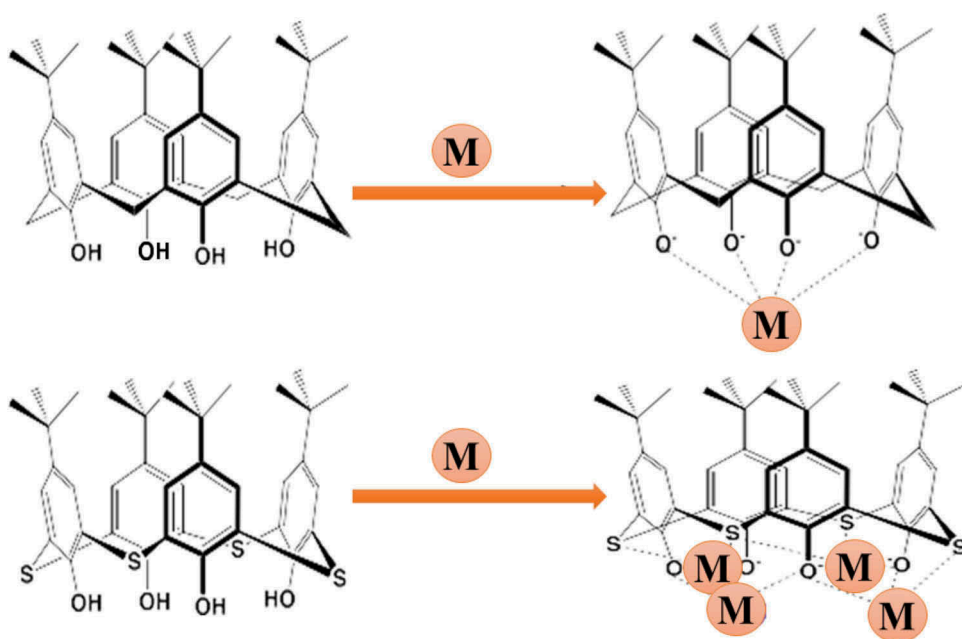
Figure 6. A comparison of the complex formation (By means of cationic metal ion) between p-tert-butylcalix[4]arene and p-tert-butylthiacalix[4]arene.
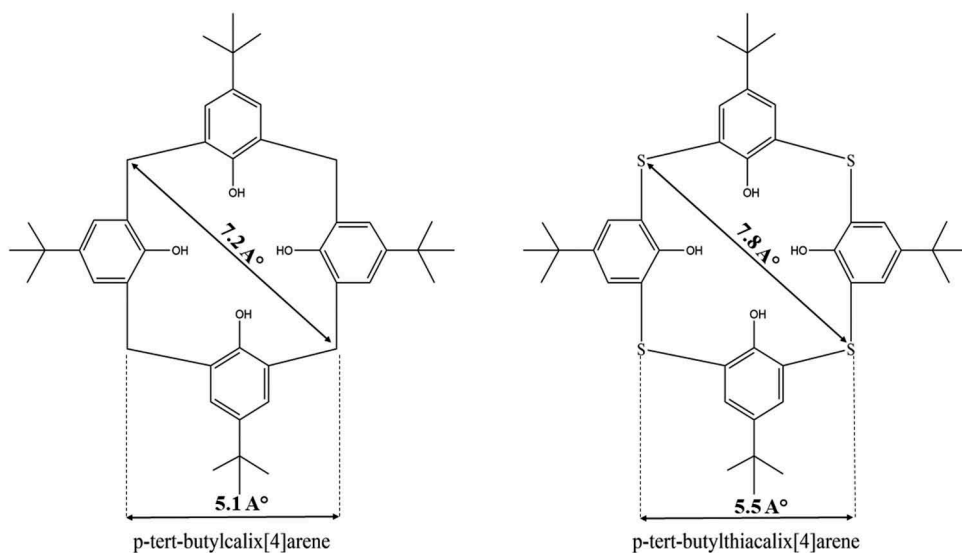
Figure 7. Size cavity comparison between p-tert-butylcalix[4]arene and p-tert-butylthiacalix[4]arene.

Many researchers demonstrated calixarenes as complexing, extracting and coordinating agents for metals ions. O'Connor and his team reviewed the use of calix[n]arenes as recognition reagents in electroanalysis [78]. Yordanov and his research group prepared the compound 25,26,27,28-tetra-(2 dimethyl-dithio-carbamoyl-ethoxy) calix[4]arene as an extracting material for heavy metal ions; this compound was effective for Ag^+, Pd^{2+} and

Table 2. Spectroscopic properties of p-tert-butylcalix[4]arene and p-tert-butylthiacalix[4]arene.

Calixarene name	Coalescence temperature (°C)	Free activation energy ΔG (Kcal.mol^{-1})	v OH (cm^{-1})	δ OH (ppm)
p-tert-butylcalix[4]arene	58.00	15.50	3160	10.34
p-tert-butylthiacalix[4]arene	17.00	13.50	3300	9.53

Au^{3+}, but much less effective for both Hg^{2+} and $MeHg^+$ [79]. Navakun and collaborators have synthesised a series of p-tert-butylcalix[4]arene derivatives containing azathiol receptors and investigated their complexation ability for Zn^{2+}, Cd^{2+} and Hg^{2+} ions by potentiometric titration; the compounds selectively form 1:1 complexes with Hg(II), and their stability constants (log Ks) were estimated to be 4.47 and 3.20, respectively [80]. Liu and his group have synthesised a novel series of double-armed p-(tert-butyl)calix[4]arenes in 80–86% yield, which formed ISEs for Pb^{2+}. These results indicated that the electrodes, based on calix[4]arene-derived amides as neutral ionophores were all Pb^{2+} selective and revealed nearly theoretical Nernstian slopes for Pb^{2+} over a fairly wide concentration range [81]. Wang and co-workers prepared numerous, new nitrogen-containing calixarene derivatives and analysed by UV spectroscopy and solvent extraction their ion-binding properties with Pb ions by using UV spectroscopy and solvent extraction. The UV spectra showed their capability to transform Pb picrate ion pairs into detached ones by means of Pb^{2+} complexation, in tetrahydrofuran [82].

Halouani fabricated a new series of beta-ketoimine calix[4]arene derivatives and determined their molecular structures by X-ray diffraction. These novel receptors can selectively complex with Cu^{2+}, Hg^{2+}, and Ag^+ cations [83]. In the meantime, Macros recognised the binding properties of the tetra(diethyl) amide derived from p-tert-butyldihomooxacalix[4] arene in the cone conformation, towards alkali, alkaline earth, transition (Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) and heavy (Ag^+, Cd^{2+}, Hg^{2+} and Pb^{2+}) metal cations by extraction methods [84,85]. Sgarlata and his research group investigated the binding affinity of the synaptic acid-calix[4]arene hybrid for Pb^{2+}, Cd^{2+} and Hg^{2+} using a UV-Vis study. The UV-Vis analysis showed that the hybrid calixarene noticeably favours Pb^{2+} over Cd^{2+} and Hg^{2+} while the NMR data indicated that all three metal ions are located in the cavity of the calixarene scaffold and the sinapyl pendants [86].

Furthermore, Hamdi synthesised a spirobiscalix[4]azacrown (a), and a calix[4]azacrowns (b and c). They stated the extraction properties of all three (a, b and c) toward Cu^{2+}, Zn^{2+}, Pb^{2+}, Ag^{2+} and Cd^{2+}. The results showed that complexation is the main factor affecting extraction with ligands [87]. Uysal and collaborators used pyrimidyl-thioamide functionalised calix[4] arene to extract selectively the transition metal ions (Cu^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Hg^{2+} and Cd^{2+}). The experimental results show better efficiency and affinity for Pb^{2+} and Hg^{2+} ions, the antibacterial and antifungal effects were also investigated [88]. This was a short summary about the progress of the use of calixarenes in this field of metal ion complexation over two decades.

Recently, Russo and his analysis cluster used polarimetry to analyse the binding skills of a chiral calix[4]resorcinarene with L-proline subunits, towards a group of fittingly chosen organic guests. A synchronal formation of 1:1 and 2:1 complexes were discovered in many cases [89]. Göde and his team likewise invented a GC modified electrode, they exploited it for synchronal voltammetric detection of many metal ions in solution [90].

Ovsyannikov reviewed a series of coordination polymers supported by calixarene. A special thought was drawn towards the structural and purposeful properties of those

extended networks: magnetic, luminescence, sorption and chemical change properties [91]. Lu research group studied the extraction behaviours of various acids changed with calixarenes towards Eu^{3+} and Nd^{3+}, a high extraction ability was observed [92]. Moradi and his collaborators represented a novel technique to construct two-dimensional metal-organic coordination networks. It may be applied to an oversized functionalised organic building blocks, conjointly on the far side macrocycles, which may be interconnected by various metal nodes [9].

Shivappa and his colleagues invented calixarene modified screen-printed electrodes, which were employed as disposable electrochemical sensors for simultaneous measurement of toxic metal ions Pb^{2+}, Cu^{2+} and Hg^{2+} within environmental samples using cyclic voltammetry and differential pulse anodic stripping voltammetry techniques [93].

Sgarlata and his group obtained a new series of supramolecular assemblies through the interaction of 3-pyridylmethyl-calixarenes and Cu^{2+} or Zn^{2+}. The formed complexes were characterised both in solution and in the solid state. The results have shown how the lower rim was crowded and how the different coordination modes of the metal centres had a great impact on the complexes conformation with the formation of monomeric, dimeric, or oligomeric polymeric species [94].

Additionally, Smirnov and his co-workers studied the extraction of Cs-137 and Am-241 with perchloroethylene solutions of O-substituted p-alkylcalix[8]arenes (alkyl: tert-butyl, iso-nonyl) from carbonate-alkaline media. They confirmed the pH-dependence distribution in the aqueous phase, and determined the composition of caesium and americium solvates with calix[8]arenes. Additionally, it was shown that tert-butylcalix[8] arene with oxybis(ethane-1,2-diyl) bridging group possesses superior efficiency towards caesium in alkaline media and that the most efficient extractants for americium are 'mixed' iso-nonyl-tert-butylcalix[8]arenes with ethane-1,2-diyl and oxybis(ethane-1,2-diyl) bridging groups [95].

Likewise, Kumar and co-workers described a one-step synthesis of a singly bridged biscalix[6]arene and evaluated its recognition properties towards alkali metal ions. They studied the complexation ability by liquid-liquid extraction using alkali metal (Na^+, K^+, Cs^+) picrates and the conclusion was that in the transport process, the predominant role of an ion exchange action mechanism was observed [52].

Furthermore, Horvat and co-researchers studied the complexation of alkali metal cations by lower rim N,N-dihexylacetamide (L1) and newly synthesised N-hexyl-N-methylacetamide (L2) calix[4]arene tertiary-amide derivatives in acetonitrile, benzonitrile, and methanol by means of direct and competitive microcalorimetric titrations [96].

Additionally, De Leener synthesised a novel calixarene, and explored its coordination chemistry. The X-ray diffraction studies of the metal complexes disclosed a six-coordinate Zn-II and a five-coordinate Cu-II complex. The studies of cyclic voltammetry in numerous solvents showed a reversible system [97]. Lavande tested the formation of several complexes between lucigenin and p-sulfonatocalix[n]arenes, the creation of 1:1 and 1:2 host-guest complexes with lucigenin was observed, and the binding affinities were up to 10^9 M^{-1} [98].

Recently, Sayin and collaborators synthesised a new 1-(2-furoyl) piperazine-appended calix[4]arene derivative, the results show that it has great selectivity concerning Cd^{2+} and other ions [99].

5.1.3. Calixarene-based sensing agents

The recognised selective receptor properties and easiness of structural alteration makes calixarene derivatives as attractive materials for applications in chemical sensors. In 1986, Diamond and his co-workers described the receptors (Figure 8(a,b), as excellent sensors for sodium. These sensors have been found to be useful in the estimation of Na^+ in blood. It was the first publication on calixarene-based sensing agents [100].

In 1993, Van Dienst and co-workers reviewed the synthetic methods of selectively functionalised calix[4]arenes. They discussed a number of practical applications of calix [4]arenes like non-linear optics, organ imaging, ion sensitive field effect transistors and transport through liquid membranes [101]. The McKervey group is one of the pioneers in the development and synthesis of new and novel calixarenes for use in many applications; they appraised many calixarene derivatives prepared as electrochemical sensors, optical sensors, chiral recognition devices, solid phase extraction phases, stationary phases and modifiers [102].

Arora and his research team offered an overview on the synthesis and evaluation of calixarene based molecular receptors. They demonstrated that calixarenes could be used for recognition, chemical separation and detection of metal ions. This group reviewed some molecular receptors based upon calix[n]arenes [63] such as:

- calixarene-based receptors for alkali and alkaline earth metal ions,
- calixarene-based receptors for transition and heavy metal ions, and;
- calixarene-based receptors for f-block elements.

Similarly, Cragg and his group reviewed briefly the history of calixarenes and their nomenclature; they examined colorimetric calixarene sensors, fluorescent calixarenes with excimer activity, electrochemically active calixarenes, and calixarenes as modifiers
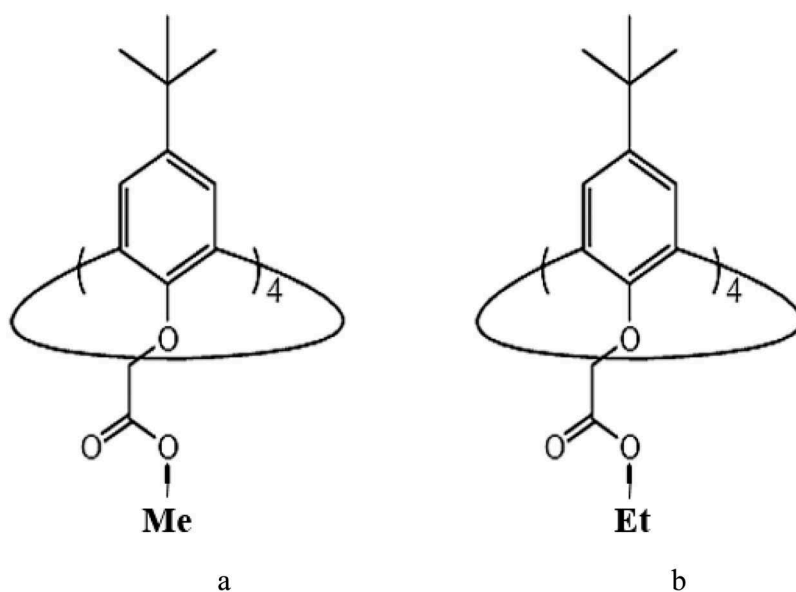

Figure 8. Receptors based on polymeric calixarenes [100].

on QCM resonator and they considered the prospective of applying calixarene sensors in biomedicine [103].

Recently, Deska and collaborators reviewed the applications of calixarenes as sensors, for the extraction of actinides and lanthanides, for the extraction of uranium, and for the sensing of Pb^{2+}, Sr^{2+}, Li^+, Al^{3+}, Ni^{2+}, Hg^{2+}, $Cr_2O_7^{2-}$, $HCr_2O_7^-$ ions [104]. Patra and co-researchers reviewed calixarenes as molecular sensors for ion recognition studies [105].

Many calixarenes based receptors were designed for selective sensing of alkali and alkaline earth metal ions [106–110]. The influence of steric hindrance was studied on ion-selectivity for calix–crown hybrid ionophores [108,111]. Likewise, fluorescent sensors were used as receptors where the $[Ru(bpy)_3]^{2+}$ was the fluorophore and calix–crown hybrid molecule the ionophore [107,112,113]; fluorescent molecular sensors with excimer emission and the solvent effect on the ion selectivity were also studied [114–116].

Other types of fluorescent sensors are cation-induced fluorescent excimers in molecular sensors bearing quinoline as fluoregenic unit [117,118]; for the detection of anions calixarenes based fluoroionophores were used [119].

5.2. Polymers as sensing agents

The concept of polymer application seems simple and logical today, but was not accepted until the 1930's when the extensive research work of I-I. Staudinger (Nobel Prize winner in Chemistry in 1953) finally became appreciated. Prior to Staudinger's work, polymers were believed to be colloidal aggregates of small molecules with quite nonspecific chemical structures.

Polymers are substances made up of recurring structural units, each of which can be regarded as derived from specific compound called monomers. The number of monomeric units usually is large and variable, with different molecular weights. The range of molecular weights is sometimes quite narrow. Polymers are used extensively in various fields including the detection and recognition of heavy metals ions in the environment.

5.2.1. Polymers in heavy metals ions sensing

In heavy metal detection many polymers were applied as coating materials, for example Sartore and his group made a polymer-grafted QCM chemical sensor, which can selectively adsorb heavy metal ions such as copper, lead, chrome and cadmium from aqueous solutions over a wide range of concentration from 0.01 to 1000 ppm [120]. Yang and his team developed a novel QCM sensor coated with copolymer to detect heavy metal ions, in the order of detection frequency of $Cu^{2+} > Co^{2+} > Cd^{2+} > Pb^{2+} > Ni^{2+} > Zn^{2+}$; for Cu^{2+} in aqueous solution, the lowest detection limit can reach as low as 10 ppm, also Yang and co-workers fabricated a QCM sensor based on the modification of Cu^{2+} ion-imprinted polymer (Cu(II)-IIP) film onto a quartz crystal, the obtained MIP-QCM sensor presents high-selectivity monitoring of Cu^{2+} ions, better reproducibility, shorter response time (6 min), wider linear range (0.001-50μM) and lower detection limit (8×10^{-4} μM) [121]. Deshmukh and co-workers appraised composites based on conducting polymers and carbon nano-materials for heavy metal ion sensing [122].

5.2.1.1. CNTs-based electrodes for the determination of heavy metal ions.

Carbon nanotube-based electrodes were widely applied for the heavy metal ions detection, for example, Ouyang and his group used a bimetallic Hg–Bi/single-walled carbon nanotube

composite electrodes for the detection of Zn^{2+}, Cd^{2+}, Pb^{2+}; the limits of detection were 2 µg/L, 0.98 µg/L, 0.98 µg/L respectively [123]. The same metals were detected by a screen printed carbon nanotube electrode and the detection limits were 11, 0.8, 0.2 µg/L, respectively [124]. CNTs-based nanoelectrode arrays (NEAs) were also used for the detection of Cd^{2+} with a detection limit of 0.04 µg/L [125]. In another study a carbon paste, modified with multi-walled carbon nanotubes was used for the detection of Cu^{2+} with a detection limit of 1.1×10^{-6} M [126].

5.2.1.2. Electrodes based on organic conducting polymers (OCPs) applied for the determination of heavy metal ions.
Organic conducting polymers were also used in the detection of heavy metal ions. For the detection of Pb^{2+} and Cd^{2+} a polyaniline-co poly(dithiodianiline) modified carbon paste electrode was used, the detection limits were 0.03, 0.09 µg/L, respectively [127]. In another work a polyaniline Sn(iv) tungstomolybdate nanocomposite cation exchange material was fabricated for the recognition of Pb^{2+} ions with a detection limit of 1×10^{-6} M [128]; furthermore, a polyaniline modified electrode gave a detection limit of 0.02 mM for Cu^{2+} [129]. Likewise, a polyacrylic acid/ GC electrode was invented for the detection of Pb^{2+}, Cd^{2+}, Co^{2+} with detection limits of 0.9 nM, 1.9 nM, and 11.0 µM, respectively [130].

5.3. Nanostructures as sensing agents

The contamination of natural waters and soils with heavy metal ions has an important impact on the environment because their toxicity and are severely harm for the human health. The elimination of heavy metal ions could be done by traditional techniques (precipitation, electrochemical methods, ion exchange, membrane filtration, extraction, adsorption etc.). From the point of view of the cost efficiency, simplicity the removal of the traces of heavy metal ions by adsorption is the most preferential.

The follow conditions are preferential for nano-adsorbents: they should be not toxic, they must have high sorption capacity and high selectivity to the metal ions; the removal of the adsorbate should be easy and the nanosorbers should be easily recycled.

This is the reason that there are official limits for their concentrations. It makes clear why is so important to measure/follow the contamination of the environment.

There are several possibilities to determine and quantity/concentration of the undesired heavy metal ions. In sensors for monitoring heavy metal ions in aqueous environment nanomaterials and nanostructures are often used as they can monitor the metal ion concentration in situ and ex situ, they are sensitive and could be very selective. Nanotechnology has an always increasing importance on several research fields. Nanomaterials have interesting characteristics that differ from the bulk materials in two aspects: their surface area is extremely high, which enable them to sensitive surface processes. Nanomaterials follow rather the laws of quantum chemistry than the classical physics. The importance and application of nanostructures that can help in the quantification of ions is continuously increases.

The nanomaterials could be nanoparticles and nanostructured materials. From the point of view of the heavy metal sensors nanoparticles are formed from nano-sized metals and metal oxides (silver nanoparticles, manganese/ferric/titanium/magnesium/copper/cerium oxides) that have minimal impact on the environment and low solubility [131].

6. Detection and selectivity

Detection means to find a material (atom, molecule) in a complex system by extraction of some information from a larger stream. In the field of heavy metals sensing, it indicates the discovery of the presence of a heavy metal ion in the media. Selectivity means making a selection among materials or, in other terms the ability to distinguish the different components. In sensor applications, it stands for the detection of a specific heavy metal cations among the others.

6.1. Detection

There are several research groups that investigated heavy metal cations detection; Cao and his team fabricated a novel QCM sensor to detect heavy metal ions [42]. Aragay and his coworkers reviewed the advantages of a series of materials that enhance the selectivity, sensibility, and reproducibility of heavy-metal detection [132]. Li and his collaborators summarised the progress in sensors for heavy metal detection [57]. Gumpu's team highlighted numerous electrochemical biosensors with various interfaces employed in the detection of metal ions [24].

6.2. Selectivity

In terms of sensor selectivity, numerous research work have been done; Su and his team fabricated an innovative Cu^{2+} ion sensitive sensor by electrochemical coating of functionalised calix[4]arenes with benzoyloxy or nitrophenylazo groups, a linear response to the negative logarithm of Cu^{2+} ion concentration in the range of 1.0×10^{-16} to 1.0×10^{-10} M, a good selectivity towards Co^{2+}, Ni2+, Zn^{2+} and Ag^+ ions, a high reproducibility and a low detection limit (3.8×10^{-17} M) were found [133].

Chawla and his research group synthesised and evaluated a single molecular receptor based on calixarene for multiple analytes. The results revealed that calix[4]arene based molecular receptor shows a highly selective response towards Cu^{2+} and F^- ions with detection limits of 0.5 µM and 0.7 µM, respectively [134]. Likewise Gupta and collaborators fabricated a new cadmium-selective potentiometric sensor through p-tert-butyl calix[6] arene, the sensor works well in the concentration range 9.7×10^{-5} to 1×10^{-1} mol.dm^{-3}, the working pH range of this sensor is 2.8 to 6.2, and had an excellent selectivity for Cd^{2+} over alkali, alkaline and other heavy metal cations [135].

Recently Sayin and coworkers synthesised a new 1-(2-furoyl) piperazine-modified calix[4] arene derivative. It's metal ion extraction capabilities towards Pb^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+} and Zn^{2+} ions were evaluated, and the results showed high selectivity towards Cd^{2+} and other ions [99]. PVC-based membranes incorporating 1,3-alternate thiacalix[4]crown ionophore, was used for the selective sensing of Hg^{2+} [136], and an environmentally friendly process was elaborated for the selective recovery of Cr^{3+}, Cu^{2+}, Ni^+, and Zn^{2+} [137].

7. Conclusions

Research in the area of design and manufacture of sensors and biosensors for the detection of heavy metals is of increasing interest to many scientific communities ranging from biological and chemical sciences to engineering communities. As extensive summary on the materials applicable for metal/heavy metal ion detection was given; in the focus

were different calixarene derivatives, which are able not only sensing special molecules and metal ions, but they do it with high sensitivity and selectivity. Several tools and techniques for detecting heavy metals based on the latest trends in nanomaterials and micro and nanotechnologies are being developed. These offer new opportunities for new heavy metal detection technologies with advantages such as high sensitivity and selectivity, quickness and cost-effectiveness through the possible integration of simple platforms and existing technologies into development. Several measuring techniques were demonstrated that are able to measure the metal ions at very low concentration. New technologies like QCM, QCM-D and QCM-I were induced that were elaborated for sensing heavy metal ions and special molecules.

This review aimed to assess the research progress in the QCM applications for detection of heavy metals cations in water, to show the wide application possibilities of the QCM techniques, and to demonstrate the structural changes resulting from the interaction of metal ions with polymer, macrocyclic 'calixarenes' and nanostructural coating on the sensors. However, QCM will find a particular place in certain sensing applications in the near future. Recently it has already been demonstrated that the development of a combined system, such as application of QCM and electrochemical measurements parallel would be very useful as it would provide a lot of additionally important information on the comparison of individual analytical techniques.

QCM-based sensing concept has been demonstrated for a wide range of analytes, but a wide-spreading, multifunctional technology comparison with several commercially available instruments still needs to be critically evaluated to demonstrate its pros and cons with respect to the existing technologies.

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