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Chapter

Low Dimensional Nanostructures: Measurement and Remediation Technologies Applied to Trace Heavy Metals in Water

María Luisa García-Betancourt, Sandra I. Ramírez Jiménez, Apsahara González-Hodges, Zandra E. Nuñez Salazar, Ismailia Leilani Escalante-García and Jeannete Ramírez Aparicio

Abstract

A nanostructure is a system in which at least one external dimension is in the nanoscale, it means a length range smaller than 100 nm. Nanostructures can be natural or synthetic and determine the physicochemical properties of bulk materials. Due to their high surface area and surface reactivity, they can be an efficient alternative to remove contaminants from the environment, including heavy metals from water. Heavy metals like mercury (Hg), cadmium (Cd), arsenic (As), lead (Pb), and chromium (Cr) are highly poisonous and hazardous to human health due to their non-biodegradability and highly toxic properties, even at trace levels. Thus, efficient, low-cost, and environmentally friendly methodologies of removal are needed. These needs for removal require fast detection, quantification, and remediation to have heavy metal-free water. Nanostructures emerged as a powerful tool capable to detect, quantify, and remove these contaminants. This book chapter summarizes some examples of nanostructures that have been used on the detection, quantification, and remediation of heavy metals in water.

Keywords: nanostructures, remediation, water nanobioremediation, immobilized biological substrates, heavy metals

1. Introduction

Pollution due to heavy metals possesses a serious issue not only to human health but also to the environment and urban infrastructure. Heavy metals can be found in wastewater, groundwater, lakes, and streams, but also in soils or sediments. Heavy metals come from natural sources, but they can also originate from different anthropogenic activities (**Figure 1**). Human exposure to them has risen dramatically as a result of an exponential increase in their use in several industrial, agricultural, domestic, and technological applications [1]. Even though metals such as cobalt (Co), copper (Cu), iron (Fe), manganese (Mn), selenium (Se), or zinc (Zn)
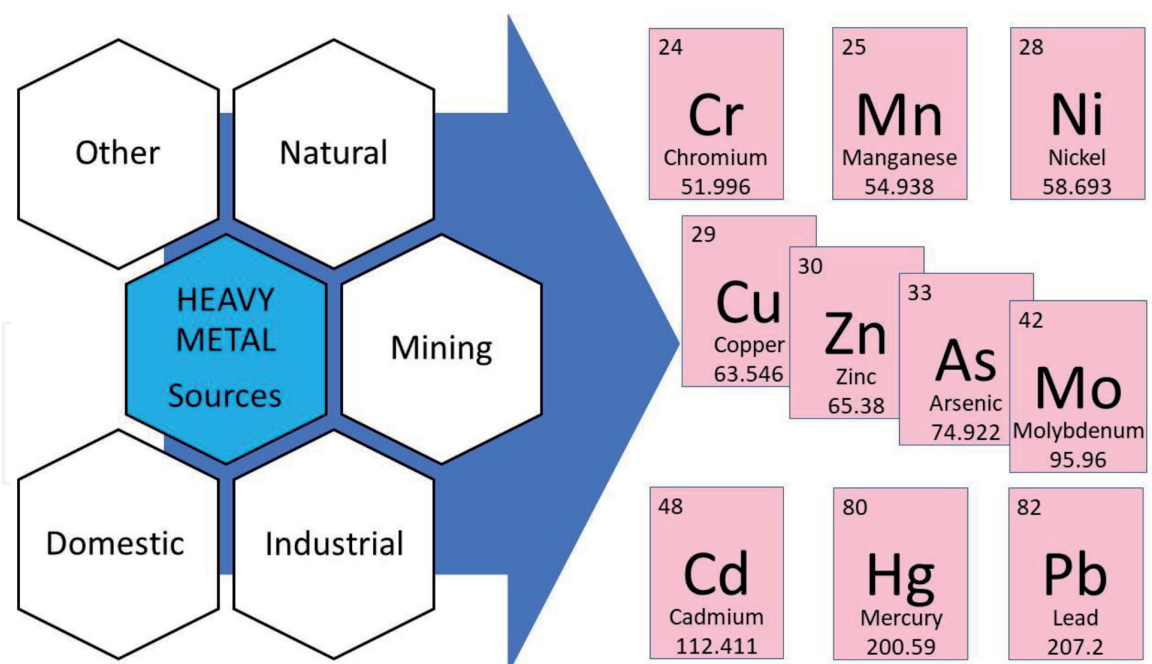
Figure 1.
The origin of some of the heavy metals released to the environment.

play essential biochemical roles in the cells of living beings, in high concentrations or as a result of long-term exposure, they are associated with cellular and tissue damage leading to adverse effects and diseases [2]. Notably, arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), and mercury (Hg) are ranked among the metals of great public health significance [1].

In order to minimize the damage to public health and other living organisms due to heavy metals, remediation appeared to rectify and redeem the environment after anthropogenic disturbance [3]. Remediation aims to implement and realize efficient actions for the eradication of diverse forms of pollution in three main activities: (1) remove formation damage, (2) testing before each remediation, and (3) routine treatment applications (maintenance) [4].

Remediation is just one of the multiple promising applications of nanotechnology. The utilization of nanotechnology concerning the environment classifies as follows: (1) the design and production of sustainable materials, (2) remediation using nanostructures, and (3) nano-based sensors [5]. Nanotechnology may contribute to any of the remediation facets, listed above, providing high selectivity (speciation and clean-up) and sensitivity (preconcentration) [6] to achieve trace levels in water, usually 100 microgram per gram.

The nanomaterials mainly used for removal are metal and iron oxides as they facilitate the precipitation and reduction of heavy metals to less harmful ionic species [7]. They are followed by carbonaceous materials such as fibers, carbon nanotubes, graphene, and graphene oxide. The porosity and surface area of carbonaceous materials allow them to easily form membranes for an efficient metal removal; besides, they serve as support of nanometals for easy recovery [8–10]. Other nanostructures based on silicon, such as silica and zeolite, are widely used due to its versatility and availability. The reactive and high surface area of porous silica allows the functionalization for multiple adsorptions of heavy metals, and zeolite allows selective separation of cations by ion exchange and adsorption from water [11, 12].

From this brief review, three main facts can be listed: (1) the importance of removing toxic heavy metals, (2) the role of nanotechnology on remediation, and (3) the use of diverse nanostructures for the removal of heavy metal from water.

In this context, the need for rapid and efficient removal of pollutants focused on toxic heavy metals with high selectivity and sensitivity from water is addressed in this work [1, 5–6], considering the advantages offered by nanostructures. This book chapter summarizes some examples of nanostructures employed for wastewater treatment considering the three aspects listed above, as well as ways to reach heavy-metal concentrations lower than trace-level limit, after removal.

2. Nanotechnology and nanostructures classification

Nanotechnology is a multidisciplinary science focused on the design, processing, manipulation, and application of new materials at the nanoscale; it means between 1 and 100 nanometers (nm). It also comprises the modification of some properties of bulk materials. Nanostructures are nanometric materials with a defined morphology. They form a self-assembling of atoms, molecules, or macromolecules.

Nowadays, thanks to the application of nanostructures, nanotechnology can contribute to the solution or mitigation of part of the worldwide problems involving environmental pollution [13]. The main strategies focus on different categories: (1) sustainable design and synthesis of nanostructures; (2) new generation technology using functionalized nanostructures to remove contaminants from water, air, and soil; (3) sensor design for the estimation and quantification of pollutants; (4) study of toxicity and evaluation of environmental and health implications associated with the use of nanostructures for remediation; (5) emerging solutions [5, 14, 15].

Nanostructures are materials or structures with at least one dimension in the nanometer scale (1–100 nm) [16]. A zero-dimension (0D) material has a nanometer scale in each of the three directions (x, y, z), while a one-dimension (1D) material has a nanometer-scale only in two directions. A two-dimension (2D) structure contains a nanometer-scale only in one direction. Three-dimensional (3D) nanostructures are included in this classification even though their dimensions are higher than 100 nm, but their construction is a hierarchical architecture that grows in all directions using 0D, 1D, and 2D nanostructures. **Figure 2** presents a scheme
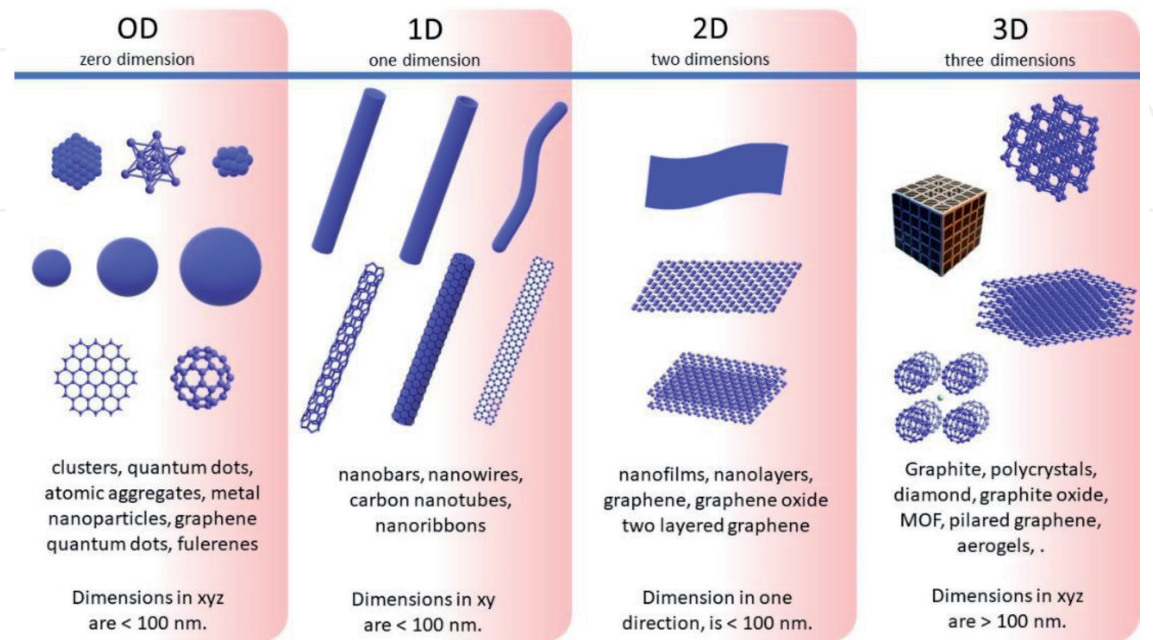

0D	1D	2D	3D
zero dimension	one dimension	two dimensions	three dimensions
clusters, quantum dots, atomic aggregates, metal nanoparticles, graphene quantum dots, fulerenes	nanobars, nanowires, carbon nanotubes, nanoribbons	nanofilms, nanolayers, graphene, graphene oxide two layered graphene	Graphite, polycrystals, diamond, graphite oxide, MOF, pilared graphene, aerogels, .
Dimensions in xyz are < 100 nm.	Dimensions in xy are < 100 nm.	Dimension in one direction, is < 100 nm.	Dimensions in xyz are > 100 nm.

Figure 2.
Schematic for the classification of low dimensional nanostructures: zero dimension (0D), one dimension (1D), two dimension (2D), and three dimension (3D). Examples for each dimension are mentioned in the text.

classification of some examples of nanostructures: 0D nanostructures are quantum dots, nanoparticles, fullerenes, clusters, metal nanoparticles, or graphene quantum dots, among others. One-dimensional structures are carbon nanotubes, single layer graphene nanoribbons, graphite nanoribbons, or nanobars. Two-dimensional nanostructures include nanofilms, graphene, graphene oxide, and two layered graphene. Three-dimensional nanomaterials include graphite, metallic-organic frameworks, aerogels, and composites.

3. Measurement methods using nanostructures

All the elements from the periodic table are suitable to form nanostructures in all dimensions, individually or combined, increasing in this way the variety of properties, behavior, and functionality. As a result, new opportunities are now available with nanotechnology to enhance the efficiency of existing methods for detection, quantification, and remediation of pollutants. However, environmental remediation is still a challenge and some important facts should be considered, such as selectivity, efficiency, reusability, eco-friendly, and low cost. It is important to notice that nanomaterials are non-biodegradable and so they tend to accumulate in organisms, leading to serious health problems when ingested by humans [17]. Thus, using nanotechnology either as a remediation strategy or measurement method needs to consider the recuperation and reutilization of nanomaterials as mandatory steps.

Some authors have conducted relevant investigations to know the levels of heavy metals in water. Florence Lagarde and Jaffrezic-Renault proposed complementary methods for the monitoring and treatment of metal-contaminated water [18], which Agostino et al. resumed in two main sections: fast and conventional [19]. The first consists of the development of in-situ, low cost, non-specific early warning systems to operate online. The second one is focused on accurate detection and quantification using conventional methods that are expensive, more time consuming, and require manual operation.

Detection and quantification of heavy metals are crucial tasks in the characterization of different water types: surface water, groundwater, tap water, and wastewater. Nowadays, the monitoring of toxic effects becomes mandatory since water resources are being scarce, and the development of monitoring tools is essential for an easy, fast, and accurate detection of heavy metals in a few steps. Sensing is an integral part of both fast and conventional measurement methods for the quantification of heavy metals proposed in nowadays research [20]. Nanotechnology used in sensing improves not only the efficiency but also the selectivity and reduces the time needed in each step of the methodology of quantification of heavy metals in water. Sensing using nanotechnology can be implemented in-situ for a faster detection of heavy metals in water with a low-cost technique, followed by the quantification with a sensitive and accurate analytical method on-lab such as atomic absorption spectroscopy, X-ray fluorescence, electrochemical techniques, and among others that are described below.

Some of the 0D nanostructures used for the detection and quantification of heavy metals in water are the metal nanoparticles. These nanoparticles can be made of gold (Au), silver (Ag), titanium oxide (TiO_2), iron oxide (Fe_3O_4), zinc sulfide (ZnS), or cadmium sulfide (CdS) due to the facility that these materials offer to modify their surface, and the easiness they offer to control their reproducibility and flexibility in an aqueous medium [21]. The heavy metals are detected by a spectroscopic, electrochemical, or optical technique. The methodologies adapted to these strategies using nanostructures have some advantages and disadvantages as can be expected [22]. The spectroscopic methods allow not only the detection but also

the quantification step, and they are usually very sensitive to multiple heavy metal ions. Some examples of spectroscopic techniques are ICP-MS (inductively coupled plasma mass spectrometry), AAS (atomic absorption spectroscopy), HR-SPS (high-resolution surface plasmon resonance spectroscopy), and SERS (surface-enhanced Raman spectroscopy). SERS is useful for sensing applications since the surface plasmon resonance of metal nanoparticles can be identified with a detection limit of 10 ppt in a pH buffered solution, and of 70 ppt in a real sample when compared with AAS, whose detection limit is around 0.2 ppb [22]. ICP-MS quantifies a wide variety of elements in one-single analysis step with high accuracy, sensitivity, and selectivity. Low detection limits for metal ions can be achieved by using ICP-MS, normally in the ppt range [23, 24]. Such techniques are typically used for quantification but not for sensing. The main disadvantage of the spectroscopic methodologies is the high cost of the analytical instrumentation, the time-consuming procedures, and the use of sophisticated equipment that requires trained personnel [22, 25]. On the other hand, electrochemical methods are low cost, low time-consuming, and easy to handle. They can be conducted under any of the following techniques: potentiometric, amperometric, voltammetric, impedimetric, or electrochemiluminescence. They have a high sensitivity and low detection limits (from 0.25 ng/L to 0.12 μg/L) [26–28]. The main advantage of the electrochemical methods is the possibility of sensing or monitoring of pollutants with in-line systems coupled with water streams. However, the design and miniaturization of the electrodes needed to build portable sensors are one of their major challenges [22, 28]. The use of optical methods for the detection of heavy metals is also an economical and fast option. Optical procedures usually utilized for this purpose are absorption, reflection, or luminescence spectrometry. The main limitations could be that some non-optical indicators interfere with some metal ions [22].

Table 1 summarizes some examples of detection and quantification of heavy metals using nanostructures, reported in recent literature, where the spectroscopic, electrochemical, and optical methodologies have been applied.

For a fast and in situ detection, some authors propose an innovative and cheap methodology based on an online operation aided by a smartphone. The strategy uses the wavelength shifting of the resonant plasmon. It means that nanoparticles suffer a color change, from red to purple, when cadmium (Cd^{2+}), mercury (Hg^{2+}), or copper (Cu^{2+}) ions are present on a solution [29–31]. The nanosensor uses a gold nanoparticle-based assay platform that records, processes signals within the range of 1 ng/mL–32 ng/mL of Hg^{2+}, and proposes a concentration of 0.28 ng/mL as the limit of detection [29]. The *in situ* detection of Cd^{2+} with the nanogold-based detection system controlled by the smartphone is fast and reliable as it displays a linear range for the Cd^{2+} concentration, between 2 and 20 μg/L with a detection limit of 1.12 μg/L [30]. This range is below the permissible limit of Cd^{2+} ion in water and smaller than those based on non-portable and other nano-based technologies [32]. The main advantage for these types of systems is the portability, as well as the immobilization of metal ions to gold nanoparticles that allows the tuning of sensitivity. For example, the aptamer is a particular recognition of Cd^{2+} [33], with a low recognition of Pb^{2+}, and acceptable detection even though the specimen contains other metal ions in high concentration [30].

The quenching of quantum dot (QD) was studied for cadmium (Cd^{2+}), mercury (Hg^{2+}), and lead (Pb^{2+}) to understand the colorimetric/visual sensors. The composite formed by Mn-doped ZnS QD and graphene oxide detects Pb^{2+} down to 0.4 ppb. Further, the interaction between the metal ion and the passivating ligands attached to the QD also contributes partway to the specific detection combined with the quenching of QD [34]. The green approach is also present on the fast detection, which is vital since the production of nanostructures requires to minimize the use

Ion	Nanostructure and sizes	D	Main methodology	Ref.
Cd^{2+} Hg^{2+} Cu^{2+}	Spherical gold nanoparticles ~15 nm	0D	Smartphone-based colorimetric reader system	Xiao et al., Gan eta al., and Cao et al. [29–31]
Hg^{2+} Pb^{2+} Cd^{2+}	Mn–doped ZnS quantum Dots ~5 nm	0D	Detection through the quenching of QD emission	Devaiah Chonamada et al. [34]
Hg^{2+}	Spherical silver nanoparticles (10–30) nm	0D	Green approach using aqueous extract of *Vigna mungo* beans for reduction	Choudhary et al. [35]
Ag^{+} Cu^{2+} Hg^{2+}	Core-shell nanoparticles. ZnS coated up conversion nanoparticles 60 nm in diameter and 20 nm in the shell	0D	Detection of residuals in water using ion metals	Chu et al. [36]
Pb^{2+} Cd^{2+} Cu^{2+} Zn^{2+}	Rhodium/ antimony co-doped TiO_2 nanorod and titanate nanotube ~20 nm	2D in 2D	Quantification and removal of metals and degradation of organic pollutants. The adsorbed metal enhanced the photocatalytic degradation of organic pollutants	Dhandole et al. [37]
Pb^{2+} Cd^{2+}	Functionalized Fe3O4/ NaP zeolite nanocomposite ~30 nm	0D in 3D	Quantification of metals and removal of bacteria	Zendehdel et al. [38]
Pb^{2+} Cd^{2+}	SnS-decorated Bi_2O_3 nanosheets (3–4) nm	2D in 3D	Electrochemical detection of Cd(II) and Pb(II) in real samples from lake and tap water	Jin et al. [39]

Table 1.
New methodologies using nanostructures for sensing and quantification of heavy metals.

of solvent, energy, time, and the release of odd substances to the environment. An extract of *Vigna mungo* beans was used as a reducing agent of nanoparticles to minimize the use of traditional chemical compounds and solvents; the detection limit for Hg^{2+} ions was near 0.13 μM [35].

In previous investigations, two processes were combined to enhance the implementation of nanostructures on heavy metal detection [36–38]. The main advantage of this approach is that after the detection and quantification steps, the removed metal agglomerates in a nanometric size scale that is useful for further remediation. After quantification and removal of any heavy metal, it is possible to convert core-shell nanoparticles, such Ag^{+}, Cu^{2+}, and Hg^{2+} coated on ZnS and use them for the detection of another kind of contaminants. The ZnS nanoparticle can remove up to 3.98 μmol of Ag^{+} [36]. The metal adsorbed on TiO_2 nanostructures enhanced the photocatalytic degradation of organic pollutants. The degraded pollutants were orange (II) dye and bisphenol-A. Metals increased photodegradation

after 5 hours in a batch experiment (70% of dye and 80% of Bisphenol A) due to the photodeposition of metal ions on the TiO_2 nanoparticle surface [37]. Functionalized Fe_3O_4/NaP zeolite nanocomposite removed metal, more than 95%, after removed bacteria (*Bacillus subtilis*) [38]. A different methodology was employed for *in situ* measurements by electrochemical detection using SnS-decorated Bi_2O_3 nanosheets. The composite exhibited high sensitivity and efficient detection for the removal of heavy metals with high toxicity, which limits of detection was 1.50 nM for Cd^{2+} and 1.40 nM for Pb^{2+} [39].

Quantification of metallic ions is essential during the different steps of the water cycle that goes through various biological processes. The main quantification techniques are atomic absorption spectrometry, inductively coupled plasma mass spectrometry, anodic stripping voltammetry, X-ray fluorescence spectrometry, and microprobes. These techniques require sample pretreatment procedures, analyte pre-concentration steps, and expensive instrumentation [40]. Due to the presence of dangerous heavy metal ions in water, an instantaneous measurement and quantification are desirable. The use of nanotechnology, along with the investigation of novel approaches, will allow the quantification of heavy metals in an inexpensive, rapid, and simple way. For example, Stenberg, Massad-Ivanirb, and Ester Segal presented a nanostructured porous silicon (Si) biosensor for the detection and quantification of copper ion in real water samples. The monitoring is based on the Laccase relative activity. Lacasse is an enzyme, a multi-copper oxidase, immobilized within the oxidized nanostructured porous silicon. The Laccase-based biosensor exhibited a lower detection limit of 1.30 μM, smaller than other values [41].

Quantification of the metal ion content, as well as the chemical speciation of the different chemical forms of a specific metal in water, becomes essential to estimate its toxicity and persistence in living organisms. The environmental health effects can be understood by the study of natural chemistry, quantification, and speciation of chemical species of metal ions. The chemical form of any metal depends strongly on the chemical conditions in which it is exposed, and the toxicity not only relays on its ionic form but also on the chemical species that formed. For example, the methylmercury ion (CH_3Hg^+) is the toxic specie of the inorganic mercury II (Hg^{2+}). Speciation analysis requires complex, expensive, and time-consuming pre-separation analyses, which are incompatible with *in situ* measurements. Guerrini et al. [42] presented a Surface-Enhanced Raman Scattering (SERS) methodology for the chemical speciation of Hg^{2+} and CH_3Hg^+. In this work, the SERS consisted of an active platform of closely spaced spherical gold nanoparticles anchored on polystyrene microparticles. The ion receptor, mercaptopyridine (MPY), forms strong bonds between the gold atoms and the mercaptan group, and coordinates a nitrogen group with both species Hg^{2+} and CH_3Hg^+. The coordination with nitrogen is determined by the changes in vibrational SERS of MPY, which could give insights on the qualitative and quantitative modifications correlated with Hg^{2+} or CH_3Hg^+.

4. Nanoremediation

Tague defines remediation as "all measures taken for treatment of damaged wells for restoring an optimal performance" [4]. Nowadays, the environment requires those actions for the protection of human health and all living systems on Earth. Environmental remediation consists of the eradication, removal, or transformation of contaminants from natural resources [43]. Although remediation is a complex task, nanoremediation has emerged as an optimal alternative for the removal of pollutants from different waters (groundwater, surface water, and residual water), soil, air, and sediments [43].

Water is by far, one of the most contaminated resources in the planet; that is why the remediation and removal of contaminants are an urgent need together with easy and fast monitoring tools. The available treatments used for removal of heavy metals from water are classified as follows: chemical precipitation, membrane filtration, ion exchange, reverse osmosis, and adsorption [44]. The adsorption using nanomaterials has been of great interest since several nanostructured adsorbents have demonstrated a high performance [44–46]. Adsorption on nanostructured materials is complicated, but some authors have proposed possible mechanisms that depend mainly on the nature of the surface area. The fundamental mechanisms are based on physical adsorption (physisorption), chemical adsorption (chemisorption), electrostatic attraction, and sorption-precipitation [9, 47, 48]. **Figure 3** shows a schematic representation for the adsorption mechanisms of heavy metal on porous nanomaterials. Lu et al. reported that biochar, a 3D network, is a material rich in cations and surface interaction sites for lead adsorption. Electrostatic cation exchange or metal exchange reactions mechanisms may occur when calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), and sodium (Na^+) ions released from biochar in the adsorption of Pb ions, but the electrostatic interaction and surface complexation with pi-cationic and functional groups interaction, may also happen in the adsorption of Pb ions [48].

4.1 Carbonaceous nanostructures

The removal of heavy metals with carbon nanotubes (CNT) varies because the adsorption mechanisms depend on the affinity order of metals ions and the surface functionalization of CNT. Some examples of adsorption have been summarized by Ihsanullah et al. [47]. The mechanism is based on the release of protons (H^+) from the surface when oxidation of CNT was achieved. After that, the attachment of divalent metals occurs on the surface. This process depends on the concentration of the metal ion. A higher number of ions increase the pH value due to the increment of H^+ in the solution. It was found that the adsorption of divalent ions, such as Cd^{2+} and Zn^{2+}, is dominated by a combination of physisorption (Van deer Waals forces) and sorption-precipitation when the pH is increasing in the solution. It means that the acid treatment and surface modification have a significant effect on the adsorption capacity of CNT. Some examples of carbon materials used for metal removal under different metal concentrations in the ppm range are listed in **Table 2** [49–52]. Those experiments were performed without temperature or pH
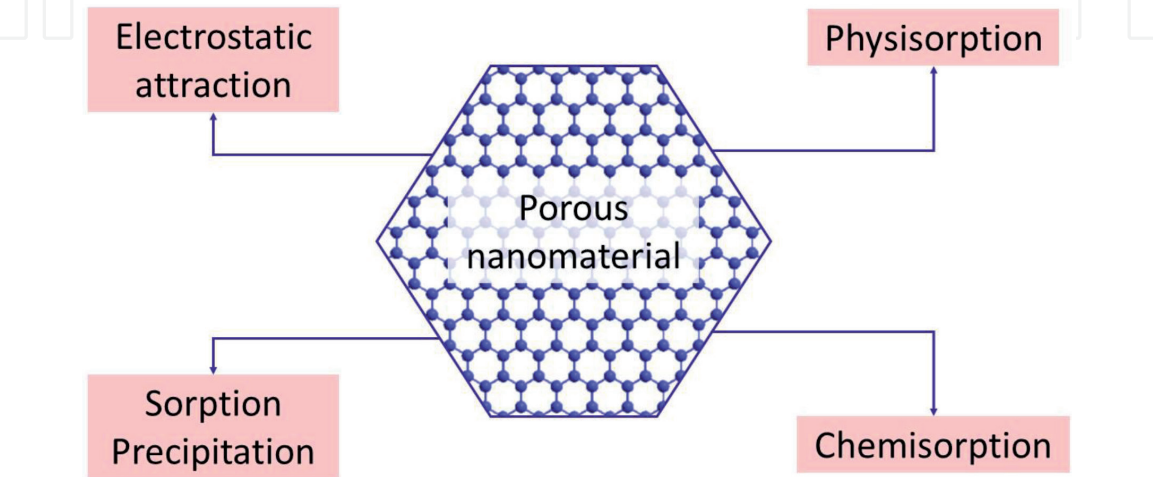

Figure 3.
Fundamental mechanisms for the adsorption of heavy metal ions on porous nanostructured materials.

Material	Copper	Lead	Other metals	Reference
Activated carbon	—	30 ppm – 83% 50 ppm – 74%	**Chrome** 30 ppm – 50.6% 50 ppm – 48.2% **Nickel** 30 ppm – 90% 50 ppm – 87.8% **Cadmium** 30 ppm – 86% 50 ppm – 84%	Karnib et al. [49]
Activated carbon (coconut waste)	126 ppm 73% pH 5	709 ppm – 100% pH 4	**Nickel** 996 ppm – 92% pH 4	Kadirvelu et al. [50]
Graphite oxide	—	30 ppm – 85% 50 ppm – 84%	**Chrome** 30 ppm – 63% **Nickel** 30 ppm – 89.9%	Sheet et al. [51]
Carbon nanotubes	100 ppm – 41%	40 ppm – 83%	**Chrome** 0.5 ppm – 66% **Nickel** 15 ppm –75.4% **Cadmium** 6 ppm - 87%	Mubarak et al. [52]
N-doped carbon nanotubes growth on red volcanic rock	10 ppm – 82% 20 ppm – 84% 40 ppm – 51%	10 ppm – 91% 20 ppm – 90% 40 ppm – 93%	—	Gonzalez Hodges [53]
N-doped carbon nanotubes growth on black volcanic rock	10 ppm – 90% 20 ppm – 95% 40 ppm - 71%	10 ppm – 91% 20 ppm – 81% 40 ppm – 98%	—	Gonzalez Hodges [53]
N-doped carbon nanotubes growth on yellow volcanic rock	10 ppm – 92% 20 ppm – 83% 40 ppm – 63%	10 ppm – 100% 20 ppm – 89% 40 ppm - 99%	—	Gonzalez Hodges [53]
Red volcanic rock	5 ppm – 15%	5 ppm – 14%	—	Mabel et al. [54]

Table 2.
Heavy metal removal percentages using different carbon-based materials.

variation, except for the analysis that uses activated carbon from coconut waste, where the pH was adjusted.

Table 2 presents higher percentages of copper and lead removal when using nitrogen-doped carbon nanotubes grown on volcanic rock [53] than other carbon materials or red volcanic rock [54] without any treatment. The increased efficiency of these carbon nanotubes grown on volcanic rock can be correlated with the presence of nitrogen on their graphitic lattice. Doping carbon nanostructures with heteroatoms, such as nitrogen, increases the adsorption capacity without any acid treatment [4]. Nitrogen has a similar atom diameter but an extra electron as carbon, favoring the atom replacement, and the electron-donating properties [55]. N-doping occurs in different forms, such as pyridine, pyrrole-like, and quaternary-N salts, but may include nitrogen oxide groups and amines [56]. In particular, quaternary nitrogen atoms are considered to increase the adsorption capacity by electrostatic interaction, as the surface carbon nanostructures doped in this way are more negatively charged than the undoped ones [55, 57]. Besides, nitrogenated carbon nanostructures act as reducing agents for toxic Cr^{6+} converting it into harmless Cr^{3+} [55].

4.2 Silica-based nanostructures

The high surface area found on porous materials, such as the silica-based ones, is attributed to the 3D network that displays a hierarchical organization that can be found at different scales (nano, micro, and milli). The nanostructured organization is mainly attributed to the form and size of the pore, which allows the accommodation of other nanostructures, as well as the functionalization of the surface. The methodology to produce nanostructured porous silica is based on the liquid-crystal template mechanism. This allows getting pores around 2–10 nm in size [58]. A surfactant at high concentration is set at a specific pH and temperature values to form a liquid-crystalline phase. Then, the crystalline form may be organized by spherical or rod-shaped micelles arranged on a periodic 3D structure, which serves as a template to be filled with tetraethoxysilane (TEOS) or tetramethylorthosilica (TMOS). Finally, the surfactant is removed to form a mesoporous material [59].

Surface functionalization is a useful tool for the realization of a well-defined set of functions which improves the adsorption properties of silica. It can be carried out by chemical bonds or physical interactions. Silica surface functionalization is of interest due to the multiple options that it offers for heavy metals removal. For example, the thiol-functionalization of mesoporous silica has been proved to exhibit a high affinity for thiophilic heavy-metal ions like Cu^{2+}, Zn^{2+}, Cr^{3+}, and Ni^{2+} but focused on highly toxic metals such Hg^{2+}. At the same time, the amino functionalization increases the efficiency of the adsorption of Hg^{2+} [59, 60]. For some specific types of silica materials such as SBA-15 (Santa Barbara Amorphous-15), the imidazole functionalization improves the selective affinity adsorption of Pd^{2+} and Pt^{2+}, despite the high concentration of Ni^{2+}, Cu^{2+}, and Cd^{2+} in the mixture [61]. Specific morphologies, such as PMO-like (periodic mesoporous organosilica) or spherical mesostructured, increased the surface area and the particular site of functionalization, consequently, affinity, and selectivity are improved [62, 63].

4.3 Zeolites

Zeolites are known as microporous materials with a crystalline structure composed by tetrahedral building blocks of alumina (AlO_4) and silica (SiO_4) that give rise to a three-dimensional network linked by oxygen atoms [64]. Zeolites are an effective, economical, and eco-friendly option to remove heavy metals and organic contaminants from wastewater [64–66]. There are more than 40 naturally occurring zeolites each with different physicochemical properties. Among their most interesting characteristics are their high chemical stability, molecular sieve, adsorption, and ion exchange capacity [67].

The Si/Al ratio in the structure of a zeolite determines its adsorption and ion exchange capacities, which are directly related to the amount of aluminum contained in the natural zeolite [66], so the isomorphic replacement of Si^{4+} by Al^{3+} (aluminum-rich zeolites) will have a more negative charge on the framework, providing a higher affinity for polar molecules. The negative charge is balanced with interchangeable cations (generally sodium, potassium, or calcium), therefore these cations are used for cation exchange processes in solutions containing lead, chromium, or mercury, among others ions [68]. The adsorption capacity of zeolites also depends on the charge density and the diameter of the hydrated ion, which is why zeolites have a great potential to remove heavy metal ions from wastewater [64].

Natural zeolites such as clinoptilolite, mordenite, and chabazite were investigated for the removal of heavy metals [64, 65]. The natural zeolite clinoptilolite has attracted attention because of its abundance. The selectivity of the sodium form of clinoptilolite, extracted from natural deposits, was found to be

$Pb^{2+} > Cd^{2+} > Cs^+ > Cu^{2+} > Co^{2+} > Cr^{3+} > Zn^{2+} > Ni^{2+} > Hg^{2+}$. This behavior confirmed that natural zeolites have a great ability to selectively remove metallic ions from wastewater. In particular, sodium loaded zeolites resulted the most effective because sodium acts as an exchangeable ion with heavy metals [69]. Further, clinoptilolite exhibited a higher capacity than carbonaceous materials such as carbon nanotubes (CNTs) for lead removal (up to 15.5 times higher) [70, 71].

Nano zeolite [72] and modified zeolites [73–75] demonstrated a higher removal capacity of lead than that reported by natural zeolites, even much higher than functionalized reduced graphene oxide (RGO) [71]. The silica nano-zeolite X [72] presented an adsorption capacity of 909.09 mg/g of Pb^{2+} being 5.5 times higher compared to that reported for natural clinoptilolite (166 mg/g) [69]. The main characteristic of nano zeolites and modified zeolites is a larger surface area and pore size, which make them more efficient and facilitate the adsorption of heavy metals and organic molecules, compared to natural zeolites [76]. The efficiency in the removal of heavy metals and other cations will strongly depend on the high surface area of the zeolites, and in their efficiency in removing the metal ions present in wastewater. The surface area in porous materials is determined by the specific surface area (BET) by standard multipoint techniques of nitrogen adsorption. There are several studies where the largest surface area is for nano zeolites (692 m^2/g) [76], followed by modified silica natural zeolites (702 m^2/g) [72]. A smaller surface area is found for the sodium form of clinoptilolite (70.4 m^2/g) [77], and the smallest area is for the simple natural zeolite clinoptilolite (15.36702 m^2/g) [78].

4.4 Iron oxides

Iron oxide nanostructures are gaining attention for metal removal from water due to their high surface area, excellent adsorption capacities, innocuousness with the environment, and easiness of separation as one can make good use of their magnetic properties. Despite their advantageous characteristics, their use in real scenarios has not been proved. It is essential to explore their removal mechanisms, not only for iron oxides but also for zerovalent iron nanomaterials.

Zerovalent iron nanoparticles (nZVI) are considered a strong reducing agent that is bringing degradation to less harmful substances from a wide range of organic and inorganic pollutants. Sorption of co-precipitation of heavy metals on the surface forms an iron oxide or hydroxide shell when nZVI is exposed to air [79]. The most cited example is the transformation of Cr^{6+}, which precipitates on nZVI with corrosion products. However, this property usually depends on the surface functionalization of the nZVI. Functionalization is important since iron nanoparticles form aggregates very easily and suffer oxidation under acidic and oxygenated environments. The best approach is to coat the nanoparticle surface with Fe_3O_4 or some polymer to reduce the contact with the environmental oxygen, but maintaining the reactivity [79].

Previous studies on the adsorption of Cr^{6+} on the surface of Fe_3O_4 show the formation of a different crystalline structure by chemical adsorption. For chromite ($FeCr_2O_4$), the Cr^{6+} is reduced to Cr^{3+}, followed by the precipitation of Cr^{3+} onto the F_3O_4 nanoparticles. Low desorption is indicative of adsorption because desorption is due to physical adsorption, mainly by electrostatic interactions. This adsorption process predominates on γ-Fe_2O_3, as previously demonstrated by X Ray Photoelectron Spectroscopy (XPS). Another evidence of the physical adsorption is the non-modification of the crystallographic structure, an indication that the removal process was not due to a chemical interaction [80, 81]. The positively charged surface on the iron oxide nanoparticles determines the attraction for negatively charged pollutants; the positive charge of iron oxides depends on the
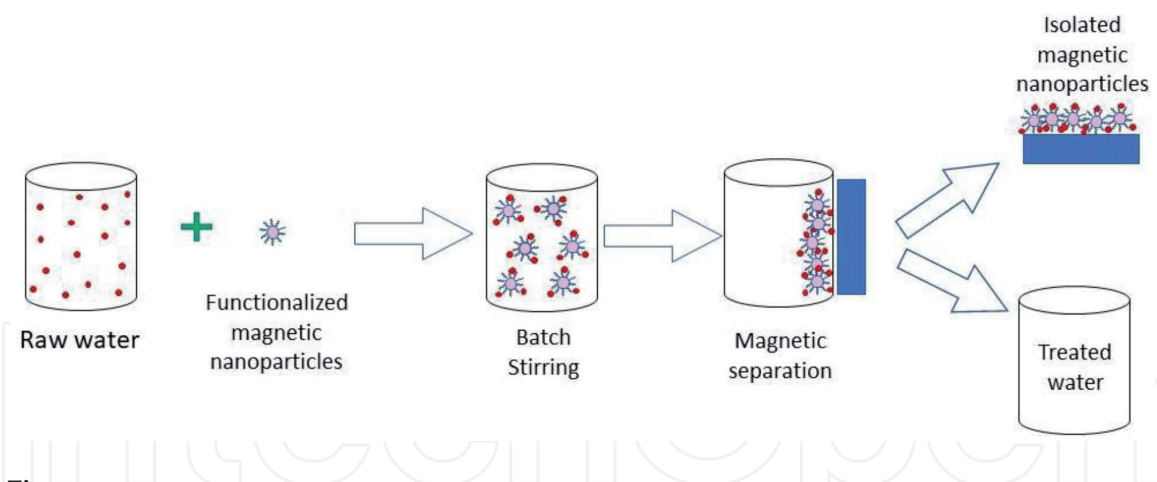
Figure 4.
The different steps on removal of contaminants from water using magnetic nanoparticles.

polarization of oxygen atoms on the surface, which can be modified by pH. The successful removal of pollutants such as Cr^{6+} and As^{5+} is highly pH-dependent [82].

4.4.1 Recovery and reuse of nanostructures using iron oxides

Some of the problems faced when iron nanostructures are used in water reme-diation are related to their capture, recovery, and reuse. Sometimes complicated steps are required. Many authors have proposed to take advantage of the magnetic nanoparticles as an alternative to capture contaminants and nanostructures that could remain in the environment. Goon et al. [45] studied the capture and quantifi-cation of cupric ions at trace level using a composite formed by polyethyleneimine (PEI-) coated with Fe_3O_4 nanoparticles. They captured trace levels (~2 ppb) of Cu^{2+}. The PEI is amine-rich, so it captures the Cu ions easily, while the magnetite nanoparticles allow the magnetic separation of the material from water. Hu and coworkers [44] used graphene oxide coped Fe_3O_4 nanoparticles for highly efficient removal of Pb^{+2}.

The particularity of the composite with graphene oxide is that adsorption capac-ity improved at pH 7, the natural pH value found in a faucet. They also observed that the system graphene oxide/Fe_3O_4 could be recyclable because it maintains an 80% adsorption capacity after 10 adsorption-desorption cycles. This process can be generalized to the removal, or capture, of any contaminant by the interaction with a specific functionalized nanoparticle followed by its recovery from water (see the scheme in **Figure 4**). Tang and Lo [79] consider that magnetic separation could be a low-cost and a convenient method over the use of a membrane-separation filtration method because the separation of tiny magnetic nanoparticles with the adsorbed heavy metal is easier. The magnetic separation usually occurs with the help of a magnetic field or with a hand-held magnet [79].

5. Remediation based on nanobiotechnology

Natural resources, such as biological systems as microorganisms and plants can also be mixed with nanostructured nanoparticles, usually by cross-linking bond-ing using a bifunctional reagent; nanoparticles should be inert and biocompatible materials. Even though this methodology is fast, simple, and exhibits an electron transfer, the main disadvantage is the formation of covalent bonds between the functional groups at the outer membranes of the biological living system [18]. Biological systems can be used to directly originate nanomaterials for heavy metal

remediation, but they can also be the active coating on nanostructured materials for similar purposes. Even more, the utilization of microbes for intracellular/extracellular synthesis of nanoparticles with different chemical composition, size/shapes, and controlled monodispersity can be a novel, economically viable, and eco-friendly strategy that can reduce toxic chemicals in the conventional protocol [83]. Studies were conducted on some bacteria to produce an iron sulfide compound, which acts as an adsorbent for several toxic metal ions [84]. Nanoparticles obtained from the plant *Noaea mucronata* were used for the accumulation of heavy metals, such as Pb, Cu, Cd, Zn, Fe, and Ni in groundwater, streams, and rivers [85]. The study conducted on plant species such as *Centaurea virgata*, *Scariola orientalis*, *Noaea mucronata*, *Chenopodium album*, *Cydonia oblonga*, *Reseda lutea*, and *Salix excelsa* revealed that these plants are very good heavy metal accumulators. Specifically, *Noaea mucronata* is a suitable accumulator for Pb to a level higher than 1000 ppm [86].

Biological substrates like bacteria, fungi, algae, yeast, and plant derivatives can be immobilized on nanomaterials or nanoparticles and play an essential role in the retention of metal ions. They offer several advantages, namely biodegradability, natural abundance, low cost, simple production, high surface to volume ratio, and various active sites such as carboxyl, hydroxy, amino, sulfate, or phosphate groups [8]. Besides, immobilized biological substrates have been employed as living and non-living cells. The use of dead bacteria offers the possibility to develop continuous flow systems on different solid supports [87]. The main advantage is that dead microorganisms avoid the risk of contamination of water with bacteria. Some examples were summarized by Escudero et al. [87] in an extensive literature review of biological substrates, which includes composites with biological materials and nanostructures as a green alternative in trace elemental preconcentration and speciation analysis. Such nano-based technology has been proved successful on the laboratory scale, but only a few have been used for small-scale testing or commercialization [88]. Specific studies are summarized in the following lines to exemplify the advantages of the biological substrate-based methods in the removal of heavy metals from water. According to the information reported by Escudero and collaborators, the most employed biological substrates are plant-derivatives, bacteria, and fungi, and they are mainly used for water treatments [87].

Heat inactivated *Fusarium verticillioides* filamentous fungi has been immobilized on nano-silica particles for biosorption of calcium (Ca^{2+}) and magnesium (Mg^{2+}) cations, in helping the preconcentration technique of solid-phase extraction to reduce the hardness of aqueous solutions. Maximum capacities were found to be 1000.0 μmol/g for magnesium and 1333.3 μmol/g for calcium [89]. Lead (Pb) has also been removed using a chromatographic column filled with biomass of this same fungal species immobilized on TiO_2 nanoparticles and using hydrochloric acid (HCl) as eluent [90]. Dead coliform bacteria have been immobilized on nanoparticles of titanium oxide (TiO_2) for Pb preconcentration which was then analyzed using a flow injection analysis system coupled to a flame atomic absorption spectrometer [91]. The biosorption of aluminum (Al^{3+}) and cadmium (Cd^{2+}) ions over an exopolysaccharide obtained from the bacterium *Lactobacillus rhamnosus* was possible due to the presence of hidroxyl (—OH) and carboxyl (—COOH) groups that facilitated a complex formation with the target analytes [92]. The well recognized bacteria *Escherichia coli* was immobilized on multiwalled carbon nanotubes to help in the determination of trace elements such as Cd, Co, Cu, and Ni by flame atomic absorption spectrometry [93]; while the metallothionein of the cyanobacterium genera Synechococcus decorated graphene oxide nanosheets for the selective adsorption of Cd from different waters [94]. Different mechanisms are involved in the extraction of metal ions by biological substrates. They include ion exchange, microprecipitation, complexation,

and oxide-reduction processes whose adequate election depends basically of the target contaminant and the type of sample to be treated.

6. Perspectives

There is still a need to develop smarter nanomaterials for remediation purposes on different environments, particularly at trace levels. Significant facts can be listed as follows:

- Laboratory experiences on the removal of heavy metals based on the use of nanomaterials must be extended toward real environments potentializing their advantages, but also having in mind their potential risks to human health and to the ecosystems, areas which are poorly understood and might lead to unintended consequences.

- The mobility, bioavailability, toxicity, and persistence of a wide variety of manufactured nanoparticles that are already in use, need to be studied [95]. This will provide qualitative and quantitative information for a better understanding of their potential risks, beyond their use in the heavy metal removal. For this issue, full-scale ecosystem-wide studies can be carried out by machine learning programs [96, 97].

- More studies focused on profitable strategies applied to the recovery and reuse of nanostructures need to be achieved. They will also allow the proposal of safe handling and disposal guidelines for the already used nanoparticles not only in environmental remediation protocols but in any other area that is already releasing them into the environment.

- Accessible and low-cost pollution sensors based on an electrochemical or an optical response that can be easily implemented in an electronic device such as a smartphone, are urgently needed. These technologies are much less expensive that the traditional spectroscopic techniques and can transform every device into a mobile sensor, with probably thousands displayed in huge territorial areas.

- Strategies for the maintenance or the improvement of water quality become mandatory in times when water access is becoming more and more difficult. In this context, the presence of different nanomaterials as an efficient, low-cost, and environmentally friendly alternative for the removal of heavy metals from waters to keep healthily environments [98] is a research and educational area that is just emerging.

7. Conclusions

The increasing pressure that the exacerbated demand on primary goods and commodities is placing to our environment by the development of larger communities will lead us to catastrophic and irreversible damages if a change of actions is not taken. Toxic and dangerous pollutants that are discharged in increasing quantities mean negative impacts to our natural resources, among which water is one of the most vulnerable as it is an absolutely necessary requisite for any form of life on

Earth. Palliative solutions have been proposed in different scenarios with variable degrees of success. In this sense, we have presented a summary of some of the alternatives that have been explored to help in the remediation of water reservoirs, based on the application of a variety of nanomaterials coupled with traditional analytical techniques, and on the other hand supported with some innovations in terms of the design, reuse or efficiency.

One of the multiple promising applications of nanotechnology is remediation. The current work mentioned some examples of applied nanotechnology such as testing before and after a remediation strategy is applied. The presented low dimensional (0D, 1D, 2D, and 3D) nanomaterials were coupled with traditional analytical techniques, and on the other hand, supported with some innovations in terms of the design, reuse, or efficiency. Most of the examples showed that concentration values lower than trace levels can be reached, which is an important fact concerning highly toxic metals.

The combination of nanotechnology and remediation opens an avenue of multiple options for environmental improvement strategies. It is an efficient alternative for the sensing, quantification, and removal of contaminants from water, specifically the cleaning of heavy metals, ideally to quantities lower than trace levels, as was exemplified in this chapter. The main advantages of the nanomaterials used for this purpose reside in their high sensitivity and selectivity that can be achieved at a reduced cost and with a lower time-consumption than other non-processed materials (for example volcanic rock shown in **Table 2**). Also, the nanoscale size means an impressive increment of the surface area of nanomaterials that can be translated into a higher reactivity. The reactivity allows the tuning of selectivity or combined selectivity; it means that any molecule with a specific affinity to any metal can be anchored to the nanostructure surface. Besides, nanostructured materials could be adapted for subsequent remediations and magnetic removal, reducing secondary contamination.

The combination of living systems, nanotechnology, and remediations extends the possibilities. Some microorganisms (dead or dead) are natural accumulators at trace levels and combined with nanostructures make a synergistic effect with improved sorption capacity; such combination allows the production of sustainable materials. Toxicity also concerns with this field, due to one of the main concerns about the extensive use of nanomaterials resides on the fact that the details on the nanostructure interaction with the environment and with different living organisms are still unknown. It means that systematic and extensive studies are required to aid to fill the current voids of data or information. Then, the toxicity is still a limitation on the use of nanomaterials in real samples. Other limitations such as the industrial manufacture tackle multiple difficulties due to do not readily exist regulation neither guidance on information requirements nor safety assessment. Apart from regulation, the right on intellectual property delays the industrial application.

It is true that one of the main concerns about the extensive use of nanomaterials resides on the fact that the details on the nanostructure interaction with the environment and with different living organisms are still unknown. It means that systematic and extensive studies are required to aid to fill the current voids of data or information. Another important issue is the recuperation of the nanomaterials once used. In some cases, the magnetic removal represents a practical option for recovery and reuse, but additional innovative strategies are needed. Overall, the application of nanomaterials to the removal of heavy metals from water is still a vast research opportunity area to be covered by current and future generations of scientists.

Conflict of interest

The authors declare no conflict of interest.

Author details

María Luisa García-Betancourt[1*], Sandra I. Ramírez Jiménez[1],
Apsahara González-Hodges[1], Zandra E. Nuñez Salazar[1],
Ismailia Leilani Escalante-García[2] and Jeannete Ramírez Aparicio[3]

1 Center of Chemical Research, IICBA, Autonomous University of the State of Morelos, Cuernavaca, Mexico

2 Department of Chemical Sciences, Autonomous University of Zacatecas, Zacatecas, Mexico

3 CONACYT - National Institute of Electricity and Clean Energies, Cuernavaca, Mexico

*Address all correspondence to: mluisa.garcia@uaem.mx

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References

[1] Bradl H, Kim C, Kramar U, StÜben D. In: Heavy Metals in the Environment: Origin, Interaction and Remediation. UK: Elsevier; 2005. p. 28-164. DOI: 10.1016/s1573-4285(05)80021-3

[2] Tchounwou PB, Yedjou CG, Patlolla AK, et al. Heavy metal toxicity and the environment. EXS. 2012;**101**:133-164. DOI: 10.1007/978-3-7643-8340-4_6

[3] Elliott M, Burdon D, Hemingway KL, et al. Estuarine, coastal and marine ecosystem restoration: Confusing management and science - a revision of concepts. Estuarine, Coastal and Shelf Science. 2007;**74**:349-366. DOI: 10.1016/j.ecss.2007.05.034

[4] Civan F. Formation damage abatement—Guidelines, methodology, preventive maintenance, and remediation treatments. In: Reservoir Formation Damage. Amsterdam: Elsevier; 2016. DOI: 10.1016/b978-0-12-801898-9.00023-0

[5] Tratnyek PG, Johnson RL. Nanotechnologies for environmental cleanup. Nano Today. 2006;**1**:44-48. DOI: 10.1016/S1748-0132(06)70048-2

[6] Smichowski P, Londonio A. A retrospective and prospective of the use of bio- and nanomaterials for preconcentration, speciation, and determination of trace elements: A review spanning 25 years of research. Analytical and Bioanalytical Chemistry. 2020:1-4. DOI: 10.1007/s00216-020-02536-5

[7] Khin MM, Nair AS, Babu VJ, et al. A review on nanomaterials for environmental remediation. Energy and Environmental Science. 2012;**5**:8075-8109. DOI: 10.1039/c2ee21818f

[8] Zhao G, Li J, Ren X, et al. Few-layered graphene oxide nanosheets as superior sorbents for heavy metal ion pollution management. Environmental Science and Technology. 2011;**45**:10454-10462. DOI: 10.1021/es203439v

[9] Lee LZ, Zaini MAA, Tang SH. Porous nanomaterials for heavy metal removal. In: Handbook of Ecomaterials. Switzerland: Springer; Vol. 1. 2019. pp. 469-494. DOI: 10.1007/978-3-319-68255-6_27

[10] Qu X, Alvarez PJJ, Li Q. Applications of nanotechnology in water and wastewater treatment. Water Research. 2013;**47**:3931-3946. DOI: 10.1016/j.watres.2012.09.058

[11] Mohan D, Pittman CU. Arsenic removal from water/wastewater using adsorbents – A critical review. Journal of Hazardous Materials. 2007;**142**:1-53. DOI: 10.1016/j.jhazmat.2007.01.006

[12] Hassan AM, Wan Ibrahim WA, Bakar MB, et al. New effective 3-aminopropyltrimethoxysilane functionalized magnetic sporopollenin-based silica coated graphene oxide adsorbent for removal of Pb(II) from aqueous environment. Journal of Environmental Management. 2020;**253**:109658. Epub ahead of print. DOI: 10.1016/j.jenvman.2019.109658

[13] Theron J, Walker JA, Cloete TE. Nanotechnology and water treatment: Applications and emerging opportunities. Critical Reviews in Microbiology. 2008;**34**:43-69. DOI: 10.1080/10408410701710442

[14] Patil SS, Shedbalkar UU, Truskewycz A, et al. Nanoparticles for environmental clean-up: A review of potential risks and emerging solutions. Environmental Technology and Innovation. 2015;**5**:10-21. DOI: 10.1016/j.eti.2015.11.001

[15] Diallo MS, Fromer NA, Jhon MS. Nanotechnology for

sustainable development: Retrospective and outlook. In: Nanotechnology for Sustainable Development. 1st ed. Vol. 2050. 2014. pp. 1-16. DOI: 10.1007/978-3-319-05041-6_1

[16] Azmi MA, Shad KF. Role of nanostructure molecules in enhancing the bioavailability of oral drugs. In: Nanostructures for Novel Therapy: Synthesis, Characterization and Applications. Amsterdam: Elsevier; 2017. Epub ahead of print. DOI: 10.1016/B978-0-323-46142-9.00014-1

[17] Lu F, Astruc D. Nanomaterials for removal of toxic elements from water. Coordination Chemistry Reviews. 2018;**356**:147-164. DOI: 10.1016/j.ccr.2017.11.003

[18] Lagarde F, Jaffrezic-Renault N. Cell-based electrochemical biosensors for water quality assessment. Analytical and Bioanalytical Chemistry. 2011;**4**:947. DOI: 10.1007/s00216-011-4816-7

[19] Agostino V, Massaglia G, Gerosa M, et al. Environmental electroactive consortia as reusable biosensing element for freshwater toxicity monitoring. New Biotechnology. 2020;**55**:36-45. DOI: 10.1016/j.nbt.2019.09.005

[20] Ahmad L, Arshid M, Aaliya B, et al. Detection and removal of heavy metal ions: A review. Environmental Chemistry Letters. 2019;**17**:1495-1521. DOI: 10.1007/s10311-019-00891-z

[21] Kumar A, Gupta K. RNA-mediated fluorescent colloidal CdSe nanostructures in aqueous medium-analysis of Cd2+ induced folding of RNA associated with morphological transformation (0D to 1D), change in photophysics and selective Hg2+ sensing. Journal of Materials Chemistry A. 2017;**5**:6146-6163. DOI: 10.1039/c6ta10795h

[22] Dalmieda J, Kruse P. Metal cation detection in drinking water. Sensors. 2019:5134. Epub ahead of print;**19**. DOI: 10.3390/s19235134

[23] Zeiner M, Rezić I, Steffan I. Analytical methods for the determination of heavy metals in the textile industry. Journal of Chemists and Chemical Engineers. 2007;**56**:587-595

[24] Helaluddin ABM, Khalid RS, Alaama M, et al. Main analytical techniques used for elemental analysis in various matrices. Tropical Journal of Pharmaceutical Research. 2016;**15**:427-434. DOI: 10.4314/tjpr.v15i2.29

[25] Scherzer RD, Gasparov LV, Stagon SP. Enhanced morphological stability of silver nanoparticles supported on rough substrates at high temperatures. Micro & Nano Letters. 2018;**13**:498-501. DOI: 10.1049/mnl.2017.0526

[26] Aragay G, Merkoçi A. Nanomaterials application in electrochemical detection of heavy metals. Electrochimica Acta. 2012;**84**:49-61. DOI: 10.1016/j.electacta.2012.04.044

[27] Bansod BK, Kumar T, Thakur R, et al. A review on various electrochemical techniques for heavy metal ions detection with different sensing platforms. Biosensors and Bioelectronics. 2017;**94**:443-455. DOI: 10.1016/j.bios.2017.03.031

[28] Hernandez-Vargas G, Sosa-Hernández JE, Saldarriaga-Hernandez S, et al. Electrochemical biosensors: A solution to pollution detection with reference to environmental contaminants. Biosensors. 2018;**8**:29. DOI: 10.3390/bios8020029

[29] Xiao W, Xiao M, Fu Q, et al. A portable smart-phone readout device for the detection of mercury contamination based on an aptamer-assay nanosensor. Sensors. 2016;**16**:1871. DOI: 10.3390/s16111871

[30] Gan Y, Liang T, Hu Q, et al. In-situ detection of cadmium with aptamer functionalized gold nanoparticles based on smartphone-based colorimetric system. Talanta. 2020;**208**:120231. DOI: 10.1016/j.talanta.2019.120231

[31] Cao Y, Liu Y, Li F, et al. Portable colorimetric detection of copper ion in drinking water via red beet pigment and smartphone. Microchemical Journal. 2019;**150**:104176. DOI: 10.1016/j.microc.2019.104176

[32] Awual MR. A facile composite material for enhanced cadmium(II) ion capturing from wastewater. Journal of Environmental Chemical Engineering. 2019;**7**:103378. DOI: 10.1016/j.jece.2019.103378

[33] Huang CC, Chang HT. Aptamer-based fluorescence sensor for rapid detection of potassium ions in urine. Chemical Communications. 2008;**12**:1461-1463. DOI: 10.1039/b718752a

[34] Devaiah Chonamada T, Sharma B, Nagesh J, et al. Origin of luminescence-based detection of metal ions by Mn–doped ZnS quantum dots. ChemistrySelect. 2019;**4**:13551-13557. DOI: 10.1002/slct.201903769

[35] Choudhary MK, Garg S, Kaur A, et al. Green biomimetic silver nanoparticles as invigorated colorimetric probe for Hg2+ ions: A cleaner approach towards recognition of heavy metal ions in aqueous media. Materials Chemistry and Physics. 2020;**240**:122164. DOI: 10.1016/j.matchemphys.2019.122164

[36] Chu Z, Wang W, Zhang C, et al. Monitoring and removal of trace heavy metal ions via fluorescence resonance energy transfer mechanism : In case of silver ions. Chemical Engineering Journal. 2019;**375**:121927. DOI: 10.1016/j.cej.2019.121927

[37] Dhandole LK, Kim SG, Bae HS, et al. Simultaneous and synergistic effect of heavy metal adsorption on the enhanced photocatalytic performance of a visible-light-driven RS-TONR/TNT composite. Environmental Research. 2020;**180**:108651. DOI: 10.1016/j.envres.2019.108651

[38] Zendehdel M, Ramezani M, Shoshtari-Yeganeh B, et al. Simultaneous removal of Pb(II), Cd(II) and bacteria from aqueous solution using amino-functionalized Fe3O4/NaP zeolite nanocomposite. Environmental Technology. 2019;**40**:3689-3704. DOI: 10.1080/09593330.2018.1485750

[39] Jin W, Fu Y, Hu M, et al. Highly efficient SnS-decorated Bi2O3 nanosheets for simultaneous electrochemical detection and removal of Cd(II) and Pb(II). Journal of Electroanalytical Chemistry. 2020;**856**:113744. DOI: 10.1016/j.jelechem.2019.113744

[40] Forzani ES, Zhang H. Detection of heavy metal ions in drinking water using a high-resolution differential surface Plasmon resonance sensor. Environmental Science & Technology. 2005;**39**:1257-1262. DOI: 10.1021/es049234z

[41] Shtenberg G, Massad-ivanir N, Segal E. Detection of trace heavy metal ions in water by detection of trace heavy metal ions in water by nanostructured porous Si biosensors. Analyst. 2015;**140**:4507-4514. DOI: 10.1039/c5an00248f

[42] Guerrini L, Rodriguez-Loureiro I, Correa-Duarte MA, et al. Chemical speciation of heavy metals by surface- enhanced Raman scattering spectroscopy: Identification and quantification of inorganic- and methyl-mercury in water. Nanoscale. 2014;**6**:8368-8375. DOI: 10.1039/C4NR01464B

[43] Ingle AP, Seabra AB, Duran N, et al. Nanoremediation: A new and emerging technology for the removal of toxic contaminant from environment. In: Microbial Biodegradation and Bioremediation. Amsterdam: Elsevier; 2014:233-250. DOI: 10.1016/b978-0-12-800021-2.00009-1

[44] Hu Z, Qin S, Huang Z, et al. Recyclable graphene oxide-covalently encapsulated magnetic composite for highly efficient Pb(II) removal. Journal of Environmental Chemical Engineering. 2017;**5**:4630-4638. DOI: 10.1016/j.jece.2017.09.003

[45] Goon IY, Zhang C, Lim M, et al. Controlled fabrication of Polyethylenimine-functionalized magnetic nanoparticles for the sequestration and quantification of free Cu2+. Langmuir. 2010;**56**:12247-12252. DOI: 10.1021/la101196r

[46] Pyrzynska K. Carbon nanostructures for separation, preconcentration and speciation of metal ions. TrAC, Trends in Analytical Chemistry. 2010;**29**:718-727. DOI: 10.1016/j.trac.2010.03.013

[47] Ihsanullah AA, Al-Amer AM, et al. Heavy metal removal from aqueous solution by advanced carbon nanotubes: Critical review of adsorption applications. Separation and Purification Technology. 2016;**157**:141-161. DOI: 10.1016/j.seppur.2015.11.039

[48] Lu H, Zhang W, Yang Y, et al. Relative distribution of Pb 2+ sorption mechanisms by sludge-derived biochar. Water Research. 2012;**46**:854-862. DOI: 10.1016/j.watres.2011.11.058

[49] Karnib M, Kabbani A, Holail H, et al. Heavy metals removal using activated carbon, silica and silica activated carbon composite. Energy Procedia. 2014;**50**:113-120. DOI: 10.1016/j.egypro.2014.06.014

[50] Kadirvelu K, Thamaraiselvi K, Namasivayam C. Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste. Bioresource Technology. 2001;**76**:63-65. DOI: 10.1016/S0960-8524(00)00072-9

[51] Sheet I, Kabbani A, Holail H. Removal of heavy metals using nanostructured graphite oxide, silica nanoparticles and silica/graphite oxide composite. Energy Procedia. 2014;**50**:130-138. DOI: 10.1016/j.egypro.2014.06.016

[52] Mubarak NM, Sahu JN, Abdullah EC, et al. Removal of heavy metals from wastewater using carbon nanotubes. Separation and Purification Reviews. 2014;**43**:311-338. DOI: 10.1080/15422119.2013.821996

[53] Gonzalez Hodges AN. Nanotubos de carbono multicapa dopados con nitrógeno crecidos sobre roca volcánica y su aplicación en la remoción de metales pesados. México: Tesis de Licenciatura; 2019. pp. 1-105

[54] Mabel VM, Laura MC, Mónica SC, et al. Tratamiento Terciario De Aguas Residuales Por Filtración E Intercambio Iónico. Available from: https://www.researchgate.net/profile/Mabel_Mier/publication/237211478_Tratamiento_Terciario_De_Aguas_Residuales_Por_Filtracion_E_Intercambio_Ionico/links/546494c90cf2c0c6aec58c6d.pdf

[55] Zhang T, Wei S, Waterhouse GIN, et al. Chromium (VI) adsorption and reduction by humic acid coated nitrogen-doped magnetic porous carbon. Powder Technology. 2020;**360**:55-64. DOI: 10.1016/j.powtec.2019.09.091

[56] Byrne TM, Gu X, Hou P, et al. Quaternary nitrogen activated carbons for removal of perchlorate with electrochemical regeneration. Carbon. 2014;**73**:1-12. DOI: 10.1016/j.carbon.2014.02.020

[57] Chu B, Amano Y, Machida M. Preparation of bean dreg derived N-doped activated carbon with high adsorption for Cr(VI). Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2019;**586**:124262. DOI: 10.1016/j.colsurfa.2019.124262

[58] Hoffmann F, Cornelius M, Morell J, et al. Silica-based mesoporous organic-inorganic hybrid materials. Angewandte Chemie, International Edition. 2006;**45**:3216-3251. DOI: 10.1002/anie.200503075

[59] Zhou Y, Quan G, Wu Q, et al. Mesoporous silica nanoparticles for drug and gene delivery. Acta Pharmaceutica Sinica B. 2018;**8**:165-177. DOI: 10.1016/j.apsb.2018.01.007

[60] Nooney RI, Kalyanaraman M, Kennedy G, et al. Heavy metal remediation using functionalized mesoporous silicas with controlled macrostructure. Langmuir. 2001;**17**:528-533. DOI: 10.1021/la000720j

[61] Kang T, Park Y, Choi K, et al. Ordered mesoporous silica (SBA-15) derivatized with imidazole-containing functionalities as a selective adsorbent of precious metal ions. Journal of Materials Chemistry. 2004;**14**:1043-1049. DOI: 10.1039/b315829b

[62] Zhang L, Zhang W, Shi J, et al. A new thioether functionalized organic-inorganic mesoporous composite as a highly selective and capacious Hg2+ adsorbent. Chemical Communications. 2003;**2**:210-211. DOI: 10.1039/b210457a

[63] Walcarius A, Sayen S, Gérardin C, et al. Dipeptide-functionalized mesoporous silica spheres. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2004;**234**:145-151. DOI: 10.1016/j.colsurfa.2003.11.010

[64] Erdem E, Karapinar N, Donat R. The removal of heavy metal cations by natural zeolites. Journal of Colloid and Interface Science. 2004;**280**:309-314. DOI: 10.1016/j.jcis.2004.08.028

[65] Vaca Mier M, López Callejas R, Gehr R, et al. Heavy metal removal with mexican clinoptilolite: Multi-component ionic exchange. Water Research. 2001;**35**:373-378. DOI: 10.1016/S0043-1354(00)00270-0

[66] Egashira R, Tanabe S, Habaki H. Adsorption of heavy metals in mine wastewater by Mongolian natural zeolite. Procedia Engineering. 2012;**42**:49-57. DOI: 10.1016/j.proeng.2012.07.394

[67] Ramírez-Aparicio J, Sánchez-Martínez A, Ramírez-Bon R. Photodecolorization of rhodamine under sunlight irradiation driven by chabazite. Solar Energy. 2016;**129**:45-53. DOI: 10.1016/j.solener.2016.01.050

[68] Shaheen SM, Derbalah AS, Moghanm FS. Removal of heavy metals from aqueous solution by zeolite in competitive sorption system. International Journal of Environmental Science and Development. 2012;**3**:362-367. DOI: 10.7763/ijesd.2012.v3.248

[69] Zamzow MJ, Eichbaum BR. Separation science and technology removal of heavy metals and other Cations from wastewater using zeolites. Separation Science and Technology. 1990;**25**:1555-1569. DOI: 10.1080/01496399008050409

[70] Santhosh C, Velmurugan V, Jacob G, et al. Role of nanomaterials

in water treatment applications: A review. Chemical Engineering Journal. 2016;**306**:1116-1137. DOI: 10.1016/j. cej.2016.08.053

[71] Online VA, Kam CS, Leung TL, et al. RSC advances form of carbon and surface functionalization. Separation and Purification Technology. 2018;**47**:18355-18362. DOI: 10.1039/ c8ra02264j

[72] Rasouli M, Yaghobi N, Hafezi M, et al. Adsorption of divalent lead ions from aqueous solution using low silica nano-zeolite X. Journal of Industrial and Engineering Chemistry. 2012;**18**:1970-1976. DOI: 10.1016/j.jiec.2012.05.014

[73] Oliveira JA, Cunha FA, Ruotolo LAM. Synthesis of zeolite from sugarcane bagasse fly ash and its application as a low-cost adsorbent to remove heavy metals. Journal of Cleaner Production. 2019;**229**:956-963. DOI: 10.1016/j.jclepro.2019.05.069

[74] Liu H, Peng S, Shu L, et al. Magnetic zeolite NaA: Synthesis, characterization based on metakaolin and its application for the removal of Cu2+, Pb2+. Chemosphere. 2013;**91**:1539-1546. DOI: 10.1016/j.chemosphere.2012.12.038

[75] Tran HN, Lien Nghiem TH, Duong Vu TT, et al. Dye-doped silica-based nanoparticles for bioapplications. Advances in Natural Sciences: Nanoscience and Nanotechnology. 2013;**4**:043001. DOI: 10.1088/2043-6262/4/4/043001

[76] Pham T-H, Byeong-Kyu L. Aqueous Phase Adsorption : Theory, Simulations, and Experiments. United Kingdom: Taylor & Francis; 2019. pp. 181-210

[77] García-Mendieta A, Solache-Ríos M, Olguín MT. Evaluation of the sorption properties of a Mexican clinoptilolite-rich tuff for iron, manganese and iron–manganese systems. Microporous and Mesoporous Materials.

2009;**118**:489-495. DOI: 10.1016/j. micromeso.2008.09.028

[78] Bekta N, Kara S. Recent advances in functionalized micro and mesoporous carbon materials: Synthesis and applications. Chemical Society Reviews. 2004;**39**:189-200. DOI: 10.1016/j. seppur.2003.12.001

[79] Tang SCN, Lo IMC. Magnetic nanoparticles: Essential factors for sustainable environmental applications. Water Research. 2013;**47**:2613-2632. DOI: 10.1016/j.watres.2013.02.039

[80] Hu J, Lo IMC, Chen G. Comparative study of various magnetic nanoparticles for Cr(VI) removal. Separation and Purification Technology. 2007;**56**: 249-256. DOI: 10.1016/j. seppur.2007.02.009

[81] Hu J, Lo IMC, Chen G. Performance and mechanism of chromate (VI) adsorption by δ-FeOOH-coated maghemite (γ-Fe2O3) nanoparticles. Separation and Purification Technology. 2007;**58**:76-82. DOI: 10.1016/j. seppur.2007.07.023

[82] Hu J, Lo IMC, Chen G. Removal of Cr(VI) by magnetite nanoparticle. Water Science and Technology. 2004;**12**:139-146

[83] Juwarkar AA, Singh SK, Mudhoo A. A comprehensive overview of elements in bioremediation. Reviews in Environmental Science and Biotechnology. 2010;**9**:215-288. DOI: 10.1007/s11157-010-9215-6

[84] Mahmoud ME, Yakout AA, Abdel-Aal H, et al. Enhanced biosorptive removal of cadmium from aqueous solutions by silicon dioxide nano-powder, heat inactivated and immobilized Aspergillus ustus. Desalination. 2011;**279**:291-297. DOI: 10.1016/j.desal.2011.06.023

[85] Mohsenzadeh F, Rad AC. Bioremediation of heavy metal pollution by nano-particles of Noaea Mucronata. International Journal of Bioscience, Biochemistry and Bioinformatics. 2012;**2**:85. DOI: 10.7763/ijbbb.2012.v2.77

[86] Rizwan M, Singh M, Mitra CK, et al. Ecofriendly application of nanomaterials: Nanobioremediation. Journal of Nanoparticles. 2014;**2014**:7. DOI: 10.1155/2014/431787

[87] Escudero LB, Maniero MÁ, Agostini E, et al. Biological substrates: Green alternatives in trace elemental preconcentration and speciation analysis. TrAC, Trends in Analytical Chemistry. 2016;**80**:531-546. DOI: 10.1016/j.trac.2016.04.002

[88] Tripathi S, Sanjeevi R, Anuradha J, et al. Nano-bioremediation: Nanotechnology and bioremediation. In: Biostimulation Remediation Technologies for Groundwater Contaminants. Singapore: Springer; 2018. pp. 202-219. DOI: 10.4018/978-1-5225-4162-2.ch012

[89] Mahmoud ME, Yakout AA, Abdel-Aal H, et al. Immobilization of Fusarium verticillioides fungus on nano-silica (NSi-Fus): A novel and efficient biosorbent for water treatment and solid phase extraction of Mg(II) and Ca(II). Bioresource Technology. Singapore: Springer; 2013;**134**:324-330. DOI: 10.1016/j.trac.2016.04.002

[90] Bakircioglu Y, Bakircioglu D, Akman S. Biosorption of lead by filamentous fungal biomass-loaded TiO2 nanoparticles. Journal of Hazardous Materials. 2010;**178**:1015-1020. DOI: 10.1016/j.jhazmat.2010.02.040

[91] Bakircioglu D, Ucar G, Kurtulus YB. Coliform bacteria immobilized on titanium dioxide nanoparticles

as a biosorbent for trace lead preconcentration followed by atomic absorption spectrometric determination. Microchimica Acta. 2011;**174**:367-374. DOI: 10.1007/s00604-011-0630-3

[92] Polak-Berecka M, Szwajgier D, Waśko A. Biosorption of Al+3 and Cd+2 by an exopolysaccharide from *Lactobacillus rhamnosus*. Journal of Food Science. 2014;**79**:T2404-T2408. DOI: 10.1111/1750-3841.12674

[93] Aydemir N, Tokman N, Akarsubasi AT, et al. Determination of some trace elements by flame atomic absorption spectrometry after preconcentration and separation by Escherichia coli immobilized on multiwalled carbon nanotubes. Microchimica Acta. 2011;**175**:185. DOI: 10.1007/s00604-011-0668-2

[94] Yang T, Liu LH, Liu JW, et al. Cyanobacterium metallothionein decorated graphene oxide nanosheets for highly selective adsorption of ultra-trace cadmium. Journal of Materials Chemistry. 2012;**22**:21909-21916. DOI: 10.1039/c2jm34712a

[95] Nowack B. Pollution prevention and treatment using nanotechnology. Nanotechnology. 2010;**2**:1-15. DOI: 10.1002/9783527628155.nanotech010

[96] Odedele TO, Ibrahim HD. Modelling toxicity behaviour of engineered nanomaterials using computational intelligence approach. In: Procedings of the SPE International Conference and Exhibition on Health, Safety, Security, Environment, and Social Responsibility; 16-18 April 2018; United Arab Emirates. Abu Dabi; ADNOC and SPE; 2018. p. 190498

[97] Cohen Y, Rallo R, Liu R, et al. In silico analysis of nanomaterials hazard and risk. Accounts of Chemical

Research. 2013;**46**:802-812. DOI:
10.1021/ar300049e

[98] Chen X, Yu L, Zou S, et al. Zeolite
cotton in tube: A simple robust
household water treatment filter
for heavy metal removal. Scientific
Reports. 2020;**10**:1-9. DOI: 10.1038/
s41598-020-61776-8