



Implementing nanoparticles for competitive drinking water purification

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Abstract

The implementation of nanotechnology in drinking water treatment is a very promising field for applied research. A major part of this effort focuses on the reduction of the dimensionality of the conventional cost-effective adsorbents that have been successfully used for decades. The development of engineered nanoparticles has the potential to provide improved uptake efficiencies and sustainability if issues related to cost, technical incorporation and environmental safety are overcome. In this study, we review: (1) the technical and economic conditions for potential implementation of inorganic nanoparticles as alternative adsorbents of heavy metals from drinking water, (2) the reported studies referring to the capture of heavy metals ionic forms by inorganic nanoparticles giving emphasis to those succeeding residual concentrations below the regulation limit and (3) the indirect health and environmental risk related to the application of nanosized materials in a water treatment line. A part of the review is devoted to the identification of an optimum nanoparticle profile that complies with the unique characteristics for each and every heavy metal with respect to the chemical affinity, charge interactions, aqueous speciation, redox reactions and ion-exchange processes. Importantly, in order to bridge fundamental research with the requirements of the technical and commercial sector dealing with water treatment plants, we introduce an evaluation path for the preliminary qualification of candidate nanoparticulate materials, based on a universal index which is derived by adsorption isotherms recorded under realistic conditions of application.

Keywords Drinking water · Inorganic nanoparticles · Heavy metals · Uptake mechanisms · Maximum contaminant level · Environmental impact · Fate

Introduction

Water treatment has become a major field of interest during expansion of nanotechnology to more traditional sectors of human applications. In general, it involves a variety of

separation, catalytic, sensing and quality controlling processes aiming to secure health or environmental protection, water resources management and sustainable development. Based on recent research and technological trends, the development of nanomaterials capable of removing heavy metals

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from water appears as the most pronounced case of nanotechnology's incorporation in water treatment. Particularly, the aqueous soluble forms of elements such as arsenic, cadmium, lead, antimony, chromium, mercury and nickel are considered as emerging water pollutants regulated by strict legislation, especially referring to their long-term exposure through drinking water consumption. Therefore, whenever the problem comes up, a water purification method oriented to the removal of heavy metals should be included as an extra task into the conventional treatment sequence. Such need is usually addressed by proper adsorbents which show high affinity and selectivity to specific heavy metals as a result of their surface configuration. To this point, owed to their small dimensions and tunable surface features, the possible use of nanostructured materials is rather challenging as a way to overcome limitations and improve efficiency of conventional adsorbents.

Nanoparticles are the most representative type of nanostructured materials. Met at a wide variety of shapes, nanoparticles are characterized as self-existent material units completely isolated by adjacent particles with a uniform size lying in the nanoscale. During the last 2 decades, plenty of research work has been devoted in the synthesis of engineered nanoparticles and their optimization for various technology fields including electronics, biomedicine and catalysis. More frequently, nanoparticles consisting of inorganic phases (metal, alloys, oxides, composites) are preferred due to the offered diversity of advanced electronic, optical, magnetic and mechanical properties and the further opportunities arising by nanoscale coupling effects. From another point of view, inorganic nanoparticles appear to be very compatible to the aqueous chemistry which is the base of most industrial, environmental and biological processes. Nanoparticles were also suggested as potential heavy metal adsorbents during drinking water purification. Numerous preliminary studies support the ability of particles with specific compositions to irreversibly capture one or more heavy metals from the aqueous phase. However, it is not always clear whether such observations are reproducible under realistic water treatment conditions and, even worse, whether nanoparticles application can fulfill all technical/economic limitations and regulations for drinking water. Becoming competitive to conventional adsorbents requires at least an equal efficiency and a similar production cost for nanoparticles. Furthermore, the benefit from the small dimensions may turn into a serious drawback considering the need to design a different application setup followed by a corresponding recovery process.

This review summarizes the current state of the art related to the potential of inorganic nanoparticles to be used as efficient adsorbents for heavy metal ionic forms able to comply with the drinking water regulations. Importantly, it emphasizes to reported technologies and research studies which provide sufficient data allowing their evaluation under realistic

terms of water treatment. Furthermore, it attempts to give an approach for facing common heavy metal pollutants providing the optimum nanoparticle profile for each case. This article is an abridged version of the chapter published by Simeonidis et al. (2018) in the series Environmental Chemistry for a Sustainable World (ECSW, volume 14, <https://link.springer.com/bookseries/11480>) (Simeonidis et al. 2018).

Synthesis of engineered nanoparticles

Despite the ancient origin of the term “nanoparticle”—*νάνο* = dwarfish and *ἀπάρτησις* = detachment (Liddell et al. 1996)—the use of this term exclusively refers to modern science and technology. Nevertheless, materials with identical texture were developed throughout human history or even found naturally as a result of biological or anthropogenic procedures. All these cases are separate to the engineered nanoparticles, those intentionally designed and produced to cover the specifications of technological applications. Synthesis of engineered nanoparticles may be realized by two routes: (1) bottom-up, building nanoparticles from small nuclei in the atomic scale, and (2) top-down, splitting coarse materials to smaller dimensions. Chemical wet methods are classified in the bottom-up approach where nanoparticles are formed after the oversaturation of soluble species triggered by the controllable modification of specific parameters defining their stability. Mechanical treatment and vapor condensation processes are the most important top-down techniques for nanoparticles preparation.

Ideally, a successful synthetic route should be able to provide well-defined nanoparticles with respect to chemical composition, structural stability and sufficient segregation. In practice, a compromise between the degree of surface activity, aggregation tendency and resistance against phase changes should be considered according to the targeted application of nanoparticles. More importantly, proportionality between the cost of the selected production method and the added value by nanoparticles incorporation in the corresponding technological field should be always maintained. For instance, drinking water treatment requires nanoparticles with extremely low cost, ton-scale availability, water compatibility, zero toxicity and high surface activity. Therefore, in the majority of cases, the available synthesis methods are limited to those operated in a simple and scalable setup, using low temperatures and pressures, in an environmentally friendly process free of any toxic reagents (Table 1).

Nanoparticles in water purification

As the management of drinking water is a priority for the sustainable development of organized societies within the centuries, controlling the water quality by treatment

Table 1 Evaluation of commonly applied methods for nanoparticles synthesis with respect to their potential for large-scale production oriented for drinking water purification systems

Method	Cost	Production rate	Water compatible	Energy demands	Special facilities	Eco-friendly
Thermal decomposition	High	Medium	No	High	Yes	No
Solvothermal	High	Medium	Can be	High	Yes	No
Precipitation	Low	High	Highly	Low	No	Yes
Electrochemical	Medium	High	Highly	High	No	Yes
Ball milling	Low	High	Can be	Medium	Yes	Yes
Vapor condensation	Very high	Low	Yes	High	Yes	Yes

facilities remains an achievement of high importance. Water intended for consumption by human is obtained by underground aquifers or surface reservoirs. The long-term contact of water with the surroundings of source causes the dissolution or the drift of components originating by the earth background or anthropogenic byproducts. Suspended solids, dissolved species and microorganisms are considered as the main categories of such components. Dissolved water pollutants like heavy metals may be captured by the application of conventional non-selective or species-oriented methods. Reverse osmosis is the most representative case of a non-selective technique accompanied by high cost and water quality parameters very close to those of deionized water, i.e., non-potable. On the other side, ion-exchange, air-stripping, chemical precipitation and adsorption by solids are characterized by relatively high selectivity and much lower cost for application. The major class of selective methods for the removal of dissolved pollutants from water is adsorption by various solids. The general mechanism of adsorption is described by the initial approach of the solid/water interface by soluble pollutants and their attachment to the solid's surface by means of van der Waals (physisorption) or chemical (chemisorption) bonds. Adsorption processes are usually adapted to column bed filter setups which are very popular for large-scale and point-of-use water treatment solutions due to their simplicity and low cost.

Since the increase in specific surface area is a critical task for the improvement of adsorption efficiency, the development of nanomaterials for adsorption comes as an obvious sequence in the evolution of the field, especially if low-cost availability and recycling are achieved. Based on the principles of nanoscale engineering, tuning adsorbents' surface configuration and charge density may be also realized. But the small dimensions of nanoparticles may turn into a serious drawback for their successful implementation into water treatment units. More specifically, it is almost impossible to get the benefit of utmost in specific surface area without meeting severe difficulties in the design of the proper operation setup with respect to their separation. In summary, there

are three potential approaches able to employ nanoparticles-based processes in a water purification line:

- (1) Dispersion of nanoparticles in water and separation by filtration,
- (2) Use of nanoparticles aggregates or composites in typical column beds and
- (3) Supported on substrates.

In the first case, nanoparticles are initially added in the water under treatment as a dried product or highly concentrated suspension. This part requires a simple but relative large continuous-stirred vessel in which contact of nanoparticles with water for sufficient time allows for the removal of the targeted pollutant. However, the outflowing water still contains the dispersed nanoparticles that need to be completely separated. The recovery of solids with dimensions lying in the nanoscale should be accomplished by nanofiltration in order to be on the safe side against possible leakage. But referring to common water purification strategies, the introduction of nanofiltration may become the cost-determining step of the whole process.

The filtration bed, which operates as a plug-flow reactor, is considered as the best way to bring an adsorbent in contact with the polluted water resulting in high removal efficiency within short time. A large quantity of the material is packed in a column or cartridge being able to operate for a long period without the need for any maintenance until replacement. However, to ensure the normal flow of water through the filter and avoid occlusion problems, the applied nano-adsorbent should be in the form of aggregates (> 200 μm) or attached to other phases.

In specific systems, nanoparticles are used in secondary processes to integrate a main water treatment step. For instance, a small quantity of an adsorbent may be introduced as a filtration step to guard the periodical or possible appearance of a pollutant in the treatment line. Here, there is an option to apply highly activated nanoparticles supported on substrates or immobilized on membranes, porous materials or graphene oxide. Such methodology exploits the

maximum efficiency of nanoparticles but probably has a limited lifetime.

Removal of heavy metals

Mechanisms

Adsorption is a favorable mechanism for heavy metals removal as, under optimized conditions, it can achieve both high capacities and non-reversible binding of the pollutant on the nanoparticle. It comes as the result of surface energy and the tendency of surface atoms to occupy their outer side by other atoms from the surrounding phase. Chemisorption is characterized by the formation of strong covalent bonds usually through oxygen bridges when the process takes place in aqueous environment. A representative system is the case of As(V) adsorption by ferric oxy-hydroxides where a variety of complexation types (mononuclear monodentate or bidentate and binuclear bidentate inner-sphere complexes shown in Fig. 1) may appear according to the proximity of Fe octahedra and As(V) oxy-anions (Cornell and Schwertmann 2003). Positively charged adsorbents not only favor the attraction of As(V) oxy-anions but

also induce a corner/edge-connectivity of the Fe octahedra, while a face-connectivity is promoted when surface charge is negative (Pinakidou et al. 2015). Direct adsorption is not always spontaneous, especially when the targeted heavy metal form is very mobile or uncharged. In this occasion, modifying metal's oxidation state is a sophisticated approach to enable its removal. This can be realized by using adsorbents which potentially act as reducing or oxidizing intermediates and exchange electrons with aqueous species. For example, tetravalent Mn can be incorporated into a single-phase adsorbent by substituting iron in ferrihydrite to oxidize As(III) to As(V) before adsorption of the last as shown in Fig. 1d (Pinakidou et al. 2016b).

When activated by photons through solar or UV lamp radiation, titanium dioxide but also ZnO, ZrO₂, CeO₂ and Ag are known for their photocatalytic properties. Photocatalysis is initiated by the excitation of an electron from the valence band which is promoted to the conduction band producing a pair of electron and a hole. The photo-excitation results in the release of electrons, hydroxyl radicals ($\cdot\text{OH}$), superoxide anions (O_2^-) and other forms depending on co-existing compounds (Fig. 1e) and, therefore, can provide multiple mechanisms for the removal of heavy metals for water by involving direct or indirect reduction and oxidation

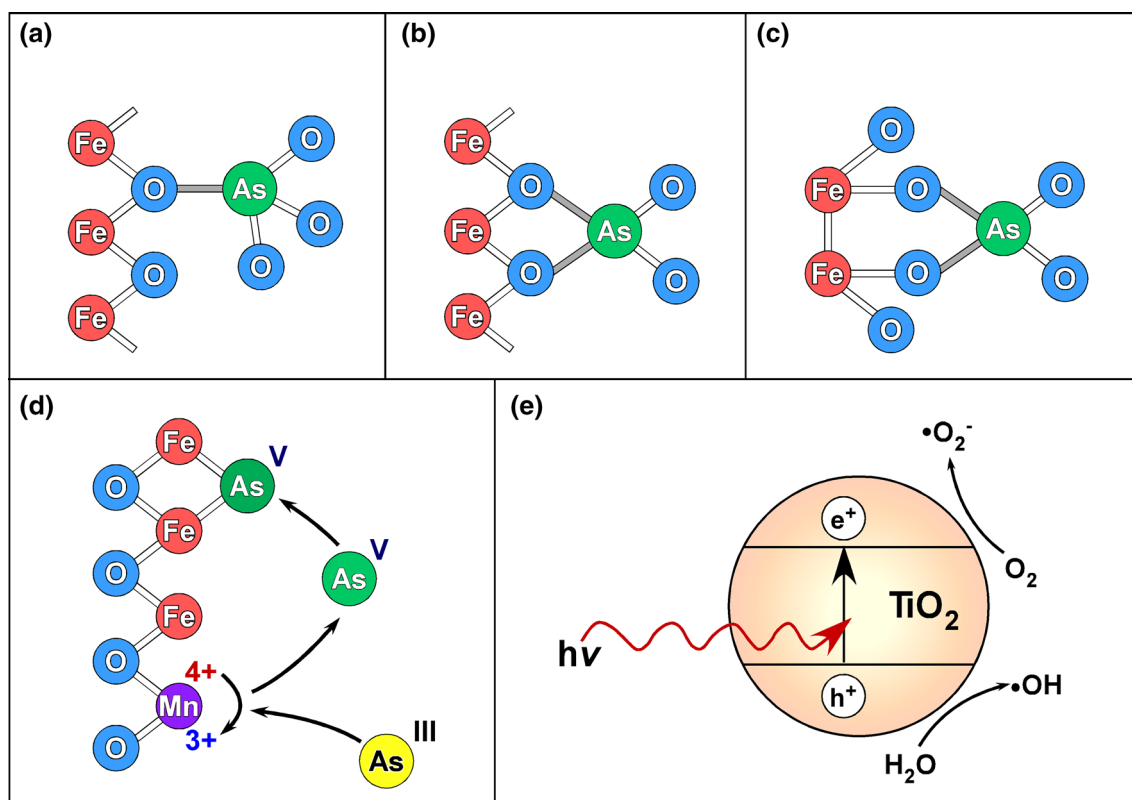


Fig. 1 Representative scheme of possible uptake mechanisms of heavy metals by inorganic nanoparticles. Monodentate (a) bidentate-mononuclear (b) and bidentate-binuclear (c) adsorption complexes of

As(V) on an iron oxy-hydroxide. Oxidation-mediated adsorption of As(III) in a Mn(IV)-substituted iron oxy-hydroxide (d). Photocatalytic mechanisms releasing free radicals on TiO₂ nanoparticles (e)

processes (Litter 2015). Another common mechanism which results in the removal of heavy metals from the aqueous phase is the modification of their solubility by a change in the oxidation state. For instance, Cr(VI) is a soluble state of chromium, whereas Cr(III) has the tendency to form insoluble hydroxides. Therefore, electron donors can be employed as adsorbents to favor such reduction step with the grown solid to be precipitated on adsorbent's surface. Finally, amalgamation refers to the purification of water from soluble mercury through the formation of insoluble solid solutions with various metals or alloys. In this mechanism, divalent Hg is first reduced to Hg^0 and then diffused to the metal structure resulting in a very stable alloy.

Evaluation methodology

The performance of adsorbents oriented to meet the drinking water specifications should be initially evaluated by bench-scale experiments followed by their validation in pilot operational units. However, an overview of the literature indicates the absence of a common approach to determine the efficiency of heavy metal adsorbents, done in most cases under "ideal laboratory conditions" very different to those found in drinking water treatment processes. In the following, the prerequisites which ensure the reliable estimation of nanoparticles efficiency are analyzed, whereas a universal quality evaluation index specified for heavy metals removal in compliance to drinking water limitations is introduced.

A major modification observed during the transition from wastewater treatment to drinking water purification is related to the much lower initial concentrations of the pollutant that need to be handled. Particularly, a polluted groundwater source hardly provides concentrations of heavy metals higher than $100 \mu\text{g/L}$. Proportionally, the permissible concentration after purification should be at most equal to the corresponding drinking water regulation limit for each heavy metal, usually below $10 \mu\text{g/L}$. Therefore, considering that recording of adsorption isotherms is the common methodology to estimate adsorption efficiency of a material, the bench-scale experiments should deliver detailed results in a range of residual concentrations starting from zero up to $100\text{--}200 \mu\text{g/L}$. In addition, the conditions during a laboratory experiment should be as close as possible to those met in natural water. For this reason, any study should be carried in the pH range 6–8 which is compatible with drinking water purification processes. Furthermore, anions like HCO_3^- , Cl^- , SO_4^{2-} , SiO_2^- , PO_4^{3-} and cations like Ca^{2+} , Mg^{2+} , Na^+ may act in competition to the targeted heavy metal forms and cause a significant reduction of the removal efficiency. It is known that a decrease of around 50% in the overall efficiency is expected when adsorption experiments are carried out in natural water compared to similar tests in deionized water. Accordingly, the investigation of nanoparticles

performance should consider a representative water composition of ions at their average levels of concentration.

An important task is the proper evaluation of obtained results with respect to the need for direct comparison with other studies and the compliance to the maximum contaminant limit (MCL) for each pollutant. Unfortunately, in the majority of bench-scale experiments, the efficiency of adsorbents is judged through the maximum adsorption capacity (Q_{max}) which is defined by the plateau of the recorded isotherm observed at extremely high residual concentrations (see curve A in Fig. 2). In some other cases, the percentage of decrease in initial pollutant concentration after treatment is given as a criterion for the successful adsorbent's performance (see curve C in Fig. 2). The weakness of both approaches is that they usually point to high initial and residual concentrations which indeed bring high adsorption capacities and percentage removals but provide no data for the ability to reach low concentrations such as the regulation limits. For this reason, a better way to monitor the efficiency of various nanoparticles is by the introduction of an index defined after the adsorption capacity that corresponds to a residual concentration equal to the regulation limit of each pollutant (Q_{MCL}). In practice, this index directly indicates the operational capacity and lifetime of the

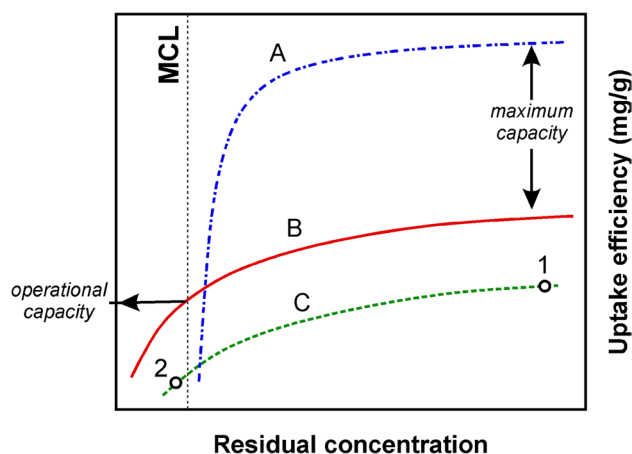


Fig. 2 Simplified approach to evaluate applicability of nanoparticles in drinking water purification by adsorption isotherms. Case A: material succeeding high maximum capacity but completely fails to decrease pollutant concentration below the MCL. Case B: high performing material in the concentration range of the MCL; effective operational capacity is pointed at the section of the curve with the MCL. Case C is an example of mistaken use of percentage removal for the evaluation of nanoparticles independently of the residual concentration. Point 1 indicates the removal of 95% of an unrealistic initial pollutant's concentration (e.g., $> 10 \text{ mg/L}$) succeeding a high residual concentration. Point 2 corresponds to the removal of 70% of a realistic initial pollutant's concentration (e.g., $40 \mu\text{g/L}$) reaching residual concentration below the MCL. Reproduced after modification by Simeonidis et al. (2016) with permission of The Royal Society of Chemistry

material and it is estimated by the projection of adsorption isotherm to the MCL of the studied heavy metal (see curve B in Fig. 2). For example, the evaluation index for nanoparticles used to remove arsenic should be determined by the adsorption capacity from isotherms at the residual concentration of 10 µg/L (Q_{10}). The value of this index is expected to provide a good estimation of the nanoparticles efficiency during the operation of a large-scale unit indicating the maximum operational capacity before their replacement.

Heavy metals' categories

The qualification of the proper adsorbent for a particular heavy metal is based on a number of conditions defined by the uptake mechanism of pollutant's species. High chemical affinity, proper adjustment of surface charge, and incorporation of ion or electron exchange potential are commonly mentioned as possible directions of optimization. This section discusses the most favorable approaches for the removal of heavy metals from drinking focusing on cases where potential implementation for purposes in drinking water purification is supported, at least indirectly (Table 2). A

Table 2 Summary of research studies on heavy metals adsorption by nanoparticles with potential technological interest for drinking water treatment

Phase	Type	Size (nm)	Heavy metal	pH	Water	Estimated Q_{MCL} (mg/g)	References
<i>Divalent cations (Pb, Cd, Ni, Hg)</i>							
TiO ₂	Particles	8.3	Pb Cd Ni	8	Tap	4.0 4.5 1.8	Engates and Shipley (2011)
α -Fe ₂ O ₃	Particles	30	Pb Cd	8	Tap	2.0 0.2	Shipley et al. (2013)
(Fe, Mn)OOH	Spheres	200	Cd Ni	7	Tap	5.2 7.1	Kokkinos et al. (2018)
Au	Particles	13	Hg	7	Ground	20	Lo et al. (2012)
Fe ₃ O ₄ @SiO ₂	Particles	50	Hg	6	Tap	5	Hakami et al. (2012)
(Fe, Mn)OOH	Spheres	200	Hg	7	Tap	2.5	Kokkinos et al. (2017)
<i>High-valent ions (Cr, Se, Mo, U)</i>							
Fe ₃ O ₄	Particles	30	Cr(VI)	7	Tap	1.8	Simeonidis et al. (2015)
Fe ₃ O ₄	Aggregated	30	Cr(VI)	7.2	Tap	4.5	Kaprara et al. (2016)
Sn ₆ O ₄ (OH) ₄	Particles	30	Cr(VI)	7	Tap	19	Kaprara et al. (2017)
Fe ₃ O ₄	Supported particles	15	Se(IV) Se(VI)	7	Distilled	1.9 –	Fu et al. (2014)
ZVI	Particles	5	U(VI)	7	Ground	300	Li et al. (2015)
(Fe, Mn)OOH	Spheres	200	U(VI)	7	Tap	4	Dimiropoulos et al. (2015)
<i>Oxy-ionic species (As, Sb)</i>							
FeOOH	Spheres	200	As(III) As(V)	7	Tap	1.9 13.5	Tresintsi et al. (2012)
(Fe, Mn)OOH	Spheres	200	As(III) As(V)	7	Tap	6.7 11.7	Tresintsi et al. (2013)
ZVI	Particles	15	As(V)	7	Ground	5	Kanel et al. (2006)
MgFe ₂ O ₄	Particles	3.7	As(III) As(V)	7	Tap	9 10	Tang et al. (2013)
TiO ₂	Aggregated particles	6	As(III) As(V)	7	Ground	4 3.5	Jing et al. (2009)
CeO ₂	Particles	4	As(III) As(V)		Distilled	13.5 12	Li et al. (2012)
ZrO ₂	Spheres	600	As(III) As(V)	7.2	Distilled	5 4.5	Cui et al. (2013)
CeO ₂ /ZrO ₂	Spheres	90	As(III) As(V)	7	Distilled	9.2 27.1	Xu et al. (2013)
FeOOH	Spheres	200	Sb(III) Sb(V)	7	Tap	3 –	Simeonidis et al. (2017b)

thorough overview of recent progress in the research related to nanoparticles and heavy metal removal is given in (Tang and Lo 2013; Gómez-Pastora et al. 2014; Ray and Shipley 2015; Adeleye et al. 2016; Lata and Samadder 2016; Santhosh et al. 2016; Simeonidis et al. 2016; Gómez-Pastora et al. 2017).

Divalent cations

Lead Dissolved lead in water is usually correlated to the flow through lead-containing pipes which stayed in use till recently. Lead appears in the positively charged forms Pb^{2+} and $\text{Pb}(\text{OH})^+$ in the pH range of natural water, with the percentage of the hydroxylated form increasing at higher pH values. A number of works studied different kinds of inorganic nanoparticles for the removal of lead from water providing indications about their potential efficiency under drinking water treatment conditions that comply also with the regulation limit of 10 $\mu\text{g/L}$. Titanium dioxide nanoparticles with a size of 8.3 nm were examined for the removal of Pb and other divalent metals (Engates and Shipley 2011). Due to the low point of zero charge, TiO_2 nanoparticles appear efficient to adsorb at least 4 mg Pb/g from polluted tap water with pH 8, while keeping a residual concentration well-below MCL. It was suggested that TiO_2 nanoparticles introduce a much faster adsorption kinetic rate compared to the bulk material being also many times more efficient than Fe_3O_4 counterparts or activated carbon. Yet, hematite nanoparticles, despite a smaller capacity (2 mg Pb/g), could succeed in achieving residual concentrations below MCL (Shipley et al. 2013).

Cadmium The presence of cadmium in natural water is usually attributed to anthropogenic activities and especially to the leaching from galvanized pipes, fittings and water coolers. Unlike lead, cadmium appears exclusively in the form Cd^{2+} in the whole pH range of natural water, thus presenting more or less the same requirement of negatively charged surface by potential adsorbents. In most cases, cadmium adsorption by inorganic nanoparticles is discussed in comparison with that of lead. Among published works, TiO_2 nanoparticles offered a high uptake capacity for Cd according to the drinking water standards reaching a capacity of around 4.5 mg Cd/g at pH 8 using polluted tap water (Engates and Shipley 2011). At the same levels, tetravalent manganese ferrihydrite nanospheres brought a capacity of around 4 mg Cd/g at pH 7 that increases to 5.2 mg Cd/g in a column filter of granulated aggregates (Kokkinos et al. 2018). Zirconia nanoparticles with a mean diameter of 13 nm showed also some weak tendency to capture Cd at low concentrations (Gusain et al. 2016). Disappointingly, relevant research performed by applying zero-valent iron (Boparai et al. 2011) and ZnO (Sheela et al. 2012) nanoparticles cannot be evalu-

ated due to the absence of any information on the adsorption pH and the extremely high concentrations of Cd test solutions. However, given thermodynamic data for uptake at high concentrations describe a spontaneous endothermic adsorption on Fe and an exothermic process on ZnO.

Nickel Nickel appears in water supplies as a result of corrosion processes on steel construction but under specific conditions has the potential to dissolve from the soil. Although nickel's naturally occurring forms are highly insoluble hydroxides or sulfides, whenever nickel becomes soluble it is very stable at neutral pH. A very limited number of works is focused on the removal of nickel from water employing nanoparticles of inorganic phases. Even worse, none of them clearly examines the possibility of their use as drinking water adsorbents. The most promising result comes from the negatively charged tetravalent manganese ferrihydrite nanospheres with an efficiency of 7.1 mg Ni/g in tap water at a residual concentration of 20 $\mu\text{g/L}$ which stands as the current MCL (Kokkinos et al. 2018). High enough was also the corresponding capacity of TiO_2 nanoparticles estimated from the given data to be around 1.8 mg Ni/g (Engates and Shipley 2011). In comparison with the corresponding values for Pb and Cd, it is clear that Ni shows a significant lower affinity for adsorption. Finally, alumina nanoparticles (20 nm) indicate some good removal efficiencies at large concentrations, but given data indicate a very low performance at concentrations below 1 mg/L which is attributed to the high PZC (7.9) of the material (Srivastava et al. 2011).

Mercury Mercury's presence is not so frequent in natural water resources; however, its removal from drinking water is a very challenging field taking into consideration the high toxicity of mercury species and the low MCL of 1 $\mu\text{g/L}$. The origin of its presence can be both natural and industrial (volcanos, fires, combustion processes). A variety of nanoparticle systems have been tested for Hg removal from water. Gold nanoparticles embedded on activated Al_2O_3 adsorbent show high selectivity against Hg^{2+} species explained by the formation of Au–Hg amalgams (Lo et al. 2012). The study was performed using low concentrations of Hg (200 $\mu\text{g/L}$), but still a capacity of 20 mg Hg/g (reduced to the mass of Au) was achieved for total removal of Hg. Nevertheless, the high cost of Au restricts the application of such systems only for analytical purposes rather than large-scale water purification. A better expectancy comes from functionalized silica-coated Fe_3O_4 nanoparticles which gave relatively good efficiency for the removal of Hg below its MCL when tested in polluted tap water (Hakami et al. 2012). The observed efficiency of 5 mg Hg/g is mainly attributed to the selectivity of thiol groups, while nanoparticles are considered as a carrier for the application and magnetic separation

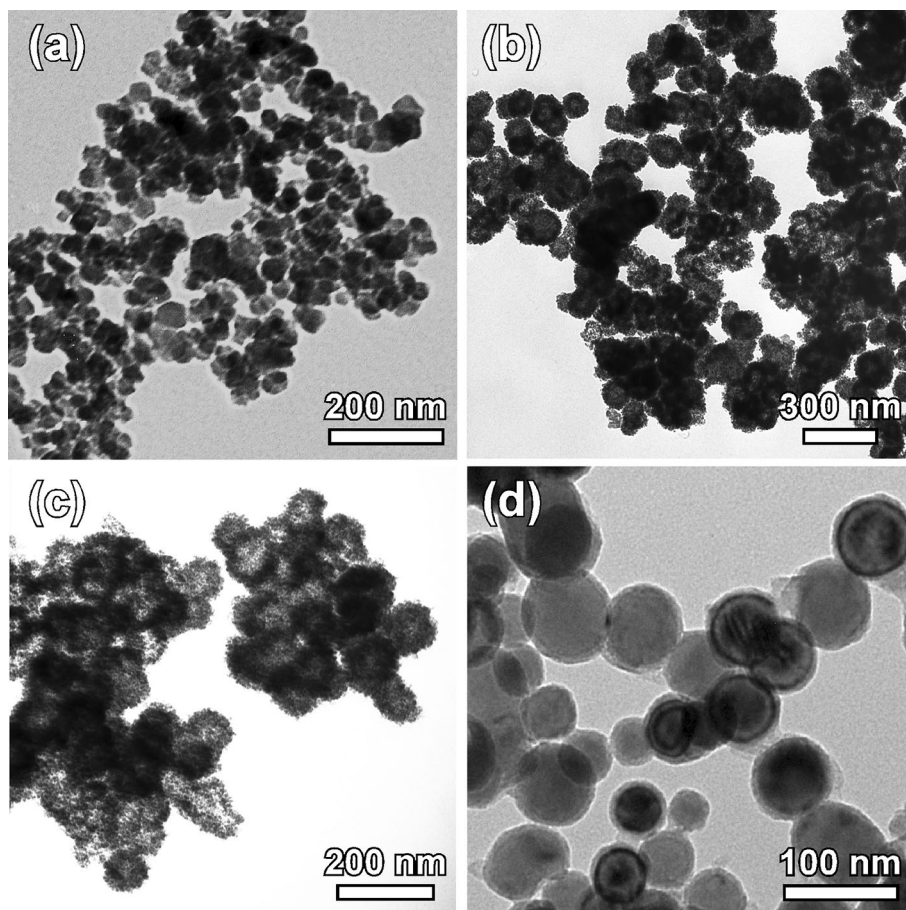
of the nanoadsorbents. So far, the study of Mn-substituted iron oxy-hydroxide nanospheres is the best established case for the development of mercury adsorbents (Kokkinos et al. 2017). The application of negatively charged (Fe, Mn) OOH as granules (aggregated nanospheres) in a column filter setup showed a capacity of 2.5 mg Hg/g while keeping residual concentration below the MCL.

High-valent ions

Chromium Hexavalent chromium is by far the most studied form in this category of heavy metal species. Such interest was triggered by the recent extended discussion on its toxicity by the drinking water consumption path in combination with the practical absence of any specific regulation beyond the total chromium MCL of 50 or 100 $\mu\text{g/L}$. Furthermore, studies revealing a high frequency of Cr(VI) presence among drinking water resources have exacerbated the intensity of the problem (Kaprra et al. 2015). Aqueous speciation of Cr(VI) indicates CrO_4^{2-} as major species in the pH range of drinking water (Kazakis et al. 2015). Much research effort has been devoted to the development of redox-active nanoparticles capable of eliminating Cr(VI) by the reduction-precipitation of Cr(III). Numerous stud-

ies refer to zero-valent iron (ZVI) and Fe_3O_4 nanoparticles, whether as pure nanomaterials or embedded on supports, due their potential to provide electrons for the reduction of Cr(VI). However, results so far are only of fundamental research interest since extreme Cr(VI) concentrations and adsorption pH values are applied. There are hopefully a bunch of works that successfully face Cr(VI) removal from drinking water or at least provide enough data for an indirect estimation of nanoparticles' potential. For instance, ZVI nanoparticles supported on mesoporous silica (Sun et al. 2014), carbon (Dai et al. 2016) or humus (Fu et al. 2017) were tested at pH values 5–6.3 in distilled water presenting a significant ability to decrease Cr(VI) concentration below the 50 $\mu\text{g/L}$. Although such pH range cannot be directly assigned to the drinking water conditions, values such as the 118 mg Cr(VI)/g of ZVI content should be taken into serious consideration. Magnetite nanoparticles with a size of 30 and 80 nm either dispersed or in aggregates were evaluated according to their capacity at residual Cr(VI) concentrations of the current MCL and even lower (Simeonidis et al. 2013, 2015; Kaprra et al. 2016) (Fig. 3). In particular, granules formed by particle aggregates and used in column filters almost doubled the removal capacity compared to that from the dispersion of the separated counterparts. Further

Fig. 3 Transmission electron microscopy images of iron-based nanoparticles successfully tested for drinking water treatment. **a** Fe_3O_4 nanoparticles with a mean size of 30 nm applied for Cr(VI) reduction/precipitation (Reprinted from Simeonidis et al. (2015), Copyright (2015), with permission from Elsevier). **b** Schwertmannite nanospheres optimized for As(V) adsorption in a column bed setup (reprinted from Tresintsi et al. (2012), Copyright (2012), with permission from Elsevier). **c** Tetravalent Mn-feroxyhyte developed for the oxidation/adsorption of As(III) (Reprinted with permission from Tresintsi et al. (2013), Copyright (2013) American Chemical Society). **d** MgO-coated ZVI nanoparticles used for the regeneration of a saturated arsenic adsorbents. Reproduced after modification by Simeonidis et al. (2017a) with permission of The Royal Society of Chemistry



analysis of the uptake mechanism of Cr(VI) by Fe₃O₄ nanoparticles indicated that Fe²⁺ ions work as electron donors to activate the precipitation of Cr(VI) to Cr(III) (Pinakidou et al. 2016c). The Cr(III) oxy-anions are then adsorbed on nanoparticles' surface forming bidentate-binuclear or monodentate complexes. Tin-based nanoparticles include a high perspective for a redox-active material able to overcome passivation problems (Pinakidou et al. 2016a). The developed Sn₆O₄(OH)₄ nanoparticles are advantageous not only because of the large number of electrons delivered by the Sn²⁺ for Cr(VI) reduction but also due to their surface stability against secondary oxidation processes resulting in Q₁₀ values close to 20 mg Cr(VI)/g (Kaprra et al. 2017).

Molybdenum For the time, hexavalent molybdenum is not a priority pollutant of emerging concern. This is signified by the absence of a MCL, whereas some advisory guidelines for 40 or 70 µg/L are only valid according to the essential daily requirement for human. Even though it appears very similar to Cr(VI), Mo(VI) is a weaker oxidant with little evidence on possible health effects caused by its consumption through the drinking water path. The research related to the removal of Mo(VI) from water is rather limited. Direct adsorption or reduction to less soluble forms at a lower oxidation state, e.g., Mo(IV) is a potential way for its uptake by adsorbents. Adsorption of Mo(VI) on inorganic oxyhydroxides is mentioned to take place by ligand exchange with hydroxyl ions resulting in inner-sphere complexation (Goldberg et al. 1996). A small number of works refer to the use of nanoparticles oriented for Mo(VI) removal from water. Suggestively, γ-Fe₂O₃ (Afkhami and Norooz-Asl 2009), ZnFe₂O₄ (Tu et al. 2016) and CuFe₂O₄ (Tu et al. 2014) nanoparticles were tested in this direction but under evaluation conditions and concentration levels much different than those met in drinking water treatment. Thus, the validity of such works should be considered more for wastewater treatment or molybdenum recovery procedures.

Selenium Selenium is dissolved in water resources by the weathering of calcareous sedimentary rocks or by agricultural activities. It is controversial that selenium can be a nutrient and, at the same time, a toxic trace element for human depending on its concentration and oxidation state. For this reason, some countries have regulated the strict MCL of 10 µg/L, while in others a guideline is considered unnecessary. An increasing number of publications are dealing with nanoparticles implementation for the removal of selenium species from water with few of them providing sufficient data to be evaluated for drinking water purification. In general, Se(VI) is strongly captured only after its reduction to insoluble Se²⁻ compounds with Se(IV) species to be preferably removed by direct adsorption. Magnetite nanoparticles are frequently tested as potential selenium

adsorbents but only with poor efficiency. An exception appears for the composite consisting of Fe₃O₄ nanoparticles embedded on graphene oxide which gave a capacity of 1.9 mg Se(IV)/g of Fe₃O₄ at the MCL (Fu et al. 2014). Redox-active nanoparticles consisting of ZVI (Olegario et al. 2010; Ling et al. 2015) and FeS (Mitchell et al. 2013) were introduced as alternatives for the reduction of Se(VI); however, carried experiments were not focused on drinking water treatment conditions.

Uranium Mining activities are the main origin of groundwater pollution by U(VI). Regarding its radioactivity, dissolved uranium is not as dangerous as the metallic form. However, overexposure by ingestion can result in severe damages, especially to the kidney. Few research works deal with U(VI) uptake by inorganic nanoparticles. ZVI is used in order to introduce a reduction mechanism to the less mobile U(IV) form. To this end, ZVI nanoparticles were found to provide extremely high U(VI) capacities reaching 300 mg U(VI)/g under anoxic conditions (Li et al. 2015). However, during the process huge amounts of iron corrosion products are released to water; at the same time, in the presence of dissolved oxygen the ZVI surface is rapidly passivated and the precipitated U(IV) is easily redissolved. Magnesium oxide nanoparticles indicated limited potential to decrease U(VI) concentration below the MCL (Camtakan et al. 2012). Best results were found for Mn(IV)-substituted ferrihydrite nanospheres tested under conditions simulating a drinking water treatment unit which were able to capture around 4 mg U(VI)/g for residual concentrations below 30 µg/L (Dimiroopoulos et al. 2015).

Oxy-ionic species

Arsenic Water treatment for arsenic is the most discussed subject related to heavy metal removal. The frequency of appearance in ground and surface water, the significant decrease in the MCL from 50 to 10 µg/L at the beginning of this century and the remarkable chemistry and complexation of its aqueous species are some of the reasons explaining such interest. The high request for arsenic adsorbents is also demonstrated by the numerous available commercial products usually based on iron oxy-hydroxides, activated alumina and titania. Arsenic usually enters water resources by geological deposits or even from agricultural and industrial activities on the surface. Depending on the oxygenation of the reservoir, arsenic is met in two oxidation states, the As(III) and the As(V). It should be noted that compared to the cases of other heavy metals, the field of arsenic removal is rather competitive since commercial adsorbents are offered at a very low cost achieving high efficiencies, while alternative methods (coagulation) are also applicable. Expectations by inorganic nanoparticles mainly

arise from the possibility of tuning their surface charge and morphology. A wide variety of phases, usually metal oxides or their hydrated counterparts, have been tested for As(III) and As(V) removal in the form of nanoparticles. Iron-based nanoparticles are a frequent choice due to the relatively low cost and the good affinity to arsenic species. In this category, the best results are coming from phases like iron oxyhydroxides (FeOOH) and α -Fe₂O₃ due to the high specific surface area, the positive charge and the strong sorption binding through inner-sphere complexes. More specifically, schwertmannite nanospheres showed an enhanced capacity, especially for the uptake of As(V), reaching a value of 13.5 mg As(V)/g (Tresintsi et al. 2012). In order to incorporate sufficient As(III) adsorption, the same nanoparticles were modified by partial substitution of Fe³⁺ by Mn⁴⁺ (Tresintsi et al. 2013) (Fig. 3). This increased As(III) adsorption up to 6.7 mg As(III)/g while keeping residual concentration below 10 µg/L by adding an oxidation step to As(V) after reaction with Mn⁴⁺ (Tresintsi et al. 2014).

Not very high but competitive capacities are also provided by zero-valent iron, Fe₃O₄ and γ -Fe₂O₃ nanoparticles, which are nonetheless many times preferable for their magnetic properties. Under drinking water treatment conditions, zero-valent nanoparticles usually result in efficiencies below 2 mg/g for both As(III) and As(V) (Kanel et al. 2005; Zhu et al. 2009; Gupta et al. 2012). However, an exceptional value of around 5 mg As(V)/g was reported for 15 nm Fe nanoparticles (Kanel et al. 2006). Magnetite and maghemite nanoparticles whether as single or surface-modified do not show significant adsorption capacities against arsenic. The highest reported capacities are estimated around 2 mg/g (Yavuz et al. 2006; Park et al. 2009; Lunge et al. 2014). The potential for magnetic separation also triggered some studies with other ferrite nanoparticles (Phu et al. 2009; Dey et al. 2014; Garcia et al. 2014). In one of the cases, MgFe₂O₄ nanoparticles showed very good results when tested in tap water (Tang et al. 2013).

Some other metal oxides nanoparticles have been recently introduced in drinking water treatment technology. A separate case is TiO₂ nanoparticles since it came as the first commercial product based on nanoparticles for drinking water treatment against arsenic. Its activity is based on the photocatalytic properties and the fast kinetic it succeeds, though it is to be noted as a disadvantage the requirement for sun or UV lamp illumination. Indeed, when exposed to light, TiO₂ nanoparticles showed significant capacities, especially for As(III) which is most difficult to capture. In particular, aggregated TiO₂ nanoparticles achieved an efficiency of around 4 mg/g for both As(III) and As(V) in groundwater (Jing et al. 2009) with this value falling to 1.2 mg As(V)/g (Sun et al. 2007) and to 2 mg As(V)/g when combined with γ -Fe₂O₃ nanoparticles (Yu et al. 2013). Improved efficiencies were reported for CeO₂ and ZrO₂ nanoparticles.

Surprisingly, cerium oxide nanoparticles presents the best capacities among any kind of nanoparticles reaching 13.5 mg As(III)/g in distilled water (Li et al. 2012; Sun et al. 2012). Zirconia nanospheres or particles have a lower but not negligible removal ability (Hang et al. 2012; Cui et al. 2013) but when combined with CeO₂ ones they produce by far the maximum available performance of 27.1 mg As(V)/g (Xu et al. 2013).

Antimony Antimony is classified as a very toxic compound for water supplies as signified by its low MCL of 5 µg/L. However, compared to arsenic, not much attention has been dedicated in the understanding of its chemistry in correlation to the development of proper treatment methods for polluted water delivered for drinking purposes. This is explained by the lower frequency of Sb detection than As, due to its limited solubility, and the absence, until recently, of regular sampling control by authorities. Literature presents very few examples of antimony removal from water by inorganic nanoparticles. Some of them show a potential to decrease concentration at the levels of the MCL but they refer only to Sb(III) species. More specifically, hematite-coated Fe₃O₄ nanoparticles showed a removal capacity of around 1 µg Sb(III)/g at the MCL (pH 7) (Shan et al. 2014), while FeOOH nanospheres were able to capture around 3 mg Sb(III)/g when tested in natural-like water in both batch adsorption and column experiments (Simeonidis et al. 2017b). Titanium oxide nanoparticles indicated a removal capacity of around 0.8 µg Sb(III)/g though this value was obtained under variable pH conditions between 10 and 5 while the efficiency of corresponding chitosan-coated TiO₂ nanoparticles was practically zero (Nishad et al. 2014). In any case, none of the reported systems presented any efficiency against Sb(V).

Technical and economic aspects

Acceptance of nanoparticles-based technologies for the removal of heavy metals during drinking water treatment does not only require the development of the proper materials. Qualified nanoparticles should be able to deliver their nominal efficiency under the intense conditions met in real processes while being adopted by properly designed facilities sometimes very different than the conventional ones. At the end, the competitiveness of the system will be judged by the overall cost defined not only by the nanoparticles price but also by the capital investment, the maintenance and the operational cost. Furthermore, environmental and technical limitations or even the social impact may determine the promotion of nanoparticle-assisted water purification.

A fundamental task of laboratory research is the optimization of synthesized nanoparticles in order to acquire the

appropriate features with respect to the heavy metal forms which are expected to remove. Surface configuration is the most advantageous property for using nanoparticles instead of conventional materials. The tuning of such properties is usually performed during synthesis of nanoparticles especially when aqueous methods are preferred. Optimum conditions of synthesis for a specific nanoparticulate system are the key to decrease operational cost as soon as the effective lifetime of nanoparticles can be significantly extended. However, selecting to work with nanoparticles consisting of low-cost phases, even with some deduction in removal capacity, should be always considered and balanced. For example, it is unreasonable to use Au nanoparticles for large-scale mercury uptake, in spite of their extremely high efficiency, because their cost is exclusionary.

The intense conditions met in real processes are another critical factor. Preliminary tests should be carried out to identify whether nominal efficiency is preserved in a water matrix with acidity, redox potential and interfering/competing ions similar to those of a typical drinking water resource. The exact behavior of qualified nanoparticles at the initial concentration levels of the pollutant and the targeted MCL should be also considered.

The determination of an appropriate setup which implements nanoparticles contact with the polluted water is another major requirement. Nanoparticles can be used whether aggregated, supported or dispersed. In the first two cases, traditional packed bed filters are the ideal way of application taking the advantage of the longtime technical experience of their design and operation together with the compatibility of their adoption in the water treatment line. Things become more complicated when nanoparticles are going to be dispersed in the polluted water. Recovery of nanoparticles is possible by membranes (Stancel et al. 2015) or by the application of an external magnetic field. It is clear that the numerous research works with magnetic nanoparticles point not only to the low cost of these phases but to the option for their magnetic recovery as well (Westerhoff et al. 2016). An example of magnetic separation of nanoparticles after their use in heavy metals removal was reported by (Mayo et al. 2007) where the suspension flowed through a vertical column located in a high-gradient magnetic field generated by an electromagnet. Furthermore, a continuous-flow system consisting of a contact tank sequenced by a horizontal tube placed between permanent magnets was tested for Cr(VI) removal by Fe_3O_4 nanoparticles (Simeonidis et al. 2015).

Finally, since water adsorbents are usually considered as consumables being regularly replaced after reaching their effective lifetime, the safe handling of saturated nanoparticles should be a priority. Their disposal in organized landfills is controlled by strict legislation demanding a laboratory study of leaching potential under specific experimental

protocols (California Office of Administrative Law 1985; U.S. EPA 1986; European Standard EN 12457-4 2002). Failure to provide evidence that nanoparticles can be handled as an inert waste would have a dramatic impact in the viability of developed technology since the inertization process can multiply the overall cost to the customer.

Fate in soil and aquatic systems

The importance of understanding the effects that engineered nanoparticles can display in the environment through potential accidental releases has generated multiple research initiatives that try to shed light on this matter (Bernhardt et al. 2010). In addition, atmospheric emissions from waste incineration (Tourinho et al. 2012), and sludge from wastewater treatment units (Sánchez et al. 2011; Pan and Xing 2012), are two examples of pathways that contribute prominently to soil and water pollution with engineered nanoparticles (Klaine et al. 2008). In the case of nanoparticles used as water adsorbents, the strength of pollutants' adsorption is an extra parameter dealing with the environmental issues raised for spent nanoparticles loaded with extremely high pollutant quantities.

The effects of nanoparticles are already present at the most tiny organism; it has been independently stated the ecological effect of CuO and Fe_3O_4 nanoparticles (Ben-Moshe et al. 2013) and TiO_2 and ZnO (Ge et al. 2011) at reducing the microbial biomass and altering the bacterial composition of soils. Changes in the nanoparticle context from the controlled manufactured origin to the reactive organic final fate are likely to modify their physicochemical properties (composition, size, stability, etc.) (Rivera-Gil et al. 2013; Wang et al. 2016). In this regard, the aqueous, non-toxic organic matter (humic, fulvic and tannic acids) present in water and soils plays a key role. The particular details of the interaction between organic matter and the engineered nanoparticles will promote aggregation/agglomeration, sorption to surfaces, surface transformation and/or dissolution to the ionic metal (Tourinho et al. 2012; Batley et al. 2013; Wang et al. 2016), thus modifying their dissemination and impact on biosphere (Anjum et al. 2013). The preservation of the particle stability increasing their ability to disperse in the different media is another possible scenario.

For instance, it is worthy to mention the special ionic strength conditions of marine systems, which ease aggregation/agglomeration processes (Klaine et al. 2008). And therefore, physiological alterations of mussel *Mytilus galloprovincialis* due to the ingestion of agglomerated TiO_2 and SiO_2 have been reported. Additionally, Ag and ZnO nanoparticles were described to be toxic for phytoplankton and diatoms such as *Thalassiosira pseudonana*, *Cyclotella gracilis*, and *Phaeodactylum tricornutum*. Afterward, humans

could be exposed to those nanoparticles through trophic transference (Matranga and Corsi 2012).

The major mechanisms that nanoparticles can induce toxicity at cellular level are generation of reactive oxygen species, cell membrane interaction/damage by particles sorption, retention of electrons produced in cell energy generation processes, and alternation of cell signaling pathways by their sorption onto proteins (Pan and Xing 2012). Batley et al. reported the disruption of membrane transport mechanisms due to adsorption of ZnO, CeO₂, Ag, Zn²⁺, Ce³⁺, Ag⁺ on the cell membrane of the freshwater algae *Pseudokirchneriella subcapitata* (Batley et al. 2013). Despite these findings, no effect on photosynthesis efficiency was detected upon TiO₂, ZrO₂, Al₂O₃, and CeO₂ nanoparticle interaction.

Regarding the interaction of engineered nanoparticles with plants, metal oxide nanoparticles can influence their growth and development. Once the plants absorb nanoparticles from the soil, they may be distributed along the leaves, stem, roots and fruits, to the interstitial/intracellular space. As a result, main plant processes can be deregulated by events such as activation of the oxidative stress signaling (Hossain et al. 2015), alterations in microRNAs or DNA. Examples of DNA damage are the case of radish (*Raphanus sativus*) and ryegrass (*Lolium perenne* and *Lolium rigidum*) after exposition to CuO nanoparticles. Interestingly, maize plants can reduce CuO to Cu₂O and Cu₂S, and cucumbers, lettuces, soybean pods and kidney beans can biotransform CeO₂ into Ce(III) and Ce(IV) species (Zhang et al. 2012; Du et al. 2016), which opens the door to bioremediation mechanism (Siddiqi and Husen 2017).

Despite the efforts made to understand engineered nanoparticles fate and behavior in different environmental scenarios, standardization of protocols and more research are needed to ease a quantitative assessment of the ecological risk (Sánchez et al. 2011).

Conclusions

The application of engineered inorganic nanoparticles for the purification of drinking water is a very ambitious perspective of nanotechnology aiming the improvement of an everyday human need and a fundamental sustainability element. The present review attempts to bring a summary of the current knowledge on the field by considering the many different aspects that should be handled for a successful and safe implementation of nanoparticles for heavy metals removal. For the first time, to our knowledge, reported studies are evaluated under the prism of their potential to produce nanoparticles able to comply with the demands of drinking water technology and to become competitive to existing technologies. In particular, whenever applicable, given results of laboratory removal

experiments are projected to the corresponding maximum contaminant level so as to provide a direct estimation of the uptake capacity for the tested nanoparticles.

Conclusively, an overview of the up-to-date research related to the removal of emerging heavy metals met in drinking water sources, indicates only a very small amount of effort directed to realistic solutions for drinking water treatment based on nanoparticles. This gap should be attributed to the absence of common experimental protocols and universal methods for the evaluation of obtained results. Working independently on the design of nanoparticles aiming ideal compositions and morphologies or conversely testing nanomaterials in heavy metals adsorption without providing a feedback for the optimization of their features is not the proper strategy. Interdisciplinary projects employing experts from materials science, surface chemistry and water technology appear as the only valid way to understand uptake mechanisms, tune the properties and adapt nanoparticles to conventional or even novel water treatment schemes.

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