# Remediation of mercury contaminated saltwater with functionalized silica coated magnetite nanoparticles

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## HIGHLIGHTS

- Magnetic NP was efficient for Hg removal from single or multi contaminated seawater.
- Hg removal rate in the presence of As and Cd remained unaffected.
- Chemical remediation provoked a decrease in water toxicity to some species.
- Microalgae *Phaeodactylum tricornutum* appears to be the most sensitive to the tested solutions.

## GRAPHICAL ABSTRACT
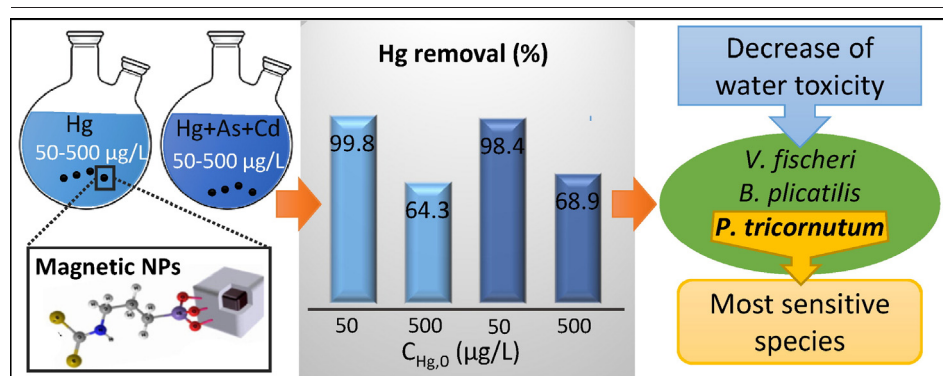


## ARTICLE INFO

## ABSTRACT

The study aimed to evaluate the efficiency of dithiocarbamate functionalized silica coated magnetite nanoparticles (NPs) for Hg decontamination of saltwater either contaminated with Hg alone or with As and Cd. For this, the residual levels of Hg in seawater were assessed and Hg-contaminated or Hg + As + Cd-contaminated seawater toxicity to aquatic biota, before and after the sorption process, was compared. The results showed that under highly competitive conditions (water salts, Cd and As), the removal of Hg from seawater, by using these magnetic NPs, for the lowest concentration (50 μg/L) was superior to 98% and for the highest concentration (500 μg/L) ranged between 61% to 67%. Despite the great affinity of the magnetic NPs for Hg, they were not effective at removing As and Cd from seawater. In relation to the ecotoxicity endpoints after remediation, the mixture with lower Hg concentration exhibited no toxicity to rotifer *Brachionus plicatilis* and bacteria *Vibrio fischeri*; however, the mixture with higher concentration revealed toxicity. In addition, the toxicity of bacteria *V. fischeri*, rotifer *B. plicatilis* and algae *Phaeodactylum tricornutum*, whose responses where inhibited during its exposure to the non-remediate sample was considerably reduced after treatment with NPs. Furthermore, microalgae *P. tricornutum* appears to be most sensitive species while *Artemia franciscana* showed no toxic effects to the tested solutions. Both chemical and ecotoxicological approaches revealed a high efficiency for the remediation of Hg-contaminated saltwater.

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## 1. Introduction

Mercury (Hg) is one of the most hazardous contaminants reported in aquatic environments (Chételat et al., 2015; Lillebø et al., 2011; Pereira et al., 2009), being among the highest priority environmental pollutants in the scope of the European Water Framework Directive (WFD) and on a global scale (Pereira et al., 2009). Most Hg enters aquatic systems in its inorganic form *via* anthropogenic point discharges, mostly related to chlor-alkali plants, mining activities or through diffuse sources (Lillebø et al., 2011). Despite the existing restrictions on anthropogenic sources of Hg, historically contaminated sediments may still constitute a source of Hg to the aquatic environment and consequently to the biota (Taylor et al., 2012; Covelli et al., 2012; Ma et al., 2013).

Once in the biota, several processes may occur, namely the increase of Hg concentrations through the trophic web (biomagnification), which makes predators and consumers particularly susceptible (Coelho et al., 2008; Pereira et al., 2009; Lillebø et al., 2011; Sandheinrich and Weiner, 2011). Mercury toxicity causes behavioral, reproductive, and genotoxic effects in aquatic fauna. Specific symptoms include decreased feeding behavior (Berntssen et al., 2003), decreased feeding efficiency (Fjeld et al., 1998), decreased shoaling behavior (Webber and Haines, 2003), and impaired immune and reproductive system function (Hammerschmidt et al., 2002; Sandheinrich and Miller, 2006; Drevnick and Sandheinrich, 2003; Drevnick et al., 2006) in aquatic organisms (Sandheinrich and Weiner, 2011). A study evaluating the risk posed by trace metals on the culture of seawater bivalves reflected that the Hg is the most toxic among others trace metals for bivalve embryogenesis (Beiras and Albentos, 2004). The high toxicity of Hg, mainly in organic forms, is related to its high affinity to sulphide groups (Guzzi and La Porta, 2008), binding readily to proteins and disturbing the functions where they are involved. Furthermore, its lipophilicity allows it to pass through lipid membranes of cells and facilitates its distribution to all tissues (EPA, 2001).

Keeping in view the previous toxicity aspect, it is equally important to study the complex phenomena controlling the transference of Hg to seawater organisms and develop new techniques for its removal from waters. Various technologies such as ion exchange, reverse osmosis, adsorption, precipitation, membrane filtration and flocculation have been reported for the removal of Hg from water (Lopes et al., 2014a; Lopes et al., 2014b; Zhou et al., 2013; Urgun-Demirtas et al., 2012; Lopes et al., 2009). Each of these processes present advantages and disadvantages. Although some of these technologies are simple, rapid, quantitative and selective under proper conditions, some require high-energy or large quantities of chemicals that involves high operating and maintenance costs and expensive equipment. Others produce large volumes of solid wastes (*e.g.* precipitation) generating toxic residual sludge, which give rise to another major problem that is the disposal of toxic sludge (Monteagudo and M.J., 2000; Pacheco et al., 2006), and, finally, others do not achieve the target concentrations after treatment since the Hg removal is incomplete. Chemical precipitation, ion-exchange and adsorption are probably the three processes most used for the removal of Hg from contaminated water (Fu and Wang, 2011).

Recently, nanoparticles (NPs) have emerged as new class of sorbents for recovery, separation and/or pre-concentration of metals. Ngomsik et al. (2005) wrote a mini review on the application of magnetic nano and microparticles in the removal of metals in wastewaters. In particular, magnetic iron oxides such as magnetite ($Fe_3O_4$) and maghemite ($\Upsilon$-$Fe_3O_4$) have been investigated intensively for Hg removal from water (Girginova et al., 2010; Li et al., 2011; Hakami et al., 2012; Figueira et al., 2011; Tavares et al., 2013; Zhang et al., 2013; Rahbar et al., 2014; Shan et al., 2015; Zhang et al 2015; Mehdinia et al., 2014). Recently, Shan et al. (2015) reported the synthesis of $Fe_3O_4@SiO_2$ magnetic nanoparticles modified by grafting poly(1-vinylimidazole) oligomer as a novel adsorbent to remove Hg(II) from water. This material showed a high adsorption capacity toward the metal that was not inhibited with the increase of ionic strength. Tavares et al. (2013) explored the sorption efficiency of the synthesized magnetite particles coated with siliceous shells and with different degree of dithiocarbamate functionalization in the removal of Hg ions from aqueous solutions by magnetic separation, while Figueira et al. (2011) also took advantage of the high affinity between Hg and sulphur, and used magnetite ($Fe_3O_4$) NPs functionalized with dithiocarbamate groups as a new type of sorbent to remove Hg(II) from synthetic and natural spiked waters. These studies, like most of the approaches driven in the field of water treatment, aim only the quantification of the residual levels of metals and the amount of the metal effectively sorbed by the material applied (Lopes et al., 2009; Lopes et al., 2011; Girginova et al., 2010; Figueira et al., 2011; Tavares et al., 2013). However, chemical analysis alone is not suitable to test for water good quality status, therefore, it is important to establish a cause-effect relationship between the concentration of chemicals and consequent environmental damage. Thus, for a proper evaluation of the feasibility of a water treatment, an approach combining both chemical and ecotoxicological assays should be designed, and to the best of our knowledge, the studies following this approach on the subject of reducing or eliminating the toxicity of waters contaminated with metals are scarce (Mishra and Tripathi, 2008; Lopes et al., 2014a; Rocha et al., 2014) or inexistent for salt waters.

Moreover, particular attention is also required to understand the efficiency of removal technologies under more realistic conditions for example in the presence of other contaminants like arsenic (As) and cadmium (Cd) since they are non-essential elements and due to their persistent nature and tendency toward bioaccumulation are rated among the most hazardous potentially toxic elements. Cadmium is classified as "priority hazardous substance" by the European Union water framework directive (http://ec.europa.eu/environment/water/water-framework/index_en.html) and As occupies the first position in the ATSDR, Agency for Toxic Substances and Disease Registry (2011)Substance Priority List (http://www.atsdr.cdc.gov/spl/index.html).

Thus, the main question of this study was to known the real efficiency of dithiocarbamate functionalized silica coated magnetite NPs as a saltwater decontamination material toward Hg, in absence and presence of other hazardous contaminants (As and Cd).

In order to answer to this question a combined chemical and ecotoxicological approach was designed. This approach included the assessment of the residual levels of Hg in seawater, the modelling of the sorption process, and the evaluation of the seawater toxicity to biota before and after the proposed treatment. The toxicity measurement was carried out through a battery of bioassays, with organisms from different taxonomic groups and exhibiting different key functions at the ecosystem levels, namely the bacterium *Vibrio fisheri* (decomposer), the green algae *Phaeodactylum tricornutum* (producer), the rotifer *Brachionus plicatilis* (primary consumer) and the *Artemia franciscana* (primary consumer). The selection of these species was based on the fact that they are available at low cost, easy to maintain in the laboratory, have been widely used in other ecotoxicological studies as model species, and (ideally) have commercial or ecological importance (Widdows, 1993). Additionally, the possible toxic effects caused by the NPs applied in the decontamination process will also be contemplated. Moreover, the use of a natural seawater instead of a synthetic one allowed us to achieve conditions close to the ones found in aquatic systems and to evaluate the influence posed by this natural matrix (chemically very complex) on the speciation and dynamics of Hg, that can eventually hinder or enhance the sorption process and as well the toxicity to biota.

## 2. Materials and methods

### 2.1. Experimental design

The efficiency of dithiocarbamate functionalized silica coated magnetite NPs ($Fe_3O_4@SiO_2/SiDTC$) in the remediation of spiked seawater was evaluated in four different scenarios, according with the details in Table 1.