Science of the Total Environment 565 (2016) 165–180

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Review

Bio-rescue of marine environments: On the track of microbially-based metal/metalloid remediation

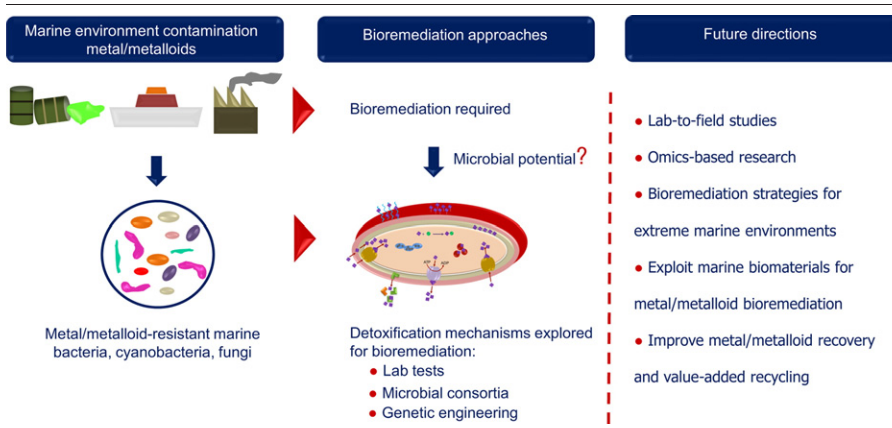
Catarina R. Marques

Departamento de Biologia & CESAM, Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

HIGHLIGHTS

- Marine microbes have metal/metalloid detoxification paths useful for bioremediation.
- Biotic and abiotic factors limit metal/metalloid (*in situ*) bioremediation efficiency.
- Microbial consortia and engineering can enhance bioremediation in marine environments.
- Lab-to-field studies on metal/metalloid microbial remediation are urgently demanded.
- Omics have been fulfilling knowledge gaps on resistance mechanisms of marine microbes.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 March 2016
Received in revised form 17 April 2016
Accepted 18 April 2016
Available online xxxx

Editor: D. Barcelo

Keywords:
Bacteria
Cyanobacteria
Fungi
Detoxification pathways
Microbial consortia

ABSTRACT

The recent awareness of the huge relevance of marine resources and ecological services is driving regulatory demands for their protection from overwhelming contaminants, such as metals/metalloids. These contaminants enter and accumulate in different marine niches, hence deeply compromising their quality and integrity. Bioremediation has been flourishing to counteract metal/metalloid impacts, since it provides cost-effective and sustainable options by relying on ecology-based technologies. The potential of marine microbes for metal/metalloid bioremediation is the core of many studies, due to their high plasticity to overcome successive environmental hurdles. However, any thorough review on the advances of metal/metalloid bioremediation in marine environments was so far unveiled. This review is designed to (i) outline the characteristics and potential of marine microbes for metal/metalloid bioremediation, (ii) describe the underlying pathways of resistance and detoxification, as well as useful methodologies for their characterization, (iii) identify major bottlenecks on metal/metalloid bioremediation with marine microbes, (iv) present alternative strategies based on microbial consortia and engineered microbes for enhanced bioremediation, and (v) propose key research avenues to keep pace with a changing society, science and economy in a sustainable manner.

Abbreviations: BMFCs, benthic microbial fuel cells; DGGE, denaturing gradient gel electrophoresis; EPSs, extracellular polymeric substances; GST, glutathione S-transferase; MS, mass spectrometry; MTs, metallothioneins; NGS, next generation sequencing; NMR, nuclear magnetic resonance; PCR, polymerase chain reaction; SRB, sulfate-reducing bacteria; T-RFLP, terminal restriction fragment length polymorphism.

E-mail address: crmarques@ua.pt.

http://dx.doi.org/10.1016/j.scitotenv.2016.04.119
0048-9697/

Contents

1. Introduction . . . 166
2. Microbial resistance mechanisms & potential . . . 166
2.1. Uptake and efflux . . . 167
2.2. Extracellular sequestration . . . 167
2.3. Intracellular sequestration . . . 172
2.4. Biotransformation . . . 172
3. Bottlenecks on metal/metalloid bioremediation . . . 174
3.1. Interfering factors . . . 174
3.1.1. Abiotic . . . 174
3.1.2. Biotic . . . 174
3.2. Limitations of in situ bioremediation . . . 174
4. Alternatives for enhanced metal/metalloid bioremediation . . . 175
4.1. Microbial consortia and bioaugmentation/biostimulation strategies . . . 175
4.2. Engineered microorganisms . . . 175
5. Concluding remarks and future challenges . . . 177
Acknowledgements . . . 177
References . . . 177

1. Introduction

The marine environment has been increasingly subjected to metal and metalloid contamination, both due to natural occurrences (geochemical processes) and anthropogenic activities. Among the latter, shipping, accidental spills, mine activities, waste disposal, fossil fuel extraction, dredging, urbanization, agricultural practices and industrial processes are major sources of direct (i.e., open sea effluent discharges) and/or indirect (i.e., land-based river runoff and groundwater discharges) input of metals, metalloids and metallic radionuclides into the sea (Machado et al., 2016). These inputs reduce the quality of seawater and sediments, especially in coastal areas (e.g., estuaries), which are strongly exposed to human pressure and may present high metal burdens (Ortega-Morales et al., 2010). An additional concern is the environmental persistence and accumulation of metals/metalloids in marine food webs, thereby posing serious risks to wildlife and marine ecosystem services (Deng and Wang, 2012). This is particularly worrying for toxic metals and metalloids (e.g., Cd, Pb, As, Hg), while essential metals can also become noxious if above optimal concentrations (e.g., Cu, Zn, Fe) (Valls and de Lorenzo, 2002; Machado et al., 2016). The fate, bioavailability and toxicity of a metallic/metalloid element depend on its chemical speciation, and biotic- (e.g., microbial transformations) and abiotic-mediated processes (e.g., organic content, pH, temperature) (Dell'Anno et al., 2009). Based on these traits, Hg, Cd, Cr, As, Pb are considered to be priority elements for the quality of seawater and marine sediments (UK Marine SACs Project website, 2016), and have been the target of many remediation programs or studies (Daffonchio et al., 2012). Furthermore, recent European legislation (e.g., Directive 2008/56/EC) encourages the implementation of measures to protect and conserve marine ecosystems that in part is to be achieved through the development of metal/metalloid removal strategies (Ali et al., 2015).

Conventional metal/metalloid remediation techniques are usually directed to marine sediments, since these are the major sink of metal/metalloid accumulation. They consist of sediment dredging, natural recovery, *in situ* capping, and *in situ* confined aquatic disposal (Akcil et al., 2015). These methods are, however, quite destructive, time-consuming and expensive. Besides, they turn out to fail often, particularly when metal concentrations are low (1–100 mg L^{-1}) (Ali et al., 2015). An up-to-date and sustainable alternative is the use of bioremediation techniques, which are broadly accepted due to their cost efficiency and ecological character associated with the exploitation of nature-based technology (Harms et al., 2011). In the literature can be found scattered studies on metal/metalloid bioremediation measures applied to the marine context , but a thorough overview is yet to be accomplished. For this reason, the present review will highlight major studies on the exploitation of marine microorganisms (and their derivative components), more specifically marine archeae, bacteria, cyanobacteria and fungi, for the bioremediation of marine environments contaminated with metals/metalloids. Additionally, it will be described the detoxification mechanisms underlying the bioremediation abilities of marine microorganisms, together with the most applied methods and techniques for their characterization. Enhanced bioremediation strategies based on marine microbial consortia and engineered microorganisms will be also herein covered. Overall, ranging from laboratory trials up to *in situ* approaches, this pioneer review intends to provide a fundamental basis for (re)defining future breakthrough frameworks that aim the creation of new scientific knowledge and innovative bioremediation methods for the sustainable rehabilitation of marine environments contaminated with metals/metalloids.

2. Microbial resistance mechanisms & potential

In order to prevent the occurrence of toxic effects from metal/metalloid exposure, the microorganisms have evolved physiological and biochemical resistance mechanisms to guarantee metal/metalloid homeostasis, detoxification and/or biotransformation (Huertas et al., 2014). Understanding these mechanisms and their genetic basis has been the focus of many works (e.g., Silver and Phung, 1996; Nies, 1999, 2003; Tsai et al., 2009; Gadd, 2010), which provide invaluable information for developing efficient bioremediation strategies. The researchers have been highlighting major resistance pathways in bacteria and fungi, either for avoiding metal/metalloid exposure or for reducing their bioavailability. Overall, metal/metalloid bioaccumulation by microbes may comprise essentially two uptake processes:

i) passive uptake - an initial non-metabolic and rapid metal/metalloid sequestration onto cellular structures, following their biosorption by electrostatic interaction with functional groups present at the cellular structures. This process includes chemical interactions like physical adsorption, ion exchange, chelation, complexation, precipitation and entrapment in the cell wall. It can be performed either by living or dead biomass;
ii) active uptake - a much slower process that requires the active transport of metals/metalloids across the membranes for their subsequent transformation and/or accumulation in the intracellular environment. This process only takes place in living cells once it is metabolism-dependent (Malik, 2004).