Chemosphere 182 (2017) 707–719

Contents lists available at ScienceDirect

Chemosphere

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

Review

Possible developments for ex situ phytoremediation of contaminated sediments, in tropical and subtropical regions – Review

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HIGHLIGHTS

- Phytoremediation for dredged sediments is successfully tested in temperate belt.
- We explore the possibility to implement systems based on the use of mangroves.
- Humic acids mitigate abiotic stress effects and improve remediation efficiency.
- A multidisciplinary approach could improve phytoremediation for dredged sediments.

ARTICLE INFO

Article history:
Received 16 September 2016
Received in revised form
23 March 2017
Accepted 20 April 2017
Available online 22 April 2017

Handling Editor: T Cutright

Keywords:
Avicennia
Humic acids
Peroxidase
Sediments
ROS
Auxin

ABSTRACT

The growing problem of remediation of contaminated sediments dredged from harbor channels needs to be resolved by a cost effective and sustainable technology. Phytoremediation, by *ex situ* remediation plants, seems to have the potential to replace traditional methods in case of moderately contaminated sediments. On the other side, the need to mix sediments with soil and/or sand to allow an easier establishment of most employed species causes an increase of the volume of the processed substrate up to 30%. Moreover the majority of phytoremediating species are natives of temperate climate belt. Mangroves, with a special focus on the genus *Avicennia* – a salt secreting species – should represent an effective alternative in terms of adaptation to salty, anoxic sediments and an opportunity to develop ex situ phytoremediation plants in tropical and subtropical regions. The use of humic acid to increase root development, cell antioxidant activity and the potential attenuation of the "heavy metals exclusion strategy" to increase phytoextraction potentials of mangroves will be reviewed.

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http://dx.doi.org/10.1016/j.chemosphere.2017.04.093
0045-6535/© 2017 Published by Elsevier Ltd.

1. Introduction

Since many decades harbors produce and accumulate contaminated sediments due to navigation and surrounding industrial and urban settlements activities (Taylor et al., 2004). Sediments dredging is necessary to prevent flooding and allow a normal shipping traffic, but it produces polluted substrates to be disposed avoiding risks of environmental contamination. Contaminated sediments annual world production is estimated in ten millions of m^3 (Bortone et al., 2004; Le Guyader, 2013). Brazil, a country characterized by a rapid economic growth, is modernizing and reorganizing ten harbors: among those sediment dredging is carried on in Itaguaí harbour (RJ), Itaiaí harbour (SC), Maceió harbor (AL) and many others (http://www.pac.gov.br/infraestrutura-logistica/portos, 2016). In this scenario sediment decontamination lays on the top of environmental priorities and needs to develop a sustainable solution, in terms of safe disposal, clean up and recycling of dredging products. Physical, chemical, and thermal decontamination treatments are not cost effective nor ecofriendly as they employ a great quantity of energy and dangerous chemical reagents to remove contaminants and due to the huge amount of sediments that must be treated every year (Robinson et al., 2000; Pollard et al., 2002; Lors et al., 2004; Meers et al., 2005). The phytoremediation technique, consisting in the use of photoautotrophic vascular plants to remove (phytoextraction), inactivate (phytostabilization) or destroy (phytodegradation) inorganic and organic contaminants, starts to be considered as an ecological and economic effective option. It is up to 25 times cheaper than chemical and thermal treatments (FRTR, 2007; Wan et al., 2016) and sustainable for a natural way to clean up contaminated sediments (Ghosh and Singh, 2005; Doni et al., 2013). There are two main sediment remediation techniques: *ex-situ* and *in-situ*. *In-situ* remediation involves treating contaminants on-site, whereas *ex-situ* requires physically extracting media from a contaminated site and moving it to another location for treatment. Both techniques have specific benefits and costs: *in-situ* remediation, although less efficient, is preferred due to the high costs of excavation and transport of polluted media needed for *ex-situ* remediation and the concomitant risk of contaminant mobilization (Kuppusamy et al., 2016). However, harbor sediment dredging is continuously applied worldwide and dredged material is only feasible for *ex-situ* techniques. Nowadays the standard model for an ex-situ phytoremediation facility is basically constituted by an open-air tank isolated from soil by a plastic layer on the bottom, a drainage system done with PVC tubes and a coarse draining layer placed between plastic membrane and sediments and an irrigation system to facilitate plant growth and sediment desalination; this facility could also be placed in a harbor sediment tank (Iannelli and Masciandaro, 2012). As demonstrated by several pilot scale experiments carried on with the settlement described above, selected plant species help to convert moderately contaminated sediments into a matrix with characteristics similar to those of a natural soil (Bianchi et al., 2010a,b, 2011), defined as techno-soil (Lehmann and Stahr, 2007). Furthermore many works demonstrate effectiveness of soil phytoremediation for different classes of pollutants, like oil hydrocarbons and heavy metals (Padmavathiamma and Li, 2007; Bandiera et al., 2009; Vamerali et al., 2010; Macci et al., 2012): Doni et al. (2013) reported in a two years treated harbor sediments a decrease of 20% in Pb, Cr, Zn and Ni and of 50% of polyaromatic hydrocarbons. Vervaeke et al. (2003) demonstrated that willows planted in contaminated river sediments are able to extracts heavy metals and degrade polyaromatic hydrocarbons: Pb decreased in 18 months from 240 mg/kg down to 142 mg/kg, Zn from 662 to 447 mg/kg, Cd from 4,6 to 3 mg/kg. Authors suggest that, with 11 rotations in 3 years, a 40% of Cd concentration cut off is feasible, leading to values under law limits.

The evolution of sediments begins since the moment of dredging. Once placed in an aerobic environment, several parameters start to change: in anoxic sediments, contaminants such as As, Zn, Cd, Pb, Se, Ni are often in thermodynamic equilibrium under reducing conditions, and generally form various sulfur compounds depending on oxygen conditions (Caille et al., 2003; Lions et al., 2010; Popenda, 2014). The mineralization of organic matter, which plays an important role in the mobility of metal ions, is slow in anoxic environments and tends to accumulate in sediments (Couvidat et al., 2017). Dredging operations induce aeration and, as a result, deeply change redox conditions, owing to a shift from an anoxic to oxic environment. Exposure of sediments to aerobic conditions results in a sequence of oxidative reactions, leading to a decrease in pH, an increase in redox potential, an increase in sulfate levels in the water, and solubilization of the most cationic metals (Popenda, 2014). In dredged sediments, where phytoremediation occurs, the mobility of toxic metals in sediment can be influenced by a variety of factors, including, pH, redox potential (Eh), Ca/Fe/Mn/Al/P and natural organic matter content, sediment size, microorganisms (Li and Cai, 2015), and cation exchange capacity (Bert et al., 2009). Redox conditions as well as the pH are considered to be of prime importance in determining the mobility of trace metals from sediments (Zhong et al., 2011). These parameters affect processes related to metal binding, such as sorption and desorption to soil particles, formation and dissolution of carbonate bound metals, formation and decomposition of soluble and insoluble metal organic complex compounds, formation and dissolution of hydroxides and oxyhydrates, sorption and co-precipitation of metals by Fe/Mn-oxides, particularly in oxidic environments at neutral pH, precipitation of metal sulfides in strong reducing environments, and dissolution as sulfates under oxic conditions (Popenda, 2014). Natural organic matter could play a dual role in metal mobility by either resulting in higher environmental availability of heavy metals in the pore water, in particular under moderately acidic up to alkaline conditions (Kim et al., 2015) or binding with metals which would then be retained in sediment (Li and Cai, 2015). Plants may promote metal immobilization or availability due to different interactions with soil/sediments: *Arabidopsis halleri* enhanced metal sulfide oxidation probably due to both abiotic and biotic processes, that were enhanced by the plant activity (Huguet et al., 2015). Mangrove species can release phenols into the rhizosphere trough roots turn over and decomposition: this process can increase the acid volatile sulfides that, in anoxic conditions, can bind several metal ions. For example Cd can replace Fe in metal-sulphides reducing its own bioavailability but increasing Fe bioavailability (Li et al., 2016). On the other hand the oxygen supplied to rhizoshpere by mangrove roots aerenchyma, coupled with sediment oxygenation caused by dredging, can rapidly oxidize sulfides and limits metal precipitation (Jacob and Otte, 2003).

The soil or sediment texture is an important factor in heavy