Review

A review of approaches and techniques used in aquatic contaminated sediments: metal removal and stabilization by chemical and biotechnological processes

Ata Akcil, Ceren Erusta, Sevda Ozdemiroglu, Viviana Fontib, Francesca Beolchini

Mineral-Metal Recovery and Recycling Research Group, Mineral Processing Division, Department of Mining Engineering, Suleyman Demirel University, TR32260 Isparta, Turkey
Department of Life and Environmental Sciences, Università Politecnica delle Marche, Via Brecce Bianche, 60131 Ancona, Italy

Abstract

The contamination of aquatic sediments with metals is a widespread environmental problem. Coastal aquatic ecosystems with low hydrodynamics need to be periodically dredged in order to maintain the navigation depth and facilitate sailing; consequently large volumes of contaminated sediments need to be managed. Conventional remediation strategies include in-place sediment remediation strategies (e.g. in situ-capping) and relocation actions; in particular, landfill disposal and dumping at sea are still widely applied. Both these options are becoming unsustainable, due to problems associated with contaminant transport pathways, the uncertainties about long-term stability under various environmental conditions, the limited space capacity, costs and environmental compatibility. Alternative approaches have received increased attention; treatment and reuse of contaminated sediments is politically encouraged, but its application is still very limited. Because of the potential human health and environmental impacts of contaminated sediment, different chemical treatments are conventionally applied for contaminated sediments before reuse in other environmental settings. Environmentally friendly techniques developed for soils and other environmental matrices have been investigated for applications with sediments. Biotechnological approaches are gaining increasing prominence in this field and they are often considered as a promising strategy for the eventual treatment of contaminated sediments. In this paper an overview of the main treatment strategies potentially available for sediment contaminated with metals is given, together with a brief overview of the issue associated with the problem of the sediment management.

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1. Introduction

The contamination of aquatic sediments is a global scale environmental problem, that national and international authorities and regulators have faced since the last two decades (Fürstner and Apitz, 2007; Apitz, 2008). Human’s activities and hydrographical characteristics are responsible for the accumulation of high concentrations of contaminants in estuaries, harbours, ports and coastal marine zones (Pellegrini et al., 1999; Tanner et al., 2000). In all the aquatic systems, the sediment is the compartment where particulate and dissolved substances in the water column (as well as contaminants) tend to accumulate, due to scavenger agents and adsorptive components (Mulligan et al., 2001a,b; Tabak et al., 2005; Peng et al., 2009).

The problem of contaminated sediment management is closely related to the need for periodical dredging activities for the maintenance of the navigational depth in ports and waterways, but also for remediation and flood management (Fürstner and Apitz, 2007; Rulkens, 2005; Agius and Porebski, 2008). This implies that very large volumes of contaminated sediment can be produced (e.g. around 100 to 200 million cubic metres per year in Europe, according to SedNet estimations) and need to be properly managed (Bortone et al., 2004). Landfill disposal, confined aquatic disposal or dumping at sea are still the most applied management strategies all over the world, despite they also offer several disadvantages (e.g. limited space capacity, costs, low or lack in sustainability and environmental compatibility; Bortone et al., 2004; Adriaens et al., 2006; Agius and Porebski, 2008). Among other management
strategies, the “natural attenuation” has become unsustainable, due to political and social reasons, as well as to a difficulty in quantifying contaminant transport events. Contaminated sediment remediation deals with either the removal or the control of contaminants from polluted environmental media in or under a land site, to protect human health and the environment (Hou et al., 2014). Conventional management/remediation strategies of polluted sediment involve either in-place actions or relocation actions. In the first group, those strategies that do not require dredging operations are included, like natural recovery, that consists in allowing that natural attenuation processes achieve remediation objectives without human intervention, and in-situ capping, where the sediment is isolated by the environment by inert or reactive barriers. In the other cases, dredging is followed by disposal in submerged or partially saturated facilities, landfill disposal or dumping at sea (Bortone et al., 2004; Adriaens et al., 2006). All these options offer several disadvantages (Bortone et al., 2004; Rulkens, 2005) and more environmentally sustainable alternatives (Agius and Porebski, 2008; Apitz, 2008) are needed. The application of in-situ capping and in-situ confined aquatic disposal are limited because of the uncertainties about long-term stability under various environmental conditions (Apitz, 2008; Juwarkar et al., 2010; Liu et al., 2001).

The ‘beneficial use’ of dredged materials is highly encouraged. Dredged sediment can be relocated in the same water system it came from, e.g. for maintenance of ditches and rivers. Nevertheless, such type of operations allows the relocation of small volumes and sediments are often too contaminated to be used as received. As a consequence, the treatment for decreasing pollutant concentration has become part of sediment management process (Bortone et al., 2004). Today, a particular attention is paid to identify the most effective treatments for dredged contaminated sediments, with purpose of beneficial reuse either in building industries or in beaches nourishment (Lee, 2000; Ahlf and Förstner, 2001; US EPA, 2005). Furthermore, also because of the potential human health impacts of contaminated sediment, a treatment may be required before reuse in another environmental setting (Barth et al., 2001). Many treatment strategies proposed for the remediation of metal contaminated sediments derive from techniques developed for soils, other environmental matrices or for solid urban and industrial wastes (Fig. 1). Nevertheless, the differences in the sediment properties compared to soils and solid wastes make the application very limited and often characterized by very high costs and low feasibility. The only technique really used is the separation of the sandy fractions (less polluted), in order to minimize the contaminated volumes that require dumping. Biotechnological approaches are object of an increasing attention, but in general clean-up procedures for the removal/recovery of metals from contaminated sediments refer still to laboratory- or pilot-scale studies. On the contrary, there is an urgent need for large scale, environmentally friendly and cost-feasible techniques, in order to allow sediment beneficial reuse. Cleaner production requires responsible environmental management and evaluating technology options (Radonji and Tominc, 2007). Researchers often need to evaluate different alternative designs for a given chemical and biological process and this evaluation procedure might contemplate the environmental impacts of each alternative. Therefore, depending on the chemical and biological process, the most relevant environmental aspects to be taken into account should be selected and researchers should evaluate the suitable treatments to obtain a final index that will serve as the basis for the final decision (Carvalho et al., 2014). Moreover, all studies demonstrate that further research is needed to assess the overall sustainability of the developed approaches, so that all the three aspects of triple bottom line are considered: social, economic and environmental (Kim et al., 2014).

The contamination in the sediment is often due to both organic and inorganic pollutants (mostly metals), but the latter are of sustained and growing concern in the field of water quality management: heavy metals are toxic, persistent and unlike organic pollutants they cannot be degraded (Zoumis et al., 2001; Sun et al., 2009). Very recently, development and implementation of techniques for metal removal from fresh water, estuarine and marine contaminated sediments are gaining prominence not only as tools for the management of an environmental problem, but also as a secondary source of base valuable metals and raw materials for metallurgy and other industries. In some special cases, the sediment of high priority areas can accumulate concentrations of base valuable metals much higher than areas with high anthropogenic pressure: it has been hypothesized that the recovery of some metals from the sediment of such sites could be economically feasible (Fathollahzadeh et al., 2014). This change of perspective about contaminated sediments could offer new strategies to solve the dilemma of the management sediment with reduced environmental footprints. Another very important point in the debate about dredged sediment management is the controversy between the so-called “conventional” technologies (based on chemical or physical approaches) and biotechnologies, which are based on the exploitation of microorganisms and/or their metabolic products. The former are usually considered as more efficient but also more costly, while biological strategies would offer environmentally friendly methods (especially when the contamination is mainly due to hydrocarbons) but they would require longer treatment time and uncertain efficiencies.

In this work, the newest findings about chemical and biological technologies for the removal/stabilization of metals from contaminated sediments are summarized.

2. Sediment contamination with heavy metals

Heavy metals from natural and anthropogenic sources can enter a natural aquatic system by a result of multiple processes: atmospheric deposition, erosion of the bed-rock minerals, in-stream of industrial effluents are just examples (Colacico et al., 2010; Perrodin et al., 2012). As mentioned above, the sediment is the compartment where heavy metals settle and accumulate, till reaching concentrations very higher than in the overlying waters (Goldsmith et al., 2001; Warren and Haack, 2001). Salomons and Stigliani (1995) postulated that the far less than 1% of the metal contaminants (and other pollutants) are dissolved in the water,
while more than 99% are stored in the sediment. Very often, adsorbed heavy metals are not readily available for aquatic organisms but the variation in physical and chemical characteristics (i.e., pH, salinity, redox potential etc.), natural resuspension phenomena, dredging activities and disposal actions may lead to the release of the heavy metals back to the aqueous phase, so that the sediment may become an important source of pollution (Singh et al., 2000; Jain, 2004; Juwarkar et al., 2010; Jain et al., 2012).

The sediment is a complex and heterogeneous matrix of many different components and phases (including crystalline minerals, hydrous metal oxides, salts, biogenic calcareous particles and organic substances (Usero et al., 1998; Brils, 2008) to which heavy metals associate by several mechanisms: particle surface absorption, ion exchange, co-precipitation and complexation with organic substances (Wang et al., 2010). Heavy metals deposited to the different geochemical fractions in the sediment, with different mobility. Since the composition of the sediment varies from site to site (due to the geology, hydrography, local climate and socioeconomic significance of the area (Preda and Cox, 2003; Perrodin et al., 2012), heavy metals distribute among various geochemical phases in a site-specific way and with different grade of adsorption and retention (Brils, 2008; Peng et al., 2008; Wang et al., 2010). As a consequence, the determination of their concentrations does not provide an accurate estimate of the magnitude of pollution and of the potential environmental impact (Chon et al., 2012; Okoro and Fatoki, 2012). An indication of the potential bio-availability of heavy metals is given indirectly by procedures of selective extraction (Quevauviller, 1998; Gleyzes et al., 2002; Ure et al., 2006). For this reason a wide number of studies have been aimed at identifying the partitioning of metal contaminants in areas of interest, like ports, lakes, estuaries and marine coastal zones with high anthropogenic pressure.

Unlike organic pollutants, heavy metals cannot be degraded but are infinitely persistent and cannot be subjected to biological and chemical degradation processes. Heavy metals can just be transformed in more soluble/insoluble substances and/or in less toxic species. For this reason, many remediation strategies attempt to increase either metal solubility (mobilization) or their stability, reducing their bioavailability (immobilization). Indeed, actions addressed to the speciation have consequences on solubility and transport properties, which together determine the bio-availability and affect their toxicity (Tabak et al., 2005; Van Hullebusch et al., 2005).

3. Physical–chemical strategies for toxic metal removal and stabilization from the sediment

The majority of the remediation strategies aimed at moving heavy metals away from the sediment are based on physical–chemical strategies, often implemented in other field, like mining or soil remediation (US EPA, 2005). These technologies attempt to transfer contaminants from the sediment particles to the solution phase, for a beneficial use of cleaned sediment.

An analysis of the scientific literature has pointed out that the strategies for the removal of heavy metals from the sediment can be roughly classified in 1) sediment washing techniques, aimed at solubilizing metal contaminants by aqueous solutions of extracting chemical reagents or chelating agents; 2) electro-chemical treatments, where metal cations are separated by applying a electromagnetic field; and 3) thermal treatments, in which dewatered or partially dewatered sediment is treated by heat (Table 1). Due to the nature of water ecosystems, physical–chemical strategies can be applied almost exclusively ex-situ/on-site.

Purely physical strategies (i.e., particle separation processes) find large application in soil remediation field (Dermont et al., 2008); nevertheless, when applied to sediment treatment, the physical techniques often come down to a simple gravimetric pre-treatment aimed at removing uncontaminated coarser fractions and at reducing the volume to be treated (Mulligan et al., 2001b). Indeed, heavy metal removal by particle separation processes is applicable only when metal contaminants are under particulate forms (discrete particles or metal-bearing particles (Dermont et al., 2008), while in natural aquatic sediments heavy metals are mostly present in sorbed forms (i.e., adsorbed or bound to the different geochemical phases) and their concentration levels are relatively low. The characteristics of the sediment usually do not allow the use of the physical approaches: usually, natural aquatic sediments have very poor hydraulic characteristics and too high content in organic matter or, anyway, the particle size is often too small for hydro-classifiers, gravity concentrators and centrifuges (Mulligan et al., 2001b; Bianchi et al., 2008). Flotation and ultrasonic-assisted extraction are physical techniques that appear to be feasible for ex-situ treatment of sediments but their actual application is highly affected by the particle size, that determines the efficiency (Cauwenberg et al., 1998; Meegoda and Perera, 2001; Kyllonen et al., 2004). However, physical properties of the sediment, like size, density, magnetism and surface hydrophobicity can be exploited in combined physical–chemical strategies (Peng et al., 2008).

Physical–chemical stabilization strategies have also been proposed as a in-situ/ex-situ remediation solution for sediments contaminated with metals. In this case, the aim of the treatment is to reduce the mobility rather to extract metals. Mineral-based amendments have been reported for contaminated soils (Xenidis et al., 2010) and, more recently, for contaminated sediments (Qian et al., 2009; Peng et al., 2009; Chiang et al., 2012). Among the various tested amendments, iron-bearing materials (e.g. zero-valent-iron, goethite, hematite, and ferrihydrite), other adsorbents such as alumino-silicates (clays, zeolites) and phosphate minerals (e.g. apatite) were demonstrated efficient to stabilize metals in polluted soils and sediments (Mamindy-Pajany et al., 2013). Mamindy-Pajany et al. (2013) have also upscaled the technique from the laboratory to field application, to assess the effect of hematite, zero-valent iron and zeolite on metal/semi-metal (As, Cd, Cu, Mo, Ni, and Zn) mobility in a marine sediment sample: the results of the pilot-scale experiment showed that Fe containing minerals at 5% amendment rate were sufficient to efficiently stabilize several elements in the dredged marine sediments. Owing to nano-material with higher reactivity and sorption ability than the same material of normal size, some nano-material (e.g. nano-hydroxiapatite, nanosized metal oxides) have also been very recently used as amendment to metal contaminated matrices (Zhang et al., 2010; He et al., 2013; Bolan et al., 2014).

3.1. Sediment washing

Sediment washing treatments are aimed to strip off contaminants at the surface of sediment particles and to remove soluble pollutants (Rulikens and Bruning, 2005); this involves two steps: the solubilization of metals and the removal of solubilized metals by washing the sediment with water (Löser et al., 2006, 2007). The physical action of high pressure water jets is combined with the chemical action of various type of additives, which enhance the performance of sediment washing (Dahrazma and Mulligan, 2007; Di Palma and Mecozzi, 2007; Peng et al., 2009): inorganic acids (e.g. nitric acid, sulphuric acid and hydrochloric acid), organic acids and chelating agents (e.g. acetic acid, citric acid, EDTA), surfactants (e.g. rhamnolipid).

Hydrochloric acid and nitric acid, and other inorganic acids, are known as effective in extract heavy metals from soil/sediments (Dermont et al., 2008). In particular nitric acid could be...
<table>
<thead>
<tr>
<th>Strategy</th>
<th>Site</th>
<th>Contaminants</th>
<th>Operating conditions</th>
<th>Efficiencies of treatment</th>
<th>References</th>
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</thead>
<tbody>
<tr>
<td><strong>Sediment washing</strong></td>
<td>Penrhyn Basin and Okinawa Trough</td>
<td>Fe, Mn</td>
<td>Mixtures of dilute hydrochloric acids (0.1–0.3 M) and hydrogen peroxide (1.5% with 0.25% surfactin from <em>Ricillus subliris</em> at 37 °C and pH control at 6.7)</td>
<td>83–100% Fe, 395–100 Mn</td>
<td>Chen et al. (1996)</td>
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<td></td>
<td></td>
<td>Cu, Zn</td>
<td>with 0.25% surfactin from <em>Ricillus subliris</em> at 37 °C and pH control at 6.7</td>
<td>70% Cu, 22% Zn</td>
<td>Mulligan et al. (1999)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu, Zn</td>
<td>70% of the copper with 0.1% surfactin/1% sodium hydroxide, 5100 of the zinc with 4% sophorolipid/0.7% hydrochloric acid at 4% sophorolipid solution with 0.7% hydrochloric acid (pH 5.4)</td>
<td>~100% of the Cu and Zn</td>
<td>Mulligan et al. (2001d)</td>
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<td></td>
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<td>Cu, Zn</td>
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<tr>
<td></td>
<td></td>
<td>Cu, Zn</td>
<td>Chelating agents: Ethylenediamine tetraacetate (EDTA), nitritolriacetic acid (NTA), citric acid and the SS-isomer of the ethylenediaminedisuccinic acid ([S,S]-EDDS)</td>
<td>78–86% Pb (with 0.02–0.2 M EDTA), 76% Cu (with 0.2 M EDTA), 585 Zn (using 0.2 M citric acid) and 55–85% Cd (with 0.02 M citric acid)</td>
<td>Polettini et al. (2006)</td>
</tr>
<tr>
<td><strong>Dredged sediments from the Italian port</strong></td>
<td></td>
<td>Cd, Cu, Pb, Zn</td>
<td>Chelating agents: Ethylenediaminedisuccinic acid (EDDS), EDTA, NTA, citric acid</td>
<td>70% Cu, 65% Zn, 98% Pb and 14% Fe using EDTA; 10% Cu, 82% Zn, 27% Pb and 40% Fe using citric acid</td>
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<td></td>
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<td>Cu, Zn</td>
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<tr>
<td></td>
<td></td>
<td>As, Cu, Zn, Pb</td>
<td>Chelating agents: EDTA and citric acid, end of 144 h</td>
<td>70% Cu, 65% Zn, 98% Pb and 14% Fe using EDTA; 10% Cu, 82% Zn, 27% Pb and 40% Fe using citric acid</td>
<td>Di Palma et al. (2012)</td>
</tr>
<tr>
<td><strong>Dredged sediments from an Italian harbour in the Tirrenian Sea</strong></td>
<td></td>
<td>Cu, Zn, Pb, Fe</td>
<td>Chelating agents: EDTA and citric acid, end of 144 h</td>
<td>70% Cu, 65% Zn, 98% Pb and 14% Fe using EDTA; 10% Cu, 82% Zn, 27% Pb and 40% Fe using citric acid</td>
<td></td>
</tr>
<tr>
<td><strong>Weisse Elster River sediments</strong></td>
<td>Heavy metals (sum of Zn, Ni, Cu, Cd, Cr and Pb)</td>
<td>With 624 mmol/kg sulphuric acid at 20 °C, on a rotary shaker at 130 rpm for 1 h</td>
<td></td>
<td>&gt;70% heavy metals</td>
<td>Löser et al. (2007)</td>
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<td><strong>Lachine Canal, Canada</strong></td>
<td>Cu, Zn, Ni</td>
<td>With adding 1% sodium hydroxide to 0.5% rhomnolipid EDTA, citric acid and humic substances (HS)</td>
<td></td>
<td>37% Cu, 13% Zn, 27% Ni</td>
<td>Dahrazma and Mulligan (2007)</td>
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<tr>
<td><strong>Port of Livorno (Italy)</strong></td>
<td>Cu, Zn</td>
<td>Range of pH 5–8</td>
<td></td>
<td>58% Cu, 50% Zn using EDTA (480 mg/l) and 32% Cu, 5% Zn, using HS (1000 mg/l), no significant effects with citric acid</td>
<td>Bianchi et al. (2008)</td>
</tr>
<tr>
<td><strong>Not available</strong></td>
<td>Zn, Hexachlorobenzene (HCB)</td>
<td>Used agents: EDTA, TritonX100</td>
<td></td>
<td>HCB 41%; Zn 30.0%</td>
<td></td>
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<tr>
<td><strong>Anconca port(Italy)</strong></td>
<td>Zn, Cr, Ni, As</td>
<td>Complexing agents: citric acid, oxalic acids and diluted sulphuric acid</td>
<td></td>
<td>About 50% for all metals</td>
<td>Beolchini et al. (2013)</td>
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<td><strong>Namhang (NH), Banggeejin (BE), and Haengam (HA) bay sediments, South Korea</strong></td>
<td>Cu, Pb, Zn</td>
<td>Used agents: EDTA</td>
<td></td>
<td>30%, 43%, and 9% of Cu; 48%, 66%, and 8% of Pb; 31%, 60%, and 14% of Zn from NH, BE, and HA sediments, respectively</td>
<td>Yoo et al., 2013</td>
</tr>
<tr>
<td><strong>Electro-chemical process</strong></td>
<td>Port of Haakonsvern, Bergen, Norway</td>
<td>Cu, Zn,Pb, Cd</td>
<td>Complexing agents: citric acid, lactic acid, in pH 7.5, lasting 14 days, and current strength 50 mA</td>
<td>67–87% Cu, 79–98% Cd, 90–97% Zn, 91–96% Pb</td>
<td>Nystroem et al. (2005)</td>
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<td></td>
<td>Port of Haakonsvern, Bergen, Norway</td>
<td>Cu, Zn,Pb, Cd</td>
<td>Complexing agents: hydrochloric acid (0.6 M), sodium chloride (0.6 M) and distilled water (DW), ammonium citrate (0.5 M), lactic acid (1 M), and citric acid (1 M), lasting 14 days, and current strength 50 mA</td>
<td>12% Cu and Pb, 10% Zn and 18% Cd using HCl; 6% Cu and Cd, 12% Zn and 5% Pb using NaCl; 48% Cu, 80% Zn, 96% Pb and 98% Cd using DW; 30% Cu, 40% Zn, 13% Pb and 18% Cd using ammonium citrate; 70% Cu, 78% Zn, 90% Pb and 98% Cd using lactic acid; 25%Cu and 20% Zn using citric acid</td>
<td>Nystroem et al. (2006)</td>
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<td></td>
<td>Port of Sisimiut (Greenland)</td>
<td>Cu, Cd</td>
<td>pH = 2, d = 1.2 mA/cm² in 28 days</td>
<td>Cu from 97 to 16 mg/kg</td>
<td>Ottosen et al. (2007)</td>
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<td></td>
<td>Norway</td>
<td>Cu, Pb, Zn, Cd</td>
<td>pH &lt; 2, in 14 days Aerobically d = 0.6 mA/cm², 1 mA/cm² 1.4 mA/cm²</td>
<td>Cu from 0.55 to 0.03 mg/kg</td>
<td>Kirkelund et al. (2009)</td>
</tr>
<tr>
<td><strong>Chemical-thermal process (Novosol process)</strong></td>
<td>Dunkerque (France) and Calais (France)</td>
<td>Cu, Cr, Cu, Pb, Zn</td>
<td></td>
<td>97% Cd, 99% Cr, 98% Cu, 99% Pb, 99% Zn for sediment from Dunkerque; 99% Cd, 91% Cr, 94% Cu, 99% Pb, 98% Zn for sediment from Calais</td>
<td>Zoubeir et al. (2007)</td>
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</table>
 advantageous for its oxidizing properties and could effective in destroying more metal–organic complexes than hydrochloric acid (Kim et al., 2010, 2011). A recent study conducted by Yoo et al., 2013 has investigated inorganic acids and different extracting agents (sodium citrate and sodium chloride) as additives in washing contaminated sediment coming from marine areas. Very interestingly, hydrochloric acid and nitric acid washing solution maintained an acidic pH through the washing experiments, due very likely to the particular characteristics of the sediment sample. However, hydrochloric acid showed a similar or lower heavy metal removal efficiency than nitric acid. Since chloride is known to be a very important ligand for metal cations and since sea water contains 3.5% sodium chloride, that study has also investigated the possibility to enhance metal solubilization by sodium chloride; nevertheless, complexation with chloride was not effective. Beolchini et al. (2013) have tested the efficiency of sulphuric acid as well as organic acids in heavy metal removal from marine contaminated sediments. Cr and Zn showed extraction efficiencies of about 34% while the highest mobilization of Ni was about 40% with sulphuric acid. In the case of As, the performance of the sulphuric acid were 58%.

A number of chelators have been studied and applied to increase the solubility of heavy metals, some of which are readily biodegradable and others that are fairly recalcitrant (NABIR 2004). Ethylene diamine diuccinate (EDDS) is relatively biodegradable, while EDTA tends to persist in the environment for long (Gorby et al. 1998; Bohuslavek et al. 2001). Chelators are also of interest in bioremediation by phytoextraction, since chelators promote the metal uptake by plants (Meers et al. 2005). Organic acid such as citric, oxalic, gluconic and ascorbic acids can be applied as chemical extractants, due to their ability to chelate heavy metals in soluble complexes. These compounds are naturally produced by bacteria and fungi and may offer advantages, like low environmental impact and high removal efficiency (Di Palma and Mecozzi, 2007; Peng et al., 2009). In a very recent study, has pointed out the efficiency of heavy metal removal by organic acids is strongly dependent upon the metal partitioning in the sediment (Beolchini et al., 2013) and that citric acid may mobilized higher concentrations of metal contaminants than oxalic acid (i.e., about 50%). Furthermore, an approach of Life Cycle Assessment (LCA) was used to investigate the environmental impact (potential abiotic depletion, acidification, eutrophication, global warming, ozone layer depletion and photo-chemical ozone creation) and has revealed that the use of highly diluted sulphuric acid is also a valid alternative, both in terms of mobilization efficiency and environmental compatibility. Poletti et al. (2006) have tested the efficiency of four chelating agents in heavy metal removal from a marine contaminated sediment: EDTA, NTA, citric acid and the [S,S]-EDDS. This study has demonstrated that EDTA can remove Cd, Cu, Pb and Zn with the efficiencies ranging between 65 and 86%. Among the investigated heavy metals, Pb exhibited the highest removal yield (up to about 78–86% in the case of 0.02 and 0.2 M EDTA), followed by Cu (76% with 0.2 M EDTA, 57% with 0.2 M EDDS) and Zn (65% with 0.2 M citric acid, 63% using 0.2 M EDTA). Cd showed the lowest solubilization efficiencies when compared with the other elements. In addition, Cd removal was highly affected by the washing time: after 8 h of treatments the solubilization reached 55–65% values, with a decrease to <1% in a 48 h washing treatment with 0.2 M NTA. Other studies have shown similar results for the application of EDTA on other sediment samples (see Table 1), while Bianchi et al. (2008) have reported no significant effects of heavy metal mobilization by washing with aqueous solutions of citric acid have. In addition, the same study has suggested that humic substances could be also used in sediment washing treatments, especially for the removal of Cu (i.e., 38% Cu removal with 1000 mg/l humic substances). In general, EDTA was a more efficient extraction agent compared to other agents, because EDTA can form very stable complexes with metals (Begum et al., 2012; Yoo et al., 2013), although the removal efficiencies are also affected by the partitioning of metals in the sediment (Begum et al., 2012; Beolchini et al., 2013). Di Palma and Mecozzi (2007) reported that the extraction efficiencies of Cu and Pb by EDTA washing/extraction from Italian port sediments were higher than those by citric acid washing/extraction. Li et al. (2010) showed that zinc and lead in different sediment samples can be partly dissolved by using solutions of citric acid, tartrate acid and malic acid, with descending efficiencies. Therefore, the use of organic acids as chelating agents appears to be suitable to solve the problem of dredged sediments with moderate level of contamination.

Surfactants are another group of compounds that can be added to washing solutions to enhance the solubilization, dispersal, and desorption of metal contaminants from contaminated sediments (Edwards et al., 1994, 1991; Finnerty, 1994). Due to their ability to reduce the attractive forces at the liquid’s surface, surfactants have been investigated in the removal of organic contaminant removal at first (Christoff and Ishihana, 2002; Dermont et al., 2008) but they can also be advantageous for the treatment of metal contaminated sediments (Mulligan et al., 2001a). In the last decade, microbial originated macromolecules with amphiphatic characteristics, namely “biosurfactants” (e.g. rhamnolipids and sophorolipids), are gaining prominence in bioremediation field. These molecules are very interesting due to their ion complexation activity. The mechanism for heavy metal removal by biosurfactants involves the formation of aggregate of biosurfactant molecules into micelles (spherical bilayers, less than 50 nm in diameter): biosurfactant molecules are sorbed onto sediment particle surface and complexate with the metals (ad-)sorbed to various sediment fractions, detach of metal contaminants and transfer them in the solution phase as micelles (Tabak et al., 2005; Meers et al., 2005). It has been demonstrated that a solution of 0.25% surfactin (a lipopeptide produced by Bacillus subtilis) in 1% sodium hydroxide can remove 15% of Cu and 6% of Zn from freshwater sediment samples (Mulligan et al., 1999). Rhamnolipid, a glycolipid biosurfactant, can be applied without other additives and obtain the removal of up to 37% of Cu, 13% of Zn, and 27% of Ni from sediments (Dahrazma and Mulligan, 2007). Mulligan et al. (2001c) tested the efficiency of biosurfactants in heavy metal removal from marine contaminated sediments. A single washing with 0.5% rhamnolipid removed 65% of the Cu and 18% of the Zn, whereas 4% sophorolipid removed 25% of the Cu and 60% of the Zn. At the same time, sediment washing experiments were performed at two surfactin concentrations with and without sodium hydroxide and hydrochloric acid for the sediment: Cu 70% and Zn 40% were solubilized by using 0.1% surfactin and 1% sodium hydroxide, while 4% sophorolipid and 0.7% hydrochloric acid removed 100% of Cu and Zn. Such results indicate clearly that anionic biosurfactants are suitable extractants even though metals in the exchangeable fraction were very low (Mulligan et al., 2001c). In addition, the biodegradability of biosurfactants may offer advantages in sediment remediation, but long-term studies of the impacts on the ecosystem should be performed before full-scale applications. For instance, surfactin is a non-specific cytotoxic antibiotic and a massive application on field could cause the depletion of ecological functions played by the bacterial community.

According to the scientific literature, sediment washing is appropriate for heavy metals weakly associated to the sediment particles, when hydroxides, oxides and carbonates are the main phases involved (Ortega et al., 2008). The acid neutralizing capacity of the sediment is also a major constrain. The pH of the solution affects the ability of chelating agents (EDDS, EDTA, and NTA) to bind
heavy metals as well the speciation of metals into soluble/insoluble forms (Bordas and Bourg, 1998). The treatment with inorganic acid may be not appropriate for very calcareous sediments, since protons would be consumed by dissolution of calcite and carbonates (Fonti et al., 2013). Additionally, sediment washing appears to be more appropriate for sediment with coarse particles (Peng et al., 2009) and this is an important limitation for this technique: dredged materials are usually fine and, anyway, the finest particles are more contaminated, due to the high surface available for adsorption. For these reasons, extraction tests should be conducted to determine optimal conditions (chemical type and dosage, contact time, agitation, temperature and extraction steps to meet regulatory requirements (Di Palma and Ferrantelli, 2005).

Techniques of sediment washing imply the potential release of chemicals in the environment or the management of liquids containing contaminants and extractants. Heavy metals can be more mobile and potentially more toxic, due to their speciation as chelator—metal complex. It follows that the development of full scale strategies of sediment washing is based on the selection of chemicals with characteristics of low environmental impact (low toxicity, high bio-degradability) and high removal efficiency.

3.2. Electro-chemical separation

Electro-chemical separation involves the application of static or alternating electro-magnetic field. A cathode and an anode are imbedded in the contaminated sediment in wet conditions and a low intensity electric current is applied. Anions move towards the positive electrode and cations towards the negative one (Dermont et al., 2008). Heavy metals as soluble ions and bound to oxides, hydroxides and carbonates can be removed by this method but other non-ionic components can be transported due to the flow (Mulligan et al., 2001a; Ottosen et al., 2007; Kirkelund et al., 2009). The process can be used to recover ions from soils, muds, dredged sediments and other materials. Wet high intensity magnetism separation (WHIMS) has been successfully applied on soils to remove Cr, Cu, Ni, Pb, and Zn (Rikers et al., 1998; Sierra et al., 2014). Once the remediation process is over, the contaminants that are accumulated at the electrodes can be extracted by electroplating, precipitation/co-precipitation, pumping water near the electrodes, complexing with ion-exchange resins or other methods (Krishna et al., 2001). The recovery of heavy metals could improve the process economics to achieve partial cost-effectiveness.

An electro-chemical process example was applied on sediment samples from Haakonsvern (Norway), where different leaching agents were used (hydrochloric acid, sodium chloride, citric acid, lactic acid). The highest removal efficiencies were obtained working with dry sediment (L/S 8) and with 70 mA applied current, for 14 days: 67–87% Cu, 79–98% Cd, 90–97% Zn, and 91–96% Pb were removed (Nystroem et al., 2005). In subsequent 14 day electro-dialytic experiment by Nystroem et al. (2006), lactic acid was used as desorbing agent with efficiencies of 70, 78, 90 and 98% for Cd, Cu, Zn and Pb, respectively, in conditions of 50 mA constant current.

3.3. Thermal treatments

Treating contaminated sediment by heat (after a dewatering pretreatment) is an advantageous strategy since the organic pollutants are completely destroyed by an oxidation due to the high temperatures useful strategy for destroying organic pollutants. During this type of treatment, many heavy metals are in immobilized in the sediment matrix but other metals, like Hg, As and Cd, can be volatilized or became more leachable. Like As, Mo and V due to the formation of oxanions. Either desorption or immobilization can be obtained by working at different temperature range (Rulkens, 2005). Temperature between 100 and 500 °C is used to remove pollutants by the thermal desorption. In this way, pollutants are not destroyed but vaporized from the sediment together with water and then concentrated in a small volume. This process can be used to remove low molecular hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) to prepare the sediment for further treatment; nevertheless, the presence of unstable volatile pollutants such as chlorinated hydrocarbons special equipment and conditions can be necessary to prevent formation of dioxins and furans; residue can be treated subsequently. At higher temperatures inorganic contaminant in the sediment can be immobilized by melting (vitrification) and organic pollutants can be completely destructed. Complete destruction of the volatilized organic compounds and its destruction products often requires an after-burning process operating at appropriate conditions. Depending on the process conditions and type of sediment the slag can be suitable as building material.

There are several commercially available thermal chemical treatment processes. The X-Trax process is a heat treatment with relatively low temperatures (400–650 °C) compared to conventional chemical—thermal processes. The X-Trax process has been used in experiments for the removal of organic matter and mercury in various dredges and sediments (Mulligan et al., 2001a). Cement Lock, developed by the Institute of Gas Technology (IGT), has been used for dredged sediment in the New York/New Jersey Harbour (Stern et al., 1998). The sediment contained metal contamination by As, Cd, Cr, Pb, Hg, Se and Ag and was mixed with lime into a rotary kiln reactor smelter at 1200–1600 °C. The sediment passed the toxicity characteristic leaching procedure (TCLP) for all metals. Volatilized heavy metals and acid gases and other combustion products were treated in the offgas by filtration to remove particulates and activate carbon to remove heavy metals gas (Rodsand and Acaar, 1995). On the contrary, the X-Trax™ process uses a relatively low-temperature process for removal of organics and mercury from soils, sludges, and sediments, which was developed by Chemical Waste Management Inc. The contaminated sediment is fed into a rotary dryer (400–650 °C). Hg was then desorbed. Oxide and sulfide forms were reduced to Hg. Nitrogen carries the vapours to the gas treatment systems. Approximately 10%–30% of the Hg is removed by the dust scrubber (Palmer, 1996). The Novosol® process by the Solvay Company is a patented chemical-thermal treatment in which phoshatation and calcination are combined. In the first stage, heavy metals are stabilized by mixing sediments with phosphoric acid (2–3.5%) in a tubular reactor; in the presence of calcite, the addition of phosphoric acid allows the formation of calcium phosphates minerals (e.g. hydroxyapatite). In the second stage, the phosphated sediments is calcining at high temperature (650 °C) in order to break down the organic contaminants (polycyclic aromatic hydrocarbons, dioxins and pesticides). With this process the polluted sediment becomes inert and can be used as raw material for brick making in construction industries (Agostini et al., 2005; Lafhaj et al., 2007).

4. Biological strategies for heavy metal removal from contaminated sediments

Bioremediation strategies have been recently considered as a promising answer to the problem of contaminated sediment (Guevara-Riba et al., 2004; Tabak et al., 2005). As explained above, metal contaminants are not absolutely fixed in the sediment; unlike organic pollutants, they cannot be degraded since they are not subjected to biological and chemical degradation processes occurring in the sediment but can be mobilized by changing their speciation (Van Hullebusch et al., 2005; Peng et al., 2009). Bioremediation strategies for heavy metal removal from sediments
attempt to exploit natural biological processes leading to bio-
imobilization of metals that are components of natural biogeo-
chemical cycles (White et al., 1997). In this group of remediation
techniques, the metabolic products of key microorganisms are the
driving force in dissolving metal species into aqueous solutions
(Erust et al., 2013). Indeed, metal mobilization can be mediated by
a range of microorganisms and processes, including autotrophic
and heterotrophic leaching, chelation by microbial metabolites and
methylation.

Microorganisms applied in bioremediation may be endogenous
in the contaminated area or they may be isolated from different
systems and brought to the contaminated site. In the first case,
microorganisms are already adapted at the environmental condi-
tions and bioremediation strategies consist basically into stimulate
and exploit the microbial function leading to the bioremediation
objectives (Biostimulation). In the second one, microorganisms are
chosen on the basis of their metabolic properties, including their
tolerance of high concentration of metals and other contaminants,
and added to contaminated sediments to lead to prefer biotrans-
formation (Bioaugmentation). This could require changes in the
natural environmental conditions (e.g. concentration of oxygen,
ph, etc.) to favour microbial activity. Bioremediation strategies can
be applied directly in the contaminated site, without moving
sediments (“in-situ”), in the contaminated area but with small scale
movimentation of the sediment to treat (“on site” or “in-place”), or
in areas or reactors designed on purpose for sediment treatment,
that require removal and transportation.

Leaching of metals mediated by microorganisms (i.e., Bio-
leaching) is a well-established technology in mining; in particular,
non-phylogenetic group of acidophilic, aerobic and chemo-
lithotrophic strains, known as Fe/S oxidizing bacteria are exploited
for large-scale operations of metal recovery from ores. In biore-
mediation process in which elemental sulphur (S0) is used as a
substrate, the rate of microbial sulphur oxidation is a limiting step
governing the efficiency of the process (Seidel et al., 2002, 2006;
Ilyas et al., 2014).

The main products of the metabolism of such strains are sul-
phuric acid (and a list of sulphur oxidation intermediates) and ferric
ions. The most known and studied strains in this group are Acid-
ithiobacillus ferrooxidans, At. thiooxidans and Leptospirillum fer-
rooxidans, but many other species are known, today (Dopson and
Johnson, 2012; Johnson, 2012) In addition, iron-oxidizing and
sulphur oxidizing strains among Archaea have been identified, so
the microbial diversity in bioleaching and bio-oxidation processes
is much wider than previously hypothesized (Brierley and Brierley,
2013; Vera et al., 2013). The solubilization of metal sulfides by Fe/S
oxidizing bacteria has long been described as a process based on
two independent mechanisms: a ‘direct mechanism’ (i.e., the direct
enzymatic oxidation of the sulphur moiety of the metal sulfide) and
an ‘indirect mechanism’ (i.e., the non-enzymatic metal sulfide
oxidation by Fe(III) ions combined with enzymatic (re)-oxidation of
the resulting Fe(II) ions; Sand et al., 2001). However, it is now
generally accepted that the ‘direct mechanism’ of biological metal
sulphide oxidation does not exist. Conversely, the true effectors for
metal solubilization from ores are the products of bacterial meta-
bolism, previously known as the ‘indirect mechanism’ (Rohwerder
et al., 2003). According to Rohwerder and Sand (2007), the Fe/S
oxidizing bacteria approach the mineral surface by creating a bio-
film, in a contact sub-mechanism), while some planktonic bacteria
cells remain floating in the bulk solution (non-contact sub-
mechanism). In either case, the dissolution of metal-bearing min-
erals can follow two different reaction pathways, which depend on
the acid-solubility of the sulfides involved: acid-insoluble metal
sulfides (e.g. pyrite, molybdenite, tungstenite) are exclusively
oxidized via electron extraction (the thiosulfate pathway), while

acid-soluble metal sulfides (e.g. sphalerite, galena, arsenopyrite,
chalcopyrite, hauerite) are dissolved by the combined actions of
Fe(III) oxidative attack and proton attack (the ‘polysulfide pathway’.
Schippers and Sand, 1999). These two pathways are simplified in
Fig. 2.

Inorganic source of reduced sulphur or elemental sulphur and/
or ferrous iron, can be used as energy source to favour the microbial
activity. The use of pyrite as an energy source in bioleaching
experiment for heavy metal solubilization form marine sediments
has also been reported (Wong et al., 2004).

As bioleaching consists of a combination of proton attack and
oxidation processes, sediments with high contents of metal sul-
phides and other reduced forms of metals should be particularly
suitable for clean-up strategies based on bacterial leaching.
Nevertheless, a very recent study have demonstrated that metals
in the other geochemical fractions can be solubilized by bio-
leaching, too (Fonti et al., 2013). On the contrary, the concentration
of the sediment to be treated and its content in carbonate and
particulate organic matter are among the main constraints to be
considered.

Table 2 reports some of the main scientific papers about bio-
logical strategies for metal removal from contaminated sediments.
The majority of the studies were performed at laboratory scale and
no feasibility assessment was carried out, with few exceptions. In
their works on river sediment samples, Seidel et al. (1998) and
Löser et al. (2007) were among the first scientists to show that S-
oxidizing bacteria can be applied for sediment remediation, with
metal removal efficiencies higher than those obtained by chemical
leaching with H2SO4. Further studies have investigated factors
affecting bioleaching efficiencies: sediment concentration in the
process, microorganisms involved, type and concentrations of
growth substrata for Fe/S oxidizing bacteria, initial pH, T and so on.
Some studies have used synthetic sediment samples, spiked with
metal sulfides. For instance, in their study Kim et al. (2005) have
reported solubilization efficiencies of 80% and 60% for Cd and Ni,
respectively, on artificially contaminated sediment. Control tests
showed that their results were significantly affected by the pres-
ence of Acidithiobacillus ferrooxidans. Studies have also pointed out
that a bacterial adaptation to the sediment is needed (Beolchini
et al., 2012).

![Fig. 2. Schematic comparison of the thiosulfate (A) and polysulfide (B) mechanisms in (bio)leaching of metal sulfides. MS: metal sulfides, M2–: metal cations, At: Acidithiobacillus ferrooxidans, At. thiooxidans and Lf: Leptospirillum fer-
roxidans (Schippers and Sand, 1999; Schippers et al., 1996; Rohwerder et al., 2003).](image)
The real application of biological strategies for metal removal from sediment is complicated by various problems, which are still unsolved. The required time for pilot scale studies, research, development and technology commercialization is estimated to be 10 years at least, or even more (Brierley, 2010). Anyway, research and development time is not the sole problem and other aspects need to be faced by the scientific community and authorities. Our analysis of the scientific literature suggests that sediment bioremediation technologies have very site-specific effects. Therefore, nearly every process that is developed it does require on-site piloting and, perhaps, even large-scale demonstrations, which are very costly and time-consuming. Furthermore, competitiveness with consolidated chemical and thermal processes make biotechnological processes not always preferable. In addition, the costs that may occur during the commercialization of new bio-technologies should be examined in detail, because they probably require a high capital investment (Brierley, 2010; Gahan et al., 2012). Notwithstanding, biophydmetallurgical strategies are considered as environmentally friendly and it is thought that they will make significant contributions to research and development in the future (Watling, 2006; Gahan et al., 2012).

Biosorption and bioaccumulation processes could provide an alternative solution for the remediation of sediments contaminated with metals. Biosorption is a physical—chemical and metabolically-independent process based on a variety of interactions among biological material and metal, including adsorption, ion exchange, surface complexation and precipitation (Veglio’ and Beolchini, 1997; Veglio et al., 1997, 2000). More recently, a wider definition of the term “biosorption” is used, including both passive and active processes in case of living biomass and often referred to as bio-accumulation (Valls and de Lorenzo, 2002; Fomina and Gadd, 2014). A wide variety of active and inactive organisms have been employed as biosorbsents to sequester metal ions from aqueous environments. Over the past two decades, much effort has been devoted into identifying readily available non-living biomass capable of effectively removing toxic metals/semimetals. These biosorbsents typically include algae (Pennesi et al., 2012; He and Chen, 2014), fungi (Gadd, 2008), bacteria (Vijayaraghavan and Yun, 2008), and agricultural waste (Veglio et al., 2003).

However, most of the available research papers and patents (Fomina and Gadd, 2014) deal with biosorption applied to water systems (e.g. industrial wastewater, groundwater), while literature lacks of studies addressing biosorption as a bioremediation strategy for sediments. Indeed, few examples are available were fungal strains are reported to successfully stabilize metals in soils (e.g. copper and cadmium) (Li et al., 2014) and biosorption is rather reported as one of the processes responsible for metal stabilization within phytoremediation strategies (Mani and Kumar, 2014).

Also organic amendments (e.g. compost), that are low in metal/semi-metal can be used as a sink for reducing the bioavailability of

### Table 2
Research and development works on biophydmetallurgical treatments of contaminated sediments.

<table>
<thead>
<tr>
<th>Microbe used</th>
<th>Efficiencies of treatment (%)</th>
<th>Temperature (°C)</th>
<th>Time</th>
<th>Scale/Type of reactor</th>
<th>Adjusted pH</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphur-oxidizing bacteria</td>
<td>Zn, Cd, Mn, Co and Ni 61–81%, Cu 21%</td>
<td>35</td>
<td>21d</td>
<td>Batch reactor</td>
<td>2.8</td>
<td>Seidel et al. (1998)</td>
</tr>
<tr>
<td>Acidithiobacillus thiooxidans and Acidithiobacillus thiooxidans and Acidithiobacillus ferrooxidans</td>
<td>Cu 95–96%, Zn and Pb</td>
<td>30</td>
<td>5h</td>
<td>Completely mixed batch (CMB) reactor</td>
<td>2–4 (Acidithiobacillus thiooxidans), 5–7 (Acidithiobacillus thioparus)</td>
<td>Chen et al. (2003)</td>
</tr>
<tr>
<td>Acidithiobacillus thiooxidans and Acidithiobacillus ferrooxidans</td>
<td>Ni, Zn, Cu and Cr &gt;90%, Pb 60–95%</td>
<td>37</td>
<td>18d</td>
<td>Continuous reactor</td>
<td>&lt;2.0</td>
<td>Tsai et al. (2003)</td>
</tr>
<tr>
<td>Acidithiobacillus ferrooxidans and Acidithiobacillus ferrooxidans</td>
<td>Cr and Mn &gt;80%, Pb 63%</td>
<td>30</td>
<td>48d</td>
<td>Bioreactor</td>
<td>2–3.5</td>
<td>Akinci and Guven (2011)</td>
</tr>
<tr>
<td>Acidithiobacillus ferrooxidans and Acidithiobacillus ferrooxidans</td>
<td>Mn &gt;88%, Zn and Ni &gt;40%</td>
<td>25</td>
<td>14d</td>
<td>Bioreactor</td>
<td>2.0</td>
<td>Beolchini et al. (2013)</td>
</tr>
</tbody>
</table>

### Table 3
Descriptions of sediment remediation technologies (Reis et al., 2007).

<table>
<thead>
<tr>
<th>In situ technologies</th>
<th>Physical/Chemical Treatments</th>
<th>Capping</th>
<th>Containment Barriers</th>
<th>Solidification/Stabilization</th>
<th>Confined Disposal Facility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ex Situ Technologies</td>
<td>Biological Treatments</td>
<td>Bioslurry</td>
<td>Containment Land</td>
<td>Composting</td>
<td>Chelation</td>
</tr>
<tr>
<td>Physical/Chemical Treatments</td>
<td>Thermal Treatments</td>
<td>Thermal Destruction</td>
<td>Inversion</td>
<td>Pyrolysis</td>
<td>High-Pressure Oxidation</td>
</tr>
</tbody>
</table>
metal semi-metals in contaminated soils and sediments through their effect on the adsorption, complexation, reduction and volatilization (Kumpiene et al., 2008; Park et al., 2011). Most of the research work has been performed on soils contaminated with copper (Farrel et al., 2010; Soler-Rovira et al., 2010; Beesley et al., 2014) arsenic (Farrel et al., 2010; Beesley et al., 2014), cadmium (Beesley et al., 2014), lead (Farrel et al., 2010; Beesley et al., 2014), zinc (Farrel et al., 2010) and it has been poorly addressed to sediment remediation. Nevertheless, taking into account both the high potential of this approach in reducing metal toxicity and possible differences in the responses of soils and sediments, it is considered as strategic to address further research work to assess the effect of compost on the remediation of sediments contaminated with metals.

5. Technological application and patent analysis

Potentially available remediation options for contaminated sediments have been summarized by Reis et al. (2007) and they are shown in Table 3. The majority of the techniques reported in Table 3 are based on the ex-situ/on-site approaches. Indeed, periodical dredging activities are requested for the preservation of navigation depths in ports. Consequently huge amounts of contaminated sediments need an ex-situ/on-site treatment and cannot be left in place, either for their high contamination or for the port maintenance activities. Nevertheless, in the case of moderate contamination and out of port sites, in-situ strategies would be preferable, since they could decrease sediment handling and, consequently, the exposure of contaminants caused by resuspension/volatilization processes (Table 4).

6. Strategies and future recommendations

There are currently several patents existing at international level related to technologies of contaminated soils which, with the necessary precautions, can also be applied to sedimentary matrix. As reported above, since the efficiency of the treatment changes as a function of the characteristics of the contaminated matrix, processes developed for the remediation of soils are not always effective to achieve adequate quality standards when applied to dredging sediment (US EPA, 1993; Rulkens and Bruning, 2005). Consequently, a number of processes specific for management/remediation of contaminated sediment have been patented. These patents deal with both in-situ (Table 5) and ex-situ application (Table 6), in the case of contamination with metals. The aim of such patents is to offer sustainable alternatives to landfill and dumping at sea. For the in situ application, most of patents deal with active capping of the contaminated site, with stabilization through specific sorbents, with solidification/stabilization by injection of cementitious materials and, more recently, with biotechnological approaches addressed at stimulating microbial communities. In the case of the ex situ/on-site application, targeted technologies are based on thermal treatments, on sediment washing, eventually integrated with advanced oxidation in the case of mixed contamination, on stabilization with sorbents, and, last, but not least, on biotechnological approaches (bioaugmented slurry bioreactors and phytoremediation). As a whole, the temporal evolution of patents suggest that a shift is in progress, from the high impact thermal processes and cement solidification towards the more environmentally friendly approaches (chemical and biological treatments).

Table 4
Main advantages and disadvantages of in situ treatment (Reisholds, 1998).

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relatively inexpensive</td>
<td>Lack of process control</td>
</tr>
<tr>
<td>Usually results in less resuspension of contaminated sediments than removal technologies</td>
<td>Poor environmental conditions for treatment</td>
</tr>
<tr>
<td>Treats, does not contain, contaminants</td>
<td>Lower treatment efficiency than ex situ treatment</td>
</tr>
<tr>
<td>Reduces handling and exposure of sediments</td>
<td>Limited experience with in situ treatments</td>
</tr>
</tbody>
</table>

Table 5
The main patents related to in situ treatment of sediments contaminated with metals (European Patent Office, 2014).

<table>
<thead>
<tr>
<th>Year</th>
<th>Code</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>2011</td>
<td>WO2011061300</td>
<td>Method for the cleanup of contaminated site/sediments</td>
</tr>
<tr>
<td>2013</td>
<td>US20113193066</td>
<td>Anaerobic mesophilic bacteria for the remediation of sites contaminated with metals and polychlorinated biphenyls</td>
</tr>
<tr>
<td>2009</td>
<td>JP2009074301</td>
<td>Noxious chemical substance diffusion prevention mat</td>
</tr>
<tr>
<td>2009</td>
<td>WO2009038476</td>
<td>Active capping layer</td>
</tr>
<tr>
<td>2009</td>
<td>WO2008070293</td>
<td>Product and method for creating an active capping layer across surfaces of contaminated sediments</td>
</tr>
<tr>
<td>2008</td>
<td>WO2008090992</td>
<td>Low-impact delivery system for in-situ treatment of contaminated sediment</td>
</tr>
<tr>
<td>2008</td>
<td>US2008090992</td>
<td>Mix of sorbent material, bentonite and sand</td>
</tr>
<tr>
<td>2008</td>
<td>WO2007070293</td>
<td>Injection apparatus for solutions targeted at decontamination</td>
</tr>
<tr>
<td>2007</td>
<td>US2006051601</td>
<td>Cylindrical rotating equipment that contains the contaminated sediments and allows the treatment through specific reagents</td>
</tr>
<tr>
<td>2007</td>
<td>US2006051601</td>
<td>Cylindrical rotating equipment that contains the contaminated sediments and allows the treatment through specific reagents</td>
</tr>
<tr>
<td>2006</td>
<td>KR2003009170</td>
<td>Sediment remediation agent and in situ remediation method of sediment using the same</td>
</tr>
<tr>
<td>2005</td>
<td>CA2441259</td>
<td>Coating by a thin layer of gas microbubbles</td>
</tr>
<tr>
<td>2005</td>
<td>US2005046055</td>
<td>Sorbent material enriched with electron acceptors</td>
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<tr>
<td>2002</td>
<td>US2002151241</td>
<td>Active capping layer</td>
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<tr>
<td>2002</td>
<td>FR2781702</td>
<td>Sorbent material, consisting of a hydrate of marine algae</td>
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<tr>
<td>1993</td>
<td>US5256001</td>
<td>Cylindrical system for in-situ treatment of underwater contaminated material</td>
</tr>
<tr>
<td>1993</td>
<td>WO9301899</td>
<td>Cylindrical equipment that contains the contaminated sediments and allows the injection of cementitious materials</td>
</tr>
<tr>
<td>1993</td>
<td>WO9301899</td>
<td>Injection of cementitious materials</td>
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</table>
the analysis of the environmental impact should not be overlooked, also for the strategies widely considered as environmentally friendly by the scientific community. Literature and patent analysis has evidenced that an evolution is in progress towards environmentally sustainable solutions: from high impact (thermal treatment and cementification) to low impact (chemical and biological) processes. In the future, full scale applications for sediment decontamination are expected to be found; nevertheless, a new thinking is necessary for a really sustainable management of dredged sediments, in order to consider such solid matrix as a resource rather than an environmental problem, taking into account its richness in oligoelements, microelements and organic nutrients.

The cost of remediation application will depends on several factors including the needs for mixing the mineral with the contaminated sediment, and whether the application and mixtures can be accomplished on the wet contaminated sediment or need to be performed after pre-treatments. The high activity of the heavy metals and the competitive price of this techniques (in comparison with others available disposal and remediation technologies) make the proposed technology a sustainable solution for in shore management of contaminated sediments. A large-scale study will provide valuable information to address concerns about the full cost of remediation application and long-term accumulation of heavy metals.

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References


