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Review

The remediation of heavy metals contaminated sediment

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A B S T R A C T

Heavy metal contamination has become a worldwide problem through disturbing the normal functions of rivers and lakes. Sediment, as the largest storage and resources of heavy metal, plays a rather important role in metal transformations. This paper provides a review on the geochemical forms, affecting factors and remediation technologies of heavy metal in sediment. The in situ remediation of sediment aims at increasing the stabilization of some metals such as the mobile and the exchangeable fractions; whereas, the ex situ remediation mainly aims at removing those potentially mobile metals, such as the Mn-oxides and the organic matter (OM) fraction. The pH and OM can directly change metals distribution in sediment; however oxidation–reduction potential (ORP), mainly through changing the pH values, indirectly alters metals distribution. Mainly ascribed to their simple operation mode, low costs and fast remediation effects, in situ remediation technologies, especially being fit for slight pollution sediment, are applied widely. However, for avoiding metal secondary pollution from sediment release, ex situ remediation should be the hot point in future research.

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1. Introduction

Nowadays, heavy metals originating from anthropogenic activities are frequently detected in sediments and water columns of river/lake, which cause a considerable number of the world's rivers/lakes severely contaminated [1–4]. Heavy metals pollution had gradually become a major concern worldwide.

In aquatic environment, heavy metal is usually distributed as follows: water-soluble species, colloids, suspended forms and sedimentary phases. However, unlike organic pollutants, natural processes of decomposition do not remove heavy metals. On the contrary, they usually are enriched in sediment by organisms or some other compounds. In some conditions, more than 99% of heavy metal entering into river can be stored in river sediments in various forms [5]. However, heavy metals cannot fix in sediment forever. With the variation of the physical–chemical characteristics of water conditions, part of these fixed metals will re-enter the overlying water and become available to living organisms. Thus, sediment often acts as both carriers and potential sources for metals in aquatic environment [1]. Heavy metals usually possess significant toxicity to aquatic organisms, and then affect human health through food chain. Therefore, investigating the transformation and distributions mechanisms of heavy metal in sediment becomes necessary.

The main purpose of this paper is to provide a review on the geochemical forms, affecting factors and remediation technologies of heavy metal in sediment, depending on literatures and practical working experiences. Only based on these, the optimization of remediation technologies fitting for polluted sediment can be achieved.

2. Metals species in sediment

In sediments, metals can be bound to various compartments in different ways: occluded in amorphous materials; adsorbed on clay surfaces or iron/manganese oxyhydroxides; presenting in lattice of secondary minerals like carbonates, sulfates or oxides; complexed with organic matter (OM) or lattice of primary minerals such as silicates [6,7]. Since each form has different remobilization potential, and then affects its respective bioavailability and toxicity, the measurement of total metal may not be able to provide exact information about the characteristics of pollution [8].

To clearly investigate the toxicity of heavy metal to aquatic biota, in the past decades, different sequential extraction procedures for partitioning the metals bound to various mineral components had been developed [9]. Based on these, the community Bureau of Reference of the Commission of the European Union initiated a major effort to harmonize these extraction procedures. Their works produced the definition of an extraction protocol (the BCR protocol) and a purely operational definition of sequential fractionation. For enlarging the research scopes, depending on the different partition conditions among various metals, some assistant sequential extraction procedure were also established and popularized. Some primary characteristics of them are shown in Table 1.

In all of these sequential extraction methods, the four steps method mainly established by Tessier et al. won the most popular application [6]. This method partitions the heavy metals into five fractions: extractable and exchangeable, carbonate bound, iron and manganese oxides bound, organic matter bound and residual metal.

Exchangeable fraction, usually extracted with magnesium chloride solution or sodium acetate solution (1 M) at pH 8.2 for 1 h, refers to the metals directly adsorbing on sediments [16]. Through some typical sorption–adsorptions processes, these metals can be exchangeable and are in equilibrium with the ionic content in water. Generally, this fraction is usually used to represent the environmentally available components.

Carbonates fraction, continuously extracted with NaOAc or HOAc solution (1 M) at pH 5.0 for 5 h, mainly refers to the metals that are precipitated or co-precipitated with carbonate. This fraction is sensitive to pH variations.

Fe–Mn oxides fraction includes the soluble metal oxides/hydroxides under slightly acidic pH as well as the metal associated with reducible amorphous Fe–Mn oxyhydroxides, which was extracted with 25% (v/v) acetic acid containing some $NH_2OH \cdot HCl$ at 96 °C for 6 h. This fraction can be dissolved with oxidation–reduction potential (ORP) varying.

Organic fraction may be associated with various forms of organic material such as living organisms, detritus or coatings on mineral particles through complexation or bioaccumulation process. It is extracted mainly with 0.02 M nitric acid and 30% hydrogen peroxide at pH 2.0 and 85 °C. This kind of metals can exist in sediment for longer periods, and can also be released with OM decomposition.

Residual fraction, namely the metals still remained in sediment after the above extraction procedures, usually presents as consolidated oxides, co-precipitates, and strongly held complexes, which keeps relatively stable and does not show significant transformation in various conditions.

Normally, the summation of the mobile and the exchangeable fractions can be used to assess the environmentally available components. The fractions bound to Mn oxides and organic material are supposed to represent the potentially mobile component under changing conditions, which are reviewed as the most important components in sediments for metals binding. While the residual fraction represents the more stable metal forms associated with anthropogenic or geogenic components, the influence of which to ecological system is much less than the others in major conditions.

3. Influence factors for heavy metal distributions

It has been validated that each environmental factor presents unique influence on metals distribution in sediment. The influences of some factors, such as pH, ORP and OM are more crucial than the others. Only a slight variation of them, the distributions of metals would be producing some significant variations. Correspondingly, some other factors (e.g. salinity, temperature) can only alter metals distribution to a less extent. In this paper, only those relatively important factors are introduced.

3.1. The influence of pH values

The pH is a key parameter controlling heavy metal transfer behavior in sediment. Normally, with pH decreasing in sediment, the competition between H^+ and the dissolved metals for ligands (e.g. OH^-, CO_3^{2-}, SO_4^{2-}, Cl^-, S^{2-} and phosphates) becomes more and more significant. It subsequently decreases the adsorption abilities and bioavailability of the metals, and then increases the mobility of heavy metal. Sometimes, only with a few lower of pH units, the fixation percentage of heavy metals on sediment particles may range from almost a 100% to none [17]. In sediment, due to the OM degradation and the acid volatile sulfide oxidation, the pH of sediment usually decreases from the neutral in the initial to acid, sometimes even decreasing to pH 1.2, which often results in some metals being released into water again even under stable water conditions [15,18].

Table 1
Characteristic of different sequential extraction procedures

Sequence number	Total extraction steps	Extracted metal species	Reference
1	Three steps	Acid soluble fraction; reducible fraction; oxidizable fraction; residual fraction	[10,11]
		Exchangeable fraction; OM fraction; carbonate fraction; residual fraction	[12]
2	Four steps	Extractable/exchangeable fraction; carbonate fraction; iron and manganese oxides fraction; OM fraction; residual fraction	[6]
3	Five steps	Exchangeable Cations fraction; carbonates fraction; easily reducible fraction (e.g. manganese oxides); moderately reducible fraction (e.g. amorphous iron oxyhydroxides); oxidizable fraction (organic phase + sulfides); residual fraction	[1,8]
		Exchangeable metals fraction; iron and manganese oxides fraction; weakly bound to organic matter fraction; strongly bound to organic matter fraction; sulfide phase fraction; residual fraction.	[13]
4	Six steps	Mobile fraction; exchangeable fraction; Mn-oxide fraction; organic fraction; amorphous Fe oxides fraction; crystalline Fe oxides fraction; residual fraction.	[14]
5	Seven steps	Mobile fraction; exchangeable fraction; Mn-oxides fraction; OM fraction; Fe oxides (anthropogenic) fraction; Fe oxides (geogenic) fraction; sulfide fraction; residual fraction.	[15]

In sediment, there exists a limit pH controlling heavy metal mobility. And the trace metal would be released only as they reaching such pH value. For different metals, this limit pH is different correspondingly, which can be found in Table 2. Therefore, under similar pH value, the potential mobility of heavy metals in sediment is different significantly. For example, when pH was controlled at 4.0, the potential mobility of metal decrease as follows: Zn > Cd > Ni > As > Cu > Pb [19].

3.2. The influence of OM species

Organic compounds in sediment, frequently existing in considerable amounts in particle form, play an important role in heavy metal transformation. For example, in the sediment of some rivers or lakes, the heavy metal bound to OM generally takes up the largest fraction. Additionally, in sediment, the solubility of organic matters usually directly determines the mobility of heavy metals. Normally, the complexation of metal ions with insoluble organic compounds can strongly lower their mobility, whereas the formation of soluble metal complexes with dissolved organic compounds would enhance their mobility [20].

In natural rivers or lakes, OM is mainly composed of humic and fulvic substances. The complexation reaction between heavy metals and organic complexants is usually recognized as the most important reaction pathway, due to this reaction determining, to a large extent, the speciation and bioavailability of metal, and then influencing the mobility of trace metal in natural water environment. However, in severely polluted river, due to the complexity of organic matter, the reaction types between organic complexes and

metals are difficult to predict. In most conditions, precipitation, co-precipitation or flocculation usually plays the most important role in heavy metal fixation.

3.3. The influence of ORP

It is generally accepted that sediment ORP is also a most important factors controlling heavy metal mobility [5]. In anaerobic sediment, Acid volatile sulfide (AVS), a key component controlling the activities of some divalent cationic metals, usually present naturally [21]. Initially, the majority of AVS contained in the anaerobic sediment is bound to iron as solid iron monosulfide (FeS), crystalline mackinawite (FeS), pyrrhotite (FeS), greigite (Fe_3S_4), or exits as free sulfides. However, if divalent metals, such as cadmium, copper, chromium, lead or zinc are present, the iron in iron-sulfide are displaced and one of these heavy metals rapidly bind to AVS with stronger affinity [22]. Finally, in those sediment contaminated, the metal bound with sulfide usually takes up a rather high proportion.

When ORP in sediment increases, the oxidization rate of metal sulfides and the degradation rate of organic compounds will increase correspondingly. Both can accelerate the release of the adsorbed/complexing heavy metal [23]. The reaction can be expressed as: $MS_2 + (15/4)O_2 + (7/2)H_2O = M(OH)_3 + 2SO_4^{2-} + 4H^+$. The release of H^+ ions into porewater would decrease the pH of sediment and then cause a secondary release of heavy metals. Part of this released material will be re-adsorbed, especially onto the more labile binding fractions. For example, with ORP in sediment increase, the Cd bound to organic sulfide, a stable metal forms, would decrease from 65% to 30% and form a more mobile form [1,24].

Accordingly, with the annual variations of ORP in sediment, the heavy metal presents seasonal release and fixation. These phenomena are very significant in some seasonally flooding rivers. For example, in Mulde reservoir, approximately 18 t of Zn can be released from sediment into water only due to the sediment being disturbed and oxidized in flooding, which led to a significant increase of Zn concentration in water [1].

Therefore, in the dredging process of river or lake, for decreasing the release of metal from sediment, oxidation of sediment should be avoided.

Table 2
The limit pH values of different metals in sediment

Metal species	pH limit
Zn	6.0–6.5
Cd	6.0
Ni	5.0–6.0
As	5.5–6.0
Cu	4.5
Pb	4.0
Al	2.5
Fe	2.5

3.4. The influence of some other factors

Except pH, OM and ORP, some other factors, such as temperature, salinity, metal species and retention time, can also affect the distributions of heavy metal in sediment. For example, due to the differences of cation exchange capacity among different metal, their mobility capacity varies correspondingly, and usually ranges as follows: Cs > Zn > Cd > Fe > Ag > Co > Mn [25]; with temperature increasing, the adsorption content of heavy metal on sediment often decreases gradually; with salinity in porewater increasing, the total adsorption content of heavy metal would decrease ascribed to the competition among heavy metal and some other cations [26]. Additionally, long time kinetic adsorption–desorption experiments also show that the metal freshly associated with particles presents less stable and higher potential bioavailability than those associated for a long time.

4. Remediation technology

Just like soil remediation, a two-tiered remediation strategy has also been adopted for remedying the sediment contaminated by heavy metal. The first tier aimed at in situ increasing the stabilization of metals on sediment particles (e.g. immobilization) and the second tier aimed at ex situ extracting or separating metals from sediment (e.g. washing, flotation) [4,27].

The first strategy focus on improving metal stabilization, in which mainly by enhancing metal sorption, precipitation and complexation capacity on sediment, the potential mobility or bioavailability of the toxic metals to environment are lowered. Due to these stabilization techniques usually being carried out "in situ", their remediation cost is relatively low [28,29]. Noteworthily, these techniques just improve the immobility of heavy metal on sediment and their total content in sediment does not lower. Therefore, in some special conditions, part of these immobilized metals will be released into the water again.

The other strategy is extraction, in which sediment polluted is dredged from the river bed and heavy metal is extracted from the sediment through a series of chemical, physical, biological methods in a specially designed reactor. This kind of remediation techniques is usually carried out "ex situ", and can remove almost all mobile metal. However, it also implies the sediment structure deterioration and high costs, which limit their popularization on vast contaminated areas [30,31].

Compared with ex situ remediation techniques, the key advantage of in situ stabilization approach is that only need a simple mixture of amendments with sediment. And the major disadvantage of this approach is that the final product of remediation, although existing in inactive form, still remains in sediment.

4.1. In situ remediation technology

Due to low cost and non-disruptive to natural hydrological conditions than conventional ex situ extraction technologies, in situ metal immobilization technologies developed rapidly in the past several decades. Several typical in situ remediation technologies are introduced as follows.

4.1.1. Amendments

Amendment, usually possessing high cation exchange capacity, can lower metal mobility and bioavailability in sediment by precipitation or sorption, thereby decreasing their solubility. The in situ immobilization of metals, usually using inexpensive amendments such as minerals (e.g. apatite, zeolites, steel shot, or beringite), is considered as a promising alternative to the currently available remediation methods. Compared to the amendments used in soil, that used in sediment usually has higher sorption capacity, lower water solubility (Ksp = 10^{-40}), higher stability under reducing and oxidizing conditions, and lower cost [28].

Apatite is usually selected as an ideal amendment for sediment remediation. Generally, it is formulated in the form of $Ca_{10-a-b}Na_a Mg_b(PO_4)_{6-x}(CO_3)_xF_{2+0.4x}$ with isomorphic substitution of carbonate for phosphate, F for hydroxy, and minor substitution of Ca^{2+} by Na^+ and Mg^{2+} atoms. In sediment remediation process, metal firstly incorporates into the apatite lattice through ion exchange with Ca^{2+}. This reaction can stimulate apatite dissolution and phosphate is released correspondingly. Due to the lower solubility between metal ions and phosphate, a new metal-phosphate solid phase (such as $Ca_{10-x}Pbx(PO_4)_6(OH)_2$) would form [32]. Through these fixing process, apatite minerals can effectively immobilize almost all Pb, Mn, Co, Cu, Cd, Zn, Mg, Ba, U, and Th in sediment [28,33].

4.1.2. Sand cap

Normally, decreasing the direct contact area between water and the contaminated sediment is a good choice for lowering the release content of heavy metal. Therefore, capping the contaminated sediment with sandy materials, such as clean sediment, sand, or gravel becomes an effective remediation technique. Through physical isolation, chemical isolation or sediment stabilization, the mobile and the exchangeable metals are transformed from the contaminated sediment into the clean cap and combined with particles in more stable forms. When properly designed, the placement of a relatively coarse-grained cap does not disturb or mix with underlying very soft fine-grained sediments. Some researchers also showed that a good cap thickness was approximately 50 cm; and through capping the sediment by sands materials, the heavy metal concentration in water could reduce to 80% [1]. Additionally, compared with other in situ remediation methods, this approach has a lower cost.

However, this remediation technique can only reduce the transfer rate of metal in sediment, while their immobilization effect for heavy metal is small. Therefore, for enhancing their immobilization capacity, some amendments (such as apatite, rock phosphate, lime or zeolite) can also be added into the sand cap. These reactive materials would demobilize heavy metals from solution and enhance the cap quality. For example, Jacobs and Förstner found that through adding the natural zeolite in sand cap, their fixation capacity for heavy metals and organic contaminants increases sharply [34].

4.1.3. Phytoremediation

Phytoremediation is the use of plants to extract, sequester, or detoxify pollutants. This technology is widely viewed as an ecologically responsible alternative to the environmentally destructive chemical remediation methods currently practiced [35]. This technology is popularly applied in soil remediation, and also shows some excellent remediation effects in some shallow rivers, lakes and wetlands. At present, this technology had presents good immobilization effects for Zn, Fe, Mn and Cd in sediment.

Phytoremediation is comprised of two tiers, one by plants themselves and the other by the root colonizing microbes, which degrades the toxic compounds to further non-toxic metabolites. Normally, hydrophytes have the ability to uptake and accumulate various heavy metals by the action of phytochelatins and metal lothioneins [36]. However, mass balance experiments show that metal uptake by hydrophytes were not high enough for phytoextraction. This indicates that in hydroremediation, the direct uptake of hydrophytes is small, and the indirect reactions, such as stimulation of microbial activity, redox reactions/formation and

precipitation of insoluble metal compounds in the rhizosphere, may play a relative important role [37]. Therefore, the direct uptake capacity of phytoremediation for heavy metal can be achieved by most plant species able to grow in the contaminated sediment. Correspondingly, the choice of hydrophytes would not depend on their apparent uptake capacity, but on their practical immobility capacity for metal.

4.2. Ex situ remediation technology

In situ remediation techniques are usually applied for the sediment slightly polluted by heavy metal. However, for the sediments heavily polluted, their remediation effects can be ignored to a large extent. Under such conditions, ex situ sediment remediation becomes the first choice [38]. Most ex situ remediation technologies for soil or mineral ores can be used for dredged sediment. However, due to higher workload and different environmental characteristics in sediment, some technologies have higher costs and more complex when used in sediment remediation. Only those promising alternative technologies are introduced as follows.

4.2.1. Washing

Sediment washing is a relatively simple and useful ex situ remediation technology, which involves through adding washing water, heavy metal can be transferred from the dredged sediment to wash solution. To enhance the performance of sediment washing, various additives can be employed, such as acid washing (e.g. H_2SO_4 and HNO_3), chelating agents (e.g. EDTA, DTPA and EDDS) or surfactants (e.g. rhamnolipid). These additives can assist in the solubilization, dispersal and desorption of metal from dredged sediments. This technology is most appropriate for the weaker bound metals in the form of exchangeable, hydroxides, carbonates and reducible oxides fraction. Residual fractions, the most difficult ones to remove, are not affected during the washing process [38,39]. Additionally, fine grain sediments are difficult to decontaminate through washing solutions, therefore washing is most applicable to sands and gravels.

Acid leaching, as a typical washing method, refers to the remediation of sediment through extracting the metals with sulfuric acid. Considering the sources of leaching agent, acid leaching can be divided into abiotic leaching and microbial leaching [40,41]. In abiotic solid-bed leaching, the H_2SO_4 is supplied to the sediment by circulating water with a rate highly dependent on the solid-bed height and percolation flow. However, in microbial solid-bed leaching, elemental sulfur added to the sediment is oxidized to sulfuric acid within the package which, in turn, solubilize the heavy metals. Here, the percolation flow and the solid-bed height do not affect the rate of metal solubilization [42,43]. Both methods present perfect removal efficiencies (>90%) for total extractable Ni, Zn, Cu and Cr. And the pH ranges are controlled depending on the heavy metal species. For example, Al is markedly solubilized at pH < 4, and Fe at pH < 2.4. However, due to a lesser requirement for acid and lime, which subsequently lower the operational difficulties of the microbial solid-bed leaching, the microbial process is 80% cheaper than an abiotic solid-bed leaching [29]. Additionally, when solid-bed leaching is performed on a larger scale, microbial leaching is much faster than abiotic leaching [40]. Therefore, microbial solid-bed leaching presents great attraction in sediment remediation.

Chelating agents used in sediment remediation usually possess higher chelating affinity for metal. They can combine with aqueous metal to form chelate complex, which subsequently lower the metal concentration in water. Through the adsorption/release balance between sediment and water, the toxic and bioavailable metals adsorbed on sediment will be transferred to chelate complex gradually, and finally removed with solution. This method is especially

suitable for treating the dredged sediment contaminated concurrently by organic pollutants and heavy metal. EDTA, as a chelating agent popularly applied, can effectively remove Cd, Cu, Pb and Zn with the removal efficiencies ranging between 65 and 86% [44]. However, due to possible adverse health and environmental effects, EDTA is currently under scrutiny. Therefore, the optimization of chelating agents should be the research direction in future.

Surfactants, especially biosurfactants, usually possess excellent surface active properties, anionic nature and low toxicity. Through adsorbing onto sediment surface, complexing with metal, detaching the metal from the sediment into the porewater and hence associating with surfactant micelles, surfactant can effectively remove the metals adsorbed on sediment particles. For example, when rhamnolipid, a glycolipid biosurfactant, without additives was applied, the removal of heavy metals from sediments was up to 37% of Cu, 13% of Zn, and 27% of Ni [45].

4.2.2. Electrochemical remediation

Electrochemical remediation involves applying a low DC current or a low potential gradient to electrodes that are inserted into the sediment and encompass the contaminated zone [46]. When DC electric fields are applied to the contaminated sediment, migration of charged ions occurs. Positive ions are attracted to the negatively charged cathode, and negative ions move to the positively charged anode. For example, under an induced electric potential, the anionic Cr(VI) migrated towards the anode, while the cationic Cr(III), Ni(II) and Cd(II) migrated towards the cathode. Once the remediation process is over, the contaminants that are accumulated at the electrodes are eventually extracted by methods such as electroplating, precipitation/co-precipitation, pumping water near the electrodes, or complexing with ion-exchange resins [16]. Because the electric conductivity is the highest in the fine particles of the sediment on which also most metals are adsorbed, and the electric field is the strongest where the metals are mainly found. This method is well suited for fine-grained dredged sediment.

In electrochemical remediation, there are four mechanisms, namely electromigration, electro-osmosis, electrophoresis and diffusion, affecting the migration of metals in an imposed electric field. Electromigration is considered as the dominant transfer mechanism for metal due to the transfer rate from electromigration is one to two orders greater than the others [46]. Using inert electrodes, the electrode reactions will produce H^+ at the anode and OH^- at the cathode, which means that if pH is not controlled, the H^+ in the anode migrate through the sediment towards the cathode, whereas the OH^- migrate towards the anode. Depending on the extent of migration of H^+ and OH^-, pH will vary across the sediment. An increase in the OH^- concentration causes an increase in the pH near the cathode. It has been proved that when heavy metals enter into basic conditions, they are likely to be adsorbed onto soil particles or form precipitate as hydroxides, oxyhydroxides, etc., and in acidic conditions, those ions desorb, solubilize and migrate. The high pH region in the proximity to the cathode is the main obstacle to heavy metal removal.

In order to solubilize the metal hydroxides and carbonates formed, or other species adsorbed onto sediment particles, as well as protonate organic functional groups, acidification may be a very effective method. Generally, in electrochemical remediation process, the development of an acidic front is often couple with a successful remediation [47]. However, this acid addition also has some evident drawbacks. Achieving these acidic conditions might be difficult due to higher sediment buffering capacity; in addition, acidification of dredged sediment may be not an environmentally acceptable method. Surfactants can increase the solubility and mobility of heavy metals during electrochemical remediation, depending on its function on decreasing the ζ potential of sediment

Table 3
The immobilization technologies for heavy metal in dredged sediment

Amendments	Immobilization mechanisms	Key components	Metal species removed	Reference
Red mud	Shift exchangeable metals to Fe-oxide fraction; decrease acid extractability metals; chemisorption; diffuse into oxide particles; increase pH values	A kind of alkaline material rich in iron (Fe) (typically 25–40%) and Al oxides (15–20%).	Cd, Zn, Pb, Ni and Cu	[29,55,56]
Lime	Precipitated as carbonates or hydroxides;	OH^-	Cd, Zn, Pb, Ni and Cu	[55,56]
Beringite	Increase pH values; directly adsorb and fix metals	Fe and Mn-bearing materials; aluminosilicate.	Cd, Zn, Pb, Cu and Ni	[29,57]
Iron oxides/hydroxides	Adsorption	Steel shot; limonite; goethite	Cd, Cu, Zn and As	[29]
Clays	Adsorption	Sepiolite; palygorskite; palygorskite; bentonite	Cd, Cu and Zn	[58]
Rock phosphate	Shift non-residual metal to residual fraction	Apatite	Pb, Mn, Co, Cu, Cd, Zn, Mg, Ba, U, Th and Cr	[59,60]
Zeolites	High cation exchange capacity;	Aluminosilicates	Cd, Cu and Zn	[58]

and then reducing the Van der Waals interactions [46]. Therefore, using surfactants to improve the metal removal became an effective method [48].

4.2.3. Flotation

Flotation, using gas bubbles attachment to dispersed phase, is a separation method of hetero-phase systems. The formed aggregates are floated and separated from the dispersing medium. Flotation is widely used in mining industries to separate valuable mineral ores [49]. Presently, flotation technology, as a possible treatment procedure for metal sulfides, shows some advantages in the remediation of anaerobic sediment, especially fine-textured substrates (20–50 μm) of sediment. It is expected that various metal ions (e.g. Ca, Cu, Pb and Zn) would be present as sulfides in dredged anaerobic sediments. The surface of these metal sulfides is hydrophobic in nature, and then can be selectively separated from suspensions by means of collectorless flotation. For most heavy metals in sediment, up to 80% of removal efficiencies can be achieved in flotation process [50,51].

However, Flotation can be either advantageous or disadvantageous for metal removal depending on the oxidation degree of sulfides [52]. Low oxidation intensity cannot form enough oxygen concentration gradient, lower particle resuspension, and then decrease the possibility of particle removal. However, high oxidation intensity would lead to excessive sulfides be oxidized to sulfate, and metal, originally fixed on particles, dissolve into the water again, which would also lower the removal efficiencies. Noteworthily, even in moderate oxidation intensity, the redistribution of heavy metal cannot be avoided, and the metals became more easily bioavailable. In flotation process, some metal sulfides are oxidized, released and subsequently redistributed in other fractions, such as freshly precipitated iron oxides, which would lower the efficiency of flotation. Consequently, in general, the froth fractions have a lower extractability than other remediation technology [51].

4.2.4. Ultrasonic-assisted extraction

One of the key limitations of traditional heavy metal remediation technologies is that they are extremely time consuming. However, the use of ultrasound coupled with vacuum pressure can effectively improve the extraction efficiencies of heavy metal from dredged sediment [53].

Ultrasound can cause high-energy acoustic cavitation: the formation, growth and implosive collapse of bubbles in liquid. During cavitational collapse, intense heating of the bubble occur. These localized hot spots roughly have the temperatures of 5000 °C, the pressures of 500 atm, and a lifetime of a few microseconds, the impact of which is sufficient to melt most metals. These bubbles collapse creates very minute, but high-energy movements of the

solvent that results in localized high shear forces, which can remove the material adhering to particles surface. Additionally, these "cavities" or areas of low pressure provide a sink of the metal into which adsorbed material will be desorbed.

Depending on particles sizes, the removal efficiencies for heavy metal change correspondingly. When ultrasound is applied to treat coarse grains, almost all metal can be separated from sediment and 92% can be removed in the whole remediation process; when used for silt (>2 μm), separation efficiency still can reach 100%, but only 82% of the removal efficiency can realize; when used for clay (<2 μm), no significant removal can be found [53]. Further research shows that the metal associated with clay is too stable to be removed in most remediation processes. Therefore, the ultrasound technology is an effective and economical remediation process, especially for those sediments with lower clay contents [54].

4.2.5. Immobilization

Most amendments used for sediment remediation are also used to heavy metal immobilization in dredged sediment, whose characteristics are introduced in Table 3. Though these immobilization methods cannot remove metal from sediment, due to their low cost and fast remediation effect, they are still popularly applied.

5. Conclusions

Nowadays, heavy metals pollution in river/lake has gradually become a major concern worldwide. Most metals flowing into river would store in sediment and keep available to living organisms for a long period. The remediation of sediment is necessary.

For different sediment contaminated by heavy metal, the adoption of remediation technology usually depends on some special characteristics of sediment, such as metal loads, size distributions of particles, metal species distribution. Generally, for the sediment contaminated severely, ex situ remediation technologies, such as sediment washing, flotation, ultrasound, electrochemical remediation should be considered priorly; for those contaminated slightly, in situ remediation technologies (e.g. phytoremediation, amendment and sand cap) usually are a perfect choice. If the sediment is mainly composed of larger particles (such as sand, grains and silt), washing and ultrasonic-assisted extraction should be given the priority; if the sediment is mainly composed by smaller particles (<63 μm), flotation, electrochemical remediation, immobilization and ultrasonic-assisted extraction should take the priority. Additionally, when metals in sediment are mainly composed of the mobile and the exchange fraction, such methods as amendment, ultrasound, electrochemical remediation, immobilization and washing can effectively lower the release of metal adsorbed; when the Mn-oxides fraction and the OM fraction take

up a large proportion of sediment, such methods (e.g. ultrasound, electrochemical remediation, amendment, sand cap and chelating reagents washing) often present better remediation effects.

In all environmental factors, the pH, ORP and OM are the most important factors affecting heavy metal distributions. The pH and OM can directly change metals distributions in sediment. However, mainly through oxidizing metal sulfide or changing pH values, ORP indirectly alter metal distribution.

In situ remediation technologies, due to their easy operation, low costs and fast remediation effect, are applied widely. However, the immobilized metal still remains in sediment and may be released into water again under some special conditions. Therefore, for avoiding a possible pollution of the sediment remedied, the ex situ remediation should be advocated in future.

Acknowledgement

References

[1] Z.U. Theofanis, S. Astrid, G. Lidia, W.G. Calmano, Contaminants in sediments: remobilisation and demobilization, Sci. Total Environ. 266 (2001) 195–202.
[2] M.A. Arribere, G.S. Ribeiro, R.S. Sanchez, M.I. Gil, R.G. Roman, L.E. Daurade, V. Fajon, M. Horvat, R. Alcalde, A.J. Kestelman, Heavy metals in the vicinity of a chlor-alkali factory in the upper Negro river ecosystem, Northern Patagonia, Argentina, Sci. Total Environ. 301 (2002) 187–203.
[3] H. Akcay, A. Oguz, C. Karapire, Study of heavy metal pollution and speciation in BuyakMenderes and Gediz river sediments, Water Res. 37 (2003) 813–822.
[4] O.R. Susana, D.L.R. Daniel, L. Lazaro, W.G. David, D.A. Katia, B. Jorge, M. Francisco, Assessment of heavy metal levels in Almendares River sediments—Havana City, Cuba, Water Res. 39 (2005) 3945–3953.
[5] W. Salomons, W.M. Stigliani, Biogeodynamics of Pollutants in Soils and Sediments: Risk Assessment of Delayed and Non-linear Responses, Environmental Science, Springer-Verlag, New York, 1995, pp. 331–343.
[6] A. Tessier, P.G.C. Campbell, M. Bisson, Sequential extraction procedure for the speciation of particulate trace metals, Anal. Chem. 51 (1979) 844–850.
[7] K.C. Yu, L.J. Tsai, S.H. Chen, S.T. Ho, Chemical binding of heavy metals in anoxic river sediments, Water Res. 17 (2001) 4086–4094.
[8] M. Kersten, U. Förstner, Effect of sample pre-treatment on the reliability of solid speciation data of heavy metals implications for the study of early diagenetic processes, Mar. Chem. 22 (1987) 299–312.
[9] C.K. Jain, Metal fractionation study on bed sediments of River Yamuna, India, Water Res. 38 (2004) 569–578.
[10] P. Quevauviller, G. Rauret, J.F. Lopez-Sanchez, Certification of trace metal extractable contents in a sediment reference material following a three-stage sequential extraction procedure, Sci. Total Environ. 205 (1997) 223–234.
[11] G. Rauret, J.F. López-Sánchez, A. Sahuquillo, Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials, J. Environ. Monit. 1 (1999) 57–61.
[12] S.P. McGrath, J. Cegarra, Chemical extractability of heavy metals during and after long-term applications of sewage sludge to soil, J. Soil Sci. 43 (1992) 313–321.
[13] L. Campanella, D. Dórazio, B.M. Petronio, Proposal for a metal speciation study in sediments, Anal. Chim. Acta 309 (1995) 387–393.
[14] E. Martley, B.L. Gulson, Heavy metal partitioning in soil profiles in the vicinity of an industrial complex and potential health implications, in: International conference on heavy metals in the environment NO12, Grenoble, France, vol. 107, 2003, pp. 831–834.
[15] K. Uta, W. Jens, Long-term effects of the Aznalcóllar mine spill—heavy metal content and mobility in soils and sediments of the Guadiamar river valley (SW Spain), Sci. Total Environ. 367 (2006) 855–871.
[16] R.R. Krishna, C.Y. Xu, C. Supraja, Assessment of electrokinetic removal of heavy metals from soils by sequential extraction analysis, J. Hazard. Mater. 84 (2001) 279–296.
[17] P. Gundersen, E. Steinnes, Influence of pH and TOC concentration on Cu, Zn, Cd, and Al speciation in rivers, Water Res. 37 (2003) 307–318.
[18] P. Bonnissel-Gissinger, M. Alnot, J.J. Ehrhardt, Surface oxidation of pyrite as a function of pH, Environ. Sci. Technol. 32 (1998) 28–39.
[19] C. Valérie, S. Rudy, V. Jiska, Assessment of acid neutralizing capacity and potential mobilization of trace metals from land-disposed dredged sediments, Sci. Total Environ. 333 (2004) 233–247.
[20] L.R.S. Amina, R. Mandal, M.H. Nouri, J. Murimboh, C.L. Chakrabart, M.H. Back, D.C. Grégoire, W.H. Schroeder, Effect of metal/fulvic acid mole ratios on the binding of Ni(II), Pb(II), Cu(II), Cd(II), and Al(III) by two well-characterized fulvic acids in aqueous model solutions, Anal. Chim. Acta 402 (1999) 211–221.
[21] T.D.M. Di, J.D. Mahony, D.J. Hansen, Toxicity of cadmium in sediments: the role of acid volatile sulfide, Environ. Toxicol. Chem. 9 (1990) 1487–1502.
[22] D.J. Hansen, W.J. Berry, J.D. Mahony, W.S. Boothman, T.D.M. Di, D.L. Robson, G.T. Ankley, D. Ma, C.E. Pesch, Predicting the toxicity of metal-contaminated field sediments using interstitial concentrations of metals and acid-volatile sulfide normalizations, Environ. Toxicol. Chem. 15 (1996) 2080–2094.
[23] W. Calmano, J.F. Hong, U. Forstner, Binding and mobilization of heavy metal in contaminated sediment affected by the pH and redox potential, Water Sci. Technol. 28 (1993) 223–235.
[24] P. Kelderman, A.A. Osman, Effect of redox potential on heavy metal binding forms in polluted canal sediments in Delft (The Netherlands), Water Res. 41 (2007) 4251–4261.
[25] M.L. Emile, R.P. Jonathan, The effect of salinity on binding of Cd, Cr, Cu and Zn to dissolved organic matter, Chemosphere 37 (1998) 861–874.
[26] J.M. Garnier, P. Ciffroy, B. Lakhdar, Implications of short and long term (30 days) sorption on the desorption kinetic of trace metals (Cd, Zn, Co, Mn, Fe, Ag, Cs) associated with river suspended matter, Sci. Total Environ. 366 (2006) 350–360.
[27] I.K. Iskandar, D.C. Adriano, Remediation of soils contaminated with metals: a review of current practices in the USA, in: I.K. Iskandar, D.C. Adriano (Eds.), Remediation of Soils Contaminated with Metals, Advances in Environmental Science, Northwood, UK, 1997, pp. 1–26.
[28] S. Raicevic, J.V. Wright, V. Veljkovic, J.L. Conca, Theoretical stability assessment of uranyl phosphates and apatites: selection of amendments for in situ remediation of uranium, Sci. Total Environ. 355 (2006) 13–24.
[29] L. Enzo, F.J. Zhao, G.Y. Zhang, B. Sun, W. Fitz, H. Zhang, S.P. McGrath, In situ fixation of metals in soils using bauxite residue: chemical assessment, Environ. Pollut. 118 (2002) 435–443.
[30] P.D.M. Alfredo, J.O.C. Julio, F. Cabrera, E.M. ngracia, Changes in enzyme activities and microbial biomass after "in situ" remediation of a heavy metal-contaminated soil, Appl. Soil Ecol. 28 (2005) 125–137.
[31] C. Rafael, C.M. Almela, B. Pilar, A remediation strategy based on active phytoremediation followed by natural attenuation in a soil contaminated by pyrite waste, Environ. Pollut. 143 (2006) 397–406.
[32] R. Shrestha, R. Fischer, D. Rahner, Behavior of cadmium, lead and zinc at the sediment–water interface by electrochemically initiated processes, Colloids Surf. A: Physicochem. Eng. Aspects 222 (2003) 261–271.
[33] S. Raicevic, T. Kaludjerovic-Radoicic, A.I. Zouboulis, In situ stabilization of toxic metals in polluted soils using phosphates: theoretical prediction and experimental verification, J. Hazard. Mater. 117 (2005) 41–53.
[34] P.H. Jacobs, U. Förstner, Concept of subaqueous capping of contaminated sediments with active barrier systems: ABS using natural and modified zeolites, Water Res. 33 (1999) 2083–2087.
[35] R.H.B. Meagher, Phytoremediation of toxic elemental and organic pollutants, Curr. Opin. Plant Biol. 3 (2000) 153–162.
[36] B. Suresh, G.A. Ravishankar, Phytoremediation—a novel and promising approach for environmental clean-up, Crit. Rev. Biotechnol. 24 (2004) 97–124.
[37] R. Clemente, D.J. Walker, M.P. Bernal, Uptake of heavy metals by *Brassica juncea* grown in a contaminated soil in Aznalcóllar (Spain): the effect of soil amendments, Environ. Pollut. 138 (2005) 46–58.
[38] N.M. Catherine, R.N. Yong, B.F. Gibbs, An evaluation of technologies for the heavy metal remediation of dredged sediments, J. Hazard. Mater. 85 (2001) 145–163.
[39] L.M. Ortega, R. Lebrun, J.F. Blais, R. Hauslerd, P. Drogui, Effectiveness of soil washing, nanofiltration and electrochemical treatment for the recovery of metal ions coming from a contaminated soil, Water Res. 42 (2008) 1943–1952.
[40] C. Löser, Z. Andreas, K. Görsch, H. Seidel, Remediation of heavy metal polluted sediment in the solid bed: comparison of abiotic and microbial leaching, Chemosphere 65 (2006) 9–16.
[41] C. Löser, Z. Andreas, H. Petra, H. Seidel, Remediation of heavy metal polluted sediment by suspension and solid-bed leaching: estimate of metal removal efficiency, Chemosphere 66 (2007) 1699–1705.
[42] L.J. Tsai, K.C. Yu, S.F. Chen, P.Y. Kung, C.Y. Chang, C.H. Lin, Partitioning variation of heavy metals in contaminated river sediment via bioleaching: effect of sulfur added to total solids ratio, Water Res. 37 (2003) 4623–4630.
[43] L.J. Tsai, K.C. Yu, S.F. Chen, P.Y. Kung, Effect of temperature on removal of heavy metals from contaminated river sediments via bioleaching, Water Res. 37 (2003) 2449–2457.
[44] A. Polettini, R. Pomi, E. Rolle, D. Ceremigna, L.D. Propris, M. Gabellini, A. Tornato, A kinetic study of chelant-assisted remediation of contaminated dredged sediment, J. Hazard. Mater. 137 (2006) 1458–1465.
[45] B. Dahrazma, C.N. Mulligan, Investigation of the removal of heavy metals from sediments using rhamnolipid in a continuous flow configuration, Chemosphere 69 (2007) 705–711.
[46] V. Jurate, S. Mika, L. Petri, Electrokinetic soil remediation: critical overview, Sci. Total Environ. 289 (2002) 97–121.
[47] M.N. Gunvor, J.P. Anne, M.O. Lisbeth, V. Arne, The use of desorbing agents in electrodialytic remediation of harbour sediment, Sci. Total Environ. 357 (2006) 25–37.
[48] K. Abidin, Y. Yeliz, Zeta potential of soils with surfactants and its relevance to electrokinetic remediation, J. Hazard. Mater. 120 (2005) 119–126.
[49] K.A. Matis, Flotation Science and Engineering, Marcel Dekker, New York, USA, 1995, p. 558.
[50] G. Barbery, Engineering aspects of flotation in the minerals industry: flotation machines, circuits and their simulation, in: J.K. Ives (Ed.), The Scientific Basis of Flotation, Nato Advanced Study Institute, The Hague: Martinus Nijhoff Publishers, Boston, 1982, pp. 289–348.

[51] P. Cauwenberg, F. Verdonckt, A. Maes, Flotation as a remediation technique for heavily polluted dredged material. 2. Characterisation of flotated fractions, Sci. Total Environ. 209 (1998) 121–131.
[52] R.A. Hayes, D.M. Price, J. Ralston, R.W. Smith, The collectorless flotation of sulphide minerals, Miner. Process. Extr. Metall. Rev. 2 (1987) 203–234.
[53] N.M. Jay, P. Ruvini, Ultrasound to decontaminate heavy metals in dredged sediments, J. Hazard. Mater. 85 (2001) 73–89.
[54] K. Hanna, P. Pentti, H. Väinö, P. Pekka, G. Antti, S. Hannu, Ultrasonically aided mineral processing technique for remediation of soil contaminated by heavy metals, Ultrason. Sonochem. 11 (2004) 211–216.
[55] I. Muller, E. Pluquet, Immobilization of heavy metals in sediment dredged from a seaport by iron bearing materials, Water Sci. Technol. 37 (1998) 379–386.
[56] C.W. Gray, S.J. Dunham, P.G. Dennis, F.J. Zhao, S.P. McGrath, Field evaluation of in situ remediation of a heavy metal contaminated soil using lime and red-mud, Environ. Pollut. 142 (2006) 530–539.
[57] M. Mench, J. Vangronsveld, V. Didier, H. Clijsters, A mimicked in situ remediation study of metal contaminated soils with emphasis on cadmium and lead, Environ. Pollut. 86 (1994) 279–286.
[58] S.A. García, A. Alastuey, X. Querol, Heavy metal adsorption by different minerals: application to the remediation of polluted soils, Sci. Total Environ. 242 (1999) 179–188.
[59] A.S. Knox, D.I. Kaplan, M.H. Paller, Phosphate sources and their suitability for remediation of contaminated soils, Sci. Total Environ. 357 (2006) 271–279.
[60] S.B. Chen, Y.G. Zhu, Y.B. Ma, The effect of grain size of rock phosphate amendment on metal immobilization in contaminated soils, J. Hazard. Mater. 134 (2006) 74–79.