

Chemical-induced washing remediation of metal-contaminated soils (Book Chapter)

メタデータ	言語: eng 出版者: 公開日: 2017-10-03 キーワード (Ja): キーワード (En): 作成者: メールアドレス: 所属:
URL	http://hdl.handle.net/2297/46433

Chemical-Induced Washing Remediation of Metal-Contaminated Soils

Zinnat A. Begum,^{1, *} Ismail M. M. Rahman,^{2, 3, *} Hikaru Sawai,³

Hiroshi Hasegawa^{4, *}

¹ *Department of Civil Engineering, Southern University, 739/A Mehedibag Road, Chittagong
4000, Bangladesh*

² *Department of Applied and Environmental Chemistry, Faculty of Science, University of
Chittagong, Chittagong 4331, Bangladesh*

³ *Graduate School of Natural Science and Technology, Kanazawa University, Kakuma,
Kanazawa 920-1192, Japan*

⁴ *Institute of Science and Engineering, Kanazawa University, Kakuma, Kanazawa 920-1192,
Japan*

*Author(s) for correspondence.

E-mail: Zinnat.Ara@gmail.com (ZAB); I.M.M.Rahman@gmail.com (IMMR);

hhiroshi@se.kanazawa-u.ac.jp (HH)

Tel/ Fax: +81-76-234-4792

Abstract

The immobilization or removal of toxic components using aqueous extractants, with or without additives, is one of the commonly practiced techniques for the treatment of metal-contaminated soils. However, rather than the use of water alone, the solution with chemical-additives is preferred due to the less time requirement and better separation effectiveness. There is a long-favored list of additives that have been used for the chemical-induced washing remediation of soils, which include acids, bases, chelants, surfactants, and so forth. The objective of this chapter is to provide a brief overview of the chemical-assisted soil washing approaches.

Keywords

Soil; Metal contamination; Chemical-assisted washing; Acid; Chelant; Surfactant; Remediation.

1.0 Introduction

Metal contamination of soils, which has been known as threatening for human health and the environment, has been caused from manufacturing discharges, effluents from service industries or wood preserving operations (Sposito and Page 1984; Basta et al. 2005; Khan et al. 2008). The sites of metal-contaminated soils can either be declared abandoned restricting for future exploitation, or the soils can be excavated and transported to secured disposal (Abumaizar and Smith 1999). However, the leaching possibility of the toxic metals from the contaminated soil cannot be avoided even it confined and has been considered rather as a provisional and an economically less-viable option (Leštan et al. 2008). Instead, the depollution of metal-contaminated soils has been preferred as it not only minimizes any future contamination risk but also offers an option to re-exploit the restricted locations (Abumaizar and Smith 1999; Dermont et al. 2008; Pavel and Gavrilesco 2008).

The ‘soil washing’ technique used for the treatment of metal-contaminated soils is a physico-chemical approach based on mining and mineral processing principles (Mann 1999). The target contaminant usually remains in specific particle fractions of the metal-contaminated soils, which can be concentrated into a much smaller volume of contaminated residue via washing treatment of soil (ITRC 1997). However, the effectiveness of the washing treatment is closely related to the ability of the extracting solution to separate out the metals in soil (Peters 1999). The solubility of metals in water is too limited for removing a high amount of cations in the leachates and, hence, the washing solution includes various chemical agents (e.g., acids, bases, surfactants, chelating or sequestering agents) to enhance the separation of contaminants from soils (Davis and Singh 1995; ITRC 1997).

Soil decontamination by washing treatment can be accomplished either on the excavated (i.e., physically removed) soil (*ex situ*) or on-site (*in situ*). However, the effectiveness of *in situ* washing treatment is limited due to the restricted mobility of the extractants while the soil is in the intact state. Furthermore, it is necessary to maintain site-specific control measures to prevent subsequent leaching occurrences (Abumaizar and Smith 1999). Therefore, the soil washing technique is generally performed as an *ex situ* method (Peters 1999; Pavel and Gavrilesco 2008), which have been discussed in detail in this chapter.

2.0 General outline of the *ex situ* soil washing process

In the metal-contaminated soils, the toxic components tend to be attached to the fine fractions (silt and clay) either chemically or physically, which are further bind to the coarse fraction consisting of sand and gravel (US EPA 1996). The cumulative target of the soil washing process is to treat the entire volume of a contaminated soil site, including the separation of the fine soil parts from the coarse ones. Hence, the total process of soil washing can be said to be a combination of the following basic steps: (a) Separation of the contaminated zone by excavation; (b) Segmentation of the unearthed soil to fine, sand and gravel fractions; (c) Treatment of the sand fraction using suitable extractant; (d) Rinsing with water to remove residual contaminants and extracting agents; (e) Re-deposition of the cleaned sand fraction along with the gravel parts to the site; (f) Further treatment of the fine fractions or disposed of according to the regulatory guidelines. (Griffiths 1995; US EPA 1996; ITRC 1997; Abumaizar and Smith 1999; Mann 1999; Ramamurthy et al. 2008).

The volume reduced during the washing treatment of soils is a typical performance indication of process application in a particular metal-contaminated site, which is calculated from the metal content reduction in the coarse and sand fraction in accordance with the regulatory standards using the following equation (Mann 1999).

$$\text{Volume reduction (\%)} = 1 - \left(\frac{\text{Feed soil (tons)} - \text{Clean products (tons)}}{\text{Feed soils (tons)}} \right)$$

A typical *ex situ* soil washing process (ITRC 1997) is illustrated in Figure 1.

3.0 Factors limiting the effectiveness of soil washing technology

There are several factors, which limit the effectiveness of the soil washing technology during the treatment of metal-contaminated soil. The factors include the percent distribution of soil particle sizes, organic content in the soil, the ratio of hydrophobic contaminants, the percentage of co-contaminants other than the metals, and the treatment of spent washing fluid.

The application of soil washing will not be cost-effective if the percentage of the fine-fractions of soils (silt/clay, < 63–74 microns) is in excess of 30 to 50 percent. The high organic content, such as humic substances, in soils make the separation of metal-

contaminants difficult because it provides additional binding sites for metals. An increased ratio of hydrophobic contaminants in soil requires extra additives and, in addition, a supplementary problem is created during the removal or recycling of the additives from the residual washing liquid. The volume requirements of washing liquid and the operating parameters for soil washing are determined depending on the comparative nature and concentration of metals and co-contaminants in soil, and a huge variation among those can alter the washing effectiveness of solvents to a considerable extent. Moreover, the after-use concentration of washing solvents (e.g., acids, chelating agents, surfactants, or other additives) in the treated soils evokes concerns regarding application of soil washing technology due to the environmental issues related to the disposal of residuals (US EPA 1995; ITRC 1997).

4.0 *Ex situ* soil washing: pros and cons

The *ex situ* soil washing process has several advantages, such as, quantitative removal of the contaminants, rapid cleanup of a contaminated site, reduce or elimination of long-term liability, the possibility of producing recyclable material or energy (Evanko and Dzombak 1997; Hester and Harrison 1997). Furthermore, it is one of the few permanent treatment alternatives for soils contaminated with metals and radionuclides. In addition to the metals, organic contaminants can be treated in the same system using soil washing technology. Besides, the clean coarse fractions of soils can be returned to the site at a very low cost after the soil washing treatment depending upon soil matrix characteristics (ITRC 1997).

The disadvantages of *ex situ* soil washing process include a must-requirement of further treatment or disposal of the spent washing liquid, the risk of spreading contaminated soil and dust particles during removal and transportation of excavated soils. The soil excavation can also be expensive when a large amount of soil is required to be removed, or disposal as hazardous or toxic waste is required. There are possibilities of a complication during the treatment process due to the high soil-humic contents, elevated percentage of soil fines, complex mixtures of contaminants, or excessively variable influent contaminant concentrations. Moreover, the space requirement for the installation of the treatment system

is also an issue of concern (Evanko and Dzombak 1997; Hester and Harrison 1997; ITRC 1997; Peters 1999; Dermont et al. 2008).

5.0 Extractants for soil washing

Acids, bases, chelants, surfactants, alcohols, reducing agents, or other solvents are used as the extracting agent in the soil washing processes either individually or as an additive to the aqueous mixtures. The solubilization, exchange, and/or extraction of metals by washing solutions differ considerably with the soil characteristics as well as the types and concentration of co-contaminants other than the metals (Wood et al. 1990; Yu and Klarup 1994; Griffiths 1995; Chu and Chan 2003; Gao et al. 2003; Maturi and Reddy 2008). Hence, the selection of extractants is decided on a case-by-case basis depending on the various factors as mentioned Section 3.0.

The metal immobilization in soils occurs either by forming insoluble precipitates or incorporating into the soil-crystalline structures, if the metal sorption ability of soils exceeds the limit due to the high input (Davis and Singh 1995; Pichtel and Pichtel 1997). To treat such a soils, the acids and chelants have been often studied at laboratory scale, and suggested for the commercial-scale remediation practices (Dermont et al. 2008). The selection of acids or chelants as the washing liquid is attributable to their better-responsive ability towards the metal-mobilization factors, e.g., acidity, ionic strength, redox potential and complex formation (Pickering 1986; Rampley and Ogden 1998). The acid-induced leaching of metals in soil takes place through ion exchange and/or soil matrix dissolution (Bricka et al. 1993; Peters 1999). The ability of the chelants to form stable water-soluble complexes with the metal ions is exploited during the chelant-assisted soil washing of metal-contaminated soils (Davis and Singh 1995; Pichtel and Pichtel 1997; Abumaizar and Smith 1999; Peters 1999). The application of surfactants becomes an attractive option for the extraction of contaminants from soil (Wang and Mulligan 2004; Conte et al. 2005), due to less acute toxicity relative to that of the organic solvents and considerable rate of environmental degradability to produce non-toxic substrates (Mulligan et al. 2001c; Roundhill 2001; Ehsan et al. 2006a; Ehsan et al. 2006b). The capacity of surfactants to increase the aqueous solubility of hydrophobic organic compounds at concentrations above the critical micelle concentration (CMC) is the key factor

in the surfactant-enhanced soil washing (Deshpande et al. 1999; Wen and Marshall 2011). In this work, we have concentrated our discussion on the remediation of metal-contaminated soils using acids, chelants and surfactants considering the increasing and continued research focus on the use of those extractants.

6.0 Acid-induced washing remediation of metal-contaminated soils

The acid-leaching treatment of metal-contaminated soils, sediments, and sludges is an established remediation approach, which exploit the pH of the washing fluids. The mechanisms involved, by far, can be either desorption of metal cations via ion exchange or the dissolution of metal compounds and/or metal contaminant containing soil mineral components (Tampouris et al. 2001; Kuo et al. 2006). The protons in solution, at low pH, reacts with the layer silicate minerals and/or surface functional groups (e.g., Al–OH, Fe–OH, and –COOH) of soils, and the desorption rate of metal ions increased (Isoyama and Wada 2007). The dissolution of Fe- and Al-oxides and phyllosilicates occurs when strong acidic fluid is added to the soils, and it replaces the ion-exchange process during metal extraction at $\text{pH} < 2$ (Kuo et al. 2006).

The acid-leaching treatment usually employs strong mineral acids, such as, hydrochloric (HCl), sulfuric (H_2SO_4), nitric (HNO_3), phosphoric (H_3PO_4), and so forth. Although the use of weak organic acid, such as, acetic acid (CH_3COOH) is attempted (ESTCP 1997), the efficiency was proved limited because of relative low strength and foul-smelling odors (Dermont et al. 2008). The leaching of toxic metals (As, Cu, Pb and Zn) from soils contaminated with metallurgical materials (Moutsatsou et al. 2006) can effectively be achieved with HCl compared to the H_2SO_4 and HNO_3 . Furthermore, a significant Pb-leaching (65–100%) from artificially or naturally contaminated soils is possible with HCl (Cline and Reed 1995; Reed et al. 1996; Abumaizar and Smith 1999). However, similar rates of Zn and Ni-extraction have been observed with HCl, H_2SO_4 and H_3PO_4 , while a higher As-extraction rate was achieved with H_2SO_4 and H_3PO_4 than that of HCl (Ko et al. 2005; 2006). In brief, it can be concluded that the metal-leaching efficiency of the acid-variants strongly depends on the metal-types, the geochemistry of soils, as well as the reagent concentrations.

The metal-leaching treatment of contaminated soils using acids alters soil structure and induces co-dissolution of soil components causing approximately 50% losses of soil minerals (Tampouris et al. 2001) and organic matters (Ko et al. 2005). The co-dissolution of the soil matrix is an issue of concern in terms of both environmental and economic point of view, because it not only increases the consumption of acid reagent and the complexity of the effluent management but also the acidity of treated soil is increased (Tampouris et al. 2001; Ko et al. 2005).

To minimize the destructive impact from the leaching treatment using high-concentrated acid, the diluted acidic solutions containing chloride salts (e.g., CaCl_2 , NaCl) have been proposed as the effective alternatives. The chloride salt solutions have been applied either in a mixed solution of the mineral acids of lower concentration (Kuo et al. 2006), or individually at a very high concentrations (>1 M) at a pH-controlled condition (Nedwed and Clifford 2000; Lin et al. 2001). A subsequent application of chloride salt solutions after the acid-leaching has also been evaluated, which in addition help to prevent the re-adsorption of acid-extracted metals to soils (Nedwed and Clifford 2000; Wasay et al. 2002; Isoyama and Wada 2007). However, the monitoring of Eh and pH parameters should be conducted to achieve and maintain the optimum thermodynamic conditions as well as to prevent the formation of insoluble compounds (Lin et al. 2001). The processes involved in the removal of metal ions (e.g., Pb^{2+} , Cd^{2+}) with chloride salt solutions (e.g., CaCl_2 , NaCl) can either be ion exchange of $\text{Ca}^{2+}/\text{Na}^+$ with $\text{Pb}^{2+}/\text{Cd}^{2+}$ on the reactive surface sites of the soil matrix, or the formation of stable and soluble metal chloro-complexes with Cl^- ions (e.g., $\text{Cd}^{2+} + y\text{Cl}^- \Leftrightarrow \text{CdCl}_y^{2-y}$) (Nedwed and Clifford 2000; Tampouris et al. 2001; Kuo et al. 2006). It has been observed that such a saline leaching treatment of metal-contaminated soil, with or without acid, can minimize the co-dissolution of soil matrix, and maintain the physico-chemistry and microbiology of soils close to that of source soil (Tampouris et al. 2001; Kuo et al. 2006; Makino et al. 2007).

The instances of the application of acid-leaching for the washing remediation of contaminated soils, both at laboratory and full-scale field-tests, are available from VanBenschoten et al. (1997), Steele and Pichtel (1998), Lin et al. (2001), Ko et al. (2005),

Kuo et al. (2006), Moutsatsou et al. (2006), Isoyama and Wada (2007), and Dermont et al. (2008), and are recommended for further reading.

7.0 Chelant-assisted washing remediation of metal-contaminated soils

A multi-protic chelant (H_nL), which typically contains multiple coordination sites available for complexation with a metal center, undergoes acid–base equilibrium reactions in the aqueous phase, *e.g.*,



There will be subsequent reaction steps followed by the eq (1). The total solubility of metal ion (M_{Tot}) in the presence of chelant in solution can be computed using the following relation:

$$M_{Tot} = M_{aq} + \sum M_p H_q L_r = M_{aq} + ML_{Tot} \quad (2)$$

In eq (2), p , q and r are used to denote the coefficients for metal ions, protons and chelants, respectively, and indicate that each conjugate acid or base of the chelants may form a strong complex with the metals in the contaminated soil when added to the washing solution. The complexation ability and comparative interaction quotient of the chelants towards the metals in soils can be evaluated assuming the equilibrium computation procedures formulated in eq (2). If the chelant is strong in interacting with the metals in soils, the ML_{Tot} will be much higher than that of M_{aq} . In addition, performance of a chelant can be evaluated based on their interaction with and partition potential to soil surfaces according to soil texture, particle size distribution, clay content, humic matter contents, metal and waste characteristics, mineralogy, and solution pH (Peters 1999).

A suitable chelant for the treatment of contaminated soil may be required to possess several of the following criteria (Peters 1999; Hong and Jiang 2005; Leštan et al. 2008):

- a) The chelant should have higher metal complexing abilities, as indicated by the equilibrium complexation constants, towards the heavy and transition metals compared to the hard sphere cations (*e.g.* Ca^{II} or Mg^{II}).
- b) The chelant is better to possess extraction selectivity towards the target metals. The donor atoms in the chelant decide its comparative selectivity behavior. For example,

chelants having sulfur and nitrogen as donor atoms show higher selectivity toward the transition metals (*e.g.* Cu^{II}, Ni^{II}) and soft sphere cations (*e.g.* Zn^{II}, Cd^{II}, Pb^{II}, Hg^{II}), while chelants containing oxygen as the donor atoms are more selective to the hard sphere cations.

- c) Chelants having multiple coordinating sites (*i.e.* multidentate) are capable of forming more stable metal-chelant complexes, therefore, preferable.
- d) The adsorption affinity of metal-chelant complexes towards solid surfaces of soils should be low.
- e) The reusability of chelant, including low toxicity in the environment are desirable to design a cost-effective separation scheme.

Aminopolycarboxylate chelants (APCs) such as, ethylenediaminetetraacetic acid (EDTA) and its homologs are commonly utilized in the *ex situ* soil washing processes due to their ability to interact with the majority of toxic metals (Leštan et al. 2008; Hasegawa et al. 2010; 2011). However, the free-form of classical APCs (*e.g.*, EDTA) exhibit poor photo-, chemo- and biodegradability in the environment (Means et al. 1980; Bolton Jr. et al. 1993; Kari and Giger 1995; Kari et al. 1995; Egli 2001; Nowack 2002; Nörtemann 2005) and, in most cases, metal complexation raises the threshold values for toxic effects of metals (Sillanpää and Oikari 1996; Sorvari and Sillanpää 1996; Sillanpää 2005). The requirement of using an excess amount of chelant to ensure the adequate desorption of metal-contaminants from soil, as well as to minimize the competition effect due to the coexisting elements in the soil (*e.g.* Ca^{II}, Mg^{II}, Fe^{III}, Al^{III}) further enhance the problem (Leštan et al. 2008). The consequence raise concern regarding eco-safety issues, and increasingly stringent legislative regulations regarding the disposal of soil washing fluid containing APCs have been proposed or imposed (Grundler et al. 2005; Begum et al. 2013a).

The search for eco-friendly biodegradable variants to replace the classical APCs, thus, became a topic of interest for the treatment of heavy metal-contaminated soils (Tandy et al. 2004; Begum et al. 2012a; Begum et al. 2012c; Pinto et al. 2014). Nitrilotriacetic acid (NTA) and [S,S]-ethylenediaminedisuccinic acid (EDDS) have been evaluated as the biodegradable and environmental-friendly replacement for EDTA in soil washing in the beginning phase of

such works (Elliott and Brown 1989; Pichtel and Pichtel 1997; Vandevivere et al. 2001; Tandy et al. 2004; Polettini et al. 2006). The work of Vandevivere et al. (2001) confirms that a comparable rate of efficiency for Pb, Zn, Cu and Cd extraction with EDDS to that of EDTA is possible if the contact time is sufficient and solution pH is maintained above 7. The result is, however, contradicts in the work of Yang et al. (2012), who proposes the use of pH 5.5 for Pb or Cd extraction. The performance of NTA, EDDS and EDTA for the extraction of Cd, Cu, Pb and Zn from soils by Polettini et al. (2006) and, among the biodegradable options, EDDS performed superior than the NTA. The effectiveness of NTA, EDTA, IDSA (iminodisuccinic acid) and MGDA (methylglycine diacetic acid) as potential alternatives of EDTA was investigated by Tandy et al. (2004) for the extraction of Cu, Zn and Pb from contaminated soils, which indicate EDDS as the best option among all. The removal of Cu, Pb and Zn by the action of the EDDS and MGDA has been reported by Arwidsson et al. (2010). The DL-2-(2-carboxymethyl) nitrilotriacetic acid (GLDA) and 3-hydroxy-2,2'-iminodisuccinic acid (HIDS) have been introduced as the biodegradable alternatives to EDTA, along with EDDS, IDSA and MGDA by Begum et al. (2012a). The performance of GLDA is found better than other options, in some cases even better than EDTA, at pH 4 and 7 for the extraction of Cd, Cu, Ni, Pb and Zn from contaminated soils.

The solution pH seems to be a prime deciding factor during the chelant-assisted washing remediation and the optimal pH condition for the treatment of metal-contaminated soils is frequently varied with the change in soil characteristics, the incorporation of metals within the soil phases, and the chelant employed (Begum et al. 2012b; Begum et al. 2013b). In addition, the relative stability of metal-chelant complexes in the solution is often altered due to the variation in the formation efficiency of the soluble dominant species in solution, re-sorption of the metal-chelant complexes in the active surface site of the soil solids, and so forth (Nowack 2002; Begum et al. 2012b; Begum et al. 2013b).

The basic information about the chelants (EDTA, EDDS, IDSA, MGDA, GLDA and HIDS) by far explored for the washing remediation of metal-contaminated soils is given in Table 1. The protonation and complexation characteristics of those chelants with Cd, Cu, Ni, Pb and Zn are listed in Table 2, while and the changes in the conditional stability constants of

the corresponding metal–chelant complex as a function of pH is shown graphically in [Figure 2](#). Some instances of chelant-assisted washing remediation of metal-contaminated soils are summarized by [Peters \(1999\)](#), [Tandy et al. \(2004\)](#), [Dermont et al. \(2008\)](#), and [Begum et al. \(2012b\)](#), and are recommended for further reading.

8.0 Surfactant-enhanced washing remediation of metal-contaminated soils

Surfactants are heterogeneous and long-chain molecules containing both hydrophilic (head) and hydrophobic (tail) moieties ([Mao et al. 2015](#)), and these can be classified as anionic, cationic, zwitter-ionic, and non-ionic depending on the nature of the hydrophilic group ([Rosen and Kunjappu 2012](#)). In an aqueous medium, the monomer molecules of surfactant create aggregates of a large number of molecules called ‘micelles’ when the surfactant concentration exceeds the critical micelle concentration (CMC) ([Figure 3](#)). Accordingly, the lowering of surface and interfacial tensions between the contaminants occurs followed by the displacement of contaminants ([Mulligan et al. 2001c](#); [Paria 2008](#)). The application of surfactant-enhanced remediation is more suitable for the treatment of organic contaminants in soils. Hence, the washing by surfactants can be more effective when the metals are closely associated with organic contaminants ([US EPA 1997](#); [Dermont et al. 2008](#)). The removal of metal contaminants from soils occurs either due to the surfactant-associated complexation ([Ochoa-Loza et al. 2001](#)) and/or ionic exchange ([Swarnkar et al. 2011](#)). A list of surfactants by far employed for the washing remediation of contaminated soils is provided in [Table 3](#).

Several comparative studies have been conducted to explore and select the best surfactant-types for the enhanced remediation of heavy metal-contaminated soils. For example, cationic surfactant DPC, nonionic surfactant Ammonyx KP and anionic surfactant JBR-425 have been used for the treatment of metal-contaminated soils, and the JBR-425 demonstrated the best elution effect towards Zn, Cu, Pb, and Cd among the surfactant variants ([Slizovskiy et al. 2011](#)). There was a study to evaluate the utility of 11 different kinds of surfactants, which includes 4 non-ionic, 4 anionic, one zwitter-ionic, and two charge-unknown surfactants, for the remediation of As, Cd, Cu, Ni, Pb, and Zn-contaminated

soil. The maximum remediation effectiveness has been achieved with Texapon N-40 anionic surfactant for most of the metals (Torres et al. 2012).

In comparison with the synthetic surfactants, the bio-surfactants are often preferred due to their larger molecular structure with more ligand groups, which facilitate usually high surface activity for the decontamination of both hydrophobic organics and heavy metals (Sachdev and Cameotra 2013). The potency of bio-surfactants in enhancing metal removal either as an individual solvent or as an additive to the solvent mixtures has gained advanced research focus from 1990s, and continued thereafter (Herman et al. 1995; Mulligan et al. 1999a, b, 2001a, b, c; Mulligan and Wang 2006; Dahrazma and Mulligan 2007; Song et al. 2008; Wang and Mulligan 2009a; 2009b). The findings conclude that the acidic bio-surfactant performed better in extracting the metals bound to carbonate and oxide, while the alkaline bio-surfactant expedites the release of the organically associated metals (Mulligan et al. 1999a). The release of the cationic forms of metals from contaminated soil occurs easily with anionic bio-surfactant solutions, e.g., the remediation of Cd, Zn and Pb-contaminated soil is reported with the use of rhamnolipid (Herman et al. 1995). In addition, bio-surfactants are found to be able to remove chromium and arsenic from contaminated soils (Li et al. 2002; Ozturk et al. 2012; Maity et al. 2013; Mukhopadhyay et al. 2013). The common forms of chromium and arsenic are negatively charged anionic complexes, which facilitate the cationic surfactant-assisted fixation of those species (Li et al. 2002). However, mobilization of arsenic/chromium oxyanions by negatively-charged bio-surfactant (e.g., rhamnolipids) might be due to any of following mechanisms: (a) the competition between the arsenic oxyanions and rhamnolipids for the adsorption sites on soil particles; (b) anion exchange reactions among arsenic anions and rhamnolipids; (c) electrostatic repulsive interactions because of the increase in the negative zeta potential of the soil particles through the adsorption of rhamnolipids (Wang and Mulligan 2009a; 2009b). Song et al. (2008), while investigating the performance of saponin bio-surfactant for the simultaneous removal of cadmium and phenanthrene, concluded that the external carboxyl groups of saponin micelles might have coordinated with cadmium and improved the mobilization rate. Mulligan et al. (1999a) suggested that the metal removal rate with the bio-surfactant can further be enhanced after consecutive washing. However, the surfactant-enhanced washing remediation of soils can be

ineffective if the soil has a silt and clay content more than 20–30% or have substantial quantities of organic matter (Riser-Roberts 1998; Mulligan et al. 2001c; Wen and Marshall 2011).

The surfactants are also used in combination with other extractants for the enhancement of metal removal rate from contaminated soils. The elimination of both heavy metals (Cd, Cr, Mn, Ni, Pb, and Zn) and the organic pollutants from soil were observed by the combined use of surfactant (e.g., Tween 80, Brij-98, saponin, CAS) and aminopolycarboxylate chelants (e.g. EDTA, EDDS) (Ehsan et al. 2006a; Mouton et al. 2009; Wen and Marshall 2011; Alcántara et al. 2012; Cao et al. 2013). Surfactants are also exploited in conjunction with some ligand ions to achieve an enhanced removal rate of metals from soil (Lima et al. 2011), and bio-extraction of soil heavy-metals (Ernst 1996; Langley and Beveridge 1999; Almeida et al. 2009).

9.0 Conclusion

The principles, methodologies and features of the extractant as adopted during the chemical-assisted soil washing approaches has been discussed briefly within the scope of this chapter. Although a varying range of extractant is available, we have limited our discussion on the use of acid, chelant and surfactant considering the overall frequency of extractant recommendation trend by the researchers. It should be noted that chemical-induced washing remediation of metal-contaminated soils have been often studied at laboratory scale but moderately used at field-scale or full/commercial-scale, mostly due to the higher reagent cost and treatment-issues of the spent washing liquids. Hence, there has been increasing research focus on the formation of a treatment-scheme, which consists of recycling or recovery of the washing additives.

Acknowledgment

The research has partially been supported by the Grants-in-Aid for Scientific Research (15H05118 and 25-5863) from the Japan Society for the Promotion of Science. One of the authors, Ismail M.M. Rahman, acknowledges the financial grant from the 'The Public Foundation of Chubu Science and Technology Center, Japan' to support his research in the Kanazawa University, Japan.

References

- Abumaizar RJ, Smith EH (1999) Heavy metal contaminants removal by soil washing. *J Hazard Mater* 70:71–86.
- Alcántara MT, Gómez J, Pazos M, Sanromán MA (2012) Electrokinetic remediation of lead and phenanthrene polluted soils. *Geoderma* 173–174:128–133.
- Alderighi L, Gans P, Ienco A, Peters D, Sabatini A, Vacca A (1999) Hyperquad simulation and speciation (HySS): A utility program for the investigation of equilibria involving soluble and partially soluble species. *Coord Chem Rev* 184:311–318.
- Almeida CMR, Dias AC, Mucha AP, Bordalo AA, Vasconcelos MTSD (2009) Influence of surfactants on the Cu phytoremediation potential of a salt marsh plant. *Chemosphere* 75:135–140.
- Arwidsson Z, Elgh-Dalgren K, von Kronhelm T, Sjöberg R, Allard B, van Hees P (2010) Remediation of heavy metal contaminated soil washing residues with amino polycarboxylic acids. *J Hazard Mater* 173:697–704.
- BASF (2007) Technical Information (Ti/EVD 1418 e): Trilon® M types. BASF Aktiengesellschaft, Ludwigshafen, Germany
- Basta NT, Ryan JA, Chaney RL (2005) Trace element chemistry in residual-treated soil: key concepts and metal bioavailability. *J Environ Qual* 34:49–63.
- Begum ZA, Rahman IMM, Tate Y, Egawa Y, Maki T, Hasegawa H (2012a) Formation and stability of binary complexes of divalent ecotoxic ions (Ni, Cu, Zn, Cd, Pb) with biodegradable aminopolycarboxylate chelants (DL-2-(2-carboxymethyl)nitrilotriacetic acid, GLDA, and 3-hydroxy-2,2'-iminodisuccinic acid, HIDS) in aqueous solutions. *J Solution Chem* 41:1713–1728.
- Begum ZA, Rahman IMM, Tate Y, Sawai H, Maki T, Hasegawa H (2012b) Remediation of toxic metal contaminated soil by washing with biodegradable aminopolycarboxylate chelants. *Chemosphere* 87:1161–1170.
- Begum ZA, Rahman IMM, Sawai H, Tate Y, Maki T, Hasegawa H (2012c) Stability constants of Fe(III) and Cr(III) complexes with dl-2-(2-carboxymethyl)nitrilotriacetic acid (GLDA) and 3-hydroxy-2,2'-iminodisuccinic acid (HIDS) in aqueous solution. *J Chem Eng Data* 57:2723–2732.
- Begum ZA, Rahman IMM, Hasegawa H (2013a) Management of EDTA-containing aqueous effluent: Environmental concerns and remedies. In: Molnar A (ed) *EDTA: Synthesis, Uses and Environmental Concerns*. Nova Science Publishers, Hauppauge, NY, USA, pp 163–177.
- Begum ZA, Rahman IMM, Sawai H, Mizutani S, Maki T, Hasegawa H (2013b) Effect of extraction variables on the biodegradable chelant-assisted removal of toxic metals from artificially contaminated European reference soils. *Water Air Soil Pollut* 224:1381.

- Bolton Jr. H, Li SW, Workman DJ, Girvin DC (1993) Biodegradation of synthetic chelates in subsurface sediments from the southeast coastal plain. *J Environ Qual* 22:125–132.
- Bricka RM, Williford CW, Jones LW (1993) Technology Assessment of Currently Available and Developmental Technique for Heavy Metals-Contaminated Soils Treatment (Technical Report IRRP-93-4). U.S. Army Corps of Engineers, Waterways Experiment Station, Vicksburg, MS
- Cao M, Hu Y, Sun Q, Wang L, Chen J, Lu X (2013) Enhanced desorption of PCB and trace metal elements (Pb and Cu) from contaminated soils by saponin and EDDS mixed solution. *Environ Pollut* 174:93–99.
- Chu W, Chan KH (2003) The mechanism of the surfactant-aided soil washing system for hydrophobic and partial hydrophobic organics. *Sci Total Environ* 307:83–92.
- Cline SR, Reed BE (1995) Lead removal from soils via bench-scale soil washing techniques. *J Environ Eng-ASCE* 121:700–705.
- Conte P, Agretto A, Spaccini R, Piccolo A (2005) Soil remediation: humic acids as natural surfactants in the washings of highly contaminated soils. *Environ Pollut* 135:515–522.
- Dahrazma B, Mulligan CN (2007) Investigation of the removal of heavy metals from sediments using rhamnolipid in a continuous flow configuration. *Chemosphere* 69:705–711.
- Davis AP, Singh I (1995) Washing of zinc(ii) from contaminated soil column. *J Environ Eng-ASCE* 121:174–185.
- Davis AP, Hotha BV (1998) Washing of various lead compounds from a contaminated soil column. *J Environ Eng-ASCE* 124:1066–1075.
- Dermont G, Bergeron M, Mercier G, Richer-Lafleche M (2008) Soil washing for metal removal: A review of physical/chemical technologies and field applications. *J Hazard Mater* 152:1–31.
- Deshpande S, Shiau BJ, Wade D, Sabatini DA, Harwell JH (1999) Surfactant selection for enhancing ex situ soil washing. *Water Res* 33:351–360.
- Egli T (2001) Biodegradation of metal-complexing aminopolycarboxylic acids. *J Biosci Bioeng* 92:89–97.
- Ehsan S, Prasher SO, Marshall WD (2006a) A washing procedure to mobilize mixed contaminants from soil: II. Heavy metals. *J Environ Qual* 35:2084–2091.
- Ehsan S, Prasher SO, Marshall WD (2006b) A washing procedure to mobilize mixed contaminants from soil. I. Polychlorinated biphenyl compounds. *J Environ Qual* 35:2146–2153.
- Elliott HA, Brown GA (1989) Comparative evaluation of NTA and EDTA for extractive decontamination of Pb-polluted soils. *Water, Air, & Soil Pollution* 45:361–369.
- Ernst WHO (1996) Bioavailability of heavy metals and decontamination of soils by plants. *Appl Geochem* 11:163–167.

- ESTCP (1997) Joint Small-Arms Range Remediation: Cost and Performance Report. Environmental Security Technology Certification Program (ESTCP), U.S. Department of Defense, Arlington, VA
- Evanko CR, Dzombak DA (1997) Remediation of Metals-Contaminated Soils and Groundwater (TE-97-01). Ground-Water Remediation Technologies Analysis Center (GWRTAC), Pittsburgh, PA
- Gao Y, He J, Ling W, Hu H, Liu F (2003) Effects of organic acids on copper and cadmium desorption from contaminated soils. *Environ Int* 29:613–618.
- Griffiths RA (1995) Soil-washing technology and practice. *J Hazard Mater* 40:175–189.
- Grundler OJ, van der Steen ATM, Wilmot J (2005) Overview of the European risk assessment on EDTA. In: Nowack B, VanBriesen JM (eds) *Biogeochemistry of Chelating Agents*. ACS Symposium Series. American Chemical Society, Washington, DC, pp 336–347.
- Hasegawa H, Rahman IMM, Kinoshita S, Maki T, Furusho Y (2010) Non-destructive separation of metal ions from wastewater containing excess aminopolycarboxylate chelant in solution with an ion-selective immobilized macrocyclic material. *Chemosphere* 79:193–198.
- Hasegawa H, Rahman IMM, Nakano M, Begum ZA, Egawa Y, Maki T, Furusho Y, Mizutani S (2011) Recovery of toxic metal ions from washing effluent containing excess aminopolycarboxylate chelant in solution. *Water Res* 45:4844–4854.
- Herman DC, Artiola JF, Miller RM (1995) Removal of cadmium, lead, and zinc from soil by a rhamnolipid biosurfactant. *Environ Sci Technol* 29:2280–2285.
- Hester RE, Harrison RM (eds) (1997) *Contaminated Land and its Reclamation*. Royal Society of Chemistry, Cambridge, U.K.
- Hong PKA, Jiang W (2005) Factors in the selection of chelating agents for extraction of lead from contaminated soil: Effectiveness, selectivity, and recoverability. In: Nowack B, VanBriesen JM (eds) *Biogeochemistry of Chelating Agents*. ACS Symposium Series. American Chemical Society, Washington, DC, pp 421–432.
- Isoyama M, Wada SI (2007) Remediation of Pb-contaminated soils by washing with hydrochloric acid and subsequent immobilization with calcite and allophanic soil. *J Hazard Mater* 143:636–642.
- ITRC (1997) *Technical and Regulatory Guidelines for Soil Washing*. Interstate Technology & Regulatory Council (ITRC), Washington, D.C.
- Kari FG, Giger W (1995) Modeling the photochemical degradation of ethylenediaminetetraacetate in the river Glatt. *Environ Sci Technol* 29:2814–2827.
- Kari FG, Hilger S, Canonica S (1995) Determination of the reaction quantum yield for the photochemical degradation of Fe(III)-EDTA: Implications for the environmental fate of EDTA in surface waters. *Environ Sci Technol* 29:1008–1017.

- Khan S, Cao Q, Zheng YM, Huang YZ, Zhu YG (2008) Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. *Environ Pollut* 152:686–692.
- Ko I, Chang YY, Lee CH, Kim KW (2005) Assessment of pilot-scale acid washing of soil contaminated with As, Zn and Ni using the BCR three-step sequential extraction. *J Hazard Mater* 127:1–13.
- Ko I, Lee CH, Lee KP, Lee SW, Kim KW (2006) Remediation of soil contaminated with arsenic, zinc, and nickel by pilot-scale soil washing. *Environ Prog* 25:39–48.
- Kuo S, Lai MS, Lin CW (2006) Influence of solution acidity and CaCl₂ concentration on the removal of heavy metals from metal-contaminated rice soils. *Environ Pollut* 144:918–925.
- Langley S, Beveridge TJ (1999) Effect of O-side-chain-lipopolysaccharide chemistry on metal binding. *Appl Environ Microbiol* 65:489–498.
- Leštan D, Luo C-l, Li X-d (2008) The use of chelating agents in the remediation of metal-contaminated soils: A review. *Environ Pollut* 153:3–13.
- Li Z, Alessi D, Zhang P, Bowman R (2002) Organo-illite as a low permeability sorbent to retard migration of anionic contaminants. *J Environ Eng* 128:583–587.
- Lima TMS, Procópio LC, Brandão FD, Carvalho AMX, Tótola MR, Borges AC (2011) Simultaneous phenanthrene and cadmium removal from contaminated soil by a ligand/biosurfactant solution. *Biodegradation* 22:1007–1015.
- Lin HK, Man XD, Walsh DE (2001) Lead removal via soil washing and leaching. *JOM-J Min Met Mat S* 53:22–25.
- Maity JP, Huang YM, Fan C-W, Chen C-C, Li C-Y, Hsu C-M, Chang Y-F, Wu C-I, Chen C-Y, Jean J-S (2013) Evaluation of remediation process with soapberry derived saponin for removal of heavy metals from contaminated soils in Hai-Pu, Taiwan. *J Environ Sci-China* 25:1180–1185.
- Makino T, Kamiya T, Takano H, Itou T, Sekiya N, Sasaki K, Maejima Y (2007) Remediation of cadmium-contaminated paddy soils by washing with calcium chloride: Verification of on-site washing. *Environ Pollut* 147:112–119.
- Mann MJ (1999) Full-scale and pilot-scale soil washing. *J Hazard Mater* 66:119–136.
- Mao X, Jiang R, Xiao W, Yu J (2015) Use of surfactants for the remediation of contaminated soils: A review. *J Hazard Mater* 285:419–435.
- Martell AE, Smith RM (1974) *Critical Stability Constants, Vol. 1: Amino Acids*. Plenum Press, New York
- Martell AE, Smith RM, Motekaitis RJ (2004) *NIST Standard Reference Database 46: NIST Critically Selected Stability Constants of Metal Complexes Database (Version 8.0 For Windows)*. Texas A&M University, College Station, TX
- Maturi K, Reddy KR (2008) Extractants for the Removal of Mixed Contaminants from Soils. *Soil Sediment Contam* 17:586–608.

- Means JL, Kucak T, Crerar DA (1980) Relative degradation rates of NTA, EDTA and DTPA and environmental implications. *Environmental Pollution Series B-Chemical and Physical* 1:45–60.
- Mouton J, Mercier G, Blais JF (2009) Amphoteric surfactants for PAH and lead polluted-soil treatment using flotation. *Water Air Soil Pollut* 197:381–393.
- Moutsatsou A, Gregou M, Matsas D, Protonotarios V (2006) Washing as a remediation technology applicable in soils heavily polluted by mining-metallurgical activities. *Chemosphere* 63:1632–1640.
- Mukhopadhyay S, Hashim MA, Sahu JN, Yusoff I, Sen Gupta B (2013) Comparison of a plant based natural surfactant with SDS for washing of As(V) from Fe rich soil. *J Environ Sci-China* 25:2247–2256.
- Mulligan CN, Yong RN, Gibbs BF (1999a) On the use of biosurfactants for the removal of heavy metals from oil-contaminated soil. *Environ Prog* 18:50–54.
- Mulligan CN, Yong RN, Gibbs BF (1999b) Removal of heavy metals from contaminated soil and sediments using the biosurfactant surfactin. *J Soil Contam* 8:231–254.
- Mulligan CN, Yong RN, Gibbs BF (2001a) Remediation technologies for metal-contaminated soils and groundwater: An evaluation. *Eng Geol* 60:193–207.
- Mulligan CN, Yong RN, Gibbs BF (2001b) Heavy metal removal from sediments by biosurfactants. *J Hazard Mater* 85:111–125.
- Mulligan CN, Yong RN, Gibbs BF (2001c) Surfactant-enhanced remediation of contaminated soil: a review. *Eng Geol* 60:371–380.
- Mulligan CN, Wang SL (2006) Remediation of a heavy metal-contaminated soil by a rhamnolipid foam. *Eng Geol* 85:75–81.
- Nedwed T, Clifford DA (2000) Feasibility of extracting lead from lead battery recycling site soil using high-concentration chloride solutions. *Environ Prog* 19:197–206.
- Nörtemann B (2005) Biodegradation of chelating agents: EDTA, DTPA, PDTA, NTA, and EDDS. In: Nowack B, VanBriesen JM (eds) *Biogeochemistry of Chelating Agents*. ACS Symposium Series. American Chemical Society, Washington, DC, pp 150–170.
- Nowack B (2002) Environmental chemistry of aminopolycarboxylate chelating agents. *Environ Sci Technol* 36:4009–4016.
- Ochoa-Loza FJ, Artiola JF, Maier RM (2001) Stability constants for the complexation of various metals with a rhamnolipid biosurfactant. *J Environ Qual* 30:479–485.
- Ozturk S, Kaya T, Aslim B, Tan S (2012) Removal and reduction of chromium by *Pseudomonas* spp. and their correlation to rhamnolipid production. *J Hazard Mater* 231–232:64–69.
- Paria S (2008) Surfactant-enhanced remediation of organic contaminated soil and water. *Adv Colloid Interface Sci* 138:24–58.

- Pavel LV, Gavrilescu M (2008) Overview of *ex situ* decontamination techniques for soil cleanup. *Environ Eng Manage J* 7:815–834.
- Peters RW (1999) Chelant extraction of heavy metals from contaminated soils. *J Hazard Mater* 66:151–210.
- Pichtel J, Pichtel TM (1997) Comparison of solvents for *ex situ* removal of chromium and lead from contaminated soil. *Environ Eng Sci* 14:97–104.
- Pickering WF (1986) Metal ion speciation – Soils and sediments (a review). *Ore Geol Rev* 1:83–146.
- Pinto ISS, Neto IFF, Soares HMVM (2014) Biodegradable chelating agents for industrial, domestic, and agricultural applications—a review. *Environ Sci Pollut R* 21:11893–11906.
- Polettini A, Pomi R, Rolle E, Ceremigna D, De Propriis L, Gabellini M, Tornato A (2006) A kinetic study of chelant-assisted remediation of contaminated dredged sediment. *J Hazard Mater* 137:1458–1465.
- Ramamurthy AS, Vo D, Li XJ, Qu J (2008) Surfactant-enhanced removal of Cu (II) and Zn (II) from a contaminated sandy soil. *Water Air Soil Pollut* 190:197–207.
- Rampléy CG, Ogden KL (1998) Preliminary studies for removal of lead from surrogate and real soils using a water soluble chelator: Adsorption and batch extraction. *Environ Sci Technol* 32:987–993.
- Reed B, Carriere P, Moore R (1996) Flushing of a Pb(II) contaminated soil using HCl, EDTA, and CaCl₂. *J Environ Eng-ASCE* 122:48–50.
- Riser-Roberts E (1998) Remediation of Petroleum Contaminated Soils : Biological, Physical, and Chemical Processes. Lewis Publishers, Boca Raton.
- Rosen MJ, Kunjappu JT (2012) Surfactants and Interfacial Phenomena. Wiley, Hoboken, NJ.
- Roundhill DM (2001) Extraction of Metals From Soils and Waters. Kluwer Academic/Plenum Publishers, New York.
- Sachdev DP, Cameotra SS (2013) Biosurfactants in agriculture. *Appl Microbiol Biotechnol* 97:1005–1016.
- Sillanpää M, Oikari A (1996) Assessing the impact of complexation by EDTA and DTPA on heavy metal toxicity using microtox bioassay. *Chemosphere* 32:1485–1497.
- Sillanpää MET (2005) Distribution and fate of chelating agents in the environment. In: Nowack B, VanBriesen JM (eds) Biogeochemistry of Chelating Agents. ACS Symposium Series. American Chemical Society, Washington, DC, pp 226–233.
- Slizovskiy IB, Kelsey JW, Hatzinger PB (2011) Surfactant-Facilitated Remediation of Metal-Contaminated Soils Efficacy and Toxicological Consequences to Earthworms. *Environ Toxicol Chem* 30:112–123.
- Song S, Zhu L, Zhou W (2008) Simultaneous removal of phenanthrene and cadmium from contaminated soils by saponin, a plant-derived biosurfactant. *Environ Pollut* 156:1368–1370.

- Sorvari J, Sillanpää M (1996) Influence of metal complex formation on heavy metal and free EDTA and DTPA acute toxicity determined by *Daphnia magna*. *Chemosphere* 33:1119–1127.
- Sposito G, Page AL (1984) Cycling of metal ions in the soil environment. In: Sigel H, Sigel A (eds) *Metal Ions in Biological Systems (Vol. 18: Circulation of Metals in the Environment)*, vol 18. Marcel Dekker, New York, pp 287–332.
- Steele M, Pichtel J (1998) Ex-situ remediation of a metal-contaminated superfund soil using selective extractants. *J Environ Eng* 124:639–645.
- Swarnkar V, Agrawal N, Tomar R (2011) Sorption of chromate and arsenate by surfactant modified Erionite (E-SMZ). *J Dispers Sci Technol* 33:919–927.
- Tampouris S, Papassiopi N, Paspaliaris I (2001) Removal of contaminant metals from fine grained soils, using agglomeration, chloride solutions and pile leaching techniques. *J Hazard Mater* 84:297–319.
- Tandy S, Bossart K, Mueller R, Ritschel J, Hauser L, Schulin R, Nowack B (2004) Extraction of heavy metals from soils using biodegradable chelating agents. *Environ Sci Technol* 38:937–944.
- Tejowulan RS, Hendershot WH (1998) Removal of trace metals from contaminated soils using EDTA incorporating resin trapping techniques. *Environ Pollut* 103:135–142.
- Torres LG, Lopez RB, Beltran M (2012) Removal of As, Cd, Cu, Ni, Pb, and Zn from a highly contaminated industrial soil using surfactant enhanced soil washing. *Phys Chem Earth* 37-39:30–36.
- US EPA (1995) *Contaminants and Remedial Options at Selected Metal-Contaminated Sites (EPA/540/R-95/512)*. United States Environmental Protection Agency, Washington, D.C.
- US EPA (1996) *A Citizen's Guide to Soil Washing (EPA 542-F-96-002)*. United States Environmental Protection Agency, Cincinnati, OH
- US EPA (1997) *Recent Developments for In Situ Treatment of Metal Contaminated Soils*. United States Environmental Protection Agency, Washington D.C.
- VanBenschoten JE, Matsumoto MR, Young WH (1997) Evaluation and analysis of soil washing for seven lead-contaminated soils. *J Environ Eng-ASCE* 123:217–224.
- Vandevivere P, Hammes F, Verstraete W, Feijtel T, Schowanek D (2001) Metal decontamination of soil, sediment, and sewage sludge by means of transition metal chelant [S,S]-EDDS. *J Environ Eng-ASCE* 127:802–811.
- Wang S, Mulligan CN (2004) An evaluation of surfactant foam technology in remediation of contaminated soil. *Chemosphere* 57:1079–1089.
- Wang S, Mulligan CN (2009a) Rhamnolipid biosurfactant-enhanced soil flushing for the removal of arsenic and heavy metals from mine tailings. *Process Biochem* 44:296–301.
- Wang SL, Mulligan CN (2009b) Arsenic mobilization from mine tailings in the presence of a biosurfactant. *Appl Geochem* 24:928–935.

- Wasay SA, Parker WJ, VanGeel PJ (2002) Removal of lead from a calcareous soil by chloride complexation. *Soil Sediment Contam* 11:841–859.
- Wen Y, Marshall WD (2011) Simultaneous mobilization of trace elements and polycyclic aromatic hydrocarbon (PAH) compounds from soil with a nonionic surfactant and [S,S]-EDDS in admixture: Metals. *J Hazard Mater* 197:361–368.
- Wood AL, Bouchard DC, Brusseau ML, Rao PSC (1990) Cosolvent effects on sorption and mobility of organic contaminants in soils. *Chemosphere* 21:575–587.
- Yang R, Luo C, Zhang G, Li X, Shen Z (2012) Extraction of heavy metals from e-waste contaminated soils using EDDS. *J Environ Sci-China* 24:1985–1994.
- Yu J, Klarup D (1994) Extraction kinetics of copper, zinc, iron, and manganese from contaminated sediment using disodium ethylenediaminetetraacetate. *Water Air Soil Pollut* 75:205–225.
- Zacarias-Salinas M, Vaca M, Flores MA, Bandala ER, Torres LG (2013) Surfactant-enhanced washing of soils contaminated with wasted-automotive oils and the quality of the produced wastewater. *J Environ Prot* 4:1495–1501.

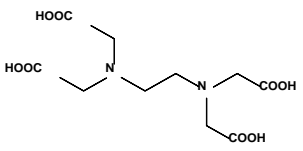
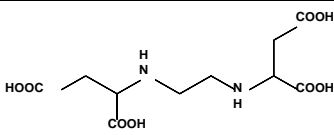
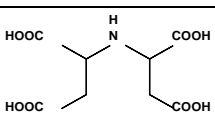
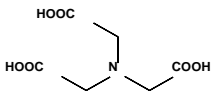
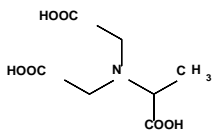
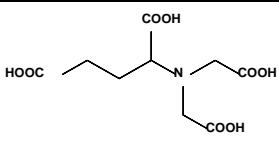
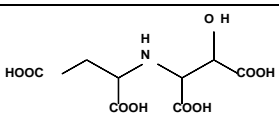
1 **List of Figures**

2 **Figure 1:** A schematic diagram of a basic soil washing process (adapted from [ITRC \(1997\)](#))

3 **Figure 2.** The changes in the conditional stability constants ($\log K'_{ML}$) of the corresponding
4 metal–chelant (ML) complexes as a function of pH (M = Cd, Cu, Ni, Pb and Zn; L = EDTA,
5 EDDS, IDSA, MGDA, GLDA and HIDS). The calculation was performed with the aid of the
6 computer program HySS2009 ([Alderighi et al. 1999](#)) using the values mentioned in [Table 1](#)
7 (adapted from [Begum et al. \(2012b\)](#)).

8 **Figure 3.** A schematic view of the variation of surface tension, interfacial and contaminant
9 solubility with surfactant concentration

10 **Table 1:** Basic information about the chelants (EDTA, EDDS, IDSA, NTA, MGDA, GLDA
 11 and HIDS) that have been explored for washing remediation of metal-contaminated soils,
 12 such as, chemical structure, acid dissociation constants (pK_a) and stability constants ($\log K_{ML}$)
 13 of metal-chelant (ML) complexes with selected toxic metals (Cd, Cu, Ni, Pb and Zn)*

APCs	Structure	pK_a				Metal	$\log K_{ML}$
		pK_{a1}	pK_{a2}	pK_{a3}	pK_{a4}		
EDTA ^a		2.00	2.69	6.13	10.37	– Cd Cu Ni Pb Zn	– 16.5 18.78 18.4 18 16.5
EDDS ^a		2.95	3.86	6.84	10.01	– Cd Cu Ni Pb Zn	– 10.9 ^c 18.36 16.7 12.7 ^c 13.4 ^c
IDSA ^a		1.97	3.24	4.24	10.00	– Cd Cu Ni Pb Zn	– 8.33 12.69 11.68 9.75 9.88
NTA ^b		1.89	2.49	9.73		– Cd Cu Ni Pb Zn	– 9.78 12.94 11.50 11.34 10.66
MGDA ^c		1.5	2.45	10.43		– Cd Cu Ni Pb Zn	– 10.61 13.88 11.99 12.07 10.98
GLDA ^d		2.56	3.49	5.01	9.39	– Cd Cu Ni Pb Zn	– 10.31 13.03 12.74 11.6 11.52
HIDS ^d		2.14	3.08	4.07	9.61	– Cd Cu Ni Pb Zn	– 7.58 12.58 11.3 10.21 9.76

14 ‘–’ stands for ‘no metal added’.

15 ^a At 25 °C ($\mu = 0.1$ M), (Martell et al. 2004); ^b At 25 °C ($\mu = 0.1$ M), (Martell and Smith 1974);

16 ^c At 20 °C ($\mu = 0.1$ M), (Martell et al. 2004); ^d At 25 °C ($\mu = 0.1$ M), (Begum et al. 2012a).

17 *A partial adaptation from Begum et al. (2012b).

18 **Table 2.** The protonation and complexation characteristics of the chelants (EDTA, EDDS,
 19 IDSA, NTA, MGDA, GLDA and HIDS) with selected toxic metals (Cd, Cu, Ni, Pb and Zn)
 20 in the aqueous medium ^{a, *}

Equilibria	EDTA	EDDS	IDSA	NTA	MGDA ^{d, e}	GLDA ^f	HIDS ^f
[HL]/[H][L]	9.52–10.37	10.01	10	9.46–9.84	10.43	9.36	9.61
[H ₂ L]/[HL][H]	6.13	6.84	4.24	2.52	2.45	5.01	4.07
[H ₃ L]/[H ₂ L][H]	2.69	3.86	3.24	(1.81)	1.5	3.49	3.08
[H ₄ L]/[H ₃ L][H]	2	2.95	1.97	(1.0)	–	2.56	2.14
[H ₅ L]/[H ₄ L][H]	(1.5)	–	–	–	–	–	1.6
[H ₆ L]/[H ₅ L][H]	(0.0)	–	–	–	–	–	–
Cd²⁺							
[ML]/[MOHL][H]	(13.2) ^b	–	–	11.25	–	10.25	10.2
[ML]/[M][L]	16.5	10.9 ^d	8.33	9.76	10.6	10.31	7.58
[MHL]/[ML][H]	2.9	4.5	4.68	–	–	4.72	5.11
[MH ₂ L]/[MHL][H]	(1.6) ^b	–	3.28	–	–	3.46	3.77
[ML ₂]/[M][L] ²	–	–	–	14.47	–	–	–
[M ₂ L]/[ML][M]	–	–	–	–	–	–	2.64
Cu²⁺							
[ML]/[MOHL][H]	(11.4)	10.38	–	9.2	–	9.91	8.9
[ML]/[M][L]	18.78	18.4	12.69	13	13.9	13.03	12.58
[MHL]/[ML][H]	3.1	3.48	4.01	1.6	–	4.13	3.65
[MH ₂ L]/[MHL][H]	2	1.95	2.65	–	–	–	2.57
[ML ₂]/[M][L] ²	–	–	–	17.4	–	–	–
Ni²⁺							
[ML]/[MOHL][H]	(11.9)	–	–	10.86	–	–	9.5
[ML]/[M][L]	18.4	16.7	11.68	11.51	12.0	12.74	11.3
[MHL]/[ML][H]	3.1	3.22	4.14	–	–	4.38	3.52
[MH ₂ L]/[MHL][H]	(0.9) ^b	–	–	–	–	2.19	2.24
[ML ₂]/[M][L] ²	–	–	–	16.32	–	–	–
Pb²⁺							
[ML]/[MOHL][H]	–	–	–	–	–	10.65	9.34
[ML]/[M][L]	18	12.7 ^d	9.75	11.48	12.1	11.6	10.21
[MHL]/[ML][H]	2.8	5.9	–	2.3 ^c	–	4.69	4.13
[MH ₂ L]/[MHL][H]	(1.7) ^b	–	–	–	–	2.11	2.41
[MH ₃ L]/[MH ₂ L][H]	(1.2) ^b	–	–	–	–	–	–
[ML ₂]/[M][L] ²	–	–	16.27	12.8 ^d	–	–	–
Zn²⁺							
[ML]/[MOHL][H]	(11.6)	–	–	10.06	–	10.64	8.96
[ML]/[M][L]	16.5	13.4 ^d	9.88	10.65	10.9	11.52	9.76
[MHL]/[ML][H]	3	6.68	4.29	–	–	4.6	3.92
[MH ₂ L]/[MHL][H]	(1.2) ^b	2.48	–	–	–	2.58	–
[ML ₂]/[M][L] ²	–	–	–	14.27	–	–	–

21 ^a Unless mentioned otherwise, all the data are from the NIST database of critically selected stability constants of
 22 metal complexes at 25 ± 0.1°C ($\mu = 0.1$ M) (Martell et al. 2004).

23 ^b $\mu = 1$ M; ^c $\mu = 0.5$ M; ^d At 20°C; ^e Data source: BASF (2007); ^f Data source: Begum et al. (2012a).

24 * A partial adaptation from Begum et al. (2012a) and Pinto et al. (2014).

25

26 **Table 3.** Basic information about the surfactants used for the washing remediation of
 27 contaminated soils *

Surfactant	Name/Components ^a	Ionic nature ^a	Mol weight (g mol ⁻¹) ^a
DPC	1- dodecylpyridinium chloride	Cationic	283.88
TX-100	<i>P</i> -tertiary-octylphenoxy polyethyl alcohol	Nonionic	628
PFOA	Perfluorooctanoic acid	Anionic	414.07
NINOL 40-CO	Cocamide DEA	Nonionic	287.44
CAPB	Cocanut amide propyl betaine	Zwitterionic	342.52
DDAC	Didecyl dimethyl ammonium chloride	Cationic	362.08
SLES	Sodium laureth sulfate	Anionic	NR
SDS	Sodium dodecyl sulphate	Anionic	288.38
SDHS	Sodium dihexyl sulfosuccinate	Anionic	388.45
JBR-425	Rhamnolipid	Nonionic	504.6/650.8
Ammonyx KP	Oleyl dimethyl benzyl ammonium chloride	Cationic	436.11
CTAB	Cetyltrialkyl Ammonium Bromide	Cationic	364.45/406.53
SDBS	Sodium dodecyl benzene sulfonate	Anionic	348.48
Texapon-40	Sodium lauryl ether sulfate	Anionic	376.48
AOT	Bis(2-ethylhexyl) sulfosuccinate sodium	Anionic	444.56
Brij-35	Poly(oxyethylene) ₂₃ dodecyl ether	Nonionic	1198
Tween 80	Polyoxyethylene sorbitan monooleate	Nonionic	1310
Empilan KR6	Alcohols, C9–C11, ethoxylated	Nonionic	NR
Tergitol NP-10	Polyoxyethylene nonyl phenyl ether	Nonionic	NR
Sophorolipid	Sophorolipid	Nonionic	NR
Surfactin	Cyclic lipopeptide	Zwitterionic	NR
Guar gam	Galactomannan	Nonionic	NR
TX-405	Polyoxyethylene (40) isooctylphenyl ether	Nonionic	NR
Brij-58	Polyoxyethylene (20) cetyl ether	Nonionic	1123.5
Brij-98	Polyoxyethylene (20) oleyl ether	Nonionic	1149.5
Saponin	Pentacyclic triterpene saponin	Nonionic	NR
CAS	Cocamidopropyl hydroxysultaine	Zwitterionic	452.69
Emulgin W600	Nonyl phenol	Nonionic	483
Canarcel 20	Sorbitan monolaureate	Nonionic	NR
Canasol BJ35	Lautyl alcohol ether	Nonionic	NR
Surfacpol 203	NR	NR	NR
Surfacpol G	NR	Anionic	NR
Surfacpol 14104	NR	NR	NR
Polafix LO	Propyl-cocoamide betaine	Zwitterionic	NR
Maranil Lab	Sodium dodecyl benzen sulfonate	Anionic	NR
Texapon N-40	Sodium lauryl ether sulfate	Anionic	NR

28 *A compilation from the work of [Torres et al. \(2012\)](#), [Zacarias-Salinas et al. \(2013\)](#) and [Mao et al. \(2015\)](#).

29 ^a ‘NR’ stands for ‘Not Reported.’