1 **The use of chelating agents in the remediation of metal-contaminated soils –**

2 **a review**

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10 ***Capsule:*** *The use of synthetic chelants for soil washing and enhanced phytoextraction by*
11 *plants has been well-studied for the remediation of metal contaminated soils in the last two*
12 *decades.*

13

14 **Abstract**

15

16 This paper reviews current remediation technologies that use chelating agents for the

17 mobilization and removal of potentially toxic metals from contaminated soils. These

18 processes can be done *in situ* as enhanced phytoextraction, chelant enhanced electrokinetic

19 extraction and soil flushing, or *ex situ* as the extraction of soil slurry and soil heap/column

20 leaching. Current proposals on how to treat and recycle waste washing solutions after soil is

21 washed are discussed. The major controlling factors in phytoextraction and possible strategies

22 for reducing the leaching of metals associated with the application of chelants are also

23 reviewed. Finally, the possible impact of abiotic and biotic soil factors on the toxicity of

24 metals left after the washing of soil and enhanced phytoextraction are briefly addressed.

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26 *Keywords:* Metal; Chelant; Phytoextraction; Soil washing; Metal leaching

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1. Introduction

The contamination of soils with toxic metals has become a major environmental concern in many parts of the world due to rapid industrialization, increased urbanization, modern agricultural practices and inappropriate waste disposal methods. In Europe, the polluted agricultural lands likely encompass several million hectares (Flathman and Lanza, 1998). In China, the degraded land associated with mining activities reached about 3.2 Mha by the end of 2004, and the figure is increasing at an alarming rate of 46,700 ha per year (Bai et al., 1999; Li, 2006).

In soils, toxic metals are present in various chemical forms and generally exhibit different physical and chemical behaviors in terms of chemical interactions, mobility, biological availability and potential toxicity (Bohn et al., 1979). Chemical speciation plays a vital role in the solubility and potential bioavailability of metals in soils (Tandy et al., 2004). Unlike organic compounds, toxic metals are not degradable in the environment, and can persist in soils for decades or even centuries. The contamination of soils by metals can have long-term environmental and health implications.

It is highly desirable to apply suitable remedial approaches to polluted soil, which can reduce the risk of metal contamination. The excavation and disposal of soil is no longer considered to be a permanent solution. The demand for soil treatment techniques is consequently growing and the development of new low-cost, efficient and environmentally friendly remediation technologies has generally become one of the key research activities in environmental science and technology. In selecting the most appropriate soil remediation methods for a particular polluted site, it is of paramount importance to consider the characteristics of the soil and the contaminants. At present, various approaches have been suggested for the remediation of metal-contaminated sites. Some of these technologies, like

53 soil washing using particle size separation and chemical extraction with aqueous solutions of

54 surfactants and mineral acids are in full-scale use (Kuhlman and Greenfield, 1999; Mann,

55 1999), while technologies addressed in this review, chelant-assisted soil washing and

56 enhanced phytoextraction, are still largely in the development phase.

57   Toxic metals and other contaminants can be isolated and contained to prevent their further

58 movement, *i.e.* by leaching through soil or by soil erosion. This can be achieved by capping

59 the site with asphalt or other impermeable materials to prevent the infiltration of water, by

60 planting permanent plant cover *(e.g.*, phyto-stabilization) or by covering the site with

61 unpolluted soil (Guo et al., 2006).

62   Smaller, but usually more polluted, soil particles can be removed from the rest of the soil

63 by various separation techniques developed and used in the mining industry. These include

64 the use of hydrocyclones, which separate larger particles from smaller ones using centrifugal

65 force; and solid-liquid separation techniques, such as gravimetric settling and flotation, which

66 are based on the different surface characteristics of particles (Mulligan et al., 2001; Vanthuyne

67 and Maes, 2002).

68   Stabilization involves fixing up the contaminants in stable sites by mixing or injecting

69 inorganic or organic soil amending agents *(e.g.*, liming agents, organic materials,

70 aluminosilicates, phosphates, iron and manganese oxides, coal fly ashes, *etc.*). Due to the

71 effects of a change in pH, such agents are effective at decreasing the bioavailability of metals

72 by introducing additional binding sites for toxic metals. Stabilized metals then become less

73 available for plants, and their bioconcentration through the food chain is reduced (Guo et al.,

74 2006). However, the toxic metals remain in the soil and can be harmful when soil dust is

75 ingested or inhaled. Many of the amendments used in soil stabilization are by-products of

76 industrial activities, and are therefore inexpensive and available in large amounts. Overviews

77 on previously successfully applied amending agents and their effectiveness for different

78 metals have been given by Knox et al. (2001) and Puschenreiter et al. (2005).

79   Another immobilization method is vitrification by heating the contaminated soil to up to

80 $2000^{o}C$. Vitrification usually involves imposing an electrical current between electrodes

81 inserted into the contaminated soil. Due to its low electrical conductivity, the soil begins to

82 heat and produces a melt that hardens into a blocks of glasslike material. Vitrification is

83 expensive but applicable to soils with mixed organic and metallic contamination, for which

84 few technologies are available (Buelt and Farnsworth, 1991).

85   Electrokinetic extraction has been proposed as an *in situ* method for the remediation of

86 blocks of contaminated soil. Electrokinetic extraction involves the electrokinetic movement of

87 charged particles suspended in a soil solution, initiated by an electric gradient. The target

88 metals can be removed by precipitation at the electrodes (Hicks and Tondorf, 1994).

89   Phytoextraction is a publicly appealing (green) remediation technology. However,

90 phytoextraction can be effectively applied only for soils contaminated with specific (and less

91 problematic) potentially toxic metals and metalloids, *e.g.* Ni, Zn and As, which are readily

92 bioavailable for plants and for which appropriate hyper-accumulating plants with a high

93 enough biomass are known. Common crop plants with a high biomass can be triggered to

94 accumulate large amounts of low bioavailability metals (*e.g.* Pb, Cr, U, Hg) when the mobility

95 of these metals in the soil is enhanced by the addition of mobilizing agents (Huang et al.,

96 1997; Wu et al., 1999; Shen et al., 2002; Luo et al., 2005). In such chemically enhanced

97 phytoextraction, chelating agents are used almost exclusively as the mobilizing agents.

98   This paper reviews the current remediation technologies for metal-contaminated soils,

99 which use chelating agents. Chelants desorb toxic metals from soil solid phases by forming

100 strong water-soluble complexes, which can be removed from the soil by plants through

101 enhanced phytoextraction or by using soil washing techniques. The latter currently consist of

102 soil flushing, the extraction of soil slurry in reactors, and soil heap/column leaching. Another

103 innovative remediation method that uses chelating agents for mobilizing metals is enhanced

104 electrokinetic extraction.

105

106 **2. Chelant assisted phytoextraction**

107

108   The idea of using plants to remediate metal-contaminated soil has attracted a great deal of

109 research in the last two decades. But due to the limited plant species with a high capacity to

110 accumulate metals, especially metals with low bioavailability in soil, such as Pb, and to

111 produce a large amount of biomass, one alternative approach using chelants to improve the

112 uptake of metals by high biomass plants has been proposed, inspired by studies on plant

113 nutrition (Marschner, 1995).

114   Careful assessment and evaluation is required to determine the biodegradation and

115 toxicity of the chelating agents and their metal complexes in soils (Means et al., 1980;

116 Borgmann and Norwood, 1995; Nörtemann, 1999; Grčman et al., 2001; Römkens et al.,

117 2002). Although EDTA (ethylenediaminetetraacetic acid) was recognized as the most efficient

118 chelant to increase metal uptake by plants, especially for the uptake of Pb, the low

119 biodegradability of the chemical does not make it a good choice for large-scale field

120 applications (Kos and Leštan, 2004; Tandy et al., 2004; Luo et al., 2005). In recent years, the

121 focus of research has shifted to some more biodegradable chelants, such as NTA

122 (nitrilotriacetate), [S,S]-EDDS (S,S-ethylenediaminedisuccinic acid), and others. The use of

123 these biodegradable chelants in improving the uptake of metals by plants and in limiting the

124 leaching of metals from soil has become an attractive field of research. Most of this kind of

125 research has been carried out in the form of studies comparing the previous EDTA results in

126 metal uptake efficiencies with additional data on the biodegradability of chelants and the

127 metal leaching potential from the application of the chemicals (Grčman et al., 2003; Kos and

128 Leštan, 2004; Luo et al., 2005; Meers et al., 2005; Luo et al., 2006b). The optimization and

129 application of this technology should be based on the full understanding of important

130 processes involved, such as metal solubilization from the application of chelants, the uptake

131 of metals by the roots of plants, and their transport upwards to the shoots of the plants. To

132 prevent the possible movement of metal-chelants into groundwater and to reduce the impact

133 of the remaining chelant on soil microorganisms, the selection of chelants and the amount and

134 process of their application are important, as well as irrigation techniques and the time of the

135 chelant application (Blaylock et al., 1997; Evangelou et al., 2007; Luo et al., 2007). The

136 following section reviews the research progresses on the phytoextraction of metals using

137 chelants in recent literature, and highlights some potential research area for future

138 devolvement.

139

140 *2.1. Theoretical considerations*

141

142   In the process of chelant-assisted phytoextraction, chelant is applied to the soils. First,

143 chelant can desorb metals from the soil matrix, and the mobilized metals move to the

144 rhizosphere for uptake by plant roots. The amounts of bioavailable metals in soil solution are

145 mainly determined by the properties of the soil and the chelant which is applied (Huang et al.,

146 1997; Kos and Leštan, 2004; Tandy et al., 2004; Luo et al., 2005).

147   The efficacy of a chelant in the extraction of metals is usually rated with the stability

148 constants *Ks* of the chelant-metal complexes. According to Elliott et al. (1989), the order of

149 magnitude of the *Ks* can be used to rank different chelants according to their general efficacy,

150 but not to rank the efficacies of a specific chelant toward different metals because the latter is

151 also influenced by the metal speciation in a given soil matrix. Huang et al. (1997) indicated

152   that a variety of synthetic chelants have the potential to induce Pb desorption from soil. Their

153   effectiveness, in decreasing order, was EDTA > HEDTA (N-hydroxyethylenediaminetriacetic

154   acid) > DTPA (diethylenetriaminepentaaceticacid) > EGTA [ethyleneglycol -bis (ß -

155   aminoethyl ether), N, N, N', N-tetraacetic acid] > EDDHA [etylenediamine-di (*o*-

156   hydroxyphenylacetic acid)]. EGTA has been shown to have a high affinity for Cd^{2+}, but not

157   for Zn^{2+}. Luo et al. (2005) found that EDTA is more efficient than [S,S]-EDDS in the

158   extraction of Pb and Cd, but that [S,S]-EDDS is more effective in the extraction of Cu and Zn.

159   The predominant theory for metal-chelant uptake is the split-uptake mechanism, by which

160   only free metal ions can be absorbed by plant roots (Chaney et al., 1972; Marschner et al.,

161   1986). Fe-EDTA is known to dissociate before plant uptake (Marschner et al., 1986; Sarret et

162   al., 2001). Another important theory suggests that some of the purportedly intact metal-

163   chelant complexes are taken up by plants (Wallace, 1983; Bell et al., 1991; Laurie et al., 1991;

164   Salt et al., 1995; Nowack et al., 2006). A schematic display of this process is shown in Figure

165   1.

166   As a typical soil metal contaminant, Pb has been extensively studied. The metal can be

167   absorbed by plant roots and transferred as a Pb-EDTA complex (Vassil et al., 1998; Epstein et

168   al., 1999). In the leaves of *Phaseolus vulgaris*, Sarret et al. (2001) detected that some of the

169   Pb was complexed to EDTA. The complexes of Pb-EDTA cannot be split through the

170   reduction or oxidation of Pb. It is also unlikely that Pb-EDTA or EDTA can diffuse across the

171   plasma membrane at any significant rate, as they are too large and polar to move the

172   plasmalemma lipid bilayer. It has been concluded that the uptake of Pb-EDTA by plants can

173   take place in the location where suberization of the root cell walls has not yet occurred and at

174   breaks in the root endodermis and the Casparian strip (Tanton and Crowdy, 1972; Bell et al.,

175   1991). Therefore, some damage to the root may be helpful for the indiscriminate uptake of Pb-

176 EDTA by plant roots. The damage could be caused by the toxicity of metals, chelants and

177 other artificial means (Vassil et al., 1998; Luo et al., 2006a).

178

179 *2.2. Application of chelants*

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181 For a given chelant, different methods of application can produce different levels of

182 phytoextraction efficiency. Exploring effective strategies for the application of chelants is

183 useful in optimizing the technology. It has been reported that placing chelant at some depth

184 near the roots of plants instead of mixing this agent into the entire soil area will lead to a

185 significantly higher accumulation of trace metals by plants (Kayser et al., 1999). Applying

186 chelant in several smaller dosages (versus in one application) can result in the enhanced

187 phytoextraction of Pb (Grčman et al., 2001; Puschenreiter et al., 2001; Shen et al., 2002). The

188 combined application of different chemicals can also greatly improve the metal

189 phytoextraction efficiency. One type of combination is the use of two chelants/chemicals,

190 which can increase the solubility of metals by lowering the pH of the soil. Blaylock et al.

191 (1997) demonstrated that the application of EDTA and acetic acid led to a two-fold

192 accumulation of Pb in Indian mustard shoots compared with the application of EDTA alone.

193 This result was explained by the lower cell wall retention of Pb as lead carbonate at a lower

194 rhizosphere pH. The second type of combination is based on the interactions between metals

195 and different chelants, in which the solubility of metals by a chelant can be increased by

196 another chelant through the reduction of competition from other metals in soil. Luo et al.

197 (2006c) found that the combined application of EDTA and [S,S]-EDDS led to a higher level

198 of efficiency (*i.e.*, a synergy effect) in the phytoextraction of Cu, Pb, Zn and Cd than could be

199 obtained by the application of either chelant alone. There are two reasons for the result: the

200 fact that EDTA and [S,S]-EDDS have different levels of efficiency in extracting metals from

soils; and a decrease in the competitive cations for trace metals with EDTA, such as soil-soluble Ca, due to the addition of [S,S]-EDDS (Tandy et al., 2004). The third type of combination is the utilization of one chemical to destroy the plant root structure to facilitate the direct uptake of metal-chelants and their translocation into the shoots. In several experiments, it was found that the application of glyphosate enhanced the Pb accumulation of the tested crops (Kayser et al., 1999; Mathis and Kayser, 2001). The mechanism of enhanced metal accumulation after the application of glyphosate was explained by a disruption of the plant's metabolism, leading to the enhanced transport of trace metals from roots to shoots (Ensley et al., 1999).

Some artificially physiological damage to roots, such as that resulting from pretreatments with MC (methanol: trichloromethane), HCl and hot water, and from treatment with DNP (2, 4-dinitrophenol, an uncoupler of oxidative phosphorylation), dramatically increased the concentrations of Pb in shoots with the EDTA treatment (Luo et al., 2006a). Applying similar treatments in a pot experiment, Luo et al. (2006d) found that when chelants were applied as hot solutions at the rate of 1 mmol kg^{-1}, the concentrations and total phytoextraction of Cu, Zn and Cd by plant shoots exceeded or at least approximated those in the shoots of plants treated with normal chelants at a rate of 5 mmol kg^{-1} (Luo et al., 2006d). This result indicated that the amount of chelant applied could be greatly decreased for the given effectiveness of chelants in enhancing the phytoextraction of trace metals from contaminated soils. The soil leaching study demonstrated that there was no significant difference in the soluble metals between the hot and normal chelant applications when the chelant was applied at the same dosage. The decreased dosage of chelant resulted in decreased concentrations of soluble metals in soils, which meant that the hot chelant application did not increase metal leaching compared with the normal chelant application. Similarly, some environmental stresses, such as excessive toxic metals, high temperatures, and drought, may also result in a breakdown of the root

226   exclusion mechanisms, subsequently influencing the chelant-enhanced accumulation of trace

227   metals in plant shoots. This result may be one of the reasons behind the different

228   phytoextraction efficiencies in using EDTA treatments reported by various researchers even

229   for the same plant species (Blaylock et al., 1997; Huang et al., 1997; Wu et al., 1999; Salido et

230   al., 2003; Walker et al., 2003; Lim et al., 2004; Meers et al., 2004).

231

2.3. Optimizing the phytoextraction process

233

234   Environmental and economic concerns require that the addition of chelants should be kept

235   to a minimum. This suggests that further improvements in the process of selecting and

236   applying chelants should be made in parallel with the selection of plant species. As for plants,

237   first, the species should be one that is able to tolerate some degree metal contamination.

238   Screening for more sensitive species/cultivars and optimizing plant growth conditions would

239   help to reduce the dosage of chelants for a given phytoextraction efficiency (Kumar et al.,

240   1995; Li et al., 2005; Luo et al., 2006b,d). Desirable plant species are those that are fast-

241   growing, have a high biomass and are easily harvested. Native plant species are better than

242   exotic species, as using the former increases the probability of success and reduces the

243   potential risk of plant invasion. Research on an easily biodegradable chelant to replace those

244   with low levels of biodegradability has led to some exciting new results. A typical example is

245   the recent reports about the use of [S,S]-EDDS in the phytoextraction application (Grčman et

246   al., 2003; Kos and Leštan, 2004; Luo et al., 2005; Meers et al., 2005; Tandy et al., 2006).

247   Different chelant application methods will also have a significant impact on the efficiency of

248   metal phytoextraction.

249   In addition, there are several new areas of development that are worthy further research to

250   reduce potential metal leaching in chelant-enhanced phytoextraction.

251   First, a new slow-releasing chelating agent can be developed by coating solid EDTA (or

252   other chelants) with a layer of silicate to slow down the mobilization of metals in soil in order

253   to match plant uptake, and thus prevent excessive mobilization (Li et al., 2005). The results

254   have indicated that the slow release of CCA (coated chelating agent) improved the

255   bioavailability of metals in soil to match the plant uptake of these metals, and that this could

256   reduce the risk of metals leaching from the soil.

257   Second, some agronomic practices should be adapted to increase the efficiency of metal

258   phytoextraction. The efficiency of phytoremediation depends on large plant yields and high

259   metal concentrations in plant shoots. Therefore, increasing plant dry biomass yields can be

260   helpful in increasing the total metal uptake by plants. It has been suggested that the use of

261   foliar-applied P to plants grown in Pb-contaminated soils can overcome P deficiencies and

262   avoid the necessity of adding P fertilizer to soils. Huang and Cunningham (1996) reported that

263   foliar P application not only increased plant biomass four-fold in goldenrod, but also

264   increased total plant Pb uptake by 115%.

265   A significant increase in the uptake and translocation of Pb has been reported for corn

266   transplanted into soil, then treated with EDTA, in comparison with the plants that were

267   germinated and grown in Pb-contaminated soil to which EDTA was subsequently applied

268   (Wu et al., 1999). Transplanting seedlings rather than planting seeds resulted in an increased

269   uptake of chelates, probably through breaks in the Casparian strip due to possible mechanical

270   damage to the roots (Wallace and Hale, 1962).

271   Using deep-rooted, higher water-use plants or trees to reduce metal leaching may be

272   another good approach. Chen et al. (2004) found that 98, 54, 41 and 88% of the initially

273   applied Pb, Cu, Zn and Cd could re-adsorbed in the soil due to the effects of vetiver grass.

274   Although the deep-rooted plants of vetiver grass could not accumulate high concentrations of

275   metals, the plant may reduce the risk of metals migrating downwards and contaminating the

276   groundwater through the evaporation of water by the roots of vetiver grass. Therefore, if other

277   high metal-tolerant plants, such as Indian mustard, are intercropped with vetivar grass, on the

278   one hand the metals will be accumulated by the shoots of mustard, and on the other hand the

279   leached metals would be reduced by their readsorption in deep soil layers due to the root

280   effect of vitiver grass.

281   Third, different phytoremediation technologies can be combined in field applications.

282   Electrodic and electrokinetic remediation is another alternative for removing trace metals and

283   radionuclides from contaminated soil and ground water (Li and Li, 2000; Yong, 2001). Lim et

284   al. (2004) reported that the addition of an electric field around the plants in combination with

285   the application of EDTA did more to enhance the uptake of Pb by Indian mustard than the

286   addition of EDTA only. The accumulation of Pb in the shoots of Indian mustard increased 2-

287   to 4-fold when 0.5 mmmol kg^{-1} of EDTA was applied with the parallel application of

288   electrodics.

289

290   **3. Soil washing using chelating agents**

291

292   Soil washing involves the separation of toxic metals from soil solid phases by solubilizing

293   the metals in a washing solution. Acids and chelating agents are the most prevalent removal

294   agents used in soil washing (Peters, 1999). Acids dissolve carbonates and other metal-bearing

295   soil material and exchange trace metals from soil surfaces where H^+ ions are attracted more

296   strongly than the cations of toxic metals. Chelating agents desorb trace metals from soil solid

297   phases by forming strong and water-soluble metal-chelant coordination compounds

298   (complexes). These complexes are very stable, prevent the precipitation and sorption of

299   metals, and do not release their metal ions unless there is a significant drop in soil pH. Since

300   acidic solutions can cause deterioration in the physico-chemical properties of the soil, using

301 chelating agents is considered to be environmentally less disruptive than using acids (Xu and

302 Zhao, 2005).

303   The important issues concerning the selection of chelants and the development of washing

304 solutions are summarized as follows (Peters and Shem, 1992; Hong and Jiang, 2005):

305 • Extraction strength. The chelant should be able to form strong, stable complexes with

306   toxic metals over a wide pH range.

307 • Extraction selectivity towards target toxic metals.

308 • The potential for recovering the spent chelant. If the chelant is to be recycled and reused in

309   the process several times, it should have low biodegradability in soil.

310 • The metal-chelant complexes should have low adsorption affinity towards solid soil

311   surfaces.

312 • The chelant should have low toxicity and a low potential to harm the environment.

313 • The chelant should be cost-effective.

314   Many different chelants (mostly aminopolycarboxylic acids) have been tested for soil

315 washing. In the literature, EDTA (Na_2EDTA) is the most frequently cited chelating agent for

316 extracting potentially toxic trace metals from soils, because of its efficiency, availability and

317 relatively low cost.

318   Since common soil constituents (e.g., Ca^{2+}, Fe^{2+}, Mg^{2+}, Al^{3+}) compete with toxic metals

319 for the binding sites of chelating agents, an excess amount of chelant is needed to ensure the

320 adequate removal of contaminants. Elliott and Brown (1989) reported that more than 95% of

321 the Pb that was present was removed when a 2:1 EDTA:Pb molar ratio was used. The removal

322 efficiency was lower when an equimolar ratio was used.

323   The stability constants of the formation of the metal-chelant complex and thus the

324 efficiency of chelant metal extraction are pH dependent. The removal of greater amounts of

325 toxic metals has most often been observed at lower pH levels (Van Benschoten and

326 Matsumoto, 1997). However, Vandevivere et al. (2001) reported that a slightly alkaline pH

327 was optimal for the removal of Pb, Zn and Cd with [S,S]-EDDS. The formation of complexes

328 in soils is controlled by the kinetic of all complexation reactions, adsorption in soil solid

329 phases, mineral dissolution and the possible degradation of the chelating agent or its metal

330 complexes (Nowack, 2002). These interactions are difficult to predict and depend on the

331 contaminants and soil conditions. Interestingly, applying chelant in several small dosages

332 often results in the extraction of considerably more toxic metals than when using one large

333 dose (Finžgar and Leštan, 2007). In practice, the choice of washing solution pH, the

334 concentration of the chelating agent and the application mode, the optimum soil/washing

335 solution ratio, the retention (reaction) time of the chelating agent solution in the soil and the

336 designated soil washing technique must therefore be selected individually for each case of

337 remediation. Technically, soil-washing techniques comprise soil flushing, extraction or

338 leaching.

339

340 *3.1. In situ soil flushing*

341

342   Soil flushing is an *in situ* soil washing technique applicable to specific soil conditions, in

343 which the contaminated zone is underlain by non-permeable materials, which allows the

344 washing solution to be pumped and treated (Gracia-Delgado et al., 1998; Khan et al., 2004).

345 The method is suitable for sandy soil or sediment with high hydraulic conductivity. As shown

346 in Figure 2, the washing solution is forced through the in-place soil matrix via injection wells

347 or is infiltrated into the soil using surface sprinklers or similar devices. The washing solution

348 is pumped from the soil using a set of recovery wells installed down a gradient of the

349 contaminated area. The washing solution must be treated to remove toxic metals and the

350 process water reused in the flushing process. Treating the washing solution could prove to be

351   more difficult than the soil remediation itself (Mulligan et al., 2001). The disadvantage of *in*

352   *situ* soil flushing is the low degree of control over the movement of contaminants into

353   undesirable areas. The hydrology of the site must therefore be precisely understood.

354

355   *3.2. Extraction of soil slurry*

356

357   The extraction of soil slurry refers to the batch treatment of soil slurry in a reactor, as

358   shown in Figure 3. Following an initial screening of the excavated soil to remove the surface

359   debris, the soil is vigorously mixed with the chelating agent solution, separated by a second

360   screening step (filtration), and then returned to the ground (Vandevivere et al., 2001). The

361   washing of soil in reactors involves stringent physical treatments. It is harsh for the soil flora

362   and can cause the physical quality of the soil (its structure, water holding capacity and

363   hydraulic conductivity) to deteriorate (Finžgar and Leštan, 2006a).

364

365   *3.3. Soil heap/column leaching*

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367   In soil leaching, the washing solution is gravitationally percolated through a soil heap or

368   column *ex situ* (Papassiopi et al., 1999; Sun et al., 2001). As shown in Figure 4, the soil which

369   is contaminated with toxic metals is excavated, screened and placed in a mound on a pad.

370   Metals are removed by passing washing solution through the soil using some type of liquid

371   distribution system. The extractant is collected in a pregnant solution pit and processed to

372   remove metals (Hanson et al., 1992). Soil leaching is operationally simple and holds the

373   potential for the economical treatment of large amounts of soil. The leaching efficiency is

374   higher for soils with higher hydraulic conductivity.

375

3.4. Chelant enhanced electrokinetic extraction

When a direct current electrical field is imposed across a wet mass of contaminated soil, the pore fluid migrates by electroosmosis and the ions migrate by ionic migration towards the electrodes. Combining these two removal mechanisms results in the electrokinetic extraction of metal contaminants from soils.

During electrokinetic soil treatment, hydrogen ions (H^+) are generated at the anode due to water electrolysis, and migrate into the bulk of the soil. A low pH develops through the soil (except at the cathode where OH^- is generated), causing desorption of metallic contaminants from the soil solid phases. The dissolved metallic ions are then removed from the soil solution by ionic migration and precipitation at the cathode (Acar and Alshawabkeh, 1993). However, a high soil buffer and ion exchange capacity can prevent soil acidification and thus decrease the efficiency of the electrokinetic extraction of toxic metals. In such conditions, the addition of a chelating agent to the soil can enhance electrokinetic extraction. EDTA has most often been tested, since EDTA form strong water-soluble chelant complexes with most toxic metals (Yeung et al., 1996). Chelant-enhanced electrokinetic extraction is promising for dealing with contamination at moderate depths in fine-grained soils and soils with a high clay or organic matter content, where the application of soil washing technologies is impractical.

3.5. Treatment of soil washing solutions

One of the main drawbacks of the soil washing methods is the vast consumption of water required for making up the washing solution, and of clean water for the removal of the mobilized metallic species that have been complexed with the chelating agent and that have been retained in the soil after the remedial treatment. Another problem is that the washing

401 solution, now rich with metal-chelant complexes, must subsequently be treated before it can

402 be safely discharged. EDTA, the chelating agent that is most often used, is toxic, especially in

403 its free form (Sillanpaa and Oikari, 1996; Dirilgen, 1998), and is poorly photo-, chemo- and

404 biodegradable in the environment (Nörtemann, 1999). In the case of conventional treatments

405 such as settling, chemical precipitation or activated carbon, it is difficult to recover chelating

406 agents from spent extraction fluid or wastewater from other processes.

407   Several strategies have been proposed for the treatment of spent soil washing solutions.

408 For Pb-EDTA soil extractant, Kim and Ong (1999) proposed the replacement of the Pb in the

409 EDTA complex with Fe^{3+} ions at a low pH level, followed by the precipitation of Pb ions with

410 phosphate or sulfate ions. Ferric iron is then separated from the EDTA with precipitation at a

411 high pH level. The method allows chelates to be recycled and reused. Similarly, Ager and

412 Marshall (2003) investigated the possibility of substituting zero-valent Mg and Pd for metals

413 in EDTA complexes. Zeng et al. (2005) proposed that metals be precipitated from the soil

414 washing solution as insoluble sulphides after the addition of Na_2S. Di Palma et al. (2003a)

415 advocated the recovery of EDTA after washing soils "artificially" contaminated with Pb or Cu

416 in two steps: using an initial evaporation treatment that leads to a reduction of the extractant

417 volume by 75%, followed by acidification, which precipitates more than 90% of the EDTA

418 complexes. The feasibility of the evaporation of the extractant is probably constrained by the

419 high cost of water evaporation, an operation that consumes a great deal of energy. The same

420 research team (Di Palma et al., 2003b) also proposed reverse osmosis to reduce the volume of

421 the extractant. Allen and Chen (1993) suggested the electrolytic separation of metals and the

422 chelating agent in the soil washing solution. A two-chamber cell separated by a cation

423 exchange membrane to prevent migration to the anode and the oxidative destruction of

424 negatively charged metal-EDTA complexes was used for this. In electrolytic separation and

425 reverse osmosis, colloidal particles (clays and humic materials) and bacteria can clog the

426 membranes and thus diminish the performance and shorten the lifetime of the membranes.

427 Tejowulan and Hendershot (1998) used a simple procedure to remove negatively charged

428 metal-EDTA complexes from the soil washing solution using an anion exchange resin.

429 However, an effective method of recycling expensive resins still needs to be developed.

430   The cost of the chelating agent can be an important issue in soil remediation. Methods that

431 recycle not only the process water, but also the chelant may therefore be economically

432 feasible. However, at the current stage of development, the proposed EDTA recycling

433 methods involve the use of other expensive chemical materials or are technically demanding.

434 For example, the substitution procedure proposed by Kim and Ong (1999) can prove difficult

435 to apply if EDTA is complexed with more than one trace metal, especially with Zn. It is rare

436 for soil to be contaminated with a single metal; rather, several toxic metals are usually

437 simultaneously present in elevated concentrations. On the other hand, EDTA, the most

438 commonly used chelating agent, is relatively inexpensive (in Europe, it costs about 1.3 euros

439 per kg^{-1} for the technical-grade chemical, according to a major European manufacturer)

440 compared to the cost of soil remediation, which can go up to 450 euros per m^{-3} for *in situ* soil

441 washing (Summergill and Scott, 2005). Chaney et al. (2000) reported that the price of

442 technical-grade EDTA in the U.S.A. was 4.3 US$ per kg^{-1}. The efficient destruction of EDTA

443 complexes and the removal of toxic metals from the washing solution could provide a simple

444 and robust treatment, and the process water can be reused.

445   To treat decontaminated wastewater from the nuclear industry and other aqueous effluents

446 contaminated with EDTA, the chemical destruction of EDTA and its complexes using

447 advanced oxidation processes (AOP) has been proposed (Korhonen et al., 2000; Munoz and

448 von Sonntag, 2000). AOP involves the use of ozone, H_2O_2, ultrasonic waves, UV irradiation,

449 Fenton's reagent (Fe^{2+} and H_2O_2), alone or in combination, and electrochemical methods, to

450 generate free hydroxyl radicals that are powerful, effective and non-specific oxidizing agents.

451   Finžar and Leštan (2006b) introduced a novel EDTA-based soil leaching method that involves

452   treating and reusing the washing solution in a closed process loop (Figure 5). An AOP

453   combination of ozone and UV was used to generate hydroxyl radicals for the oxidative

454   decomposition of EDTA-metal complexes. The metals which were released were then

455   removed from the washing solution by absorption on a zeolite-based commercial metal

456   absorbent. The method was successfully tested for soils contaminated with Pb, Zn, Cd and Cu,

457   resulting in the removal of a substantial amount of metals and in a major reduction of the

458   mobility and bioacessibility (toxicity) of metals left in the soil after remediation (Leštan and

459   Finžgar, 2007). The method produced a colorless discharge washing solution with a close to

460   neutral pH and fairly low concentrations of toxic metals and EDTA. Compared to

461   conventional soil washing methods, this method requires very little process water, and enables

462   potential emissions to be easily controlled – in short, it is environmentally and soil "friendly."

463

464   **4. The fate of metals left after soil remediation**

465

466   Toxic metals in soil are usually not entirely accessible to chelating agents. Consequently,

467   only part of the total amount of metals in soil is removed by soil washing or enhanced

468   phytoextraction, especially from soils rich in organic matter or clay. Peters and Shem (1992),

469   for example, reported that a maximum of 64.2 and 19.1% of Pb (compared with the initial Pb

470   concentration) was washed with EDTA and NTA as chelants, respectively, from contaminated

471   soil with a high clay and silt content. Similarly, Pichtel et al. (2001) reported that various

472   concentrations of EDTA and PDA (pyridine-2,6-dicarboxylic acid) removed up to 58 and

473   56% of Pb, respectively, from soil material at a battery recycling/smelting site. Metal

474   speciation and fractionation are also crucial for extraction efficiency of chelating agents.

475   Barona and Romero (1996) extracted Pb-contaminated soil with EDTA and observed that the

476   amount of Pb that was removed correlated with the amount of Pb associated with the Fe and

477   Mn-oxide and organic matter soil fractions. Finzgar et al. (2005) reported that using 40 mmol

478   kg^{-1} of [S,S]- EDDS extracted 31.1% of Pb from vegetable garden soil, which was rich in

479   organic matter. Lead was removed proportionally from the carbonate and organic matter soil

480   fractions. To evaluate the potential of EDTA, NTA, DTPA and [S,S]- EDDS to extract Pb,

481   Zn, Cd and Cu from soil, Nowack et al. (2006) compiled data from 28 publications. Except in

482   some reports for Pb, complete solubilization did not occur, even at a chelant-to-metal ratio of

483   greater than 10. The compiled data also indicated large variations in metal extraction among

484   soils for a given chelant-to-metal ratio.

485   Potentially toxic metals left in soil after remediation are likely to be present in chemically

486   stable mineral forms and bound to non-labile soil fractions. As such, they are less mobile and

487   bioavailable, and therefore less toxic in comparison with the original conditions before

488   remediation. However, the question is whether the reduced mobility and bioavailability of soil

489   residual metals is a permanent or only temporal achievement of soil remediation. Soil is a

490   dynamic natural body and, after remediation, various abiotic (i.e., climatic, hydrological) and

491   biotic soil (microorganisms and fauna) factors could presumably initiate the transition of

492   residual metals from less to more mobile/accessible forms, thus changing their toxicity status.

493   Of the biotic factors, earthworms are perhaps the most important soil organisms in terms of

494   their influence on soil properties. By ingesting organic debris, earthworms have been shown

495   to enhance the bioavailability of soil nutrients such as C, N and P, and also of trace metals.

496   For example, Udovic et al. (2007) reported that EDTA soil leaching removed 58.4% of initial

497   soil Pb and decreased Pb mobility by 83.7% (assessed by the toxicity characteristic leaching

498   procedure, TCLP). However, after the exposure of remediated soil to the earthworm species

499   *Eisenia fetid,* the Pb mobility in their casts increased by 6.2-times – back to the initial level

500   before remediation. In the process of phytoextraction, although the metals accumulated by the

501 shoots of plants are proposed to be recovered by incineration, this technology still needs

502 further research and development in the future.

503

504 **5. Conclusion**

505

506   The remediation of metal-contaminated soils using synthetic chelants for soil washing and

507 for enhancing phytoextraction by plants has become one of a number of well studied clean-up

508 techniques in the last two decades.

509   In soil washing, however, the strategies for developing chelant-washing solutions to

510 achieve optimal efficiency in the extraction of toxic metals and in the recovery of chelant and

511 process water need to be improved. Furthermore, the methods currently being proposed to

512 recycle chelating agents from spent washing solution are still encountering operational

513 difficulties and work well only within a narrow range of contamination and soil types. The

514 cost for soil washing and vitrification is estimated to be between US$ 100,000 and 1,000,000

515 per ha (Russel et al., 1991). The development of more robust recycling methods would greatly

516 increase the economic value of soil washing technologies.

517   The operational cost of chelant-enhanced phytoremediation is much lower than the soil

518 washing operation. In combination with the possible recovery of extracted metals, this

519 technology can be more promising in the future. However, the potential leaching of metals

520 into surrounding environments is the most important concern in this process. It is therefore

521 essential to optimize this technology before it can be safely adopted in field applications.

522   Since toxic metals in soil cannot be entirely removed by chelants and plants, enhanced

523 phytoextraction and soil washing generally focus on stripping the bioavailable and mobile

524 metal fractions those interact with biological targets and poses a threat to the environment and

525 human health, instead of trying to reduce the total concentration of metals in soil below limits

526 set by legislation (Hamon and McLaughlin 1999). However, the potential effect of abiotic and

527 biotic soil factors on the availability and mobility of toxic metals left in soil after soil

528 remediation requires further investigation.

529

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537 **References**
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813

Figure Captions

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816

817   Figure 1. The schematic representation of the uptake of metal-chelant complexes by plant

818   roots, their translocation upward, and the potential leaching of metals into the

819   surrounding environment in the process of chelant-enhanced phytoextraction (the red

820   circle and yellow moon represent the metals and the applied chelant in the soil,

821   respectively)

822

823   Figure 2. Flow chart of *in situ* soil flushing via the injection (A), irrigation (B) and sprinkling

824   (C) of the soil washing solution.

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826   Figure 3. Flow chart of *ex situ* extraction of the soil slurry in the reactor.

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828   Figure 4. Flow chart of *ex situ* soil heap/column leaching.
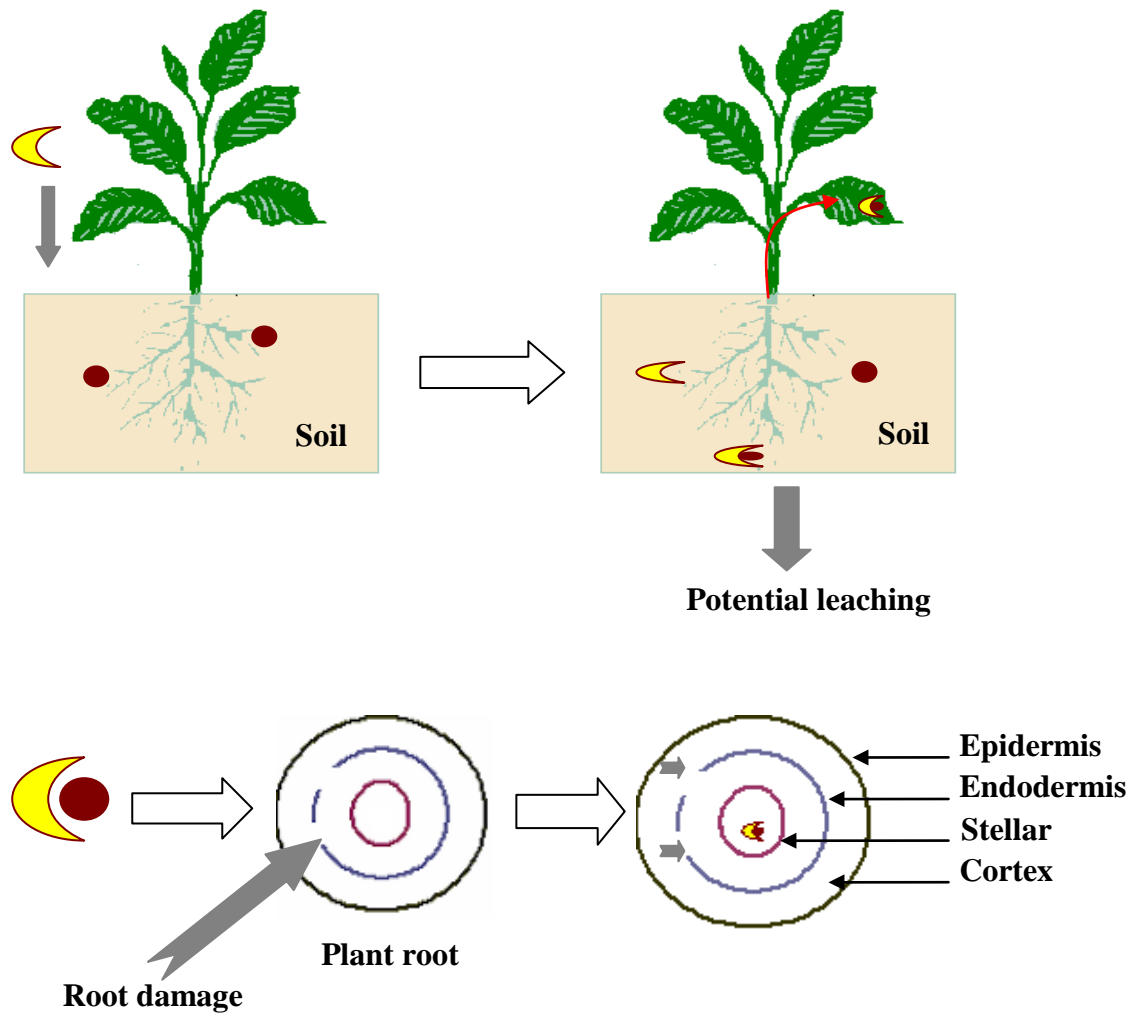
829

830   Figure 5. Flow chart of the chelant-based soil leaching method using AOP to treat and reuse

831   the washing solution in a closed process loop. The washing solution first circulates

832   solely through soil (A- washing step) until the optimal contact time for removing the

833   metals is reached, and afterwards also through the soil solution treatment units (B),

834   to remove all mobilized metal complexes from the soil.

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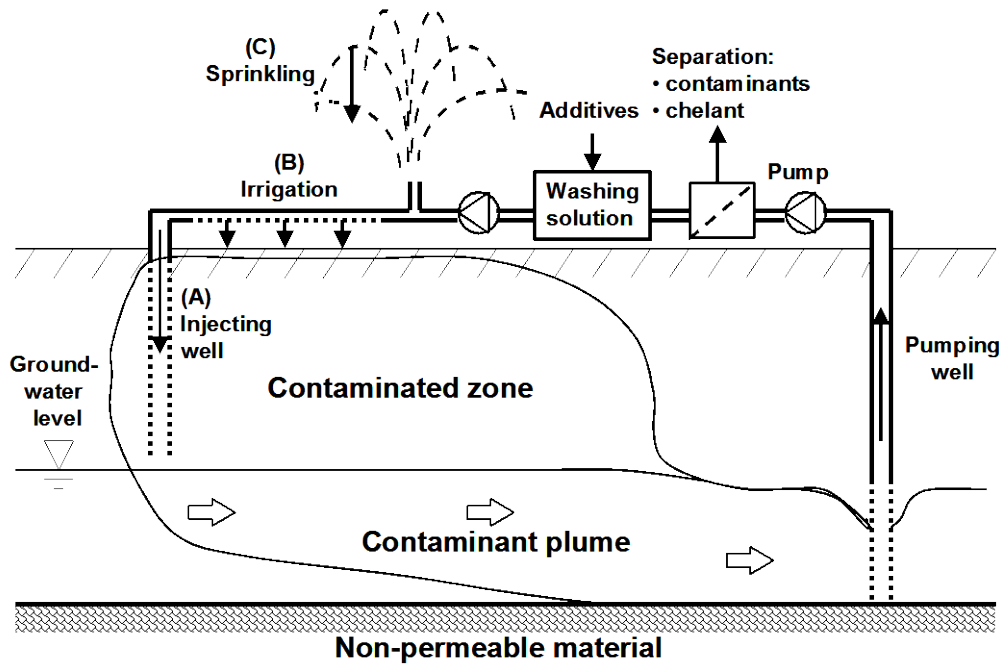837   *Figure 1*
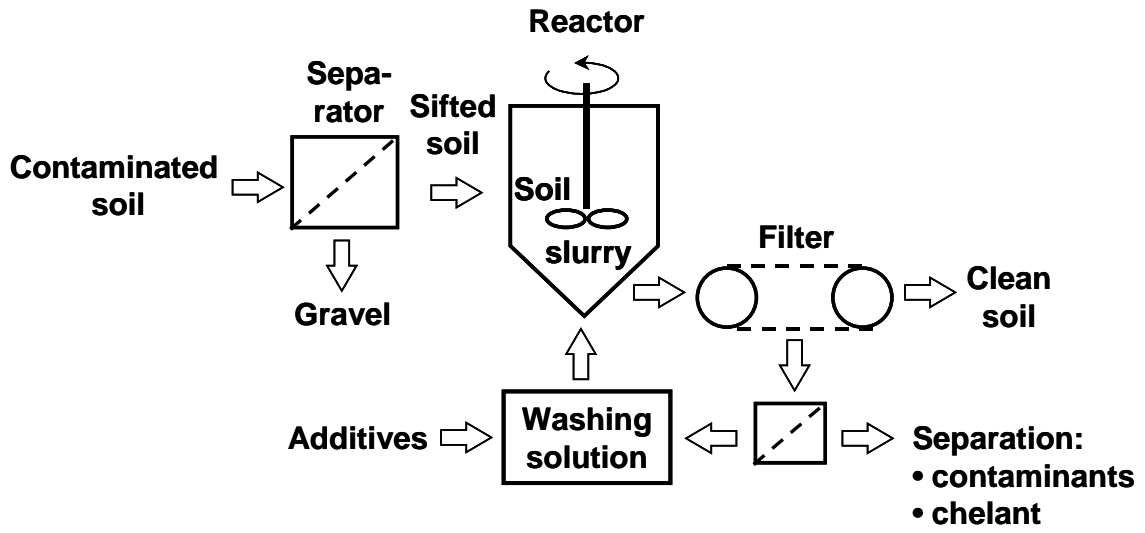838
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Figure 2

841
842

(C)
Sprinkling

(B)
Irrigation

Separation:
• contaminants
• chelant

Additives

Pump

Washing solution

(A) Injecting well

Ground- water level

Contaminated zone

Pumping well
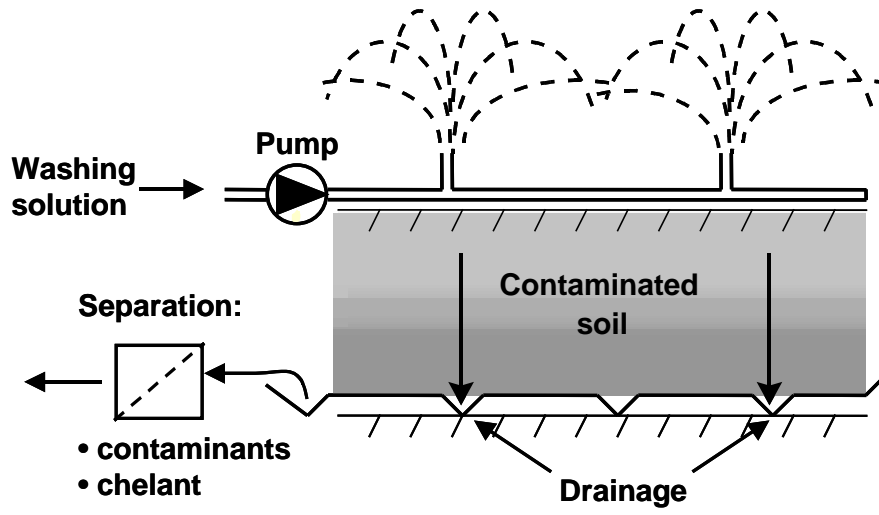
Contaminant plume

Non-permeable material

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Figure 3

Figure 4

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Figure 5

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