Metal Complexes in the Bioremediation of Industrial Contaminated Soils: Mechanisms, Applications, and Challenges

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DOI:10.37648/ijrst.v14i03.008

[1]*Received: 21 May 2024; Accepted: 22 August 2024; Published: 03 September 2024*

ABSTRACT

Industrial activities release heavy metals into soils. These metals stay in the ground for a long time and harm plants, microbes, and people. Bioremediation uses living organisms to clean the soil. Metal complexes play a key role. Chelating agents form stable complexes with metal ions. These complexes raise the amount of metal that plants and microbes can take up or immobilize (Nowack, 2002; Leštan et al., 2008). This review explains how metal complexes work in phytoextraction and microbial remediation. It covers synthetic agents such as EDTA and biodegradable options such as EDDS. It also describes natural ligands made by plants and bacteria. Tables compare efficiencies. Figures show structures and processes. Equations illustrate complex formation. All references date from June 2022 or earlier.

1. Introduction

Factories, mines, and metal-processing plants release lead, cadmium, chromium, arsenic, and other heavy metals into soil (Alloway, 2013; Kabata-Pendias, 2010). Once the metals enter the soil they bind to clay particles and organic matter. They do not break down. Over time they move into groundwater or enter the food chain. Traditional cleanup methods dig up the soil or wash it with chemicals. These methods cost a lot of money and can destroy soil structure (Mulligan et al., 2001).

Bioremediation offers a gentler approach. Plants and microbes remove or stabilize the metals (Ali et al., 2013; Garbisu & Alkorta, 2001). Metal complexes improve the results. A complex forms when a ligand wraps around a metal ion. The ligand is often a chelating agent. The complex keeps the metal soluble so roots or microbial cells can take it up more easily. In other cases the complex helps microbes precipitate the metal and lock it in place (Gadd, 2004).

This paper reviews the chemistry and practical use of metal complexes in bioremediation of industrial soils. It focuses on work published through June 2022. The goal is to show clear mechanisms, real efficiency numbers, and the main limitations.

[1] How to cite the article: Krishna K.V.; September 2024; Metal Complexes in the Bioremediation of Industrial Contaminated Soils: Mechanisms, Applications, and Challenges; *International Journal of Research in Science and Technology*, Vol 14, Issue 3, 55-62; DOI: http://doi.org/10.37648/ijrst.v14i03.008

2. Chemistry of Metal Complexes in Soil

A metal complex is a central metal ion surrounded by one or more ligands. Ligands donate electron pairs to the metal. When the ligand has several donor atoms it is called a chelating agent. The resulting structure is more stable than a simple ion pair. Stability is measured by the formation constant, often written as log K (Nowack, 2002).

For EDTA the reaction with a divalent metal can be written as:

M^{2+} + EDTA^{4-} → [M(EDTA)]^{2-}

The log K values for many common metals with EDTA exceed 15–18. High stability means the complex stays together even when the soil pH or ionic strength changes. Plants and microbes can still take up the intact complex or break it apart inside the cell (Evangelou et al., 2007).

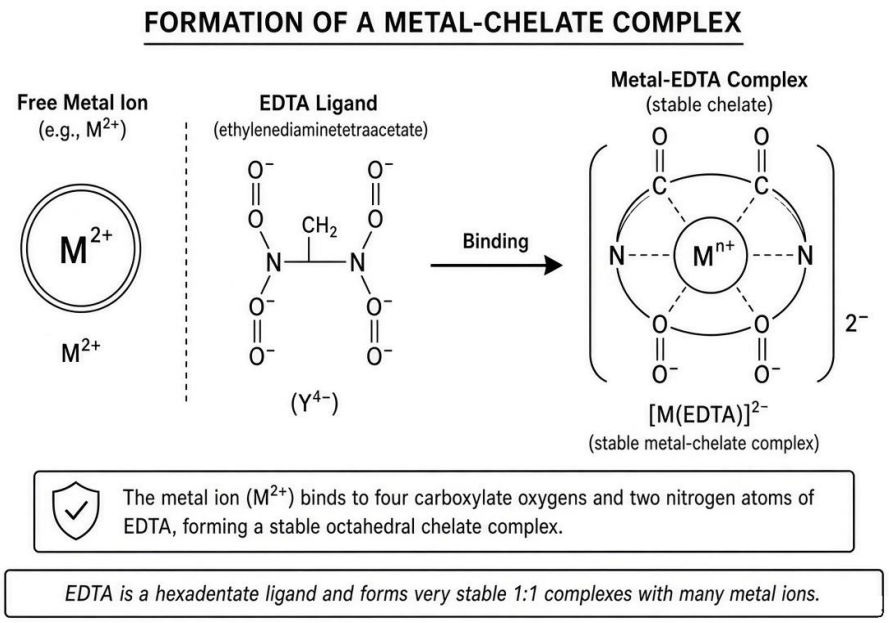
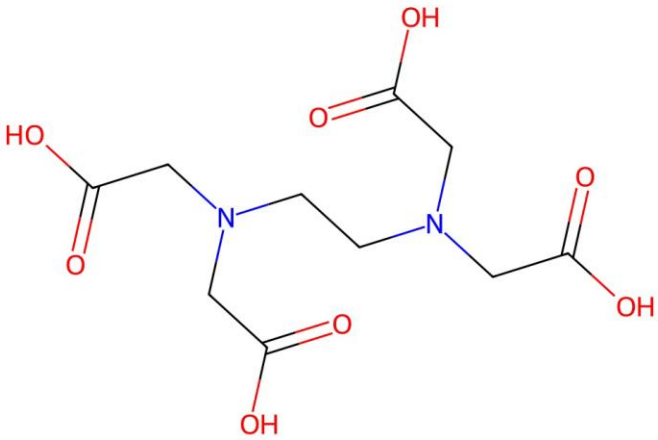


Figure 1. Formation of a stable metal–EDTA complex. The ligand wraps around the metal ion and holds it tightly.



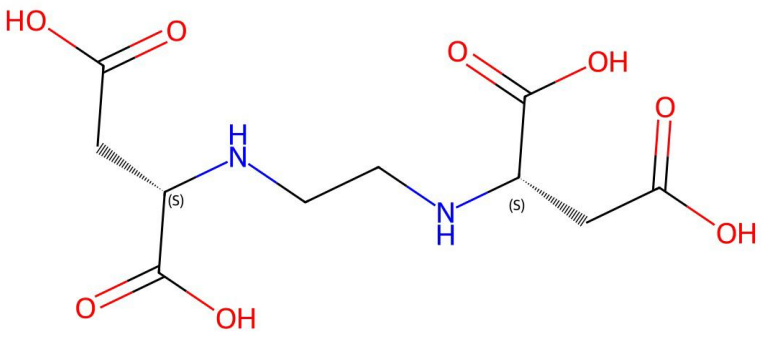
Ethylenediaminetetraacetic acid (EDTA), C10H16N2O8

Figure 2. Structure of EDTA. The four carboxylate groups and two nitrogen atoms allow hexadentate binding (Nowack, 2002).

2.1 Synthetic and Biodegradable Chelates

EDTA is the most widely studied synthetic chelate. It works well for lead, cadmium, and zinc (Blaylock et al., 1997; Huang et al., 1997). However, EDTA does not break down quickly in soil. Residual EDTA and metal–EDTA complexes can leach into groundwater (Nowack, 2002; Meers et al., 2008). Researchers therefore tested biodegradable alternatives.

EDDS is a structural analog of EDTA that microbes can degrade within days to weeks (Tandy et al., 2004; Luo et al., 2005). NTA, GLDA, and MGDA are other biodegradable options. Low-molecular-weight organic acids such as citric acid and oxalic acid also form complexes. Plants and microbes produce these acids naturally (Evangelou et al., 2007; Leštan et al., 2008).



[S,S]-Ethylenediamine-N,N′-disuccinic acid (EDDS), C10H16N2O8

Figure 3. Structure of EDDS. The molecule is biodegradable yet still forms strong complexes with many heavy metals (Tandy et al., 2004).

3. Phytoextraction Assisted by Metal Complexes

Phytoextraction uses plants that take up metals and store them in shoots (Salt et al., 1998; Pilon-Smits, 2005). Most plants cannot take up enough metal when the metal is tightly bound to soil particles. Adding a chelate raises the soluble metal concentration. Roots then absorb the metal–chelate complex (Blaylock et al., 1997).

Studies with Brassica juncea, Zea mays, and Helianthus annuus show clear increases. In pot trials, B. juncea grown on soil containing 600 mg kg^{-1} Pb and amended with EDTA accumulated up to 1.5% Pb in its shoots (Blaylock et al., 1997). In a later comparison, 5 mmol kg^{-1} EDTA raised shoot Pb in corn and beans to 270 and 487 mg kg^{-1} DW, whereas EDDS was more effective for Cu (Luo et al., 2005). Similar gains for cadmium and zinc have been reported, although usually smaller (Luo et al., 2005; Shahid et al., 2014).

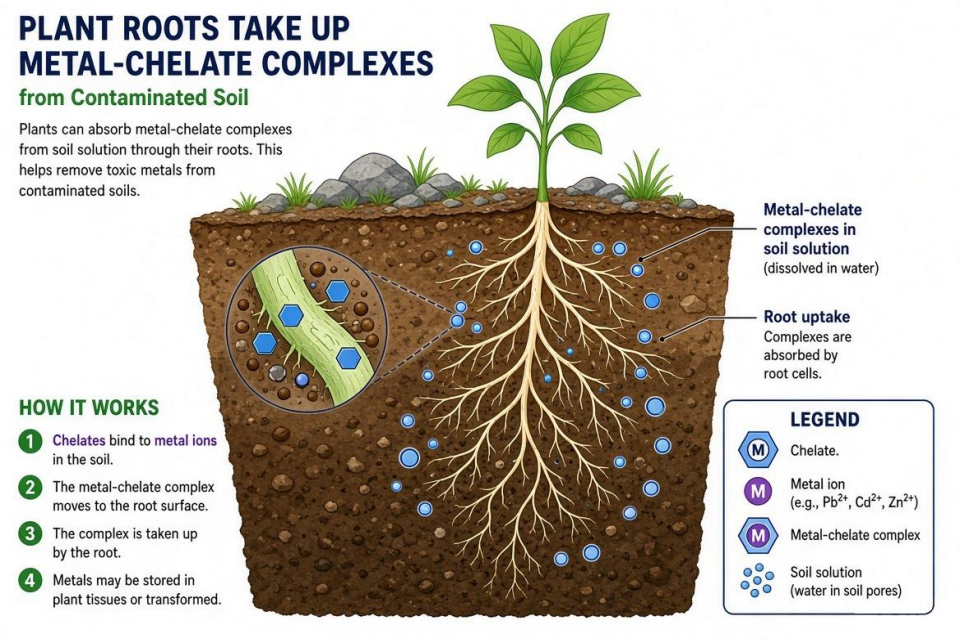


Figure 4. Plant roots take up metal–chelate complexes dissolved in the soil solution. The complexes move with water into the root and then into the shoot (Meers et al., 2008).

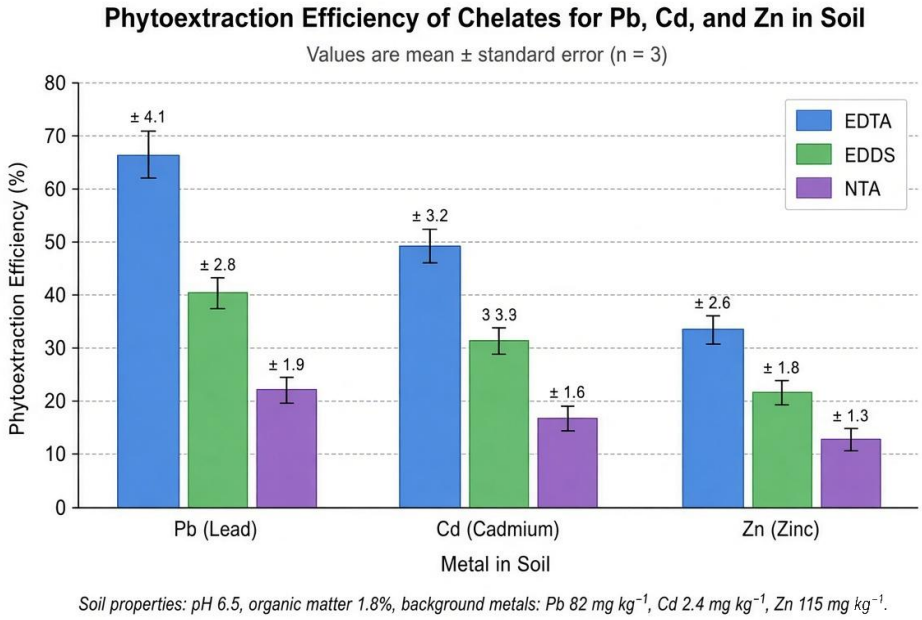


Figure 5. Schematic comparison of phytoextraction efficiency for three common chelates. The bar heights show the relative trend (EDTA > EDDS > NTA for Pb) and are not measured data. Actual values vary with soil type, metal concentration, and plant species; see Table 2 for published experimental values (trend based on Luo et al., 2005; Tandy et al., 2004).

3.1 Comparison of Chelating Agents

Table 1. Selected studies on chelate-assisted phytoextraction (references up to June 2022).

Chelate	Metal(s)	Plant	Key Result
EDTA	Pb, Cd, Zn	Brassica juncea	Large increase in shoot metal (Blaylock et al., 1997)
EDDS	Cu, Pb, Zn, Cd	Zea mays, Phaseolus vulgaris	Better than EDTA for Cu; weaker for Pb; degrades faster (Luo et al., 2005)
MGDA / GLDA	Pb, Zn	Zea mays	Pb uptake similar to EDTA, higher Zn uptake, lower leachable metal (Masoudi et al., 2020)
Citric acid	Cd, Pb	Various species	Moderate increase, low cost (Evangelou et al., 2007)

3.2 Reported Experimental Results

Table 2 summarizes measured results from published pot and batch experiments. The data show that chelates raise shoot metal concentrations by one to two orders of magnitude, but the effect depends strongly on the metal–ligand pair. EDTA remains the strongest agent for Pb, EDDS is superior for Cu, and the newer biodegradable ligands MGDA and GLDA match EDTA for Pb while leaving less leachable metal in the soil. Even so, total metal removal per crop is often small, so many cropping cycles may be needed (Wu et al., 2004).

Table 2. Published experimental results for chelate-assisted metal mobilization and phytoextraction.

Chelate and dose	Soil / plant	Measured result	Reference
EDTA (soil-applied)	Soil with 600 mg kg^{-1} Pb; Brassica juncea	Shoot Pb reached 1.5% (15,000 mg kg^{-1} DW)	Blaylock et al., 1997
EDTA, 5 mmol kg^{-1}	Contaminated soil; corn and beans	Shoot Pb up to 270 (corn) and 487 (bean) mg kg^{-1} DW, 3 and 1.6 times higher than with EDDS	Luo et al., 2005
EDDS, 5 mmol kg^{-1}	Contaminated soil; corn and beans	Shoot Cu up to 2060 (corn) and 5130 (bean) mg kg^{-1} DW, 45- and 135-fold above control	Luo et al., 2005
MGDA / GLDA / EDTA, 8 mmol kg^{-1}	Calcareous soil; Zea mays	Shoot Pb uptake rose about 39-fold over control for all three; Zn uptake rose 7.9- (MGDA), 7.1- (GLDA) and 5.3-fold (EDTA)	Masoudi et al., 2020
EDDS, pH 7 (batch washing)	Contaminated reference soils	Best balance of Cu, Zn and Pb extraction against loss of Ca and Fe among EDDS, NTA, IDSA, MGDA	Tandy et al., 2004
EDTA (pot trial)	Multi-metal soil; Brassica juncea	Shoot Cu and Pb increased, but offtake so low that ≥200 crops would be needed	Wu et al., 2004

4. Microbial Bioremediation and Metal Complexes

Bacteria and fungi also use metal complexes. Many produce siderophores. Siderophores are small molecules that bind iron tightly. They can also bind other metals and change their mobility (Gadd, 2004; Rajkumar et al., 2012). Extracellular polymeric substances (EPS) contain carboxyl and hydroxyl groups that form surface complexes with metal ions. These surface complexes allow biosorption (Nies, 1999).

Some microbes reduce toxic forms of metals. Chromium(VI) is more soluble and toxic than chromium(III). Certain bacteria reduce Cr(VI) to Cr(III). The reduced metal can then precipitate or form less mobile complexes (Lovley & Coates, 1997; Lloyd & Lovley, 2001). Other bacteria produce organic acids that dissolve metal minerals and increase bioavailability for further treatment (Gadd, 2004).

Bioleaching uses acid-producing or sulfur-oxidizing bacteria. The acids and the complexes they form solubilize metals from solid phases. Once the metals are in solution they can be recovered or stabilized (Mulligan et al., 2001).

5. Integrated Approaches and Field Considerations

Combining plants and microbes often works better than either alone. Plant-growth-promoting rhizobacteria produce organic acids and siderophores that raise metal availability for the plant. At the same time the bacteria protect the plant from metal stress (Glick, 2010; Ma et al., 2011; Sessitsch et al., 2013). Chelate addition can be timed so that the complex forms just before harvest. This reduces the window for leaching (Meers et al., 2008).

Field trials show that soil pH, organic matter, and clay content strongly affect results. Calcareous soils often need higher chelate doses because carbonate minerals compete for the ligand. Monitoring of groundwater is essential whenever strong chelates are used (Nowack, 2002; Shahid et al., 2014).

Cost and environmental risk remain the main barriers. Biodegradable chelates reduce the risk of long-term contamination but still cost more than citric acid or simple organic amendments. Researchers continue to look for low-cost, plant- or microbe-derived ligands that work well at field scale (Leštan et al., 2008; Evangelou et al., 2007).

6. Chemical Equations and Key Reactions

General complex formation:

$$M^{n+} + L^{m-} \rightleftharpoons [ML]^{(n-m)+}$$

For EDTA with lead (Nowack, 2002):

$$Pb^{2+} + EDTA^{4-} \rightleftharpoons [Pb(EDTA)]^{2-} \quad \log K \approx 18$$

Microbial reduction of chromium (Lovley & Coates, 1997):

$$CrO_{4}^{2-} + 3e^{-} + 4H^{+} \rightarrow Cr^{3+} + 4H_{2}O \quad \text{(catalyzed by bacterial enzymes)}$$

Once reduced, Cr^{3+} can form hydroxide precipitates or bind to organic ligands.

7. Discussion and Outlook

Metal complexes clearly improve bioremediation efficiency in laboratory and greenhouse studies (Blaylock et al., 1997; Luo et al., 2005). The main challenge is to keep the mobilized metal from leaving the treatment zone. Biodegradable chelates and carefully timed applications help (Tandy et al., 2004; Meers et al., 2008). Microbial

communities can also be managed so that they both mobilize and then immobilize metals as needed (Gadd, 2004; Rajkumar et al., 2012).

Research up to 2022 focused on finding cheaper biodegradable ligands and on combining chelate addition with microbial inoculation (Shahid et al., 2014). Long-term field data remain limited. More studies that track metal mass balance and groundwater quality are needed.

8. Conclusion

Metal complexes are useful tools for cleaning industrial soils. Synthetic and natural chelates raise metal solubility so plants and microbes can remove or stabilize the contaminants (Leštan et al., 2008; Ali et al., 2013). EDTA remains highly effective but carries leaching risks (Nowack, 2002). EDDS, GLDA, MGDA, and organic acids offer safer alternatives (Tandy et al., 2004). Successful application requires matching the chelate, the plant or microbe, and the soil conditions. With proper design, bioremediation that uses metal complexes can restore contaminated industrial sites at lower cost and with less disruption than excavation.

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