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Review Article

IMPACT OF CHELATION / COMPLEXATION PHENOMENON ON SOIL ENVIRONMENT

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Abstract: Economic activities in the industrialized countries in the past have resulted in significant contamination of environmental resources including soil and groundwater. These activities include vehicle operation, mining, smelting, metal plating and finishing, battery production and recycling, agricultural and industrial chemical application, and incineration processes. Chelators that have been used for extraction of heavy metals from soils include EDTA, NTA, DTPA, formic, succinic, oxalic, citric, acetic, humic, and fulvic acids, glycine, cysteine etc. These chelators are used to remediate the heavy metal contaminated soil. Nutrient management is crucial for optimal productivity in commercial crop production. Although soil contains almost all the essential nutrients, but under certain conditions, these nutrients, especially the cations, can be tightly bound to the soil and also precipitation can limit their availability to the crop. Chelators has the ability to bind with the metals in the soil depending upon competition for particular metal ions, and can aid the nutrient uptake, transport from source to sink. Organo-mineral associations and complexation of SOM with metals ions largely determines the stability and degradability of organic matter. In the light of above fact, this review mainly focuses on the remediation of heavy metal contaminated soils by the application of chelating agents depending upon their recoverability and selectivity must be considered.

Keywords: Heavy metal contaminated soil, Chelators, Complexation, Micronutrient, Fertilizer, Phytoremediation

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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. Soil is source and sink of metals. The total and bio-available concentrations of heavy metals in soils are of great importance with regard to human toxicology. It can form several bonds to a single metal ion; it can also form strong, water soluble metal complexes with di- and trivalent cations. Chelating agents upon addition to the soil bring metals into solution through desorption of sorbed species, dissolution of Ferric (Fe) and Manganese (Mn) oxides, and dissolution of precipitated compounds. They can alter the oxidation – reduction properties of transition-metal ions, such as Fe and Mn, and therefore increase or decrease the reactivity of these systems. Phytoavailability of the metals is a very important factor to achieve the productive phytoextraction ofthe heavy metals. Chelating agents like Ethylenediaminetetraacetic acid (EDTA) has ability to form water solublecomplexes by increasing uptake of metals desorbing from the solid phase of soil. Metal is basically partitioned in two phases: reversible and irreversible. Chelates first try to absorb metals from reversible phase afterwards from irreversible phase. This basic principle is used in testing the chelating agent, that how well a chelate can free the metals from the bounded phase. Chemical reactions include oxidation-reduction, precipitation-dissolution, volatilization, and surface-solution phase complexations are taking place in soil. Biological reactions include metabolism, homeostasis, reproduction, digestion, cell growth, cellular differentiation, fermentation, fertilization, germination metamorphosis *etc.* Humic substances with function groups of carboxyl, carbonyl, ether, ester, phenolic, alcohol, and methoxyl have the ability to combine or bind with considerable quantities of metal ions.

Chelation

Chelation is a type of bonding between ions and molecules to a metal ion that involves formation of two or more separate coordinate bonds between a multidentate ligand and an individual central atom. The resulting compounds by this type of bonding are mainly organic compounds that are also known as chelants, chelating agents or sequestering agents. It's a useful mechanism having beneficial role in applications such as providing nutritional supplements, removal of toxic metals from body, Magnetic Resonance Imaging (MRI) scanning, manufacturing of catalysts and fertilizers. Amino acids, glutamic acid, histidine, malate, phytochelatin *etc.* are some of the typical type of chelators in nature. Siderophores, water soluble pigments formed by many microbial species such as pyochelin and pyoverdine produced by Pseudomonas serves the function of chelating agents by binding with iron. Enterobactin, produced by *E.Coli* is also an example of chelating agents. In geology(earth science), hot chemical weathering is responsible for organic chelating agents (e.g., peptides and sugars) who extract metal ions from minerals and rocks. Some metal complexes in the environment and in nature are not found in the form of chelate ring (*e.g.*, with a humic acid or a protein). Thus, metal chelates are relevant to the mobilization of metals in the soil, their uptake and the accumulation of metals into plants and microorganisms. In order to prevent absorbed nutrients from precipitation, cationic nutrients will immediately form chelates with organic acids such as citric acids, malonic acid, and some amino acids. Thus, due to the chelation process, the nutrients can move freely within the plants.

Chelate

Chelate is a class of coordination or complex compounds which consist of a central metal atom that is attached to a large molecule, called a ligand, in a cyclic or ring structure. It's a specific kind of chemical compound which is easily dissolved and absorbed than other types of molecules and chemical compounds. It is made up of a metal ion and a chelating agent that forms multiple soluble bonds with the ion.

This chemical structure is responsible for its easy absorption in a solution. Chelates are sometimes mixedwith fertilizers to enhance a plant's ability to absorb and assimilate nutrients.

Chelating agents

Chelating agents are the natural or manmade formed chemical compounds that reacts with metal ions forming a water-soluble stable complex. They are composed of a ring-like centre forming at least two bonds with the metal ion. Organic substances in the soil that are either applied or produced by plants or microorganisms are the naturally occurring chelating agents. To prevent the chelating agent’s molecule from reacting, these molecules form several bonds with the metal ion. The bonding to the metal ions thus re-organizes the ions' core structure and chemical composition. The chemical structures in many of the metals mainly form a chain rather than a ring. The ends of this chain like structures are joined by the chelators forming a stable ring, which then can move easily through various environments. At the commercial scale, chelating agents are used for industrial, medical and biological applications.

Examples of some chelating agents

Inorganic

- EDTA (Ethylenediaminetetraacetic acid)
- GCG (L-5-glutamyl-L-cysteinylglycine)
- NTTA (Nitrilotris(methylene)triphosphonic acid)
- TMDTA (Trimethylenedinitrilotetraacetic acid)
- DTPA (Diethylene triaminepenta acetic acid)
- NTA (Nitrilo tri acetic acid)

Organic

- Formic, Succinic, Oxalic, Citric, Acetic, Humic, and Fulvic acids
- Glycine, Cysteine

Significance of Chelation Process in Soil

1. Increase in available nutrients
   In the alkaline soils, chelating agents bind to the insoluble iron and make them available to plants.
2. Prevents nutrients from forming insoluble, unavailable compounds
   Chelating agents increase the availability of metal ions for plant uptake by protecting the chelated ions from unwanted chemical reactions.
3. Chelates reduce toxicity of some metal ions
   Substrate chelation reduces the concentration of metal ions to a normal beneficial level. This is done by the humic acid and several high molecular weight compounds which are present in organic matter.
4. Chelates prevent nutrients from wash out
   Chelate forming metal ions are much more stable than free ions.
5. The chelation process increases the mobility and therefore availability of nutrients to plants.
   By this increased mobility the uptake of nutrients by plants is enhanced.
6. Chelating agents reduces the growth of plant pathogens by reducing available iron.
   Chelating agents may sometimes suppress the growth of plant pathogens by depriving iron hence favoring plant growth.

Complexation

Reaction of a metallic ion and a molecular or ionic ligand containing atleast one atom with an unshared pair of electrons is called as complexation. In complexation process, individual atom groups, ions or molecules combine to form one large ion or molecule. This atom or ion is the central atom of the complex that helps in bonding with other atoms as well as unshared electrons. The most commonly used complexing agent is EDTA. Every complexing agent commonly contributes a single pair of electrons to the central atom orbital otherwise these agents are different from each other. These agents can be positively, negatively or possess no charge. Certain factors should be kept in mind to ensure proper complexation process, such as ionic strength, temperature, pH and competing ions. Under properly controlled conditions, obtaining more accurate complexation values is the major result.

Extraction of Heavy Metals from Soil Through Chelating Agents

In a study by [4], the increase in complexing ability was observed as GCG<NTTA<TMDTA<EDTA. Selectivity towards metal contaminants was observed in the order EDTA<TMDTA<GCG<NTTA. EDTA results in increased recovery of metal ions among the rest and was found to be a very strong chelator. A batch soil washing experiments was performed by [11] on 1.0 g portions of the soil using 0.05 M chelating agents at a solid:liquid ratio of 1:25 showed that washing efficiencies varied in the order: EDTA> citric acid (CA)> tartaric acid (TA) with metal extraction yields typically following the sequence, copper> nickel> zinc> cadmium> lead. Most of the metals associated with exchangeable and reducible fractions was removed by CA, TA removed the exchangeable metal pools and EDTA was responsible for removal of non-residual metal pools. They also concluded that EDTA and CA have a greater potential as chelating agents. At the end of the 6 hours washing time, CA removed 45.60 % Ni, 50.30 % Cu, 43.50 % Zn, 38.40 % Cd and 31.00 % Pb. TA gave extraction yields of 28.30 % Ni, 30.20 % Cu, 26.60 % Zn, 19.30%Cd and 16.70 % Pb. The extraction yields of EDTA were 62.50 % Ni, 70.30 % Cu, 60.40 % Zn, 56.70 % Cd, and 50.50 % Pb. The extraction yields efficiency varied in the order as: Cu > Ni > Zn > Cd > Pb by all three organic chelants. A trend of decreased extraction ability for Cu and Ni was observed as Chitosan>EDTA> sodium citrate by [5]. They found a relationship between pH of eluents and chelating agents used. It was seen that the rate of extraction of copper and nickel was 43.36 % and 37.07 % respectively when the pH was 3-3.5. The potential of two organic acids to decontaminate a calcareous soil from Zn-Pb smelting plant was studied by [8]. Greater Zn was extracted by oxalic acid and Cd by acetic acid. By increasing the doses of chelating agents, availability of the metals can be increased. This was supported by [10] in an experiment when they increased the doses of EDTA, DTPA and NTA upto 5.0mM. Shacking time duration has also affect on availability of metals. They found that EDTA is a good extracting solution for extraction of Pb and NTA for Cr. It observed that extraction ability of Mercury and copper was decreased in the order by chelating agents as OA > CA > EDTA in the polluted water [1]. He found that removal of metals depends on the concentration of extracting agent and with increase in concentration of chelating agents, the rate of metals removal increases first for 50 min, and then decreased as the pH started to increase. In an experiment by [2] they reported that chelating agents has the ability to improve the contents of Pb, Cu and Cd in roots and shoots of Chrysanthemum.

CHELATING AGENTS FOR INCREASING NUTRIENTAVAILABILITY IN SOIL

Chelators or ligands when combined with a nutrient, can form a chelated fertilizer. Chelated fertilizers are protected from oxidation, precipitation, and immobilization in certain conditions because the organic molecule (ligand) can combine and form a ring encircling the nutrient. The pincer-like manner in which nutrient is bonded to the ligand changes the nutrient’s surface property and favors the uptake efficiency of foliarly applied nutrients.

Need of Chelated fertilizers

Due to the complex and heterogenous nature of soil, availability of nutrients is reduced or increased. Some of the nutrients gets oxidized or precipitated. Chelation prevents the nutrients from such type of chemical reactions. Chelated fertilizers not only increase the availability of micronutrients such as Fe, Cu, Mn, and Zn but also increase the productivity as well as profitability. Chelated fertilizers perform better in pH greater than 6.5. To have a good crop, Crop Nutrient Requirements (CNRs), including micronutrients, has to be satisfied first from the soil and if this is not fulfilled by soil, chelated sources need to be used. The bioavailability of iron can be reduced by various edaphic factors such as high pH, bicarbonate content, species of the plant (grass species are usually more efficient because they can excrete effective ligands), and abiotic stresses. Iron is mainly utilized as Fe^{2+} ion in plants. This can be readily oxidized to the unavailable ferric form (Fe^{3+}) in the plant when pH of the soil is greater than 5.3 [7]. Iron deficiency is often observed in soil having pH greater than 7.4. Application of chelated form of iron can prevent the conversion from Fe^{2+} to Fe^{3+}. Nutrients such as Fe, Mn, Zn, and Cu to the soil is inefficient because they are present as positively charged metal ions in soil solution and will freely reacts with oxygen and hydroxide ions.

When they react with oxygen or hydroxide ions, they form new compounds that are unavailable to plants. The chelating agents can protect the micronutrient from oxidization or precipitation. Plant roots contain some exudates that are natural chelating agents. The non-protein amino acid, mugineic acid, is example of one such natural chelate called phytosiderophore. It is produced by graminaceous (grassy) plants that are grown in low-iron stress conditions. The exuded chelate works as a vehicle, helping plants absorb nutrients in the root-solution-soil system [6]. A plant-excreted chelate forms a metal complex near the rhizosphere region in the soil with a micronutrient ion which releases the nutrients near root hair [3].

Conclusion

Chelating extraction of heavy metals from contaminated soils is a remediation technique. Addition of chelating agents to the soil can bring metals into solution through desorption of sorbed species, dissolution of Fe and Mn oxides, and dissolution of precipitated compounds. Important consideration in the application of chelating agents for soil remediation, include complexing power, selectivity, and recoverability of the chelators with respect to heavy metal contaminants. EDTA has been the best chelating agents for removing heavy metals from soil. Use of chelated fertilizers is a new approach towards increasing the nutrient availability in soil. Chelated fertilizers are less reactive to soil conditions and can significantly enhance nutrient uptake and utilization efficiencies. Chelate fertilization rates range from 0.2 to 1 lb. micronutrient per acre for vegetable production and 0.1–0.5 lb. micronutrient per acre for fruit production. Foliar application of chelated fertilizers is often more effective than soil application.

Application of review: To know about the chelation process and how it is beneficial for the availability of nutrients from the soil to the plants by which we can increase the production.

Review Category: Agriculture Chemistry

Abbreviations

EDTA: Ethylene diamine tetraacetic acid
GCG: L-5-glutamyl-L-cysteinylglycine
NTTA: Nitrilotris (methylene) triphosphonic acid
TMDTA: Trimethylene dinitrilo tetraacetic acid
DTPA: Diethylene triaminepenta acetic acid
NTA: Nitrilo tri acetic acid

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