



Remediation Technology for Copper Contaminated Soil: A Review

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Authors' contributions

This work was carried out in collaboration between all authors. All the authors made corrections, read and approved for final publication mutually

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ABSTRACT

Copper is a naturally occurring trace element present in all environmental media, including soil, sediment, air and water. It is an essential micronutrient critical for cell function, playing a vital role in processes. Copper contamination to agricultural soils is of great concern due to its wide and continuous use in agriculture and horticulture as fertilizers and fungicide. Copper contaminated soil is mainly attributed to agriculture activities such as continuous application of copper-based fungicides and pesticides application. A minireview was carried out using peer-reviewed articles published from 2000 to 2017, which methods of remediating copper soil. The AGORA and Google Scholar databases were used to conduct the search for articles using the terms copper and phytoremediation, Copper and Biological remediation, Copper and soil washing OR physical methods. Following these searches, 19 journal articles out of a total of 191 articles satisfied criteria for inclusion and were used in the final systematic review. The study showed that remediation technology for copper contaminated soil is divided into physical, chemical and biological categories. Physical methods are laborious and costly but can be applied to highly contaminated site; chemical methods have high efficiency and effective to remove the copper, but mostly popularized in a large

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scale; bioremediation methods including phytoremediation and microbial remediation are appropriate for large areas of soil contaminated by low concentrations of copper. The bioremediation methods are economical, eco-friendly but time consuming.

Keywords: Copper; remediation; physical methods; chemical methods and biological methods.

1. INTRODUCTION

Soil is defined as non-renewable resource, meaning it cannot be restored on a time scale in which its consumption rate will be sustained [1]. Soil degradation has become an issue of serious concern globally. In that regard, the EU has defined several threats to soil, which include: acidification, erosion or heavy metal pollution [2]. Heavy metal contamination refers to the excessive deposition of toxic heavy metals in the soil caused by human activities [3]. Heavy metal contamination is caused by various sources, such as industrial processes, manufacturing, disposal of industrial and domestic refuse, and agricultural practices [4]. Out of the Fifty-three of the ninety naturally occurring heavy metals elements [5], Fe, Mo and Mn are needed in minute quantity (microelements), while Zn, Ni, Cu, Co, Va and Cr are toxic elements, but play an important role as trace elements [6]. The most frequently reported heavy metals with potential hazards to soils are cadmium, chromium, lead, and zinc and copper [7]. The concentration of these toxic elements in soils may increase from various sources including anthropogenic pollution, weathering of natural high background rocks and metal deposits [8]. Campbell et al. [9] compared natural and anthropogenic quantities of trace metals emitted to the atmosphere. The results showed that around 15 times more Cd, 100 times more Pb, 13 times more Cu and 21 times more Zn are emitted by human activities than by natural processes. Amongst heavy metals, copper is one of the most common soil contaminants [10]. Copper is a trace element essential to life, yet, at high doses it can be toxic to humans. Copper-based fungicides have been used to control fungal diseases in pome and stone fruit orchards, vineyards and vegetable crops for well over 100 years [11]. Copper is not biodegradable, it accumulates in the environment and eventually reach hazardous concentrations levels [12]. However, elevated concentrations of copper are toxic and when found in soils may result in a range of effects including reduced biological activity and subsequent loss of fertility [13]. Remediation technologies use for removal of copper in the soil can be divided into physical, chemical and biological methods. Bioremediation

is divided into plant and microorganism methods. Each method has both advantages and disadvantages.

1.1 Sources of Copper

Copper is a common trace component in the earth crust. Its concentration in the soil has increased dramatically since the Industrial Revolution [14]. However, the source of copper in copper contaminated soils are pig and poultry manures, cow dung manure, copper-based fungicides, pesticides and metal finishing in which continuous application of copper-based fungicides to control diseases of crops possess the major source of copper in agricultural soils.

1.2 Copper Contamination and Damage

Copper causes soil and water contamination mainly through agriculture activities such as application of copper-based fungicides and pesticides application. The continuous use of the copper-base fungicides on crop results in the fungicides residues accumulation in the soil leading to contamination. Contaminated copper soil is attributed to soil degradation, copper phytotoxicity, causing adverse effects to the microbial function and fertility of the soil and increase transport of copper to surface and ground waters. Gyimah [14] suggested that copper suppressed the rates of nitrogen fixation by the bacteria rhizobium under some situations, at relatively high copper levels of 235 ppm. In soil, large earthworms have been eliminated by the extensive use of copper containing fungicides [15,16]. Elevated levels of copper may cause health implications such as liver and kidney failure or Wilson's disease [17].

2. METHODS

2.1 Search Procedures

Literature search was conducted for publications on relevant studies across a broad range of online databases, websites and knowledge repositories such as AGORA, Web of Science and Google Scholar, which allowed the identification of both peer reviewed and grey

literature. Boolean operators “AND” and “OR” were used to broaden the search. Keywords used for searching copper AND phytoremediation, Copper AND Biological remediation, Copper and soil washing OR physical methods. The results were screened against inclusion criteria by two independent reviewers, with additional supervision by a third. Using both sensitive as well as specific searches helped to narrow down the literature retrieved to fit into the inclusion and exclusion criteria. Full text of articles for all the articles that fitted into the inclusion criteria were retrieved.

2.2 Inclusion Criteria

In the database of Google Scholar and AGORA, searches were carried out using the following combination of search terms; copper AND phytoremediation, Copper AND Biological remediation, Copper AND soil washing OR physical methods. All articles that were found in this database using these search terms were published between 2000 and 2017.

2.3 Exclusion Criteria

In all, 198 peer-reviewed articles met the initial search criteria, but only 13 met criteria to be included in this literature review. Articles that were excluded from the research review included: studies that focused on other heavy metal remediation apart from copper, articles that focused on organic contaminated remediation. Selected articles were also limited to those that were written in English.

3. REMEDIATION METHODS FOR COPPER CONTAMINATED SOIL

Remediation of copper contaminated soils depends on the contact between remediation medium and copper ions. Remediation processes are methods for treating a contaminated media in the environment in a way that they are contained, removed or degraded. Remediation of metals and metalloids in soils might be complex due to the heterogeneous distribution (vertical/horizontal) of heavy metals in the soil since heavy metals are non-degradable and cannot be destroyed as well as the physical and chemical characteristics of metals in the soil matrix vary, as trace elements are discharged to the soil in different physicochemical forms, such as salts, ions, particle [18].

3.1 Chemical Methods for Remediating of Copper Contaminated Soil

Soil washing is the removal of copper ions from soil using various reagents and extractants [20,21] which results to the leachate of the copper ions from the soil. During soil washing, the copper contaminated soil is dug out and mixed with a suitable extractant solution depending on type of soil for a specified time [19] in which the copper ions in the soil are transferred from soil to liquid phase, through the precipitation, ions exchange, chelation or adsorption and then separated from the leachate [22]. Race et al. [23], proposed that soil washing process using EDDS as a chelating agent was efficient at removing copper and zinc from real polluted soils as Intra-particle diffusion was the main rate controlling step in this extraction of heavy metals from the solid matrix. Their results indicate that soil washing process allows the efficient extraction of only the Cu (100%) and Zn (80.9%) exchangeable and reducible fractions.

Also, Immobilization refers to decrease in metal mobility, bioavailability and bio accessibility of heavy metal(loid)s in soil by adding immobilizing agents to the contaminated soils [19] in which copper ions can be immobilized in soil by complexation, precipitation and adsorption reactions. Fan et al. [24], study the immobilization of copper in contaminated sandy soils using calcium water treatment residue. Their results showed that Ca-WTR amendment significantly raised soil pH and decreased water soluble and exchangeable Cu by 62–90% in the contaminated soils and most of the bioavailable Cu was converted into more stable Cu fractions, i.e. oxides-bound and residual Cu.

3.2 Biological Methods for Copper Remediation

The development of biological methods for the management of polluted soils is a way to reduce the cost of chemical reagents and to favour the use of environmentally-friendly techniques. Bioremediation is one of the most viable options to rectify and re-establish the natural condition of soil considered detrimental to environmental health. Bioremediation makes use of micro-organisms/plants to detoxify or remove heavy metals from the soil. Bioremediation is cost-effective, non-invasive and provides a permanent solution [19].

Table 1. Comparison of different contaminated soil clean-up methods [19]

Chemical methods	Biological methods	Physical methods
a. Soil washing b. Immobilization	a. Phytovolatilization b. Phytostabilization c. Phytoextraction	a. Soil replacement b. Soil isolation c. Verification d. Electrokinetic
Very effective and efficient but influence by soil type and chemical use.	Cost-effective and small disturbance to the environment as well as limited to moderately copper contaminated soil.	High cost and labour intensive but can remediate highly copper contaminated soil.

Soil remediation methods can be broadly divided into three categories: physical, chemical and biological methods

3.2.1 Application of phytoremediation methods in repairing copper pollution soil

Phytoremediation also known as botanoremediation, vegetative remediation, green remediation or agroremediationis which is proposed as a cost-effective alternative for the treatment of contaminated soils. Topsoil would be preserved and the amount of hazardous materials reduced significantly [25]. Phytoremediation is considered as environmentally friendly, non-invasive and cost-effective technology to clean up copper contaminated soils. Ariyakanon and Winaipanich [26], study the efficiency of copper removal from soil by *Brassica juncea* (L.) Czern and *Bidens alba* (L.) DC. var *radiata*. Their results showed that the maximum concentrations of copper of *Brassica juncea* (L.) Czern and *Bidens alba* (L.) DC. var *radiata* were 3,771 and 879 mg/kg (dry weight) in experimental pots with 150 mg Cu/kg soil respectively which indicate that *Brassica juncea* (L.) Czern could be regarded as a hyperaccumulator for copper remediation in

contaminated soils and also Andreazza et al. [27] showed that *Brachiaria decumbens* plant exhibited high capacity copper phytoextraction in a vineyard soils and copper mining waste by entire plant in which the plant exhibited greatest phytostabilization characteristics such as high shoots and roots biomass production, and high copper bioaccumulation in the roots. There are many factors affecting phytoremediation efficiency in which soil properties such as pH, water content, soil texture, organic matter content can affect plant growth conditions and the bioavailability of copper.

3.2.2 Microbial remediation of copper contaminated soil

This refer to the use of microorganisms for removal of a pollutant from the biosphere. Microorganisms can increase the mobility of metals in soil by stimulating desorption of metals from metal-bearing phases or by mediating the dissolution of metal-bearing phases themselves (mainly minerals). Microorganisms can immobilization Copper in soil through biosorption,

Table 2. Phytoremediation processes for heavy metal removal [28,29]

Phytostabilization	Phytostabilization aims to restrict copper ions in the vadose zone of plants through accumulation by roots or precipitation within the rhizosphere. Phytostabilization is helpful in achieving ecosystem restoration because it increases soil fertility.
Phytodegradation	Uptake of contaminant for transformation or degradation, products are stored in plant tissue, bond to plant lignin, degraded partially or completely.
Phytoaccumulation	Plant have the ability to uptake, relocate, accumulate mainly contaminants from soil to the roots or leaves
Phytovolatilization	Root uptake, transport and transpiration above ground of mainly organic compounds. Some metals are subject for volatilization.
Rhizodegradation	The activity in the rhizosphere derived from root exudes like enzymes and proteins are capable of degrading the contaminate. Degradation means volume reduction and increased pore space which enhances water and oxygen transport
Evotranspiration	Combined effort of plant evaporation from leaves and other parts located above ground and transpiration where water is a byproduct of plant activity.

bioaccumulation and biomineralization [30]. Kaksonen et al. [31] observed that a bioleaching culture of *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans*, *Acidithiobacillus caldus*, *Leptospirillum ferrooxidans* and *Sulfobacillus thermotolerans* was able to solubilize 62% of the Cu from Cu smelting industry slag waste in 29 days. Samal and Kotiyal, [32] reported that gram negative bacteria are capable of reducing copper contaminated soil in their study on bioremediation of Copper Contaminated Soil Using Bacteria.

3.3 Physical Methods for Remediation of Copper Contaminated Soil

The physical remediation mostly includes soil replacement method, soil isolation, verification electrokinetic and thermal desorption for copper removal from the soil. Sah and Lin, [33] conducted research on electrokinetic technology for soil remediation on three copper contaminated soils. Their results showed that, the electrokinetic process has the potential to remove carbonate and Fe-Mn oxides' copper in contaminated soils, which accounts for 70-85% of copper in the soils. The experimental tests also found that the electrokinetic process can remove copper from both acidic and basic soils. They proposed that removal efficiency in the electrokinetic process is influenced by soil properties, physicochemical reactions, electrolytic reaction/dissociation across the soils, migration of electro-osmotic flow in the specimens, electrification and pH condition. The soil replacement methods.

4. CONCLUSION

Transforming excess copper in soil into harmless form requires using one of the method or combined methods for the remediation of copper contaminated soil. The study showed that remediation technology for copper contaminated soil is divided into physical, chemical and biological categories. Physical methods are labour intensive and costly but can be applied to highly contaminated site; chemical methods have high efficiency and effective to remove the copper, but mostly popularized in a large scale; bioremediation methods including phytoremediation and microbial remediation are appropriate for large areas of soil contaminated by low concentrations of copper. The bioremediation methods are economical, eco-friendly but time consuming.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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