

Mini Review

Recent advances in chemical methods for remediation of heavy metals contaminated soils: A Review

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Abstract

Heavy metal remediation has been an important concern of agriculture sector since decades and development of new and sound remediation techniques has become the need of the hour. These potentially harmful and persistent metals (loids) are posing great threat to environment and human health. Chemical remediation techniques are long been used for the remediation of all hazardous metals and to bring them back to safe and acceptable level in soils, but these conventional methodologies have their own setbacks. These techniques ae not cost-effective, consume a lot of time and mostly generate by-products that are toxic in nature. Hence, to overcome these issues, recently scientists have come up with more refined chemical methods to ameliorate heavy metal contamination in soils. In this review, we have highlighted some of the costeffective and effective chemical methods, including precipitation, ion exchange, and chemical extraction and leaching, nanoremediation, encapsulation and soil washing. All these methods have shown effective results in the recent literature for the efficient removal of heavy metals from the contaminated soils along with economic feasibility.

Keywords advance techniques, chemical remediation, heavy metal (loids)

Introduction

Due to revolution in industrial sector and urbanization, there is high release of aqueous effluents in to the soils that mainly contain heavy metals and organic pollutants [1]. Moreover, processes like erosion, pollution and salinization are destroying physical, biological and chemical properties of soil that leads to the release and accumulation of toxic materials into the soil, thus becoming an increasing concern all over the globe. According to a report more than 10 million sites in world are contaminated and among them more than 50% of them are contaminated with heavy metals [2]. Soils are main sink of these heavy metals into environment [3] and such contaminated soils are mostly found in developed countries [4-5]. Heavy metals have high atomic weight and density, and even at low concentration (<1 ppb) they can cause potential toxicity [6]. They may damage active sites of biological molecules and can cause toxicity to both macro-organisms and micro-organisms [7]. Presently, soils are contaminated with heavy metals and with organic pollutants, a condition that is termed as co-contamination, due to which heavy metal pollution has become a serious issue all across the world and posing serious threats to animals, plants and human life.

Due to technical and financial implications and some other complexities, heavy metal clean-up of soils have become a difficult task. In past much attention has been given to remediate the heavy metal contaminated

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soils through various chemical methods, but currently there is need to develop more efficient and advance technologies to counter this increasing issue. The conventional methods that have been used for this purpose have multiple drawbacks associated with them [8-12]. Scientists have find out that site specific and innovative remediation technologies should be exploited to remove heavy metals from contaminated soil in more effective and sustainable way.

Chemical remediation of heavy metal contaminated soils

There are various approaches that are being used for remediation of heavy metal contaminated soils, but these conventional methods are inefficient and expensive. In this review, chemical methods for remediation of contaminated soils such as precipitation, ion exchange, chemical leaching, chemical extraction and oxidation, soil amendments and nano-remediation will be discussed as they are cost effective and quickly remove the toxicants from soil as compare to other methods.

Remediation of heavy metals is difficult as they cannot be mineralized, but they can be immobilized thus reducing their bioavailability, or they can be converted to less toxic forms. This can be efficiently done through chemical remediation techniques in order to remediate the contaminants that are accumulated in soil. These chemical methods are aimed to change the chemical properties of heavy metals in soil so that their toxicity can be reduced [13]. Some of the techniques being used for removal of heavy metals from soil are shown in Figure 1, and discussed below.

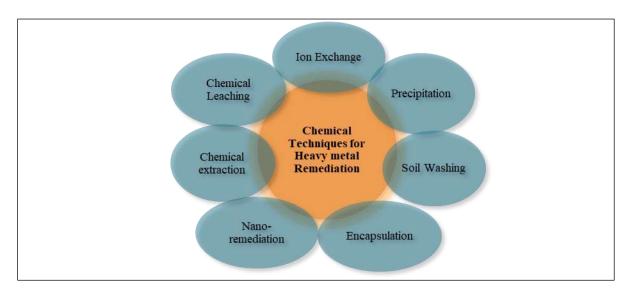


Figure 1. Chemical techniques for remediation of heavy metal contaminated soils

Precipitation

Precipitation is simple, non-toxic, cost effective and the most conventional method to remediate the contaminated soils. This process takes place at basic pH of 9-11 [14]. In this treatment organic contaminants also go through alkaline hydrolysis [15-16]. But huge amount of chemicals are required to minimize the metallic cations to acceptable limit of discharge. Some drawbacks are associated with this technique such as generation of waste, poor and slow settlement of precipitates, slow degradation process of sludge and different metal precipitates may form aggregates [17].

Ion exchange

This process is used to exchange the anions or cations from contaminants and is effectively used in industrial sectors for decreasing heavy metals concentration in effluent stream. In this technique undesirable

ions of heavy metals are swapped by cations which are not pollutants [18]. This technique can also be used for co-contaminated soils by using appropriate cation exchange matrix and substrate soil solution. The cations of heavy metals in the soil are exchanges with other cations present at matrices thus it maintains the charge transfer balance [19]. Various studies have showed that natural zeolite is being extensively exploited for heavy metals cation exchange such as Zn, Cu, Co and Mn [20-22]. Mostly the matrices used for this purpose are synthetically organic ion exchange resins. However this technique has few drawbacks such as non-selectivity of membrane, pH sensitivity and membrane fouling.

Chemical extraction and oxidation

Chelating agents which are organic compounds have metal ions as binding sites in their structure [23]. Ethylenediaminetetraacetic acid (EDTA), humic substances, cyclodextrins and surfactants nitrilotriacetic acid (NTA) and CR11 a chelating resin which is produced by Diaion is used for treatment of sludge contaminated by heavy metals [24]. EDTA is effective reagent for removal of cations of heavy metals and it can be recovered after the reaction [25]. EDTA is having higher affinity for metals and forms metal-EDTA complexes. Recently biodegradable chelants have been made by green chemistry which are used as diacetic glutamic acid (GLDA). It is being used at low pH of 4 to remove different heavy metals such as Cu contaminated sludge, Ni and Cd [26]. Citric acid (167.6 Mm) has been used as chelating agent to effectively remove Zn from contaminated soils at acidic pH (4.43). 92.8% of Zn was removed within 30 minutes [27].

Chemical leaching

It involves the dissolution of ions of heavy metals into leaching liquid and then their extraction. Generally leaching solution is acidic to increase the solubility of metal ions. Inorganic acids such HNO3, H2SO4 and HCL, are used for acidification and their pH s maintained at the level of 1.5-2.0 [28]. This method is preferred when area to be covered is huge and concentration of heavy metals is significant in that area [29]. One of the drawbacks of this technique is that large amount of acid is prerequisite for the maintenance of pH for solubilization and after that acidified sludge should be neutralized which requires hefty operational cost.

Soil amendments

This technique is mainly focused to decrease the solubility and mobility of heavy metals by the use of chemical agents such as lime, silica, cement and fly-ash. This method is used for immobilization of heavy metals and is named as chemical fixation. The chemicals which are used for this purpose are termed as amendments. Mainly it is used for Cr, As and Pb, but some other metals such as Zn, Cd and Cu can also be stabilized by this method.

Nanoremediation

For nanoremediation, iron particles (Nano-scale zero valent) are ideal for remediation of industrial waste contaminated with heavy metals. These nZVI consists of iron oxide shell and metallic iron core. The metallic iron core has good power to donate electrons. Meanwhile iron hydroxide at surface performs electrostatic and coordinative functions and attracts the adsorbed charged ions of toxic metals. So there are two nano-components of nZVI which have complementary and distinct functions to remove oxyanions. Recently zeolite aided zero valent iron nanoparticles have also been used for removal of adsorbed heavy metals. Complexes are formed with the modified nanoparticles by following co-precipitation and then removal.

ZnO nanoparticles have been used for the bio-remediation of Pb and Cd contaminated soils. Plants grown in heavy metal contaminated soils have low catalase coding gene (CAT) which leads to compromised defense mechanism in plants. Application of ZnO nanoparticles in such contaminated soils causes improves peroxidase coding gene (POX) and CAT. So due to improvement of POX and CAT plants are protected from deleterious effects of oxidative stresses [30]. Also nanomagnetite that was coated by MgO and silica showed excellent results for the removal of heavy metals from soil, mainly the mechanism



behind the removal of heavy metals is substitution which is followed by the precipitation [31]. This is technique is widely eco-friendly as nanomaterials are used in smaller amounts.

Encapsulation

It is an effective method for immobilization of toxic metals. It is used to minimize the exposure to hazardous materials by safely disposing them as landfill by their encapsulation in solid blocks [32]. In this technique contaminated soils are mixed with other products such as asphalt, concrete or lime. In this way toxic elements in the soil become immobile and their contamination to surrounding material is prevented. For building up of solid blocks many materials can be used, but cement is preferred as it is versatile, cost effective and easily available [33]. For instance, calcium aluminate cement (CAC), is effective and highly efficient to encapsulate hazardous material [34]. By encapsulation techniques leaching of organic materials can be prevented up to greater extent [35].

Soil Washing

In this method heavy metals are removed from the soil by using various extractants or reagents [36-37]. Recently this technique is being used as alternative to some of conventional techniques for cleaning the contaminated soils. In this technique contaminated soil is dug out and depending upon type of metal and soil is mixed with suitable, extractants solution. Then soil and extractants solution are mixed for specific time. Through chelation, precipitation and ion exchange, heavy metals in soil are transferred to soil solution and then they are separated from leachate [38]. After fulfilling the regulatory criteria the separated soil can be placed to original place. This technique is frequently used to remediate the contaminated sites as it completely removes all toxic metals from soil. This is rapid technique without long term liabilities. Due to high efficiency it is considered as most effective technology for soil remediation.

Conclusion

In this review, we have reviewed the advanced chemical remediation methods for heavy metal contaminated soils. As compared to the conventional methods which are expensive and inefficient, these new methods are now followed worldwide. Encapsulation and soil washing techniques are especially emerged as strong contenders in the last few years. Likewise, the exploitation of the properties and attractive features of precipitation, chemical extraction and ion exchange have been improved even more over the years. In this way, chemical remediation technology for heavy metal detoxification has been made extremely cost-effective, and efficient.

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