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RESEARCH ARTICLE

APPLICATION OF NANOTECHNOLOGY IN AGRICULTURE PART 1: SOIL REMEDIATION BY USING NANOTECHNOLOGY: A REVIEW

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ABSTRACT

Pollution of soils is becoming a major problem in the world and especially, for most of the developed countries of the world. The crops cultivated in polluted soils may be containing a high level of heavy metals and/or toxic materials that can effect on human health. So, it is necessary to use the different technologies to clean up the polluted soil and creates additional lands for agricultural uses. Nanotechnology offers a wide number of smarter and cheaper techniques can be used as alternative methods to immobilize contaminants such as; nanoremediation technology. The nanoremediation methods entail the nanomaterials application on polluted soil. Additionally, this method has the potential to reduce the high costs of soil remediation for large-scale and the time of cleanup. Also, may be reducing toxic materials concentration or heavy metals to near zero in situ. This study aims to present a review of nanotechnology application on contaminated soil remediation.

INTRODUCTION

One of the greatest problems facing most the countries is the inability to grow enough food for her ever-increasing population. To increase food production it is necessary to use the different technologies in agriculture. Nanotechnology can be used as alternative technology techniques helping to increase food production in the agriculture area. Nanotechnology can be defined as particles of size materials at a scale of 100 nanometers (nm) or less in any dimension and be using of nanotechnology in the agriculture sector are still in developing stage (Baruah and Dutta, 2009; Mousavi and Rezai, 2011). Nanotechnology has more applications in soil science (Lal, 2007), such as soil remediation through the new properties of nanomaterials (Baruah and Dutta, 2009). The polluted soil is a significant problem in food production. Crops and plants are grown on polluted soil often absorb heavy metals such as (Pb, Cd… etc.) that can affect the health of humans. The main reason of soil becomes contaminated is due to the human behavior such as the industrial waste and agricultural activities and acid rain. There are many technologies can be using to remediation (also, called cleaned up) of contaminated soils, which can be classified into: (1) Pump and treat (ex situ technologies) are one of the most common technologies used for remediation of polluted soil and must be removed from the site and treated on-site or off-site by using processes such as air stripping, carbon adsorption, biological reactors, or chemical precipitation (U.S.EPA, 2001). (2) In situ soil remediation technologies, in these methods can be treated of polluted soils directly within the subsurface (Sharma and Reddy, 2004). Other in situ treatment technologies include thermal treatment, chemical oxidation, surfactant-cosolvent flushing, and bioremediation. The Pump and treat (ex situ technologies) may be producing highly contaminated wastes through reclamation processes and must to be disposed of out site. Also, it is high average cost and tends a long time of operating periods. Because of that the use of in situ treatment technologies is increasing (Karn*et al.*, 2011; Reddy, 2013). Therefore, new types of technologies and soil amendment materials are urgently needed for polluted soil reclamation. The technologies that using nanomaterials for remediation of polluted soil recently have been developed in

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North America and Europe (USEPA, 2012; NANOREM, 2013).

Nanoremediation

Nanotechnology is an advanced modern technique and alternative for traditional remediation methods (ex-situ and in-situ technologies). It provides new kinds of materials (nanomaterials) have properties that enable both chemical reduction and catalysis to transformation and detoxification of pollutants. Nanoremediation methods entail the nanomaterials application on polluted soil.

Nanomaterials

Nanomaterials (NMs) are materials have nanoscaled dimensions of 100 nm or less in at least one dimension, these materials have highly desired and required properties for soil contamination remediation and nanoparticles are those that have at least two dimensions between 1 and 100 nm. Due to the specific properties of nanomaterials such as larger specific surface area, structure and smaller particle size, they allow significantly changed the physical, chemical, biological properties and adsorption /or reactions effects on the nanoscale with the surrounding contamination media (soil). The characteristic of nanomaterials makes its more reactive than those materials used in traditional remediation technologies for soil remediation (USEPA, 2007). Also, they many different materials in nanoscale can be using for soil remediation such as metal oxides, titanium dioxide, carbon nanotubes, and zeolites in nanoscale. Nanomaterials can be produced by different ways of technologies, and they were classified into two mainly groups: (1) the group of technology is from outside to inside (top down), in generally turning the bigger bulk material into smaller. (2) The group of technology is a bottom to top (bottom-up), in this group, small materials will build bigger bulk material (Niemeyer, 2001). In recent years, the uses of nanotechnology application for polluted soil remediation have been significant increased. The NMs can be classified according to their properties (physical/chemical) into groups: The first group is organic nanomaterials, where mostly content carbon atoms. The second is inorganic nanomaterials and can be classified into subgroups such as (i) metal (Au-Ag) (ii) metal oxide (ZnO_2-Fe2O_3) (iii) quantum dots (Cd-Se). Figure (1) showed the classification of the NMs according to their physicochemical properties (Peralta-Videa*et al*., 2011).

Nanoparticles physical and chemical properties

The NPs have specific properties such as specific surface area, particle size distribution, and morphological sub-structure of the substance, surface charge, and crystallographic characterization. These properties enhanced nanoparticle to be the key of remediation. Additionally, the natural NPs in soil include clays, organic matter, iron oxides, and other minerals are an important fraction in biogeochemical processes.

Nanomaterials for soil remediation

Pollution in the soil can be cleaned up (remediation) using a range of techniques. Nanotechnology is an advanced modern technique used in remediation of polluted soil. Recently, nanoremediation is considered a new technology and is still in progress.

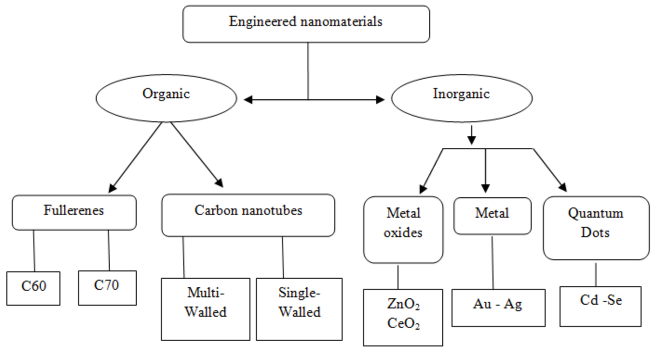

Fig. 1.Nanomaterial classification according to their physical–chemical properties

Nanoremediation methods are involves removing contamination from the soil by using nanomaterials as new techniques. Nanomaterials have specific properties and can be applied in different ways in soil remediation. The using of nanoremediation methods have advantages compared with traditional remediation technologies, that is may be due to smaller particle size and specific surface area of nanomaterial and easy to moving into the soil porous. Also, for these reasons can be used for in situ application. In addition, this method is more practice and economic for remediation because it does not travel very far from the target point (Tratnyek and Johnson, 2006). Many different nonmaterials have been suggested for soil remediation such as nanoscalezeolites, metal oxides, carbon nanotubes and fibers, titanium dioxide, zero-valent iron, iron oxides nanoparticles. Also, nanoscale zero-valent iron (nZVI) is recently more used for polluted soil remediation. Tables (1) show some examples of nanoparticles materials application in the cleanup of contaminated soil (Thome*et al*., 2015).

Table 1.Some contaminated materials have been treated with nanoparticles

Classification of materials	Example for contaminated materials
Organics	Chlorinated solvents- Organophosphorus- p-chlorophenol-Antibiotcs- Pesticidasclorados
Inorganics anions	Nitrate-perchlorate- bromate
Metals	Chrome - cobalt- lead-copper- molybdenum- nickel-silver- zinc- technetium; vanadium- cadmium

Nanoscale Zero-Valent Iron Particles (nZVI)

Nanoscale Zero-Valent Iron Particles (nZVI) are one of the most common types of nanoremediation techniques and they range from 10 to 100 nm in diameter. Generally, the nZVI can be distribution and mobility once injected into a soil to remediation of contamination by moving of nanoscale material in the soil pores (Tratnyek and Johnson, 2006). Because of their properties such as high available surface area, high reaction, and high efficiency can be used in in situ remediation technology (Henn and Waddill, 2006).

Mechanism of nZVI methods in decontamination

Nanoremediation technologies based on using NPs for remediation can be divided into two groups depending on their chemical reaction: the first group is used NPs as an electron donor to clean up the contamination in a low level of toxic with slow moving in the media (soil), and the second group the

NPs using as an agent of sorbent and it is more stable for toxic fixation, also, can be using the NPs as precipitant or co-precipitant of the contaminated materials. In particular, NPs have a high absorption ratio for metal, arsenic (As), chromium, lead (Pb), mercury, selenium, copper (Cu), uranium (anionic contaminants), natural organic matter, organic acids, and heavy metals(Thome*et al.,* 2015). The reaction between toxic materials and the NPs by using the zNIP technique depending on higher surface area of these materials and by simply of that this material can be sequestration of contaminated or toxic material by two ways firstly by encapsulation of toxic materials in interface of NP aggregates, and secondly by fixation on complexation surface (Thome*et al*., 2015). In generally, the chemical reaction processing in zero-valent iron (Fe^0) nanoparticles for removes the halogenated organic contaminants and heavy metals form soil can be expelling by following equations:

$Fe^0 \rightarrow Fe^{2+} + 2e-$ -------------------------------- (1)

$Fe^0 \rightarrow Fe^{3+} + 3e-$ -------------------------------- (2)

$RCl + H^+ + 2e- \rightarrow RH + Cl^-$------------------- (3)

$RCl + Fe^0 + H^+ \rightarrow RH + Fe^{2+} + Cl^-$---------- (4)

As showing in the above reaction the metallic iron (Fe^0) using as an electron donor (first way of clean up), and very fast transformed into Fe^{2+} (Eq.1), also, may be gradually by more time to Fe^{3+} (Eq.2). While in (Eq.3) using the reduction reaction between chlorinated hydrocarbons and the electrons for dechlorination of soil. On the other hand by thermodynamic processes may be acceptable the coupling of the reactions (Eq.1) and (Eq.3) as showed in (Eq.4)

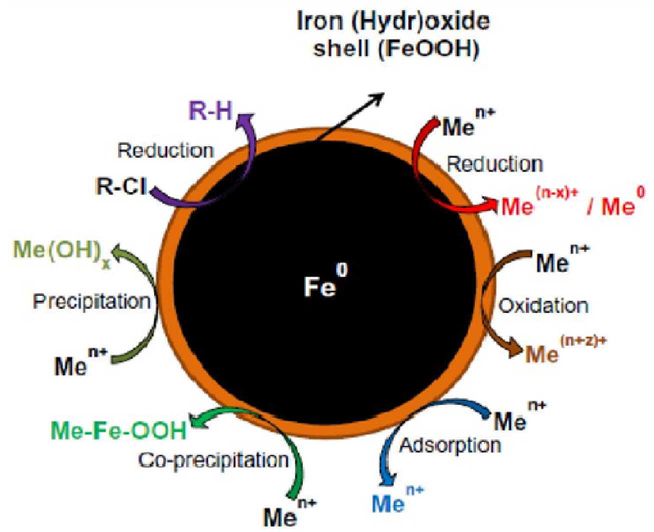

Fig. 2.The chemical mechanisms of nano-zerovalent iron (Fe^0)

In generally, the standard reduction potential (E◦) of metallic iron (Fe^0) to transfer to the (Fe^{2+}/Fe) during the reaction by dissolved in water is (- 0.44 mV), indicating that the high capacity ofmetallic iron (Fe^0) to reducing contamination of many organic compounds such as chlorinated hydrocarbons and metals (Pb, Cd, Ni, Cr). The degradation of organic contaminants by zero-valent iron (Fe^0) methods has two common processes (Li and Farrell, 2000): (i) the first process is hydrogenolysis, where in chlorinated compounds the chlorine atom is replacement by hydrogen atom as presented in equation (Eq.5), and (ii) the second process is dehalogenation, where no addition of hydrogen, but a new C–C bond can be formed and depending on carbon connected can be divided to β reaction (connected with neighbor carbon), and the α reaction may be connected with same carbon. These reactions are presented in (Eq.6) and (Eq.7), respectively (Matheson and Tratnyek, 1994; Orth and Gillham, 1996).

$ClHC{=}CCl_2 + 2e^- + H^+ \rightarrow ClHC{=}\ ClHC + Cl^-$ ------------ (5)

Reaction β: $ClHC{=}CCl_2 + 2e^- \rightarrow HC{\equiv}CCl + 2Cl^-$-------- (6)

Reaction α: $Cl_2C{=}CH_2 + 2e^- \rightarrow H_2C{=}C{:} + 2Cl^-$ ---------- (7)

In soil remediation by zero-valent iron (Fe^0) methods is better using the dehalogenation reaction than hydrogenolysis process that is because may be formation a new product more injurious than the contaminant source as result of hydrogenolysis reactions (Li and Farrell, 2000; Arnold and Roberts, 2000).

Conclusions

Recently, the world facing a rapid increase in population with decreasing of food production and agricultural soils, due to soil pollution by humans activities and we need to provide additional land for agricultural uses by adopting a new and advanced technique for the soil remediation. Nanotechnology provides the possibility of producing the product (nanomaterials) of high quality and low cost for soil remediation compared with old methods. Nanoremediation technologies entail the application of nanomaterials for absorption, detoxification, and release of pollutants from the soil in situ remediation technique. Also, the nZVI methods can be using for the destruction of chlorinated hydrocarbons in soil.

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