

Role of nano scale zero valent NZVI nano-particles in removing heavy metal pollution from soil.

Papel de las nanopartículas NZVI de valencia cero a escala nanométrica en la eliminación de la contaminación por metales pesados del suelo.

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ABSTRACT

Heavy means a sequence of metals or metalloids that are present in small concentrations can be toxic for plants and animals. Soil contamination and degradation are serious environmental problems that pose a great challenge to agricultural productivity and food security. Numerous studies on the Contamination of soil by means of heavy metal pollution were Investigated. An emerging technology called nanotechnology has gained an interest in solving this problem. Many of the nanomaterials were prepared and they are effective in removing the heavy metal pollution in the soil. In this review, we studied the application of Nano scale zero valent nZVI. The Nano scale nZVI finds a versatile application in removing the heavy metal pollution on the soil. In this work, we had discussed about Nano scale zero-valent metal nanomaterials, and Nano composites in detail. The application and observations of this nanomaterial metal and its composite are fully explained and summarized in details . This nanomaterial's exhibit great advantages as adsorbents towards heavy metals.

Keywords: Soil contamination, heavy metal pollution, nanomaterials, Nano scale zero valent nZVI

RESUMEN

Pesado significa que una secuencia de metales o metaloides que están presentes en pequeñas concentraciones pueden ser tóxicos para plantas y animales. La contaminación y degradación del suelo son problemas ambientales graves que plantean un gran desafío para la productividad agrícola y la seguridad alimentaria. Se investigaron numerosos estudios sobre la contaminación del suelo por medio de la contaminación por metales pesados. Una tecnología emergente llamada nanotecnología ha ganado interés en resolver este problema. Muchos de los nanomateriales se prepararon y son eficaces para eliminar la contaminación por metales pesados del suelo. En esta revisión, estudiamos la aplicación de nZVI de valencia cero a escala nanométrica. La nanoescala nZVI encuentra una aplicación versátil para eliminar la contaminación por metales pesados del suelo. En este trabajo, habíamos discutido en detalle acerca de los nanomateriales metálicos de valencia cero a nanoescala y los nanocompuestos. La aplicación y las observaciones de este metal nanomaterial y su compuesto se explican completamente y se resumen en detalles. Este nanomaterial presenta grandes ventajas como adsorbente de metales pesados.

Palabras clave: contaminación del suelo, contaminación por metales pesados, nanomateriales, nZVI de valor cero de nanoescala

INTRODUCTION

A per chemistry literate, we define a heavy metal or metalloid an atom with atomic number more than 20 and have specific gravity 4-5 g/cm³ few examples are cadmium (Cd), mercury (Hg), copper (Cu), arsenic (As), lead (Pb), chromium (Cr), nickel (Ni), and zinc (Zn). The word metalloid means a chemical element that shows some properties of metals and some nonmetals. The entry of theses metals or nonmetals into the environment by soil, plants, water bodies, and the animals may spread to various components of the environment. In the arctic, the heavy metals are found in water bodies, and the plants in different amounts amount [1]. The sources of heavy metals depend upon the nature of parent rock, human activities, and the physicochemical properties of soil. Among the physicochemical properties, pH and organic matter are the important parameters, which play an important role in the accumulation and accessibility of heavy metals. How the accumulation of these heavy metals and its interaction with the soil occurs is on priority in the environmental monitoring [2].

If we consider biological outlook, heavy means a sequence of metals or metalloids that are present in small concentrations can be toxic for plants and animals [3]. Because of the rapid development in agriculture and industry, the pollution caused due to heavy metals is a serious risk to the environment and food safety. It also disturbs the natural ecosystem due to the tremendous growth in the world population [4].

Heavy metal pollution is underground, determined and irreversible it only not degrades the purity of aquatic bodies, atmosphere, and plants, but also has a great impact on the health and wellbeing on the humans and organism via food chain [5].

Continuous exposure to Arsenic causes many types of problems including high blood pressure, neurological effects, respiratory problems keratosis, etc.[6].

The heavy metal pollution on the soil has now become an international environmental issue that has concerned considerable public consideration due to the increasing concern for the security of food products [7]. On worldwide, there are 5 million locations of the soil pollution covering 500 million hectares of land, in which the soils are contaminated by deferent ways of pollutions. When the concentration of soil is increased higher than the baseline or regulatory value soil gets contaminated. Heavy metal pollution in the soil has a great impact on the economic perspective.

VARIOUS SOURCES OF SOIL POLLUTION WITH HEAVY METALS

Soil condemnation by the heavy metal occurs naturally on the parent rocks as well as by the manmade activities. The earth's crust is made of 95% of ingenious rocks and the remaining 5% is made up of sedimentary rocks (Sarwar et al., 2016). The ingenious rocks are rich sources of Cu, Cd, Ni, and cobalt (Co), whereas rock shale contains large amounts of Pb, Cu, Zn, manganese (Mn), and Cd. The entry of heavy metals into the soil environment occurs naturally by meteoric, biogenic, terrestrial, and volcanic processes (Muradoglu et al., 2015).

The soil environment condemnation occurs by the heavy metals when they are transferred from one mine to the deferent environmental sites. The production of heavy metals in the industries is faster than the natural ones. The concentration of metals and metalloids in the waste products is more as compared to those in the receiving environment [8][9]. Mining and the heavy metal manufactured industries are the main sources of soil, water, air condemnation. With the speedy up in the urbanization, the rate of concentration of these heavy metals increases [10] [11][12][13]. Anthropogenic sources as if mining activities release harmful toxic gases, which persist for a long time causes harm to warm

bodies. The possible contamination of heavy metal is increased when mined ores are discarded in physical dressing processes.

Human uses fertilizers for agriculture uses. Fertilizers are important sources of micronutrients, macronutrients that are essential for plant growth. These fertilizers supply metals, which are essential for plant growth [14], [15] . The fertilizers are supplied either directly or via water. The use of some fertilizers instinctively adds some toxics to the soil that results in condemnation of soil.

Several pesticides used in horticulture and floriculture contain a higher concentration of toxic metals. Recently in the UK, 10% of the copper-based pesticides contain some toxic substances, which contain lead, mercury, copper, and zinc [16], [17] such contamination in upcoming cause's difficulties if such sites will be used for agricultural purposes [18]

Some organic solid wastes called biosolids come from wastes water treatment and are recyclable. The importance of various biosolids in municipal sewage slop, dung, and manure leads to the addition of heavy metals in the soil environment [16]. Fig 1 and Fig 2 represents either diagrammatically how contamination of soil by heavy metals occurs naturally or manmade activities.

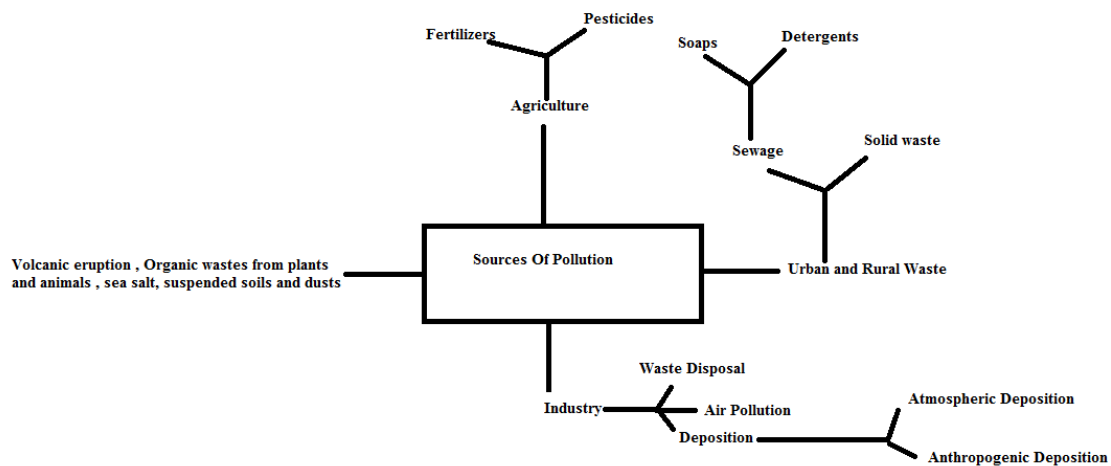


Fig 1 Diagram represents the pathway of Soil Contamination



Fig 2 Anthropogenic sources of Soil Contaminations

ROLE OF NANOTECHNOLOGY IN REMOVING THE HEAVY METALS FROM THE SOIL

Numerous new technological innovations are explored from time to time to remove the soil contamination caused by heavy metal pollution. In order to make the soil suitable for agriculture and crop production one of the techniques, which involves nanomaterials for removing heavy metal pollution? The nanoparticles (NPs) are excellent to immobilize or absorb heavy metals. Their high capacity for adsorption they have immense application in releasing the heavy metals from the soil [19]. Nanoscale zerovalent iron (nZVI) one of the most important nanoparticle. It is a composite consist of Fe (0) and Ferric oxide coating. It is the most widely used nanoparticle for the removal of both organic and inorganic pollutants from the soil. Some common inorganic heavy metals removed by Due to its large surface area, high reactivity, and reduction capability, the most widely studied nanoparticle (NP) for the removal of both organic and inorganic pollutant from the soil is Nanoscale zero-valent iron

(nZVI) are Hg (II), Cr (VI), Cu (II), Ni (II), Cd (II) [20][21][22][23]. Many experiments were done using the Nanoscale zerovalent iron nanoparticles. The results showed that nZVI not only decreases the toxicity but also decreases bioluminescence, reproduction, and lethality of the soil. Some of the important applications of nZVI used for the removal of heavy metals are given in Table 1.

Table 1. Applications of Zero Valent Nano scale metal and composites in removing of heavy metals

Zerovalant nanoparticles (nZVI)	Aimed Pollutant	Observations
nZVI	Cr(VI)	Reduction of chromium from Cr(VI) to Cr(III)
nZVI	Pb, Zn	Effective for the reduction of concentration these elements
nZVI	As, Cr, Pb, Zn	Reduces the immobilization of Cr(VI) also reduces the metal availability
CMC nZVI	Cr(VI)	Reduces the Cr in both water and soil
CMC-nZVI	Cr(VI), Zn	Removing the Cr and Zn with increasing temperature
FeS	Cr(VI)	Effective for the adsorption of Cr
Fe(II) Phosphate	Pb(II)	In situ immobilization
Ca(II) phosphate	Pb(II)	Total immobilization of heavy metals
Starch stab.nZVI	As, Ni	Decreases heavy metal accessibility

The removal of heavy metal pollution by using zero-valent nZVI occurs via the reduction mechanism given below. The removal mechanism of nZVI varies according to the standard potential E_0 of heavy metal. For example, if any metal has a more positive value than the other metal then it cannot be removed as easily by only reduction mechanism. The removal process mainly includes reduction and sorption. For heavy metals, whose standard potential is more than iron can be removed using reduction and precipitation mechanism.

In order to remove the heavy metal pollution in the soil. The pH and temperature of soil also play an important role. Some experiments suggest that with an increase in the

temperature of soil the removal rate of Cr (VI) increases. Nanoparticle nZVI incorporated with copper is used for the removal of Cr (VI) under high soil temperature. Zhu et al. (2016) reported that almost there is $< 2\text{mgL}^{-1}$ dropping of Cr (VI) concentration occurs at a high temperature within 30minutes at temperature 298K to 303K.

Wang reported that Iron sulfide nanoparticles (FeS NPS) are efficient for the immobilization of soil contamination of Cr (VI) [24]. Zhang et al. prepared starch-stabilized iron-based nanoparticles and iron sulfide (FeS [25]. He reported that the use of this nanoparticle is important for the immobilization of arsenic (As) and found that an increasing Fe/As molar concentration ratio decreased As bio accessibility and leachability in soil.

There are also some anthropogenic sources by which the condemnation of soil occurs. The condemnation of soil occurs by the use of pesticides and the persistent organic pollutants (POPs). There are large numbers of pesticides that are completely banned by the Stockholm Convention on persistent organic pollutants in the year 2004. It is in the hands of human beings to avoid the excessive use of these toxic and harmful chemicals. There are almost 12 POPs chemicals, and 8 are pesticides who was banned out of 12 which are referred as dirty zones, The other POPs includes pharmaceuticals chemicals and industrial solvents [26][27]. The POPs exhibit the properties of bioaccumulation and biomagnification.

THE POPS ARE ACCUMULATED INTO OUR BODIES THROUGH THE FOOD CHAIN.

Nanoparticles have been widely studied for their role in the degradation of POPs as well as pesticides. The mechanism involves the degradation of POPs and pesticides are photocatalysis. When light falls on the nanoparticle, it acts as a catalyst and undergoes chemical reactions with POPs and pesticides. The nanoparticles convert these complex toxic and harmful substances present in the POPs and pesticides into simpler and nontoxic molecules like CO_2 , N_2 , and H_2O . Fujishima et al., found that Titanium oxide and zinc oxide are considered as good photocatalysts for such processes [28]. Yu et al. and Kangguo also studied the degradation of three organochlorides and organophosphates and carbamate using titanium dioxide [29] [30]. Fig 3. nanoparticle and titanium dioxide doped with rhenium nanoparticle El-Temsah, studied the nanoscale zerovalent nZVI on DDT. He used soil spiked and aged soil contaminated soil. He found that the degradation rate is 50% in spiked soil and 24% aged soil [31]. El-Temsah &. and Fouad uses zerovalent Nanoscale nZVI particles for the remediation of organ chlorine and malathion [32][33]. Table 2 shows the remediation of various pesticides and POPs using deferent nanoparticles.

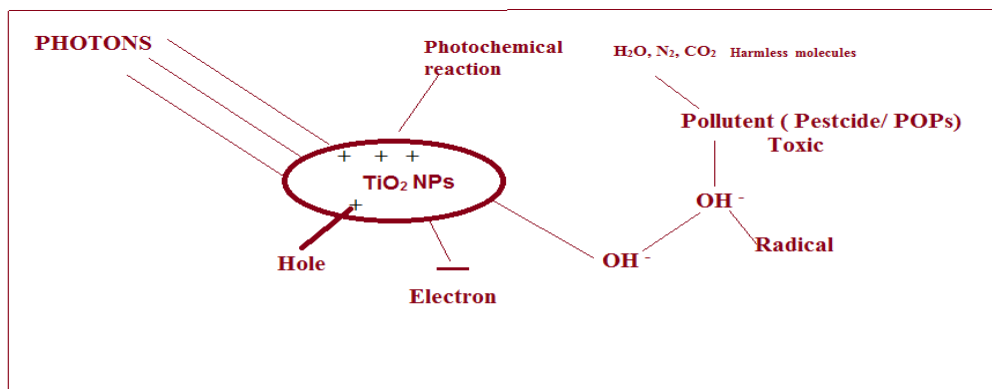


Fig 3. Mechanism involves for the photochemical degradation of pollutants using TiO₂ nanoparticles

Table 2 shows the remediation of various pesticides and POPs using deferent nanoparticles.

Nanomaterial	Pesticide	Observation
Nanoscale zero valent iron	DDT Organo chlorine pesticide, PCB Malathion	Complete oxide and release of electrons causes reduction of pesticides
TiO ₂ , Au/ ZnO coated films	Organo chloride pesticide, BHC, Cypermethrin	Catalytic photodegradation Hydroxyl radical and electron transfer enabled photocatalytic degradation
CMC stabilised nano Pd/Fe nanoscale zerovalent and Pd/Fe bimetallic NPs	Penta chlorophenol Polychlorinated Biphenyl (PCBP)	Dechlorination to phenols Hydroxyl dechlorination of pesticides
FeS NPs	Pentachloro phenol & Lindane	Solubilization of pesticide Photodegradation

Chen studies the in-situ degradation of soil contaminated with PCBs. Uses zero valent Nano scale nZVI. Zarime et al prepared a novel nanoparticle by using zero valent Nano scale nZVI incorporated with low cost bentonite Nano composite. Bentonite is low-cost natural clay it forms a soft paste when mixed with water. Bentonite- nZVI composite is effective for the photochemical degradation of Pb (II), Cu (II), Cd (II), Co (II), Ni (II), and Zn (II) in water. The mechanism involves aggregation of nZVI particles and provides the nZVI particles more adsorbing sites for heavy metals. Bentonite - nZVI Nano composite provides higher removal capacity towards heavy metals as compared to simple bantonite [34].

As conclusion, nano materials have been widely exploited to remove heavy metals from the soil owing to their exceptional properties. In this work, we had discussed about Nano scale zero-valent metal nanomaterial's, and Nano composites in detail. The application and observations of this nanomaterial metal and its composite are summarized in Table 1, 2. This nanomaterial's exhibit great advantages as adsorbents towards heavy metals.

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