Soil Remediation Applications of Nanotechnology

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ABSTRACT: With the growth of urbanization, the anthropogenic activities have increased and thus increase occurrence of soil contaminants. In order to eliminate the contaminants in soil environment, the application of nanotechnology for soil remediation has become a great concern in the world. This review discussed about the fate of contaminants in soil environment; the mechanisms of nanotechnology with various types of nanomaterials for the soil remediation; the advantages and disadvantage of nanomaterials towards the terrestrial organisms, human health as well as the soil environment; and the challenges of using nanotechnology for soil remediation. The major challenges of nanotechnology are the negative effect of the nanoparticles towards the microbes. The toxicity in nanomaterials will affect the microorganisms and inhibit the enzymes activities in the soil environment.

Keywords: Soil remediation; mechanisms of nanotechnology, immobilization, nanomaterials

1. Introduction

Soil is one of the importance parts of environment which provides a critical ecosystem benefit for life. However, due to the urbanization, the rapid growth of industrializations has created side effects towards the soil. In recent decades, soil has been contaminated by the hazardous and toxic pollutants that produced from the anthropogenic sources such as disposal of chemical wastes from industrial, abandoned use of fertilizers and pesticides, and other potential chemical sources which lead to the contamination of soil. For instance, 187 million tonnes of fertilizer and 4 milllion tonnes of pesticides have been used annually for agricultural crop in globally, which has led to the sources of soil contamination [1]. In Europe, the contaminated areas were investigated to be more than 0.5 million areas and approximately 3.5 million of sites were found to be seriously contaminated [2]. There are several soil contaminants which include heavy metals, pesticides, mineral oil and solvents. Heavy metal was found to be the dominant source of soil contaminants, which was also the main concern in many studies, due to the various sources of heavy metals, non-biodegradability and its cumulative behavior [3]. An overview of soil pollutants which conducted in Europe has been reported as presented in Figure 1, where the heavy metal was accounted for 35% of total pollutants found in soil [4]. The attention towards the contaminated soil problems has been raised with great concern as the

contaminated soil will poses potential health impacts to the human, ecosystem, agricultural as well as the environment.
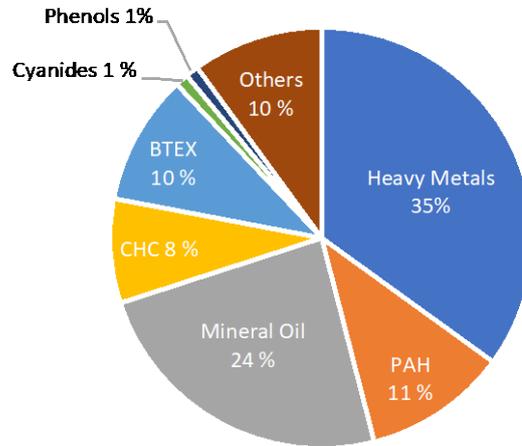

Figure 1. Proportion of soil contaminants in Europe

Nanotechnology and nanomaterials have been widely attracted the attentions from the industrial sector, and was recently being used frequently in several fields such as agricultural, energy and environmental science [5]. Small particle size of 1 to 100 nanometers was being used in the nanotechnology, with different types, high specific surface area, high reactivity and flexibility. Various types of nanomaterials are presented in Figure 2. With the vary properties of nanomaterials, nanomaterials have the potential in removing the contaminants from soil, water and air. The high specific surface area of nanomaterials significantly increases the efficiency in decontamination process. The nanometers size of the nanoparticles enhanced their effectiveness in transported into the contaminated soil. The application of nanotechnology techniques in remediation were investigated to have high efficiency, inexpensive, high flexibility and environmentally friendly [6-7].
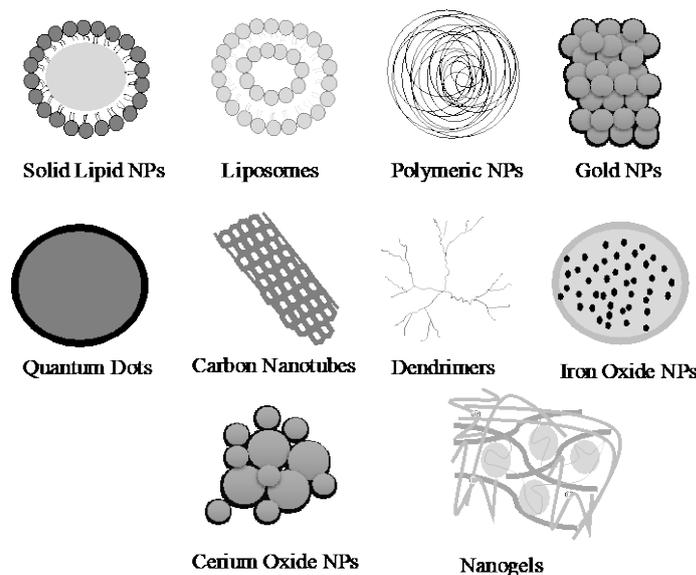

Figure 2. Types of nanomaterials

The implementation of nanotechnology not only applied in decontamination process but also used to detect the various types of pollutants due to the properties of nanomaterials. Heavy metals such as Lead, Chromium, Copper, Cadmium, Mercury, etc can be removed from soil through the applications of nanotechnology. In this review, the fate of heavy metals, the types of removal mechanism technology as well as the benefit, negative impacts and challenges of nanotechnology will be discussed.

2. Fate of Soil Contaminants

The contaminants in soil can be derived in solid, liquid and gaseous phases. There are several factors that causes the contaminants to transport into the soil which include soil properties such as pH, clay content and organic matter content as well as chemical compounds properties. The contaminants in soil are mainly produced through diffuse pollution and point source pollution [8-9]. Diffuse sources of contaminants are typically related to the occurrence of natural phenomena against the agricultural activities and discharge of pollutants from wastewater treatment plant, which will lead to the sedimentation of pollutants in soil through surface water [10]. Point sources are the activities that will produced and transferred the pollutants into the soil such as manufacturers, landfills, industrial activities [10]. The principle of volatilization, leaching and suspension are the dominant mechanisms in transporting the pollutants into the soil [10]. The pollutants that being discharged will transported through the soil and entered the pore space in the soil as well as retained on the surface of mineral or organic matters. The pollutants will also penetrate into wet soil or volatilized into the atmosphere. The most toxicity contaminants in soil are heavy metals, which include the persistent organic pollutants and inorganic pollutants as these pollutants were very resistance to degradation and cannot be destroy or degrade easily. The presence of heavy metal pollutants in soil was mainly due to the anthropogenic activities and the foundation of soil.

Soil is considered as an ultimate sink for various pollutants, especially heavy metals which can persist in soil for few decades. When the contaminants were transported into the soil system, the contaminants will transform into more steady solid phases and retained in organic phase of the soil. The process of this transportation is known as aging and it is a permanent process. The process of aging showed a degradation on soil properties as the formation of aging will reduce the permeability of soil [11]. The contaminants in soil will be sequestered due to the aging process, and the combination of diffusion and adsorption between contaminants and soil will be limited. The factors that cause the occurrence of aging are mainly depends on the quantity and behavior of soil organic matter and black carbon, inorganic components of soil and the structure of soil [11]. The sedimentation of heavy metals in the soil is highly linked to the pH value of the soil, the presence of clay mineral, content of organic matter and other possible factors.

The value of pH in soil is the key parameter that effect the mobility and concentration of heavy metals in the soil solution which regulate the occurrence of precipitation dissolution in soil environment. The availability and solubility of heavy metals tend to be decreased with the increase of pH value in the soil [12]. However, the mobility of heavy metals and toxicity towards the organisms on the soil such as the crops are excepted to be increased. In acidic conditions, the concentration of heavy metal ions in the soil was increased with the precipitation of solid phases of soil [13]. Not only that, the pH values also governed the formation of specific adsorption, ion exchange, desorption reactions in the surface of soil, and

the solubility of mineral [14]. The sorption of heavy metal ions was generally proportional to the pH value of the soil due to the relationship between the H^+ and Al^{3+} ions reaction in the adsorption sites. At high pH values condition, the adsorption of the metal ions was resulted in a hydrolysis complexes of metal compound, which the formation of metal hydroxo complexes was vary from different types of heavy metals against specific pH values [15]. The concentration of metal ions in the soil environment were significantly reduced due to the pH level in the soil reaches a limitation towards the metal ions. For instance, the adsorption of ionic organic contaminants showed a significant decrease with the increasing of pH values from 2 to 3, while remained stable at pH level of 3 to 6, and decreased again with the increasing of pH level. Thus, the threshold levels of pH for the ionic organic contaminants were within 3 to 6 [16]. On the other hand, the sorption process of the metal ions was reduced at a low pH level due to the properties of the sorption locations and the acidity of the oxide catalyzes [16]. While the complexation of metal ions with the organic matter was decreasing linearly proportional to the pH level.

The clay mineral is one of the factors that affecting the transportation of heavy metal pollutants into the soil environment. The specific adsorption as well as the exchange of ions are related to the clay minerals, where the clay minerals has the ability to absorb the metal ions in the soil [8]. The adsorption of metal ions through clay minerals was completed through the adsorption of hydroxyl ions from metal ions or directly removal the proton in the metal ions at the clay mineral's locations. Clay mineral such as kaolinite has a higher ability in retaining heavy metals than other types of clay minerals as different clay minerals has their individual sorption ability at the mineral edges [17]. For kaolinite mineral, the surface edges have greater amount of weakly acidic which enhance the capacity of kaolinite adsorbed the heavy metals to its surfaces. Moreover, the clay minerals such as vermiculite which was able be expand has greater adsorption capacity than kaolinite. This is due to the adsorption process involved the inter-layer spaces of the vermiculite mineral. The clay mineral has higher adsorption capacity compared to silty soil [18]. The organic matter content in soil can also be the factor in affecting the heavy metals content in soil by increasing or decreasing the amount of organic matter content. For instance, the soil with high organic matter content has the capacity in decreasing the presence of metal in the soil and plants through the forming of metal-organic complexes [14]. While the low organic matter content will reduce the adsorption of heavy metals in soil and remains the heavy metals in the form of ions [19]. However, the organic matter content has large impact on the mobility of heavy metals as the heavy metal pollutants were typically attached to the humid compounds in soil [13]. The formation of complexes in organic matter will increase the amount of heavy metals in soil solutions. Besides that, the functional group in metal ions will also affect the adsorption capacity in organic matter [8].The heavy metals with negatively-charged functional group are more likely to be adsorbed by organic matter and become more stable at high level of pH [8].

3. Mechanisms of Nanotechnology

The application of in situ technique is widely used in soil remediation. The technologies used for remediation of contaminants in soil are mainly adsorption, immobilization, Fenton and Fenton-like oxidation, reduction reaction and multiple combination of nanotechnology and bioremediation. The mechanism of combination of nanotechnology and bioremediation has arisen a great concern in recently [20]. Table 1 below has presented a summary of

nanomaterials and nanotechnology applied for in situ removal of contaminants from soils, where the contaminants include heavy metals, organic compound and metalloids. The inorganic contaminants such as heavy metals and metalloid were typically removed through the adsorption process by nanoparticles, while the organic contaminants were removed through reduction reaction and degradation with the presence of catalyzes. With the implementation of nanomaterials, the process of adsorption and oxidation were able to degrade as well as remove the micro-pollutants that retained in soil environment. The applications of nanotechnology in soil remediation that are widely used in removing the contaminants include the carbon nanomaterials, Iron (III) oxide (Fe_3O_4), Titanium oxide (TiO_2), Zinc oxide (ZnO), nanoscale zero-valent iron (nZVI) and nanocomposites. Among the nanomaterials, nZVI was the most common used of nanoparticles in removing the heavy metal pollutants due to the high efficiency of nZVI in eliminating the contaminants such as toxic metals, chlorinated organic compounds and inorganic compound into less harmful compounds [21].

3.1. Reduction Reaction

Reduction reaction has high potential in removing the heavy metals and organic compounds in contaminated soil with the application of nZVI nanoparticles, as well as both the water and groundwater contamination [5]. nZVI particles has been widely applied in wide field scale. Due to the nanoparticle size of nZVI and large surface area, nZVI particles were the capacity to improve the efficiency of remediation by direct contact with contaminants. nZVI particles were being applied into the contaminated soil through injection wall as shown in Figure 3. nZVI particles has a strong reduction capacity and good adsorption ability which are able to convert toxic contaminants to less toxic compound, such as Chromium(VI) converted to Chromium(III) and form a new compound such as ferrous chromite [4]. Moreover, the addition of biochar into the nanoparticles of ZVI was found to enhance the reduction reaction capacity of nZVI and increase the removal efficiency of nZVI in eliminating Chromium(VI) through reinforcement the disparity of iron particles and reduce the movement of mixture in the soil [5]. For example, the combination of biochar and nZVI has removed 66% of Chromium(VI) content in the soil [5]. It was investigated that a mass of 28% of 1 kg Chromium(VI) was reduced with 1 g of nZVI injection into the contaminated soil. In addition, 98% of Chromium (VI) was removed within 24 hours in a treatment condition with pH level at 5 [33].

Furthermore, the combination of carboxymethyl cellulose stabilizer with nZVI was reported to have high capacity in converting most of the Chromium (VI) contaminants into carbonate-bound as well as Iron-Manganese oxides-bound, where the bioavailability and leachability of Chromium will be by 50% at a condition of 1 g to 10 mL of soil to solution [26]. The combination of carboxymethyl cellulose stabilizer and nZVI was also reported to have great efficiency in removing the organic contaminants such as DDT, TCE and pesticides from soil column. For instance, 44% of TCE was dechlorinated within 30-hours treatment period through the injection of CMC-stabilized nZVI into the potting soil with 9.2% of organic matter in soil [22]. With the injection of 20% aqueous nZVI 1 kg of soil, 25% of DDT was removed in 1 kg of soil which containing 24 mg of DDT per kg soil within 72-hours. In order to enhance the reaction activity of nZVI, higher amount of nZVI was needed to remediate the soils that contaminated for long period of time [22].
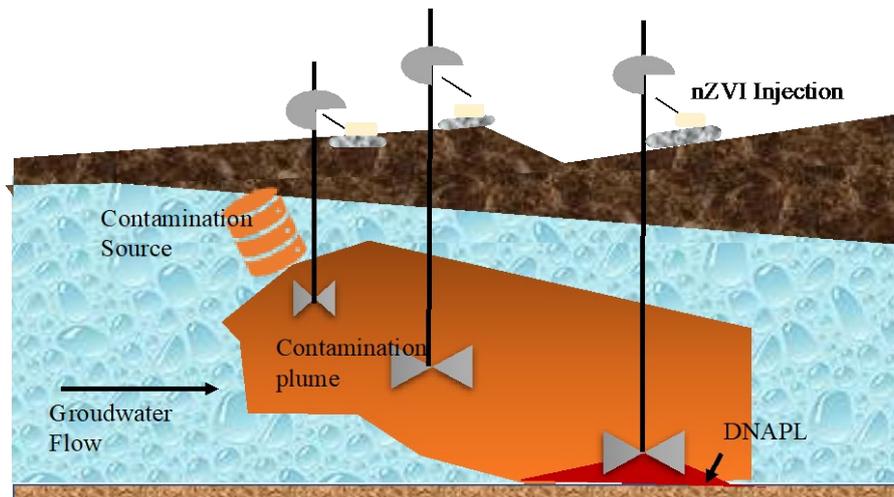
Figure 3. Injection of nZVI for in situ soil remediation

3.2. Immobilization

The mechanism of in situ immobilization of contaminants has received great attention in worldwide as immobilization is a cost-effective and environmental friendly technique for remediation of contaminated soil [1]. For immobilization remediation, the nanomaterials selected were highly depending on the properties of the contaminants and the condition of soils. Several nanoparticles additives have been selected and widely applied in the immobilization remediation of organic and inorganic pollutants in the soil environment [5]. These nanoparticles additive selected include the carbon nanomaterials and metal oxide nanomaterials. For carbon nanomaterials, the organic contaminants were being absorb through van der Waals forces and interactions between π- π. Carbon nanomaterials can be classified into various structural configurations such as fullerene, carbon nanotubes and graphene which act as an adsorbent in immobilization remediation. The characteristics of hydrophobicity surface and high adsorption ability of carbon nanomaterials enhance the potential of carbon nanomaterials in removing the organic contaminants in soils [34]. The application of carbon nanotubes was being considered due to the high adsorption properties of carbon nanotubes to the organic compounds compared to the organic matter in soils [7]. Furthermore, carbon nanotubes were found to have specific adsorption towards the ionizable organic compound such as pesticides through the interaction between π- π and cation- π. Not only that, carbon nanotubes have low-barrier surface and hydrogen bond with electron charged [7]. The application of carbon nanotubes has been widely investigated in various condition in order to reduce the organic compounds such as PAHs [5]. For instance, the presence of carbon nanotubes in soil could hinder the movement of PAHs and reduce the bioavailability of PAHs towards the crops and microorganisms in soil environment [34]. Moreover, the oxygen content can influence the adsorption capacity of carbon nanotubes. The functional group of –OH can increase the adsorption capacity of carbon nanotubes by strengthen the interaction between π-π and –OH [34].

Table 1. A summary of various mechanism of nanotechnology applications for in situ soil remediation.

Mechanism	Nano-materials	Pollutants	Pollutants Conc.	Nano-materials Conc.	Results	References
Reduction reaction	nZVI	Dichloro- diphenyl- trichloroethane (DDT)	24 mg/kg	20% aqueous	25% of DDT removal within 3 days	[22]
	nZVI	Dichloro- diphenyl- trichloroethane (DDT)	0.15 g	5 wt%	2.5% of DDT removal per nZVI	[23]
	nZVI	Chromium (VI)	50 mg/L	45.7 m²/g	62% removal within 60 min	[23]
	nZVI activated persulfate	polycyclic aromatic hydrocarbons (PAHs)	17 μg/g	3 wt% of persulfate & 0.35 wt% of nZVI	82.2% removal within 104 days	[24]
	CMC/HA @nZVI	Chromium (VI)	110 μg/g	3 wt%	74.5% reduction within 3 months	[25]
	CMC-nZVI	Chromium (VI)	800 μg/g	1.1 wt%	95% reduction within a week	[26]
	PVP-nZVI	Tri-chloroethylene (TCE)	727 μg/kg	0.4 g	84.73% dechlorination of TCE	[27]
Immobilization	Carbon nanotubes (CNTs)	polycyclic aromatic hydrocarbons (PAHs)	4000 μg/L	0.25 wt%	66.1% removal within 24 hours	[7]
	Iron (III) oxide	Cobalt (Co)	185 mg/kg	0.5 wt%	31% removal within 60 days	[28]
	nanosized hydroxyapatite nHAP	Copper (Cu)	547 μg/g	5 wt%	Fully removal of Cu	[29]
	nHAP	Zinc (Zn)	70.4 μg/g	5 wt%	Completely reduction of Zn	[29]
	nZVI	As	70.2 mg/g	5 wt%	70% removal of As	[30]
	Titanium dioxide TiO₂	diphenylarsinic acid (DPAA)	20 μg/g	5 wt%	82% removal within 3 hours	[31]
Fenton-like oxidation	Fe₃O₄	PAHs	100 μg/g	18mM	85.2% of removal at pH 3.5	[32]

For metal oxide nanomaterials, the contaminants were removed through surface complexation. Metal oxides such as Iron(III) oxide and Titanium dioxide are commonly being applied in soil remediation. Due to the high adsorption capacity of Iron(III) oxide, it can remove heavy metals such as Arsenic and Cadmium. For instance, Iron(III) oxide has a maximum of 37.03 mg/g of adsorption capacity in remediated the Cadmium under a condition with pH level of 6.0 [5]. Besides that, the maximum adsorption capacity for Titanium dioxide was found to have 94% of sorption rate in removing the Th(IV) under a condition of pH 4.0. The acidic condition of soil enhanced the sorption process by promoting the surface complexation to become the main adsorption mechanism [35].

4. Pros and Cons of Nanotechnology

With the increasing of the application of nanotechnology in soil remediation, the amount of nanomaterials will also be increased and entered the environment. The high amount of nanomaterials may produce unpredicted risk towards the soil environment and ecosystem and indirectly threaten to human health. The main concern is the transportation of nanomaterials in the soil environment may transmitted into the groundwater system and pollute the water resources as well as the drinking water system and bring adverse impacts towards the terrestrial organisms and human health [34]. The application of nanotechnology brings both benefits and disadvantages towards the ecosystem and environment.

The presence of nanomaterials in the soil environment could enhance the growth of seeds and plants due to the enrichment of useful nutrients and pesticides [5]. For instance, the various nanomaterials such as carbon nanotubes, metal and metal oxide nanomaterials has the ability to enhance the nutrient in soil by delivering the nutrient to the roots and leaves of the crops and thus improve the growth of crops [1]. The application of metal oxide nanomaterials such as CuO has the potential to enhance the crops yield as well as the growth of crops due to the presence of virulent pathogens in CuO nanomaterial [5].

The disadvantage of the application of nanotechnology is the potential of toxicity towards the terrestrial organisms and soil ecosystem. It was found that there is potential toxic from nanomaterials towards the plant's cells. For instance, the concentration of carbon nanomaterials such as fullerene was found to be high in the plant's cells due to the process of translocation as well as uptake process [26]. The translocation of the hydrophobic nanomaterials was due to the natural phenomena in the xylem, where the transport of nanomaterials was through the uptake of water and nutrients. Through the life cycle system, the uptake of toxic by the plants will indirectly impacts towards the human through the ingestion of toxic crops. Besides that, the nanomaterials will also impact towards the properties of soils due to the small size of nanomaterials and high specific surface area. The nanomaterials could increase the porosity of soil and enhance the interaction between soil particles and organic matter [14].

5. Challenges of Nanotechnology

The major challenges of nanotechnology are the negative effect of the nanoparticles towards the microbes. The toxicity in nanomaterials will affect the microorganisms and inhibit the enzymes activities in the soil environment. Several studies have been done to reduce and prevent the toxicity of nanomaterials towards the soil organisms. However, various conflict

results have been reported as some studies presented the inhibitory ability and some studies investigated the biostimulation impacts towards the microbial in soil system [1, 5, 20]. In order to overcome the negative impacts that cause by the application of nanotechnology, further research and experiment are required to be investigated.

6. Conclusions

In summary, the application of technology for soil remediation includes the mechanism of reduction reaction and immobilization. Carbon nanomaterials, nZVI and metal oxide nanomaterials are the most efficient in removing or reducing the contaminants in the soils. The fate of contaminants in the soil environment is mainly linked to the pH value of the soil, the presence of clay mineral and content of organic matter. The application of nanotechnology has high efficiency in remediated the contaminated soils as well as enhance the useful nutrient to the plants and crops and increase the growth of yield. However, the nanomaterials could bring toxicity towards the plants cells and have negative impacts towards the soil environment as well as threaten human health. Thus, the application of nanotechnology in soil remediation is still require for further more investigation in order to promote the global environment.

Acknowledgments

Competing Interest

The authors declare that they have no conflict of interest

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