Nanotechnology for Polluted Soil Remediation

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15.1 Introduction

Nanotechnology is considered to a key role in soil remediation that involves removing soil contaminants and enhancing soil quality and fertility. This can be achieved by high specific area and high reactivity of nanomaterials due to smaller particle size which make nanomaterials easier to deliver into soils. These characteristics increase its efficacy in soil remediation than other traditional materials, especially in situ remediation due to its easier delivery into soils (Panpatte et al. 2016). There are many kinds of nanomaterials that were used for soil reclamation such as carbon nanotubes, zerovalent iron nanoparticles, magnetic nanoparticles, and others. Taking into consideration their functions on soil remediation, fate and mobility and possible ecotoxicology effects will be also mentioned in this chapter.

15.2 Application of Different Nanomaterials for Reclamation of Soil Contaminated with Different Pollutants

15.2.1 Zeolites

Zeolites are defined as microporous, aluminosilicate minerals generally applied as adsorbents and catalysts for different pollutants (Grace 2010), and its porous structures contain many cations, such as Na^+, K^+, Ca^{2+}, Mg^{2+}, and others (Marakatti and Halgeri 2015). These cations are easily to contact and readily exchanged to other solutions. Natural and manufactured zeolites can be used for reclamation of soil contaminated with different pollutants, consequently decreasing the risks of those

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pollutants which might release to neighboring waterbodies or accumulated in plants/animals. For example, Edwards et al. (1999) reported that manufactured zeolites with ratio of 0.5–5% were applied successfully in mine soils contaminated with Zn, Pb, Cu, and Cd and achieved significant removal (42–72%) of fractions of the heavy metals that exist. In addition, zeolites also increase soil pH that plays an important role in metal immobilization (Edwards et al. 1999). Other scientists have got similar results that use other leaching solutions such as 0.01 M $CaCl_2$ or dilute acetate solution to estimate the stability of the heavy metals in the soil phase. The extracted amounts of metals using the above solutions were significantly decreased due to reclamation of the contaminated soils with 0.5–16% zeolites by weight (Lin et al. 1998; Shanableh and Kharabsheh 1996; Moirou et al. 2001). To evaluate the ability of zeolite minerals for remediation of heavy metals in soil, some scientists used plant to check the metal toxicity and bioavailability in zeolite-amended soils. Haidouti (1997) reported that Hg uptake by ryegrass (*Lolium perenne L.*) and alfalfa (*Medicago sativa L.*) were decreased to 58% and 86% in roots and shoots, respectively, in soils amended with zeolite at 1–5% (g g^{-1}). Chlopecka and Adriano (1996) reported that application of 1.5% (g g^{-1}) zeolite to a Zn-spike soil was able to amend the harmful effect of the metal and to increase the growth and yields of maize and barley (*Hordeum vulgare*), and accumulation of Zn was also decreased in plant tissues. The same results were got by Knox et al. (2003) who found that growth of maize and oat (Avena sativa) were increased in soil near Zn-Pb smelter when amended with 2.5–5% zeolites, and also Cd, Pb, and Zn accumulations in the plant tissues were decreased. In contrast, neither plant could grow in the unamended soil. Moreover, Mahmoodabadi (2010) found that shoot and root dry weight of soybean (*Glycine max*) were increased due to application of natural zeolites.In addition , zeolites also increase soil pH tha. However, scientists have recorded a reduction in growth of some crops and vegetables due to zeolite application (Geebelen et al. 2002; Coppola et al. 2003; Stead 2002). Generally, application of Na-type zeolites might have negative effects on growth of plants due to release of Na+ into soil solution even though the adverse effects of the heavy metals were alleviated. Therefore, Ca-type zeolites are preferred for heavy metal remediation especially in farmed lands. Additionally, zeolites are strong candidate for radioactive elements such as 139Cs and 90Sr from contaminated soils due to nuclear pollution, since it can retain radionuclides in contaminated soils and prevent plant accumulation of these pollutants (Ming and Allen 2001).

15.2.2 Iron Oxides Nanoparticles (nFeOs)

As an important constituent of soil and a necessary nutrient to plants and animals, iron (Fe) is classified as the fourth most abundant element in the earth. The Fe oxide that exist in soils and sediments usually occur as nano-crystals (5–100 nm in diameter) with reactive surfaces that can adsorb a wide range of both inorganic and organic substances through mechanisms such as surface complexation/surface precipitation (Bigham et al. 2002). Because of their noticeable absorption capacity for toxic substances and their environmentally friendly characteristics, there are many kinds of iron oxide nanoparticles that had been fabricated and used for water/soil remediation processes. For example, nano-Fe oxides (nFeOs) solution can be pumped/spread directly to polluted sites at low cost with insignificant risks of secondary contamination. The intensively studied nFeOs for heavy metal removal from water/wastewater include goethite (α-FeOOH, needle-like, 200 nm × 50 nm), hematite (α-Fe_2O_3, granular, 75 nm), amorphous hydrous Fe oxides (particles, 3.8 nm), maghemite (γ-Fe_2O_3, particle, 10 nm), and magnetite (Fe_3O_4, particles, around 10 nm) (Hua et al. 2012). Many scientists had been tested nFeOs for heavy metal removal from aqueous solution by adsorption. The target contaminants included Cu^{2+}, Cr^{6+}, Ni^{2+}, Pb^{2+}, Cr^{3+}, Zn^{2+}, As^{+5}, and As^{+3} (Hua et al. 2012). Many studies had been concluded that reclamation of soil polluted with heavy metals using nFeOs can reduce the availability and mobility of these toxins in soil by adsorption. Moreover, application of industrial wastes rich in iron oxides to contaminated soils resulted in high immobilization of heavy metals (Xenidis et al. 2010; Kumpiene et al. 2008; USEPA 2007), suggesting that application of nFeOs with the mine soils could significantly immobilize the soil-bound toxic substances. Shipley et al. (2011) reported that using a column packed with soil mixed with 15% (g g^{-1}) nano-magnetite had showed negligible adsorption. As concentrations in the effluent for up to 132 days, the influent containing 100 μg L^{-1}, and observed that As solution was injected through the column at a rate of 0.3 mL h^{-1}. While removal percentage was decreased after 208 days to 80% as compared with soil alone that had no removal efficiency for contaminant. Moreover, nFeOs were used successfully to remove another 12 heavy metals (V, Cr, Co, Mn, Se, Mo, Cd, Pb, Sb, Tl, Th, and U) from soil. Since the removal efficiency reached to 100% for all elements except Cr, Mo, Sb, and Co, the removal efficiency was lower (80%) after 35 h of the leaching test, proven that nFeOs have high adsorption capacity for multiple toxins. Nano-hematite has similar adsorption capacity to the nano-magnetite (Shipley et al. 2011). The removal efficiency of nFeOs depends on the chemical compositions, particle size, particle concentration, particle magnetism, solution chemistry, and medium property. For a given nanoparticle suspension, the particle stability is largely governed by the electrostatic repulsion between particles (O'Carroll et al. 2013). The force is caused by the particle surface charge, and surface "zeta potential" is used to quantify the magnitude of the charge or the electrostatic repulsion. Whenever zeta potential was higher, the repulsion force between particles was stronger; thus the nanosolution is more stable. Charged ions (e.g., H^+, OH^-, Na^+, or Cl^-) in the background solution can affect the suspension stability by changing the particle surface charge (zeta potential). A pH value where the net surface charge becomes zero is called "point of zero charge" (PZC), and the solution is smallest stable and greatest prone to form aggregates at pH close to the PZC. Nanoparticle stability can influenced by solution pH depends on to which extend solution pH close to the particle PZC. For example, the PZC is at pH 7.1 for magnetite nanoparticles. The suspension won't be stable at pH from 6 to 8 because the net particle surface charge decreased to around zero and fast aggregation took place due to the minimum repulsion. In contrast, the nanoparticle solutions stayed stable at pH from

3 to 5 or from 9 to 10, which were far from the PZC of magnetite nanoparticles (Hu et al. 2010). In these cases, the average particle size remained similar to the original size (60 nm) (Hu et al. 2010). Nanoparticles form aggregates and precipitate when they exist in a concentrated solution than dilute solution, due to nanoparticles that crash with each other which make them less stable and have more chance for aggregation and precipitates. He et al. (2008) and Baalousha (2009) reported that smaller hematite nanoparticles have more ability to form aggregates due to changes of the surface characteristics with particle size changes. In addition, attractive force of magnetism among the particles of nFeOs increases the probability of aggregation. Hong et al. (2009) observed that the electrostatic and magnetic interactions are two factors affecting the stability and transport of magnetic nanoparticles. Hong et al. (2009) reported during a column test with sand media higher magnetic nanoparticles are more stable in the column than less magnetic nanoparticles. The nonmagnetic nFeOs were highly transported, while magnetic nanoparticles were mostly retained, indicating that magnetically induced aggregation and subsequent straining cause a greater retention in the column. Magnetic particles include maghemite (γ-Fe_2O_3), magnetite (Fe_3O_4), and zerovalent iron (Fe^0), while a hematite (α-Fe2O3) nanoparticle is nonmagnetic. On the other hand, transport of those magnetic nanoparticles might be controlled by the magnificent of an external magnetic field to the system. Particle PZC could be changed due to adsorption of natural organic matter on nanoparticles. Therefore, the stability of nanoparticle suspension was affected by humic acids (HA) due to the acid effect on the size particle of PZC, so minimizing PZC particles caused by adsorption of HA. For example, Hu et al. (2010) found that PZC of magnetite nanoparticles decreased from 7.1 (without HA) to 5.8 at 2 mg L^{-1} HA and to 3.77 at 3 mg L^{-1} HA. When the HA concentration was high enough (e.g., 10 mg L^{-1}), the PZC was decreased to pH values out of the range (pH 3–10) that is commonly encountered by the natural environment. In this case, the suspension shows the highest stability under normal conditions (Hu et al. 2010). Similar results were got by other scientists (He et al. 2008; Baalousha 2009; Hong et al. 2009; Baalousha et al. 2008). In addition, an increase of the solution ionic strength generally improves the aggregation of the nanoparticles (Hu et al. 2010).

Fang et al. (2012) concluded that the method of combining Fe_3O_4 nanoparticles with indigenous soil microbes may lead to great benefits for the application of nanotechnology in remediation of herbicide-contaminated soil. Soil treatment with Fe_3O_4 nanoparticles combined with soil indigenous microbes achieved higher degradation efficiency for 2,4-dichlorophenoxyacetic acid (2,4-D) than the treatments with Fe_3O_4 nanoparticles or indigenous microbes alone. This was attributed to the effect of Fe3O4 nanoparticles which not only degraded 2,4-D in soils but also increased the soil microbial populations and enzyme activities (Fang et al. 2012). These results were in agreements with those obtained by Huang et al. (2014) who found that nanoscale Fe_3O_4 would eliminate the toxicity of 2,4-dichlorophenol (2,4-DCP) by reductively transforming the electron-withdrawing chlorine groups to chloride, and then the laccase was employed to combine with nanoscale Fe_3O_4 to degrade 2,4-DCP.

The use of nFeOs for soil remediation will release these nanomaterials and their transformation products into the environment. The potential toxicity and pathology of nFeOs at the ecosystem were studied by many scientists. For example, Karlsson et al. (2009) evaluated the risks of nFeOs with different sizes on cell death, mitochondrial damage, DNA damage, and oxidative DNA lesions after exposure of the human cell line A549. They found that Fe_2O_3 nanoparticles have low toxicity and the difference between the different particle sizes showed insignificant effect. Moreover, Auffan et al. (2006) found that the coated nFeOs produced weak cytotoxic effects, and no genotoxic effects were measured, while other scientists showed that nanoparticles might produce oxidative stress in cells by creating reactive oxygen species (ROS). ROS can damage proteins, lipids, and DNA and in addition give rise to necrosis and apoptosis (Karlsson et al. 2009). However, Limbach et al. (2007) referred the creation of ROS in exposed cells to the chemical composition rather than the nanoscale size. Whereas, they observed that dissolved iron ions produce ROS 20 times higher than exposure to the same amount of Fe_2O_3 nanoparticles, indicating that nFeOs do not cause more toxicity than the soluble iron or solid irons with larger particle sizes. As a matter of fact, Sadeghiani et al. (2005) reported that poly-coated magnetite such as aspartic acid coated magnetite nanoparticles may be considered as a potential precursor of anticancer drugs.

15.2.3 Nanoscale Zerovalent Iron (nZVI)Particles

Nanoscale zerovalent iron (nZVI) technology developed in the 1990s was fabricated to degrade the toxic halogenated hydrocarbon compounds and other petroleum-related products which pollute the groundwater environment through gas tank leakage, organic solvent spills, etc. (Zhang 2003). The metallic iron particles are highly effective reducing agents and able to degrade many organic contaminants to benign compounds by reduction reactions. These contaminants include chlorinated methane, chlorinated benzene, pesticides, polychlorinated biphenyls (PCBs), and nitroaromatic compounds (Zhang 2003). In addition, the high degradation efficiency technology considered an eco-friendly material for the environment and being easily delivered to the subsurface environment due to the small particle size. This technology is also having benefits in heavy metal removal from water and soil. Zerovalent iron is a strong reductant with a reduction potential ($E0$, Fe^{2+}/Fe^0) of −0.44 V (O'Carroll et al. 2013). Theoretically, some metals with E0 much more positive than −0.44 V could be reductively immobilized by nZVI. Typical examples of such metals with environmental importance include CrO_4^{2-}/Cr^{3+} ($E0$ = +1.56 V), $Cr_2O_7^{2-}/Cr^{3+}$ ($E0$ = +1.36 V), and UO_2^{2+}/U^{4+} ($E0$ = +0.27 V) (O'Carroll et al. 2013). The high-valent species (CrO_4^{2-}, $Cr_2O_7^{2-}$, and UO_2^{2+}) of those metals are usually more soluble and more toxic than their low-valent counterparts (Cr^{3+} and U^{4+}) in the natural environment. nZVI can reductant toxic forms of metals (CrO_4^{2-}, $Cr_2O_7^{2-}$, and UO_2^{2+}) to non- or low toxicity forms (Cr^{3+} and U^{4+}) through the process called reductive immobilization. For example, uranium (U) is the most common radionuclide pollutant found at many nuclear waste sites. It is mainly detected in contaminated groundwater as highly soluble and mobile U^{6+} in the form of $UO_2{}^{2+}$ (Cao et al. 2010). Fe oxyhydroxides can adsorb UO_2^{2+} in soils and in uranium mining tailings (Abdelouas 2006). However, acid mine drainage can dissolve and release the adsorbed uranium to the nearby ecosystem. These risks can be solved by converting it to insoluble U^{4+} oxides using nZVI. Many reports concluded that, compared to the other reductants (metal iron filing, galena (PbS), and iron sulfide), nZVI is more efficient to reductively immobilize U^{6+} from aqueous phase, which could be attributed to its nano-size, high reactivity, large surface area, and reactive Fe (II) produced by nZVI (Yan et al. 2010; Fiedor et al. 1998; Crane et al. 2011; Dickinson and Scott 2010; Riba et al. 2008). This literature confirmed that U^{6+} was predominantly removed by nZVI via reductive precipitation of UO_2^{2+} (U^{4+}) with minor precipitation of $UO_3 \cdot 2H_2O$ (U^{6+}) as confirmed by the X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) analyses. Oxygen level, solution pH, and presences of bicarbonates and calcium ions all affect the reductive immobilization processes (Yan et al. 2010; Fiedor et al. 1998). Similar to U, other elements could be more toxic in higher valent than lower valent, and nZVI have the ability to convert higher-valent atoms to lower valent. Franco et al. (2009) reported that nZVI were used to convert 97.5% of Cr^{+6} in a polluted soil to Cr^{+3}, which significantly reduced the chromium toxicity in the soil. Similar results were obtained by O'Carroll et al. (2013) who used nZVI to convert high-valent selenium species ($SeO_4{}^{-2}$ or Se^{6+} and $SeO_3{}^{-2}$ or Se^{4+} which are more soluble and mobile in the natural environment and more toxic) to low-valent species such as Se^0 and Se^{-2}. nZVI has been applied to remove the selenium from the solution and reduce the high-valent species to the low-valent ones; thus the toxicity and solubility of Se are greatly lowered (O'Carroll et al. 2013). Also nZVI had high adsorption capacity to remove dissolved pollutants from polluted water. Olegario et al. (2010) reported that nZVI can remove dissolved Se^{6+} up to 0.1 mole Se/mole Fe. Using X-ray absorption near-edge structure (XANES) spectroscopy and X-ray absorption fine structure (EXAFS) spectroscopy, they identified FeSe compound in the solid phase as the reduced Se^{2-} species converted from S^{6+}. They reported that nZVI can reduce soluble Se oxyanions to insoluble Se^{-2}. nZVI also had the capability to remove other toxic elements in water or soil such as Hg^{+2}, Ni^{+2}, Ag^{+1}, Cd^{+2}, As^{+3}, and As^{+5} (Li and Zhang 2006; Li and Zhang 2007; Kanel et al. 2006; Kanel et al. 2005). The mechanism inculdes reduction of higher-valent to lower-valent metals or adsorption of such elements that consist of a layer of iron oxidation products (iron oxides) (O'Carroll et al. 2013). For example, Watanabe et al. (2009) reported that use of 0.01% nZVI ($g\ g^{-1}$) to a Cd-spiked soil significantly reduced the Cd accumulations in rice (*Oryza sativa*) seeds and leaves by 10% and 20%, respectively, than control. nZVI were estimated to relocate within a few centimeters under subsurface environment (Saleh et al. 2008; Tratnyek and Johnson 2006) due to rapid nanoparticle accumulation and interactions with surfaces of the ambient porous media. Many scientists were succeeded to enhance the stability and mobility of nZVI (e.g., using nanoparticle stabilizers) and recorded during laboratory column test that nZVI diffuses the entire contaminated aquifer and degrades the pollutants in situ (He and Zhao 2005; He and Zhao 2007; Phenrat et al. 2008; Sakulchaicharoen et al. 2010). But they failed to significantly increase nZVI mobility in the field (O'Carroll 2013). O'Carroll (2013) reported that stabilized nZVI can travel around 1 m from an injection well, while high permeability formations of nZVI achieved maximum travel distance of up to 2–3 m. The differences between the lab work and the field experiments resulted from the fact that lab work uses lower Fe concentrations (<0.25 g L^{-1}), higher flow velocities (15–30 m day^{-1}), and simplified subsurface simulations by sand-packed columns, while field experiment uses much higher Fe application rates (1–30 g L^{-1}), lower groundwater flow rates (0.1–10 m day^{-1}), and much more complicated aquifer formations (O'Carroll 2013), which produce much aggregation and precipitation of nZVI. In addition, the oxidizing of nZVI can be faster by dissolved oxygen, creating maghemite and magnetite precipitates (Reinsch et al. 2010). From this approach, nZVI and other nanoparticles with extremely high mobility are not required for surface soil remediation purpose. There are some reports concerning the toxicological and ecotoxicological effects of nZVI on the environment. For example, Grieger et al. (2010) reported some possible effects of exposure to nZVI as follows:

(a) Low serious toxicity to aquatic organisms, as sublethal effects have been observed at minor concentrations (<1 mg L^{-1}).
(b) nZVI can cause histological changes and morphological changes in some species and attach to organisms and cells.
(c) Some coatings decrease toxicity by reduced adherence.
(d) Release of Fe(II) from nZVI leads to ROS production as well as distraction of cell membranes causing cell death and lysis and possible improvement of biocidal effects of Fe(II).
(e) The aging of nZVI under aerobic conditions decreases nZVI toxicity, whereby Fe^0 is speedily oxidized.

Other metal-based nanoparticles for environmental remediation include nanoscale manganese oxides and hydroxides, aluminum oxides, titanium oxides, zinc oxides, and magnesium oxides. All these nanoparticles could adsorb heavy metal from solution on surface; iron oxides also remove heavy metals using the same mechanism (Bigham et al. 2002). Among those metal oxide nanoparticles, iron and manganese nanoparticles are sensitive to the compact environment such as those in a waterlogged soils or wetlands. Those particles may be reduced to the lower-valent states and miss the adsorption capacity. For manganese-, zinc-, and aluminum-based nanoparticles, phytotoxicity might be useful for acidic soils. Moreover, Limbach et al. (2007) reported that cobalt and manganese oxide (Co_3O_4 and Mn_3O_4) nanoparticles produced more ROS (indicating more toxicity) than their respective salt solutions, while titanium oxide (TiO_2) and iron oxide (Fe_2O_3) nanoparticles were relatively inert.

15.2.4 Phosphate-Based Nanoparticles

Many kinds of nFeOs or nZVI, phosphate-based nanoparticles, were used for removal of heavy metals from polluted soils by producing highly insoluble and stable phosphate compounds. Similar mechanism was made for treatment of lead-laden soils, which shows very low solubility of common lead compounds in soils such as anglesite ($PbSO_4$), cerussite ($PbCO_3$), galena (PbS), and litharge (PbO) which were determined as $10^{-7.7}$, $10^{-12.8}$, $10^{-27.5}$, and $10^{+12.9}$, respectively (Ruby et al. 1994). In comparison, lead phosphate compounds such as pyromorphites (($Pb_5(PO_4)_3X$, X = F^-, Cl^-, Br^-, and OH^-) have solubility products fewer than 10^{-71} (Ruby et al. 1994). This fact shows that lead phosphates are significantly more stable than other Pb products that exist in soils. So to reduce the availability of Pb in soils, phosphate amendments were suggested to alter the less stable Pb products to more stable species. Some phosphate amendments had significantly led to lead precipitation in situ (Ruby et al. 1994). Phosphate amendments have been proven that they have similar action with other metals which include Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Ba^{2+}, U^{6+}, and Eu^{3+} (Ma et al. 1995; Raicevic et al. 2005; Raicevic et al. 2006; Basta and McGowen 2004). Generally, soluble phosphate salts and particulate phosphate minerals are the commonly utilized forms of the phosphates for this purpose. The former include phosphoric acid (Eighmy et al. 1997), NaH_2PO_4 (Stanforth and Qiu 2001), and $(NH_4)_2HPO_4$ (Basta and McGowen 2004), and the latter involve various forms of apatite including synthetic apatites (Peld et al. 2004), natural rock phosphates (Ma et al. 1995; Raicevic et al. 2005; Raicevic et al. 2006; Basta and McGowen 2004), and biogenic apatites such as fishbone (Knox et al. 2006). Both are significantly effective for in situ accumulation of heavy metals at the laboratory scale, they showed some problems in the field. For example, soluble phosphates are greatly mobile in the subsurface and thus more effective in heavy metal accumulation, but they might result in the harmful effects of eutrophication. Moreover, large amounts of phosphoric acids and ammonium phosphates might acidify the soils (Basta and McGowen 2004). USEPA and other scientists (2001) studied the application of 3% PO_4 (or 1% as P) by weight for soils as an amendment. They reported higher risk of the phosphate spill to waterbodies and soil acidification following the heavy metal remediation. Yet, solid phosphate application is hindered by the large size particles, which restrict the phosphate mobility and delivery and inhibit phosphate from reaching and reacting with heavy metals in subsurface layers of soil. Also the finely ground solid phosphate particles are not mobile in soils, so they need for mechanical mixing in the field for treatment processes. Considering these problems of phosphate application, Liu and Zhao (2007) fabricated nano-sized iron phosphate particles for heavy metal accumulation as the commonly used phosphates while overcoming the delivery problem and secondary contamination risks related with the latter. For example, the nanoparticle suspension, which has the same mobility as aqueous solution due to the nano-scaled particle size, is easily transported to the contamination site with conventional engineering methods (e.g., spray or well-injection). The nanoparticles are reported to be environment-friendly because the phosphate in solid form is much less bioavailable to the algae than those in soluble forms (Reynolds and Davies 2001). Algae-bioavailable P and N are primarily responsible for eutrophication in surface waters. Liu and Zhao (2007) synthesized and applied a new class of iron phosphate (vivianite) nanoparticles for in situ adsorption of Pb^{2+} in soils. Batch experiment results revealed that the nanoparticles significantly reduce the leachability and bioaccessibility of Pb^{2+} in three studied soils (calcareous, neutral, and acidic), evaluated by the toxicity characteristic leaching procedure (TCLP) and physiologically based extraction test (PBET), respectively. When the soils were treated for 56 days at a rate ranging from 0.61 to 3.0 mg g^{-1}-soil as PO_4^{-3}, the TCLP-leachable Pb^{2+} was decreased by 85–95%, and the bioaccessible fraction was decreased by 31–47%. Results from a sequential extraction technique observed a 33–93% decrease in exchangeable Pb^{2+} and carbonate-bound fractions and an increase in residual Pb^{2+} fraction when Pb^{2+}-spiked soils were amended with the nanoparticles. Additions of chloride in the treatment further lower the TCLP-leachable Pb^{2+} in soils, proposing the formation of chloropyromorphite minerals. Compared to soluble phosphate application for in situ metal immobilization, using iron phosphate nanoparticles resulted in around 50% decrease in phosphate leaching into the environment. Liu (2011) concluded an effective remediation of a lead-laden soil from a shoot range using manufactured apatite nanoparticles. Results revealed that the apatite nanoparticle solution could effectively decrease the TCLP-leachable Pb fraction in the Pb-contaminated soil from 66.43% to 9.56% after 1-month amendment at a ratio of 2 mL solution to 1 g soil, and the resulting Pb content in the TCLP solution was decreased to 12.15 mg L^{-1} from 94.33 mg L^{-1}. When the amendment ratio was raised by five times, the leachable Pb was decreased to 3.75 mg L^{-1} with only about 3% of the soil Pb leachable. The original soil sample contained an average of 2647.9 mg Pb kg^{-1} soil (Liu 2011). These phosphate-based nanoparticles also could be used as P nano-fertilizers. In addition to supplying nutrient P to the plants, these nanoparticles also have benefits of easy delivery (by spraying to the soil surface) with minimum P leaching to the neighboring waterbodies.

15.2.5 Iron Sulfide Nanoparticles

Similar to the mechanisms of phosphate-based nanoparticle application for heavy metal immobilization, sulfide-based nanoparticles have been studied for removal of mercury (Hg) and arsenic (As) in water and soil/sediment by providing sulfide (S^{-2}) ligands and/or management surfaces. As a matter of fact, reduced sulfur (S^{-2}) has been considered as a stabilizer/sink of heavy metals in the reduced environment such as in the sediments or waterlogged soils by forming highly insoluble metal sulfides (Moore et al. 1988). It has been estimated that a sediment sample would be considered safe or nontoxic to the aquatic organisms when molar ratio of the acid volatile sulfide (AVS) to the total heavy metal concentrations (e.g., Cu + Ni + Zn) was greater than 1 (Ankley et al. 1996). In this case, ideally, the heavy metals are all bound in the insoluble metal sulfide phases, and thus the soluble (bioavailable) metals in the pore water are decreased (Ankley et al. 1996). Moreover, sulfide (S^{-2}) has been widely supposed as greatly important inorganic ligand to remove the Hg from the water column and destroy the formation of the notorious methylmercury (CH_3Hg) in the natural environment. Methylmercury has been supposed to be one of the most toxic Hg species which can easily bioaccumulate and concentrate in fish and other aquatic organisms and become biomagnified through food chain. Consumption of fish and shellfish contaminated with CH_3Hg is the primary route of human exposure to mercury (Ankley et al. 1996). Dissolved, neutral mercury complexes (primarily HS0 and $Hg(HS)_2$) rather than Hg^{2+} or total dissolved Hg are considered the main Hg(II) species controlling the extent of mercury methylation in the contaminated sediments (Liu et al. 2009; Benoit et al. 1999). Iron sulfide amendments can effectively decrease the concentrations of the neutral mercury complexes by formation of charged Hg(II)-polysulfides (e.g., $HgS_2{}^{2-}$, HgSH+, HgS2H−) (Liu et al. 2009; Benoit et al. 1999; Drott et al. 2007; Xiong et al. 2009). In addition, formation of the insoluble mercuric sulfide complexes also reduces conversion of the ionic Hg to volatile metal Hg in soil (Revis et al. 1989). Liu et al. (2009) reported that synthesized mackinawite (FeS) was able to remove the aqueous Hg around 0.75 mol Hg^{2+}/mole FeS. They believed that 77% of Hg removed was through precipitation by forming in soluble HgS species and the residual 23% was removed by adsorption on the FeS surface. Meanwhile, under anoxic environments, iron sulfides have the ability to reduce the mobility and availability of toxic element As by adsorption and/or precipitation processes, depending on the solution pH and iron sulfide type and oxidation state of As (Drott et al. 2007; Xiong et al. 2009; Renock et al. 2009). For example, Wolthers et al. (2005) concluded that the maximum As(V) adsorption by FeS happened at pH 7.4 with an adsorption capacity of 0.044 mol As/mol FeS, while the capacity was 0.012 As/mol FeS to As(III) but less pH dependent. Furthermore, the reduction capacity of iron sulfides is also practical to reductive immobilization of Tc^{+6} (Liu et al. 2008), Cr + 6 (Patterson et al. 1997), and U^{+6} (Hua and Deng 2008) and reductive degradation of trichloroethylene (TCE) and tetrachloroethylene (PCE) (Butler and Hayes 1998; Butler and Hayes 1999; Butler and Hayes 2001). Again, sulfide ion (S^{2-}) plays a major role in those reduction reactions, and the decontamination mechanisms are similar to those of zerovalent iron nanoparticles as discussed before. Mackinawite is a widely reported iron sulfide synthesized for those environmental remediation studies in the laboratory. This compound is prepared by simply mixing Fe^{2+}-containing and S^{2-}-containing salts together under anaerobic condition. This method produces black-colored micrometer-sized particles (Liu et al. 2008; Xiong et al. 2009; Ankley et al. 1996), which aggregate and precipitate in a few minutes (Xiong et al. 2009). By using carboxymethyl cellulose (CMC) as nanoparticle stabilizer, Xiong et al. (2009) fabricated stable FeS spherical nanoparticle suspension which stayed suspended for at least 3 months with a particle size of 31.4 ± 4 nm diameter. Shi et al. (2006) synthesize FeS nanoparticles using the same stabilizer, creating spherical-shaped particles with an average size of 4–6 nm. Xiong et al. (2009) reported that the CMC-stabilized nanoparticles were found to enhance the adsorption of Hg in a sediment sample.

For example, when the FeS spherical nanoparticle to Hg (sediment-bound) molar ratio was up to 26.5, the Hg concentration in the sediment pore water was decreased by 97%, and the TCLP leachability of the sediment-bound Hg was decreased by 99%, indicating that the FeS nanoparticle amendment significantly decreased the labile Hg portion in the sample. In addition, significantly decreased the availability of Hg species (HgS^0 + Hg $(HS)_2{}^{\circ}$) by up to three orders of magnitude. Most essentially, the FeS spherical nanoparticle suspension was highly mobile in a clay loam sediment column, indicating the essential properties of the nanoparticles and the high mobility for soil/sediment remediation. They observed that complete breakthrough of the nanoparticles happened at around 18 pore volumes (PVs), compared to 3 PVs for the inert tracer (Br^-). In contrast, when FeS spherical nanoparticles were applied in the same tests, the majority (>99.7%) of particles were captured on top of the sediment column (Xiong et al. 2009). Xiong et al.'s (2009) work is probably the only one using real FeS nanoparticles to remediate the soil-bound contaminants (Hg). Earlier researches suggest that FeS nanoparticles were highly immobilized other heavy metals (especially As) and some organic contaminates exist in soils or in sediments. However, cautions must be taken when using it in a mine soil reclamation plan: firstly, most of the iron sulfide (S−) solids could be oxidized to soluble sulfate species ($SO_4{}^{2-}$) by the air due to their instability under the aerobic environments (Liu et al. 2008; Ankley et al. 1996); thereby their adsorption capacity is lost, and the contaminants already retained on the FeS solid surface would be rereleased to the pore water and become remobilized (Ankley et al. 1996). Processes such as draining a pond or a waterlogged land and dredging the sediments are a few examples of exposing the sediments to the air. Practically, it is hard to keep a soil/sediment under anaerobic environment for long period, and a change of the redox potential might result in a secondary contamination problem related to FeS amendments. Secondly, acid mine drainage (AMD) is a very important environmental issue at most of the abandoned mining sites. Many works had been done on investigation, inhibition, management, and remediation of AMD and acidic mine soils for many years (Blodau 2006). In fact, the acidity in the drainage and in the soils established from oxidation of the iron sulfide minerals (mostly pyrite (FeS_2)) by oxygen (O_2) after these buried minerals were exposed to the air through the mining process (Blodau 2006). Therefore, simple application of FeS minerals to the soils might exacerbate the AMD and soil acidity problems at a mining site. More stable adsorption materials such as iron oxide nanoparticles (for As) or phosphate-based nanoparticles (for heavy metals) could be better options.

15.2.6 Carbon Nanotubes

The C nanotubes (CNTs) are C macromolecules consisting of sheets of C atoms covalently bonded in hexagonal lattices that seamlessly toll into a hollow, cylindrical shape with both ends normally caped by fullerene-like tips (Niu and Cai 2012). According to their structures, CNTs could be categorized into single-walled C nanotubes (SWCNTs) and multi-walled C nanotubes (MWCNTs). The diameter of CNTs can varied from hundreds nanometers and micrometers to 0.2 and 2 nm for SWCNT and from 2 to 100 nm for coaxial MWCNT. CNTs is a promising adsorbent material for nonpolar organic contaminants such as trihalomethanes, polycyclic aromatic hydrocarbons, or naphthalene, dioxin, herbicides, DDT, and its metabolites, because of their large surface area, tubular structure, and nonpolar property (Niu and Cai 2012; Theron et al. 2008; Mauter and Elimelech 2008). Compared to an activated C, the purified CNTs possess 2–3 times higher adsorption capacities for organic contaminants (Theron et al. 2008). CNTs have nonpolar characteristics; this led to very low sorption of the polar metal ions, while the sorption was increased after modification of the CNT surface by creating a large amount of oxygen-containing polar functional groups (–COOH, –OH, or –C=O). These functional groups resulted in increasing negative charge on CNT surface, and the oxygen atoms in functional groups provide single pair of electrons to metal ions, which raise the cations adsorption capacity of CNTs (Rao et al. 2007). For example, MWCNTs, pretreated with nitric acid, showed high adsorption for many kinds of heavy metal ions, including Pb(II) (97.08 mg g^{-1}), Cu(II) (24.49 mg g^{-1}), and Cd(II) (10.86 mg g^{-1}) from an aqueous solution. In addition, SWCNTs and MWCNTs after their oxidation with NaClO proved to have better Ni (II) sorption properties. These treatments increased polarity of the CNT surface, leading them to be more hydrophilic, and, therefore, able to adsorb more charged metal ions from the aqueous solution (Li et al. 2003; Lu and Liu 2006). Although CNTs proved to be efficient adsorbents for many kinds of pollutants in both drinking and environmental waters, their practical application may be hindered by their high cost (Theron et al. 2008). However, CNTs could be applied at small scale with sludge or to other solid wastes to remove several contaminants which make these wastes safely land-applied to improve soil quality and reduce the waste disposal expenses. The pristine CNTs are prone to aggregation and precipitation in the aqueous phase due to their extreme hydrophobicity (Hyung et al. 2007; Jaisi and Elimelech 2009). Dispersion of CNTs in the aqueous phase can be achieved either by modifying the surface structure and introducing hydrophilic (polar) functional groups (Jaisi and Elimelech 2009; Jaisi et al. 2008) or by improving the interactions on the nanotubes/water interface through addition of surfactants (Jiang et al. 2003), polymers (O'Connell et al. 2001), and natural organic matter (Jaisi et al. 2008; Jiang et al. 2003; O'Connell et al. 2001). The former method directly enhances the hydrophilicity of the CNTS, while the latter options not only create a thermodynamically suitable surface in water but also provide steric or electrostatic repulsion among dispersed CNTs, thus preventing aggregation (Hyung et al. 2007). Natural organic matter may play serious roles in fate and transport of nanotubes in the environment due to its ubiquitous presence. Hyung et al. (2007) stated that the water samples taken from the Suwannee River, USA, presented a similar MWCNT stabilizing capacity as compared to fabricated solutions containing the model natural organic matter (SR-NOM). For the same initial MWCNT concentrations, the concentrations of suspended MWCNTs in SR-NOM solutions and the Suwannee River water samples were even significantly greater than that in a solution of 1% sodium dodecyl sulfate (surfactant used to stabilize CNTs in the aqueous phase). During studying the transport of carboxyl-functionalized SWCNTs in quartz sand-packed columns, Jaisi and Elimelech (2009) and Jaisi et al. (2008) reported that the performances of the nanotubes were generally similar to those traditionally got with colloidal particles and bacterial cells. For instance, ionic strength of the solution was increased due to increased SWCNT deposition in the column, and divalent cations (e.g., Ca^{2+}) decrease the SWCNT stability higher than monovalent cations (e.g., Na^{+}) at the same ionic strength. However, at very low ionic strengths even in DI water, SWCNT nature in the sand media changed slightly, reflecting that the simply physical constrains (straining) also played roles in nanotube mobility besides the complicated physicochemical interactions between particle and the medium surfaces. Jaisi and Elimelech (2009) reported that straining has serious roles on nanotube mobility in the soil media. They compared the mobility of linear nanotubes and spherical fullerene nanoparticles in columns packed with the same soils. It was found that the fullerene removal rates were fewer than those of SWCNTs at the same ionic strength. Moreover, fullerene nanoparticles were more affected by changes in ionic strength as compared with SWCNTs. Scientists suggested that linear shape and structure, particularly the very large aspect ratio and its highly bundled (aggregated) state found in aqueous solutions, were the main reason for nanotube retaining in the soil columns. Furthermore, the pore size distribution and pore geometry as well as heterogeneity in soil particle size, porosity, and permeability also participate in straining in flow through the soil media by nanotubes. Thus, SWCNT mobility in soils would be limited (Jaisi et al. 2008). Also MWCNTs reported same results (Xueying et al. 2009). On the other hand, natural soil environments are more heterogeneous and normally contain open soil structures (e.g., cracks, fissures, worm trails, and other open features) that can encourage mobility of SWCNTs in soil. Moreover, soil pore water is normally rich in dissolved organic molecules (e.g., humic and fulvic acids) that can improve the colloidal stability of nanomaterials (Jaisi et al. 2008). Due to limited work studying the nanoparticle mobility in the soil media, the discussions above reported significant suggestions on transport of all types of nanoparticles in the soil environment. On one hand, nanoparticles may reduce mobility and have greater retention rate in soil media than what were reported using sand-packed column studies in the laboratory due to the more complicated pore structures and pore distributions in soils. On the other hand, existence of the preferential flow and natural organic matter in soil media would increase the nanoparticle transport through the soil columns and enhance the risks of groundwater pollution. Other works reported that CNTs are biologically active as demonstrated by a pulmonary response via induction of pulmonary granulomas (Warheit et al. 2004; Lam et al. 2004) at a higher instance than quartz (1–3 μm crystalline silica), which is a considered chronic occupational health hazard (via inhalation routes). Both SWCNTs and MWCNTs were also recognized to cause loss of phagocytic ability and ultrastructure damage to alveola macrophages (Jia et al. 2005). Additionally, CNTs have encouraged observable toxic responses in other cell cultures (Magrez et al. 2006).

15.3 Using Nanoenhanced Materials as Solid Waste Stabilizers/Conditioners

Solid wastes have mostly different environmental contaminants (detrimental impurities, pathogens, and sometimes nauseous odors). Thus, to make these wastes to have benefits for landfill soil reclamation, secondary environmental contaminations should be eliminated. Nanoenhanced materials had proved to enhance the environmental safety and public acceptance for landfill application of these wastes in mine or agricultural remediation. For instance, Li et al. (2007) reported that a small amount of nZVI (0.1% by weight) significantly eliminate nauseous odors (caused by organic sulfur compounds), heavy metals, and organic contaminants in the biosolids, indicating that nZVI could decrease the contamination of biosolids and increase beneficial uses of these wastes. Turan (2008) concluded that co-compost of poultry litter mixing with 5% and 10% (g g^{-1}) natural zeolites had removed 66% and 89% of the end product salinity, respectively. Using 25–30% (g g^{-1}) zeolites for biosolids remediation can remove many kinds of heavy metals (100% of Cd, 28–45% of Cu, 10–15% of Cr, 50–55% of Ni and Pb, and 40–46% of Zn) and decrease the leaching of these metals (Zorpas et al. 2000). Also, Zeolites used at lower rates (0.5% and 1.0%) significantly removed labile Zn during experimental horticultural compost derived from sewage sludge (Nissen et al. 2000). Subsequent plant growth trials measuring transfer of Zn and Cu to ryegrass in successive harvests demonstrated that 1.0% zeolite caused significant reduction in total metal transfer from soil to plant over a 116-day growth period. The use of zeolites is a cost-effective amendment for compost to significantly reduce potential for soil metal mobility and soil to plant transfer (Villaseñor et al. 2011). Villaseñor et al. (2011) added three commercial natural zeolites to a pilot-scale rotary drum composting reactor, where the domestic sewage sludge and barley straws were co-composted. They observed that all three types of zeolites removed 100% of Ni, Cr, and Pb and significant amounts (more than 60%) of Cu, Zn, and Hg originated from the sludge (Villaseñor et al. 2011). It is also reported that the clinoptilolites reduced 50% of the NH_3 emission from the compost (Villaseñor et al. 2011), avoiding N loss and unpleasant odor from the compost. Villaseñor et al. (2011) claimed that addition of 10% zeolites produced composts compliant with Spanish regulations regarding heavy metal contamination. According to them, the zeolite-amended compost could either be applied directly to soil or the metal-polluted zeolites could be separated from the compost prior to application to ensure environmental safety. Using zeolites as heavy metal absorbents in compost is also verified by other researchers (Zorpas and Loizidou 2008; Zorpas et al. 2002; Zorpas et al. 1999). Gadepalle et al. (2007) applied compost containing 5% zeolite to an As-contaminated soil and observed that zeolite addition can effectively reduce the As uptake by ryegrass and that less than 0.01% of the total As content in the soil may be absorbed by the plants. Literature above showed that amending the solid wastes with relatively small amounts of nanomaterials could effectively reduce or eliminate the risk of secondary contamination associated with land applications of these wastes. This practice could expand the industrial or municipal waste lists which are safe for land application, thus saving the cost of waste disposal and ameliorating the adverse environmental impacts. In addition, agricultural soils and drastically disturbed lands (e.g., mine soils) could benefit from these most cost-effective waste materials (soil amendments). Moreover, application of the nanomaterials to stabilize or condition the conventional soil amendment materials (e.g., composts, biosolids, coal combustion by-products) could be a potential aspect of utilization of nanotechnology in the agriculture at low cost. Zeolites, nFeOs, phosphate-based nanoparticles, and sulfide-based nanoparticles are efficient in immobilizing inorganic contaminants in the solids, while C nanotubes have a high absorption capacity for organic pollutants, and nZVI can destroy the OWCs present in the wastes by reduction reactions. Finally, incubation of the nanomaterials with solid wastes could in turn stabilize the former and reduce the risks of nanomaterials spill and contaminations resulting from direct application of the nanoparticles to the environment.

15.4 Using Nanoenhanced Materials to Control Soil Erosion

Soil erosion is affected by rainfall or wind in a closed mining site can result in loss of good soil, exposure of the buried sulfide minerals, and transportation of the sediments and pollutants to nearby surface waterbodies. Therefore, soil erosion management is a high importance in a mine soil reclamation plan. Nanoenhanced materials have potentials benefits to use for combat the harmful of soil erosion. Andry et al. (2009) reported that the surface runoff and soil loss can be significantly decreased by zeolite application at rate of 10% of a Ca-type zeolite material when applied at an acidic soil under simulated rainfall. This was attributed to an enhancement of wet aggregate stability and the large particle size of the sediment due to the amendments. Andry et al. (2009) suggested that zeolites can be more effective than lime in soil erosion management. Yamamoto et al. (2004) also applied Ca type of artificial zeolite at rates of 5–25% in sodic soils to control the runoff rate and soil loss. They reported that the exchange of Ca^{2+} on zeolites with Na^+ in the sodic soil reduced the clay dispersion, resulting in increased soil hydraulic conductivity and soil aggregation, which decrease the runoff rate and soil loss. Zheng (2011) reported that using polyacrylamide (PAM, a polyelectrolyte used for soil erosion management) and magnetite nanoparticles to an As-spiked soil subject to the simulated rainfall could effectively decrease soil erosion, while the nanoparticles could reduce As leaching. Wang et al. (2007) reported that using alumina nanoparticles (Al_2O_3, 140–330 nm) in conditioning a wastewater treatment sludge results in larger flocks and better dewatering effects than the single conditioning by polyelectrolyte only. The valuable effects are more evident when finer nanoparticles (140 nm) were used. Wang et al. (2007) suggested that the nanoparticles can increase the stretch of the chain-like structures of the polyelectrolyte, resulting in more effective bridging effects and better flocculation. As a matter of fact, the PE (polyelectrolyte)-NP (nanoparticle) flocculation systems have been widely used in effectively eliminating solid particles from the solution (Ovenden and Xiao 2002; Yan and Deng 2000). The flocculation in such a system is induced by the sequential addition of a positively charged polyelectrolyte followed by negatively charged nanoparticles, such as bentonite and colloidal silica. The systems produce a better flocculation and drainage (dewatering) than conventional polymer-only flocculation systems (Yan and Deng 2000). These results suggest that double application of polyelectrolyte and nanoparticles could increase flocculation and improve soil particle size and particle stability and thus effectively manage soil erosions caused by wind or rain.

15.5 Conclusion

Despite these exciting opportunities to use nanomaterial for soil remediation, further studies are needed to investigate the toxicity and trophic transfer of these NPs under environmentally realistic and relevant conditions and also study their effect on plant, to ensure both the safe use and social acceptance of nanotechnology. This will support the establishment of blueprints for safe-by-design and use NPs.

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