



Effect of Engineered Nanoparticles on Soil Attributes and Potential in Reclamation of Degraded Lands

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Abstract

Rapid upsurge in the discipline of nanoscience and technology has led to emergence of myriads of nanoparticles. Apart from substantial application in medicine, textile, food science, and environmental technology, nanoparticles have received considerable application and immense opportunities in agricultural practices. Given the inherent potential, nanoparticle based on zinc, iron, manganese, copper, titanium, and mixtures thereof has been successfully employed in agricultural lands. Although negative consequences of nanoparticle application are well recognized, the judicious application of various nanoparticles in agriculture could improve the soil productivity in a better way in contrast to currently used strategies. Therefore, assessment of soil attributes may provide important insight on possible threats of nanoparticles in agro-ecosystem. The modulation in characteristics like pH, moisture content, soil organic matter, nutrient and mineral composition, microbial attributes, fauna and enzymatic activities to a great extent after the introduction of nanoparticle in agroecosystem is documented. Unprecedented rise in agricultural technologies and accelerated application of agrochemicals are the

important phenomena responsible for massive degradation of agricultural lands worldwide causing decline in crop productivity. Nanotechnology could provide important platform for efficient restoration of degraded land areas. This chapter has reviewed on application of engineered nanoparticles in (a) improving agricultural productivity, (b) important techniques for nanoparticle quantification, (c) impact on soil characteristics, and (d) potential in management of degraded lands.

Keywords

Agriculture • Land degradation • Nutrient cycling • Restoration • Soil enzymes • Soil organic matter

1 Introduction

Globally very large areas of lands are described to be ecologically degraded putting great risks to goal of food security (Xie et al. 2020; Morales and Zuleta 2020). Land degradation is observed as a detrimental phenomenon influencing the productivity of soils. The important factors influencing land degradation include introduction of innovative agricultural technologies and intensive application of agrochemicals (Ouyang et al. 2018). Although research and development in farm machineries have improved crop productivity multifold, negative consequences on soil productivity could not be denied (Shah et al. 2017). For instance, soil compaction, changes in soil properties and perturbation in soil organism, especially annelids and arthropods by modern plowing instruments may substantially deteriorate the soil health, eventually overall crop productivity (Beylich et al. 2010). Alteration in soil micropores, macropores, moisture content, and soil aggregate structure by agri-instruments could be important contributors for rapid decline in soil natural productivity. Excessive application of agrochemicals like fertilizers, herbicides,

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weedicides, pesticides, and insecticides is well recognized to interfere with the soil physical, chemical, and biological characteristics (Belay et al. 2002; Zhang et al. 2008; Afsar et al. 2017; Daam et al. 2020). The introduction of agro-chemicals alone or in combination with organic amendments may considerably modify pH, moisture content, aggregate structure, porosity, bulk density, metal enrichment, water holding attributes, ion exchange characteristics of soil (Hati et al. 2006; Carbonell et al. 2011; Yargholi and Azarneshan 2014) and activity of organisms including microbes (Rahman et al. 2020), arthropods, annelids (Frampton et al. 2006), etc., leading to loss in productivity potential of agro-ecosystems (Förster et al. 2006).

Land degradation exerting degenerating impacts on natural environment (Wang et al. 2020) is widely reported across the globe influencing the crop productivity, therefore economic status of both developing and developed countries. Restoration of such ecologically disturbed soil could be helpful in meeting the exponentially rising demand of food. Restoration of degraded lands is chiefly based on physico-chemical and biological strategies with each method having advantages as well as disadvantages (Silva et al. 2015; Mohammed and Denboba 2020; Singh et al. 2020). The application of nanotechnology producing enormous quantity of nanomaterials possessing potential in management of degraded soil is quite attractive and promising. The nanoparticles comprising of both metals and non-metals could be exploited to facilitate the restoration of degraded land areas (Fajardo et al. 2019; Latif et al. 2020). Some of the worth mentioning nanoparticles having significance in the management of ecologically unhealthy soil, contaminated water, and wastewater include carbon, manganese, iron, and titanium (An and Zhao 2012; Ghasemi et al. 2017; Gong et al. 2018; Yang et al. 2020).

Metal-based nanoparticles after entry into agro-ecosystem may get access to different environmental components. Incorporation of metals released, apart from nanoparticles itself in food chain, ultimately threatens human health (Tombuloglu et al. 2020; Rajput et al., 2020b). Precise determination of nanoparticles, therefore, is necessary to assess the impact to natural ecosystem. Development of rapid assessment techniques would not only help mitigate the toxicity but also transfer and accumulate in other environmental matrices.

Nanoparticles of different metals have received considerable attention in agricultural practices with an objective to improve the functionality and thereby productivity of degraded lands. Land management practices deploying nanoparticles have the potential to help resurrect the productivity of ecologically disturbed soils. For instance, nanostructured formulations of nitrogen- and phosphorus-based fertilizers could help improve the crop productivity (Sekhon 2014) by substantially modifying the

soil properties to a greater extent. The introduction of engineered nanoparticles (ENPs) into agro-ecosystems may directly and indirectly modify the soil characteristics. Alterations in humic substances and bacterial community characteristics upon the application of metal oxide nanoparticles in soil (Ben-Moshe et al. 2013; Rajput et al. 2018) are presented. In addition, minor changes in soil macroscopic attributes had also been observed. Although most of the investigations have demonstrated the negative consequences of nanoparticles application to soil environment (Rajput et al. 2020c), the beneficial impacts on soil are also documented. The contribution of iron oxide nanoparticles in sequestration of environmentally hazardous metals includes arsenic, manganese, chromium, cadmium, and lead (Shipley et al. 2011), therefore reduction in toxicity leads to improvement in soil productivity and is of immense ecological significance. Therefore, nanoparticles are helpful in soil amelioration leading to creation of additional land (Liu and Lal 2012) for agricultural activities. Extensive investigations on ENPs exhibiting compatibility with soil components may be helpful in improving the productivity of degraded lands. Exploration of the mechanism of soil productivity improvement caused by certain ENPs may provide important boulevard for the management of less productive soils in order to feed the continuously rising human population. Fate and transport in soil environment as well as detailed understandings of ENPs uptake would facilitate in escaping the toxicity to soil microbes and invertebrates.

The present chapter offers recent information concerned with ENPs application in agro-ecosystems, quantification techniques, impacts on soil physical, chemical and biological characteristics, and potential opportunities in reclamation responsible for improved productivity of less fertile soil.

2 Engineered Nanoparticle Application in Agriculture

Because of unique physico-chemical characteristics, so far, myriads of nanoparticles have been used in agriculture in order to improve the crop productivity. Nanoparticles comprising of single metal as well as complexes of metals have been employed in agriculture to meet the rising demand of global food. Additionally, the wide applications of non-metal-based nanomaterials like carbon are also reported. A systematic review dealing with contribution of considerably less explored silicon nanoparticles in agriculture is presented by Rastogi et al. (2019). Study on role of nanoformulated zinc and silicon in enhancement of mango productivity by mitigation of salt stress as achieved by foliar spray is recently demonstrated by Elsheery et al. (2020). The concentrations of nanozinc and nanosilicon used either

singly or in combination were in the range of 50–150 and 150–300 mg/L, respectively. The simultaneous combination treatment with 100 mg/L nanozinc and 150 mg/L nanosilicon was found to improve not only the resistance and fruit quality but also the productivity of mango trees under salt stressed conditions. The involvement of biologically synthesized zinc oxide nanoparticles in management of seed-borne plant pathogen is recently documented (Lakshmeesha et al. 2020). With increase in concentration, zinc oxide nanoparticle having size 30–40 nm with hexagonal structure led to growth suppression of fungal phytopathogen *Cladosporium cladosporioides* and *Fusarium oxysporum*. Treatment with nanoparticles caused alterations in level of fungal ergosterol, peroxidation of lipid molecules and modulations in membrane functionality, implying the utilization of nanoparticles as economical strategy in minimizing fungal pathogen-induced losses in crop productivity. Zinc oxide nanoparticles serving as antifungal agent against *Colletotrichum* species responsible for anthracnose disease in coffee are reported by Mosquera-Sánchez et al. (2020), suggesting implications in sustainable crop protection. At 15 mM concentration, the nanoparticle treatment was observed to significantly inhibit the fungal growth within six days. Apart from inhibition of phytopathogens, the nanoparticulate forms of fertilizers referred as nanofertilizers may be used in agriculture to enhance the productivity of important crops and the efficiency of fertilizers (Ramírez-Rodríguez et al. 2020; Yusefi-Tanha et al. 2020). Since the biological activity of ENPs is affected much by type, concentration, size (Yusefi-Tanha et al. 2020), metals and complexes, pathogen selected, and most importantly the characteristics of environmental matrices like soil and water, the selection of apposite nanoparticle is a pre-requisite for experiencing optimum beneficial effect. Furthermore, small-scale field investigations should also be conducted prior to large application in agro-ecosystems to avoid the environmental toxicity of metal and non-metal derived nanoparticles.

3 Techniques for Quantification of Nanoparticles

Extensive utilization of nanopesticides and nanofertilizers in agriculture has introduced unexpectedly large quantities of different nanoparticles in soil environment, posing undesirable effects (Carley et al. 2020). The concentrations of nanoparticles beyond certain limits are reported to exert toxicity to soil microbes and invertebrates. Surprising, to date, no regulatory limits have been set for different nanoparticles in water and soil environment. The precise identification, characterization, and determination using advanced instrumentation techniques, therefore, are

inevitable to mitigate the toxicity of nanoparticles to agricultural soils.

Quantification of engineered nanoparticles consisting of gold, silver, and cerium based on inductively coupled plasma mass spectrometry (ICP-MS) is reported by Gschwind et al. (2013) and results were comparable to other quantifying methods. The microdrop generator integrated with ICP-TOF-MS has been described for the determination of silver and gold nanoparticle mixture (Borovinskaya et al. 2014). Recently, simultaneous identification and quantification of titanium nanoparticles employing single particle ICP-MS equipped with TEM-EDS are presented by Wu et al. (2020). The developed method was able to determine the nanoparticle concentrations within the limits of 10^2 particles/ml.

Development of field-based techniques for rapid assessment of even minute concentrations of various nanoparticles from different soil components would facilitate the employment of appropriate strategies for evaluating the ecological risks (Wu et al. 2020) and maintenance of continuously deteriorating soil health. Further, the improvement in limit of detection (LOD) and limit of quantification (LOQ) could be helpful in measuring the traces of nanoparticles. In addition, the precise determination of nanoparticles is affected considerably by extraction methods, substances used for dispersion (Bland and Lowry 2020), types of soil, and instrumental sensitivity.

4 Impact of Nanoparticle Application on Soil Characteristics

Considerable rise in fabrication of varied metal and non-metal nanoparticles followed by application for multiple agricultural purposes has caused enhanced exposure and entry into soil environment (Ben-Moshe et al. 2013; Sun et al. 2020), consequently causing food chain contamination (Rajput et al. 2020a; b). The interaction of ENPs with soil is complex because of substantial variations in soil composition as well as prevailing environmental conditions. After introduction into terrestrial environment, nanoparticles may characteristically modulate the physical, chemical, and biological characteristics of soil (Samanta and Mandal 2017).

4.1 Soil pH

Soil pH is important parameter governing the growth and development of plant as well as soil microbial community structures and functions. The interaction of ENPs with soil may modulate the pH and varies significantly for different soil types (Conway and Keller 2016). The introduction of nanoparticles comprising of titanium, copper, and cerium in

the range of 100 mg/kg was exhibited to raise the pH of loam soil, nevertheless, reduction in pH was observed for sandy loam soil. The modification in pH was not influenced by varying concentrations of nanoparticles. Displacement of soil associated ions by addition of nanoparticles was considered as an important factor responsible for pH modification. Modifications in soil pH are also attributed to the interaction of ENPs with plant roots. Alteration in secretory products of plant root possibly induced by nanoparticle addition, resulting into changes in soil pH is documented by Rossi et al. (2018). Nevertheless, direct evidences regarding modification in soil pH rendered by enhancement in root exudates under the influence of nanoparticles are not reported.

4.2 Cation Exchange Capacity

Cation exchange capacity is increasingly associated with potential to hold nutrients as well as environmental contaminants, hence acting like an important parameter pointing toward soil chemical attributes. The mobilization of nanoparticles in terrestrial environment is also modulated substantially by soil cation exchange capacity. The binding of engineered nanoparticles to minerals present in soil (Zhao et al. 2012) could greatly influence the inherent cation exchange capacity. However, to date, limited studies have been conducted pertaining to impact of nanoparticle addition to soil onto cation exchange characteristics. Controlled greenhouse condition-based experiment performed by De Souza et al. (2019) demonstrated rise in rhizospheric ion exchange capacity due to presence of ENPs consisting of iron oxides. In a similar manner, increase in ion exchange potential induced by silver nanoparticles biofabricated via the action of leaf extract is described recently by Das et al. (2019). Another investigation showing modulation in cation exchange capacity galvanized by interaction of cerium oxide nanoparticle with the soil mineral kaolinite leading to surface charge density variation has been indicated by Guo et al. (2019).

4.3 Nutrient and Mineral Characteristics

Nutrients and minerals present in the soil are important constituents governing the growth and development of various agricultural crops. Terrestrial incorporation of nanoparticles is considered to modify the availability of important mineral elements present in soil, thereby nutritional quality of cultivated crops. Intergenerational impact of cerium oxide nanoparticles treatment to wheat responsible for alterations in minerals and nutrients content of root and grain as evident through synchrotron X-ray fluorescence

spectroscopy, elemental analysis and X-ray absorption near edge spectroscopy is presented by Rico et al. (2017). Both generation treatments with ENPs had considerable effect on nutritional attributes as compared to only second generation treatment. Study on the impact of ENPs including cerium dioxide and titanium dioxide nanoparticle influencing the phytoavailability of beneficial nutrient elements nitrogen, phosphorus, and zinc as well as hazardous metal ion varying with soil characteristics is demonstrated recently by Duncan and Owens (2019). The observed effects on metal and nutrient phytoavailability were ascribed to competition and antimicrobial action of investigated nanoparticles.

Addition of titanium dioxide nanoparticle into biosolids generally applied for soil fertilization is documented to reduce the bioavailability of important elements including manganese, zinc, iron, and phosphorus by 65%, 20%, and 27%, respectively (Bellani et al. 2020), and to some extent was influenced by the amount and size of nanoparticles applied. The reduced availability may be attributed to interaction between minerals and highly reactive nanoparticle surface. In addition, the soil amendment with biosolids spiked with titanium dioxide modulated the nutrient composition of grown pea plants causing decline in level of manganese, zinc, potassium, and phosphorus in root and shoot. Therefore, to avoid the non-target impact of ENPs on soil ecosystem, extensive greenhouse condition should be conducted prior to recommendation for field application.

4.4 Soil Organic Matter

The heterogeneous soil organic matter resulting from living matter both by biological and non-biological processes greatly regulates multitude of ecological functions in terrestrial environment (Wiesmeier et al. 2019). The characteristics of pores present in organic matter considerably determine acquired air volume, reaction ability, water holding potential, and environmental fate of externally sorbed substances (de Jonge et al. 1996; Pignatello 1998). Being sink of numerous environmental contaminants, different nanoparticles of anthropogenic origin from different sources are expected to accumulate in soil ecosystem. The addition of metal-based nanoparticles consisting of copper oxide and iron oxide into soil with no obvious alterations in organic materials has been registered by Ben-Moshe et al. (2013). Nevertheless, modifications in content of humic substances as deciphered through fluorescence spectroscopy were recorded. Investigation on influence of platinum nanoparticles on features of soil organic matter (SOM) has been represented recently (Komendová et al. 2019). Nanoparticles with 3 nm size diminished the evaporation enthalpy of water molecules present in SOM and facilitated loss of water from soil. Further, the addition of nanoparticle

enhanced the morphological firmness. The increased concentration of platinum nanoparticles reduced the amount of water in SOM and catalyzed the crystallization of aliphatic fractions.

4.5 Soil Microbial Characteristics

The incorporation of environmentally hazardous nanoparticles in agricultural soils may significantly hamper the normal ecological functioning of existing microbial communities (Navarro et al. 2008). Addition of nanoparticles into soil leading to variations in microbial characteristics in terms of bacterial community constitution based on denaturing gradient gel electrophoresis (DGGE) is described by Ben-Moshe et al. (2013). Diminished soil microbial performance and biomass upon challenged with multiwalled carbon nanotube (MWCNT) are narrated by different workers (Chung et al. 2011; Chen et al. 2018). Reduction in microbial biomass carbon and nitrogen, together with the upsurge in metabolic quotient by MWCNT, silver nanoparticles and titanium dioxide nanoparticle is reported by Xin et al. (2020). The observed effects were dose-dependent and much apparent at higher concentrations of MWCNT, nanosilver, and titanium dioxide. Modifications in metabolic profiles of bacterial communities surviving in three different soil types under the presence of ENPs consisting of silver and zinc oxide are recently demonstrated by Chavan and Nadanathangam (2020). However, titanium dioxide nanoparticle did not exert observable differences. The supplementation with silver and zinc oxide nanoparticle also led to substantial changes in selected diversity indices.

4.6 Soil Enzymes

Soil enzymes are important contributor of agro-ecosystem regulating cycling of different nutrients and the introduction of nanoparticles may likely hinder the natural phenomena (Shin et al. 2012). Inhibitory action of silver nanoformulation on enzymatic activities of calcareous soil is well documented (Rahmatpour et al. 2017). The silver nanoparticles exerted greater inhibition over enzymatic activities in comparison with bulk silver ions. Experimental investigation indicating restrictions in soil enzymatic activities including dehydrogenase, urease, and phosphatase by the action of MWCNT, nanosilver, and nanotitanium oxide is registered currently by Xin et al. (2020). The increased deployment of nanoformulated pesticides is considered to hinder the natural soil biogeochemical cycling of beneficial elements. The inhibitory effects of copper oxide-based nanoparticles at the concentrations 10, 100, and 500 mg/kg during 60 h

exposure affecting the enzymes involved in denitrification and electron transfer phenomenon are demonstrated (Zhao et al. 2020). The introduction of nanoparticles reduced 10–42% activities of nitrate reductase, nitric oxide reductase, and retarded denitrification process resulting into diminished emission of N_2O . The observed impacts were attributed to the inhibitory action of copper ions released from nanoparticles. The observed negative effects of nanoparticle addition on soil enzymes are considered to be the resultant of: (a) interaction of released metals with sulfhydryl group of active site of enzyme (Liau et al. 1997), and (b) direct interaction of nanoparticles with soil enzymes (Wigginton et al. 2010).

4.7 Soil Annelids and Arthropods

Soil invertebrates like annelids and arthropods are important fauna affecting the characteristics of different agricultural soils. Numbers of studies have indicated the impact of ENPs on normal cellular functioning, reproductive processes, and behavioral responses in given environmental conditions (Shoultz-Wilson et al. 2011; Schlich et al. 2013; Kwak et al. 2014). The toxicity of silver nanoparticles to model soil annelid *Eisenia fetida* through similar pathways causing perturbation in ribosomal activity, metabolic processes associated with sugar and protein, and interferences in energy generation mechanisms has been established by Novo et al. (2015). Impact assessment of powdered zinc oxide nanoparticles to annelid *Enchytraeus crypticus* in gel-based media suggesting toxicity to soil organism is illustrated (Hrdá et al. 2016). The toxicity in terms of mortality was affected by size of agglomerated nanoparticle and method of media preparation for treatment. The annelid mortality upon exposure differed in the range of 28.9–34.4% and 0–66.6% for the two different treatment methods using the nanoparticle concentrations 50, 100, 200, 500, and 1000 mg/kg. Recently, silver nanoparticle-induced toxicological effects in terms of reproduction and mortality on soil arthropod *Folsomia candida* after four week exposure is represented by Hlavkova et al. (2020). Silver nanoparticles had higher EC_{50} value as compared to bulk silver ions implying lesser toxicity to tested invertebrate. Further, silver nanoparticles in the concentration range 166–300 mg kg^{-1} dry weight did not exert toxicity.

Apart from type and amount of nanoparticles, the observed effect in agro-environment is influenced by properties of given soil (Xin et al. 2020). The impact of nanoparticle on soil characteristics is essential to investigate the ecotoxicity in order to safeguard the agricultural ecosystem. The extensive investigation would help regulate the quantity of nanoparticle to be used for agricultural

purposes. In addition, the predecided dosage of different nanoparticles, therefore, would help to improve the productivity of soil in an economical manner.

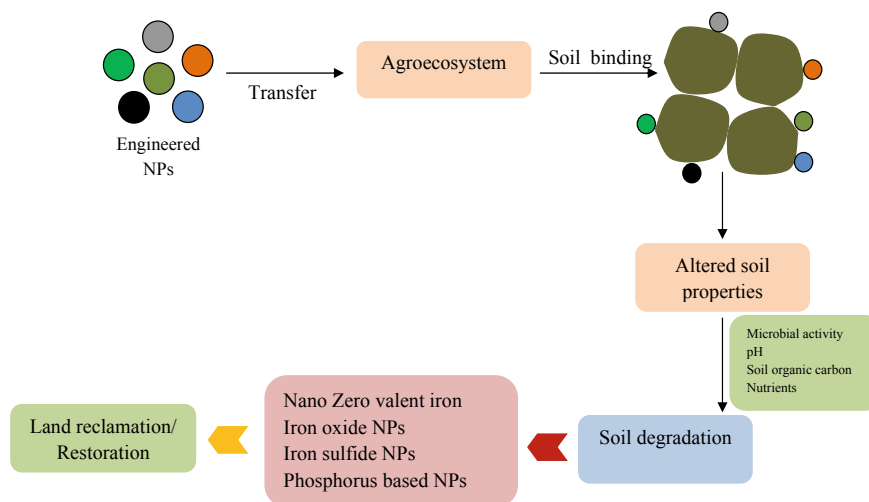
5 Application of Nanoparticles in Reclamation of Degraded Agricultural Lands

Myriads of nanoparticles with diverse application in environmental decontamination, medicine, and enhancement in agricultural productivity based on different physico-chemical methods are synthesized to date. Varying degree of influences of ENPs on crops, soil properties, and ecological functioning is reported by various authors. Apart from considerable toxicological impacts on agro-ecosystem, engineered nanomaterials could be exploited successfully for the reclamation of ecologically degraded lands. Successful reclamation would provide additional cultivable land areas to meet the rising demand of food crops. A schematic representation of ENPs impacts on different soil properties and their potential for degraded soil reclamation has been depicted in Fig. 1.

Reclamation involves sequestration of hazardous contaminants and improvement in soil characteristics leading to enhanced soil productivity. A detailed account pertaining to contribution of engineered nanomaterials in sustainable management of mine areas and other ecologically disturbed soil is elaborated by Liu and Lal (2012). The review explained the application of zeolites and nanoparticles of iron oxide, phosphorus, iron sulfide, zero-valent iron, and carbon nanotubes for efficient decontamination of land areas affected by mining activities. The combined action of synthesized nanomaterials and conventional treatment methods was also suggested to help minimize the cost required for improving the characteristics of degraded land areas.

The porous zeolites may serve as important materials for the remediation of contaminated lands (Li et al. 2018) and are described to be available in the soil, but the content typically present is very low. The most dominating zeolite existing in soil is clinoptilolite. Zeolite-based nanomaterials hold promising potential in improving the characteristics of soil due to rise in water retention potential, enhancement in clay shift proportions, augmentation of nutritional features, and efficient sequestration of toxic substances (Ming and Allen 2001). In addition, both natural and synthesized zeolites are able to potentially adsorb the noxious heavy metals occurring in contaminated soils, thereby minimizing the threats to human health and environment. Treatment of mine soil with synthetic zeolites at the rate of 0.5–5% weight basis, culminating into substantial decline of labile and readily accessible heavy metals like zinc, lead, copper, and cadmium by 42–72% is illustrated by Edwards et al. (1999). Apart from surface binding, increase in soil pH rendered by zeolite introduction into soil was also ascribed to elimination of heavy metals. Similar investigations pointing toward the decreased availability of heavy metals after soil application of zeolites at 0.5 to 16 weight % are also documented (Shanableh and Kharabsheh 1996; Lin et al. 1998; Moirou et al. 2001). In addition to extraction of heavy metals from contaminated soil, zeolites have the tendency to efficiently adsorb the radionuclides like cesium and strontium, hence potential to reduce the availability in cultivated plants (Ming and Allen 2001). Githinji et al. (2011) have presented the considerable contribution of zeolites, having size 0.55–0.60 mm, in reducing the soil bulk density and twofold enhancements in water availability. Role of zeolites in remediation of vanadium contaminated soil facilitated by stabilization process is recently demonstrated by Yang et al. (2020). The study concluded modulation in soil pH as an important factor controlling the stabilization of vanadium. The application of zeolites in a given agro-ecosystem should

Fig. 1 Effect of engineered nanoparticles (NPs) on soil attributes and potential in land reclamation/restoration



be optimized as the particle size and amount used greatly modulates the soil physical attributes.

The naturally existing soil iron oxide nanoparticles having average size ranging from 5 to 100 nm, possess reactive sites with inherent ability to adsorb varieties of organic and inorganic contaminants through the process like surface binding (Bigham et al. 2002). The efficiency in rapid adsorption, minimal chances of secondary contamination, and ecofriendly nature has fostered the engineered iron oxide nanoparticles with multiple applications including remediation of contaminated water as well as soil. Some of the widely applied iron oxide nanomaterials described for extraction of heavy metals such as copper, chromium, nickel, lead, arsenic, and zinc are goethite, magnetite, hematite, and maghemite. Column-based investigation indicating arsenic immobilization for more than four months in soil amended with 15% nanomagnetite and $100 \mu\text{g l}^{-1}$ arsenic spiked at a rate of 0.3 ml h^{-1} , in contrast to soil without amendment, has been presented by Shipley et al. (2011). However, after the elapse of 208 days, a total of 20% arsenic was noticed to be leached from column. The study further suggested the simultaneous removal of 12 other metals.

The strong reductant nanozero-valent iron (nZVI) had been synthesized with an objective to degrade the organic contaminants including pesticides and petrochemical products (Zhang 2003). Intriguingly, nZVI may also serve as an important material for sequestration of various heavy metals from terrestrial system. Because of reducing action of nZVI, metal ions with higher oxidation states like chromium and uranium are transformed to corresponding lower oxidation states and reduce the toxicity, as well as solubility and mobilization in soil environment by the process referred as reductive immobilization. Numerous studies have shown the efficiency of nZVI in immobilization of uranium in comparison with reductants including iron fillings, lead sulfide, and iron sulfide, because of large size conferred by small size, increased reactivity, and release of reactive iron produced. Reduction of approximately 98% hexavalent chromium to trivalent form assisted by the catalytic activity of nZVI, leading to reduction in toxicity to soil is demonstrated by Franco et al. (2009). Similar observation on reductive immobilization of higher oxidation state chromium (hexavalent) in soil, with the resultant decline in ecotoxicity to soil, is also documented (Ponder et al. 2000; Xu and Zhao 2007). The application of engineered graphene oxide nanoparticles as a promising tool in management of heavy metal contaminated soil responsible for immobilization of copper, lead, and cadmium, in contrast to mobilization of arsenic and phosphorus has been reported by Baragaño et al. (2020). In addition, phosphate and iron sulfide-based

nanomaterials (Liu et al. 2020; Rodríguez-Seijo et al. 2020) and carbon nanotubes (Liu et al. 2018; Egbosiuba et al. 2020) are also remarkably annotated for possessing promising potential in removal of heavy metals and organic contaminants.

The employment of ENPs, although, for reclamation of contaminated agro-ecosystem is quite attractive, the fate and toxicity to environmental components must be extensively investigated for safe application. The behavior of ENPs incorporated into soil environment is significantly modified by soil attributes, prevailing environmental conditions as well as its own size and morphology. The optimization of dose for different soil types, and different organic and inorganic contaminants are crucial steps toward application of ENPs in agro-ecosystems.

6 Conclusion and Future Perspectives

Engineered nanomaterials are continuously gaining importance in varied disciplines like medicine, electronics, environment, and agriculture. The increased applications in agriculture as nanofertilizers and nanopesticides have improved the productivity of agro-ecosystem multifold. However, the nanoparticle incorporation in food crops, toxicity to human health, and negative consequences on soil properties including enzymes, microbial diversity, soil nutrient cycling, and ecotoxicity to soil dwelling annelids and arthropods have questioned their application for enhancing the crop productivity. The employment of ENPs, therefore, must be based on extensive ecotoxicity appraisal to beneficial non-target organisms as well as humans exposed via agronomic crops. In addition to augmentation of soil productivity, ENPs could be applied for restoration of ecologically disturbed sites like mining affected cultivable sites. The soil reclamation using zeolites and iron oxide nanoparticles, however, is in infant stage, implying further research work in this direction.

Since the dose of applied ENPs varies according to the nature of nanoparticles and soil characteristics, deciding optimum dose so as to minimize the residues left over in agro-environment is a crucial step and need much experimental work. The techniques for identification and quantification of ENPs should be improved in order to minimize the impact on natural environment and associated health hazards. Investigation on sources of nanoparticles, fate, and transport in soil environment is another area of research for protection of soil health. Further, there is urgent need to set the regulatory limits for different nanoparticles currently being applied in agro-ecosystem to prevent excessive accumulation in soil as well as crop products.

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