



Showcasing work from Dr Islam Abdelhafeez and Professor Mohamed Elsayed at Soils, Water and Environment Research Institute, Agricultural Research Center, Giza, Egypt.

Nanotechnology-enabled soil management for sustainable agriculture: interactions, challenges, and prospects

The image showcases the promising effects of sustainable nanotechnologies in achieving food security and soil preservation. It illustrates nanotechnology's potential in the agricultural sector, including interactions, soil remediation (adsorption, (photo)catalysis, bioremediation), fertility, and nano-irrigation systems associated with challenges and prospects.

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Nanotechnology has recently had significant impacts across various sectors, including soil and agriculture. With increasing environmental and sustainability awareness, numerous studies have reported the role of nanotechnology in achieving food security and preserving the soil matrix. In this review, we highlight state-of-the-art sustainable nanotechnologies applicable to soil management. The mechanisms of nanomaterials' interactions with soil for nutrition and remediation are also discussed. The role of nano-irrigation, as an innovative irrigation system, is presented. Finally, the challenges and prospects of nanotechnology applications in soil management are summarized.

The land area covers 29% of the Earth's surface. Of this, only 11% is arable land, which is insufficient to meet the growing demands of population and urbanization worldwide.¹ This not only threatens food security and increases poverty rates but may also result in severe economic ramifications, hindering sustainable development goals.² The quality of food and plant production relies on the quality of terrestrial ecosystems. However, issues associated with soil deterioration raise serious concerns, including loss of fertility, high salinity, loss of useful microorganisms, loss of moisture, desertification, lack of nutrients and minerals, pH changes, high toxicity, and land degradation.³⁻⁵ This situation substantially calls for the development and innovation of new strategies to protect and restore damaged areas and reclaim new lands.

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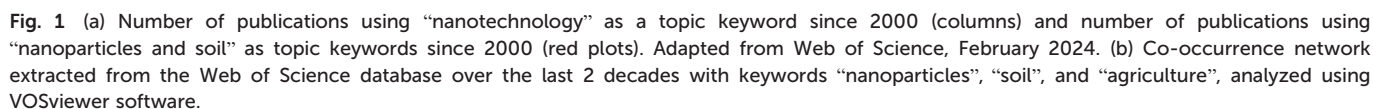
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friendly features. The number of publications using the terms “nanoparticles” and “soil” increased dramatically in 2008 (117 publications) and reached its peak in the last three years, with over “1650” publications in 2022 (Fig. 1a). This rapid growth of nanoparticles in soil science is evident from the data extracted from the Web of Science, which shows over 3400 articles published in the past two decades (Fig. 1b). The co-occurrence of the extracted keywords was analyzed using VOSviewer software, reflecting the correlation between the terms “nanoparticles”, “soil”, and “agriculture” (Fig. 1b), where the larger nodes represent a higher frequency of occurrence, while the connected lines illustrate the



relevance of the keywords.⁸ The most relevant nanoparticles applicable in soil and agriculture are silver nanoparticles, iron nanoparticles, gold nanoparticles, CeO₂, nZVI, ZnO, TiO₂, CuO, carbon nanotubes, and nano-biochar. Regarding application, the adsorption of heavy metals and degradation of organic pollutants are the most frequent keywords, followed by nanobioremediation and nanofertilizers.

With this rapidly accelerating number of literature reports, many comprehensive reviews have been recently published regarding the application of nanotechnology in soil and agricultural systems. As proposed by Usman *et al.*, nanomaterials affect the nutrient release in soil, soil biota, soil organic matter, and plant morphology and physiology, and the mechanisms involved in nanomaterial uptake and translocation within plants and their associated defence mechanisms were also explored.⁹ Saritha *et al.* summarized the potential of nanotechnology in agriculture, the environment and the food industry including seed nano-priming, smart delivery systems, and nano-food packaging.¹⁰ The limitations of nanotechnology were discussed focusing on the harmful impacts of nanotechnology on the soil microbiota, plant growth, underground water, and human health. Hofmann *et al.* explored the barriers in nanotechnology-enabled plant agriculture systems including the limitation of information about delivery methods on the field scale, regulation and safety concerns and consumer acceptance of foods produced using nano-enabled technologies.¹¹ The authors further proposed pathways to overcome these barriers including nanotechnology-based genetic engineering, fertilizers, seed coatings, plant protection, and enhanced soil microbiome. Many other reviews have described nanotechnologies as potential solutions for soil remediation,^{12–15} crop protection and growth enhancement,¹⁶ biotic and abiotic stress tolerance,^{17,18} plant quality monitoring,¹⁹ and safe food processing and packaging.^{20,21}

This review article identifies state-of-the-art of sustainable nanotechnology-based soil applications. The first section briefly describes the synthesis and properties of nanomaterials applied in soil amendment. Next, we shed light on the cutting-edge and advanced sustainable nanotechnology implemented for soil preservation and reclamation. In this part, the main remediation processes supported by interaction mechanisms with soil content include nano-based adsorption, catalysis, and bioremediation. Nano-based adsorbents are divided into four dominant classifications based on the most nanomaterials reported for soil remediation including iron, carbon, natural minerals and polymers, and metal(loid)s-derived nano-adsorbents. In addition, the advances in catalysis for the degradation of pollutants in the soil are also discussed involving advanced oxidation processes, heterogeneous catalysis, and photocatalysis. The potential of nano-induced microorganisms and phytoremediation is also highlighted as sustainable nano-bioremediation processes. We also

underline the advanced application of nano-fertilizers as green alternatives to traditional commercialized fertilizers. The emerging nanotechnology named nano-irrigation is also highlighted as a new irrigation strategy. Regarding this part, we discuss two key nano-irrigation systems, nano-pores tubes and micro/nano bubble aerated irrigation. Finally, the barriers obstructing the application of nanotechnology and the future outlook are both highlighted.

2. Synthesis of nanomaterials

The two primary strategies for synthesizing nanoparticles are bottom-up and top-down processes.^{22–24} The top-down method starts with the standard technique for nanoparticle production, and then reduces the particle size using erosion and various approaches such as mechanical alloying, reactive milling, and high-energy ball milling.^{25,26} The bottom-up approach is the most recent method, which is based on the atom-by-atom or molecule-by-molecule construction of a substance, such as molecular self-assembly, sol-gel, and chemical/physical vapor deposition.^{27,28} Each method has certain benefits and drawbacks. Crystallographic and surface structure damage during particle size reduction is the fundamental issue with the top-down method. Regardless of the flaws generated by the top-down process, it will continue to play an important role in the synthesis of nanoparticles. The two main issues with the bottom-up method are the need for chemical purification and the difficulty in large-scale production. Regardless, the bottom-up approach is the preferred technology given that it can be employed to manufacture materials with precise qualities customized to the remediation need based on the fabrication pathway chosen.²⁹ Fig. 2 shows some instances of several applicable nanomaterials manufacturing methodologies including physical, biological, and chemical methods.^{19,30–33}

Furthermore, chemical and physical methods for the synthesis of nanomaterials frequently produce nanomaterials with a defined shape and size, but these methods have been proven to be hazardous to the environment due to the use of poisonous chemical agents and high temperatures during the synthesis processes.³⁴ Given that the biological synthesis of nanomaterials is performed *via* biological entities such as bacteria,³⁵ fungi,³⁶ algae,³⁷ and plant extracts, biological methods for the synthesis of nanomaterials with a defined shape and size require further investigation.³⁸ Biological entities have been proven to be high secretors of proteins and enzymes, which are primarily responsible for reducing metal ions and controlling the produced nanomaterial. As illustrated in the microbial synthesis of nanomaterials, it can be performed *via* extracellular and intracellular mechanisms. The biogenic synthesis of nanomaterials is green and environmentally friendly technology because it does not require toxic chemicals. Furthermore, the synthesis procedure is often carried out under standard pressure and temperature conditions. As a result, rather than employing



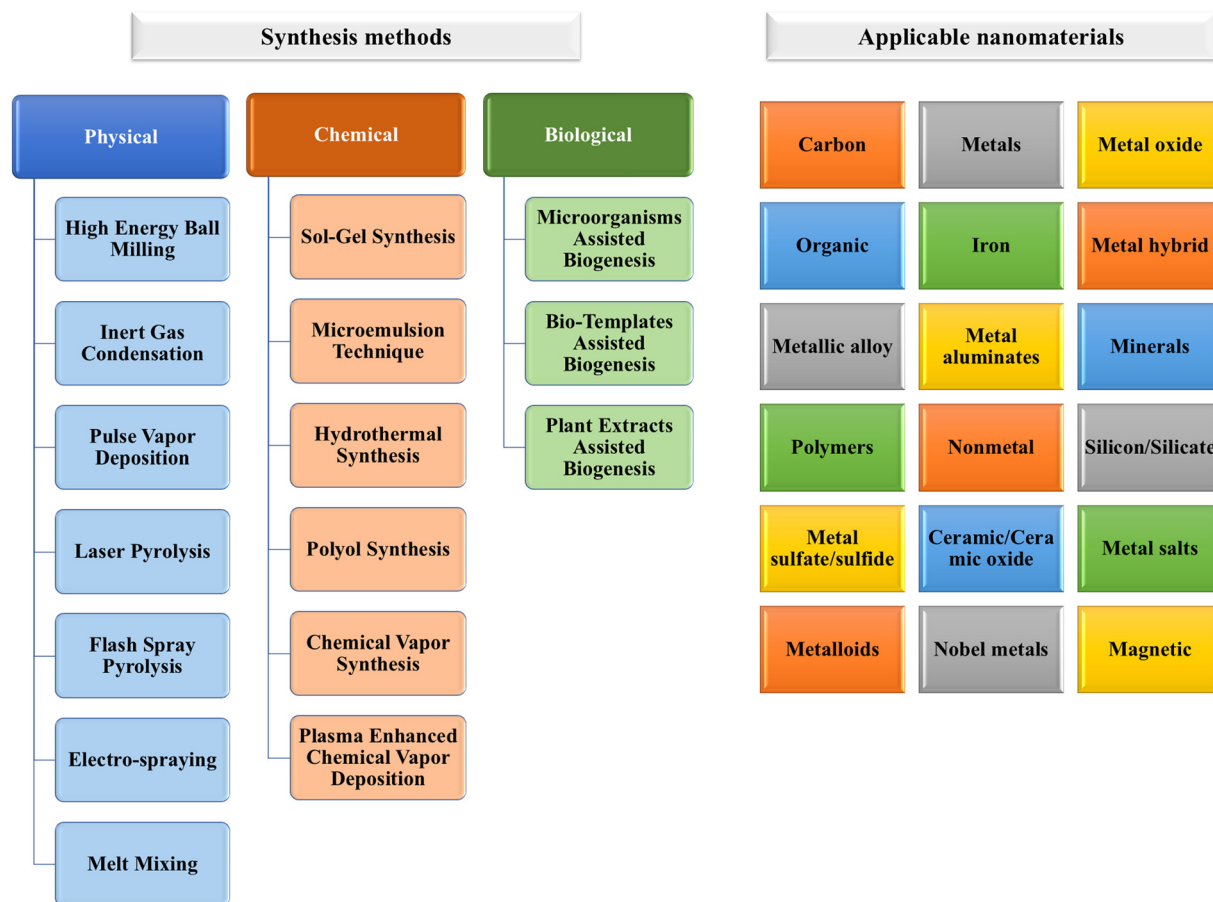


Fig. 2 Applicable nanomaterials and their manufacturing methods (physical, chemical, and biological).

chemical or physical approaches, many researchers have directed their efforts to the creation of biological nanomaterials.³⁴

3. Properties of nanomaterials

Nanomaterials have abundant desirable features, and thus they are recognized as highly efficient materials and ideal candidates for implementation in the agriculture sector. These features include enormous surface area, abundant sorption sites, low-temperature modification, short intraparticle diffusion distance, variable pore size, and surface chemistry.³⁹ The characteristics and efficacy of nanomaterials are also influenced by their form and morphology. The delicate balance among the energy from polar charges, surface area, and elastic deformation results in a variety of morphologies. According to Gatoo *et al.*, the shape, surface area and chemical composition of nanomaterials influence their behavior and activity.⁴⁰

Also, the innate surface properties, intrinsic compositions, apparent sizes, and external functionalization of nanomaterials have a significant impact on their physical, material, and chemical properties.⁴¹ The nature and distribution of active sites on the surface and the types and number of functional groups in nanomaterials contribute to

explaining their behavior and properties, such as the location of the domain atoms on their surface, high surface area, high chemical activity, high adsorptive capacity, and high surface binding energy. These distinguishable chemical and physical characteristics have led to an increase in their application compared to traditional commercial compounds.⁴²

4. Application of nanotechnology in soil management

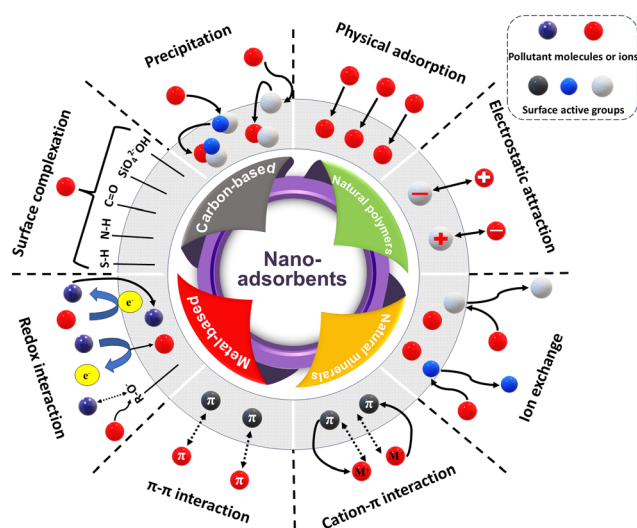
4.1. Soil remediation

The rapid pace of industrialization and urbanization growth has resulted in severe environmental issues and poses a great threat to terrestrial and aquatic resources, as well as human health. Soil contamination is a global issue that is of concern and a menace to food security. The remediation of a wide variety of soil pollutants is a challenging task, requiring highly efficient removal techniques. The major pollutants in soil can be divided into organic pollutants such as total petroleum hydrocarbons (TPHs), pesticides, herbicides, microplastic contaminants, and emerging micropollutants, and inorganic pollutants such as heavy metals (Cu, Cd, Zn, Pb, and Hg), metalloids (Sb, and As), and radioactive elements, resulting from different resources including industrial, domestic, agricultural and mining activities.^{1,43–47}



1 - Physical adsorption and pore-filling: this adsorption mechanism does not rely on chemical interactions. The adsorption process depends on the diffusion and desorption of the guest molecules/ions in the pores of nano-adsorbents until adsorption equilibrium is reached.⁴⁹ The main factor influencing physical adsorption is the conditions for the synthesis of nanoparticles. For instance, pre-treatment activation, high-temperature pyrolysis, and ball-milling utilization towards the synthesis of carbon-based nanomaterials such as nano-biochar promote the formation of mesopores and micropores and enhance the pore diameter, volume, and specific surface area.⁵⁰ Thus, the diffusion and filling of metal ions or organic molecules in

6 - Cation- π (C- π) and π - π (π - π) interactions: these interactions are considered new binding forces compared to the classical electrostatic interactions. C- π interaction is the intermolecular interaction between metal cations and the aromatic systems in nano-adsorbents.⁵⁵ Alternatively, π - π interactions occur between the aromatic moieties of organic pollutants (*e.g.* PAHs, pesticides, and antibiotics) and aromatic natures of nano-adsorbents such as graphitic structure of carbon-based nanomaterials, where π -electron interactions play the leading role. During the polarization of aromatic compounds, the residues of π -electrons in the π -bonds of the aromatic moiety groups are shared to form an aromatic π -cloud. Besides, the unique geometry positions of the aromatic moieties (face-to-face or edge-to-face), owing to their flat feature, facilitate π - π stacking.⁴⁹ The strength of both C- π and π - π interactions on the surface aromaticity of nano-adsorbents varies, where more π -conjugated aromatic



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structures have stronger electron-donating potential. The π stacking mechanism can be investigated using XPS spectroscopy.^{50,55}

Iron-based nanoparticles especially nano zero-valent iron (nZVI) have been widely applied to immobilize pollutants in contaminated soil.^{51,56} For instance, Baragaño *et al.* assessed the efficiency of nZVI and goethite nanospheres (nGoethite) for the immobilization of arsenic (As) in polluted soil (sandy loam).⁵⁷ The results showed that nZVI and nGoethite nanoparticles could reduce the As concentration based on the toxicity characteristic leaching procedure test (TCLP) by 89.5% and 82.5%, respectively. In another study, Zialame *et al.* studied the influence of manganese ferrite (MnFe_2O_4) nanoparticles on the stabilization of As in contaminated sandy soil.⁵⁸ Their study demonstrated that magnetite nanoparticles have significant potential in immobilizing As in contaminated soil by reducing the amount of arsenic leaching from the solid phase of the soil in the TCLP test by 90.2%. Furthermore, the presence of MnFe_2O_4 nanoparticles in contaminated soil could oxidize and convert some of the arsenic to the less toxic arsenate, which facilitated and enhanced its adsorption on the surface of Fe–Mn oxides in the structure of manganese ferrite. Sulfidation of nZVI (S-nZVI) is another approach that provides better conductivity, higher electron transfer efficiency, selectivity, and less toxicity compared to bare nZVI.⁵⁹ Both nZVI and S-nZVI with a concentration of 5% w/w (nanoparticles/soil) showed efficient immobilization of As in a sandy loam soil matrix by decreasing the arsenic concentration leaching by 100% and 99.6%, respectively, after 7 days.⁶⁰ However, S-nZVI exhibited considerable suppression of As bioaccumulation by earthworms (*Eisenia fetida*) more than nZVI, where the survival of the earthworms increased from 10% for nZVI to 73% for S-nZVI when the soil was treated with 0.3% adsorbent. This was ascribed to the strong stability of S-nZVI, which led to less change in pH and slower transformation, resulting in a lower impact on *E. fetida*. In another study, S-nZVI exhibited an excellent performance towards the immobilization of Cd in contaminated soil. After 30 days, the exchangeable Cd was diminished to less than 1% with an immobilization efficiency of 97.6–100% compared with the untreated soil. The proposed remediation mechanism relied on the adsorption of Cd particles onto the S-nZVI nanoparticles, followed by the formation of iron-manganese oxide bonds and the conversion of Cd to CdO and CdS, indicating that S-nZVI is a promising material for the remediation of Cd-contaminated soil.⁵⁹ The use of natural minerals and clays as a support for nZVI is also another approach to promote its immobilization. Li *et al.* investigated nZVI supported by zeolite (Z-nZVI) to immobilize Cd, Pb, and As in soil for 180 days.⁶¹ The results showed that Z-nZVI amendment with a loading of 30 g kg^{-1} was the most effective in reducing the bioavailability of Cd, Pb, and As in acidic soil by 10.2%, 73.8%, and 17.1% and in alkaline soil by 44.3%, 96.8%, and 31.0%, respectively. The divergent immobilization

efficiency of metalloids on the surface of Z-nZVI could be explained by the unique encapsulation mechanism, where the pollutants adsorbed rapidly on the surface of Z-nZVI by iron oxyhydroxides and aluminosilicates, and then a specific redox reaction of As(v), As(III) and Pb(II) occurred, which depended on soil pH and standard electrode potential (SEP). In this concurrent redox reaction, Fe^0 can reduce As(v) to As(III), and then to As^0 and Pb(II) is reduced to Pb^0 . Finally, the secondary mineralization of Z-nZVI provides a catalytic interface to form more stable B-type ternary complexes and heterogeneous coprecipitates. Alternatively, montmorillonite-supported nano-zero-valent iron (nZVI@TP-Mont) is an efficient amendment to remove chromium Cr(VI) from acidic and neutral soils. nZVI@TP-Mont showed almost complete Cr(VI) removal in acidic soil and about 84% removal in neutral soil.⁶² Its excellent Cr(VI) removal performance in acidic soil is attributed to the high H^+ concentration in soil, which facilitates the dissolution of iron oxide on the surface of nZVI@TP-Mont, releasing more Fe^{2+} and providing more active sites. The enriched active sites enhance the reduction of Cr(VI) into Cr(III) through electron loss, and then foster Cr(III) immobilization by the nZVI@TP-Mont composites in soil. Alternatively, at high pH, OH^- competes with the active sites, which hinders the reduction of Cr(VI).

Recently, nano-biochar and biochar-supported nanoparticles have been investigated as novel and promising adsorbents and amendments for the highly efficient removal of organic and inorganic pollutants in soil.^{63–68} Among the various biochar-supported nanocomposites, nZVI-doped biochar has been widely used for the immobilization of contaminants in soil.⁵¹ Biochar-supported nZVI has numerous advantages including improving the distribution of nZVI on the porous surface of biochar as discrete nanoparticles and enabling the manipulation of its particle size. This can hinder the steric and magnetic attraction between the nZVI particles and increase the surface area, thus enhancing the adsorption of pollutants.^{69–71} Thus far, Qian *et al.* studied the impact of biochar-supported nZVI (BC-nZVI) on the simultaneous stabilization of heavy metals (Cd and Pb) in clay soil.⁷² This study concluded that BC-nZVI exhibited better immobilization of Cd and Pb (high, reaching 86.49% and 80.14%, respectively) than pristine biochar and nZVI and could significantly reduce the bioavailability of these metals in contaminated soil. Furthermore, at a low concentration of 2,4-dichlorophenol (2,4-DCP) (2.65 mg kg^{-1}), BC-nZVI could effectively remove 2,4-DCP in soil by nearly 90% *via* adsorption and reduction reaction with Cd or Pb immobilization. These recent results indicate the applicability of nanoparticle-modified biochar and some recent nanocomposites include biochar-supported nZVI,⁷³ graphene oxide (GO),⁷⁴ magnetic iron oxide nanoparticles,⁷⁵ nano-hydroxyapatite,⁷⁶ Fe–Mn nanoparticle-modified biochar,⁷⁷ biochar-supported iron phosphate nanoparticles,⁷⁸ and biochar-Ni/Fe bimetallic nanoparticles⁷⁹ for the immobilization and removal of pollutants from contaminated



soil. Other carbon-based nanomaterials such as carbon nanotubes (CNTs), fullerenes (nC60), graphene oxide, and carbon black nanoparticles have been also applied for the removal of contaminants in polluted soil environments.^{80,81} Due to the unique properties of carbon nanotubes such as high surface area, abundant adsorption sites along their cylinder structure, and tunable surface chemistry, CNTs have been applied in water and soil remediation.^{82,83} Li *et al.* explored the leaching behaviors of polyaromatic hydrocarbons (PAHs) in sandy loam soil in the presence of CNTs.⁸⁴ The results showed that CNTs had significant potential to retain PAHs and reduce their bioavailability in the soil due to strong the PAH adsorption capacities of CNTs and their low mobilities. In addition to organic pollutants, CNTs showed the ability to immobilize inorganic pollutants such as phosphorus with a maximum adsorption capacity of P on sediments increasing from 0.646 to 0.996 mg g⁻¹ with an increase in the CNT content in contaminated sediment.⁸⁵

Natural minerals and polymers also play a considerable role in the adsorption of contaminants.^{86–89} For instance, halloysite nanotubes coated with carboxylic groups (HNTs@CRC) showed high efficiency in stabilizing four heavy metals, Co, Ni, Cu, and Zn, in river sediments. The stabilization of HNTs@CRC was further enhanced with the addition of Ca(OH)₂ and reached high ratios of 98.82% for Co, 83.58% for Ni, 90.71% for Cu and 73.99% for Zn.⁹⁰ These results can be attributed to the ability of carboxylic groups to adsorb heavy metals. Furthermore, the addition of Ca(OH)₂ increased the pH, leading to stronger electrostatic affinity toward positively charged metal ions. In contaminated sandy loam soil amended with sewage sludge, Feizi and Jalali recommended the use of zeolite, ZnO and MgO nanoparticles as efficient heavy metal adsorbents, which reduced the leaching of Cd, Cu, Ni, and Zn from the contaminated soil.⁹¹ In addition, hydroxyapatite nanoparticles (nHAP) also exhibited high immobilization efficiency for reducing Pb uptake by plants in Pb-contaminated soils.⁹² A field assessment was also performed to investigate the immobilization of Pb in soil. Li *et al.* monitored long-term (1 year) Pb immobilization over a new type of carboxymethyl cellulose (CMC)-bridged chlorapatite nano/microparticles (CMC-CAP) at an abandoned chemical plant site.⁹³ The pilot-scale results showed that CMC-CAP at a dosage of 0.5 wt% resulted in the highest immobilization of Pb and decreased the acid-leachable Pb in the sandy loam soil up to 99.4% after only 1 day of reaction and fixed at 99.6% after 365 days. Furthermore, the extraction data confirmed that the CMC-CAP amendment converted the more leachable Pb fractions into the less available Pb species. The use of natural polymers was also investigated as a green immobilization strategy for pollutants in the soil matrix. Tao *et al.* studied the role of three natural polymers, lignin, carboxymethyl cellulose, and sodium alginate, for soil amendment to stabilize Pb and Cd.⁹⁴ The TCLP test showed that the leaching concentrations of Pb and Cd were reduced from 5.46% and 4.25% to 71.1% and 49.6%, respectively. The

abundant oxygen groups on the surface of the natural polymers endowed them with the ability to chelate heavy metals. Compared to carboxymethyl cellulose and sodium alginate, lignin exhibited a higher immobilization performance due to its phenolic nature as a three-dimensional amorphous aromatic polymer. Embedding nanomaterials with these natural polymers paves a way toward expanding their adsorption potential with manifold interaction mechanisms. Novel metal-organic frameworks incorporated with TEMPO-oxidized nano-fibrillated cellulose/lignin/acrylamide-based hydrogel adsorbents revealed excellent adsorption capacity for Pb and Cu in contaminated soil with a decline in Pb and Cu bioavailability up to 85.9% and 74.5% within 45 days, respectively.⁹⁵ The adsorption mechanisms could be ascribed to various interactions including physical sorption by swelling, ion exchange, electrical attraction, and π -acceptor (amide-cations) interactions, and complexation through unsaturated Fe(III) sites and hydroxyl/carboxyl/carbonyl groups.

Silicon (Si), the second most abundant element in the Earth's crust, was reported to be beneficial for alleviating heavy metal bioavailability and improving plant growth.⁹⁶ Si nanoparticle amendment could enhance the immobilization of heavy metals and reduce their bioavailability in the soil, their translocation from the roots to aboveground parts, and their accumulation in plant tissues.⁹⁶ Alternatively, the application of SiO₂ nanoparticle-supported-lipid-bilayers was shown to be an effective method for the remediation of hydrophobic organic contaminants in soils using benzo-*a*-pyrene (BaP) as an example, where the lipids provided both an extraction method and stability for transport to the contaminant site.⁹⁷ Thiol-functionalized nano-silica (SiO₂-SH) was also adopted to remediate contaminated silt loam soil and decrease the biotoxicity of Pb, Cd, and Cu.⁹⁸ Although mercapto is an effective functional group for immobilizing heavy metals when grafted to various materials, it is easily oxidized, limiting its practical application to a great extent. Thus, to improve the stability of amendments, Qiu *et al.* prepared mercapto iron complex-functionalized nanosilica (RNS-SF), which had high immobilization efficiencies in Pb/Cd-contaminated soil.⁹⁹ The results showed that RNS-SF exhibited unique immobilization efficiencies in contaminated soil with immobilizing percentages of 98.7% for Pb and 97.9% for Cd, which remained unchanged from -20 °C to 50 °C, and even after 360 days storage at room temperature, the immobilization efficiencies of Pb and Cd were all about 90%.

Other nanoparticles, such as copper oxide (nCuO), can effectively reduce the mobility of As in soil and inhibit its accumulation in rice grains.¹⁰⁰ Also, selenium nanoparticles (SeNPs) can efficiently remediate Hg⁰-contaminated soils to form more stable HgSe; however, the high aggregation of SeNPs hinders their applicability.¹⁰¹ Thus, to address this issue, it was found that extracellular polymeric substances (EPS) with SeNPs were an excellent dispersant for SeNPs in soil solution and could significantly enhance the



remediation performance for Hg^0 contamination under natural conditions. The reason for the stabilization effects was the strong interaction between EPS and SeNPs, making SeNPs more negatively charged.¹⁰¹ Another novel nanoparticle is a flower-like magnetic MoS_2 nanohybrid ($\text{MoS}_2/\text{Fe}_3\text{O}_4$). This nanohybrid material showed high

adsorption capacity for $\text{Hg}(\text{II})$ (428.9 mg g^{-1}) and $\text{Pb}(\text{II})$ (263.6 mg g^{-1}) at the optimized operating parameters.¹⁰² For efficient radioactive pollutant removal from contaminated soil, Kim *et al.* proposed a novel two-step strategy for the remediation of Cs-contaminated soil assisted by magnetic polyethyleneimine-grafted Fe_3O_4 nanoparticles.¹⁰³ The

Table 1 Comparison of different nano-adsorbents for the removal of pollutants from soil

Adsorbent class	Adsorbent	Pollutant	Adsorption efficiency/removal rate	Interaction mechanism	Ref.
Iron-based nano-adsorbents	nZVI + goethite (nGoethite)	As	89.5% reduction of TLCP test	Arsenate adsorption occurs in the outer layer of the nanoparticles	57
	MnFe_2O_4	As	90.2% of TLCP test	Oxidation of As(III) to As(V) followed by adsorption of arsenate on the surface of binary Fe–Mn oxides	58
	S-nZVI	Cd	97.6–100%	Precipitation of Cd(II) to form CdS by SH^- and complexation with iron oxides	59
	S-nZVI	As	99.6% reduction after 7 days	Co-precipitation of arsenic with iron and sulfur species; the sulfhydryl ($-\text{SH}$) group in S-nZVI increases the binding sites for inorganic species, including arsenic	60
	nZVI + zeolite (Z-nZVI)	Cd, Pb, As	44.3%, 96.8%, and 31.0%, in alkaline soil	Ternary complexation by iron oxyhydroxides and aluminosilicates, along with concurrent redox reactions	61
	nZVI@TP-Mont	Cr	Complete removal in acidic soil and about 84% removal in neutral soil	Cr(VI) reduction to Cr(III) and co-precipitation on the nZVI@TP-Mont surface as combined Cr(III)/Fe(III) hydroxides	62
Carbon-based nano-adsorbents	Biochar-supporting GO/nZVI	Cu	75.16% after 14 days at soil-neutral pH	Cu complexation with the nZVI oxyhydroxide layer (Fe–OOH), electrostatic interaction and co-precipitation with biochar-GO/nZVI.	74
	Nano-biochar	Cd	~30% after 90 days	Surface complexation and electrostatic actions through core-shell structures of nano-biochar	104
	BC@ MnO_2	Pb, Cd, Zn, Ni	96.98%, 95.29%, 95.08%, 94.35% reduction in bio-concentration factor (BCF)	Formation of insoluble inorganic compounds <i>via</i> ion exchange, complexation, and precipitation in the presence of a greater number of exchangeable divalent cations such as Mg(II) in biochar	105
	CNTs	PAHs	28.8% retention in soil	Hydrophobic interactions between PAHs and CNTs, pore-filling, and π – π interactions	84
Natural mineral and polymers-based nano-adsorbents	HNTs@CRC	Co, Ni, Cu, Zn	98.82%, 83.58%, 90.71%, 73.99% stabilization ratio	Adsorption and precipitation on the surface of HNTs@CRC, along with complexation and interaction binding with $\text{Ca}(\text{OH})_2$ groups	90
	Zeolite	Cu, Cd	99.9%, 99.9% immobilization rate, and 0.005% and 0.05% leaching rate	After replacing Na^+ ions, immobilization of Cu and Cd <i>via</i> zeolitization, where Cu^{2+} strongly bonds to hydroxyl (forming $\text{Cu}^{2+}\text{--OH}$) in the small cages, and Cd^{2+} coordinates with the oxygen ($\text{Cd}^{2+}\text{--O}$) in large channels of zeolite	106
	Carboxymethyl cellulose bridged chlorapatite nano/microparticles (CMC-CAP)	Pb	99.6% stable immobilization rate from 1 day to 365 days	Surface complexation/cation exchange between Ca^{2+} in chlorapatite and Pb^{2+} , where metastable precipitates ($\text{Pb}(\text{OH})_2$ or PbCO_3) transform into the most stable lead precipitate (pyromorphite)	93
Metal(loid)-based nano-adsorbents	$\text{SiO}_2\text{--SH}$	Cd, Pb, Cu	92.02%, 68.03%, 76.34% immobilization rate	Formation of metal complexes <i>via</i> thiol groups, transforming the active fraction of heavy metals into stable ones	98
	Mercapto iron/nanosilica complex	Pb, Cd	98.7%, 97.9% immobilization rate for 360 days	Formation of insoluble and stable complexes with enriched $-\text{SFe}$ and $-\text{OH}$ functional groups	90
	ZnO nanoparticles	Carbamazepine (CBZ)	90% retention rate in the first leachate to ~99% after the fifth leaching	Adsorption of CBZ over ZnO by intermolecular forces, including hydrogen bonds, π – π , electron, electrostatic, hydrophobic interactions, and the pore-filling effect	107
	$\delta\text{--MnO}_2$	Cd	65.8% reducible Cd	Cd immobilization <i>via</i> adsorption and antagonistic effects of the released Mn ions with Cd in the wheat rhizosphere	108



magnetic composites were added to dispersion-contaminated soil (a mass of Cs-sorbed soil was dispersed in DI water using an ultrasonic bath), and then selectively bonded with clay particles through electrostatic attraction, enabling the clay particles to be easily separated from sand under an external magnetic field. After treating the residue-contaminated sand with acid, the addition of a magnetic adsorbent ($\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{KTiFC}$, where KTiFC is potassium titanium(IV) hexacyanoferrate) to the acid treatment substantially improved the desorption of Cs^+ (95.2%) by preventing the re-adsorption of Cs^+ onto the sand. Practically, this approach demonstrated high efficiency in the remediation of Cs-contaminated soil with a high radioactivity reduction of 96.7%. The performances of the above-mentioned nano-adsorbents are summarized in Table 1. However, despite the great role of nano-adsorbents in immobilizing and removing toxic heavy metals from contaminated soil, the remediation of other soil pollutants such as recalcitrant and emerging organic contaminants requires more efficient removal techniques.

4.1.2. Nano-catalysts and -photocatalysts. To overcome the drawbacks associated with the prolongation of the remaining residues and the difficulty of cleaning up pollutants, particularly organic substances, in the soil body during the adsorption process, the degradation and removal of contaminants in the soil to harmless by-products have been widely studied in the last few decades (Fig. 4). The catalytic degradation of organic pollutants in the soil by advanced oxidation processes (AOPs), a branch of chemical oxidation, has been proven to have the capability and efficiency to mineralize recalcitrant and highly toxic organic molecules such as PAHs to non-harmless substances such as CO_2 and water. Using AOPs, oxidation occurs more quickly and more

efficiently in soil, resulting in greater adaptability and performance. Typically, the effects of AOPs are primarily caused by free radical generation using oxidants such as hydrogen peroxide, persulfate, ozone (O_3), permanganate, peracetic acid, and other Fenton reagents. Several factors play a role in AOPs, particularly temperature, pH, and concentration of oxidants and catalysts involved.

Besides being broadly used as adsorbents, iron-based nanoparticles show a superior performance in advanced oxidation catalysis for the cleanup of contaminated soil. Amongst them, the effectiveness of nZVI in Fenton and persulfate oxidation and removal of organic pollutants such as PAHs from soil has been proven in several previous studies.^{109–113} Bajagain and Jeong investigated the role of nZVI in activating peroxymonosulfate (PMS) for the degradation of TPHs in aged diesel-contaminated soil.¹¹⁴ The results showed that the nZVI/PMS system (optimal concentrations were 0.2% nZVI and 3% PMS) produced more reactive oxygen species (hydroxyl and sulfate free radicals) compared to other systems, such as $\text{Co(II)}/\text{PMS}$, providing the best degradation efficiency of TPHs (61.2% in 2 h), respectively. Alternatively, Yuan *et al.* reported the degradation of tetrabromobisphenol A (TBBPA) through the activation of persulfate (PS) by nZVI.¹¹⁵ The degradation rate of TBBPA was 78.32% within 12 h in a low pH soil medium at 25 °C, where the degradation behavior of TBBPA effectively occurred at lower pH and higher temperature. The oxidative degradation of TBBPA was ascribed to the generation of active species of $\text{SO}_4^{\cdot-}$, $\cdot\text{OH}$, and $\text{O}_2^{\cdot-}$, resulting in attack of the C–Br bond, and then debromination of TBBPA, and the cleavage between the isopropyl group and one of the benzene rings completed the decomposition. Recently, honeycomb

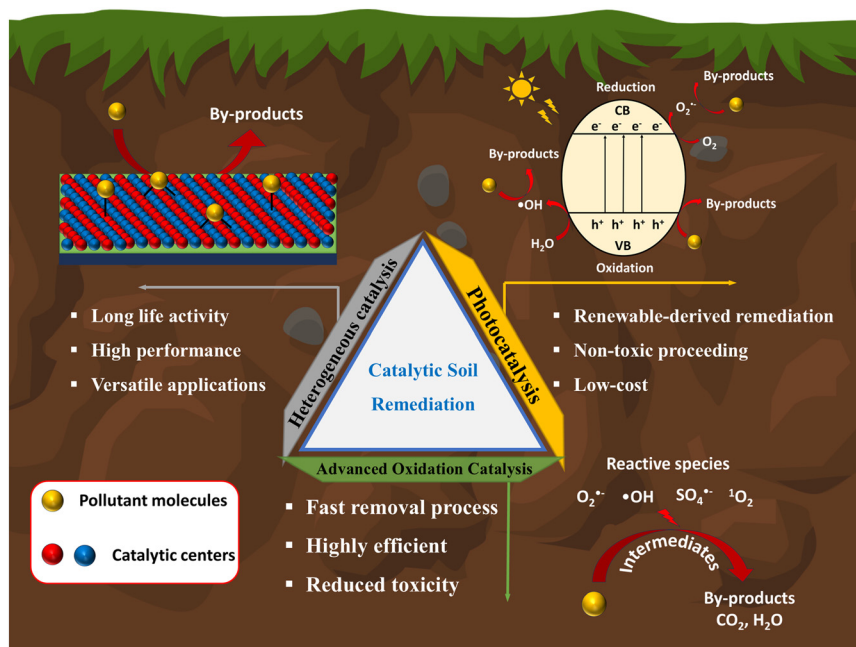


Fig. 4 Dominant green catalytic processes for soil remediation.



iron nanoparticles supported on N-doped carbon foam microstructure (Fe@CF-N) were fabricated and used as an activator of potassium peroxymonosulfate (PMS) to degrade fluoranthene (FLT) in soil.¹¹⁶ The reactive oxygen species such as hydroxyl radicals ($\cdot\text{OH}$), sulfate radical ($\text{SO}_4^{\cdot-}$) and singlet oxygen ($^1\text{O}_2$) were the major species responsible for the degradation of FLT into low molecular weight species of 1,2,3-benzenetriol and 1,3-propanediol, and finally degraded into water and carbon dioxide. The as-fabricated composite exhibited excellent degradation of FLT in soil with a degradation rate of 77.90% after 180 min. Besides, Fe@CF-N/PMS not only improved the physicochemical properties of the contaminated soil but also decreased the bioavailable toxicity of FLT. In the case of integrated processing with Fenton oxidation, Barzegar *et al.* studied the role of solo Fenton-like oxidation on the degradation of pyrene in simulated contaminated soil by Fe_3O_4 nanoparticles.¹¹² The observed pyrene removal was about 98.37% and this value was verified with a variation in H_2O_2 , nanoparticles dosage, pH, and ultrasonic power. Furthermore, the sono-Fenton oxidation was also applied for real PAH-contaminated soil. The removal rate ranged between 37.7% and 85.19% for different PAHs, which was less than that of the simulated soil, which could be attributed to the high pollution load with various aromatic and aliphatic hydrocarbons, requiring a longer reaction time for remediation. Alternatively, pyrene-contaminated soil was remediated by a microwave/magnetite-activated persulfate oxidation ($\text{Fe}_3\text{O}_4/\text{MW}/\text{PS}$) hybrid system.¹¹⁷ The presence of Fe_3O_4 nanoparticles remarkably enhanced the degradation of pyrene by 91.7% within 45 min treatment, which was three-times higher than that in the absence of Fe_3O_4 . Moreover, the pyrene removal rate in the $\text{Fe}_3\text{O}_4/\text{MW}/\text{PS}$ system was 5.18- and 3.00-times higher than that in the $\text{Fe}_3\text{O}_4/\text{PS}$ and MW/PS systems, respectively. The pyrene degradation depended on the PS concentration, Fe_3O_4 dosage, MW temperature, and soil moisture content. According to the analysis, radical species such as $\text{SO}_4^{\cdot-}$, $\cdot\text{OH}$, $\text{O}_2^{\cdot-}$, and $^1\text{O}_2$ were responsible for the degradation of pyrene. Bimetallic nanoparticles supporting biochar were also applied for the remediation of contaminated soil. Biochar-supported Ni/Fe bimetallic nanoparticles (BC@Ni/Fe) had an excellent efficiency for removal of decabromodiphenyl ether from contaminated soil with a removal efficiency of 87.7% after 72 h, which was 30.2% and 69% higher than that by neat Ni/Fe and biochar, respectively. Essentially, BC@Ni/Fe could reduce the *in situ* bioavailability of metals and adsorb the degradation byproducts after decabromodiphenyl ether degradation.¹¹⁸

Besides the high performance of catalysts for the *in situ* degradation of pollutants in soil, the use of photocatalysts provides a promising and sustainable strategy for the degradation of contaminants in polluted soil under sunlight. The mechanism of photocatalysis relies on the absorption of photons by electrons, and then the electrons are excited from the valence band to the conduction band, initiating a series of reactive radical species and redox reactions.¹¹⁹ Since the

pioneering work on the photocatalysis process for hydrogen production from water splitting in 1972,¹²⁰ the semiconductor titanium dioxide (TiO_2) has been broadly used for environmental remediation by removal of organic contaminants in wastewater and air. Recent years have witnessed the increasing application of TiO_2 nanoparticles in contaminated soil remediation. Wang *et al.* studied the role of TiO_2 nanoparticles in the degradation of diphenyl arsenic acid (DPAA) in contaminated soil under UV irradiation.¹²¹ With 5% of TiO_2 in soil and 3 h irradiation time, the removal efficiency of DPAA increased to 82.7%, and arsenate was identified as the final product, resulting from the generation of $\cdot\text{OH}$ by TiO_2 . In an alkaline medium, the TiO_2 and montmorillonite composite photocatalyst showed a higher degradation of γ -hexachlorocyclohexane (γ -HCH) in soil with a degradation efficiency of 76% within 2 h, and the photocatalytic performance was varied with the content of TiO_2 .¹²² The reason for the higher photocatalytic activity in alkaline soil was that more $\cdot\text{OH}$ radicals could be generated at higher pH *via* the photooxidation of OH^- by holes. Compared with the degradation of PAHs in water, Rachna *et al.* reported that the photocatalytic degradation rate of toxic three-membered PAHs, namely acenaphthene (ACN), phenanthrene (PHN), and fluorene (FLU), over a TiO_2 -based zinc hexacyanoferrate framework ($\text{TiO}_2/\text{ZnHCF}$) in contaminated soil (82–86%) and river sediment (81.63–85.43%) was slower than that in contaminated water (93–96%).¹²³ This was attributed to the reduced diffusion due to the interaction between PAH molecules and the organic content of soil and sediment. Shanker *et al.* studied the performance of potassium zinc hexacyanoferrate (KZnHCF) nanocubes as another photocatalyst in the degradation of different toxic PAHs (BaP, chrysene, fluorene, phenanthrene and anthracene) in soil under UV and sunlight.¹²⁴ This study concluded that the KZnHCF nanocubes have high potential for the degradation of PAHs by 70–93%. The order of degradation of PAHs depended on their molecular size, weight, structure, and aromaticity. Furthermore, small and non-toxic byproducts were investigated such as malealdehyde, 4-oxobut-2-enoic acid and ando-xylene.

Another promising and green photocatalyst is graphitic carbon nitride ($\text{g-C}_3\text{N}_4$), which has been widely applied in environmental and energy applications during the last decade.^{125–127} The unique properties of $\text{g-C}_3\text{N}_4$, such as its activity under visible light, ease of preparation, high surface area, enriched active sites, non-toxicity, and low cost, make it tremendously attractive with enormous applications for water and air purification.¹²⁸ However, there are limited reports that studied the role of $\text{g-C}_3\text{N}_4$ in the remediation of contaminated soil under visible light. Recently, Luo *et al.* studied the role of $\text{g-C}_3\text{N}_4$ synthesized using three different precursors including urea, melamine, and dicyandiamide in the photodegradation of phenanthrene in contaminated soil under visible light and natural sunlight in circumneutral pH.¹²⁹ The results showed that $\text{g-C}_3\text{N}_4$ synthesized using urea had the highest surface area ($67.10 \text{ m}^2 \text{ g}^{-1}$) and degradation





Table 2 Comparison of different nano-catalysts for the removal of pollutants from soil

Nanocatalyst	Pollutant	Process	Remediation condition	Nanocatalyst dosage	Pollutant concentration	Degradation %	Interaction mechanism	Ref.
Fe@CF-N	Fluoranthene	AOPs, PMS activation	Adding 6.08 mg PMS, reaction time within 180 min	25 mg catalyst per 5 g soil	20 mg kg ⁻¹	77.90%	PMS and FLT were rapidly adsorbed onto its surface. PMS generates ROS, such as SO ₄ ^{•-} , •OH and ¹ O ₂ via electron transfer. The 1, 2 carbon of FLT was attacked by free radicals through cycloaddition of the double bond, electrophilic attack and nucleophilic attack, which resulted in the oxidation of FLT to the intermediate 9H-fluorene-1-carboxylic acid. This intermediate was further decarboxylated to 9H-fluorene-9-ol	116
Fe ₃ O ₄ nanoparticles	Pyrene	Sono-AOPs	H ₂ O ₂ activation (concentration of 78 mM) associated with ultrasonic power of 313 W, within 60 min	18 mM	100 mg kg ⁻¹ soil	98.37%	Continuous activation of the Fe ₃ O ₄ surface produces •OH radicals via the turbulence generated by cavitation bubble collapse and related microstreaming at the surface of the sonocatalyst	112
Fe ₃ O ₄ nanoparticles	Pyrene	Microwave/AOPs	Persulfate (PS, 1.5 M) oxidation activated by microwave (MW with temperature of 60 °C) and magnetite (Fe ₃ O ₄) within 445 min	40 mg catalyst per 5 g soil	50 mg kg ⁻¹	91.7%	PS was activated by the Fe ²⁺ /Fe ³⁺ system. Fe(II) was oxidized to Fe(III) and catalyzed the activation of PS to produce SO ₄ ^{•-} . SO ₄ ^{•-} then reacted with water molecules to produce •OH. Moreover, Fe(II) could activate O ₂ to form O ₂ ^{•-} , promoting the degradation of pyrene	117
BC@Ni/Fe	Decabromodiphenyl ether (BDE209)	Heterogeneous catalysis	Adding nanocatalysts to spiked soil within 72 h	0.12 g catalyst per 2 g soil	8.7 ± 0.9 mg kg ⁻¹	87.7%	Active hydrogen is generated by the corrosion of Fe with water. The active hydrogen species then dissolved into the Ni lattice to form Ni-H ₂ . Finally, a hydrogenation-debromination reaction occurs between Ni-H ₂ and BDE209 on the surface of Ni/Fe	118
TiO ₂ nanoparticles	Diphenyl arsenic acid	Photocatalysis	UV irradiation with a 500 W high-pressure mercury lamp (40 mW cm ⁻² light intensity) for 3 h	5% w/w TiO ₂ in soil	20 mg kg ⁻¹	82.7%	Degradation of DPAA by •OH radicals results in arsenate as the final product	121
TiO ₂ /montmorillonite composite	γ-Hexachlorocyclohexane	Photocatalysis	UV-light irradiation with a 300 W high-pressure mercury lamp for 2 h under alkaline soil	2% w/w catalyst in soil	1.23 mg g ⁻¹	76%	More •OH radicals can be formed via the photooxidation of OH ⁻ by holes on the composite photocatalyst surfaces, which may contribute to the relatively high photodegradation rate	122
TiO ₂ @ZnHCF	Acenaphthene, phenanthrene, and fluorene	Photocatalysis	Under sunlight for 24 h	25 mg per 0.5 g soil	0.5 g of soil spiked with 2.5 mL of the PAH	82–86%	The encapsulated nanocomposite with a high surface area and negative charge was able to absorb PAHs. Its superior interaction with H ₂ O or O ₂ and charge carriers produced •OH radicals, which degraded and eventually mineralized the PAHs under sunlight	123

Table 2 (continued)

Nanocatalyst	Pollutant	Process	Remediation condition	Nanocatalyst dosage	Pollutant concentration	Degradation %	Interaction mechanism	Ref.
KZnHCF nanocubes	PAHs	Photocatalysis	UV light ($\lambda_{\text{max}} = 254 \text{ nm}$) and sunlight for 48 h	50 mg nanoparticles per g soil	50–200 mg L ⁻¹	70–93%	PAHs are adsorbed onto the surface of KZnHCF, where electron-hole pairs produce ·HO active species under sunlight or UV, breaking down the large, harmful PAHs	124
g-C ₃ N ₄	Phenanthrene	Photocatalysis	Under visible light (a 250 W xenon lamp with a 420 nm cutoff filter) for 3 h and natural sunlight for 10 h	60 mg g ⁻¹	200 mg kg ⁻¹	81.25% under visible light and 97.07% under sunlight	O ₂ ^{·-} and ·OH are the main active radicals for the degradation of phenanthrene in soil	129
g-C ₃ N ₄ /Fe ₃ O ₄	Phenanthrene	Photocatalysis	Under visible light (a 250 W xenon lamp with a 420 nm cutoff filter) for 120 min	30 mg g ⁻¹	200 mg kg ⁻¹	92.26% under sunlight	Fe ₃ O ₄ extends the adsorption region of the nanocomposite and suppresses the recombination rate. Phenanthrene can be oxidized by O ₂ ^{·-} and ·OH radicals, as well as photo-induced holes in g-C ₃ N ₄	130
g-C ₃ N ₄ /α-Fe ₂ O ₃	Fluoranthene	Photocatalysis	Under simulated sunlight irradiation (xenon lamp, 35 W) for 12 h	5% w/w	36 mg kg ⁻¹	88.7%	Z-scheme charge transfer route was proposed to explain the separation and transfer mechanism of photogenerated charge carriers in the g-C ₃ N ₄ /α-Fe ₂ O ₃ heterojunction, with O ₂ ^{·-} and h ⁺ being the dominant reactive species for the photocatalytic degradation of fluoranthene	131

activity (81.25%) for phenanthrene in soil compared with g-C₃N₄ synthesized using dicyandiamide (40.46 m² g⁻¹ and 72.87%, respectively) and melamine (28.19 m² g⁻¹ and 75.39%, respectively) under visible light. Furthermore, g-C₃N₄ synthesized using three different precursors could remarkably reduce the toxicity of phenanthrene-contaminated soil, which was demonstrated by promoting lettuce growth indexes and reducing the mortality and weight loss of earthworms (*Eisenia fetida*). The same research group also investigated the remediation of phenanthrene-contaminated soil over the g-C₃N₄/Fe₃O₄ nanophotocatalyst.¹³⁰ The hybrid composite exhibited excellent phenanthrene degradation with a photodegradation efficiency of 92.26% after 120 min of visible light irradiation. It was clear that the hybrid composite showed a better photocatalytic performance compared with the pure g-C₃N₄, which was attributed to the enhanced separation and transfer of electrons and inhibition of electron-hole recombination in the interface between g-C₃N₄ and Fe₃O₄. This was proven by UV-visible diffuse reflection spectra (DRS) and photoluminescence (PL) spectra. Yang *et al.* reported the application of Z-scheme g-C₃N₄/α-Fe₂O₃ in the photocatalytic degradation of fluoranthene in soil.¹³¹ The optimal fluoranthene photodegradation efficiency after simulated sunlight irradiation for 12 h at neutral pH was 88.7%, where the mass of contaminated soil was 2 g, initial fluoranthene concentration was 36 mg kg⁻¹, and catalyst dosage was 5%. Compared with P25, g-C₃N₄/α-Fe₂O₃ displayed a higher fluoranthene photocatalytic degradation with an increase in removal rate by 50.2%. The enhanced photocatalytic performance could rely on the unique interfacial charge transfer route *via* the Z-scheme between g-C₃N₄ and α-Fe₂O₃, which enhanced the separation and transfer of photogenerated electrons and holes and suppressed their recombination. The degradation mechanism analysis demonstrated that superoxide and hole radicals were the dominant active groups for fluoranthene decontamination. The performances of the above-mentioned nano-catalysts are summarized in Table 2. Lastly, the photocatalysis process paves a clean and cost-effective way for the sustainable remediation of recalcitrant contaminants in polluted soil, but the difficulty in its large-scale use and daylight dependence limit its application.

4.1.3. Nanobioremediation. Bioremediation is one of the eco-friendly and cost-effective strategies for cleaning up contaminated soil in a large area.^{132,133} The combination of nanomaterials with bioremediation can offer a viable approach for stimulating the remediation process by enhancing the growth of microorganisms or immobilizing pollutants through the production of microbial enzymes and biosurfactants in microorganisms.¹³⁴ Besides its application as an adsorbent, as mentioned above, nZVI has been investigated for initiating the nanobioremediation process, followed by the addition of bacterial strains in soil contaminated with polychlorinated biphenyls (PCB).¹³⁵ The results showed that the integrated remediation system has



the potential for the removal of PCB up to 99%. The merit of using nZVI is its ability for the dechlorination of highly substituted PCBs, which are barely degradable by bacterial strains. Zhang *et al.* studied the combination of chemical oxidation and biochar-supported nZVI in the presence of PS for the bioremediation of TPH-contaminated soil.¹³⁶ nZVI was responsible for the oxidation process of TPHs in the soil *via* the activation of PS. Alternatively, biochar played a crucial role in enhancing the bioremediation by inducing microbial metabolism activities and increasing the TPH-degradation bacterium. This was ascribed to the abundant and external carbon sources in biochar, which could both encourage the growth of carbon-specialized metabolism microbes and enhance the microbial metabolic efficiency.

Phytoremediation is also a green approach to achieve the bioremediation of contaminated soil.^{137,138} In this process, tolerant plants have the potential to remove pollutants from the soil either by phytostabilization, phytoextraction, rhizodegradation, or phytovolatilization.¹³⁹ The interaction between nanoparticles and plants for soil cleanup has also been widely investigated to assess the performance of hybrid systems towards biological and environmental systems. For instance, Zand and Heir studied the impact of TiO₂ NPs on the growth of *Sorghum bicolor* and their potential in Sb-contaminated soil remediation.¹⁴⁰ According to the data, it was concluded that TiO₂ NPs enhanced both the biomass of *Sorghum bicolor* and bioaccumulation of Sb in the plant parts, especially in the shoots. Based on this evidence, Chen *et al.* investigated the role of multi-walled carbon nanotubes (MWCNTs) in the growth of *Sorghum bicolor* and the alleviation of the phytotoxicity and bioavailability of Cd and As in contaminated soil.¹⁴¹ The application of MWCNTs significantly enhanced the growth of *Sorghum bicolor*, where carbon nanotubes agglomerated on the surface of the plant roots and restrained the bioavailability of Cd and As by MWCNTs in the rhizosphere area. The reduction of the bioavailability of Cd and As reinforced the plant growth and biomass, leading to an enhancement in the phytoextraction efficiency. Besides heavy metals, MWCNTs also played an important role in alleviating the phytotoxicity of herbicides compared with biochar by inhibiting their bioavailable concentration.¹⁴² In addition, MWCNTs also promoted the growth of tobacco, and even prolonged MWCNT exposure had no significant effect on the soil microbial diversity. In another study, Romeh and Saber reported that coupling of nanoparticles (Fe⁰ and Ag⁰) with P-major plants boosted the removal of chlorfenapyr from the polluted soil.¹⁴³

4.2. Nano-fertilizers

Two billion people or more around the world suffer from various forms of nutrient deficiencies, causing intense diseases such as anemia for women and blindness for children according to the FAO announcement.¹ Considering the limited agricultural arable land (40%) and growing food demand, agricultural production should enormously increase.¹⁴⁴ Thus,

providing innovative and sustainable ways to improve the productivity of crops is critical for eliminating hunger and malnutrition.¹⁴⁵ In this context, fertilization plays a remarkable role in crop productivity given that the crop yield (30–50%) is highly dependent on the input of macronutrients (N, P, K, S, Ca, and Mg) and micronutrients (B, Fe, Mn, Cu, Zn, Mo, and Cl) in the agricultural field.^{146,147} However, despite the benefits gained from fertilization, the nutrient use efficiency of plants is still less than 50%; this reduction is due to the physical and chemical properties of soil, leaching, gaseous losses, and fertilizer characteristics.¹⁴⁸ Utilizing nanomaterials in fertilization for developing novel types of fertilizers (nano-fertilizers) offers a promising trajectory for sustainable agriculture.^{149,150} Nano-fertilizers are nutrients encapsulated by nanomaterials, enabling slow release for the controlled delivery of essential plant nutrients.¹⁵⁰ Recently, significant effort has been devoted to developing smart nano-fertilizers that offer distinct advantages over conventional ones. Nano-fertilizers provide the following advantages: i) sustainable and slow release of nutrients, together with higher nutrient use efficiency, ii) significantly higher uptake due to their ability to freely transport to nano-sized pores, plasmodesmata, and root exudates, iii) economic benefits because they require smaller amounts and result in fewer losses compared to synthetic fertilizers, and iv) eco-friendly with less environmental impact by reducing nutrient leakage and emissions.^{151,152} The application of nano-fertilizers typically resembles traditional fertilizers and involves foliar spraying, seed impregnation, and soil fertilization. Despite the widespread use of soil fertilization, most applied fertilizers are not readily available to plants.^{153,154} For instance, 40–70% of nitrogen (N), 80–90% of phosphorus (P), and 50–90% of potassium (K) are lost or fixed in soils, leading to economic losses.¹⁵³ Therefore, utilizing nano-fertilizers is a favourable avenue for efficient plant nutrition, particularly when applied through soil irrigation, which improves the soil fertility and enhances the nutrient absorption by the roots.^{153,155} The roots of plants serve as the site of interaction between plants and the soil, facilitating the absorption of nutrients, water, and essential physiological substances.¹⁵⁵ Due to their unique physicochemical properties, TiO₂-NPs are one of the most widely used nanomaterials worldwide. In the agricultural sector, TiO₂-NPs offer a promising agrochemical for enhancing agricultural production.¹⁵⁶ The utilization of TiO₂ NPs as nano-fertilizer improved the performance and adhesion of plant growth-promoting rhizobacteria (PGPR) to the plant roots, promoting reproducible field usage and sustainable agriculture productivity.^{157,158} A zinc aluminosilicate (ZnAl₂Si₁₀O₂₄) mesoporous nanocomposite, as a new nano-fertilizer carrier, was synthesized, and then loaded with urea.¹⁵⁹ This nanocomposite could hold urea longer than bulk aluminosilicates, meeting the demand for the slow release of both zinc and urea. When used as a nano-fertilizer on *Oryza sativa* L., the urea-loaded ZnAl₂Si₁₀O₂₄ nanocomposite resulted in a significantly higher yield compared to commercial urea.



For preferable sustainable agricultural practices, it is essential to adopt innovative economic and environmental appraisal models using multi-criteria evaluation analysis to estimate the benefits of nanofertilizers. These criteria include irrigation water and nitrogen use efficiency, nitrate leaching, greenhouse gas change, energy input, crop yield, *etc.*¹⁶⁰ Heiba *et al.* developed a novel sustainable irrigation matrix (SIM)-based model in tomato cultivation using four irrigation scenarios, furrow and drip techniques and chemical and nanomaterial fertilizers.¹⁶¹ The analysis results demonstrated that the combination of drip irrigation and the use of nanofertilizers was the best irrigation technique and was highly influenced by the environmental and economic dimensions, followed by the social pillar of sustainability. Moreover, this study concluded that the SIM-related model can be employed to ensure the sustainable performance of crop irrigation treatments globally. Thus, it has been found that utilizing nano-fertilizers in combination with other techniques can effectively and sustainably increase plant productivity.

4.3. Micro/nano-irrigation technology

The water body is essential for both soil maintenance and agriculture security. Over the ages, flood irrigation has been employed for irrigating cultivated areas, consuming excess capacity and wasting clean water sources. Thus, the last century has witnessed tremendous efforts to develop more water-economical technology to save water and provide a minimum water capacity required for cultivation. In this case, drip irrigation technology is the most efficient among modern irrigation systems and ideal for delivering nutrients to the root zone, optimizing nutrient use efficiency.⁴ During the last decade, nanotechnology drip irrigation has sparked novel concepts in the field of agricultural water management.^{162,163} This strategy can reduce the water consumption by up to 80% compared with traditional irrigation systems. Nano-irrigation systems can be divided into two main categories, nano-pores pipes or tubes and micro/nano bubble aerated irrigation. An early nano-pore irrigation system was developed from moulded clay mixed with sawdust for an emitter diaphragm.¹⁶⁴ A clay diaphragm mixed with sawdust at a ratio of 7:3 (clay to sawdust) was quite suitable for meeting the discharge of water quantity (2 L per day) equivalent of the water requirement of okra and pumpkin vegetables. Furthermore, it was found that the nano-emitter was 100 times cost effective than that of other pottery wares around the study area. Al-Issawi *et al.* compared two trickle irrigation systems, a mobile system and a subsurface nano-irrigation system, using root guard drippers to evaluate the water use efficiency and yield of beans.¹⁶⁵ The results showed that the water use efficiency of subsurface nano-irrigation (1.73) was higher than that of the mobile system (1.14). Moreover, the bean productivity significantly increased under the subsurface nano-irrigation system, producing 7.71 tons per ha compared to 6.62 tons per ha obtained from mobile trickle irrigation.

Recently, nano irrigation has been applied and developed on a large scale such as the Moistube irrigation system.¹⁶⁶ In this system, subsurface water flows out of the Moistube nanopores as a function of soil water potential and operating pressure and it consists of two semipermeable layers, as shown in Fig. 5a. The inner semipermeable layer has approximately 100 000 nanopores per square centimeter with a pore diameter range of 10–900 nm.¹⁶⁷ When the soil is dry, water oozes out from the Moistube nanopores until potential equilibrium between the two sides of the membrane is achieved. At this point, the water seepage will reduce or stop. The Moistube flow due to soil water potential is shown in Fig. 5b.^{167,168} As illustrated in Fig. 5c, Moistube shows superior water consumption efficiency and does not need mechanical power to operate the system, which reduces the consumed energy to 95% compared to traditional drip irrigation systems.¹⁶⁸

Instead of nano-pores pipes, tubes, or pottery, micro/nano bubble (MNB) water oxygenation or aerated irrigation has been also reported to investigate its effects on the irrigation water use efficiency and crop yield and quality.^{170,171} In this technique, MNB can be mostly generated by a Venturi oxygenation generator, where air bubbles are broken to narrower sizes, *i.e.* micro and nanoscale, under low pressure and high velocity, and transmitted through tapered output flow.¹⁷² Moreover, MNB can be also generated by ultrasonication or by chemical reactions such as electrolysis.^{173,174} MNB irrigation can foster soil fertility through enhanced nutrient utilization efficiency, save water and fertilizer quantity, improve hypoxia stress, and promote plant production and quality.^{172,175,176} Besides, MNB irrigation can reinforce the potential bacterial functions related to nitrification and nitrogen fixation and enhance the dynamic mutual feedback between soil fertility and microorganisms.^{177,178} Liu *et al.* investigated the role of integrating MNB water and groundwater with different oxygenation frequencies on the yield and quality of cucumber and tomato cultivation.¹⁶² The results indicated that the integrated micro-nano bubble water oxygenation system could significantly increase the quantity and quality of cucumber and tomato yield, as well as the irrigation water use efficiency. This is due to the longer retention time, stronger mass transfer ability of micro-nano bubbles, and the increment in soil oxygen content. Recently, Khan *et al.* treated water with CO₂ and air to obtain MNB, using tap water as a control.¹⁷⁹ According to the results, it was concluded that MNB + CO₂ enhanced both the physical and chemical parameters of the amaranth plant compared to MNB + air and the control (tap water). The chemical parameters of amaranth promoted by the MNB + CO₂ treatment included amino acid content, soluble sugar content, protein content, plant height, and significant enhancement in leaf area. MNB not only directly enhanced the quality and yield of the plant, but also improved the quality of the drip irrigation emitter. For example, Li *et al.* reported that micro/nano aeration efficaciously hindered the formation of clogging materials



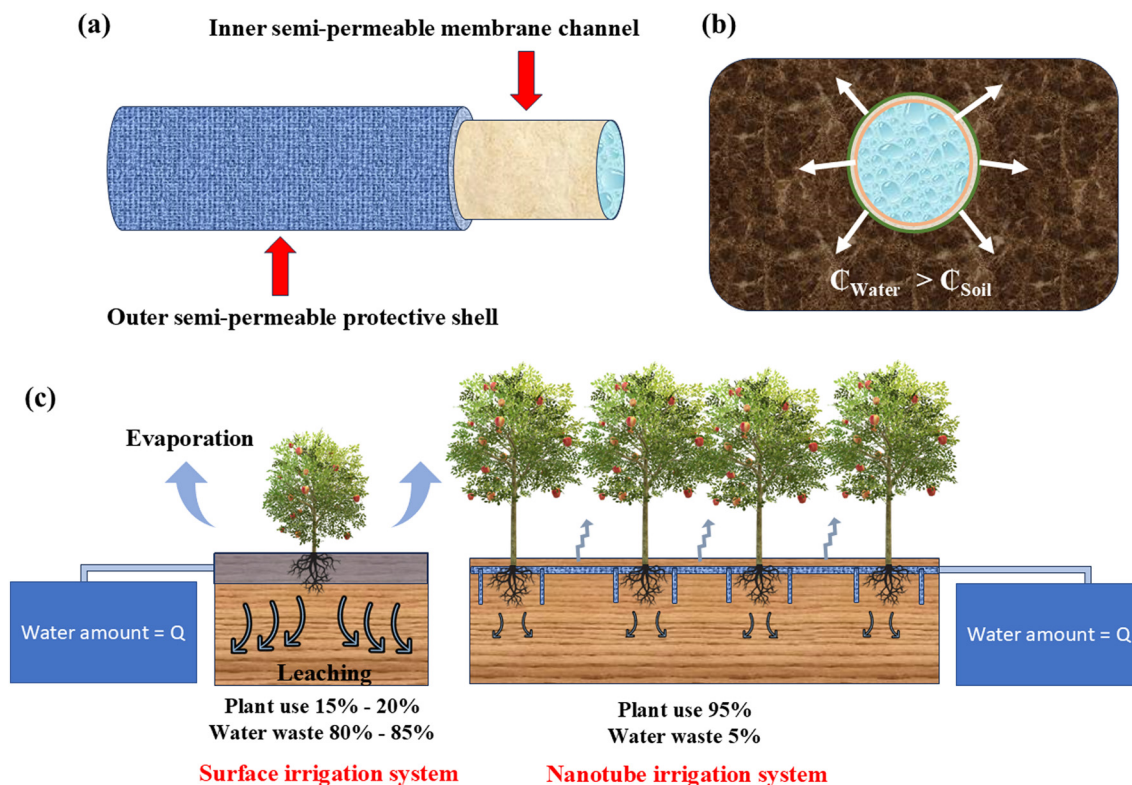


Fig. 5 (a) Internal structure of Moistube,¹⁶⁹ (b) water flow from Moistube to the surrounding soil, depending on soil water potential, and (c) irrigation water use efficiency of Moistube compared to the conventional surface drip irrigation system.

connected to the emitter flow channel.¹⁸⁰ The influential effect of MNB is attributed to the significant depression of the abundance and diversity of the microbial communities in the clogging material attached to the emitter and reduction in the number of core flora affecting the clogging of the emitter. In conclusion, nano-irrigation systems open a sustainable way toward achieving optimal water consumption and high crop quality and yield.

5. Challenges in the application of nanotechnology in soil management

Despite the promising application of nanotechnology in enhancing soil quality and ensuring food security, critical barriers should be addressed before its practical enforcement, including a lack of mechanistic understanding of nano-bio (plants and microorganisms) interactions, the actual impact of the fate and transportation of applied nanotechnology on the surrounding environment, and insufficient grasping of human health risks from the chain food impacted by nanomaterials. In addition, the prolonged stability and performance of nanoparticles in the soil matrix and how long they can maintain their performance are also crucial.

5.1. Environmental toxicity

The application of nanomaterials in the agricultural sector has become popular for solving agricultural problems and

achieving sustainability.¹⁸¹ However, employing nanomaterials in agriculture (*i.e.*, soil) has drawbacks related to their ecological and toxicological impacts that are not observed with bulk particles.¹⁸² Nanomaterial-based agrochemicals can be prepared from several types of nanoparticles with extraordinary physical and chemical properties (specific surface structures and reactivity), and these nanoparticles can generate reactive oxygen species (ROS).^{183,184} As a result, the formation of ROS leads to non-targeted cell death/apoptosis, besides the premature cell death caused by the undesirable involvement of nanoparticles.¹⁸⁴ The toxicity of nanoparticles depends on distinct factors including particle size, applied dose, composition of the fabricated material, functionality, and crystallinity.¹⁸⁵ Recent studies have shown that exposure to higher concentrations of nanomaterials has negative effects on plants, whereas utilizing a lower dose under specific conditions has beneficial effects.¹⁸⁶ However, the poor understanding of how nanomaterials transform and behave in the environment is an obstacle in entirely assessing their potential risk in the long term.¹¹ Moreover, there is uncertainty regarding how nanofertilizers may impact the overall greenhouse gas emissions from their production and use.¹⁶⁰ This is why the Food and Drug Administration (FDA) considered the potential harmful impacts of nanomaterials, not regarding them as completely safe or dangerous for use.¹⁵¹ Thus, future research should focus on expanding the knowledge about nano-bio interactions and increasing the information on nanomaterial-associated environmental toxicity.



5.2. Performance stability

The long-term stability of the performance of nanoparticles in soil bodies is also important for their lasting benefits. For instance, soil organic matter may exhibit a paradoxical effect on the stability and mobility of nanomaterials in the soil depending upon their nature. Organic matter tends to accelerate the aggregation of nanomaterials by bridging flocculation, which impacts the surface area, and thus the feature and potential of nano-based substances such as nano-adsorbents and catalysts.⁹ Regarding the bioremediation process, its prolonged remediation periods and its limitation to high pollutant concentration may obstruct its applicability, particularly in contaminated areas requiring an urgent call.^{187,188}

Alternatively, controlling the delivery behaviour of nano-fertilizers and nanocarriers of nutrients into plants, either through soil irrigation application or foliar spray, at the appropriate dose, place, and time remains a formidable challenge. In nutrient delivery to roots in soil irrigation application, the untargeted transportation of nano-fertilizers into the soil, even at low concentrations, is likely to be energy inefficient, owing to the sheer amount of soil to be treated and the relatively high embodied energy of many nanomaterials. The applicability of the foliar spray technique is restrained by climate-related stressors such as weather (rain or wind can remove the applied nanomaterials) and ultraviolet degradation of nano-fertilizers.¹⁸ Thus, developing smart nanomaterials with surface functionality or coating that are not suppressed by biomacromolecules, such as proteins in plant cells and organic matter in the soil, and tolerance to climate and environmental triggers, such as pH and salinity, is urgently demanded to achieve the utmost benefits and long-lasting food security.

Clogging or fouling issues of nanopores in Moistube, as another example, may hinder its performance stability. The clogging of Moistube is mainly affected by the presence of dissolved solids, suspended solids and microbiological impurities such as bacteria, algae, and vegetative matter in water sources. In addition, the existence of soil particles in the irrigation water causes the clogging of its pores, where the soil particle concentration and size are positively correlated with the clogging degree of nanopores.¹⁸⁹ In contrast, some factors positively influence the performance of Moistube such as the temperature and pressure, owing to the elastic and polymeric semi-permeable nature of Moistube. Nevertheless, the evidence of how the Moistube discharge dynamics is affected by other water sources such as wastewater and saline water is limited and needs further research to reduce the pressure on the freshwater resources.¹⁹⁰

5.3. Scalability and cost-effectiveness

The commercialization rate of nanotechnology in the agricultural sector has vastly accelerated during the last few years. However, several parameters may suppress the pace of its growth including the high-cost manufacturing of nano-

based materials and the extravagant scaling up and implementation of nanotechnology with a sheer area of real soils. Besides, given that most promising nanotechnology applications in soil science are still on the lab scale, their scalability without compromising their function and quality remains a great hurdle.

In the case of nano-fertilizers, for example, considering the total cost of N, P, and K nano-fertilizers, utilizing lower dosages is estimated to be about \$350 per ha compared to \$200 per ha for conventional fertilizers in wheat cultivation.¹⁶⁰ Su *et al.* performed a preliminary cost-benefit analysis of employing nano-fertilizers compared to traditional fertilizers.¹⁶⁰ The cost-benefit analysis showed that current nano-fertilizers, partially replacing their conventional counterparts, can potentially increase net revenues from crop production while reducing the environmental impact. Moreover, their study concluded that further innovation is needed to improve the efficiency of nano-fertilizers for their widescale adoption.

Alternatively, the scalability of nano-irrigation technology faces some obstacles. One of them is the abovementioned clogging effects on Moistube nanopores, limiting its scalability. In this context, the maintenance of pores fouling requires additional chemical treatment or a pre-handling process, which increases the costs and environment impact. To minimize or prevent the fouling impact, chlorine and phosphoric acid will be added to prohibit bacteria film growth inside the lines. Besides, acid injections are required to dissolve the chemical precipitates such as magnesium and calcium carbonates. Filtration systems may be also demanded for the pretreatment elimination of the suspended solids, which need high energy for occasionally flushing these particles.¹⁸⁹ In addition, the large-scale application of Moistube is unsuitable for all crops requiring high irrigation water amounts such as rice, sugarcane, and cotton. On the contrary, it will be more promising and appropriate for nanotechnology in arid or semi-arid regions.

6. Prospective trends

6.1. Life cycle assessment

Performing a life cycle assessment (LCA), which is based on the concept of life cycle thinking, of nanotechnology-based soil applications is considered a valuable tool for evaluating the potential of their environmental footprints.¹⁹¹ LCA can furnish pervasive insights in assessing the ecological impacts of applied nanotechnologies from the inception to the conclusion, by considering all stages from nanomaterials synthesis to transportation, field applications, and final pathways. The application of the nano-soil-plant nexus can benefit from LCA to identify potential zones for improvement, identify potential “environmental hotspots”, and enhance their environmental sustainability.¹⁶ Therefore, it is essential to conduct specific nanotechnological LCAs to optimize green synthesis methods, maximize cost-effectiveness, and address potential environmental risks.



It is necessary to develop an accurate step-by-step LCA evaluation system for agricultural nanomaterials to address the lack of knowledge regarding the availability, variability, and uncertainty associated with elevating emerging nanotechnologies between laboratory-scale and full-scale applications.^{16,192} In this respect, field-scale studies are required to track nanotechnology flows and allow a comprehensive and reliable data inventory. LCA systems should adopt and incorporate complete literature data on nano-specific properties to enhance their fate, behavior, and persistence in agricultural soil. Besides, developing nano-specific fate models to understand transformations and interaction mechanisms, such as aggregations, stability, dissolution and nano-eco-bio interactions, with different types of soil invertebrates and plants should be integrated with full toxicological assessments and analyses on the entire life cycle.¹⁹³ By applying an anticipatory approach, alternatives are ranked probabilistically based on their environmental preferences, allowing researchers and practitioners to prioritize research opportunities to advance the methodology. These pathways are identified and suggested as potential trials towards incorporating nano-specific behaviors, reducing the data uncertainty and facilitating decision-making.¹⁹²

6.2. Machine learning

Owing to the global population growth, diminishing number of farmers, and labour shortage associated with the complexity of available heterogeneous data of smart nanotechnology applications, new automated approaches are essential to meet the requirements of agriculture sustainability and facilitate the performance and decision-making by farmers. Researchers have been working on “smart farming” by using nanotechnologies to improve the quality of the soil microbial diversity and quantity of agricultural products, making them intelligent, cost-effective, and sustainable.¹⁹⁴ In recent years, artificial intelligence (AI) has become more accessible to a wider range of parts of the world economy, with inroads into almost all industries due to advances in computational capabilities and increased cloud penetration. The agricultural sector is one of the main fields that has started to reap the benefits of AI.¹⁹⁴ Similar to other computer-based techniques, machine learning (ML) models can reveal complex relationships and project future trends with great effectiveness. The use of machine learning and integrating lab and field data will boost the precision and sustainable nano-enhanced soil quality and agricultural production by analyzing variable covariance and making predictions at the local and global scales.¹⁹⁵

As a baseline for using eco-friendly nanoparticles, ML can provide a profile of nanoparticle properties, which can maximize their performance. In addition, ML can be used for environmental risk assessment (ERA) of nanomaterials to ensure sustainability.¹⁹⁶ One of the main ML tools relevant to ERA is automated image analysis, which is mainly performed

using classification techniques. It can improve nanoparticle identification in transmission electron microscopy (TEM)/scanning electron microscopy (SEM) images and speed up the semi-quantification of particle size and number with convolutional neural networks. Additionally, automated image analysis has also been used for environmental monitoring by identifying species in digital images of soil, sediment, and water using ML algorithms.¹⁹⁶ ML can combine information from different molecular levels within organisms and from population data, together with nanomaterial descriptors. Using this approach, it is possible to discover mechanisms of toxicity and develop safe and sustainable nanomaterials by design and for grouping or read-across. Alternatively, a spatial-temporal analysis (for example, fate over time in a diverse landscape) and omics analysis (*e.g.*, determining transcript-, proteome-, and metabolomics over time) are particularly useful for ERA, which involves highly complex multidimensional datasets.^{196,197} In modern agriculture, machine learning integrating laboratory and field studies will promote the development of nanomaterials and enhance agriculture and soil quality standards.¹⁹⁵

6.3. Guidelines and regulation policies

The use of nanotechnologies in soil applications requires regulatory guidelines to ensure their safety. Governments and legislative bodies should work together with scientists, industries, and other collaborators to develop appropriate guidelines for the green and cost-effective synthesis, spacious and productive application, and safe fate and disposal of nanomaterials. In this way, the potential negative environmental impact of nanomaterials will be minimized, and the sustainable use of nanotechnology will be enhanced. Moreover, adopting dynamics and reliable guidelines and regulations will rely on the research results obtained under real-field conditions on a large scale.¹⁶ Using green and sustainable nanotechnologies should be marketed more effectively to the public and farmers, making them aware of their benefits and safety protocols.

7. Conclusion

This review shed light on the advancements of sustainable nanotechnology applications in enhancing soil quality *via* nano-enabled soil reclamation, nutrition and efficient irrigation water use. Owing to their abundant features and unique physical and chemical characteristics, nanomaterials are recognized as highly efficient materials and ideal candidates for implementation in all sectors including the agricultural sector compared to traditional compounds. Nanomaterials can be prepared using two primary strategies, “bottom-up and top-down processes”. The bottom-up approach is the preferred technology given that it can be employed to manufacture materials with precise qualities customized to the task requirement based on the fabrication pathway chosen. Nanomaterials play an important role in the



sustainability of soil management including the remediation and recovery of contaminated soil, providing nano-fertilizers, and enhancement of micro/nano-irrigation technology in agriculture production. Reducing the mobility and bioavailability of contaminants is crucial in the sustainable remediation of contaminated soil. Nanomaterials have sparked tremendous attraction in the immobilization and conversion of pollutant molecules to harmless byproducts in the soil matrix. Iron-based nanoparticles especially nano zero-valent iron (nZVI) and other nanomaterials, *e.g.*, nano-metal oxides, nano-carbon, nano-biochar and biochar-supported nanoparticles, have been widely applied to immobilize the pollutants in contaminated soil. In addition, natural polymers and minerals demonstrate promising and green adsorption performances. As sustainable nano-enhanced catalytic processes, TiO_2 and $\text{g-C}_3\text{N}_4$ nanocomposites show propitious pollutant removal, particularly for recalcitrant organic pollutants. Alternatively, nano-enabled bioremediation and phytoremediation are considered promising strategies for green and cost-effective field-scale cleaning up.

Fertilization is vital in crop production given that their yield depends on macronutrients and micronutrient inputs. Herein, we summarized the development of green and smart nano-fertilizers, offering innovative and sustainable methods to improve soil nutrition and enhance crop productivity. Alternatively, developing more water-efficient technology to minimize water wastage and ensure a sufficient water supply for cultivation has been achieved by utilizing nano-irrigation technology. Nanotechnology drip irrigation also introduces innovative concepts in agricultural water management, reducing water consumption by 80% compared to traditional irrigation systems. Despite the tremendous advantages of nanotechnology for enforcing soil quality and promoting crop production yields, there are still gaps that should be carefully managed including the unclear mechanistic fate and behaviour of nanomaterials and their stability in the environment. Besides, the scalability and cost of the manufacturing and application of nanotechnology compared to the sheer area of the existing land may be a real challenge for upscaling this promising technology. Thus, integrating life cycle assessment and machine learning coupled with embracing active and reliable guidelines and regulations will create new opportunities towards achieving sustainable nanotechnologies in soil and agricultural applications.

Data availability

The data presented in Fig. 1a were obtained from the Web of Science (<https://access.clarivate.com/login?app=wosalternative=trueshibShireURL=https:%2F%2Fwww.webofknowledge.com%2F%3Fauth%3DShibbolethshibReturnURL=https:%2F%2Fwww.webofknowledge.com%2Ffoaming=true>) and designed by OriginLab (<https://www.originlab.com/>).

The co-occurrence network in Fig. 2b was extracted from the Web of Science database and analyzed using VOSviewer software (<https://www.vosviewer.com/>).

Fig. 5a was redesigned from <https://doi.org/10.1016/j.jhydrol.2024.131083>.

Fig. 2–5b and c were generated using Microsoft PowerPoint (<https://www.microsoft.com/en-us/microsoft-365/powerpoint>).

Conflicts of interest

There are no conflicts to declare.

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