Nanomaterials for sustainable remediation of chemical contaminants in water and soil

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Graphical abstract
Abstract

Rapid growth in population, industry, urbanization and intensive agriculture have led to soil and water pollution by various contaminants. Nanoremediation has become one of the most successful emerging technologies for cleaning up soil and water contaminants due to the high reactivity of nanomaterials (NMs). Numerous publications are available on the use of NMs for removing contaminants, and the efficiencies are often improved by modifications of NMs with polymers, clay minerals, zeolites, activated carbon, and biochar. This paper critically reviews the current state-of-the-art NMs used for sustainable soil and water remediation, focusing on their applications in novel remedial approaches, such as adsorption/filtration, catalysis, photodegradation, electro-nanoremediation, and nano-bioremediation. Insights into process performances, modes of deployment, potential environmental risks and their management, and the consequent societal and economic implications of using NMs for soil and water remediation indicate that widespread acceptance of nanoremediation technologies requires not only a substantial advancement of the underpinning science and engineering aspects themselves, but also practical demonstrations of the effectiveness of already recognized approaches at real world in-situ conditions. New research involving green nanotechnology, nano-bioremediation, electro-nanoremediation, risk assessment of NMs, and outreach activities are needed to achieve successful applications of nanoremediation at regional and global scales.

Key Words: Environmental protection; Green and sustainable remediation; Sustainable development goals; Soil remediation; Soil pollution; Wastewater treatment
1. Introduction

One of the biggest problems faced currently by most countries in the world is the deterioration of environmental quality due to wastewater generation, groundwater contamination, and land degradation. Providing a clean environment to humankind is a major challenge to the global community. The challenges of contaminated environment are represented by the United Nation’s Sustainable Development Goals (SDGs): ‘Clean Water and Sanitation’, ‘Life on Land’, and ‘Life Below Water’ (UN, 2016).

Continuous accumulation of toxic trace elements in soil and water environments accelerate their bioaccumulation. Human exposure to cadmium (Cd), lead (Pb), arsenic (As) and fluoride (F) via drinking water and the consumption of contaminated food can lead to severe health problems in the skin, lungs, kidneys and brain (Schaefer et al., 2020; Wang et al., 2019). Organic contaminants such as industrial dyes are difficult to treat due to their recalcitrance and sensitivity on physicochemical properties of the surrounding environment for degradation (Lellis et al., 2019). Likewise, the excessive application of pesticides in agriculture has contaminated soil and water resources globally (de Souza et al., 2020). Anthropogenic and natural activities including coal gasification, coal-tar pitches and open burning can produce large quantities of polycyclic aromatic hydrocarbons (PAHs) due to the incomplete combustion of hydrocarbons (Li et al., 2020). Pharmaceuticals and personal care products (PPCPs) are contaminants of emerging concern found in wastewater due to discharge from households, healthcare facilities, and the pharmaceutical manufacturing industry (Meyer et al., 2019).

There is a need to develop cost-effective and ecologically benign materials for cleaning up contaminated soil and water. Nanotechnology offers rapid, inexpensive and environmentally safe solutions, and has great potential to reduce contaminant levels to ‘nearly zero’ (Bardos et al.,
Nanoremediation of the environment can be defined as the process whereby suitable nanomaterials (NMs) are used for cleaning up environmental contaminants in the soil, water, and air. Nanoremediation technologies can eliminate the need for excavating and transporting contaminated soils because the cleanup process often takes place *in-situ* (Cai et al., 2019; Fajardo et al., 2020). Furthermore, several approaches can be applied to regenerate and reuse nanomaterials in contaminant treatment applications (e.g., magnetic separation of iron nanoparticles, recovery of metals from spent nanosorbents) (Mehta et al., 2015).

Nanoparticles (NPs) are particles with sizes of <100 nm in all dimensions (e.g., metal oxides), while NMs require only one dimension to be <100 nm (e.g., carbon nanotubes) (Khan et al., 2019). Nanocomposites are defined as multiphase materials consisting of at least one nanoscale phase that is dispersed in another phase to obtain a combination of the individual properties of its constituents (Bassyounia et al., 2019; Mukhopadhyay et al., 2020). Therefore, one of the constituent materials in nanocomposites should have a dimension <100 nm (Schaefer and Justice, 2007; Zhao et al., 2011). Nanoscale metal oxides, nano-scale zero valent iron (nZVI), bimetallic nanoparticles (BNPs), carbon nanotubes (CNTs), graphene oxides, silica-based NPs, polymers, clay minerals and zeolites have been shown to decontaminate soil and water (Awad et al., 2020; Mukhopadhyay et al., 2020; Sarkar et al., 2018; Zou et al., 2016). Applications of NMs supported on clay minerals, zeolites, activated carbon and biochar have also improved the reactivity and contaminant removal performances of NMs (Mandal et al., 2018). Reactive nanomaterials can chemically reduce and/or aid in the catalytic reactions to degrade, detoxify and transform specific pollutants (Kumar et al., 2020a). Expediting the cleanup of contaminants in water and soil using NMs holds the potential to improve environmental health for human civilization in meeting multiple SDGs.
Based on the functions of various NMs, they can be classified as adsorbents (for adsorption of contaminants), catalysts (for degradation/transformation of pollutants) and membranes (pressure-driven technique for wastewater and seawater treatment) (Anjum et al., 2019). However, most of the literature focuses on the remediation of aqueous systems, and most of these studies are at the bench scale. Cleanup of contaminated soils using NMs has received less attention. Multiple technological, societal and economic bottlenecks (e.g., high preparation and implementation costs of NMs, a lack of desired contaminant removal efficiency under in-situ conditions) have hindered the widespread application of nanotechnologies in environmental remediation.

No comprehensive critical review is currently available that discusses both water and soil remediation using various types of nanomaterials, their fates and concurrent effects on living organisms, feasibility in field-level applications, environmentally benign and inexpensive synthesis methods, and scientific, societal and economic bottlenecks hindering widespread application, which are addressed for the first time in this work. Specifically, focus has been made on toxic trace elements, pesticides/herbicides, dyes and selected aromatic compounds, which are most encountered in various industrial systems/discharges, wastewater, contaminated irrigation water and agricultural systems.

2. Nanomaterials for contaminants remediation in water

Nanomaterials can be grouped into: (i) metal-based or inorganic NMs, (ii) carbonaceous NMs, (iii) polymer-based NMs, and (iv) composite NMs (Guerra et al., 2018). Fig. 1 depicts a schematic representation of various types of NMs used for the removal of environmental contaminants. Metal based NMs (e.g., Fe-based NPs, Cu-based NPs, BNPs) are widely used in environmental remediation followed by carbonaceous NMs (e.g., CNTs, graphene and graphene
oxides), while polymer (e.g., chitosan, alginate) and composite (e.g., clay-polymer nanocomposites, zeolite and biochar supported) NMs have received considerable research attention but limited practical applications (Guerra et al., 2018; Mukhopadhyay et al., 2020). Fe-based NPs have been successfully used in the field, in addition to a few examples of Cu-based NPs, BNPs, other metal oxide NPs (e.g., TiO$_2$, ZnO) and CNTs. The main motivations for using NMs for water and soil treatment are: their high selectivity, high adsorption capacity (due to high specific surface area and numerous adsorption sites), and easy regeneration after use.

2.1 Iron-based nanoparticles

Iron-based NPs include various oxidic NPs (either magnetic or non-magnetic) as well as nZVI, as discussed below:

2.1.1 Iron oxide NPs

Iron-based NPs (Fe NPs) such as iron oxides (e.g., hematite ($\alpha$-Fe$_2$O$_3$), maghemite ($\gamma$-Fe$_2$O$_3$), and magnetite (Fe$_3$O$_4$)) and oxy-hydroxides (e.g., goethite ($\alpha$-FeOOH) and lepidocrocite ($\gamma$-FeOOH)) were reported to be effective adsorbents of As and other heavy metals (Supplementary Information: Table S1) in water. For instance, a novel nano-adsorbent was prepared by using Fe$_3$O$_4$ magnetic core shelled by mesoporous silica (Vojoudi et al., 2017). The obtained material was then modified with bis(3-triethoxysilylpropyl) tetrasulfide and used to remove heavy metals from aqueous solution. The adsorbent removed 303, 256.4 and 270.3 mg/g of Hg(II), Pd(II) and Pb(II) ions, respectively (Vojoudi et al., 2017). The magnetic Fe$_3$O$_4$ NMs were found suitable for the remediation of aqueous Cu$^{2+}$, Ni$^{2+}$, Cd$^{2+}$ and Zn$^{2+}$. The amount of Cu$^{2+}$, Ni$^{2+}$ and Zn$^{2+}$ adsorption by Fe$_3$O$_4$ were 11.5, 6.07, 9.68 and 11.1 mg/g, respectively, at pH 6.0 after 50 min of
reaction time (initial metal concentration = 50 mg/L for each metal ion; adsorbent dose = 6 g/L) (Ebrahim et al., 2016). Following modification with 2-mercaptobenzothiazole, magnetic Fe₃O₄ NPs removed 98.6% Hg(II) from a solution that initially contained 50 ng/mL Hg(II) in just four minutes through a complexation mechanism, versus 43.7% removal by the unmodified NPs (Parham et al., 2012). Green-synthesized α-Fe₂O₃ NPs using banana peel extracts showed high As(V) adsorption capacity (2.72 mg/g) (Majumder et al., 2019). Similarly, Fe oxide NPs synthesized from green tea leaf extracts removed 13.7 mg/g As(V) from aqueous solution (Kamath et al., 2020). Fe NPs supported on inert materials such as clay minerals, zeolites and biochar can improve the speed and efficiency of contaminant remediation by enhancing the dispersion of NPs and preventing their passivation and/or degradation (Supplementary Information: Table S1; Section 2.9). Apart from adsorption, Fe oxide NPs such as Fe₂O₃ and Fe₃O₄ can degrade phenol, aniline, and dye compounds via photochemical oxidation reactions (Fig. 2) (Saharan et al., 2014).

2.1.2 Nano-scale zero valent iron (nZVI)

ZVI (Fe⁰) applied to groundwater was shown to be a strong adsorbing and reducing agent of redox-sensitive contaminants (e.g., Cr(VI), As(III), chloroethylene compounds), and displayed a low toxicity to biota living in the surrounding environment (Chekli et al., 2016). Considering these advantages, researchers have used nZVI for decontaminating oxyanion (e.g., CrO₄²⁻, TcO₄⁻, AsO₃³⁻/AsO₄⁵⁻, and SeO₃²⁻/SeO₄²⁻) and oxycation (e.g., UO₂²⁺, VO₄³⁻) contaminants in water (Supplementary Information: Table S1).

In some cases, nZVI was further modified to prepare advanced nanoremediation agents. For example, bare nZVI (B-nZVI) was modified with hydroxyethyl cellulose (E-nZVI) and hydroxyl
propylmethyl cellulose (P-nZVI) to remediate dye compounds in water (Wang et al., 2015b). The
discoloration efficiency was 93.4, 96.3, and 98.6% by B-nZVI, E-nZVI, and P-nZVI,
respectively, at 0.7 mg/L initial dye concentration (Wang et al., 2015b).
The colloidal forms of ZVI (µm and nm particle sizes) can be mixed into natural aquifers to
readily degrade or adsorb various pesticides (e.g., alachlor), dyes (e.g., malachite green, reactive
green) and other organic contaminants (e.g., trichloroethylene, pentachloroethylene) (Lin et al.,
2018). The nZVI interacts with heavy metals and metalloids through precipitation (Cu(II), Pb(II),
Cd(II), Co(II) and Zn(II)), co-precipitation (Ni(II), Cr(VI), Se(VI)), redox reactions (As(V),
Pb(II), Hg(II), Cu(II), Ag(II) U), and adsorption (Cr(VI), Ni(II), Se (VI)) (Pasinszki & Krebsz,
2020). The catalytic activity of nZVI at field conditions can be compromised due to its poor
stability and agglomeration behavior (Stefaniuk et al., 2016). However, peroxide free Fenton-
type reactions can catalyze organic contaminant degradation to overcome these limitations of
nZVI (Pasinszki & Krebsz, 2020). The agglomeration of nZVI at large scales in aquifers may be
problematic as this can cause the clogging of pores and reduce inherent hydraulic conductivity.
Hence, future research should be concentrated on the modification of nZVI to reduce its
agglomeration behavior at field conditions.

2.2 Copper-based nanoparticles

Copper based nanoparticles (Cu NPs) have chemical, photocatalytic, optical and electro-thermal
properties applicable to remediation. Specifically, copper oxides (CuO and Cu₂O), are well-known
p-type semi-conductors with a high thermal stability and chemical reduction potential (Isherwood,
2017). Positive surface charge, optical properties at visible wavelength, and the high surface area
of Cu NPs are the beneficial properties for degradation, reduction, and adsorption of inorganic and
organic contaminants (Khalaj et al., 2018) (Supplementary Information: Table S2). For example, 
CuO NPs synthesized via a sol-gel procedure was used for Cd\(^{2+}\) and Ni\(^{2+}\) removal from aqueous 
solution, wherein high pH of the aqueous medium generated surface negative charge on the 
adsorbent, and stimulated metal adsorption by electrostatic attraction (Hassan et al., 2017). Zero 
valent Cu NPs (Cu\(^0\)) (dose=2 g/L, pH=7.0) degraded 2,4-dichlorophenol (7.5 mg/L) to the tune of 
60% within 5 days of reaction (Chang et al., 2019). Nutrients removal (N, P) from activated sludge 
using Cu-based NPs were investigated where phosphate removal capacity reached 98%, and N 
removal reached ~73% at a 5 mg/L dosage of NPs (Chen et al., 2012). CuO NPs also degraded 
nitrobenzene in aqueous solution upon sonication for 25 min via a Fenton reaction (•OH radicals) 
(ElShafei et al., 2014). Furthermore, green synthesized Cu-based NPs using Punica granatum leaf 
electrostatic attraction, with an adsorption capacity of 166 mg/g MB 
extracts improved the functionality of nanoparticles for removing methylene blue (MB) from 
aqueous solution through electrostatic attraction, with an adsorption capacity of 166 mg/g MB 
(Vidovix et al., 2019). However, the increasing application of Cu-based NPs raised concerns of 
negative environmental impacts to living organisms (Chen et al., 2012). The phytotoxicity of Cu 
NPs on wheat (Perreault et al., 2014), the cytotoxicity of the NPs on human epithelial cells 
(Moschini et al., 2013), NP-caused growth inhibitions, the Cu uptake of Arabidopsis thaliana upon 
application of Cu NPs (Wang et al., 2016), and their toxic effects on aquatic organisms such as 
Hydra magnipapillata have been reported (Murugadas et al., 2016). Therefore, it is prudent to 
synthesize encapsulated or supported Cu NPs, which have low toxicity toward organisms while 
retaining a high contaminant removal capability.

2.3 Bimetallic nanoparticles (BNPs)
BNPs contain two metallic elements, exhibiting properties related to each metal and resulting from synergistic interactions between two metals. The assembly of BNPs can be as random alloys, alloys with an intermetallic compound, cluster-in-cluster or core-shell structures (Zaleska-Medynska et al., 2016). The shape and size of metallic NPs are strictly dependent on their mode of preparation that also influences the physicochemical properties of the final product (Zaleska-Medynska et al., 2016). Preparation methods for the production of BNPs include chemical reduction, green synthesis, microemulsion method, photodeposition, and radiolysis (Zaleska-Medynska et al., 2016).

BNPs can remediate multiple contaminants in aqueous systems (Scaria et al., 2020). A Fe$_{0.9}$/Cu$_{0.1}$ BNP removed As(V) (60.22 mg/g) from aqueous solution (initial As(V) concentration = 200 mg/L; adsorbent dose = 2.5 g/L) (Sepúlveda et al., 2018). Incorporation of relatively low amounts of Cu in the Fe/Cu BNP resulted in a non-uniform core-shell structure with agglomerate-type chains of magnetite that enhanced electron transfers among the metals (Fe/Cu) and the target metalloid (As); hence, the adsorption of As(V) increased (Sepúlveda et al., 2018).

To decontaminate Se(IV) in groundwater, Fe-Mn binary oxide NPs were synthesized and stabilized with starch and carboxy methyl cellulose (CMC) (Xie et al., 2015). The starch-stabilized NPs were more effective than CMC stabilized NPs in adsorbing Se(IV), with maximum adsorption capacities of 109 and 95 mg Se/g for the starch- and CMC-stabilized NPs (Xie et al., 2015).

Ascorbic acid-stabilized Fe/Pd BNPs and silica-based Fe and Fe/Fe-oxide NPs were successfully tested for degrading trichloroethylene in water (Meeks et al., 2012). Due to high catalytic activity of BNPs, Fe/Ni-polystyrene cation exchange resin composites showed nearly 91% degradation and/or dechlorination of trichloroethylene (20 mg/L initial concentration) (Zhou et al., 2016).
Similarly, biochar-supported Ni/Fe BNPs also enhanced the reduction of 1,1,1-trichloroethane (1,1,1-TCA) in groundwater remediation (Li et al., 2017). The 1,1,1-TCA removal efficiency increased up to 99.3% when the BC to Ni/Fe mass ratio reached 1.0 (Li et al., 2017).

2.4 Other metal oxide nanoparticles

The oxides of Ti, Mg, and Zn have proven useful for removing contaminants from the environment although the application of metal oxide nanoparticles can influence mineral nutrition, oxidative stress and photosynthesis of plants (Rizwan et al., 2017). Some nanoparticles synthesized with the mediation of plants and/or plant products (e.g., Au NPs from *Cassia fistula*, FeO from *Rumex acetosa*) have been reported to be beneficial in environmental, agricultural and biomedical applications (Rai et al., 2018). TiO$_2$ NPs displayed a high photocatalytic degradation efficiency of 90.24% at a 20 mg/L initial concentration and pH 5.0 for imidacloprid in an aqueous system (Akbari Shorgoli & Shokri, 2017). The catalytic activity of flower-like nanostructured rutile (TiO$_2$) was used to rapidly degrade methyl orange (MO) and inactivate drug-resistant bacteria such as *Klebsiella pneumonia* (Körösi et al., 2016). Similarly, photodegradation of levofloxacin by ternary nano Ag$_2$CO$_3$/CeO$_2$/AgBr photocatalysts under visible-light irradiation was investigated and a double Z-scheme photocatalytic mechanism was proposed, which involved an electron transfer process by the active participation of radicals such as h$^+$, O$_2^-$ and OH in the photodegradation (Wen et al., 2018). Naphthalene was effectively removed (148.3 mg/g) from wastewater using ZnO NPs modified with 1-butyl-3-methylimidazolium tetrafluoroborate, and the removal capacity of the modified adsorbent was 122% higher than the bare ZnO NPs (Kaur et al., 2017). In spite of their capacity to remove a
wide range of contaminants, metal oxide NPs may cause ecotoxicological effects towards various organisms. Therefore, care should be taken in terms of dosage during their application.

2.5 Carbon nanotubes

Single and multi-walled CNTs (SWCNTs and MWCNTs) are widely used as adsorbents for wastewater purification. The rolling of a single graphene layer into a cylindrical shape creates a SWCNT, while the rolling of many concentric SWCNTs into a tubular shape creates an MWCNT (Gusain et al., 2020). The removal of contaminants through adsorption is more rapid for CNTs than other carbonaceous adsorbents (activated carbon, graphene, graphene oxides, and biochar) due to availability of reactive adsorption sites and short diffusion distance (Lee et al., 2018). The major surface functional groups (e.g., -COOH and -OH) of CNTs participate in the bulk adsorption of contaminants. Studies have been conducted to graft other functional groups (e.g., -NH₂ and -SH) onto the surface of CNTs to enhance the adsorption capacities (Supplementary Information: Table S3). The adsorption affinity of CNTs can be increased by functionalizing the surfaces of CNTs through various processes such as oxidation, nonmagnetic metal oxide coating and grafting of magnetic iron oxides (Sarkar et al., 2018). The mechanisms involved in the adsorption process of contaminants by CNTs are dependent on the surface properties of CNTs and the chemistry of the contaminant ions or compounds. The mechanisms may include chemisorption or physisorption, while the ionic radius and hydration energy of the contaminants are important factors that determine the adsorption mechanisms (Sarkar et al., 2018).

The most prominent application of CNTs in environmental remediation includes the removal of organic contaminants through membrane filtration due to the high stability and large specific
surface area of CNTs (Jame & Zhou, 2016). An electrochemically activated CNT filter was able
to generate ‘OH’ radicals from H₂O₂ to remove phenol from aqueous solution to the tune of 87%
within 4 h (Liu et al., 2015). CNTs also show catalytic activity to clean wastewater due to their
cylindrical hollow tubes, high mechanical strength, and electrochemical properties. Ruthenium
(Ru) precursor impregnated MWCNTs converted 100% aniline in wastewater within 45 min of
reaction time (Garcia et al., 2006). However, the catalytic activity of CNTs is limited due to their
hydrophobic nature, and the presence of impurities (Lee et al., 2018). Another prominent
application of CNTs is in sensor-based approaches for contaminant detection. A selective sensor
for Hg(II) was developed by adsorbing cold mercury vapor on SWCNTs in industrial wastewater
(Safavi et al., 2010). The sensor was able to sense as low as 0.64 μg/mL Hg(II) in various types
of wastewater samples (Safavi et al., 2010). Future research should be focused on the application
of CNTs for real water decontamination using membrane filtration, catalysis, and sensing
approaches while also concentrating on the ecotoxicity assessment of CNTs.

2.6 Graphene and graphene oxide

Graphene is a 2D structured material having a single atomic layer of sp² bonded carbon atoms,
with each atom bonded to 3 others in a hexagonal lattice. Graphene shows high strength,
durability and specific surface area (Meyer et al., 2007). Graphene oxide (GO) has a structure
similar to that of graphene, while having more oxygen containing functional groups (Ma et al.,
2017). The presence of hydrophobic moieties and π–π interactions in GO lead to high removal
efficiencies for aromatic pollutants (Ersan et al., 2017). Oxygen-containing surface functional
groups (-COOH, -OH and –C=O) may also be present in GO due to the incomplete reduction of
GO. Another oxidized form of GO is exfoliated graphene oxide (EGO), which contains various
surface functional groups such as hydroxyl, carboxyl, and epoxy groups (Ramesha et al., 2011).

The advantages of graphene oxides for water treatment are their colloidal stability and high dispersibility in water, while graphene-based nanocomposites (modified with organic molecules and magnetic graphene nanocomposites) show higher specific surface areas and improved functionality than unmodified graphene (Perreault et al., 2015). In addition, reduced GO (rGO) shows high electron transport capacity and increased interaction with metal contaminants (Gollavelli et al., 2013; Lin et al., 2019). The adsorption of dyes such as MB, methyl violet, and rhodamine B onto EGO and reduced GO (rGO) sheets has been widely studied in water (Supplementary Information: Table S4). The elevated negative charge density assists in the effective adsorption of cationic dyes on EGO. In contrast, rGO, which has a high surface area, is effective in anionic dye adsorption due to van der Waals interactions (Ramesha et al., 2011).

The prevalence of surface charges and different functional groups on EGO, GO, and rGO play important roles in the adsorption of polar contaminants such as phenolics and naphthol, charged heavy metals (Ahmad et al., 2020; Ersan et al., 2017), antibiotics such as sulfamethoxazole, sulfapyridine, and sulfathiazole (Çalışkan Salıhi et al., 2020), and volatile organic compounds (Kumar et al., 2020b). The adsorption of phenolic compounds generally increases with increasing reduction degree in GO, whereas the adsorption of heavy metal ions shows the reverse trend (Wang & Chen, 2015). Likewise, Cd(II) and organic pollutants were co-adsorbed onto graphene via surface-bridging mechanisms (Wang & Chen, 2015). The adsorption affinity of four aromatics on GO increased in the following order: naphthalene (NAPH) < 1,2,4-trichlorobenzene (TCB) < 2,4,6-trichlorophenol (TCP) < 2-naphthol (Pei et al., 2013). The \( \pi-\pi \) interaction was the main mechanism involved during TCB, TCP and 2-naphthol adsorption onto graphene (Zhou et al., 2015), whereas H-bonding and O-containing surface functional groups
were responsible for the adsorption of TCP and 2-naphthol onto GO (Pei et al., 2013). However, graphene-based NMs often suffer from low densities of reactive sites, including less oxygen-containing functional groups, while graphene-based nanocomposites show variable colloidal stability depending on modification type (Perreault et al., 2015). Future research should focus on the development of highly functionalized and stable graphene-based NMs for bulk removal of contaminants from aqueous solutions.

### 2.7 Polymer nanoparticles

The synthesis of polymer NPs follows two approaches: top-down and bottom-up (Krishnaswamy & Orsat, 2017). The top-down approach involves the dispersion of preformed polymers to produce polymer nanoparticles, while the bottom-up approach involves the polymerization of monomers to produce polymeric nanoparticles. Following the bottom-up approach, researchers synthesized hybrid polymer NPs from the ring-opening polymerization of pyromellitic acid dianhydride and phenylaminomethyl trimethoxysilane, followed by a sol-gel process to remove heavy metals such as Cu(II) and Pb(II) from water (Liu et al., 2010). These zwitterionic hybrid polymers adsorbed 0.28 and 1.56 mmol/g of Cu(II) and Pb(II), respectively, via electrostatic attraction when the initial metal concentrations were in the range of 0.001 to 0.1 mol/L, and the dose of adsorbent was 1 g/L (Liu et al., 2010). The development of a negative charge on the hybrid polymer NPs was mainly due to −COOH groups in the polymer hybrid which deprotonated to −COO− groups in aqueous system at pH > 4.0 and 5.0 during Cu(II) and Pb(II) adsorption, respectively, and was thus bound to positively charged metal ions on the NP surfaces (Liu et al., 2010).
MO was removed in an aqueous solution using polyamine nanoadsorbents. The MO adsorption capacity was increased by 32.04 and 30.28 mg/g, respectively, when the initial dye concentrations were increased from 10 to 100 mg/L at 65 °C and 25 °C, respectively. The MO adsorption was endothermic in nature, and the maximum MO adsorption capacity was 75.9 mg/g within 60 min of reaction time when pH of the medium was 6-10. Strong electrostatic attraction was the primary mechanism that caused maximum MO adsorption (Tanzifi et al., 2017).

Chitosan, a biopolymer, is widely used to synthesize NPs for environmental remediation due to its low toxicity and high biodegradability. In a recent study, chitosan NPs were synthesized through ionotropic gelation for encapsulating enzymatic activity (Alarcón-Payán et al., 2017). The chitosan-NPs were loaded with versatile peroxidases and were successful in the biodegradation of phenolic compounds. The chitosan-based enzymatic NPs had a higher affinity constant toward phenolic compounds, were more thermostable than free enzymes, and their operational stability was further enhanced in a real-world wastewater situation when modified with different aldehydes (Alarcón-Payán et al., 2017). Similarly, chitosan NPs prepared through ionotropic gelation between chitosan and tripolyphosphates showed a 98% Congo red (CR) removal efficiency and adsorbed 5,107 mg CR/g of adsorbent in an aqueous solution (Alver et al., 2017). CR removal was dependent on the pH, ionic strength, encapsulation time and tripolyphosphate concentration. The mechanism involved was a strong electrostatic attraction between the protonated amino groups, with anionic CR at low pH (Alver et al., 2017). However, chitosan suffers from poor solubility in water (soluble in acid) and stability, which restrict its applicability in a wide range of contaminant removal applications (Saheed et al., 2020). Future research should be carried out in order to remove these barriers by using novel modifications.
2.8 Nanomaterials supported on inert materials and polymers

Environmental applications of NMs supported on inert materials (bulky, stable and non-toxic to organisms) such as activated carbon, BC, clay minerals, biodegradable polymers, and zeolites have recently attracted widespread attention (Mandal et al., 2018). Their availability, low-cost, and less toxic nature made these support materials popular in the field of soil and water remediation (Krasucka et al., 2021; Lazaratou et al., 2020). Pristine clay minerals, zeolites, and biochar often suffer from low contaminant adsorption and poor regeneration capacity, which can be improved by supporting NMs (e.g., nZVI) on the former materials leading to improved functionality and dispersion of the NMs (Mukhopadhyay et al., 2020; Premarathna et al., 2019; Alam et al., 2020). For example, granular activated carbon (GAC) was used to impregnate NPs (e.g., nZVI), and the supported material subsequently removed nitrobenzene from water (Mines et al., 2018). Reduction of nitrobenzene (with an initial concentration of 500 μM) was achieved at up to 56.6% by GAC-nZVI, which further improved to 63.6% following an additional modification step of the material with a covalent organic polymer (Mines et al., 2018). The π-π interaction between the aromatic groups of covalent organic polymer materials and nitrobenzene likely facilitated the removal of the contaminant (Mines et al., 2018).

Clay minerals were used extensively to support NMs for environmental remediation applications. For instance, a cationic surfactant cetyltrimethylammonium bromide (CTMAB) was used to improve the hydrophobic property of Fe-NPs supported on palygorskite clay, and the nanocomposite removed acid orange 7 (AO-7) by 98.4% (initial concentration of 20 mg/L) within 2 h of reaction from aqueous solution. At low pH, dissolved oxygen in the solution enabled hydrogen ions to produce H2O2 and ·OH radicals, which provided more oxidants to degrade AO-7 (Quan et al., 2018). Palygorskite-carbon nanocomposites were prepared through
two methods: composite 1 involved a hydrothermal carbonization with starch on palygorskite, while composite 2 included a thermal activation (550°C for 3 h in a CO₂ environment) of composite 1 (Sarkar et al., 2015). Composite 2 adsorbed a large amount of anionic orange II dye (23.0 mg/g), whereas composite 1 efficiently adsorbed cationic MB (46.3 mg/g) (Sarkar et al., 2015). Similarly, a nanocomposite synthesized in-situ by embedding magnetite NPs into the palygorskite structure through the co-precipitation method had a maximum Pb(II) adsorption capacity of 26.6 mg/g (Rusmin et al., 2017).

nZVI can aggregate in aqueous solution when its concentration is high. Therefore, to avoid rapid aggregation and to improve its reactivity, zeolite supported nZVI (Z-nZVI) was prepared via the liquid phase reduction of Fe(III) salts (Suazo-Hernández et al., 2019). The maximum adsorption capacity of Z-nZVI was 11.52 mg As(III)/g, 48.63 mg Cd(II)/g, and 85.37 mg Pb(II)/g at pH 6, involving mechanisms such as electrostatic attraction, ion exchange, oxidation, reduction, co-precipitation, and complexation depending upon the ionic nature of heavy metal(loid)s (Li et al., 2018). nZVI supported on CTMAB-modified organobentonite was used as a reducing agent for organic contaminants such as 2-chlorophenol(2-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and pentachlorophenol (PCP) in an aqueous system; their removal efficiencies were 95.4, 96.8, 97.8, and 100%, respectively (Li et al., 2013).

Similar to clay minerals, biochar is another inert material used widely for supporting NMs (Liu et al., 2020). A novel GO-coated BC nanocomposite achieved a 30% enhancement in sulfamethazine sorption through π-π interactions between the antibiotic molecules and NPs (Huang et al., 2017). A ZVI-BC-chitosan nanocomposite was also shown suitable for removing heavy metals such as Pb(II) and As(V) and MB dye (Zhou et al., 2014). The novel nanocomposite removed Pb(II), As(V) and MB at 93, 95 and 68%, respectively (the initial
concentrations of Pb(II), As(V) and MB were 40, 21 and 20 mg/L, respectively) (Zhou et al., 2014). The Cr(VI) removal in an aqueous system was also achieved by using nZVI assisted BC composites where the adsorbent showed 58.82 mg/g Cr(VI) removal via electrostatic attraction, complexation, metal reduction, and precipitation reactions (Zhu et al., 2018). The nZVI/biochar composite can play a dual role, firstly by converting the contaminant into a less toxic form by nZVI, and then adsorbing the contaminant via the active surface functional groups present on biochar, involving electron donor-acceptor reactions, chemisorption, and electrostatic attraction mechanisms (Fig. 3).

Attempts were made to stabilize CNTs on BC to remove heavy metals from wastewater (Inyang et al., 2015). Pb(II) was removed from wastewater using multi-walled CNTs dispersed on BC hickory chips (pyrolysis at 600°C in N₂ environment for 1 h), and the nanocomposite adsorbed 31.05 mg Pb(II)/g (initial concentration of 40 mg/L) (Inyang et al., 2015). The authors (Inyang et al., 2015) also found that bagasse BC modified with sodium dodecylbenzenesulfonate-CNTs (prepared using the same conditions above) was successful in fixing sulfapyridine by 56% (the initial concentration was 20 mg/L, solid: solution = 2:1, reaction time 24 h) in wastewater.

Chitosan-based composite NMs were also successful in removing heavy metals. The efficiency of alginate-coated chitosan NPs (Alg-CS-NPs) in removing Ni(II) from industrial effluents was investigated (Esmaeili & Khoshnevisan, 2016), showing that nearly 95% of Ni(II) was removed from solution under the following conditions: pH = 3, initial Ni(II) concentration = 70 mg/L, adsorbent dose = 0.3 g, and contact time = 30 min (Esmaeili & Khoshnevisan, 2016). At pH 3.0, the formation of sparingly soluble hydroxides of metals occurred, which contributed to overall metal removal from solution. At a high initial Ni(II) concentration (70 mg/L), the competitive adsorption of Ni(II) on the outer surface of the NPs led to a high adsorption capacity, whereas a
high biomass dose (0.3 g) provided an increased surface area for the Ni(II) biosorption process (Esmaeili & Khoshnevisan, 2016).

Like chitosan, entrapment of nZVI in Ca-alginate beads (polymer) showed promising results for NO₃⁻ removal from groundwater. Ca-alginate beads acted as a bridge to bind the nZVI particles. Between 50-73% NO₃-N was removed by the alginate-entrapped nZVI, which was statistically similar to bare nZVI within the 2 h reaction period (Bezbaruah et al., 2009). Like NO₃⁻, TCE degradation was also achieved, up to 81-90%, due to encapsulation of nZVI within Ca-alginate beads. The encapsulation resulted in greater mobility of nZVI particles than the entrapment method, and the required amount of Ca-alginate was significantly lower than for the entrapment method (Bezbaruah et al., 2011).

Entrapped nZVI in the alginate polymer matrix showed enhanced removal capacity of 1,1,2-trichloroethane (TCA) during the treatment of hydraulic fracturing wastewater (Lei et al., 2018). Results suggested that nZVI entrapment in alginate with or without polyvinyl alcohol removed 1,1,2-TCA from water (62.6-72.3%) with lower Fe aggregation after 90 days. The nZVI provided a chemically reducing condition, while the polymers adsorbed 1,1,2-TCA during wastewater remediation. Sun et al. (2018) reported that alginate-polyvinyl entrapped nZVI, aged for 2-months, showed a high removal capacity for Cu(II) (84.2%) and Cr(VI) (70.8%), much higher than for freshly prepared beads. The corresponding removal efficiencies were 31.2 and 39.2% in case of Zn(II) and As(V), respectively. The aging effect of the adsorbent for removing heavy metals was dependent on electrostatic interaction and specific bond formation mechanisms (Sun et al., 2018).

2.9 Carbo-iron nanomaterials
Carbo-iron is a composite NM consisting of nZVI clusters on activated carbon colloids (ACC) with a particle size of 0.8 µm. The material is especially designed for the in-situ generation of reactive zones and contaminant source removal when applied in groundwater remediation processes (Bleyl et al., 2012; Mackenzie et al., 2012). The carbo-iron colloids (CIC) can overcome the limitations of nZVI during in-situ groundwater remediation. The ACC gets reduced by H₂ in order to form CIC. The ACC have sorption properties, while nZVI provides strong reactivity to degrade or immobilize the contaminants. For example, CIC produced 60% chlorine-free-C₂-hydrocarbons when degrading TCE (Mackenzie et al., 2012). Similarly, pentachloroethane (PCE) dechlorination in groundwater was achieved at field scale in Germany with NM transport lengths of several metres and fast PCE decomposition without forming toxic vinyl chloride (Mackenzie et al., 2016). However, the release of Carbo-iron NM (in g/L concentration) in the environment during groundwater treatment may have ecotoxicological effects on amphipod *Hyalella azteca* leading to inhibited weight, length, and feeding rate of the animal (Weil et al., 2016). However, the ecotoxicological data on *Daphnia magna* (Crustacea), *Scenedesmus vacuolatus* (Algae), *Chironomus riparius* (Insecta), and nitrifying soil microorganisms revealed no effect at 0.1 mg/L NM concentration in acute or chronic toxicity tests in groundwater contaminated with chlorohydrocarbons (Weil et al., 2019). The risks to organisms were minimized by around 50% after the first injection of Carbo-iron NM in heavily contaminated aquifer zones, which suggested more benefits of remediation than detriments due to toxicity effects (Weil et al., 2019).

### 2.10 Other nanomaterials

NPs such as NiFe₂O₄ and zinc aluminate were reported to degrade dyes in aqueous solution. For example, 77% degradation of MO (initial concentration of 10 mg/L) was achieved by NiFe₂O₄
NPs within 5 h of exposure to sunlight, compared to no significant degradation under dark conditions (Hirthna et al., 2018). The dye removal mechanism in this study followed an electron paramagnetic resonance type of photodegradation (Hirthna et al., 2018). Likewise, 98.28% photodegradation of MB (initial concentration 10 mg/L) was achieved in 150 min using bismuth doped zinc aluminate NPs (Kirankumar & Sumathi, 2017). Bismuth doping into zinc aluminate decreased the band gap energy significantly, which in turn increased the photocatalytic degradation of MB. A hybrid-nano Ag$_3$PO$_4$ composite was synthesized by a two-step solvothermal process using reduced graphene oxide (rGO), Ag$_3$PO$_4$ NPs and molybdenum dichalcogenides (MoS$_2$, 99%); the synthesized hybrid-nano Ag$_3$PO$_4$ composite was suitable for the degradation of 4-nitrophenol, with a greater photocatalytic activity and stability than pure Ag$_3$PO$_4$ NPs (Zhang et al., 2018a).

3. Nanomaterials for contaminants treatment in soil

Several studies have reported the immobilization of toxic metal(loids) in soils using NMs (Baragaño et al., 2020; Matos et al., 2017; Tafazoli et al., 2017). However, the fates of NMs after their application to soils for contaminant removal require proper understanding. Currently, available soil contaminant remediation strategies follow two main directions: (i) lowering the concentration of pollutants to well below a critical limit, and (ii) stabilization of pollutants within the soil to reduce their immediate risk to environmental receptors (Floris et al., 2017; Hou et al., 2020). There is a growing interest in NMs for soil remediation because of their large specific surface area, high chemical reactivity and selectivity, although their reactivity may vary with geochemical conditions. Reports are available on the use of NMs for the remediation of inorganic contaminants in soil (Supplementary Information: Table S5). Recently, nZVI$^*$s have
attracted widespread research attention in detoxifying soil due to their effectiveness in reducing or inactivating various metallic species present in soils (Jiang et al., 2018). An nZVI/Cu treatment reduced Cr(VI) by 99% at pH 5.0 (Zhu et al., 2016), while the Cr(VI) reduction efficiency increased from 14.58 to 86.83% without maintaining pH of the soil (Singh et al., 2012b). In the presence of diethylenetriaminepentaacetic acid (DTPA), Cr release decreased up to 81% due to the application of 4% bentonite supported nZVI (prepared using green tea leaf extract and FeSO$_4$.7H$_2$O). The reduction in Cr release by the same material was 79% in the presence of CaCl$_2$ in the soil. The mechanisms involved precipitation and surface complexation reactions on the bentonite-nZVI (Soliemanzadeh & Fekri, 2017).

The bioavailability of single and multi-metal(loid)s (As, Cd, Cr, Pb, and Zn) in contaminated soils in the presence of nZVI was assessed under acidic and calcareous soils. The availability of heavy metals and metalloids such as As, Cr and Pb was reduced by 82% upon an application of 10% nZVI (w/w), whereas the corresponding values for Zn and Cd varied from 31 to 75% and 13 to 42% (Gil-Díaz et al., 2017b). Furthermore, the stability and effectiveness of nZVI-s were confirmed in contaminated soils (Cd, Cr, and Zn) grown with barley plants. A 10% dose of nZVI enhanced the development of the barley plants and decreased the As uptake by decreasing the bioavailable As fraction (Gil-Díaz et al., 2016a; Gil-Díaz et al., 2016b). A nZVI/Ni BNPs prepared using NaBH$_4$ were applied to remediate Cr(VI) contaminated soils, and the reduction of Cr(VI) in the soil leachate reached as high as 99.84% at pH 5.0 (Zhu et al., 2017a).

Three commercial nZVI slurries from Toda (bare RNIP and RNIP-D; D denotes an organic dispersant) and from Nano Iron (25S) were used at different doses (1, 5 and 10%) to immobilize As and Hg in soils. A 5% application of nZVI showed a decreasing trend of exchangeable As (by >70%) in soil, whereas a 10% application of nZVI was necessary to achieve a reduction of
exchangeable-Hg between 63 and 90% depending on the nZVI and soil types. Overall, the 5% nZVI application rate was more effective in the reduction of exchangeable As, whereas RNIP and RNIP-D were most effective at a 10% application rate for the reduction of exchangeable-Hg (Gil-Díaz et al., 2017a). A long-term soil heavy metal(loid) immobilization study (6-15 years) using nZVI concluded that nZVI remained “reactive” after 6-15 years, corresponding to an observation that available Cu and As were lower in the nZVI-treated soil than in the untreated soil and pH was considered the factor most responsible for both As and Cu immobilization (Tiberg et al., 2016). A similar type of investigation on the impact of pH (4-8) and time (48 and 192 h) on nZVI-mediated Pb, Cd, Zn and As immobilization in soils was conducted. The Zn and Cd concentrations in soils decreased by 29-34% and 38-44%, respectively, at pH 8, while the corresponding values for Pb and As were 98 and 96%, respectively (Vítková et al., 2017). The authors (Vítková et al., 2017) confirmed that Fe/Al oxides or hydroxides, organic matter and aluminosilicates played a major role in governing the solubility of metals and metalloids in soils, along with soil pH.

The immobilization and degradation of organic contaminants by NMs in soil is sporadically studied. The removal efficiency of hexachlorobenzene by nZVI was investigated in the presence of competing or coexisting anions present in the soil (Su et al., 2012). HCO$_3^-$ had no effect on the decomposition of hexachlorobenzene, but Cl$^-$ and SO$_4^{2-}$ promoted rapid decomposition rates, while NO$_3^-$ competed with the contaminant molecules (Su et al., 2012). $p,p'$-DDT degradation using nZVI-B (prepared using the sodium borohydride method) and nZVI-T (commercially purchased) in soil showed a low rate of DDT degradation (22.4 and 9.2%) due to the presence of organic matter and other soil constituents (El-Temsah et al., 2016). Han et al. (2016) reported degradation half-lives of 37.5, 73.7 and 24.1 h for DDT in flooded soil at 35°C by nZVI, nZVI
coated with polyimide, and nZVI coated with sodium oleate, respectively. Similarly, the positive effect of Ni/Fe BNPs in reducing the phytotoxicity of polybrominated diphenyl ethers (PBDEs)-contaminated soil to Chinese cabbage was evaluated (Wu et al., 2016a). The germination rate, and shoot and root lengths of the Chinese cabbage in the Ni/Fe BNPs treated soil increased by nearly 15, 60, and 63%, respectively, compared to the control (Wu et al., 2016a).

Biochar supported nanoparticles have shown promise in heavy metal immobilization in soils, as they provide additional active sites for capturing metal ions (Zhu et al., 2017b). Biochar-supported nano iron phosphate particles were synthesized to remediate Cd(II) contaminated soil. The Cd(II) immobilization efficiency of the adsorbent was 81.3% after 28 days, and Cd(II) bioaccessibility (physiological-based extraction test) was reduced by 80.0%. Plant growth experiments proved that the composite inhibited the Cd(II) uptake to the below-ground and above-ground parts of cabbage mustard by 44.8% and 70.2%, respectively (Qiao et al., 2017).

Application of BC–supported nano hydroxyapatite reduced Pb by 56.8% after 28 days of application in a Pb-contaminated soil (Yang et al., 2016b), and a column experiment showed significant mobility of BC–supported nano hydroxyapatite. The immobilization rate of Pb in the soil was 74.8% after nano hydroxyapatite-biochar remediation (Yang et al., 2016a).

Heavy metals such as Pb, Cu, and Zn were also immobilized by calcium phosphate nanoparticles (CPNs) in shooting range soils. Application of these NPs to the soil decreased Pb and Cu concentrations by more than 90%, and Zn by 50% (Arenas-Lago et al., 2016). Other examples include nano-hydroxyapatite, which reduced Pb(II) concentrations in Ryegrass by 2.86-21.1% and 13.19-20.3% in the roots and shoots, respectively, due to the secretion of tartaric acid in the root rhizosphere that enhanced Pb adsorption onto the NPs (Ding et al., 2017).
BNPs and carbonaceous NMs have also been used for soil remediation. For example, CMC-stabilized Pd/Fe\(^0\) BNPs displayed a nearly 7-fold greater efficiency for \(\gamma\)-hexachlorocyclohexane degradation in soil as compared to Fe\(^0\) NPs (nFe\(^0\)) alone (Singh et al., 2012a). Similarly, biochar-supported Ni/Fe BNPs debrominated decabromodiphenyl ether at 30.2 and 69.0% higher rates than pristine Ni/Fe and biochar in soil, respectively (Wu et al., 2016b). Similarly, GO was used to remediate Cd-contaminated soils; results suggested that GO could adsorb up to 103.3 mg/g Cd(II) when applied at a high dose (1 g/kg), and could be used for remediating highly contaminated sites (Xiong et al., 2018a).

4. Approaches for contaminant nanoremediation

Nanoremediation involves various technical approaches such as adsorption, photodegradation, heterogeneous catalysis, the involvement of microorganisms (nano-bioremediation), and deployment of electrical fields (electro-nanoremediation) for applying NMs to remove or immobilize contaminants in the environment. Hence, it is important to understand how the above approaches work while employing NMs for remediation.

4.1 Adsorption

Adsorption of contaminants occurs on the surface of an adsorbent at the solid-liquid interface (Fig. 4). The solid surface of the adsorbent interacts with the adsorbate/solute in the solution, and they are attracted to each other by solid-liquid intermolecular forces (Sadegh et al., 2017). In the case of bulk adsorbents, various bond (e.g., ionic, covalent and metallic) requirements of the constituent atoms in the adsorbent are filled by other atoms in the material. Since the bonds of atoms at the surface of the adsorbents are not fully satisfied, they adsorb the adsorbate to achieve
a charge/bond balance. However, the nature of adsorption is highly dependent on the nature of the adsorbate species present in the liquid solution. Adsorption processes mainly include van der Waal’s forces, electrostatic attraction, and chemisorption (covalent bonding) (Gupta et al., 2016; Sadegh et al., 2017; Sadegh et al., 2016). In addition, adsorption also involves a mass transfer process in which a solute mass is transferred to the surface of a solid and bound by chemisorption or physical adsorption. High specific surface area of an adsorbent can considerably control the degree of adsorbate deposition onto the adsorbent (Sadegh et al., 2017).

4.2 Photodegradation

Photocatalysis has been one of the most successful processes to remove contaminants from the environment due to its low cost and environmental compatibility (Al-Mamun et al., 2019; Raizada et al., 2019). Photocatalysis is a photoreaction that can be enhanced in the presence of a catalyst (Fig. 5). During photocatalytic activity, electron-hole pairs are generated depending upon the type of catalyst. These electron-hole pairs also generate the superoxide radicals that degrade contaminants. TiO₂ NPs were used as catalysts for practical applications. A novel nano-TiO₂ photocatalyst doped with neodymium (Nd³⁺) was employed to remove Cr(VI) by catalytic reduction, obtaining a >99% efficiency in Cr(VI) reduction. Here, Nd³⁺ ions deposited on the TiO₂ surfaces facilitated the creation of sites for electron accumulation, and hence achieved a high Cr(VI) reduction rate (Rengaraj et al., 2007). However, TiO₂ promotes photodegradation primarily under UV-light, while other catalysts such as CeO₂ show rapid photodegradation rates under visible light (Qi et al., 2014). An Ag₂CO₃/CeO₂/AgBr nano-photocatalyst was designed by the in-situ loading of Ag₂CO₃ onto CeO₂ spindles via the corrosion process, and the material showed visible light degradation of levofloxacin (Wen et al., 2018). Various carbon-based
nanomaterials such as graphene composites containing NPs (e.g., TiO$_2$ NPs) showed enhanced photocatalytic activity. Under UV irradiation, the energy of photons was greater than the band gap of carbon materials, which generated valence band holes ($h^+$) and band electrons ($e^-$). The holes produced superoxide radicals that degraded the organic contaminants, while electrons from superoxide radicals reduced heavy metal contaminants (Raizada et al., 2019).

Likewise, the rGO/MS$_2$ (M= M$_0$, W) hybrid-nano Ag$_3$PO$_4$ composite was more suitable for a photocatalytic degradation of 4-nitrophenol than was pure Ag$_3$PO$_4$ (Zhang et al., 2018a). The Ag$_3$PO$_4$@MS$_2$/rGO composite photo-catalyst displayed a >98% degradation efficiency for 4-nitrophenol after four cycles of use. The MS$_2$/rGO hybrid strongly enhanced the photocatalytic stability of Ag$_3$PO$_4$ due to the reduction of Ag$_3$PO$_4$ to Ag$_0$ by photo-generated electrons (Zhang et al., 2018a). Khairy and Zakaria (2014) reported photocatalytic degradation of MO by Cu-doped TiO$_2$ NPs under both UV and visible light. Doping of metals (e.g., Cu) did not change the structure of the crystal, but a significant change was observed in the particle size and photodegradation rate. Cu-doped TiO$_2$ NPs had a higher MO degradation efficiency under UV irradiation (73%) than visible light irradiation (50%). The doping of metals in the pure oxide matrix served as electron-holes separation centers, which enhanced the degradation of MO (Khairy & Zakaria, 2014). Therefore, the introduction of doping metal ions can improve the catalytic activity of TiO$_2$ NPs under visible light illumination.

4.3 Heterogeneous catalysis

In heterogeneous catalysis, the phase of the catalyst must be different from the phase of the reactant. In general, heterogeneous catalysis involves a solid phase catalyst and a liquid phase reactant. The catalysts are employed to enhance the reaction or adsorption rates. However, mass,
heat transfer and thermodynamic parameters also affect the reaction rate (Sievers et al., 2016).

The most important parameter affecting the reaction rate of the catalyst is its surface area.

Heterogeneous catalysts can be used with NPs to improve the degradation of organic contaminants due to the advanced oxidation capacity of the catalysts. Several oxidants such as persulfate (PS), peroxymonosulfate (PMS) and hydrogen peroxide (HP) have been successfully used for removing contaminants. nZVI coupled with common oxidants such as NaClO, KMnO₄ and H₂O₂ resulted in high removal efficiencies of As(V), Cd(II), and Hg(II) within only 10-30 min (Guo et al., 2016). nZVI with PS showed a high removal capacity of 1,4-dioxane and As(III) from contaminated water, where the As(III) removal capacity of PS/nZVI was 115.27 mg/g, and the 1,4-dioxane degradation rate was 0.0347 h/mg/min (Kang et al., 2018). Similarly, PS/nZVI removed nearly 97% of trichloroethene (TCE) in the presence of ethylenediaminetetraacetic acid (Dong et al., 2017).

Bimetallic nZVI NPs were used for dual Fenton oxidation and reductive dechlorination of 2,4-dichlorophenol. A nZVI-Fe/Pd heterogeneous catalyst composite showed an approximate 16% reductive dechlorination efficiency, and a 28% Fenton oxidation efficiency for 2,4-dichlorophenol (Li et al., 2015). A combined application of nZVI and bisulfite (S(IV)) revealed that an increased Fe⁰ concentration in the Fe⁰/S(IV)/O₂ system improved sulfamethoxazole removal from aqueous media due to an accelerated activation of S(IV) and Fe⁰ corrosion (Du et al., 2018).

4.4 **Electro-nanoremediation**

Pre-magnetization by the application of a weak magnetic field was suitable for promoting the corrosion of Fe⁰, which might enhance the removal rates of contaminants by nZVI in soil and water.
systems (Pan et al., 2017). In view of this principle, electrolysis was applied to micro-sized Fe\(^0\) (mFe\(^0\)) for \(p\)-nitrophenol (PNP) removal (Xiong et al., 2018b). The results suggested that the rate constants of PNP removal by electrodialysed-mFe\(^0\) (Ele-mFe\(^0\)) were 1.72-144.50 fold higher than those of pristine mFe\(^0\) under various conditions because the electrolysis aggravated the corrosion of mFe\(^0\) by releasing Fe(II) ions (Xiong et al., 2018b). Similarly, a combined system of nZVI and electro-kinetic remediation was used to study the transport and degradation of molinate in soils. Molinate was degraded by nZVI in soils at slower rates than in an aqueous system due to the heterogeneous nature of the soil (Gomes et al., 2014). The molinate degradation occurred via the oxidative pathway, which involved oxygen and the formation of hydrogen peroxide and hydroxyl radicals (Gomes et al., 2014). nZVI was employed along with electrokinetic treatment for the degradation of chlorinated ethenes (CEs) in the presence of *Dehalococcoides* spp. and *Desulfitobacterium* spp. (Czinnerová et al., 2020). The combined treatment resulted in a rapid 75% decrease of cis-1,2-dichloroethene (cDCE) concentration in the contaminated area, and produced methane, ethane, and ethene as the end products. The treated aquifer showed increased activity of organohalide-respiring bacteria, and cDCE-oxidizing methanotrophs and ethenotrophs proliferated near the anode under low oxygen conditions. The nZVI treatment resulted in mild negative effect on indigenous bacteria, but the microbiome was restored within 15 days (Czinnerová et al., 2020). Application of nZVI with a direct current (DC) electric field led to a greater increase of CE remediation efficiency than nZVI alone in a study in the Czech Republic (Černíková et al., 2020). This method was environmentally sound for improving CE reduction efficiency by improving the longevity, migration and reactivity of the nZVI, and reduced the cost of treatment by five times compared to bare nZVI (Černík et al., 2019; Černíková et al., 2020). Only a limited number of studies have been conducted on the electro-nanoremediation of
contaminants assisted by NM s, but the potential of this method must be explored in the future for practical applications.

4.5 Nano-bioremediation

Biological technology offers cost-effectiveness and a low generation rate of toxic substances, but a relatively slower rate of remediation (Hou et al., 2020). Nano-bioremediation may be defined as the remediation of a contaminant using NPs and biological technology together for accelerating the removal/degradation rate of contaminants (Cecchin et al., 2017). The focus of the nano-bioremediation technique is to reduce the concentration of contaminants to a level where it becomes prone to biodegradation, and further reduce the contaminants to a safe limit through biodegradation. TCE was dechlorinated using a long-lasting emulsified colloidal substrate (LECS) that contained nZVI and microorganisms such as Dehalococcoides spp. and Desulfitobacterium spp. (Sheu et al., 2016). The supplement of LECS in TCE-polluted groundwater effectively stimulated the TCE dechlorination rate under anaerobic conditions (Sheu et al., 2016). Moreover, the population of Dehalococcoides sp. increased from $2 \times 10^3$ to $1.2 \times 10^7$ cells/L, and Desulfitobacterium sp. increased from $1 \times 10^3$ to $7.4 \times 10^6$ cells/L after 60 days. Similarly, TCE removal efficiency was promoted when nZVI was integrated with Dehalococcoides sp. BAV1 compared to systems with nZVI and Dehalococcoides sp. alone, and the optimum dose of nZVI for maintaining microbial activity was found to be 0.05 g/L (Shanbhogue et al., 2017).

Integration of anaerobic bacteria such as organohalide respiring bacteria, sulfate reducing bacteria (SRB) and iron reducing bacteria (IRB) with nZVI also showed promising results in removing inorganic and organic pollutants (Dong et al., 2019). Here, nZVI provided reducing
conditions, where the generated hydrogen acted as an electron donor for hydrogenotrophic bacteria, resulting in the degradation of halogenated compounds. Xu et al. (2014) reported that ZVI was able to reduce higher congeners of PBDEs to lower congeners, and subsequently degradation was promoted by *Dehalococcoides* sp. CBDB1. Thus, complete degradation of PBDEs was achieved by the integration of nZVI with *Dehalococcoides* sp. CBDB1.

The combination of nZVI and SRB has also improved heavy metal removal from contaminated systems. Yi et al. (2009) reported that 98.1% of U(VI) was removed by a nZVI+SRB integrated system within 4 h of reaction, while the removal rate of the individual system of ZVI and SRB was 17.4 and 67.3%, respectively. Under anaerobic conditions, SRB transformed sulfate into sulfides (e.g., H$_2$S, S$^{2-}$ and HS$^-$) via the metabolism of organic matter. Then sulfide could bind with heavy metals to form stable complexes with SRB metabolites (Kumar et al., 2015).

Similarly, Vogel et al. (2018) investigated the microbial degradation of PCE in the presence of *Sulfospirillum multivorans*, *Desulfitobacterium* spp. and *Dehalococcoides mccartyi* together with Carbo-iron NM. The study suggested that embedded nZVI decreased the redox potential of the groundwater due to their reaction with oxygen, leading to nZVI-corrosion-induced formation of H$_2$ within 190 days after the injection, the latter promoting sulphate-reducing conditions.

A similar approach to test the effectiveness of a hybrid system using nano scale zinc oxide (n-ZnO) and lindane-degrading yeast *Candida* VITJzN04 for lindane degradation was evaluated (Salam & Das, 2015). The half-life of the lindane was lower (9 h) with an embedded bio-nano hybrid as compared to yeast *Candida* VITJzN04 (28 h); the enhanced lindane degradation by the bio-nano hybrid was attributed to the increased porosity and permeability of the yeast cell membranes (Salam & Das, 2015). SiO$_2$ NPs coated with a zwitterionic lipid derivative were used in the bioremediation of benzo[a]pyrene (Wang et al., 2015a). The authors used *Pseudomonas*...
aeruginosa, a gram-negative bacterium, and 1,2-dimyristoyl-sn-glycero-3-phosphocholine as a source of lipids, which adsorbed and sequestered benzo[a]pyrene and maintained the colloidal stability of NPs for their transport to the contaminant source (Wang et al., 2015a).

Another study using CMC-stabilized Pd/Fe\(^0\) (CMC-Pd/nFe\(^0\)) BNPs, and the microorganism *Sphingomonas* sp. Strain NM05 targeted the degradation of hexachlorocyclohexane (γ-HCH) in soil and found that the γ-HCH degradation efficiency was \(\sim 1.7–2.1\) times greater in the integrated system than the control system (Singh et al., 2013). Dechlorination of the PCB Aroclor 1248 was performed using Pd/nFe BNPs and *Burkholderia xenovorans* LB400 under anoxic conditions. Toxic equivalent values of polychlorinated biphenyls (PCBs) decreased from \(33.8 \times 10^{-5}\) μg/g to \(9.5 \times 10^{-5}\) μg/g after the nano-bioremediation treatment (Le et al., 2015).

Apart from organic contaminants, attempts have been made to immobilize heavy metals in soil through nano-bioremediation. *Citrobacter freundii* Y9, a Se reducing organism, secreted biogenic nano-Se\(^0\), which converted 46-57 and 39-49% of elemental mercury (Hg\(^0\)) in soils to its insoluble mercuric selenide (Hg-Se) form under oxygen-rich and oxygen-free conditions, respectively. Furthermore, an addition of sodium dodecyl sulfonate enhanced soil Hg\(^0\) remediation due to the increased release of intracellular nano-Se\(^0\) from the bacterial cells (Wang et al., 2017).

5. **Practical applications**

Studies on *in-situ* remediation using NMs are important, but available literature is limited. Most field studies are confined to nZVI applications for contaminants removal from groundwater. Therefore, we discuss *in-situ* remediation applications focusing on various practical modes of
nanoremediation along with a few examples of real field scale studies as well as issues that need to be resolved for the large-scale field application of NMs for environmental remediation.

5.1 Field-scale application of nZVI for groundwater remediation

Nanoremediation using nZVI requires specific conditions to be met for achieving the most effective outcome. Appropriate site characteristics in terms of location, geological conditions, soil hydrogeological conditions (e.g., porosity, hydraulic gradient, groundwater velocity), and soil physico-chemical composition (e.g., pH, type and concentration of contaminants, dissolved oxygen level, concentration of other ions, redox potential) need to be determined before the injection of nZVI for contaminant remediation. The above would ascertain effective infiltration of nZVI in the contaminated zone, and help to ensure the efficient degradation or adsorption of specific contaminants at in-situ conditions (Karn et al., 2009). At the field-level, most of the applications of nZVI are concentrated on the degradation of chlorinated solvents. However, field studies were also found successful for treatment of halogenated organic compounds, PAHs, heavy metals (Ni, Cr(VI)), diesel fuel, PCBs, and pesticides (Bardos et al., 2018). In a case study, three types of non-pumping reactive wells (slanting, horizontal and vertical) were mixed with zero valent micro- (dose 0-4 g/L) and nano-sized iron (Fe⁰) (dose 0-2 g/L) for nitrate removal in groundwater (Hosseini et al., 2018). Removal was primarily dependent on the contact time of the reactant with nitrate and the zone captured by the tube wells. Slanted non-pumping reactive wells showed higher NO₃⁻ reduction rate (57%) compared to the vertical (38%) and horizontal (41%) configurations (Hosseini et al., 2018). Earlier, nZVI was used to remove TCE from a groundwater aquifer (80 m³) with 1300 L total water capacity (Elliott & Zhang, 2001). Here, approximately 1.7 kg of nZVI equivalent, yielding a 0.75-1.5 g/L loading, was used to completely dechlorinate TCE
over a period of 2 days. Similarly, Gavaskar et al. (2005) reported the field application of nZVI (at
2 g/L loading) for TCE removal in 68000 L water in 7300 m³ of aquifer volume. Furthermore,
complete reduction of TCE in groundwater was observed using emulsified nZVI (at 140 g/L
loading) in an aquifer of 40 m³ with a 8500 L water capacity (Quinn et al., 2005). Chlorinated
hydrocarbons including TCE in the groundwater were also successfully removed using nZVI (at
30 g/L loading) in 75000 L of water in a 15000 m³ aquifer (Varadhi et al., 2005).

5.2 Permeable reactive barriers and direct injection

Permeable reactive barriers (PRB) consist of a permeable matrix that supports and anchors a
reactive material to retain contaminants when a plume passes through the matrix. The main
challenge of PRB systems is the costliness of the reactive barrier materials in removing target
contaminants at desired levels (Tasharrofi et al., 2020). A nZVI-zeolite composite was evaluated
to overcome the cost limitation of reactive materials in a PRB system to remediate aqueous
Cd(II) (Tasharrofi et al., 2020). The zeolite was able to disperse nZVI well, and prevented its
agglomeration. The nZVI-zeolite composite adsorbed 20.6 g/kg Cd(II) within 90 min (initial
Cd(II) concentration 50 mg/L), and discharged very low levels of Cd(II) back into the
environment, making the material suitable for application in PRBs (Tasharrofi et al., 2020).

Under a pilot scale application in the Czech Republic, nZVI was injected to successfully remove
chlorinated hydrocarbons on a short-term basis before the installation of a complete PRB
remediation system. The nZVI injection prevented the migration of contaminants to adjacent
areas outside the PRB (Bone et al., 2020). Direct injection can be used for both contaminant
source and pathway treatments. A known quantity of nZVI is applied to a known depth of an
aquifer either by gravity or by introducing pressure. The injection processes may include: (a)
direct push or a stationary injection point to emplace a nZVI slurry in the treatment zone, (b) hydraulic fracturing using air or water to create preferential flow, (c) liquid atomization (i.e., pulses of pressure during injection), and (d) injection through a carrier (e.g., surfactant) for delivery of nZVI in the vadose zone (Ding et al., 2013). Apart from trialling PRB and direct injection technologies under field conditions, future research should concentrate on the development of inexpensive and efficient modes of \textit{in-situ} nanoremediation.

\section*{5.3 Issues with field application of nanomaterials for remediation}

Field scale applications of various NMs in addition to nZVI are urgently needed for environmental remediation including soil contaminants treatment. However, the following issues should be considered to enhance the practical utility of nanoremediation.

\begin{enumerate}
\item One of the key concerns of NMs application is the lack of dose optimization. High application rates of NMs in water may be useful for removing a target contaminant, but it can be a serious concern when applied to soil. The large quantity of NMs required for remediating contaminated soils at the field scale is unmanageable using conventional production facilities. In addition, high concentrations of NPs (e.g., nZVI) may cause toxicity to microorganisms (Dong et al., 2019).
\item Standard protocols to apply NMs for environmental remediation are still lacking. Therefore, appropriate application procedures for different NMs need to be documented and updated for field scale applications.
\item Regeneration of applied NMs in soil needs further investigation. It is difficult to separate NMs from soil once they are added or injected because soil itself is a highly heterogeneous medium. Adsorbed contaminants may desorb from the nanoadsorbents after some period.
\end{enumerate}
Various NMs such as CNTs and GO, and NPs such as BNPs, polymer NPs, and Cu- and Fe-based NPs are quite expensive but have enormous potential for both organic and inorganic contaminant remediation at the field scale. Green synthesis techniques (as applied for nZVI) should also be considered for these NMs to minimize environmental toxicity.

The impact and fate of applied NMs on aquatic and soil organisms should be studied thoroughly before application to test their ecological and environmental safety (Besha et al., 2020).

Optimum operational factors (e.g., competing ions, pH, time, organic matter, temperature) of various NMs for remediating various contaminants requires standardization at the field level due to the heterogeneous nature of field sites.

6. Environmental risk of nanomaterials

The potentially vast applications of NMs for remediating contaminated soil and water have earned widespread research attention; studies have specifically vied to understand the mechanisms of NM interactions with environmental components, microbial communities and target contaminants (Biswas & Sarkar, 2019; Rai & Biswas, 2018). The deposition of NMs in the environment through soil and wastewater treatment processes has been reported to cause toxicity to microorganisms such as bacteria including plant growth promoting rhizobacteria (Lewis et al., 2019). nZVI is the most widely used NPs for the remediation of various contaminants in the environment. The fate of NPs, particularly in soils, depends on several key parameters, such as soil texture, pH and organic matter contents. nZVI might have toxic effects on microbial communities (Lefevre et al., 2016). For example, nZVI disrupted microbial cells by producing reactive oxygen species that caused cytotoxicity and changed the population and functional
composition of the microbial community (Lefevre et al., 2016). Similarly, nZVI particles at high concentrations showed a strain dependent antibacterial effect on *Escherichia coli* leading to cell inactivation via oxidative stress (Chaithawiwat et al., 2016a). Gram negative bacteria were more susceptible to nZVI toxicity than Gram positive bacteria (Chaithawiwat et al., 2016a).

Chaithawiwat et al. (2016b) reported that the *rpoS* gene was mainly responsible for resisting nZVI toxicity at cellular level. Unlike *E. coli*, *Pseudomonas putida* F1 exhibited high tolerance to nZVI at a 0.1 g/L dose by virtue of the rigid cell membrane of the bacterium (Kotchaplai et al., 2017).

Since nZVI is an efficient As(V) removal agent in aqueous systems, the effects of its excessive application on plants was studied using *Arabidopsis thaliana* grown hydroponically (Zhang et al., 2018b). Biosensors for inorganic phosphate (Pi) and Mg-ATP$^2^-$ were used to monitor *in vivo* Pi and Mg-ATP$^2^-$ levels in the cells. An excess nZVI exposure resulted in Pi starvation in plants, leading to adverse effects on plant growth (Zhang et al., 2018b). Additionally, earthworm species such as *Eisenia fetida* and *Lumbricus rubellus* were also affected by the application of nZVI in soil at a high dose (500 mg/kg). However, aging or oxidation of nZVI may reduce its toxicity level (El-Temsah & Joner, 2012). For example, Fajardo et al. (2015) reported that aged nZVI had no adverse effects on soil physico-chemical properties and *Caenorhabditis elegans* in a Zn-contaminated soil, although the Fe content in the soil was increased. However, in contrast to the Zn-contaminated soil, the growth of *C. elegans* was decreased in a nZVI-treated Pb-polluted soil (Fajardo et al., 2015).

Based on ecotoxicity tests performed by Hjorth et al. (2017), most nZVI products would receive no environmental hazard classification according to European regulations, except for the ball-milled nZVI particles; none of the other nZVI particles showed toxicity below a 100 mg/L.
An injection of nZVI to Cr(VI)-contaminated water rapidly decreased total Cr(VI) in the groundwater, whereas an ecotoxicological test on *Vibrio fischeri* with nZVI did not indicate any negative changes on the toxicity of the groundwater (based on the cultivable psychrophilic bacteria population and phospholipid fatty acid analysis) (Němeček et al., 2014). It is not clear whether NPs of metal oxides or metal salts are toxic to aquatic organisms. Microarray results suggested that exposure of *Daphnia magna* to CuO and ZnO NPs and their metallic salts had no significant differences between the species’ transcribed gene fragments (Adam et al., 2015). It was elucidated that the toxicity of ZnO and CuO NPs to *D. magna* was solely caused by toxic metal ions (Adam et al., 2015). Ti-based NPs also showed deleterious effects on microorganisms in soil (Li et al., 2016); hence, they should be replaced with less toxic metal oxide NPs such as Zn, Fe and Cu, where possible.

Toxicity of the NPs in water, particularly Fe NPs (e.g., nZVI), also depends on the mixing and dispersing agents present. There may be residual NPs in water even after pollutant removal is complete (Peeters et al., 2016). The dispersion of Fe NPs with tetramethylammonium hydroxide (TMAH) resulted in a slower settling of the iron aggregates. In Milli-Q and forest spring waters treated with Fe NPs and dispersed by TMAH, the nano iron remained in solution for a day after the treatment, which represented a residual effect and may pose a threat to aquatic ecosystems (Peeters et al., 2016). Likewise, during the use of nano-TiO$_2$ in aqueous systems, a combination of humic acid and HCO$_3^-$ increased the release of Ti in water. Olabarrieta et al. (2018) reported that the nano-TiO$_2$ rejection rate was generally above 95% in a low-pressure membrane filtration pilot plant, and 2.3 g of the NPs could be released when treating 31 m$^3$ of tap water with 2 mg/L nano-TiO$_2$. 
CNTs can be toxic toward bacteria at the cellular level. SWCNTs with varying functional groups altered the gene and protein expressions of *E. coli* at even a low SWCNT concentration (10 μg/mL) causing cell perturbation (Anh Le et al., 2019). In contrast, CNT toxicity to bacteria could be eliminated by entrapping CNTs using polymeric gels such as alginate and poly vinyl alcohol (Le et al., 2016).

One of the key concerns in the treatment and remediation of chemical contaminants with NMs is the introduction of little-known man-made materials to the environment/nature. This stigma needs to be overcome to gain public acceptance of nanoremediation technologies. Risk assessments of engineered NMs have been conducted for at least two decades, and the perception of risk has begun to change to some extent. For example, Ag-based NPs, which are mainly used for antimicrobial activity and were thought to be very harmful to the environment, were found to pose a small overall risk to terrestrial environments because (1) only a small fraction of Ag NPs ultimately enter into the soil, (2) the nano-properties and activities of Ag NPs are diminishable quickly when present in the soil, and (3) only minor bioaccumulation of Ag occurs in edible plant parts (Wang et al., 2018). Moreover, researchers have advocated the application of NM-based fertilizers and pesticides (e.g., Fe-, Cu-, Mg-, Mn-, Si-based NMs) directly to soil and/or on the plant bodies because these NMs pose negligible environmental risks but support crop production (Adisa et al., 2019; Kopittke et al., 2019). Nevertheless, NMs of various types may be associated with different risks, which should be researched thoroughly before their application for environmental remediation.

7. Risk management applications of nanoremediation
Risk management includes three strategies: (i) contaminant removal at the source, (ii) plume control or pathway treatment, and (iii) limiting the use of resources. Risk management can be achieved by eliminating contaminants at their source point and destroying the linkage between contaminant sources, pathways (migration of contaminants), and receptors (Nathanail & Bardos, 2004). However, complete mass removal of contaminants at the source is quite difficult due to residues and the presence of non-aqueous phase liquids (NAPL) (e.g., chlorinated solvents), contributing to low concentrations of contaminants that are still in excess of regulatory groundwater threshold values (Gavaskar et al., 2005). nZVI is capable of managing source and pathway treatments under in-situ conditions in the host geologic material as well as in groundwater. The application of nZVI in geologic media through direct injection can cause the in-situ degradation of organic contaminants, and adsorption and transformation of inorganic contaminants due to pH and redox potential changes (Pasinszki & Krebsz, 2020; Stefaniuk et al., 2016). In groundwater, nZVI application by direct injection into the in-situ source zone, or via groundwater funnelling to an in-situ treatment zone (e.g., PRB), and using integrated approaches (e.g., nano-bioremediation, electro-nanoremediation) are effective risk management applications of nanoremediation (Bardos et al., 2015). Bioengineering approaches such as using biomarkers (a tool of biological monitoring) to track nZVI during contaminant treatment may effectively minimize the risk of release of contaminant-loaded NMs into the environment (Patil et al., 2016). Permeable iron barriers in shallow aquifers capable of collecting nZVI after use could also be useful for minimizing the further release of NMs into the system (Patil et al., 2016). However, risk management studies involving other NMs under field conditions are currently scarce, and warrant future research.
8. Societal and economic implications

Sustainable remediation involves the elimination or control of a contamination risk in a safe and timely manner, while optimizing the environmental, social, and economic values of the work (Nathanail et al., 2017). Sustainable remediation may comprise of one or multiple remediation technologies including in-situ and ex-situ treatments, and a combination of physical, chemical, thermal and biological processes (Nathanail et al., 2017). The International Standard for Organization (ISO) has taken the policy, legislations, and practices for risk management around the world through committee draft ISO/CD 18504, and published international standard ISO/DIS 18504. To make the concept widely popular and comprehensive to end users (practitioners, regulators, and stakeholders in land quality), clear definitions of the approaches, standard methodologies, and demonstrations of specific remediation strategies are the need of the hour. The approaches should meet the three pillars of sustainable remediation: (a) inexpensive, (b) eco-friendly, and (c) acceptable to society.

8.1 Societal implications

While in-situ nanoremediation has become environmentally and socially sustainable (Corsi et al., 2018), exposures of human beings to NMs through drinking of water, inhalation of polluted air, and contact with skin, potentially leading to health problems involving the lungs, liver, respiratory system, and brain. To overcome these barriers, monitoring and interventions must be performed. To promote this technology without causing harm to humans, the following steps must be considered (Corsi et al., 2018):

1) Nanoremediation techniques (success stories) requires documentation in a simple and comprehensive manner.
(2) Development of standard protocols is needed to evaluate the ecosafety and economic sustainability of NMs.

(3) Manufacturers need to inform the consumers via proper labeling of products of the level of risks, potential ecotoxicity, health impact and risk management of nanoproducts.

(4) Science-Policy-Interfacing in needed through conversations among scientists, Government/non-Governmental officials and extension workers about the benefits and potential hazards of NMs, and the hazard mitigation strategies.

(5) High quality and thoroughly validated information (including levels of risks) are needed for a policy framework to encourage in-situ uses of NMs for treating contaminated soil and water.

8.2 Economic implications

The costs of remediation technologies encompass capital costs, reagent costs, maintenance, overhead costs and operational costs. The use of nZVI's for remediating organic pollutants such as TCE, chloramphenicol, lindane, and heavy metals such as Pb, Zn, As, Cr, Cd, and Pb, is less expensive than existing advanced technologies such as membrane and ozonation (Adeleye et al., 2016). Current technologies such as adsorption and precipitation for heavy metal remediation generate substantial solid waste production that can be mitigated by the effective application of nanoremediation technologies (metal oxides and nZVI). For As and NO₃⁻ remediation, using nZVI appears to be less expensive than carbon-based nanotechnologies (Adeleye et al., 2016). Although a laboratory scale experiment requires substantially lower amounts of nZVI's, costs for a field scale application are still high. nZVI production costs are approximately $0.05-0.10/g, whereas micro and bulk Fe⁰ cost less than $0.001/g to produce (Adeleye et al., 2016). TiO₂ NPs are currently available at prices ranging from roughly $0.03/g to $1.21/g (Lu et al., 2011).
Photocatalysts can potentially be regenerated, as they are hardly degraded during oxidized radical production (Kim et al., 2012), and have potential to further decrease the overall costs associated with using photocatalytic metal oxide NPs for water treatment. Similarly, for carbon-based NMs, the cost of nanotechnology varies widely depending upon the material type, functionalization, purity level (wt. %), and grade. Currently, prices range between $2.50 - 1000/g for graphene and derivatives, $0.10 - 25/g for MWCNTs and $25 - 300/g for SWCNTs. Aqueous Pb(II) removal using SWCNTs via adsorption may cost an average of $2.2/g-Pb (Adeleye et al., 2016). However, carbon-based NMs are extremely expensive from a remediation point of view. The best way to reduce the cost is to further develop regeneration and recycling strategies for nanomaterials. Improved marketability of nanoremediation technology can potentially be achieved via: (1) encouraging NM synthesis from inexpensive renewable sources such as leaf extracts, agro-wastes, microorganisms, and natural clay minerals, and (2) identifying factors that govern the acceptability of the technology among various stakeholders, and taking regional and need-based adoption strategies.

9. Conclusions and future outlooks
The NMs discussed in this article exhibit high potential for the remediation of contaminated soil and water. Inorganic and organic modification of NPs along with supporting agents such as clay minerals, biochar, biodegradable polymers, and minimal amounts of zeolite improves the contaminant removal capacity of the NMs. The high degradation capacities and photodegradation efficiencies of NMs, and their possible uses as mediums to target multiple contaminants hold great promise. The practical field application of NMs is, however, still limited to nZVI for soil and groundwater remediation. NMs may pose positive or negative impacts on
living organisms, the environment, society and economy, which should be evaluated in a case-specific context. Appropriate documentation of NM risks, field scale validation of remediation results, science-policy interface consultations, and suitable market development initiatives are ways to increase the popularity and acceptability of nanoremediation technologies.

We put forward the following research challenges for a wider acceptability of nanoremediation technologies:

(1) Future research on both the fundamental and practical aspects of nano-bioremediation is recommended. The operational conditions of nano-bioremediation such as pH, dosage, temperature, and solution composition should be optimized to work in real, field contaminated systems.

(2) Molecular mechanisms of biological degradation and removal in nano-bioremediation techniques need further investigation.

(3) Since soil is a complex and heterogeneous system, efficient soil remediation techniques must be developed. The influence of the application of NMs on soil geochemistry, microbiology, and ultimately toxicity in soil systems should be further studied.

(4) Most extant research on nanoremediation is confined to laboratory studies and modeling. Transferring these studies to in situ conditions is a challenge. Systematic experimentation of the impact of NMs on soil environments is needed in order to develop standard protocols and doses for the application of NMs at the field level.

(5) Supporting NMs on inert materials such as activated carbon (e.g., Carbo-iron), clay minerals, polymers, zeolite, and biochar is believed to improve contaminant remediation performance while simultaneously reducing unwanted risks of NMs to terrestrial and aquatic organisms. This requires future research attention for field validation and uptake by industry.
(6) Ecotoxicological and risk assessment studies of NMs are still limited to specific bacteria and their strains. Studies on the effect of NMs on diverse living organisms, including humans, and evaluation of toxicity transmission along the food chain are the need of the hour.

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Conflicts of interest

There is no conflict of interest to declare.

Contributions

RM, BS and YSO conceptualized the work. RM and BS prepared the first draft, and revised the manuscript. All authors provided input on sections in later drafts and edited the manuscript.
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Fig. 1. Types of nanomaterials used for the removal of environmental contaminants.
**Fig. 2.** Factors and processes affecting the adsorption and degradation of contaminants by metal-based NMs.
Fig. 3. Mechanisms of contaminants removal by nZVI/biochar composites (adapted from Zhu et al., 2018)
Fig. 4. Adsorption of contaminants onto nanoparticles, and mechanisms involved (adapted from (Mukhopadhyay et al., 2020; Uddin, 2017)).
Fig. 5. Photodegradation of contaminants in the presence of a photocatalyst nanoparticle (adapted from (Chong et al., 2010)).
Supplementary Information for:

Nanomaterials for sustainable remediation of chemical contaminants in water and soil

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Table S1. Contaminant adsorption, degradation and removal efficiencies by Fe NPs in water systems.

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<tr>
<td>Starch modified nZVI</td>
<td>NO₃⁻</td>
<td>91%</td>
<td>-</td>
<td>Force electromagnetism</td>
<td>Mofradnia et al., 2019</td>
</tr>
<tr>
<td>Zero valent (Fe/Ni) BNP</td>
<td>Profenofos</td>
<td>94.51%</td>
<td>-</td>
<td>Degradation by deprotonation at high pH</td>
<td>Mansourieh et al., 2019</td>
</tr>
<tr>
<td>Potassium persulfate modified Fe₂O₃</td>
<td>Aldrin, eldrin and lindane</td>
<td>Aldrin: 24.7 mg/g, Eldrin: 33.5 mg/g, Lindane: 10.2 mg/g</td>
<td>10 min</td>
<td>Removal by chemisorption</td>
<td>Lan et al., 2014</td>
</tr>
<tr>
<td>nZVI-B (Sodium borohydride method) and nZVI-T (Commercially purchased) Zeolite-supported Fe NPs</td>
<td>DDT [1,1,1-trichloro2,2-bis(p-chlorophenyl) ethane]</td>
<td>nZVI-B: 92%, nZVI-T: 78%</td>
<td>24 h</td>
<td>Degradation due to highly reactive functional surface sites</td>
<td>El-Temsah et al., 2016</td>
</tr>
<tr>
<td>nZVI</td>
<td>Methomyl</td>
<td>100%</td>
<td>4 h</td>
<td>Degradation via photocatalytic oxidation</td>
<td>Tomašević et al., 2010</td>
</tr>
<tr>
<td>nZVI</td>
<td>Alachlor</td>
<td>92-96%</td>
<td>72 h</td>
<td>Reductive degradation by nZVI</td>
<td>Bezbaruah et al., 2009</td>
</tr>
<tr>
<td>nZVI</td>
<td>Tributyltin and trimethyltin</td>
<td>Tributyltin: 96%, Trimethyltin: 40%</td>
<td>7 days</td>
<td>High pH (8.0) followed by acidification with citric acid at pH 3.0</td>
<td>Peeters et al., 2015</td>
</tr>
<tr>
<td>Clinoptilolite/nZVI composite</td>
<td>MB and MO</td>
<td>MB: 96.6%, MO: 90.2%</td>
<td>MB: 15 min, MO: 30 min</td>
<td>Adsorption under wider dispersion of Fe nanoparticle chains in clinoptilolite matrix</td>
<td>Nairat et al., 2015</td>
</tr>
<tr>
<td>Fe-NPs</td>
<td>MO</td>
<td>100% degradation</td>
<td>6 h</td>
<td>Strong electrostatic attraction between anionic MO and Fe-NPs below point of zero charge of Fe-NPs</td>
<td>Xingu-Contreras et al., 2020</td>
</tr>
<tr>
<td>nZVI</td>
<td>Reactive yellow</td>
<td>59.9%</td>
<td>5 min</td>
<td>Removal via corrosion of nZVI and Fe(II) consumption</td>
<td>Mao et al., 2015</td>
</tr>
<tr>
<td>----------------------</td>
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<td>-------</td>
<td>-----------------------------------------------------</td>
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</tr>
<tr>
<td>nZVI/H$_2$O$_2$ (Fenton like system)</td>
<td>MB</td>
<td>94.5%</td>
<td>1 h</td>
<td>-OH radical oxidation</td>
<td>Yang et al., 2019</td>
</tr>
<tr>
<td>Granular reinforced ZVI activated by persulfate</td>
<td>Acid orange 7</td>
<td>90.78%</td>
<td>2 h</td>
<td>Diffusion mediated reduction</td>
<td>Du et al., 2020</td>
</tr>
<tr>
<td>Biochar supported nZVI</td>
<td>Ciprofloxacin</td>
<td>70%</td>
<td>1 h</td>
<td>-OH radical oxidation</td>
<td>Mao et al., 2019</td>
</tr>
<tr>
<td>Wheat straw supported nZVI</td>
<td>Cu(II), chlorotetracycline</td>
<td>Cu(II): 376.4 mg/g Chlorotetracycline: 1280.8 mg/g</td>
<td>2 h</td>
<td>Chemisorption and redox reaction</td>
<td>Shao et al., 2020</td>
</tr>
<tr>
<td>Polyethylenimine (PEI) surface-modified zero-valent iron NPs (PEIenZVI)</td>
<td>Trichloroethylene, perchloroethylene, and 1,2-dichloroethene</td>
<td>99%</td>
<td>2 h</td>
<td>Removal through high surface area (53.4 m$^2$/g) particles</td>
<td>Lin et al., 2018</td>
</tr>
<tr>
<td>Sulfide-modified nZVI</td>
<td>Trichloroethylene</td>
<td>66%</td>
<td>1 h</td>
<td>Strong corrosion of Fe◦</td>
<td>Wang et al., 2020</td>
</tr>
<tr>
<td>$Sulfide$-modified $nZVI/graphene aerogel composite$</td>
<td>Trichloroethylene</td>
<td>100%</td>
<td>50 min</td>
<td>Electron transfer from Fe core to trichloroethylene</td>
<td>Bin et al., 2020</td>
</tr>
<tr>
<td>$Heat$ treated $biochar$ impregnated $nZVI$</td>
<td>Trichloroethylene</td>
<td>88%</td>
<td>20 min</td>
<td>Chemisorption</td>
<td>Mortazavian et al., 2019</td>
</tr>
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</table>

‘-‘ indicates unavailability of information on contact time.

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<table>
<thead>
<tr>
<th>Copper based nanoparticles</th>
<th>Contaminants</th>
<th>Amount removed/removal efficiency</th>
<th>Contact time</th>
<th>Mechanism(s)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitosan encapsulated CuO</td>
<td>As(V)</td>
<td>28.1 mg/g</td>
<td>3.5 h</td>
<td>Adsorption by electrostatic attraction</td>
<td>Elwakeel &amp; Guibal, 2015</td>
</tr>
<tr>
<td>CuO-Fe₃O₄</td>
<td>As(V)</td>
<td>118.11 mg/g</td>
<td>1 h</td>
<td>Removal through protonation and improved electrostatic gravity under acidic conditions</td>
<td>Sun et al., 2017</td>
</tr>
<tr>
<td>CuFe₂O₄</td>
<td>As</td>
<td>45.7 mg/g</td>
<td>5 h</td>
<td>Bonding with reactive surface sites</td>
<td>Masunga et al., 2019</td>
</tr>
<tr>
<td>Cu NPs intercalated into CNTs</td>
<td>As(III)</td>
<td>&gt;90%</td>
<td>66.7 h</td>
<td>Adsorptive filtration and partial oxidation</td>
<td>Luan et al., 2019</td>
</tr>
<tr>
<td>CuO NPs</td>
<td>Cr(VI)</td>
<td>18.51 mg/g</td>
<td>3 h</td>
<td>Removal by chemisorption</td>
<td>Gupta et al., 2016</td>
</tr>
<tr>
<td>Alginate-coated chitosan/CuO</td>
<td>Ni(II)</td>
<td>94.48% removal</td>
<td>30 min</td>
<td>Removal through formation of less soluble hydrolyzed products such as NiOH and Ni(OH)₂ at pH 3.0</td>
<td>Esmaeili &amp; Khoshnevisan, 2016</td>
</tr>
<tr>
<td>Nano structured CuO granules</td>
<td>Pb(II)</td>
<td>55.24 mg/g</td>
<td>5 h</td>
<td>Adsorption via strong electrostatic attraction under alkaline conditions</td>
<td>Ahmadi et al., 2012</td>
</tr>
<tr>
<td>Amine-functionalized copper ferrite chelated with La(III)</td>
<td>PO₄³⁻</td>
<td>12.6 mg/g</td>
<td>40 min</td>
<td>Chemisorption</td>
<td>Gu et al., 2018</td>
</tr>
<tr>
<td>Cu NPs coated biochar (bamboo shoot shell)</td>
<td>Re(VII)</td>
<td>20.91 mg/g</td>
<td>5 h</td>
<td>Complexation</td>
<td>Hu et al., 2018</td>
</tr>
<tr>
<td>CuI-CuO NPs loaded activated carbon</td>
<td>Malachite green</td>
<td>136.67 mg/g</td>
<td>≥25 min</td>
<td>Adsorption via electrostatic attraction at low pH</td>
<td>Nekouei et al., 2015</td>
</tr>
<tr>
<td>3.025% Cu-embedded chitosan</td>
<td>Rhodamine B</td>
<td>99% degradation</td>
<td>1 h</td>
<td>Degradation through active •OH radicals</td>
<td>Senthil Kumar et al., 2015</td>
</tr>
<tr>
<td>CuO nano-needles on GO sheets</td>
<td>Coomassie brilliant blue (CBB), MB, Congo red (CR) and amido black 10B (AB)</td>
<td>&gt;98% removal</td>
<td>13.33 h</td>
<td>Adsorption via strong electrostatic attraction and high surface area of CuO nano-needles on GO sheets</td>
<td>Rajesh et al., 2016</td>
</tr>
<tr>
<td>30% Cu₂O/TiO₂</td>
<td>Acid red B</td>
<td>&gt;70% decolorization</td>
<td>1 h</td>
<td>Adsorptive decolorization via electrostatic attraction and large surface area of Cu₂O/TiO₂</td>
<td>Fei et al., 2015</td>
</tr>
</tbody>
</table>

Table S2. Cu NPs for contaminant adsorption/removal/degradation in water.
<table>
<thead>
<tr>
<th>Bio-engineered Cu NPs</th>
<th>Alizarin Yellow R</th>
<th>89.71%</th>
<th>36 h</th>
<th>Combination of van der Waals forces, electrostatic attraction and H-bonding</th>
<th>Usman et al., 2019</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO/nanoTiO₂</td>
<td>MB</td>
<td>99% degradation</td>
<td>5 h</td>
<td>Degradation via electron scavenging effect of Cu⁺²⁺ in seawater</td>
<td>Simamora et al., 2012</td>
</tr>
<tr>
<td>Cu-oxide NPs annealed at 600°C</td>
<td>MB</td>
<td>91% degradation</td>
<td>2.5 h</td>
<td>Generation of more electro-hole pairs and reduction in the electron-hole recombination rate</td>
<td>Nwanya et al., 2019</td>
</tr>
<tr>
<td>Cu₃O-zeolite</td>
<td>1,2-Dichloroethane</td>
<td>83.8% removal</td>
<td>2 h</td>
<td>Removal under UV irradiation at low relative humidity (15%)</td>
<td>Lin et al., 2014</td>
</tr>
<tr>
<td>Zero valent Cu</td>
<td>Dichloromethane</td>
<td>90% degradation</td>
<td>1 h</td>
<td>Degradation through hydrodechlorination with a high dose of zero valent Cu (2.5 g/L)</td>
<td>Huang et al., 2012</td>
</tr>
<tr>
<td>Zero valent Cu and reductant NaBH₄</td>
<td>Mono chloroaromatic</td>
<td>90% dechlorinated</td>
<td>12 h</td>
<td>Dechlorination through breaking of Ar-Cl bond by e⁻ produced by NaBH₄ and formation of Ar-H bond on zero valent Cu (Cu⁰).</td>
<td>Raut et al., 2016</td>
</tr>
<tr>
<td>Nano CuO</td>
<td>Nitrobenzene</td>
<td>100% degradation</td>
<td>25 min</td>
<td>Degradation by •OH radicals</td>
<td>ElShafei et al., 2014</td>
</tr>
<tr>
<td>Cu-doped TiO₂</td>
<td>Phenol</td>
<td>52% degradation</td>
<td>3 h</td>
<td>Degradation through electron (e⁻) scavenging effect of Cu⁺²⁺ and prevention of recombination of electron hole pairs</td>
<td>Sohrabi &amp; Akhlaghian, 2016</td>
</tr>
<tr>
<td>Chitosan embedded Cu NPs</td>
<td>4-nitroaniline</td>
<td>Rate of reduction: 7.51*10⁻³ /s</td>
<td>&lt;4.5 min</td>
<td>Cu NP-assisted reduction by NaBH₄</td>
<td>Bakhsh et al., 2019</td>
</tr>
<tr>
<td>Chitosan embedded Cu NPs</td>
<td>Metronidazole</td>
<td>92%</td>
<td>2 h</td>
<td>•OH radical</td>
<td>Xu et al., 2019</td>
</tr>
<tr>
<td>Graphene-wrapped zero-valent Cu NPs</td>
<td>Ibuprofen</td>
<td>36.0 mg/g</td>
<td>1 h</td>
<td>Chemisorption</td>
<td>Husein et al., 2019</td>
</tr>
<tr>
<td>Bentonite supported green nZVI-Cu nanocomposite</td>
<td>Tetracycline</td>
<td>95%</td>
<td>1.5 h</td>
<td>•OH radical production due to galvanic corrosion of nZVI-Cu</td>
<td>Gopal et al., 2020</td>
</tr>
</tbody>
</table>
Table S3. Adsorption of different contaminants onto various carbon nanotubes in water.

<table>
<thead>
<tr>
<th>Types of CNTs</th>
<th>Modification</th>
<th>Contaminants</th>
<th>Amount adsorbed/removal efficiency</th>
<th>Contact time</th>
<th>Mechanism(s)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNTs</td>
<td>TiO$_2$ grafted</td>
<td>Pb(II)</td>
<td>137 mg/g</td>
<td>1 h</td>
<td>Electrostatic attraction</td>
<td>Zhao et al., 2010</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>Nano iron oxide coated</td>
<td>Cr(III)</td>
<td>&gt;90%</td>
<td>2 h</td>
<td>Cr (III) removal related to flow rate (inverse relation)</td>
<td>Gupta et al., 2011</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>Iron oxide-coated</td>
<td>As(V) and As(III)</td>
<td></td>
<td>30 min</td>
<td>Simple electrostatic Attraction</td>
<td>Addo Ntim &amp; Mitra, 2011</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>Al$_2$O$_3$</td>
<td>Cd(II)</td>
<td>27.2 mg/g</td>
<td>4 h</td>
<td>Sorption</td>
<td>Liang et al., 2010</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>Oxidized</td>
<td>Cd(II)</td>
<td>22.4 mg/g</td>
<td>30 min</td>
<td>Precipitation</td>
<td>Vuković et al., 2010</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>Iodide</td>
<td>Hg(II)</td>
<td>123.5 mg/g</td>
<td>2 h</td>
<td>Chemisorption</td>
<td>Gupta et al., 2014</td>
</tr>
<tr>
<td>SWCNTs</td>
<td>Thiol derived</td>
<td>Hg(II)</td>
<td>131.0 mg/g</td>
<td>1 h</td>
<td>Chemisorption</td>
<td>Bandaru et al., 2013</td>
</tr>
<tr>
<td>Magnetic CNTs</td>
<td>N-doped</td>
<td>Cr(III)</td>
<td>2.07 mmol/g</td>
<td>30 min</td>
<td>Electrostatic attraction</td>
<td>Manilo et al., 2017</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr(VI)</td>
<td>970.87 mg/g</td>
<td>10 min</td>
<td>Acid medium and reduction reaction between Fe$^0$ NPs and Cr(VI)</td>
<td>Huang et al., 2019</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>Fe$_3$O$_4$</td>
<td>As(V)</td>
<td>39.1 mg/g</td>
<td>1 h</td>
<td>Inner sphere complex</td>
<td>Mishra &amp; Ramaprabhu, 2010</td>
</tr>
<tr>
<td>Purified SWCNTs</td>
<td>-</td>
<td>Zn(II)</td>
<td>41.8 mg/g</td>
<td>1 h</td>
<td>-</td>
<td>Lu et al., 2006</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>2-(5-Bromo-2-pyridylazo)-5-(diethylamino)phenol</td>
<td>U(VI)</td>
<td>83.4 mg/g</td>
<td>20 min</td>
<td>Trinuclear, (UO$_2$)$_3$(OH)$^{5+}$ formation</td>
<td>Khamirchi et al., 2018</td>
</tr>
<tr>
<td>CNTs</td>
<td>Oxidized</td>
<td>Co(II)</td>
<td>69.6 mg/g</td>
<td>20 min</td>
<td>Chemical interaction</td>
<td>Tofighy &amp; Mohammadi, 2011</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>Amidoamine</td>
<td>Hg(II)</td>
<td>45.05 mg/g</td>
<td>3 h</td>
<td>Chemisorption</td>
<td>Singh Deb et al., 2017</td>
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<tr>
<td>MWCNTs</td>
<td>Polypyrrole-coated and oxidized</td>
<td>Pb(II) and Cu(II)</td>
<td>Pb(II): 26.3 mg/g</td>
<td>1 h</td>
<td>Deprotonation of NH$_2$ and nitrogen</td>
<td>Nyairo et al., 2018</td>
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<tr>
<td>MWCNTs</td>
<td>Chitin/magnetite</td>
<td>Cr(VI)</td>
<td>11.30 mg/g</td>
<td>45 min</td>
<td>Strong interaction with reactive functional groups</td>
<td>Salam, 2017</td>
</tr>
<tr>
<td>Material</td>
<td>Adsorbent</td>
<td>Contaminant</td>
<td>Adsorption Yield (mg/g)</td>
<td>Contact Time (min)</td>
<td>Interactions</td>
<td>Reference</td>
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<tr>
<td>MWCNTs</td>
<td>Al₂O₃</td>
<td>Cd(II)</td>
<td>27.21</td>
<td>1 h</td>
<td>Electrostatic attraction</td>
<td>Verma &amp; Balomajumder, 2020</td>
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<tr>
<td>CNTs</td>
<td>Chitosan sponge</td>
<td>F⁻</td>
<td>975.4</td>
<td>20 min</td>
<td>Functional groups of chitosan and CNTs</td>
<td>Affonso et al., 2020</td>
</tr>
<tr>
<td>CNTs</td>
<td>Carbon graphite</td>
<td>Cu(II)</td>
<td>25%</td>
<td>-</td>
<td>Oxidation effect</td>
<td>Zghal et al., 2020</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>Oxidation</td>
<td>Diuron</td>
<td>29.82</td>
<td>1 h</td>
<td>Electrostatic interaction</td>
<td>Deng et al., 2012</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>Oxidation</td>
<td>Methyl orange (MO)</td>
<td>306</td>
<td>3.5 h</td>
<td>Electrostatic interaction</td>
<td>Mahmoodian et al., 2015</td>
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<tr>
<td>MWCNTs</td>
<td>Graphene oxide</td>
<td>Methylene blue (MB)</td>
<td>87.9</td>
<td>2 h</td>
<td>Electrostatic interaction</td>
<td>Ai &amp; Jiang, 2012</td>
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<tr>
<td>MWCNTs</td>
<td>-</td>
<td>Isoproturon</td>
<td>8.1</td>
<td>-</td>
<td>Strong attraction between surface reactive sites and contaminant</td>
<td>Sotelo et al., 2012</td>
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<tr>
<td>SWCNTs</td>
<td>-</td>
<td>Atrazine</td>
<td>4.97</td>
<td>-</td>
<td>Chemisorption</td>
<td>Jung et al., 2015</td>
</tr>
<tr>
<td>CNTs</td>
<td>Chitosan hydrogel scaffold</td>
<td>Food red 17 and Food blue 1</td>
<td>1508</td>
<td>50 min</td>
<td>Strong interaction with surface functionalized groups</td>
<td>Gonçalves et al., 2020</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>COOH-carboxylate</td>
<td>Amido black 10B COOH-cysteamine</td>
<td>90/131</td>
<td>18 min</td>
<td>Chemisorption and protonation due to pH of the medium</td>
<td>Sadegh et al., 2016</td>
</tr>
<tr>
<td>CNTs</td>
<td>Trimesoyl chloride and m-phenylenediamine grafting</td>
<td>Phenol</td>
<td>261.6</td>
<td>50 min</td>
<td>Electrostatic attraction</td>
<td>Saleh et al., 2019</td>
</tr>
<tr>
<td>CNTs</td>
<td>Fe/Ni NPs supported</td>
<td>2,6 dichlorophenol</td>
<td>82.6% (dechlorination)</td>
<td>50 min</td>
<td>Bonding with reactive sites of Fe/Ni NPs</td>
<td>Liu et al., 2020</td>
</tr>
<tr>
<td>CNTs</td>
<td>Chitosan hydrogel scaffold</td>
<td>Phenol</td>
<td>404.2</td>
<td>20 min</td>
<td>Chemisorption</td>
<td>Alves et al., 2019</td>
</tr>
<tr>
<td>Magnetic CNTs</td>
<td>Polyethyleneimine</td>
<td>Alizarin Red S</td>
<td>196.08</td>
<td>40 min</td>
<td>Interaction with active sites and multiple interactions</td>
<td>Zhang et al., 2019</td>
</tr>
</tbody>
</table>

“-” indicates unavailability of information on contact time.
Table S4. Contaminant adsorption capacities of graphene oxide (GO) and GO composites in water.

<table>
<thead>
<tr>
<th>Heavy metals</th>
<th>Adsorbents</th>
<th>Amount adsorbed/removal efficiency</th>
<th>Contact time</th>
<th>Mechanism(s)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)</td>
<td>GO</td>
<td>46.6 mg/g</td>
<td>-</td>
<td>Electrostatic attraction and coordination between Cu(II) and carboxyl groups</td>
<td>Yang et al., 2010</td>
</tr>
<tr>
<td>Cd(II), Ni(II)</td>
<td>GO</td>
<td>Cd(II): 83.3 mg/g Ni(II): 62.3 mg/g</td>
<td>10 min</td>
<td>Lewis acid base interaction</td>
<td>Tan et al., 2015</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>Few layered GO</td>
<td>842 mg/g</td>
<td>24 h</td>
<td>Surface complexation</td>
<td>Zhao et al., 2011</td>
</tr>
<tr>
<td>Sb(III)</td>
<td>Reduced GO (rGO)</td>
<td>8.1 mg/g</td>
<td>4 h</td>
<td>van der Waals force</td>
<td>Leng et al., 2012</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>GO</td>
<td>245.7 mg/g</td>
<td>20 min</td>
<td>Ion exchange and electrostatic attraction</td>
<td>Wang et al., 2013</td>
</tr>
<tr>
<td>Eu(III)</td>
<td>GO nanosheets</td>
<td>175.4 mg/g</td>
<td>48 h</td>
<td>Mononuclear and binuclear complexes</td>
<td>Sun et al., 2012</td>
</tr>
<tr>
<td>Hg(II), Cu(II), Pb(II)</td>
<td>EDTA^−-GO</td>
<td>Hg(II): 268.4 mg/g Cu(II): 301.2 mg/g Pb(II): 508.4 mg/g</td>
<td>Hg(II): 50 min Cu(II): 90 min Pb(II): 40 min</td>
<td>Electrostatic attraction</td>
<td>Cui et al., 2015</td>
</tr>
<tr>
<td>Co(II)</td>
<td>GO-NH₂</td>
<td>116.4 mg/g</td>
<td>5 min</td>
<td>Complexation with carboxyl and amino groups on GO surfaces</td>
<td>Fang et al., 2014</td>
</tr>
<tr>
<td>U(VI)</td>
<td>rGO/CoFe₂O₄/polyaniline</td>
<td>2430 mg/g</td>
<td>4 h</td>
<td>Strong electrostatic attraction</td>
<td>Dat et al., 2018</td>
</tr>
<tr>
<td>As(V)</td>
<td>GO/CuFe₂O₄ held onto Fe-Ni foam</td>
<td>125 mg/g</td>
<td>30 min</td>
<td>Ligand exchange</td>
<td>Wu et al., 2018</td>
</tr>
<tr>
<td>As(V)</td>
<td>GO/MnFe₂O₄</td>
<td>240 mg/g</td>
<td>20 min</td>
<td>Bonding with active sorption sites</td>
<td>Huong et al., 2016</td>
</tr>
<tr>
<td>Pb(II), Cr(III), Cu(II)</td>
<td>Magnetic GO</td>
<td>Pb(II): 200 mg/g Cr(III):24.3 mg/g Cu(II): 62.8 mg/g</td>
<td>Pb(II): 25 min Cr(III): 35 min Cu(II):25 min</td>
<td>Electrostatic attraction and precipitation</td>
<td>Ain et al., 2020</td>
</tr>
<tr>
<td>Compound</td>
<td>Modification Method</td>
<td>Adsorption Capacity</td>
<td>Contact Time</td>
<td>Adsorption Force</td>
<td>Reference</td>
</tr>
<tr>
<td>------------------------</td>
<td>--------------------------------------------------------------------------------------</td>
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<td>-------------------</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>Polyamine modified rGO in hydrothermal method</td>
<td>63.8 mg/g</td>
<td>10 min</td>
<td>Chemisorption</td>
<td>Yap et al., 2020</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>Sulphur-doped carbon nitride/graphene oxide</td>
<td>40 mg/g</td>
<td>2 h</td>
<td>Electrostatic attraction</td>
<td>Li et al., 2020</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>Graphene oxide</td>
<td>82.4%</td>
<td>10 min</td>
<td>Interaction with active functional groups</td>
<td>Xiao et al., 2019</td>
</tr>
<tr>
<td>Phenanthrene, biphenyls</td>
<td>GO</td>
<td>Phenanthrene: 174.6 mg/g</td>
<td>-</td>
<td>van der Waals force</td>
<td>Apul et al., 2013</td>
</tr>
<tr>
<td>TCP, TCB, 2-napthol, NAPH</td>
<td>GO</td>
<td>TCP: 3.5 mg/g TCB: 1.6 mg/g 2-naphtol: 4.2 mg/g NAPH: 0.9 mg/g</td>
<td>24 h</td>
<td>π–π interaction</td>
<td>Pei et al., 2013</td>
</tr>
<tr>
<td>MB</td>
<td>Exfoliated GO (EGO)</td>
<td>17.3 mg/g</td>
<td>2 h</td>
<td>Electrostatic attraction/ van der Waals force</td>
<td>Ramesha et al., 2011</td>
</tr>
<tr>
<td>Methyl violet (MV) and Rhodamine B, (RhB)</td>
<td>EGO</td>
<td>MV: 2.5 mg/g RhB: 1.2 mg/g</td>
<td>MV: 2 h RhB: 25 min</td>
<td>Electrostatic attraction/ van der Waals force</td>
<td>Ramesha et al., 2011</td>
</tr>
<tr>
<td>MB</td>
<td>rGO/ZnFe$_2$O$_4$</td>
<td>9.7 mg/g</td>
<td>30 min</td>
<td>Bonding with reactive functional groups</td>
<td>Park et al., 2019</td>
</tr>
<tr>
<td>2,4-Dichlorophenol</td>
<td>Polysulfone-iron oxide/GO composite</td>
<td>96.5%</td>
<td>-</td>
<td>Oxygen-enriched functional groups and hydrophilicity</td>
<td>Modi &amp; Bellare, 2020</td>
</tr>
<tr>
<td>Rhodamine-B</td>
<td>Polysulfone-GO</td>
<td>&gt;90%</td>
<td>4 h</td>
<td>Chemisorption</td>
<td>Zambianchi et al., 2017</td>
</tr>
<tr>
<td>MB, RhB, MV</td>
<td>SiO$_2$-GO hybrid</td>
<td>MB: 300 mg/g RhB: 258 mg/g MV: 178 mg/g</td>
<td>3 min</td>
<td>Interfacial catalytic process</td>
<td>Czepa et al., 2020</td>
</tr>
<tr>
<td>MB</td>
<td>Sulfated-cellulose GO</td>
<td>421.90 mg/g</td>
<td>&lt;1 h</td>
<td>Chemisorption</td>
<td>Wang et al., 2019</td>
</tr>
<tr>
<td>2, 4-Dichlorophenol</td>
<td>α-Fe$_3$O$_4$@Fe$_3$O$_4$ shell–core magnetic nanoparticles and GO</td>
<td>&gt;60% degradation</td>
<td>2 h</td>
<td>Large surface area accompanied by pore size diameter</td>
<td>Pang et al., 2020</td>
</tr>
</tbody>
</table>

*EDTA: Ethylenediaminetetraacetic acid; ‘-’ indicates unavailability of information on contact time.
**Table S5.** List of nanomaterials and their contaminant removal capacities in soil.

<table>
<thead>
<tr>
<th>Contaminants</th>
<th>Nanomaterials</th>
<th>Removal capacity/degradation efficiency</th>
<th>Contact time</th>
<th>Mechanism(s)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(II)</td>
<td>Nano-hydroxy apatite</td>
<td>Concentration decreased by 3-21% in roots and 13-20% in shoots of ryegrass</td>
<td>30 days (rye grass crop cycle)</td>
<td>Secretion of tartaric increased the Pb adsorption</td>
<td>Ding et al., 2017</td>
</tr>
<tr>
<td>Pb(II), Cu(II) and Zn(II)</td>
<td>Calcium phosphate nanoparticles (CPNs)</td>
<td>Pb: &gt; 90% Cu: 50% Zn: 50%</td>
<td>10 days aging of CPNs and soil mixture</td>
<td>Insoluble complex formation between CPNs and heavy metals</td>
<td>Arenas-Lago et al., 2016</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>nZVI/citric acid</td>
<td>87% in farmland soil</td>
<td>4 h</td>
<td>Organic acid and metal chelate formation</td>
<td>Wang et al., 2014</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>CMC-stabilized FeS NPs/biochar composite</td>
<td>11.9 to 0.63 mg/L in the leachate</td>
<td>180 days</td>
<td>Strong interaction with reactive surface sites</td>
<td>Lyu et al., 2018</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>nZVI/Cu</td>
<td>99%</td>
<td>10 min</td>
<td>Reduction of Cr(VI) to Cr(III) at low pH and generation of more electrons</td>
<td>Zhu et al., 2016</td>
</tr>
<tr>
<td>As</td>
<td>nZVI</td>
<td>40.4%</td>
<td>3 days</td>
<td>Bioaccessibility reduced through surface complexation</td>
<td>Zhang et al., 2010</td>
</tr>
<tr>
<td>As</td>
<td>Green iron oxide NPs</td>
<td>67.3%</td>
<td>120 days</td>
<td>Covalent bonding and high Fe content of soil due to application of Fe-oxide NPs</td>
<td>Su et al., 2020</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>Biochar supported nZVI</td>
<td>54.68%</td>
<td>90 days</td>
<td>Co-precipitation and secondary Pb-Fe mineral formation under alkaline environment</td>
<td>Peng et al., 2019</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>CMC stabilized FeS NPs</td>
<td>Leachate Cr(VI) immobilized by &gt;90% nZVI: 89.5% n-goethite: 82.5% (decrease in As bioavailability)</td>
<td>42 h</td>
<td>Co-precipitation, adsorption and reduction</td>
<td>Wang et al., 2019</td>
</tr>
<tr>
<td>As</td>
<td>nZVI and n-goethite</td>
<td>-</td>
<td>-</td>
<td>Inner-sphere complexation</td>
<td>Baragaño et al., 2020</td>
</tr>
<tr>
<td>Compound</td>
<td>Immobilization Method</td>
<td>Conditions</td>
<td>Mechanism</td>
<td>Authors</td>
<td></td>
</tr>
<tr>
<td>--------------------------</td>
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<tr>
<td>Cd(II)</td>
<td>nZVI/palm BC</td>
<td>Pronounced</td>
<td>Sorption and precipitation in soil</td>
<td>Qiao et al., 2018</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>immobilization</td>
<td>(Rice life cycle)</td>
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<tr>
<td></td>
<td></td>
<td>in soil</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Sb(V)</td>
<td>nZVI</td>
<td>&gt;90%</td>
<td>Chemisorption</td>
<td>Dorjee et al., 2014</td>
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<tr>
<td>Cd(II)</td>
<td>GO</td>
<td>103.3 mg/g</td>
<td>Adsorption via chelation to form stable Cd-complexes</td>
<td>Xiong et al., 2018</td>
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<tr>
<td></td>
<td></td>
<td>60 days</td>
<td>Mass transfer and Generation of active H_2 species due to Fe corrosion</td>
<td>Xie et al., 2014</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>72 h</td>
<td>in water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Decabromodiphenyl ether</td>
<td>Ni/Fe BNPs</td>
<td>72%</td>
<td>Corrosion of Fe</td>
<td>Xie et al., 2016</td>
<td></td>
</tr>
<tr>
<td>(BDE-209)</td>
<td></td>
<td>72 h</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Decabromodiphenyl ether</td>
<td>nZVI immobilized in mesoporous silica</td>
<td>78%</td>
<td>Hydro-dechlorination by generation of H^+ in anode</td>
<td>Gomes et al., 2015</td>
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<tr>
<td>(BDE-209)</td>
<td>microspheres covered with FeOOH (SiO_2@FeOOH@Fe)</td>
<td>120 h</td>
<td></td>
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<tr>
<td>Polychlorinated Biphenyls</td>
<td>nZVI</td>
<td>83%</td>
<td>Generation of free radicals or reactive oxygen species</td>
<td>Dong et al., 2018</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5 days</td>
<td>Active sites and functional groups of biochar</td>
<td>Oleszczuk &amp; Kołtowski, 2017</td>
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</tr>
<tr>
<td>PAHs</td>
<td>Fe_3O_4/persulfate</td>
<td>75%</td>
<td>Hydrolysis of chlorpyriphos due to presence of Cu in laccase molecules</td>
<td>Das et al., 2020</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>24 h</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAHs</td>
<td>nZVI/BC</td>
<td>40%</td>
<td>Fenton like degradation</td>
<td>Deng et al., 2018</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>30 days</td>
<td></td>
<td></td>
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<tr>
<td>Chlorpyriphos</td>
<td>Laccase immobilized iron oxide NPs</td>
<td>K_d: 112.3 L/kg</td>
<td>Hydrolysis of chlorpyriphos due to presence of Cu in laccase molecules</td>
<td>Das et al., 2020</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>30 days</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Sulfamethazine</td>
<td>nZVI/corn stalk biochar</td>
<td>74%</td>
<td>Low pH and faster reactivity</td>
<td>Deng et al., 2018</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>12 h</td>
<td></td>
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<tr>
<td>Ibuprofen</td>
<td>nZVI using grape vine leaf extract</td>
<td>66%</td>
<td></td>
<td>Machado et al., 2013</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>73 h</td>
<td></td>
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</table>

‘-’ indicates unavailability of information on contact time.
References


