Critical Reviews on Engineered Nanoparticles in Environmental Remediation

ABSTRACT

Environmental contamination is one of the important issues that the world is facing today, it is always expanding and leading to grave and harmful effect to the Earth. Nanoparticles have diameter less than 100 nm exhibit new size – dependent properties compared with the bulk material. Engineered nanoparticles (ENPs) have unique characteristics in addition to high surface area -to-volume ratio, which may increase their toxicity relative to bulk materials. Due to high volume production of ENPs products such carbon nanotubes, titanium dioxide, silver, zinc oxide environmental exposure to these compounds is very common. ENPs have their unique properties and applications in the areas of medicine, food& drink, construction, automotive, textiles, energy, electronics, environment etc. Present critical review is focused on recent development of the applications of ENPs in the environmental remediation and their toxic effects.

Keywords: Nanotechnology. Engineered nanoparticles, environmental remediatio, carbonaceous materials, metal oxides, zerovalent metals, polymers, semi-conductor devices.

Definition:

According to ISO [1] nanoparticles processes at least one dimention of 1 – 100 nm. Particles have diameter less than 100 nm exhibit new size dependent properties compared with the bulk material. These are several engineered nano materials such as carbon nanotubes, nanocomposites, quantum dots, fullerenes, quantum wire and nanofibers [2]. Nanomaterials are purposely manufactured by humans to achieve the specific characteristics of materials at nanometric scale. Natural nanoparticles are erosion dust or volcanic eruption dust or marine spray. Other nanoparticles produced unintentionally during burning wood or burning diesel engines [3]. Nanotechnology is the creation of materials, devices and systems by controlling matter at the nanometer scale (1 – 100 billionths of a meter).

Classification:

Nanoparticles are mainly classified into four types [4].

(i) Zero-dimensional (0D) nanostructure: All of the three dimensions are in the nanometric range. Ex. Well separated nano powders.

(ii) One dimensional (1D) nanostructure: Two dimensions are in the nanometric range and third dimension remains large. Ex. Nanotubes, nano rods etc.

(iii) Two – dimensional (2D) nanostructure: Only one dimension is in the nanometric range while other two dimensions remains large. Ex. Nano thin films, nano rods etc.

(iv) Three – dimensional (3D) nanostructure: All three dimensions are outside the nanometric size range. It may consist of group of nano wires, nano tubes, or different distribution of nano particles.

Nanoparticles have novel characteristics due to their high surface/volume ratio which make them more reactive than bulk forms of same materials [5]. Living organism required trace amounts of some heavy materials including Co, Cu, Fe, Mn, Mo, Sr and Zn these are essential metals but their excessive levels can be toxic to organism. Heavy metals including

Hg, Cr, Cd, As, Pb, Sr are non-essential metals and considered to be great threat for aquatic life. The iron oxide nano materials have potential nonasorbent properties in extraction of these heavy metals from ground water [6]. Fujishima and Konda [7] demonstrated the potential of TiO_2 semiconductor material to split water into oxygen and hydrogen in photo electrochemical cell.

The TiO_2 band gap is 3.2 eV, therefore UV light ($\lambda \leq 387$ nm) is required. The absorption of photon excites an electron to the conduction band ($e^-{}_{CB}$) generate a positive hole in the valency band ($h^+{}_{VB}$) (Eq.1)

$$Tio_2 + h\nu \longrightarrow h^+{}_{VB} + e^-{}_{CB} \quad (1)$$

The charge carriers can be trapped as Ti^{3+} and O^- defect sites in the TiO_2 lattice, or they can recombine, dissipating energy [7]. Alternatively, the charge carrier can migrate to the catalyst surface and initiate redox reactions with adsorbates [8]. Positive holes can oxidize OH^- or water at the surface to produce *OH radicals (eq. 2), which, are extremely powerful oxidants. The hydroxyl radicals can subsequently oxidize organic pollutants with mineralization producing mineral salts, CO_2 and H_2O (eq. 5) [9]. Electrons in conduction band can be rapidly trapped by molecular oxygen adsorbed on the titania particles, which is reduced to form superoxide radical anion (O_2*) (eq. 4) that may further react with H^+ to generate hydroperoxyl ($^*OOH$) (eq. 6) and further electrochemical reduction yields H_2O_2 (eq. 7) [10, 11]. These reactive oxygen species may also contribute to the oxidative pathways such as the degradation of pollutant [eq. 8 and 9] [7, 9, 10]. The photocatalytic reactions mentioned above expressed as equations.

$$e^{-}_{CB} + h^{+}_{VB} \longrightarrow \text{energy} \qquad (2)$$

$$H_2O + h^{+}_{VB} \longrightarrow {}^{*}OH + H^{+} \qquad (3)$$

$$O_2 + e^{-}_{CB} \longrightarrow O_2^{*-} \qquad (4)$$

$${}^{*}OH + \text{pollutant} \longrightarrow \longrightarrow \longrightarrow H_2O + CO_2 \; (5)$$

$$O_2^{*-} + H^{+} \longrightarrow {}^{*}OOH \qquad (6)$$

$$^{*}OOH + {}^{*}OOH \longrightarrow H_2O_2 + O_2 \qquad (7)$$

$$O_2^{*-} + \text{pollutant} \longrightarrow \longrightarrow \longrightarrow CO_2 + H_2O \qquad (8)$$

$${}^{*}OOH + \text{pollutant} \longrightarrow CO_2 + H_2O \qquad (9)$$

Applications:

Nanotechnology is fueling a revolution in manufacturing and production, creating new materials used in variety of different fields, such as cosmetic, pharmaceutical, energy, catalytic material and environmental applications [12 – 14]. Nanotechnology areas of applications are summarized in **Table 1.**

Table 1: Nanotechnology areas of application:

Areas	Applications
Automotive:	Lightweight construction; catalysts; Painting; Tires; Sensors; Windshield and body coating
Construction:	Materials; insulation; Flame retardants; Surface coatings; Mortar
Electronics:	Display; Data memory; Laser diodes; Fiber optics; Optical switches; Filters; Conductive coatings; Antistatic coatings; Transistors
Engineering:	Protective coatings for wood; machines; Lubricant-free bearings.
Food and Drink:	Packaging; Storage life sensors; Additives; Juice clarifiers.
Medicine:	Drug delivery system; Contrast medium; Rapid testing systems; Prostheses and implants; Antimicrobial agents; in body diagnostic systems.
Textiles:	Surface coatings; "Smart" clothes (anti-wrinkle, stain resistant, temperature controlled).
Chemical:	Filter for paint; Composite material; Impregnation of papers; Adhesives; Magnetic fluids.
Cosmetics:	Sunscreen; Lipsticks; Skin creams; Toothpaste.
Energy:	Lighting; Fuel cells; Solar cells; Batteries; Capacitors.
Environmental:	Environmental monitoring; Soil and groundwater remediation; Toxic exposure sensors; Fuel changing catalysts; Green chemistry.

Household: Ceramic coatings for irons; Odor removers; Cleaner for glass; Ceramics; Metals.

Sports: Ski wax; Tennis rackets; Golf clubs; Tennis balls; Antifouling coatings for boats; Antifogging coatings for glasses; goggles.

Military: Neutralization material for chemical weapons; bullet-proof protection.

The nanotechnological applications in different environmental areas reported by Mansoori et al. [15] are given in **Table 2.**

Table 2: Nanotechnological applications in different environmental areas

Type of nanoparticles	**Type of treatment**	**Removal target**	**Advantage**	**Disadvantage**
Nanoparticles based TiO_2	Photocatalyst oxidation	Organic pollutant	Non toxicity, water insolubility under most conditions, photo-stability	High operation cost, Hard to recovery, sludge generation
Nanoparticles based iron	Reduction adsorption	Heavy metals, anions, Organic pollutant (dechlorination)	In situ remediation, soil and water treatment, low cost, safe to handle	Hard to recovery, sludge generation, cost for sludge disposal, health

				risk
Nanoparticles based Bimetallic	Reduction adsorption	Dechlorination, Denitrification	Higher reactivity than the iron nanoparticle	Hard to recovery, sludge generation
Nanoclay	Adsorption	Heavy metals, anions, Organic pollutant	Low cost, Unique structures, Long-term stability, reuse, High sorption capacity, Easy recovery, large surface and pore volume	Sludge generation
Nanotube & fullerene	Adsorption	Heavy metals, anions, Organic pollutant	Treatment of pollution from air and water, exceptional mechanical properties, unique electrical properties, Highly chemical stability	High capital cost, low adsorption capacity, hard to recovery, sludge generation, Health risk
Dendrimers	Encapsulation	Heavy metals, Organic pollutant	Simple separation, renewable, large binding capacity, cost-effective, no sludge	Costly

			generation, reduce pollutant to the level of a few ppb, Treatment of pollution from soil and water	
Micelles	Adsorption	Organic pollutant from soil	In situ treatment, high affinity for hydrophobic organic pollutant	Costly
Metal-sorbing vesicles	Adsorption	Heavy metals	Re-use, high selective uptake profile, high metal affinity	
Magnetite & nanoparticles	Adsorption	Heavy metals, Organic pollutant	Simple separation, no sludge generation	External magnetically field are required for separation, Costly
Nanofiltration &nanosieve membranes	Nanofiltration	Organic and inorganic compound	Low pressure than RO	Costly, prone to membrane fouling

The application of engineered nanoparticles9 (ENPs) reported by several researchers [16-21] are given in **Table 3**.

Table 3: Applications of Engineered Nanoparticles.

ENP	**Applications**
Carbonaceous compounds	
CNTs and their derivatives	Electronics, computers, plastics, catalysts, batteries, conductive coatings, supercapacitors, water purification systems, orthopedic implants, aircraft, sporting goods, car parts, concrete, ceramics, solar cells, textiles
Fullerenes	Removal of organometallic compounds, cancer treatment, cosmetics, magnetic resonance imaging, X-ray contrasting agent, anti-viral therapy
Metal Oxides	
TiO_2	Sunscreen lotion, cosmetics, skin care products, solar cells, conductive coatings, sporting goods, paints, cement, windows, electronic coating, bioremediation
ZnO	Skin care products, bottle coatings, gas purification, contaminant sensors
CeO_2	Combustion catalyst in diesel fuels, solar cells, oxygen pumps, coatings, electronics, glass/ceramics, ophthalmic lenses
Semi-conductor Devices	

Quantum dots	Medical imaging, targeted therapeutics, solar cells, photovoltaic cells, security links, telecommunications

117 **Zero-valence Metals**

Zero-valent iron	Remediation of water, sediments and soils to remove nitrates, detoxification of organochlorine pesticides and polychlorinated biphenyls
Nanoparticulate silver	Textiles (e. g., socks, shirts, pants), disinfectant sprays, deodorants, laundry soaps, wound dressings, air filters, toothpaste, baby products (milk bottles, teethers), cosmetics, medical instruments, hardware(computer, mobile phones), food storage containers, cooking utensils, food additive/supplements, appliances (hair dryers, vacuum cleaners, washing machines, refrigerators), coatings/paints
Colloidal elemental gold	Tumor therapy, flexible conducting inks or films, catalyst, cosmetics, pregnancy tests, anti-microbial coatings

118 **Polymers**

Dendrimers	Drug delivery, tumor treatment, manufacture of macrocapsules, nanolatex, coloured glasses, chemical sensors, modified electrodes

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Use of graphene for the treatment of greenhouse gases (CO_2, NH_3, SO_2, H_2S and N_2) described by several researchers [22 – 24]. The application of fullerene B40 and fullerene – like boron nitride nano cage for the treatment of greenhouse gases CO_2 and N_2O are also reported by workers [25, 26]. The impacts of nanomaterials, carbon nanotubes [27 – 32], silver nanoparticles [33 – 35], ZnO and TiO_2 nanoparticles [36 – 37] and cerium oxide on human health described by several researchers [38, 39]. Nanoparticles also have several applications in drug delivery [40], imaging [41], sensor [42], blood purification [43, 44] and tissue engineering [45 - 47].

Umar et al. [48] has investigated that the simple synthesized α- Fe_2 O_3 nanoparticles can effectively be used as efficient photocatalyst for the photocatalytic degradation of organic dyes and effective electron mediators for the fabrication of highly sensitive chemical sensors in aqueous medium. A review summarizes the use of nanomaterials such as zero valent iron (NZVI) and carbon nanotubes (CNT) in environment cleanup like ground water remediation for drinking and reuse, reported by Rajan [49]. Mansouri et al. [50] described various environmental treatment and remediations using different types of nanostructured materials from air, contaminated waste-water, groundwater, surface water and soil. The nanoparticles studies include titanium dioxide, iron, bimetallic, catalytic particles, clays, carbon nanotube, dendrimers, fullerenes and magnetic nanoparticles. Their advantages and limitations in the environment applications are evaluated and compared with each other and with the existing techniques.

The use of inorganic, carbon-based and polymeric-based nanomaterials has been demonstrated by Guerra et al. [51]. These researchers have reviewed the use of these nanomaterials for the remediation of different environmental contaminants such as dyes.

Organophosphorous compounds volatile organic compounds, halogenated herbicides, heavy metals, chlorinated organic compounds, etc.

Li et al. [52] studied engineered superparamagnetic ion oxide nanoparticles for environmental applications. The 8 nm iron oxide nanoparticles were synthesized and transferred into water as stable suspensions by way of an interfacial oleic acid bilayer surface. Once stabilized and characterized, particles-particles and model surface interactions were quantitatively investigated and described as a function of ionic strength, zeta potential, dynamic light scattering and real-time quartz crystal microbalance with dissipation monitoring measurements. The use of metal nanoxides, tungstates and molybdates for the removal of toxic and radioactive species was discussed by Rajkumar [53]. The surface charge of nanomaterials was of great importance as this decided the applications. Antimony phosphate nano ribbons showed a clean separation of uranyl ion from its various mixtures. Nano crystalline manganese oxide was used for the separation of uranium from different metal ions.

Patil et al. [54] examined the application of nanoscale zero valent iron, carbon nanotubes and nano-fibers for the remediation of a variety of contaminants including chlorinated compounds, hydrocarbons, organic compounds and heavy metals.

Ecofriendly applications of several nanomaterials that have been used in bioremediation of waste and toxic materials have been discussed by Rizwan et al. [55]. Nanomaterials not only directly catalyzed degradation of waste and toxic materials, which is toxic to microorganism, but also it helps enhance the efficiency of microorganism in degradation of waste and toxic materials. This also shows that phytoremediation can be applied in the removal of heavy toxic metal from contaminated soil. This work focused on immense applications of nanomaterials in bioremediation.

Khin et al. [56] gives an overview of the applications of nanomaterials in various shapes/morphologies, such as nanoparticles, wires, tubes, fibers, etc. function as adsorbents and catalysts and their composites with polymers are used for detection and removal of gases, chemicals, organic pollutants and biological substances such as viruses, bacteria, parasites and antibiotics. Nanomaterials have better environmental remediation properties due to its high surface area and reactivity. They have developed dendritic nanopolymers for low pressure filtration process to remove perchlorate and uranium from contaminated water.

A review on recent development of the commercial available engineered nanoparticles in the environmental remediation and their toxic effects was reported by Kamali et al. [57]. The comparative study of the effectiveness and the toxicity of the engineered nanoparticles for environmental remediation indicated that advanced bimetallic materials such as Fe/Pd, or Fe/Ni can exhibit a better performance in degrading the recalcitrant, environmental pollutants on one hand, and a lower observed toxicity on the other hand. The copper oxides engineered nanoparticles have shown relatively high level of toxicity. Nano zero valent iron (nZVI) is emerging as a new option for the treatment of contaminated ground water. Taghizadeh et al. [58] has given an overview on the characteristics and application of nano zero valent iron and summarizes its use in ground water remediation. The nZVI effectively reduces chlorinated organic contaminants (e.g. perchlorobenzene, pesticides, tetrachloroethylene, perchloroethylene) and inorganic anion perchlorate. The nZVI is more effective at reaching deep zones of contamination, and is more effective at contaminant degradation than iron of larger size.

Karn et al. [59] has discussed nanoscale zero valent iron in environmental remediation. Nanoscale Fe particles are effective for the remediation and transformation of a variety of environmental contaminants. No ground water is pumped out for above-ground treatment, and soil is transported to other places for treatment and disposal. Because of the high cost and lengthy operating periods for pump and treat remedies, in situ ground water treatment technologies are increasing.

A review on use of nanomaterials for the remediation of environmental contaminants viz, heavy metals, dyes, organophosphorous compounds, chlorinated organic compounds, and halogenated herbicides described by Guerra et al. [51]. This review provides an overview of inorganic, carbon-based and polymeric-based nanomaterials for environmental remediation.

Muller and Nowack [60] has described three examples of the use of engineered nanomaterials in soil remediation are nanoscale zero-valent iron for the degradation of halogenated organic compounds, nanoscale calcium peroxide for the destruction of organics (e.g. gasoline) and nanoscale metal oxide for adsorption of metal. The nanoscale zero valent iron is the only application of nanomaterials in soil and ground water remediation that has been successfully commercialized. A short review on application of nanotechnology in the remediation of contaminated ground water was explained by Agarwal and Joshi [61]. The quantitative removal of chlorpyrifos and malathion pesticides achieved by gold and silver nanoparticles supported on activated alumina.

Chen et al. [62] presented review which highlights the application of nano zero valent iron (nZVI) in treating refractory compounds. The use of nZVI has some drawbacks such as (i) magnetic attraction between nano iron particles causes the rapid aggregation of particles (ii) nZVI are more prone to react with dissolved oxygen and oxygen rich compounds (iii) nZVI exert some degree of toxicity studies suggest that cell membrane disruption and oxidative stress through the generation of Fe^{2+} and oxidative stress through the generation of Fe^{2+} and reactive oxygen species by nZVI are the main mechanism contributing to nZVI cytotoxicity. These drawbacks overcome by immobilizing nZVI particles on suitable solid supports and also to expand the effective pH range of the Fenton reaction.

The nanoparticles made by mechanical and/or microbial action with fundamental building blocks are among the smallest human made objects and exhibit novel physical, chemical and biological properties: which has wider application for detection, prevention, monitoring and remediation of pollutants. This review paper reported by Pandey and Fulekar [63] highlights that nanotechnology offers great promise for delivering new and improved remediation technology to clean up the environment. Present review discussed methods of synthesis (milling of large particle, precipitation of nanoparticles, SCF technology, emulsion and biogenic) size measurements and characterization (TEM, SEM, XPS and XRD etc.) of nanoparticles use of nanoparticles as sensors (Bio, electrochemical, mass, optical, gas) has also been discussed.

Firozjaee et al. [64] described a review on application of nanotechnology in pesticides removal from aqueous solutions. The aim of this review is to compile and study current publications regarding pesticides removal by nanotechnology. This study discusses the applications, advantages and limitations various technology processes for removal of pesticides.

A review on different management approaches to reduce level of metal contamination in soil and finally to the food chain discussed by Singh and Prasad [65]. The heavy metal pollution is very much concerned because of their toxicity for plants, animals and human being and their lack of biodegradability. The applications of nanoparticles for metal remediation have been attracting great research interest due to their exceptional adsorption and mechanical properties, unique electrical property, highly chemical stability and large specific surface area.

Mohamed [66] reported a review on application of nanotechnology in air pollution monitoring. He also gave definition, classification, properties and application of nanoparticles. Air mostly contained pollutants like CO, chlorofluorocarbons, volatile organic compounds, hydrocarbons and nitrogen oxides.

Biogenic uranite nanoparticles and their importance for uranium remediation have been described by Bargar et al. [67]. First step in biogenic uranite formation is the reduction of U (VI) to U (IV). Electron transfer presumed to be mediated by C-type cytochromes localized either in the periplasm or on the outer membrane. The second step in biogenic uranite formation entails the precipitation of the mineral. The hydrated biogenic uranite due to its diminutive size, the molecular-scale structure, energetic appear to be similar to those of courser-particles, abiotic, stoichiometric UO_2. These properties of biogenic uranite nanoparticles make it suitable for the bioremediation of subsurface U (VI) contamination.

Adeleye et al. [68] presented review on the performances of traditional technologies and nanotechnology for water treatment and environmental remediation were compared with the goal of providing an up to-date reference on the state of treatment techniques for researchers, industries and policy makers. Case studies were conducted on emulsified zero-valent nanoscale iron for ground water remediation and nanosized silver-enabled ceramic water filters for drinking water treatment. This review submits that nanotechnology is emerging as a promising alternative to traditional methods of water treatment and pollution remediation.

The use of iron oxide nanomaterials for the extraction of toxic heavy metals viz. Cd, Cr, As, Pb and Hg from ground water studied by Neyaz et al. [69]. Naturally occurring iron oxide nanoparticles are magnetite (Fe_3O_4), maghamite (γ-Fe_2O_3) and hematite (α-Fe_2O_3) found in environmental sources such as volcanoes and fires. Metal ferrites such as $MnFe_2O_4$, $CoFe_2O_4$ and Ni Fe_2O_4 can be formed by constituting Fe (II) with the corresponding metal cations. The selection of best method for water purification should follow four conditions (i) Treatment flexibility and final efficiency (ii) Reuse of treatment materials (iii) Environmental friendliness (iv) Low cost. Surface modified iron oxide nanoparticles with various functional groups (like – COOH, NH_2, - OH, -SH) tend to be a hot research field due to its unique physico-chemical characteristics such as easy and fast separation by applying external magnetic field, chemical inertness, less toxic by-products, biologically safe and biocompatible etc.

Buzea et al. [7o] conducted studies on sources and toxicity of nanoparticles. Nanotoxicity is now concept to service, present review reveals the results of life long history of evolution in the presence of nanoparticles, and how the human body in particular has adapted to defend itself against nanoparticulate intruders. The key to toxicity of nanoparticles is their minute size, penetrate basic biological structure and disrupt their normal function. The toxic effect included tissue inflammation and cell death. Human have always been exposed to tiny particles via dust storms, volcanic ash, and other natural processes, and that our bodily systems are well adapted to protect us from potentially harmful intruders.

The overview of development of nanotechnology in waste water treatment and their adverse effect on human health has been described by Zekic et al. [71]. This overview discussed main nanotechnological processes such as nanofiltration, catalysis, photocatalysis, water disinfection, adsorption of pollutants and nanoscale zero valent iron, the nanomaterials used for water disinfection include chitosan, silver nanoparticles, titanium dioxide, fullerene, carbon nanotubes etc. Present review also described effect of nanomaterials used in wastewater treatment on human health and ecosystem.

Nayana and Pushpa [72] has synthesized nanozero valent iron (nZVI) borohydride reduction method for the treatment of wastewater in terms of colour and chemical oxygen demand. The nZVI characterized by scanning electron microscope and particle size analyzer. Batch experiments were carried out under various conditions of pH, dosages and contact time. The COD was reduced to 85% from initial concentration of 9,600 mg/L. The colour was reduced to 55% from initial absorbance value of 0.6596 at 655 nm at a pH of 2.48 at 150 min of contact time and at adsorbent doses of 1.5 g. Colour removal increased with a decrease in pH.

The potential for improving the effectiveness of photocatalytic processes by means of semiconductor-metal nanocomposites and merits of combining two advanced oxidation processes was discussed by Kamat and Meisel [73]. Present work described semiconductor nanoparticles as photocatalyst (TiO_2) and semiconductor-metals viz: (Ag, Au, Cu and Pt) nanocomposites for improving the efficiency of photocatalyst. Sensing potential of SnO_2 and ZnO based semiconductor system has also been discussed. The TiO_2 photocatalysis is most useful to degrade polar compounds. When highly polar compounds are formed during the oxidation of organic contaminants, complete breakdown to CO_2 and H_2O is quickly realized.

Ruttkay-Nedecky et al. [74] has summarized that the latest findings on the phototoxicity of nanomaterial products based on essential metals used in plant protection. Phototoxicity of nanoparticles may be as a result of the toxicity of substances, which are used for its preparation. The nanoparticles may have potentiating of inhibitory effects on plant growth in different developmental stage. It is concluded from present study that the nanoparticles prepared from essential heavy metals and their oxides have proven to be suitable for use in the agriculture. The least phototoxic of these appear to be nanoparticles made from iron oxides and manganese oxides.

The overview of current knowledge of magnetic nanoparticles zero valent iron (nZVI), magnetite (Fe_3O_4) and maghamite (γ-Fe_2O_3) reported by Tang and Lo [75]. This review presented contaminant removal mechanism by magnetic nanoparticles along with factors affecting the ability of contaminant desorption. This review has also discussed aggregation of magnetic nanoparticles, methods for enhancing stability and toxicological effects owing to magnetic nanoparticles.

Grieger et al. [76] has discussed environmental benefits and risks of use of zero valent iron nanoparticles (nZVI) for soil and ground water remediation. They have apply a best and worst case scenario evaluation as a first step to quantitatively evaluate the current state of knowledge regarding the potential environmental risk of nZVI.

A review on application of nanoscale zero valent iron and its composites for the removal of heavy metal ions from the environment studied by Zou et al. [77]. Present review show excellent removal capacity and environmental remediation of nZVI based materials for various heavy metal ions [Pb(II), Cr(III), Cd(II), As(III), Cu(II), ZN (II), Ni(II), Sb(II)]. A new look on nZVI based materials [nZVI @ $Mg(OH)_2$, nZVI –KOOL, chitosan based nZVI, bentonite and beta zeolite supported nZVI] and possible interaction mechanism (e.g. adsorption, reduction and oxidation) and latest environmental applications are discussed. The effects of various environmental conditions (e.g. pH, temperature, coexisting cations and oxoanions) and potential problems for the removal of heavy metal ions on nZVI-based materials with the DFT theoretical calculations and EXAFS technology are also discussed.

Verma [78] has summarized sustainable synthetic processes developed during the past two decades involving the use of alternate energy inputs and greener reaction media. Titanium dioxide can be doped with metal (Ag) and non-metal atoms such as S, N, C to enhance its activity in visible light. The evolution in the development of “greener processes” continues from solvent-free reactions to the use of alternative energy-input systems, such as microwave or mechanochemical mixing in benign reaction media such as polyethylene glycol and water. The generation of recyclable nanocomposites, especially originating from biomass and waste that is not even consumed by animals (algal and sorghum residues) can be used as agents for the removal or degradation of pollutants and toxins under visible light, thus encompassing several green chemistry principles concurrently.

A review on synthesis, structure, sizes compositions and surface properties and applications of bimetallic Fe nanoparticles has been reported by Liu et al. [79]. Reactions between

the bimetallic nanoparticles (NPs) and those pollutants categories into four types (i) catalytic replacement reaction for heavy- metal removal, (ii) hydrodehalogenation for halogenated hydrocarbons, (iii) nitro and azo hydrogenation for nitro and azo compounds and (iv) hydrodeoxygenation for oxyanions. The composition for some bimetallic nanoparticles are Fe CO_3, Fe_2Pt_5, $FePt_3$, Fe $_{0.6}$ Au_2, Fe Ni_5, $Fe_{45}Pt_{55}$ etc. Compared with monometallic Fe NP’s, bimetallic Fe NP’s have considerable separability and catalytic ability of degrade nanobiodegradable pollutants.

Metal and metal oxide nanoparticles exhibit unique properties such as sorption, magnetic, chemical reduction, ligand sequestration etc. and have separation, catalysis, environmental remediation sensing and biomedical applications. This review on broad coverage of nanoparticles and polymeric/biopolymeric host materials and their properties have been reported by Sarkar et al. [80]. This review also discusses the role of the donnan membrane effect exerted by the host functionalized polymer in harnessing the desirable properties of metal and metal oxide nanoparticles for intended application. Present work is a good channel for the development of new types of hybrid ion exchangers for applications in areas such as heterogeneous catalysis, sensors, health and medicine and drug-delivery.

Mukherjee et al. [81] discussed review on the recent developments and approaches made in synthesis of nano zero valent iron (nZVI), structure and characterization of nZVI, challenges faced in the transport of nZVI in the surface environment and the augmentation of the motility of nZVI. They have discussed the effective use of nZVI in remediating organic pollutants (halogenated organic compounds, pharmaceutical waste and azo dyes) and inorganic pollutants (Ni^{2+}, PO_4^{3-}, Co^{2+}, Cu^{2+}). Aggregation of nZVI has been reported to be the major drawback for its applications. The modification of nZVI in order to overcome the challenges faced in the transport of nZVI through the soil has also been discussed.

The review focuses on the synthesis, protection, functionalization and application of magnetic nanomaterials (Fe_3O_4, γ-Fe_2O_3, $MgFe_2O_4$, $MnFe_2O_4$, $CoFe_3O_4$, $CoPt_3$, Fe pt) as well as magnetic properties of nanostructured systems reported by Lu et al. [82]. Methods such as co-precipitation, thermal decomposition, micelle synthesis and hydrothermal synthesis are discussed to control size and shape of magnetic nanoparticles. The protection strategies surfactant/polymer coating, silica coating and carbon coating of nanomaterials are also discussed in order to protect them from corrosion. Suitable polymers for coating are includes poly (pyrrole), poly (aniline), poly (alkylcaenoacrylates), poly (methylidene malonate) and polyesters such as poly (lactic acid) poly (glycolic acid) and their copolymers. The application of protected nanomaterials in catalysis and biotechnology are briefly reviewed.

Kemp et al. [83] investigated a review deals with wide-ranging environmental studies of graphene-based composite material (Fe- rGO, Fe_3O_4, Fe_3 O_4- rGO, M Fe_2O_4 – rGO , Fe C_2 O_4- rGO, rGO = reduced graphene oxide) on the adsorption of hazardous materials and photocatalytic degradation of pollutants for water remediation. This review also addressed biological toxicity of graphene applied to environmental remediation. The photocatalyst (TiO_2- rGO, SnO_2 - rGO, CuO - rGO, WO_3 - rGO, Cu- rGO, Au – rGO) for the degradation of organic pollutants are also discussed.

The synthesis and applications of magnetic graphene nanocomposites (MGNCS) for the removal of heavy metals (Cr, As, Pd, Hg) from the environment was described by Zhu et al. [84]. Their focus is to reveal potential of MGNCS to reduce the level of heavy metals below EPA requirements. Adsorption behaviour of heavy metals on MGNCS included adsorption kinetics, solution pH effects, concentration effect of both contaminants and adsorbents.

Auffan et al. [85] has defined nanoparticles are the particle that has sizes between 1 and 100 nm (10^{-9} m) which show properties that are not found bulk samples of the same material. They reviewed the size dependent properties of a variety of inorganic nanoparticles and found that about 30 nm do not in general show properties that could require regulatory scrutiny beyond that required for their bulk counterparts.

A review with a set of recommendations for the advancement of understanding of the role of nanoscale silver in environment and ecotoxicological research investigated by Fabrego et al. [86]. Present review summarizes synthesis, characterization and bioaccumulation mechanism of silver nanoparticles. It also present effects of Ag NPs to aquatic organism fish prokaryotes, invertebrates algae and microbes mechanism of toxicity indicated that Ag NPs are more toxic than dissolve silver ion.

Bhattacharya et al. [87] have synthesized mixed oxides such as iron-cerium, iron-manganese, iron-zirconium, iron-titanium, iron-chromium, cerium-manganese, thoroughly characterized in sophisticated instruments like SEM, TEM, FTIR, AFM and employed for water treatment. The rapidly growing use of engineered nanoparticles in a variety of industrial scenarios and their potential for waste water purification still have challenge how these nanoparticles can be removed in the water cycle.

A review on core/shell nanoparticles: classes, properties, synthesis mechanism characterization and applications described by Chaudhuri and Paria [88]. Core/shell nanoparticles categories as inorganic/inorganic; inorganic/organic; organic/inorganic; organic/organic materials. The choice of shell material of the core/shell nanoparticles is generally strongly depend on the end application and use. The magnetic and fluorescence core materials coated with inorganic materials are extensively studied because of their wide applications in the biomedical and electronics fields. The efficiency of a core/shell semiconductors enhanced by selective coating of core material with higher band gap shell materials. The core/shell has potential of direct use in both imaging and selective drug release.

The increasing use of nanomaterials for treatment of ground water results their release in aquatic environment and also their toxic effect to aquatic life nanoparticles are more toxic than larger particle of same substance. Liu et al. [89] present brief summary of technique for nanoparticles removal in water and wastewater but it looks that no treatment can absolutely protect the public from exposure to a large scale dissemination of nanoparticles separation from aquatic environment such as coagulation, electrocoagulation, flotation process, filtration process, biological process, magnetic filtration, capillary electrophoresis etc, are also discussed in the review.

Bezbaruah et al. [90] has investigated trichloroethylene (TCE) remediation using encapsulated nanoscale zero valet iron (nZVI) in Ca- alginate biopolymer. Encapsulation expected to offer distinct advances over entrapment. This study has demonstrated that nZVI particles can be encapsulated in Ca – alginate without significant reduction in their reactivity. The TCE removal using encapsulated nZVI was 89 – 91% when compared to 88 – 90% removal using bare nZVI over a 2h period. This TCE degradation followed pseudo first order kinetics for encapsulated nZVI systems. The use of Ca – alginate encapsulated nZVI can overcome the mobility and settlement problems associated with bare nZVI and can be a potential technique for in situ remediation of groundwater.

An article on preparation, characterization and application of nanoparticles in preconcentration, separation and determination of trace pollutants from various environmental samples was investigated by Kaur and Gupta, [91]. Nanoparticles are suitable replacement for organic solvent and reactive complexants in the extraction and preconcentration of trace metals and organic compounds from natural water and environmental samples. Chemically modified nanoparticles of silica , titania , zirconia and magnesia with (dithizone , gallic acid , PAN, 8-hudroxiquinilone etc.) are found effective , highly selective and more efficient for the preconcentration of environmental pollutants .

Uzum et al. [92] synthesized nano zero valent iron (nZVI) from borohydride reduction and examined for the removal of aqueous Co^{2+} ions over a wide range of concentrations from 1.0-1000.0 mg/L. The size of nZVI particles was predominantly within the range of 20.0-80.0 nm. Experiment investigated the effects of V/m ratio, concentration, contact time and pH for the removal of Co^{2+} ions. Iron nanoparticles demonstrates very rapid uptake and large capacity for the removal of Co^{2+} ions. X- photoelectron indicate that fixation of Co^{2+} ions takes place through the interaction of their ions with the oxohydroxyl groups on the iron nanoparticle surface in addition to spontaneous precipitate formation on high loading.

Synthesis, properties, toxicology and applications of silver nanoparticles was reported by Tran et al. [93]. Transmission of infectious pathogens to the community has caused outbreaks of disease such as influenza (A/H_5N_1), diarrhea (Escherichia coli), cholera (vibrio cholera) etc. throughout the world. This review presented the synthesis and antimicrobial effects of Ag – NPs against various pathogens including bacteria fungi and virus. Some current applications Ag-NPs in water, water – air, surface – disinfection are described. Toxicology considerations of Ag – NPs to humans and ecology are discussed in detail. The future prospects of Ag – NPs for treatment and prevention of currently emerging infections are also discussed. Kharisov et al. [94] has discussed review on iron containing nanomaterials, their synthesis, properties and environmental applications. Attention is also paid to and polymorphic forms of iron oxides and Fe OOH. Greener methods, coated, doped, supported with polymers or inert inorganic materials, core-shell nanostructure of iron oxides and gold was discussed. Water disinfection (against viruses and bacteria), toxicity and risks of iron nanomaterial and applications were examined. This review also described use of iron – containing nanomaterials for the remediation of organic contaminants (chlorine – containing pollutants, benzoic and formic acids, dyes) and inorganic cations Zn(II), Cu(II), Cd(II), and Pb(II) and anions (nitrates, biomates, arsenates) from the environment.

Enhanced chitosan/ Fe^o – nanoparticles beads for hexavalent chromium removal from wastewater studied by Liu et al, [95]. Fe^o nanoparticles (nZVI) were successfully immobilized on epichlorohydrin/chitosan beads (ECH-CS-nZVI beads) for reduction of Cr (VI) from wastewater. ECH-CS-nZVI beads were characterized by SEM and FTIR. The removal of Cr (VI) using ECH – Cs – nZVI beads was consistent with pseudo first - order reaction kinetics. This study demonstrated that SCH –CS – n ZVI beads could became an effective and promising technology for in situ remediation of Cr (VI).

The nanoscale zerovalent iron – rectorite (nZVI-R) composite was successfully synthesized through incorporation of nZVI into the natural rectorite as support by Lou et al. [96]. Iron ions were imbedded in the interlayer of rectorite, and then the exchangeable Fe (III) cations were reduced to nZVI by $NaBH_4$ in solution. Prepared nZVI-R composite material was characterized using XRD, HR-TFM, XPS and XRF etc. In comparison to commercially available nZVI-Junye, nZVI- Lab and Na^- rectorite the synthesized nZVI- R composite in this study showed higher decolourization potential for orange (II). The mechanism for nZVI-R in discoloration of orange (II) was postulated by FTIR. The nZVI- R has potential applications in cleaning up environmental contaminants such as organic dyes or halogen compounds.

Metal nanoparticles of Au, Ag, Pd and Pt have been synthesized in aqueous media using red grape pomace as a reducing agent and a copping agent described by Baruwati and Verma

[97]. The particles are formed within a few seconds when expose to microwave irradiation at a power level as low as 50 W. Particles could be formed at room temperature, but they tend to be amorphous in nature except for gold. A detailed study of the morphology of the ensuring particles with various reaction conditions has been carried out.

Nanoscale zerovalent iron (nZVI) became more effective to remove heavy metals from electroplating wastewater when enhances chitosan (CS) beads were introduced as a support material in permeable reactive barriers (PRBS).Investigated by Liu et al. [98]. The SEM images showed that CS – nZVI beads enhanced by ethylene glycol diglycidyl ether (EGDE) had a loose and porous surface with a nucleus – shell – structure. At low concentration (< 40 mg/L), heavy metals were removed in order Cd (II) > Cu (II) >Pb (II) > Cr (II). As concentration increased the removal order was changed into Pb (II)> Cu (II) > Cd (II) > Cr (VI). The finding revealed that EGDE – CS – NZVI – beads PRB_s had the capacity to remediate actual electroplating wastewater and may become an effective and promising technology for remediation of heavy metals:

Scott et al. [99] reported the effect of vacuum annealing on the structure and surface chemistry of iron nanoparticles (INP). The corrosion resistance and longevity imbued by vacuum annealing of nanoparticles material may prove favourable for applying remediation technologies more effectively in natural and industrial situations. A multidisciplinary approach was used to investigate changes induced by vacuum annealing (< 5 X 10^{-8} m bar) at 500 ^{0}C on the bulk and surface chemistry of INP, in vacuum annealing of INP particle size did not change but surface oxide thickness decreases from 3 – 4 nm to 2 nm. The XRD confirmed that recrystallization of metallic core had occurred converting a significant fraction of poorly crystalline iron to bcc α–Fe and Fe_2 B phases. The XPS indicated a change in the surface oxide stoichiometry from magnetite ($Fe_3 O_4$) towards wustite (Fe O) and migration of boron and carbon to the particle surface.

A novel biosorbent prepared by the immobilization of phanerochaete chrysosporium with iron oxide magnetic nanoparticles (MNPs) and Ca – alginate by Xu et al. [100]. The structure of prepared MNPs – and Ca – alginate immobilized P. Chrysosporium was confirmed by ESEM, EDS, FTIP and XRD characterization. The prepared MNPs – and Ca – alginate immobilized P. Chrysosporium was capable of removing Pb (II) ions from solution efficiently, in terms of its performance and cost. Present work provide a potential and unique technique for heavy metals removal by enhanced removal capacity and application stability.

Corte et al. [101] reported innovated method for biological synthesis of Pd nanoparticles (bio – Pd). Present review discussed different bio – Pd precipitating microorganisms (Escherichia coli, Klebsiella pneumoniae, anabaena, calothrix, clostridium pasterianum, citrobacter Braaki, etc.) and application of catalyst for the degradation of environmental contaminants (e.g. Cr (VI), ClO_4^-, Lindane, Chlorophenol, Trichloroethylene etc.). The microbial scaffold allows a green synthesis of NPs and offers some advantages and perspectives for the development of reactor technologies for metal recovery, soil and water treatment.

A short review on application of nanotechnology in the remediation of contaminated ground water was described by Agarwal and Joshi [102]. Present article reviewed status of groundwater quality, basic idea of nanotechnology for remediation and its practical applicability, ongoing projects and future scope of nanotechnology in India. The use of nano zero valent iron (nZVI) in the treatment of chlorinated hydrocarbons and metals from hydrocarbon discussed in the article. The practical applicability of Fe^o particles lies in the fact to get oxidized into +2 and +3 oxidation states thereby reducing other organic as well as inorganic impurities. The metallic iron (Fe^o) served effectively as electron donor

$$Fe^0 \longrightarrow Fe^{2+} + 2e^- \quad (1)$$

Chlorinated hydrocarbons accept the electrons and undergo reductive dechlorination

$$RCl + H^+ + 2e^- \longrightarrow RH + Cl^- - (2)$$

from a thermodyamic perspective the coupling of the reactions (1) and (2) is often energetically highly favourable

$$RCl + Fe^o + H^+ \longrightarrow RH + Fe^{2+} + Cl^- - (3)$$

The standard reduction potential of ZVI, (Fe^{2+}/Fe^{3+}) is 0.44 V, which is lower than many organic compounds like chlorinated hydrocarbon and metals such as Pb, Cd, Ni, and Cr, hence these organic compounds and metals are thus prone to reduction by ZVI nanoparticles.

Chandhuri and Paria [103] reported an easy synthesis technique a sulfur doped hollow TiO_2 nanocatalyst for photodegradation of organic dye under solar light. The sulfur doped hallow TiO_2 nanoparticles synthesized by template base sacrificial core technique. The photocatalytic potential of synthesized catalyst was tested by degradation of methylene blue dye under solar light. The surface area of synthesized hallow doped nanoparticles comparatively higher (318.11 m^2g^{-1}) than TiO_2 particles (130.94 m^2g^{-1}) because of the hallow and porous structure, Sulfur doping on TiO_2 decreases the band gap from 3.2 – 2.5 eV which make the material more suitable as photocatalyst under solar light. This catalyst can be used effective for environmental remediation purposes because of high surface area and low band gap.

The biodegradability of fullerenes, single, double, multi-walled as well as COOH functionalized carbon nanotubes and cellulose and starch nanocrystals in aqueous environment has been investigated by Kummerer et al. [104]. The cellulose and starch nanocrystals are actually better biodegradable than their macroscopic counterparts in aqueous environments whereas fullerenes and CNTS are not at all biodegradable. None of the particles were found to be toxic to micro-organism necessary for oxygen take-up.

Gawande et al. [105] has synthesized $Fe_3 O_4$ – cysteine MNPs without any additional source of linkers. The $Fe_3 O_4$ – cysteine, MNPs were successfully used for the synthesis of P-amino carbonyl and hydroquinoline. Magnetic organocatalysts can be easily recovered by simple magnetic decantation and their catalytic activity remains unaltered after nine consecutive cycles making them environmentally friendly and widely applicable due to their efficiency, easy of handling and cost effectiveness.

Synthesis, characterization and manipulation of dendrimer – stabilized iron sulfide nanoparticles were studied by Shi et al. [106]. The Fe S nanoparticles were synthesized using ethylenediamie core poly (amidoamine) (PAMAM) dendrimer of generation 4 terminated with amino (G4 – NH_2), hydroxyl (G4 –NglyOH) and carboxyl (G_4 – SAH) groups, respectively as stabilizers. Deposition of FeS NPs on to mesoporous silica gel microparticles was confirmed by zeta potential and SEM measurements. Study shows that dendrimer – coated silica particles facilitate the much more effective loading of FeS NPs. The synthesis and manipulation of FeS NPs onto mesoporous silica microparticles provide remediation applications.

The potential of nano zero valent iron application for removal of different organic contaminants in different scenario (i. e. ground water, waste water etc.,) is studied by Raychaudhury and Scheytt [107]. The reaction efficiencies of nZVI for reduction of nitro organic compounds are found high. The halogenated compounds with high molecular weights or complex structures (i.e. iodinated contrast media, DDT, polychlorinated biphenyls etc.) has showed lower reaction rates with nZVI compared to the widely studied chlorinated hydrocarbons (i.e. trichloroethylene).

A review on recent applications nanotechnology is agro-environmental studies with particular attention to the fate of nanomaterials once introduced in water and soil to the advantages of their use and their possible toxicology reported by Mura et al. [108]. Finding show that the use of nanomaterials can improve the quality of the environment and help to detect and remediate polluted sites. It is noted that not all nanomaterials induce toxic effects e.g. TiO_2, carbon black show low toxicity.

Xu et al. [109] investigated review which outline the applications of iron oxide nanomaterials ($Fe_3\,O_4$ – silica, flower like iron oxides, hydrous iron oxide MNPs, cysteine coated $Fe_2\,O_3$ MNPs, amino modified $Fe_3\,O_4$ MNPs etc.) for the removal of heavy metals (Cu (II), Cr (VI), As (V), Hg (II), Ni (II) Pb (II) etc.) from waste water. Present review described the use of iron oxide as nanosorbents for heavy metals, organic contaminants, as photocatalyst in photodegradation reactions. The $Fe_2\,O_3$ can be applied as a sensitizer for TiO_2 photocatalyst, photo – Fenton like system has been set up with the existence of iron oxides and oxalate. The outlook for potential applications and further challenges as well as the likely fate of nanomaterials discharge to the environment were discussed.

A review on application of nanoparticles in agriculture (improving seed germination, plant protection, pathogen detection, pesticide/herbicide etc.) and the role these can play in future agriculture production described by Khot et al. [110]. Toxicity of the ecosystem, potential, residue carried – over in food stuff and nanomaterials phototoxicity are some of the major concerns for the application of nanomaterials in agriculture. There is also need to evaluate the toxicokinetics and toxicodynamics of nanomaterials used for agricultural production. About 1045 residues reported by Food Administration Department (FAD) as pesticide residue, nanomaterial based nanosensors can be used to detect such pesticide residue.

Ariga et al. [111] focused especially on materials for environmental remediation based on the concept of materials nano architectonics. Study classified into three categories: (i) Continuous arising problem: Such as removal and degradation of toxic substances including waste due to fossil fuel uses and organic pollutants (ii) Current urgent problem: current emerging topics concerning oil spills and nuclear waste (iii) Breakthrough for future development: advanced method based on supramolecular chemistry and nanotechnology. Toxic substances include removal of fossil waste, degradation of organic pollutants, removal and filtration of other hazardous substances. Current emerging topics included oil spills, nuclear waste, future technology for materials detection include advanced supramolecular systems for sensing. The good knowledge of both basic science and practical usage is required for environmental remediation.

Bhuyan et al. [112] investigated biosynthesize zinc oxide nanoparticles from Azadirachta indica for antibacterial and photocatalytic applications. The present work reported low cost, green synthesis of ZnO nanoparticles using 25% (W/V) of neem leaf extract: synthesized nanoparticles characterized by TEM, EDX, XRD, UV-VIS, FTIR. Biosynthesized ZnO were of size 9.6 – 25.5 nm, band gap 3.87 eV and have wurtzite structure. The ZnO nanoparticles have shown good antibacterial (S. Aureus, S. Pyogenes and E. coli) and photocatalytic (methylene blue degradation) activity. Synthesized ZnO nanoparticles found to act as an effective antimicrobial and photocatalytic agent.

The biosynthesis of inorganic nanoparticles including metallic nanoparticles (Au, Ag, Hg, CdFe, AuAg, Se, Pt) oxide nanoparticles ($Fe_3 O_4$, $Fe_2 O_3$, TiO_2, $BaTiO_3$, ZrO_2) sulfide nanoparticles (ZnS, CdS, FeS) and other typical nanoparticles ($PbCO_3$, $CdCO_3$, $SrCO_3$, CdSe) described by Li et al. [113]. The biosynthesis of nanoparticles by microbes is taught to be clean, nontoxic and environmentally acceptable "green chemistry" procedure. The use of microorganism (bacteria, yeast, fungi and actinomycetes) classified into intracellular and extracellular according to location where nanoparticles are formed. The applications of these biosynthesized nanoparticles include drug delivery, cancer treatment, gene therapy, DNA analysis, antibacterial agent, biosensors, enhancing reaction rates, separation science and MRI. The main drawback of biosynthesis of nanoparticles are slow process (several or even a few days) instability (nanoparticles formed by microorganism may be decomposed after certain period of time). These two drawbacks need further study.

Bi et al. [114] demonstrated that metallic Ag nanocrystals can be selectively formed on the entire surface, edges and partial [100] facets or only edges of simple – crystalline $Ag_3 PO_4$ submicro-cubes by simple adjusting the concentrations of ammonia. The photocatalytic performance studies for decomposition of shodamine B indicates that Ag/Ag_3 PO_4 heterocubes exhibit much higher photocatalytic properties than pure $Ag_3 PO_4$ cubes and Ag nanoparticles under visible light irradiation, which may be due to efficient charge separation at contact interface as well as the enhanced visible light absorption.

The effect of alumina nanoparticles an algal growth investigated by Sadiq et al. [115]. The growth inhibitory effect of alumina nanoparticles was observed on both algal species/72h EC_{50} value, 45.4 mg/L for chlorella sp: 39.35 mg/L for scenedesmus sp). Bulk alumina also showed toxicity through a lesser extent (72 h EC_{50} value, 110.2 m mg/L for chlorella sp; 100.4 mg/L for scenedesmus sp). The concentration dependent decrease in the chlorophyll content is may be due to the shading effect of alumina particles. The FT – IR, optical and scanning electron microscopic images suggest interaction of the nanoparticles with the cell surface. The entrapment of algal cells in aggregates of alumina nanoparticles may play a pivotal role in toxicity to the algal species.

Chidambaram et al. [116] develop and apply an efficient biomediation method based on in situ biosynthesis of bio-Pd nanoparticles and hydrogen. The C. Pasteurianum BC1 was used to reduce Pd (II) ions to form Pd nanoparticles (bio-Pd) that primarily precipitated on the cell wall and in the cytoplasm. The C. Pasteurianum BC1 cells, loaded with bio-Pd nanoparticles in the presence of glucose were used to fermentative produce hydrogen and effectively catalyze the removal of soluble Cr (VI) via reductive transformation to insoluble Cr (III) species. Batch and aquifer microcosm experiments using C. Pasteurianum BC1 cells loaded with bio-Pd showed efficient reductive Cr (VI) removal, while in control experiments with killed or viable but Pd-free bacterial cultures no reductive Cr (VI) removal was observed. The process offer significant advantages over the current ground water treatment technologies that rely on introducing performed catalytic nanoparticles into groundwater treatment zones and the costly addition of molecular hydrogen to above ground pump and treat system.

Silica colloid-polyelectrolyte-iron oxide nanocomposites with both magnetic and catalytic properties have been synthesized via layer by layer assembly by Che et al. [117]. Dynamic light scattering (DLS) and electrophonetic mobility measurements were employed to monitor the evolution of these structures from silica colloid to silica colloid – polyelectrolyte – iron oxide composite. The experiment was conducted to test dyes (methylene blue, methyl orange) removal capabilities of synthesized nanoparticles silica colloid, polyelectrolyte 0 functionalized silica colloid (silica PDDA) and silica colloid – polyelectrolyte iron oxide composite (silica – PDDA – IOMMPS). The silica – PDDA – IOMMPS composite is found superior for pollutant removal from aqueous environment mainly due to catalytic property. The finding was rationalized by Langmiur and Freuedlish absorption analysis. The silica – PDDA – IOMMPS nanocomposites hybrid material were remain catalytically active after six months of storage.

Khan et al [118] described review for remediation of contaminated soil and ground water by chlorinated organic pollutants (PCB, TCE, TCA, pesticides, solvents), inorganic anions (perchlorates) metal ions [Cr (VI) , Zn (II), Cu (II), Pb (II), Cd(II)] by use nano zerovalent iron . Iron and nickel nanoparticles use for removal of uranium.

A report on restriction of nanoparticles in environmental clean up discussed by Snousy and Zawrah [119]. The objective of the work is to point major challenges facing environmental nanoscience and urges developing ecofriendly techniques to ensure good quality of life. The use of nanomaterials in environmental applications requires a better understanding of their mobility, bioavailability and toxicity. This work includes subjects on risk assessment/toxicity, exploring the ecological assessment, toxicity, fate, transport and limitations facing nano zerovalent particles in the ecosystems. Future pollution remediation nanomaterials based techniques may include pollution transport by nanoparticles which will have medical, radiological and national defence implications in terms of human health, safety and the environment.

CONCLUDING REMARKS

1. In this critical review applications of engineered nanoparticles (carbonaceous compounds, metal oxides, semi- conductor devices, zerovalent metals, polymers etc) in various environmental remediation areas have been discussed.
2. The nano zerovalent iron , carbon nanotubes , nanoclay, dendrimers , nanoparticle silver, colloidal elemental gold are found to be an effective tool for removal of heavy metals , dyes, phenols , organochlorine , organophosphorus etc from the environment.
3. Carbon nanotubes are found to be a adsorbent for a wide variety of organic compounds from aquatic environment which include DDT , chlorobenzene , chlorophenols , trihalomethanes ,dyes , pesticides , herbicides , polynuclear aromatic hydrocarbon , p-nitrophenol etc.
4. The inorganic nanoparticles including oxide nanoparticles (Fe_2O_3, TiO_2, ZrO_2, Fe_3O_4), metallic nanoparticles (Ag, Au, Hg, Pt, CdFe, Se, AuAg) , sulphide nanoparticles (ZnS, FeS, CdS) are found to have well established environmental remediation potential.
5. There are three main challenges for the production and use of nanomaterials (i) cost effectiveness (ii) impact on human life and environment (iii) use of a particular nanotechnologies.
6. The nanocatalysts , nanomembranes and and nanoadsorbents are found to be most used nanomaterials.

7. The use of nanoparticles in environmental remediation are invariable lead to release of nanoparticles in the environment. The potential risk of these nanoparticles in the environment can be assessed by knowing their bioavailability, toxicity, persistence and mobility. The growing use of engineered nanoparticles in environmental remediation raises question how these nanoparticles can be removed from the environment. This may also be a challenging field of research for relevant researchers.

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