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Role of Nanomaterials in Environment Clean Up technologies: Toward a Sustainable Tomorrow

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ABSTRACT: Nanotechnology has a major part to play in providing novel and fruitful solutions to a wide array of environmental problems including soil, water and atmosphere pollution caused by various human activity or industrial processes. In recent years application of nanomaterials has been found as a new method for the removal of contaminants from water, soil and air due to their infinitesimal size, huge surface-area-to-volume ratio, great reactivity, high mobility, quantum size effect, great biocompatibility and strong adsorption property. Among all present nanomaterials, carbon-based nanomaterials (fullerenes, carbon nanotubes and graphene), zero-valent metal nanoparticles (silver, iron) and metal oxide nanoparticles (titanium dioxide, zinc oxide and iron oxide) have captivated a great deal attention due to their capability of monitoring, sensing and treating such small amounts of environment contaminants. This critical review discusses the role of engineered nanomaterials for different technologies linked with environmental clean-up process. The technical challenge associated with the use of engineered nanomaterials is to produce them in desired shape and size with the use of advanced physical, chemical and biosynthesis techniques and once used for any application study its effect on ecosystem. This paper also highlights the potential risks linked with the discharge of nanomaterials into the environment and possible solutions of nanomaterial discharge implications in order to revolutionize nanotechnology in environmental applications.

Keywords: Nanotechnology; contaminants; soil; water; air

I. INTRODUCTION

During the past few years, increase in global population has forced rapid development of industrialization in order to provide a better quality of life to each citizen. In developed country, the atmosphere is occupied by various pollutants present in the form solid particles liquid droplets and gases such as carbon monoxide (CO), nitrogen oxides, carbon dioxide, heavy metals (arsenic, chromium, lead, cadmium, mercury, zinc), volatile organic compounds and sulphur oxide generated by several human activities include burning of coal or by industrial processes. The existence of nitrogen and sulphur oxide in the air produce acid rain that pollute the soil. Water pollution is induced by countless factors such as sewage, oil spills, leaking of fertilisers, pesticides and from by-products of burned fossil fuels. Presence of different types of contaminants in environment cause various diseases such as cancer, neurological disorder, nausea, muscular weakness and many other harmful effects on human health [1]. Research has shown that nanotechnology possess the ability to block, minimize, identify and treat environment pollution by controlling the matter at the nanoscale level with at least one dimension between 1-100 nm. Nanomaterials are synthesized by three important methods such as physical (high energy ball milling, electron beam lithography, inert gas condensation, laser pyrolysis method, melt mixing, physical vapor deposition, sputter deposition, electric arc deposition, molecular beam epitaxy), chemical (chemical co-precipitation, sol-gel, spin coating, dip coating, solvothermal, electrochemical deoposition, microemulsion, hydrothermal)and biological methods (bacteria, yeast, fungi and plant extracts) [2-5]. In the past few years, nanomaterials are found to be useful in various fields such as biomedical [6], energy [7], agriculture [8], information and communication technology [9], environment [10] and many more. Presently, nanomaterials such as titanium dioxide, zinc oxide have been used as an additive in food products, cosmetics and paints, fullerene composites are used in solar cells, medicine and tennis rackets, silica nanoparticles are used as solid lubricants, silver nanoparticles are used in food storage, textiles, disinfectants, soaps, bandages and carbon nanotubes are used in in solar panels [11]. It has been found that currently worldwide nanotechnology products requirement appears to be 17% in soils, 21% in water and 2.5% in air and the rest appearing in landfills[12].

In particular, tiny size, large surface-to-volume ratio, strong adsorption and high reactivity of nanomaterials has drawn wide attention for the detoxification of vast variety of environmental pollutants. Reported contaminants that successfully eliminated in environment by the use of different types of nanomaterials are heavy metals (arsenic, lead, mercury, copper, cadmium, chromium, nickel), radioactive, organic (polychlorinated biphenyls, benzoic, phenols, dyes) and microbial contaminants (bacteria, viruses) [13]. Literature review indicated that zero valent metal nanoparticles, carbon and metal oxide based nanomaterials are considered to be potential candidates for the treatment of polluted water, air, soil [14]. These are found to be very attractive for the fabrication of nanosensors, nanofilters, nanoadsorbents and nanomembranes [15]. Conceptually, any technology which satisfy following conditions must be considered effective for environmental clean-up process: (1) operation flexibility (2) final productivity (3) recovery of treatment agents (4) ecological clean and (5) economical and the incorporated engineered nanomaterials must possess the following properties: (i) high reactivity and longevity (ii) sufficient mobility within porous media and (iv) low toxicity [16-17].

Numerous studies have indicated that nanomaterials show great promise in decomposing chemicals present in the form of pollutants into less toxic species. This technology also called as green technology as it helps in minimizing the production of harmful wastes obtained during manufacturing process by using less material quantity and less toxic compounds. This paper presents an overview of nanomaterials extensively used for decontamination mainly comprise zero-valent metal nanoparticles (silver, iron), metal oxides nanoparticles (TiO_2, ZnO and iron oxide)and carbon nanomaterials. Advantages of current nanotechnology over traditional environmental clean-up methods, potential risks associated with the release of nanomaterial into the environment together with possible solutions to overcome its implications are explored in order to achieve a better future.

II. NANOMATERIALS USED IN DIFFERENT TECHNOLOGIES FOR TREATING ENVIRONMENTAL POLLUTION

Availability of fresh, affordable and fast delivery of clean water is one of the greatest problems that today people are facing in our country. Its demand is continuously rising because of increase in population and industrialization. Different pollutants present in water, waste water, ground water, oil spill and soil cannot be removed effectively via traditional methods includes (a) filtration (b) osmosis (c) coagulation (d) pump and threat (e) permeable reactive barriers (f) soil vapour extraction (g) soil washing [18]. These methods are quite expensive, time consuming and not able to detect and treat contaminants concentration at ppb levels [19]. Nanotechnology enhances the productiveness of remediation methods to a large extent through the use of nanoscale particles due to its tunable physical, chemical, electrical, magnetic and structural properties. Nanoadsorbents, photocatalysis, nanofilters, nanomembranes and nanosensors are found to be useful for prevention, control and reduction of pollution. These applications are discussed below which are either in the stage of laboratory or field research together with role of applied nanomaterials.

A. Nanoadsorbents

Nanotechnology facilitates the possibility of solving many problems related to water quality using nanoadsorbents. Traditional adsorbents such as activated carbon possess small surface area, lack of selectivity and slow adsorption kinetics which limit its efficiency. Nanoadsorbents overcome all these limitations by providing extremely high adsorption capacity, high selectivity, high surface area, short intraparticle diffusion distance, improved sensitivity, fast kinetics and tunable pore size making it suitable for industrial use. Factors that determine the adsorption capacity of any nanomaterial are surface area, pore volume, and average pore diameter [20-21]. They offer design flexibility either install as fixed-bed reactors in the form of pellets/beads doesn’t require future separation process or can be integrated in the powder form in slurry reactors but need secondary unit to collect the nanoparticles. Nanoadsorbents made up carbon nanomaterials and metal oxides (iron oxide) are proven to be powerful for transporting of different types of environmental contaminants. It has been reported that as the particle size of nanoadsorbents decreases, metal adsorption capacity increases [22]. The large adsorption power, easy separation and regeneration make carbon based and metal oxide based nanoadsorbents technologically beneficial.

(a) *Carbon Nanoadsorbents*

Carbon nanostructures like fullerenes, carbon nanotubes (CNTs) and graphene are considered to be the most fascinating and promising materials for molecule adsorption due to their unique morphology, extremely high surface area, abundant porous structure, high strength and good electrical properties. CNTs are made by rolling up graphene sheets in cylindrical shape having diameter as small as 1 nm [23]. CNTs structure is classified into two types (1) multiwalled carbon nanotubes (MWCNTs) containing different stacks of concentric cylinders with a separation of about 0.34nm between the neighbouring stacks and (2) single-walled carbon nanotubes (SWCNTs) containing single layers of graphene sheets turn round into cylindrical dimension [24]. Presently, both MWCNTs [25-27] and SWCNTs [28] have been used for the degradation of contaminants in water.

Fullerenes are fabricated by burning of benzene in an oxygen–argon flame with careful control of gas flow [29]. The adsorption capacity of fullerenes against organic pollutants such as organic and organometallic compounds [30], polycyclic aromatic hydrocarbon [31] and naphthalene and 1,2-dichlorobenzene [32] in aqueous solutions have been reported. Investigation has shown that compared to traditional adsorbents, CNTs act as better adsorbents for the adsorption of various bulky organic molecules such as dichlorobenzene [33], ethyl benzene [34], dyes [27] and heavy metals include Zn^{2+}[25], Pb^{2+}, Cu^{2+}, Cd^{2+} [26] due to diverse contaminant CNTs interactions and fast adsorption kinetics [35]. Conventional adsorbents carry notable number of small pores unreachable to sizeable organic molecules such as many antibiotics and pharmaceuticals [36] and possess small uptake tendency for low molecular weight polar organic compounds. Graphite oxide is a good alternative for CNTs due to its low cost and wide spectrum nature. Regeneration and reuse are the important factors that decide the practical effectiveness of any absorbent. Adsorbed metal ions on carbon nanoadsorbents can be recover by decreasing the pH of solution. Studies have shown that using SWCNTs and MWCNTs adsorption of zinc ions reduces to 25% after 10 regeneration cycles whereas using activated carbon, it reduces to 50% after one regeneration cycle [37]. They are often incorporated with other types of materials to enhance the adsorption, dispersibility, surface area, mechanical, optical and electrical properties [38]. Some review papers suggested that addition of CNTs with iron oxide nanomaterials was successfully able to eliminate chromium from water which can be easily isolated from water by using external magnetic field. Carbon nanomaterials are found to display good antibacterial properties, However, possible mechanisms accountable for such toxicity are not clearly known [23]. Regardless of the extraordinary properties of CNTs, its production and applications are mainly bounded by high cost and requirement of supporting medium to form structural components [39].

(b) *Iron oxide nanoadsorbent*

Iron oxide possess innumerable fascinating properties that can be use in diverse applications such as catalysis [40-42], environment protection [43-44], magnetic sensors [45], data storage media [46] and biomedicine [47]. In recent years, iron oxide nanomaterials have shown great potential for environment protection by the removal of different types of contaminants present in water and soil due to its simplicity of design, easy availability, low toxicity, low cost, easy regeneration with the assistance of external magnetic field, strong adsorption capacity, chemical inertness, excellent magnetic properties, superpara magnetism and great biocompatibility. Different forms of iron oxide such as magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3) and hematite (α-Fe_2O_3) are generally used as nanoadsorbents. Among all iron oxides, magnetite (Fe_3O_4) is of great interest because of its excellent magnetic properties. Magnetite (Fe_3O_4) has a cubic inverse spinel structure in which oxygen establishing face centered closed packed geometry and Fe cations reside interstitial tetrahedral sites and octahedral sites [48].Hematite is extremely stable at ambient conditions and maghemite is metastable with respect to hematite. Hematite is weakly ferromagneticat room temperature and changes to an antiferromagnetic state at 260 K [49] and has a Curie temperature of 956 K, above which it shows paramagnetic state. Magnetite is ferrimagnetic at room temperature and has a Curie temperature of 850 K [50]. Maghemite is ferrimagnetic at room temperature and loses its magnetization with time and temperature [51].

It has been investigated that synthesis techniques play a crucial role in controlling the shape, size surface chemistry of nanomaterials [52]. Numerous studies show that chemical stability and dispersibility of iron oxide nanomaterials can be increase by surface modification with suitable ligands containing wide array of functional groups, such as phosphonic acids, carboxylic acid, biomolecules, polymer, organic molecules and amine to ensure the properties of iron oxide nanoparticles are intact. Different structures of iron oxide such as nanocrystals [53–55], particles [56-57], cubes [58], spindles [59], rods [60-61], wires [62], tubes [63], flakes [64] and 3D flower [65] have been favorably produced by different techniques. The adsorption capacity and efficiency of these materials is higher than bulk material due to the highly porous structure and high surface area [43-44]. Based on the chemistry involved iron-based technologies for environmental remediation can be classified into two groups: sorptive or stabilisation technologies in which iron is used as a sorbent to immobilise contaminant agent and reductive technologies in which iron is used as an electron donor to transform pollutants into less poisonous form. It is well known that multiple technologies utilise both operation for both in-situ and ex-situ applications.

The small size of iron oxide nanomaterials is beneficial for the dispersal of metal ions from emulsion onto the active sites of the adsorbents surface. It has been reported that carbon-encapsulated magnetic nanoparticles were found to be very functional for the disposal of copper, cadmium metals [66] and Fe_3O_4 hollow nanospheres for removal of red dye in water [67]. Lot of research has been done on arsenic removal which shows that nanosized magnetite have superior adsorption performance compared to activated carbon due to sticking nature of iron oxide [68-69]. The ascorbicacid-coated Fe_3O_4 having diameter less than 10 nm and Fe_2O_3nanoparticles in cellulose matrix display superior adsorption capacity for arsenic [70-71]. Iron oxide nanoadsorbents containing amine group on their surface possess the capacity of taking away 98% copper from polluted river and tap water [72]. α-Fe_2O_3 were able to eliminate, a common azo-dye Orange II, used in the fabric industry due to the electrostatic attraction between the iron oxide surface and the Orange II species in solution. Furthermore, the iron oxide carrying Orange II could be reproduced by catalytic combustion at 300℃ in air for 3h, and the recovered α-Fe_2O_3 material were found to bear the same adsorption performance [65].

(c) Dendrimers and Aerogels based nanoadsorbents

Nanoscale dendrimers containing highly branched polymers used in ultrafiltration system are employed to capture heavy metals and organic compound. The interior shells of dendrimers usually made nonpolar for adsorption of organic compounds while the outer shell can be customized to different functional groups (e.g., hydroxyl- oramine-terminated) for adsorption of heavy metals. Mechanism responsible for adsorption phenomenon is constructed on the ground of complexation, electrostatic interactions, hydrophobic and hydrogen bonding effect [73].

Aerogels are used to solve the problem of oil spills in seawater leading harmful effect on environment. They act as a sponge and absorb very large amount of oil due to large surface area which can be easily removed from seawater. The drawback of this technique is that used materials are very costly, so possible substitute materials are in search.

B. Nanomembranes

The main objective of nanomembranes and nanofilters for water treatment is to eliminate unwanted materials from water. It provides a physical fencing for the separation of components based on their size. Benefit of using this technology is that it offers upper level of computerization, needed small area of land and the movable layout permit flexible structure. The main limitation of this method is high energy consumption, expensive clean-up and change of membranes during membrane fouling. Membrane fouling is created by discarded colloids, chemicals and microbes [74]. Nanomembrane performance, structure and functionalities depend on material properties.

Nanomaterials can be incorporated into membranes for enhancement of flux, membrane permeability, mechanical, thermal stability and for reducing fouling resistance. Used nanomaterials are metal oxide nanoparticles (e.g., Al_2O_3, TiO_2, silica and zeolite) and antibacterial nanoparticles (e.g., nano-Ag and CNTs). Nanomembranes can be constructed by gathering tailored nanoparticles into permeable membranes [75] or combining them with polymeric or inorganic membranes [76]. Membranes manufactured using metal oxide nanoparticles yield extra applicability that can catalysed reactions to decay foulants during oxidizing state. Existing literature review shows that excessive bacterial suppression has been accomplished using 3wt% polyvinyl-N-carbazole-SWNT nanocomposite [77]. Fabrication of thin film nanomembrane is in progress that integrate nanomaterials into the thin film sheet of composite membranes resulting in higher dye rejection .Thin film nanomembrane have been manufactured in situ by interfacial integration of TiO_2 nanoparticles functionalized with amine and chloride compounds along the boundary of copolyamide network on a polyimide support [78]. The membrane penetrability and refinement depend on the type, size and quantity of used nanoparticles. Nano-zeolites have shown great capacity in improving the permeability of thin film composite membranes.

Studies have suggested that iron oxide ceramic membranes and reverse osmosis (RO) membrane are used for the extraction of organic waste in water and seawater desalination. Reverse osmosis (RO) membrane is fabricated of cross-linked array of polymers embedded with nanoparticles constructed in such a way that it attracts water ions but repel bacteria and organics. Compared with traditional RO membrane, nanomembranes are less inclined to choking and have larger lifetime. However, lot of attempts have been made to grow low-fouling membranes using different nanomaterials, future research work is still required to interpret the potential of nanoparticles in design and operation of membranes.

(a) *Zero-Valent Iron nanoparticles (nZVI)*

Nano size zero-valent iron nanoparticles **(**nZVI)is another class of extensively studied nanomaterial that could address viable outcome of few environmental clean-up issues. It is extremely useful for the treatment of insitu and exsitu contaminated groundwater and surface water as shown in Fig. 1. It acts as a strong reducing agent because of moderate reduction potential (-0.440) [79]. Zero-valent zinc nanoparticles also has a moderate reduction potential (-0.762) but Fe is preferred over Zn for ground water contamination treatment applications because it leads to adsorption, oxidation, reduction and precipitation in the existence of dissolved oxygen, possess favourable quantum size properties and increased transport efficiency [80].

In the oxidation-reduction reaction between nZVI and contaminants, under anaerobic conditions, Fe^0 can be oxidized by H_2O or H^+ and generates Fe^{2+} and H_2, both of which act as potential reducing agent for contaminants. With increase of solution pH, Fe^{2+} may undergo further oxidative transformation to Fe^{3+}, which can make $Fe(OH)_3$, an effective flocculant for the elimination of contaminants, for example, Cr(VI) [81]. In the presence of dissolved oxygen, Fe^0 will be oxidized to Fe^{2+} by transferring two electrons to O_2 to produce H_2O_2 which can be reduced to H_2O by Fe^0. Further, the addition of $H_2O_2$and Fe^{2+} (known as Fenton reaction) can produce hydroxyl radicals having powerful oxidizing capacity with respect to large number of organic compounds [82].

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \tag{1}$$

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \tag{2}$$

$$Fe^0 + O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O_2 \tag{3}$$

$$Fe^0 + H_2O_2 + 2H^+ \rightarrow Fe^{2+} + 2H_2O \tag{4}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + OH^- \tag{5}$$

Fe^{2+} has found to be the supreme dangerous iron state for microorganisms and get quickly change to Fe^{3+}in the framework of neutral and alkaline conditions. In deficiency of oxygen, Fe^0 is likely to be changed into either magnetite (Fe_3O_4) or maghemite (Fe_2O_3, γ - Fe_2O_3) based on oxidation ambient [83].

The potentiality of the nZVI core to function as an electron donor for reductive immobilization and the oxide shell offer adsorptive sites by the formation of precipitates during corrosion makes nZVI one of the most technically mature and multifunctional remediation agent [84]. Zero-valent iron particle having size in the micron range is by no means very beneficial for waste water treatment due to its low reactivity and decrease in reactivity with time nZVI have several advantages such as easy availability, inexpensive and non-toxic nature. Its chemical reactivity can be improved further by using bimetallic iron nanoparticles in which the iron nanoparticles are covered with a secondary metal such as Fe/Pd [85], Fe/Pt[86], Fe/Ag [87] and Fe/Ni [88] proven to be more active and stable than nZVI. Application of bimetallic iron systems show improved reaction rates, more saturated end products and result in small build-up of chlorinated intermediates [89]. Compared to the currently available techniques, such as centrifugation and filtration systems, this method is found to be simple and does not require electricity found to be apt for remote areas having limited access to power supply. The utility of this technology is not just bounded to laboratory scale but can be successfully applied for real water contaminated sites in commercial scale.

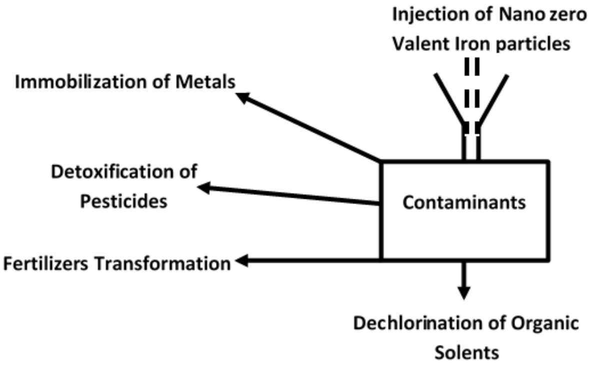

Fig. 1. Use of zero valent iron nanoparticles for treatment of contaminated water.

Discovery of nZVI was led by Gillham and O'Hannes in, who found that iron permeable-reactive barriers (PRB) filled with bulk zero valent iron particles were possess the capacity to convert a group of acyclic halogenated compound present in groundwater into less toxic compound [90]. PRB is not consider beneficial for long term use for processing deep aquifers or contaminated area due to its decrease permeability and high installation costs. Decrease in permeability is because of the deposition of iron oxidation products. nZVI are considered by many as an alternative option to PRB owing to their small size [91]. nZVI can be introduced straight into the origin of contaminated groundwater under pressure and by gravity as slurry for in situ treatment or it can be utilized in membranes for ex situ applications offering a highly flexible treatment technology. This technology is found to be very effective for deactivating heavy metals and radionuclides. The nanoparticles continue to remain active around contaminants present in soil and water for prolonged span of time (>4–8 weeks). The reaction mechanism of nZVI for contaminant transformation has been extensively studied [92].

nZVI has been identified as exceptionally fruitful for the detoxification of large variety of chemical pollutants such as azo dyes [93], chlorinated solvents (PCE, TCE, DCE) [94], pesticides (lindane, DDT) [95], halogenated organic compounds [96], nitroaromatic compounds [97], phenols [98], heavy metals such as chromium, copper, lead, arsenic, cadmium [99-104], inorganic anions such as phosphates, nitrates [105-106], metalloids [107], and radio elements such as uranium, plutonium [108]. These particles were also found to be useful for inactivation and control of certain gram-positive bacteria (Bacillus subtilis) and gram-negative bacteria (Pseudomonas fluorescens) [109].

nZVI can be synthesized by two approaches top-down and bottom-up. Bottom-up approaches require chemical reduction of ferrous or ferric salts [110]. Borohydride reduction of ferrous salts is the most commonly explore synthesis process. This approach generate considerably reactive and often polydisperse nanoparticle which may susceptible to agglomeration [111]. Expensive reagents, involvement of various separation steps, creation of huge amount of wastewater and hydrogen gas restricted its commercial application [112]. nZVI procured by making use of borohydride reduction method was effectively employed for the elimination of cobalt ion Co^{2+} over a wide concentration range. In order to minimize the cost production, it is synthesized by the ball milling method [113]. The degradation of iron pentacarbonyl ($Fe(CO)_5$) in organic solutions in the proximity of high-intensity ultrasonic waves was also used to synthesized nanoscale particles. This method produces ultrafine iron (10–20nm) with small size disperion but not useful for industrial applications due to highly toxic nature of precursor [114]. Presently, commercial-scale production is achieved by electrolytic reduction of ferrous iron employing an applied current [115]. In recent years, the synthesis of iron nanoparticles from tea leaves and sorghum bran extracts that contain polyphenolic compounds has drawn much attention [116].

Inspite of numerous benefits of using nZVI, it carries certain drawbacks, such as aggregation, easily oxidation upon exposure to air and difficulty of isolating from degraded system. In order to enhance its performance, it is coated with layer of polyelectrolytes, surfactants and dispersed in oil–water emulsions [117]. nZVI has been fortunately conjugated to a range of supports including silica, clays, zeolites and reverse osmosis membranes [118]. Surface-stabilization of nZVI has also been achieved with polymer [119], carbon [120] and noble metal [121] to provide control over shape, size and core–shell morphology of particles. Emulsified nZVI is used for treating dense nonaqueous phase liquid [122]. Future researchers need to develop effective clean-up scheme by working on the following key areas: mechanism of material reactivity with wide spectrum of contaminants, methods to improve colloidal stability by mitigating aggregation, construction of models to determine the transport properties in porous media, connecting laboratory investigations to field implementation and studying its release effects on ecosystem and human health.

(b) *Zero-Valent Silver Nanoparticles (Nano-Ag)*

Nanotechnology has shown that antimicrobial nanomaterials are found to be very effective for disinfection and microbial control in wastewater treatment. Traditional disinfectants used for water cleaning such as chlorine can result toxic disinfection by-products. Application of antimicrobial nanomaterials can increase the power of disinfection by minimizing formation of toxic by-products. Examples of effective antimicrobial nanomaterials are nano-Ag, nano-ZnO, nano-TiO_2, nano-Ce_2O_4, CNTs and fullerenes. Among all, Nano-Ag is the most extensively utilized nanomaterial. Highly toxic nature, being simple to use and broad antimicrobial spectrum made it a favourable choice for the treatment of large variety of microorganisms includes viruses [123], bacteria [124] and fungi [125]. Considerable research on silver nanoparticles shows that several theories have been presented to understand the exact mechanism of antimicrobial activity but precisely not published and will remain interesting topic of current research. Presently it is well admitted that the antimicrobial activity of nano-Ag mainly originates from the discharge of silver ions which can destroy the cell membrane and hence responsible for the destruction of cells [126]. It is also reported that silver ions can be attach with thiol groups of many vital proteins, producing enzyme damage and can destroy cell normal functions [127]. Studies have suggested that the release rate of silver ions play crucial part in determining the antimicrobial activity. The release kinetics of silver ions based on the size, shape and type of ligand used. The existence of ordinary ligands minimizes the bioavailability of silver ions and hence its toxicity [126]. It is reported that small application of silver ions results in increasing the growth of E. coli [128]. Direct use of nano-Ag pose some difficulty in existing cleaning technology due to their tendency of aggregation in aqueous media [129]. It is found to be useful in improving the performance of filters and membrane by providing barrier against waterborne pathogens. It has been reported that application of colloidal nano-Ag can eliminate Escherichia coli in the rate between 97.8% and 100% [130].

C. Nano-Sensors

It is a sensitive device used for fast identification of foreign matter and bacteria with molecular accuracy for the safety of human health and environment by producing a digital electronic signal. It is generally employed for the detection of poisonous chemical compounds present at ultra-low levels (ppm and ppb) in commercial products and in biological systems. Sensors made up of nanomaterials are more accurate, have high selectivity, high sensitivity, high speed, allow multiplex target detection, able to detect very lower concentration of targeted analyte (e.g. bacteria) and permit continuous, real-time monitoring due to their exceptional physical, chemical, optical, and magnetic properties. Conventional sensors are deliberate and unsuccessful in detecting the existence of arising pathogens particularly with respect to viruses and bacteria. Nano-sensors are generally made up of magnetic nanoparticles, quantum dots, noble metals, dye-doped nanoparticles and carbon nanotubes. Broad absorption and narrow emission spectra of quantum dots make it worthy for multiplex detection by employing single excitation light source. The emission spectrum of quantum dot is luminous and more stable than conventional dyes.

D. Photocatalysis

Photocatalysis seems to be one of the emerging and promising green technologies as it converts solar energy into chemical energy being used for solving many problems related to energy and environment such as photodegradation of pollutants, water purification, hydrogen production, carbondioxide photoreduction, photoelectric sensing and photodynamic therapy [131]. Semiconducting nanomaterials such as titanium dioxide (TiO_2), zinc oxide (ZnO) have been widely used for the removal of microbial pathogens and trace contaminants using photocatalytic oxidation method due to its high photocatalytic activity, low toxicity, chemical stability, biological stability and low cost. These materials generate electron-hole pair on absorption of photon having energy of the range of material band gap. The generated electron-hole pair travel individually to the semiconductor surface, take part in the redox reactions through charge transfer to organic contaminants and produce less harmful low molecular weight by-products such as CO_2, H_2O [132] as shown in Fig. 2. In this way several semiconductors can photodegrade numerous toxic compounds into be products by employing light.

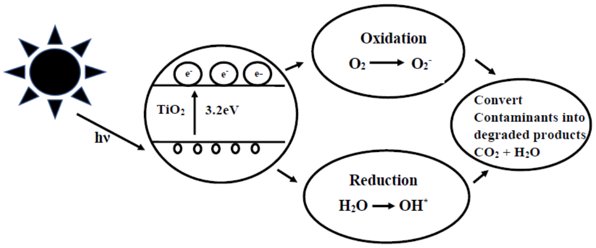

Fig. 2. Mechanism of TiO_2 photocatalytic process.

The major drawback of this technology is its slow kinetics due to limited range of light absorption of the solar spectrum and fast recombination of charge carriers. Recently, lot of research has been done to improve the photocatalytic activity with the help of nanotechnology by following ways:

1. By doping with noble metals to prevent the fast recombination of electrons and hole in the semiconductor and enhances the performance of the photocatalysis process.
2. By surface modification with organic or inorganic dyes.
3. By optimizing the shape and size of nanoparticles.

It has been presented that on reducing the particle dimension of TiO_2, tendency of electron-hole recombination decreases which further help in improving interfacial charge carrier transfer [133]. TiO_2 nanotubes were proven to be more effective than TiO_2 nanoparticles for degradation of organic compound [134]. Existed literature shows that WO_3 and Amino fullerene can decay pharmaceutical compounds and make viruses immobile under visible light irradiation in photocatalytic water treatment process [135].

(a) *Titanium dioxide (TiO_2)*

The commonly used photocatalysts are metal oxide semiconductor nanomaterials, among which TiO_2 is one of the most investigated photocatalytic material due to little contaminant selectivity. Three main crystalline phases of TiO_2 are anatase, rutile and brookite. Numerous studies reveal that anatase phase of TiO_2 exhibit large photocatalytic activity in contrast to other crystalline phases of TiO_2 [136]. A lot of effort has been made in order to improve photocatalytic activity but still not yet able to be achieved due to the fast electron-hole pair recombination and large band gap (E_g> 3.2 eV) [137]. Wide band gap nature of TiO_2 shows that light absorption is possible for wavelength below 388 nm (ultra-violet range) constituting only 7% of solar spectrum [138]. Key for making TiO_2 a powerful visible light photocatalyst is to minimize its band gap energy. Extensive work has been done to understand the photocatalytic mechanism of TiO_2 [139-140], impact of the photocatalysis operational variables with the change of TiO_2 characteristics [141-142] and applications of TiO_2 photocatalyst in large scale. TiO_2 produce reactive oxygen species and hydroxyl radicals on intake of UV light which can entirely deteriorate all types of contaminant in very short response time. It has been reported distinct nanostructures (0D, 1D and 2D) of TiO_2 may produce diverse photocatalytic properties which can be attained by using large range of synthesis techniques [143-144]. TiO_2 nanoparticles can be synthesized by hydrolysis, calcination, and flame furnace reactor method by ignition of vaporizable compounds (e.g., $TiCl_4$), emerge as one of the most effective industrial method for gas-phase synthesis of TiO_2 nanoparticles [145-146].

The photocatalytic activity depends on various factors such as initial concentration of titanium precursor, pH of the solution, temperature, treatment time, oxygen content and the type of chemical species being utilized [147]. Parameters responsible for reducing photocatalytic activity of TiO_2 are fast recombination of charge carriers and non-absorption of visible light [148-149]. In order to overcome these drawbacks, various methods have been suggested to use it for visible light and to impede electron-hole recombination such as surface modification with metals (iron, cobalt, chromium, copper, silver, platinum and gold), non-metals (carbon,nitrogen, sulphur) and coupling with other semiconductor materials [150-152].

It has been demonstrated that doping with metallic atoms help in producing localized energy levels between the valence band and the conduction band which facilitates electron-hole separation and increase visible photocatalytic activity [153]. Among all, Ag is immensely studied due to its easy production, antibacterial properties and economical nature [154]. Different techniques have been explored such as chemical reduction, UV irradiation, hydrothermal method and electrospinning to fabricate Ag/TiO_2 nanostructures. It has been reported that addition of Ag nanoparticles prevents the recombination of photo-generated electron-hole pairs in TiO_2 and cause a red shift of TiO_2 absorption edge wavelength [155-157]. Enhancement of visible photocatalytic process by doping with chromium metal is possible due to the absorption of Cr^{3+} ions on the surface of TiO_2 because of high surface energy, strong electrostatic interaction which lead to gradual diffusion of ions into the bulk of TiO_2 grains and then finally get inserted into the Ti^{4+} vacancy. This charge transfer band ($Cr^{3+} \rightarrow Ti^{4+}$) result in reducing the band gap of TiO_2 and hence increases the absorption for visible light [158]. Electron-hole pair separation using platinum photocatalyst is also reported [159]. In spite of the fact that metal-TiO_2 catalysts act effective visible photocatalyst, still they are not preferred as to suffer from multiple demerits such as high cost, difficult to recover, receptive to gas poisoning and produce harmful impact on the atmosphere. In order to recover TiO_2 easily from the treated system, research on integrating it with membrane and filtration technology has drawn much attention in recent years [160-161]. Existing publications shows that TiO_2 is also doped with non-metals (Carbon materials and nitrogen) in order to reduce the cost of this technology as demanded by industrial applications. Lot of work has been done on nitrogen doped TiO_2 photocatalyst because of its huge stability and little ionization energy [162-163]. For TiO_2 to work as effective visible light photocatalyst, it is also coupled with small band gap semiconductor includes WO_3, SnO_2, FeO_3 and CdS [164-165].

The TiO_2 based photocatalyst can be employed in diverse environmental and energy storage applications such as wastewater treatment, hydrogen generation, water disinfection and photocatalytic reduction of CO_2 into energy fuel. Various kinds of organic and inorganic contaminants have been released into the environment through water pollution caused by textile, agriculture and other industries. Different types of dyes including methylene blue [166], methyl orange [167], rodamine B [168], brilliant green [169], phenol [170] and acid red [171] have been photodegraded using visible TiO_2 based photocatalyst. It can also be used for destroying a large number of microorganisms present in water such as fungi, algae, protozoa and viruses [172]. It has been reported that Cu-TiO_2 photocatalyst synthesized using electrochemical anodization can effectively remove 97% lead from the environment [173]. This technology can also be used to produce hydrogen directly from water and from the decomposition of polluted effluents. Three Mechanisms responsible for hydrogen production are alcohol dehydrogenation, Water splitting, and alcohol reforming [174-176]. Despite achieved high photocatalytic efficiency in laboratory scale using different methods, TiO_2 is not considered very useful for large scale commercial applications. Hence, more efforts are required in investigating new effective methods to enhance the photocatalytic performance of TiO_2 in the visible light span for large applications.

(b) *Zinc Oxide (ZnO)*

In wastewater treatment using photocatalytic technology, besides TiO_2, ZnO has come out another potential member because of its direct, wide band gap nature, powerful oxidation ability, strong antimicrobial property and low cost [177-178]. The photocatalytic efficiency of ZnO is limited by the absorption of small range of solar spectrum and fast recombination of photogenerated charge carriers due to photo corrosion [179]. To increase its photocatalytic activity, ZnO is doped by various types of metal and couple with different types of semiconductor materials such as CdO [180], CeO_2 [181], SnO_2 [182], TiO_2 [183], grapheneoxide (GO) [184] and reduced graphene oxide (RGO) [185].

III. IMPLICATIONS OF USING NANOMATERIALS

Although use of nanotechnology proved to be beneficial for environmental remediation, but there are many uncertainties associated with its use. Application of nanomaterials could lead adverse effects on ecosystem and on people wellness. Ecological hazards linked with the utilization of nanomaterial include (i) dispersal in the environment due to high mobility(ii) ecotoxicity (iii) persistency due to small size (iv) bioaccumulation (v)ability to inverse their initial entry from atmosphere [186].

The major ecosystem concern is that nanoparticles due to small size remain present in atmospheric frame damaging drinking aqua bodies and thus effecting the stamina of humans and animals. Human health risks are caused by the inhalation of nanoparticles through polluted air, water and through the application of cosmetics products [187]. Exposure of nanomaterial cause a number of harmful effects on human health such as oxidative stress, genotoxicity, lung diseases, inflammation, pulmonary pathological changes etc [188-189].These implications may confine the large-scale implementation of nanomaterials for environmental decontamination. Hence, in order to build this technology more efficient than dangerous additional research is required to perform sooner than later.

IV. POTENTIAL SOLUTIONS OF NANOMATERIAL IMPLICATIONS

After reviewing the implications of nanomaterial on ecosystem and on human health. This section presents sustainable solutions to solve problems associated with discharge of nanomaterials into environment.

1. Use of green technology for formation of nanoparticles from various plant parts. For example: extracts of green tea leaves, oak, pomegranate having huge anti-oxidant capacities have been employed for the synthesis of nZVI [190-191]. Benefit of using this method is its simplicity, environmentally friendly nature, low cost, prolonged reactivity, easily availability of plant extracts and release of less toxic by-products into the environment causing less harm to aquatic and human health.
2. Use of biological method for synthesis of nanoparticles using microorganisms (bacteria, yeast and fungi) [192].
3. Application of emulsified zero valent iron particles in which iron particles are confined in a biodegradable oil

membrane result in breaking insoluble pollutants into harmless compounds.

4. Development of effective and fast analytical tools that can measure nanomaterials dispersion in water and soil.
5. Development of 'smarter' nanomaterials by providing coatings of suitable functional groups which can improve durability, transport and reactivity of nanoparticles [193-194].
6. Need to install persistent, semi-persistent or detachable permeable iron barriers combine with nZVI for shallow aquifers.
7. Need to watch the usage of nanomaterials in the ecosystem by local legal and national regulatory bodies rigorously.
8. Need to do valid testing of regulations specific to each nanomaterial with the requirement to revise them regularly and follow strictly to give accurate ecotoxicological information.
9. Requirement of integrated approach of modern research, people awareness programs, media exposure and statutory provisions in order to make nanotechnology an eco-friendly, sustainable and economical technology in environmental applications [187].

V. CONCLUSION

Nanotechnology being one of the fastest expanding section of world resources has guided the evolution of a large range of unique technologies in both household and commercial scale for the processing of organic, inorganic and bacterial contaminants present in atmosphere through water, soil and air. Nanomaterials such as carbon nanomaterials, metal oxides (TiO_2, ZnO and iron oxides) and zero valent metal nanoparticles (Ag and Fe) undoubtedly considered to be promising candidates over conventional materials for environmental applications because of its small size, large sensitivity, unique physical, chemical, electrical and magnetic properties. Traditional methods of environmental remediation such as discharge to landfill, pump-and-treat are not endurable whereas use of nanomembranes, nanofilters and nanosensors are found to be highly effective and versatile. The efficiency of different technologies depends on the properties of used nanomaterials which in turn depends on their synthesis techniques and enhancements in surface stability.

In future, lot of research is required in overcoming the drawbacks of discussed nanomaterials such as aggregation and oxidation of nanoscale zero valent iron particles, limited ultraviolet light adsorption by TiO_2 and ZnO nanoparticles and high production cost of carbon nanotubes.

It can be concluded that nanotechnologies provide the opportunity to minimize the environmental pollution through various process such as reducing the production of waste product during manufacturing processes, use of less harmful chemicals, minimize material usage, reduction in used amount of energy, minimize release of green house gases during fuel buring and utilization of biodegradable plastics. For field applications, these methods need to be cost effective and capable to treat low contaminant concentrations. Generation, utilization and discharge of nanomaterials will surely cause their appearance in air, water and soil. The unknown risks or impact linked with the usage of nanomaterials on people wellness and on ecosystem need to be addressed before their large scale application. At present there is requirement to make strict guidelines related to its implementation for remediation technology. In future, complete evaluation of the toxicity, economical efficiency and reactivity of different nanomaterials will remain an interesting subject of research for ensuring real field environmental applications.

VI. FUTURE SCOPE

As discussed, contaminants present in environment mainly comes from industrial, agricultural pesticides and medical waste. Experimentally, several techniques are found to be effective for control of pollution includes nanoadsorbents, photocatalysis, nanofilters, nanomembranes and nanosensors. However, still there are bottlenecks of mentioned technologies such as low conversion efficiency of light energy in photocatalysis method due to the presence of large factors in environment (pH, ionic strength) [195].

In the future, following work can be proposed for increasing the efficiency of laboratory based nanotechnologies:

1. Production of green, economical nanomaterials of desired shape and size.
2. Once synthesized, potential hazards associated with its use need to be investigated.
3. The effect of different environmental parameters on different nanotechnologies should be investigated.
4. Though ab initio models and simulation models, behaviour of the nanomaterial during the design of technology can be study.

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