

Chapter 6

Nano Remediation, a Novel Approach to Sustainable Environment

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Abstract:

Human activities are increasingly destroying ecological balance by releasing huge amounts of anthropogenic hazardous toxicants into the environment, contaminating soil, water, and the atmosphere, and jeopardising human public health. The use of beneficial nanotechnology to traditional environmental remediation procedures in an attempt to adopt a suitable treatment technology for cleaning up all of the waste left behind by the industrial revolution. Furthermore, this investigation highlighted the barriers that restrict nanomaterials' application and suppress the benefits of their superior properties; these barriers include environmental conditions (e.g., humidity, temperature, acidity, etc.), particle aggregation, and separation problems. Nanotechnology has been discovered to offer exceptional properties for complex, resilient, and multifunctional treatment techniques that can increase pollution monitoring and treatment performance while overcoming all of the aforementioned limits. In conclusion, nanotechnology has the potential to enhance environmental remediation by reducing the production of secondary byproducts, dissolving certain hazardous pollutants utilising zero-waste processes, and avoiding future soil contamination by converting pollutants from labile to non-labile phases. Finally, nanotechnology will pave the way for adaptable and dynamic systems that use cutting-edge approaches to detect and monitor a wide range of hazardous compounds and toxins in diverse environmental media.

Keywords: Nano Remediation, hazardous toxicants, the environment, contaminating soil, environmental remediation, nanotechnology, zero-waste processes

Introduction:

Environmental pollution is the introduction of contaminants into the natural environment that cause adverse change to their physical or biological components. The Major Types of Environmental pollutions are Air pollution, Water pollution, Soil pollution, Noise pollution. Pollution can be either man-made pollution or naturally occurring. Pollution can be a chemical substance or in the form of energy such as noise (Vehicle movement, wind mills etc.), heat (thermal pollution) or light that causes pollution. Environmental contamination is without a doubt one of the most serious issues confronting civilization today. New technology for the clean up of pollutants in the air, water, and soil are constantly being updated (*Guerra et al 2018*). Materials with at least one exterior dimension of 100 nanometers (nm) or internal structures of 100 nm or less are known as nanomaterials. Nanomaterials with the same chemical composition as recognized bulk materials may have distinct physical and chemical properties. Top-down techniques can be used to generate very small structures from bigger pieces of material, such as etching to create circuits on the surface of a silicon microchip.

Bottom-up approach, they can also be built from the ground up, atom by atom or molecule by molecule. Self-assembly is one method for accomplishing this, in which atoms or molecules arrange themselves into a structure based on their natural features. Because of the unique physical features of nanoscale materials,

nanotechnology has received a lot of interest in recent decades. Remediation is the process of restoring and maintaining the quality of air, water and soil, that are contaminated and become unfit for any use. Nano-remediation is the application of reactive nanomaterials to mitigate the env. pollutant by adsorption, transformation and detoxification process. These nanomaterials have properties that enable both chemical reduction and catalysis to mitigate the pollutants. Nano-remediation has become the main focus of research and development. This method has a lot of potential for cleaning up contaminated places and protecting the environment from pollution. Nanomaterials are best suited for in situ applications due to their unique characteristics.

Pollution Hazard and threat to Environment:

Pollutants are particles that harm the environment by polluting it. Life can be harmed when exposed to these pollutants, and the consequences for humans and other organisms are well known. Pollutants can enter the environment in a variety of ways, both naturally and through human activity. Pollutants of various types include dyes, heavy metals, pesticides, and polyaromatic hydrocarbons.

Dyes are synthetic organic chemicals that are used in many industries, including textiles. As a result, they have become common industrial environmental contaminants during their manufacture and, eventually, during fabric dyeing. Synthetic dyes in textile effluent reduce light penetration into rivers, affecting aquatic vegetation's photosynthetic efficiency and, as a result, aquatic species' food resources. The thin layer of released dyes that may form on the surfaces of receiving waters reduces the amount of dissolved oxygen, posing a major threat to aquatic life.

Heavy metal pollution is now becoming more of an issue and a subject of concern, Because of the detrimental impacts, it causes all across the world. Titanium (Ti), iron (Fe), vanadium (V), chromium (Cr), manganese (Mn), cobalt (Co), copper (Cu), zinc (Zn), arsenic (As), molybdenum (Mo), nickel (Ni), cadmium (Cd), silver (Ag), tin (Sn), platinum (Pt), gold (Au), mercury (Hg), and lead (Pb) are among the most common heavy metals that causing pollution.

Pesticides have been used in agriculture for decades to protect crops and animals from bug infestations and prevent productivity losses. Pesticides are chemicals that are used in gardens, farms, and other public places to kill undesired organisms. Pesticide exposure has poisoned almost 1 million people, according to a survey undertaken by the World Health Organization (WHO).

Polyaromatic hydrocarbons are a type of persistent and pervasive environmental contaminants that are also hazardous to individuals due to their toxic, mutagenic, and carcinogenic potential. The increase in demand for petroleum products has resulted in an increase in emissions. Combustion in the absence of oxygen in organic materials, such as coal and firewood, is one factor.

Nano Remediation of polluted environment:

The removal of pollution or contaminants from water (including groundwater and surface water) and soil is known as environmental remediation. These waste materials are removed for the sake of human health and environmental restoration. Brownfield properties are either redeveloped or returned to their natural form through remediation. Cleaning up sites where hazardous trash was disposed of presents a particular problem. Environmental remediation include soil, sediment, groundwater, and surface water, among other environmental media. Groundwater and surface water are included in water remediation, while topsoil, subsoil, and sediment are included in soil remediation. Depending on the nature and amount of the pollution, soil and water cleanup may be done individually or jointly. Water remediation is the procedure for removing contaminants from water. Surface water in lakes, streams, and rivers can be contaminated by pollutants poured directly into the water or runoff from the ground. Groundwater, which is underground water that saturates porous material, can be harmed by contaminants seeping through the soil and silt above it.

Nano remediation cleans polluted media with designed nanoparticles, and it is less expensive and more effective than most traditional approaches. The interest in using nanomaterials for environmental remediation is based on the nanostructure's features, in addition to its cost-effectiveness. Nanoparticles (NPs) have high

surface-area-to-mass ratios, excellent electrical characteristics, and catalytic action (Corsi *et al.*, 2018). Nano particles may also spread in narrow spaces, making them more useful in soil and water cleanup. Membranes made of nanoparticles have also been employed in water nanofiltration (NF) because the membrane pores have the potential to retain large components in wastewater. Furthermore, the contact with the membrane separates the minor chemicals selectively. Metal oxides, carbon nanotubes, quantum dots, and biopolymers are among the nanomaterials used in water, soil, and air remediation. Schematic representation of various approaches for nano remediation of environmental pollution is represented (Figure.1.)

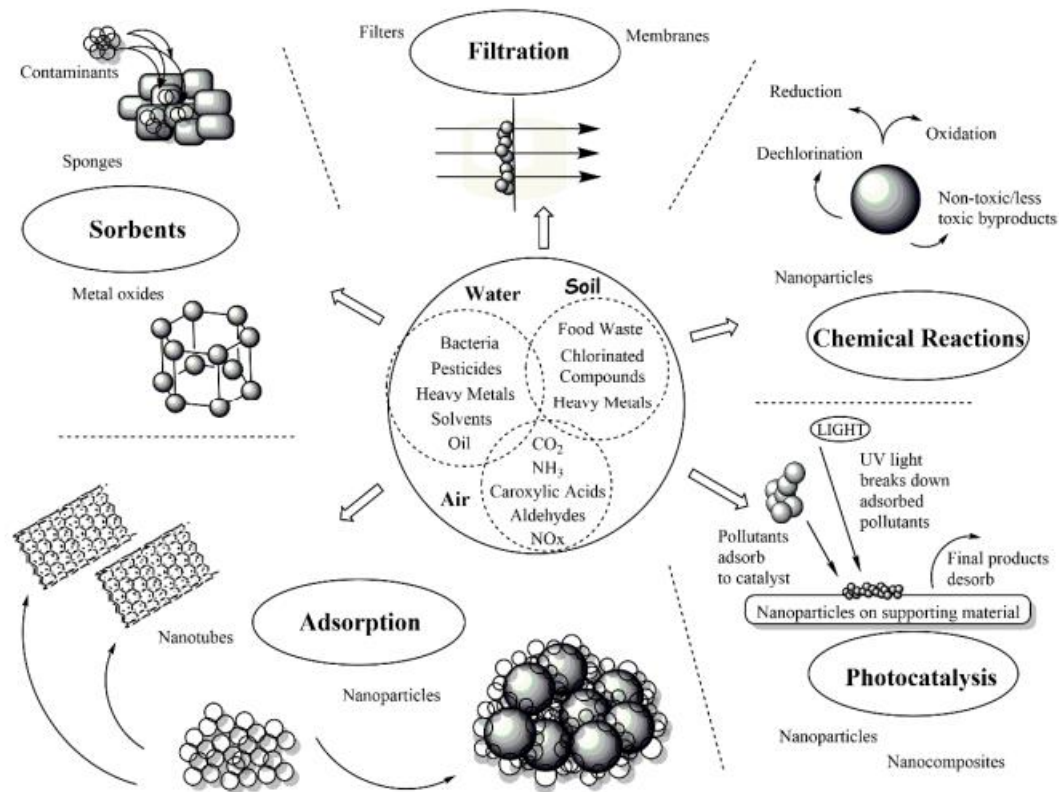


Figure.1. Environmental remediation approaches (Guerra *et al* 2018).

Properties of Nano-materials in environmental remediation:

Nano-size - Nanoparticle (100-nm) or any one of the dimensions of nanomaterial should be less than 100 nm. When compared to large-sized particles, their small size and new surface coatings allow them to spread further and wider. Other essential nanoparticle features for environmental cleanup.

- Increased surface area or sorption capacity.
- High reactivity.
- Readily tailored for application in several environments.
- Easy dispersibility.
- Nanoparticles can be prepared in different forms or shapes: Nanotube, nanofibers, nano-powder

These properties of nanoparticles can potentially provide a faster solution and more cost-effective site remediation.

Nanomaterial used in environmental remediation

- Metallic nanoparticles : Zero valent Iron (ZVI)
- Metal oxide nanoparticles : Iron oxide Nanoparticles (Fe_2O_3/Fe_3O_4)
- Titanium dioxide (TiO_2) Nanoparticles
- Zinc oxide

- Carbon based nanoparticles : Carbon nanotube
Graphene oxide nanoparticle
- Clay minerals : Zeolite
Halloysite nanotube
- Polymer based nanoparticles : Dendrimers
- Lipid based nanoparticles : Liposomes/Solid lipid nanoparticles.

Some environmental applications of nano materials include Nanoscale TiO₂ for the photocatalytic degradation of contaminants in water (e.g. microorganisms, organic materials) Nanofiltration for wastewater treatment and drinking water purification (e.g. removal of hardness and desalination). Nanoscale zero-valent iron for Heavy metal adsorption for soil and groundwater remediation. Nano clays are used as adsorbents for Carbon capture or GHG mitigation. Different types of nanomaterials are employed for nano remediation is explained (Figure.2.)

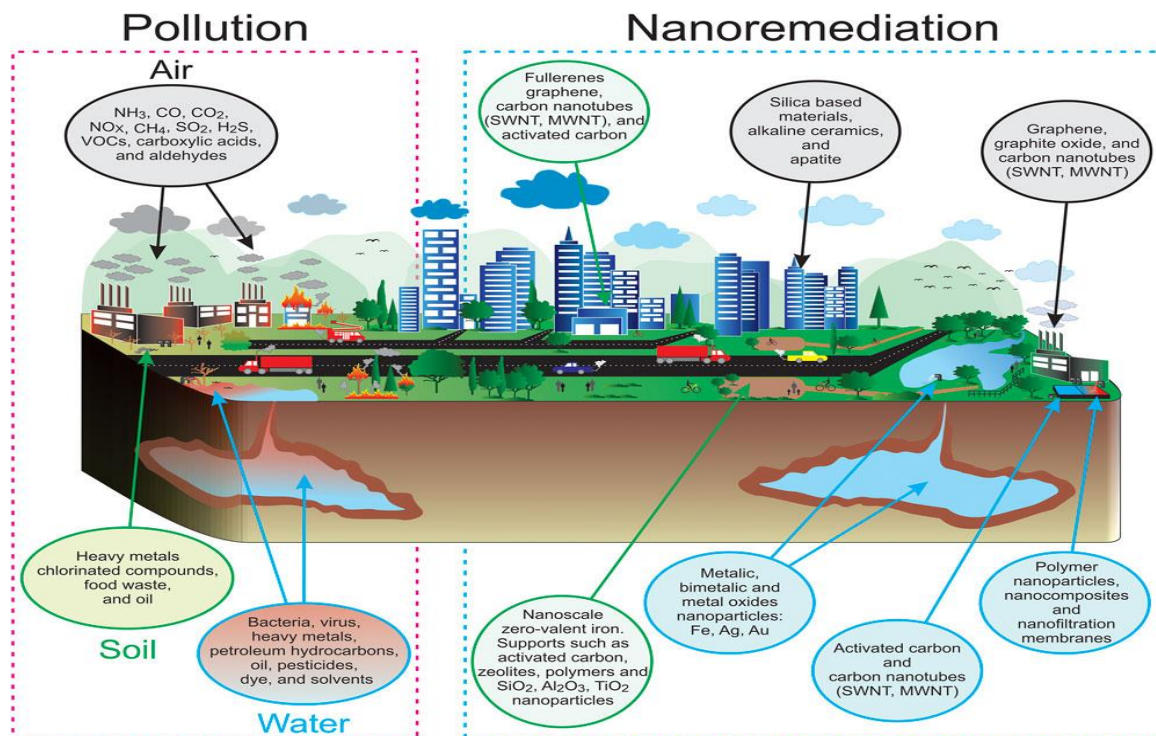


Figure.2. Different types of nanomaterials are employed for Nano Remediation

Nano Sensors:

Nanosensors are used for Sensing and detecting pollutants which is the first step in pollution control. Nano sensors are tiny devices that measure physical quantities and turn them into detectable and processed signals. The sensing portion of the sensor devices are at the nanoscale range i.e., it has nanostructured materials like Nanotubes, nanofibers and the nanoparticles /nanomaterials. They Can identify and can also aid in monitoring the contaminants. Characteristics of an ideal sensor are High conductivity, High Specificity, High Sensibility (detect the pollutant at a lower concentration), Rapid response, Detection of numerous analytes in the same device (Multiple analysis) and Cost- effective.

Advantages of Nano sensors are

- High Specificity –Like lock and key model the nanoparticles are able to be coated with several chemical and biological ligands helping to improve the sensor specificity.
- High sensibility (detect the pollutant at a lower concentration). Nano sensors are presently being utilized for the detection of several toxic compounds at ppm and ppb levels in different environmental systems.

- Multiplex sensor- The surface/volume ratio of the nanoparticles allowed to vary the size and shape of the nanoparticles thus controlling the interaction with the pollutant molecule.
- Rapid response - The conductivity and sensitivity are improved via construction nanoparticles of different metals.
- Cost- effective - Nanotechnology will permit the production of very-small ‘multiplex’ sensors, thus leading to the decrease in the analysis cost and the number of devices used for the analysis.

Air Pollution and Nano remediation strategies:

Air pollution is one of the world's most serious issues, and it's described as a change in the natural composition of the atmosphere produced by the introduction of chemical, physical, or biological substances emitted by anthropogenic, geogenic, or biogenic sources. According to the World Health Organization (WHO) report in 2014, around seven million people died in 2012 as a result of air pollution exposure.

Global warming is the most significant source of outdoor air pollution, as it causes numerous changes in the atmosphere, land, and water supplies around the planet. Greenhouse gases (GHGs) are thought to be the primary cause of global warming. Carbon dioxide, methane, nitrous oxide, and fluorinated gases are the most common greenhouse gases. Human activities are adding to the problem of GHG emissions (*Metz et al. 2007*). Because greenhouse gases tend to remain in the atmosphere for hundreds of years, the bulk of them has long-term climatic consequences. Many control and treatment systems have been developed to reduce and monitor the emissions of these gases, as well as the threats they pose to individuals and the environment. Nanotechnology is a well-enabled treatment method that uses nanomaterial features such as adsorbents, catalysts, membranes, and sensors to regulate and remediate air pollution in a variety of ways .

Based on the reversible carbonation reaction of calcium oxides, calcium-based nano-adsorbents are utilised to capture carbon dioxide at high temperatures (CaO). The capacity of high-temperature adsorbents to aggregate quickly, resulting in a sintering problem during the carbonation/calcination cycles, is a significant disadvantage. As a result, the surface coating of Ca-based nano-adsorbents is employed to prevent adsorbent aggregation and, as a result, the sintering problem. Using the adsorption phase approach. *Wang et al. (2013)* reported that titanium dioxide (TiO₂)-coated nano calcium carbonate can avoid sintering and successfully capture carbon dioxide.

Because of its direct consequences on human health, indoor air pollution has recently become a serious concern. VOCs are among the indoor air pollutants that are thought to be the leading cause of paediatric asthma, atopic hypersensitivity, and other symptoms like headache, nausea, coryza, pharyngitis, emphysema, and lung cancer. As a result, it is critical to develop an effective approach for controlling and eliminating VOC emissions (*Hauptmann et al. 2004*).

Air filtration with antimicrobial materials including silver nanoparticles, copper nanoparticles, carbon nanotubes, and natural products is the most widely used and successful method for removing bioaerosols from ventilation systems. Silver nanoparticles have been shown in several experiments to effectively remove bacterial bioaerosols during the air filtration process. The antibacterial activity of silver nanoparticles is influenced by a number of parameters, including bacterial species, concentration, relative humidity (RH), size distribution, and exposure period (*Lee et al. 2010*). Antimicrobial natural products are often regarded less harmful to humans than antimicrobial materials such as silver, carbon nanotubes, and metal oxides, and have lately been employed to improve IAQ. Essential oils extracted from natural products, for example, have been used in ventilation systems of indoor-contaminated environments to reduce bacterial inactivation rates (for example, an antimicrobial filter coated with tea tree oil inactivates 99 percent of bacterial aerosol on its surface in 2–8 minutes). Nano particles and their application in treating air pollutants and their mode of action is listed (**Table.1.**)

Table.1.Nano Particle application in air remediation

Nanoparticles	Target pollutants	Observations	References
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Silica nanoparticle (SiNPs)	Atmospheric lead (Pb)	The increased capture of Pb by SiNPs was explained by the large surface and the negative-charged groups in the SiNPs	<i>Yang et al. (2013)</i>
Zn ₁₂ O ₁₂ nanocage	Carbon disulfide (CS ₂)	At the increasing number of the CS ₂ molecules, the adsorption energy of CS ₂ per molecule decreased which may be due to the steric repulsion between the CS ₂ molecules	<i>Ghenaatian et al. (2013)</i>
Ag/SBA-15 nanocomposites	Carbon monoxide (Co)	The silver content and dispersion of the catalyst are increased with the increase of the pH value, and it gave 98 % of CO oxidation at pH = 5 and 70 °C	<i>Zhang et al. (2011)</i>
Mg ferrite nanospheres (MgFe ₂ O ₄)	Sulfur dioxide (SO ₂)	During the adsorption of SO ₂ , sulfate and sulfite species are formed on the surface of MgFe ₂ O ₄ , and Fe(III) is partially reduced to Fe(II)	<i>Zhao et al. (2010)</i>
Titanium dioxide nanoparticles (TNPs)	VOCs (ethylene)	Sol-gel method with vortex reactor was used to synthesize novel TNPs with superior characteristics and a high bandgap energy that enhanced the photocatalytic degradation of ethylene	<i>Hussain et al. (2010)</i>

Mitigation of Soil Pollution by Nano Remediation

The presence of harmful substances in the natural soil environment causes soil contamination. Heavy metals, which can be found naturally in soil but rarely at toxic levels, are the most common soil pollutants, and their main sources in contaminated soil are mining, manufacturing, landfill sites, particularly those that accept industrial wastes (e.g., paint residues, batteries, electrical wastes, etc.), and municipal or industrial sludge. Heavy metals are one of the most difficult soil pollutants to eliminate since they are nondegradable and will remain in the polluted environment once introduced; the only exceptions are mercury and selenium, which can be converted and volatilized by microorganisms. Treatments can be done in situ (on-site) or ex situ (taken and treated off-site) when vast areas of soil are polluted; however, typical treatment procedures for contaminated soil are both expensive and complicated (Natural Resources Conservation Service 2000). As a result, the best strategy to safeguard the ecosystem is to prevent heavy metal pollution or to impede heavy metal spread in soil using immobilisation techniques. Even though heavy metal activity in soil is governed by sorption-desorption reactions with other soil constituents a variety of amendment agents are being used to manipulate heavy metal bioavailability and inhibit their diffusion in soil by inducing various sorption processes, including adsorption to mineral surfaces, creation of stable complexes with organic ligands, surface precipitation, and ion exchange (*Kumpiene et al. 2008*). Nanoscale particles have sparked a lot of interest in heavy metal immobilisation in soil and groundwater in recent years.

When employing nanoparticles as amendment agents, the following two key requirements must be addressed (*An and Zhao 2012*):

(1) They must be able to reach contaminated zones, and

(2) after the external injection pressure is removed, the delivered nanoparticles must remain inside the confined domain (i.e., under natural groundwater conditions), where they will act as an immobile sink for trapping soluble metals.

In situ reductive immobilisation of heavy metals in soil is also common with zerovalent iron (ZVI) nanoparticles. The ability of ZVI nanoparticles generated using typical methods to agglomerate or react quickly with the surrounding media (e.g., dissolved oxygen or water), resulting in a loss of reactivity and mobility in soil, is the main disadvantage. As a result, multiple ZVI particle-stabilizing techniques have been reported,

including the modification of nZVI with organic coatings such as starch (Reyhanitabar *et al.* 2012), polyvinylpyrrolidone (PVP), and sodium CMC employed cetylpyridinium chloride to control ZVI nanoparticle aggregation.

Water Pollution

Water pollutants are substances that are added to water and cannot be naturally broken down, such as organic pollutants, pathogens, industrial discharge including heavy metals and various anions, and so on (Goyal *et al.* 2013). They tend to modify the properties of the water body. Human activities, in both developing and developed countries, cause water shortages by contaminating natural water resources by releasing energy, chemicals, and other pollutants that degrade the water quality for other users. Furthermore, natural contaminants such as water storm runoff, animal wastes, and so on can pollute the environment. Water contamination is divided into six categories by the United States Environmental Protection Agency (EPA): Plant nutrients, biodegradable waste, heat, sediment, dangerous and poisonous compounds, and radioactive pollutants are all examples of pollutants.

Wastewater treatment entails physical, chemical, and biological technologies, and it is commonly divided into four stages:

- (1) preliminary,
- (2) primary,
- (3) secondary, and
- (4) tertiary advanced treatment.

Coagulation and flocculation, sedimentation, dissolved air flotation, filtration, steam distillation, ion exchange, deionization, reverse osmosis, and disinfection are all common water purification procedures (Shon *et al.* 2007). Sediment filters, activated carbon, coagulants, ion exchangers, ceramics, activated alumina, organic polymers, and a variety of hybrid materials are commonly utilised in these technologies. Traditional water treatment techniques, on the other hand, may be expensive and may discharge secondary harmful chemicals into the environment.

Nanotechnology provides exceptionally efficient, adaptable, and multifunctional processes, which could be a potential way to retrofitting outdated infrastructure and developing high-performance, low-cost treatment options that are less reliant on huge infrastructures. Because of their size and adsorption efficiency, nanoscale metal oxides such as titanium dioxides, iron oxides, zinc oxides, alumina, and others have been investigated as a low-cost, effective adsorbent for water treatment. Magnetic nanoparticles have received a lot of attention, because of their potential application (Xin *et al.* 2012) and their display of remarkable magnetic properties (e.g., superparamagnetism, significant magnetic response under low applied magnetic fields). CNTs is the super organic adsorbent for environmental cleanup when compared to other carbon-based adsorbents; they act as flexible porous materials toward organic contaminants. Organic dyes (e.g., cationic, azoic, reactive, basic and acid dyes, etc.) have exhibited outstanding adsorption capability and high removal efficiency using carbon nanotubes.

Physical processes are the most common adsorption mechanisms used by CNTs to adsorb organic molecules, and they are influenced by the characteristics of the component of interest. By adding certain functional groups to electrospun nanofibers, they can be easily modified for a specific purpose and employed as affinity membranes to remove heavy metals and organic contaminants during filtration. Functionalization of polymer nanofiber membranes with ceramic nanomaterials such as hydrated alumina/ alumina hydroxide and iron oxide for heavy metal ion removal by adsorption/chemisorption and electrostatic attraction mechanisms (Ramakrishna *et al.* 2006), and use of cibacron blue to functionalize cellulose nanofiber membranes for albumin purification.

Photocatalysis

The removal of non-biodegradable organic contaminants that are resistant to traditional treatment procedures, as well as the killing of waterborne pathogens without the creation of harmful DBPs during the disinfection process, are the key issues impacting water treatment efficiency. To address these issues, it is critical to develop an innovative, low-cost, and environmentally friendly technology that can remove these contaminants with minimal energy and chemical use.

Because of their highly potent and strongly oxidising radicals research has focused on advanced oxidation processes (AOPs) as alternative robust methods capable of oxidising and mineralizing a wide spectrum of organic compounds (Comninellis *et al.* 2008). Photocatalysis, a well-known AOP, has been proven to be an effective way to improve the biodegradability of persistent organic pollutants while also removing present and emerging microbial diseases. Photocatalytic oxidation is a group of reactions that rely on the generation of strong reactive radical species such as H₂O₂, O₂ •⁻, O₃ and most hydroxyl radical (OH•) which is a strong oxidising agent that non-selectively destroys all organic molecules in water. Due to its environmentally benign merits such as low toxicity, high photoconductivity, chemical stability, and low cost and commercial availability, TiO₂ has drawn special attention in water treatment research, including photodegradation of numerous organic pollutants, photoreduction of inorganic contaminants, and inactivation of microorganisms. The photocatalysis mechanism of (TiO₂), which relies on the generation of active oxygen species such hydroxyl radicals, superoxide, hydrogen peroxide, singlet oxygen, and others, may aid in the photodegradation or disinfection of organic pollutants.

The mechanism consists of multiple phases, beginning with photoexcitation to trigger a sequence of reductive and oxidative reactions on the surface of the (TiO₂) photocatalyst via irradiation with an appropriate wavelength (typically larger than or equal to the band gap energy). Because (TiO₂) has a band gap of roughly 3.0 eV, wavelengths less than 400 nm can excite the lone electron from the valance band to the empty conduction band in femtoseconds, resulting in the production of an electron-hole pair. The reaction between photogenerated electrons and molecular oxygen, as well as the reaction between photogenerated holes and water, produces super oxide radical anions (•O₂⁻) and hydroxyl radicals (OH•). Hydroxyl radicals are the main species responsible for the breakdown of organic contaminants into water and carbon dioxide (Zhang *et al.* 2009). **Figure.3.** represents the mechanism steps of TiO₂ photocatalysis.

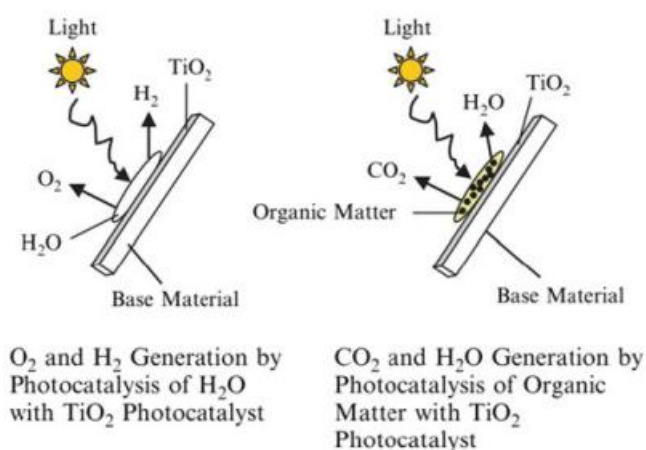


Figure.3. Light absorption by TiO₂ photocatalyst (Ohama and Van Gemert 2011)

Sensing and monitoring systems:

Monitoring the release of harmful chemicals (i.e., organic and inorganic pollutants, pathogens, and hazardous air pollutants), as well as accurately estimating the quantity and composition of these contaminants, is a major problem for environmental remediation management. As a result, several analytical techniques, such as surface plasmon resonance, high-performance liquid chromatography (HPLC), gas chromatography– mass spectrometry (GC-MS), supercritical fluid chromatography (SFC), capillary electrophoresis (CE), flow injection analysis (FIA) etc. have been used in environmental pollution detection and monitoring.

Growing advances in nanoscience and nanotechnology are having a significant impact on environmental monitoring and sensing, where a large number of nanoparticles have been introduced for detection and remediation of a wide range of contaminants in both gaseous and aqueous mediums.

Many studies have been conducted to develop high selectivity and sensitivity nanosensors for monitoring various types of gases in the ambient air in order to prevent potential explosions or poisoning, particularly for odourless, colourless, and tasteless hazardous gases like hydrogen and poisonous and irritant gases like nitrogen dioxide (NO₂).

Similarly, the use of nanomaterial-based sensors for water quality monitoring has been extensively studied for the detection of organism faecal pollution such as faecal coliforms, total coliforms, E. coli, enterococci bacteriophages, and disease-causing viruses and parasites, as well as the detection of various types of trace contaminants (pesticides, phenolic (Govindhan *et al.* 2014)

Conclusion

Increasingly severe human activities are disrupting ecological balance by releasing massive amounts of anthropogenic harmful toxicants into the environment, polluting soil, water, and atmosphere and endangering human public health. The application of advantageous nanotechnology to conventional environmental remediation methods in an attempt to adopt a compatible treatment technology for cleaning up all the trash left behind by the industrial revolution. Furthermore, this work emphasised the roadblocks that limit nanomaterials' application and suppress the benefits of their unequalled features; these roadblocks include environmental circumstances (e.g., humidity, temperature, acidity, etc.), particle aggregation, and separation difficulties. Nanotechnology has been found to have outstanding characteristics for sophisticated, robust, and multifunctional treatment procedures that can improve pollution monitoring and treatment efficacy while also overcoming all of the aforementioned constraints. In summary, nanotechnology has the potential to improve environmental remediation by minimizing the development of secondary by-products, dissolving some harmful pollutants using zero-waste operations, and preventing future soil contamination by transforming pollutants from labile to non-labile phases. Finally, nanotechnology will pave the way for flexible and dynamic systems that employ cutting-edge techniques for sensing and monitoring a wide range of dangerous substances and poisons in various environmental media.

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