

Ecotoxicology of Nanocomposite Materials

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Nanocomposites are hetero materials made up of at least one nanoscale phase called a "nanofiller" that is spread in a second phase called a "matrix" to combine the unique features of its ingredients. Contemporary uses for nanocomposites are expanding constantly, and they are being used in many different industries. Nanocomposites are used in a variety of products, such as solid polymer electrolytes for batteries, impellers and blades, oxygen and gas barriers, food packaging, thin-film capacitors for computer chips, and fuel tanks and engine parts. As drug - delivery techniques, anti-corrosion shield coatings, UV protection gels, oils, scratch-free paint, new scrape resist materials, new fire-retardant materials, superior fibres and films, etc., they also find extensive application. Extensive use of these composites led to the discloses of these stuffs into the environment and properties of these materials are greatly influenced by the presence of pollution. The physico-chemical properties of these nanocomposites are very important for predicting their fortune and behavior in the environment and their toxicity to living organisms. Limited data on the ecotoxicity of these materials are available and even those are confined to a few organisms like bacteria, algae, invertebrates, fishes and mammals. Detailed studies on the adsorption, distribution, metabolism and excretion on higher organisms is the need of the hour. Presently the environmental risk assessment of nanomaterials is being performed using the existing methodologies and modification of the methodologies are required. This review summarizes the toxicity of nanocomposites and the current toxicological tests carried out.

Keywords: CNTs; Diatom; Nanocomposites; Toxicological tests.

Ecotoxicology

Ecotoxicology is a term that was coined by Ernst Haeckel in 1866 to describe the study about how organisms behave and interact and the biology of nature. The study of the harmful effects of radiation and chemical contaminants on environmental organisms using the methods of toxicology gave rise to the field of ecotoxicology¹ (Boros et al., 2020). In nanoscience

and nanotechnology, basic research advanced rapidly, natural and manufactured nanomaterials were divided into distinct fields, theories and models about how they interact with biological and environmental systems emerged, and the issue of their plausible danger to health of people and the environment came to light² (Cattaneo et al., 2009). In light of the diverse applications of nanomaterials and the growing importance

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of environmental protection and evaluating potential contaminants' ecotoxicity, studying the ecotoxicological impacts of nanomaterials is crucial. Further evidence of the ecotoxicity of nanomaterials is provided by an increasing body of academic literature¹(Boros *et al.*, 2020). The science of environmental health offers exciting new opportunities and challenges, including addressing problems with novel materials, understanding risk, and safeguarding the environment and the general public. Many aspects of advancing technologies are shared between ecotoxicology and public health. There is a common concern with research on the fate, movement, and behavior of substances in biological and environmental matrices, as well as the manner and extent of exposure and the response of living systems to the exposure³(Tinkle *et al.*, 2008). As industrial development contaminates the environment at an accelerated rate, ecotoxicological study is progressing rapidly. Also hastening this process are serious industrial accidents. Ecotoxicity evaluation guidelines were developed as a result of ecotoxicology's growing importance in ecological and environmental risk assessment¹(Boros *et al.*, 2020). The determination of toxicity thresholds for nanoparticles and the question of whether or not currently established indicators of adverse effects are also applicable to environmental nanotoxicity and nanopathology will be key challenges for ecotoxicologists. Due to the extremely huge surface area of ultra-small particles, this could result in the direct production of harmful oxyradicals, which can harm cells by destroying their DNA, proteins, and membranes. Furthermore, it is thought that some nanoparticles' toxicity is increased by the fact that many of them naturally attract transition metals and synthetic organic contaminants⁴(Moore, 2006).

Nanoscience, however, has the potential for both benefits and problems, just like any other developing technology, because it is mostly unknown how these novel features will interact with the environment and biological systems³(Tinkle *et al.*, 2008). Since, it is crucial to recognize that particle size can influence pathology and direct toxicity, and that biodegradability may also play a key role in determining adverse biological effects⁴(Moore, 2006). When possible, comparison with equivalent bulk materials should be taken into consideration in analyses

concerning ecotoxicological risk assessment for nanocomposites. These studies should adhere to the same criteria and processes used for previously untested substances³(Cattaneo *et al.*, 2009). Due to this, it is essential that we put in place efficient risk assessment methods as soon as possible to address potential threats. Accidental spills or legal releases of untreated wastewater into streams and marine habitats may affect people right to nanoparticles by skin contact, inhalation of water aerosols, direct consumption of tainted drinking water, or particles adsorbing on vegetables or other foods⁴(Moore, 2006). Over the recent years, a vibrant community of nanotoxicologists has grown along with the handling of nanomaterials methodologies. It is important to consider a substance's exposure to or likelihood of coming into touch with an organism when evaluating whether or not it is "hazardous". This strategy seeks to tacitly link risk to the characteristics of nanomaterials. However, this technique has only produced a few numbers of practical recommendations for predicting nanomaterial danger, apart from maybe the trivial instance of anticipating that nanomaterials created from poisonous or highly reactive compounds should be harmful⁵(Wiesner *et al.*, 2017).

Possession of physicochemical properties of nanocomposites

One of the major initial obstacles for research on the health and safety of nanotechnology is the physicochemical and biological characterization of nanocomposites. The precise features of nanocomposite design and synthesis that give rise to distinctive physicochemical properties also have an impact on biological and environmental behaviors. For examples: Fullerenes, carbon-based nanoparticles and nanotubes, metal and metal oxide nanoparticles, and macromolecules. According to some studies, nanocomposite can trigger inflammatory responses, cellular processes intended to restore biological system equilibrium that, if left unattended, could result in a homeostasis disruption that is permanently irreversible³(Tinkle *et al.*, 2008). In fact, while many inorganic and polymeric nanoparticles will be hydrophilic, fullerenes are lipophilic which are the various classified sections of composites⁴(Moore, 2006). The colloidal structure and kinetics of nanomaterials, which are systems in which smaller or larger complexes might

develop in inadequately predictable ways, present the most hurdles in evaluating toxicity. This is in contrast to their large diffusion. Nanocomposite structures appear to fall well short of meeting the usage of authorized or validated standards, a fundamental prerequisite for eternal practice in toxicology test sites. The structure of the dispersed nanophase depends parallelly on the physico-chemical manufactured nanomaterials and that of the environment in all essentially existing systems such as water, clay, air, and various blends, as well as on the modalities of dispersion²(Cattaneo *et al.*, 2009).

A biological perspective on nanocomposites

Nanotechnology is a very potential and fascinating cross-disciplinary molecular technology that has various scientific and technological applications. Due to the relative novelty of this technology, relatively little has been done to evaluate the hazards to biological systems and issues over the usage of nanotechnology's products⁴(Moore, 2006). The nanocomposite material, which is made of non-metallic, metallic, and polymeric materials through a specific process, offers the additional advantage of retaining primary features to overcome flaws and express some current characteristics. It refers to a solid material made up of many phases, at least one of which has one, two, or three dimensions, all of which are nanometer-sized⁶(Omanoviæ *et al.*, 2020). They are substances to which filler components of the nanometer scale are added to enhance the qualities of the resulting substances. A unique interface separates two or more distinct elements or phases with differing physical and chemical properties to form nanocomposites⁷(Khan *et al.*, 2016). The development, characterization, and use of materials, systems, and devices with dimensions between 0.1 and 100 nm that display unique and considerably improved biological, chemical, and physical characteristics, functions, phenomena, and processes⁸(Thostenson *et al.*, 2005). A new generation of medical instruments, orthotics, and implantable devices can be made by combining bioactive qualities with mechanical features found in nanocomposite materials, such as improvements in durability, rigidity, hardness, roughness⁶(Omanoviæ *et al.*, 2020).

The term "matrix" refers to the component that is typically more plentiful. Reinforcement is

the component that is incorporated into the matrix substance to enhance the mechanical properties of nanocomposites (or nanomaterials). Usually, reinforcement takes the form of nanoscale filler materials⁷(Khan *et al.*, 2016). In composite materials, the fibre serves as a load carrier, with its strength being greatest along its axis. The alignment of the long, continuous fibres in the plane of the load results in the production of a composite material with significantly improved characteristics⁹(Tariq *et al.*, 2021). Indeed, there are naturally occurring nanocomposites, such as the abalone shell and bone's matrix. Nanocomposites differ from ordinary composites in that they have a high surface area to volume ratio and an exceedingly high aspect ratio. Minerals, metallic nanoparticles, carbon nanotubes, sheets made of exfoliated clay stacks, graphene, and fibres can all be employed as reinforcement materials⁷(Khan *et al.*, 2016). Ceramic matrix nanocomposites (CMNC), polymer matrix nanocomposites (PMNC), and metal matrix nanocomposites (MMNC) are the three categories into which the matrix components of nanocomposite materials are divided⁶(Omanoviæ *et al.*, 2020). The surface area/volume ratio of the reinforcement materials is a morphological trait that is crucial to comprehending the structure-property relationship of nanocomposites⁸(Thostenson *et al.*, 2005).

Classification of nanocomposite

Nanocomposites can be categorised into three groups based on their matrix:

- Ceramic-matrix nanocomposites
- Metal-matrix nanocomposites
- Polymer-matrix nanocomposites

Due to their exceptional qualities and extensive variety of applications in numerous industries, nanocomposites are categorized as many conventional composite materials⁶(Omanoviæ *et al.*, 2020).

Ceramic-matrix nanocomposites

A new era of engineering stuffs, ceramic matrix nanocomposites have at least one component with a nano scale and have several uses in the industrial sector. Nanoceramic composites have exceptional electro - mechanical properties as a result of their microstructure⁷(Khan *et al.*, 2016). Ceramic matrix composites (CMCs) have been developed to overcome the intrinsic fragility and mechanical inconsistency of single unified

ceramics, that are normally preferable due to their high rigidity and strength¹⁰(Cho *et al.*, 2009). Ceramics are not suited for the vibration and fatigue that are present in the majority of aerospace components. However, they are resilient, inert, and persistent at extremely high temperatures. These qualities are required for aviation parts that are subjected to high temperatures and toxic conditions. The ceramic materials have undergone extensive effort to improve toughness. Dimensionally stable phase, which increases strength and impact resistance, is added to ceramics to prevent them from breaking¹¹(Rathod *et al.*, 2017). Numerous reinforcing fibres, including all those based on SiC, carbon, alumina, and mullite, have been investigated. However, since the initial reports of their application in ceramic matrices were reported in the early 1990s, carbon fibres are among the highest end densification components explored¹⁰(Cho *et al.*, 2009). In the research, numerous techniques have been described for creating ceramic matrix nanocomposites. Micro-composites are commonly produced via the normal powder approach, the polymer precursor route, magnetron sputtering, and biochemical methods like the sol-gel process, colloidal and precipitation processes, and template synthesis⁷(Khan *et al.*, 2016).

Carbon nanotubes (CNT)

In the context of composites, carbon nanotubes (CNTs) are frequently referred to as the “future version” of carbon fibre due to the significant amount of attention they have gotten in recent years. The instinctive and functional qualities that can be attained at very moderate densities usually in the range of 1.5-2.0 gm⁻³ are what spur interest in composite materials¹⁰(Cho *et al.*, 2009). With the greatest impact of any material and the maximum thermal conductivity, carbon nanotubes are acknowledged as the ultimate form of carbon fibre. They have also been demonstrated to have exceptional field emission properties¹²(Haddon *et al.*, 2002). Even though the ideal CNT structure is highly alluring, actual materials come in a wide range of sizes, purity levels, surface physicochemical, crystallinities, graphitic configurations, grades of interaction, and costs¹⁰(Cho *et al.*, 2009). The widespread availability of nanotube materials as a result of the success in nanotube growing is a major

driving force behind the rapid advancements in base physics research and nanotube applications seen in recent years¹³(Dai *et al.*, 2002). The use of CNTs as stiffening agents in polymer, ceramic, or metal matrix composites has attracted a lot of attention over the past ten years. In industries as diverse as space aviation, sports equipment, and medicinal devices, the prospect for creating sophisticated nanocomposites that partially or fully exhibit the amazing capabilities of individual CNTs is particularly alluring¹⁰(Cho *et al.*, 2009). Nanotube applications in the real world necessitate either enormous volumes of larger particles or scaled-up device integration. It is preferred to produce high-quality nanotubes in kilograms or tone quantities utilizing straightforward, effective, and affordable growing techniques for applications including composites and hydrogen storage¹³(Dai *et al.*, 2002). Relatively few studies have examined inorganic matrices such as ceramics or glass and the prospective firming mechanisms that might be connected with CNT reinforcements, the greater part of CNT composite research has concentrated on polymer composites¹⁰(Cho *et al.*, 2009).

Metal-matrix nanocomposites

A composite material called MMC (Metal-matrix nanocomposite) must have at least two constituent pieces, one of which must be a metal or amalgam matrix and the other must be supplement. The metal matrix of the graphene-reinforced MMCs is used to categorize them¹⁴(Hu *et al.*, 2016). In other words, materials composed by nanoparticles made of ductile metal or amalgam matrix with nanoparticle reinforcement are called metal matrix nanocomposites. These composites, have entirely distinct physical, chemical, and mechanical characteristics from the matrix material. Researchers are currently studying metal matrix nanocomposites because of their improved qualities brought on by the embedding of nanoparticles, and they are finding a various range of applications in structural components⁷(Khan *et al.*, 2016). The fabrication processes for specific reinforced MMCs can be categorized into the following divisions: liquid process, solid process, and semi solid process. It has been developed and used in all industries¹⁵(He *et al.*, 2008). Metallic carbon nanotubes essentially do not emit heat; instead, they conduct electric current. They exhibit additional electrical properties and can serve as

the active semiconductor in nanoscale devices¹²(Haddon *et al.*, 2002). The fabrication of MMCs using solidification techniques has many benefits, including cost effectiveness and net-shaping capabilities. In the casting process, a variety of stirring strategies have been employed to create MMCs¹⁵(He *et al.*, 2008).

Polymer based nanocomposites

The phrase “polymer nanocomposite” now describes a system with many components, one or more of which is a polymer or a blend of polymers, and at least one of which has a dimension less than 100 nm¹⁶(Winey *et al.*, 2007). Materials called polymer nanocomposites use nano-additives as reinforcement and polymer as the matrix material. This polymer nanocomposites has received a lot of attention from both academic and commercial due to its excellent mechanical properties, such as strong elastic flexibility with a low content of metals⁷(Khan *et al.*, 2016). Inorganic-organic hybrids and molecular mixtures are appropriately referred to as polymer nanocomposite, which also includes established commercial goods such polymers with carbon black or fumed silica¹⁶(Winey *et al.*, 2007). Both chemical and mechanical processes can be used to create polymer matrix nanocomposites. One of the main issues in the production of polymer nanocomposite is the uniform and homogenous dispersal of nanoparticles in the polymer matrix¹¹(Rathod *et al.*, 2017). Other notable qualities of polymer nanocomposites include boundary resistance, incendiary factors, impact resistance, magnetic, electrical, and refractive optical properties. A filler and a polymer (matrix) are typically combined to create a polymer composite as reinforcement⁷(Khan *et al.* 2016). There are three different types of polymer nanocomposites based on the kind of reinforcement. These include nanocomposites with layered reinforcement, nanocomposites with discontinuous reinforcement, and nanocomposites with nanofiber or CNT reinforcement¹¹(Rathod *et al.*, 2017). In addition to the individual elemental properties, a range of other variables influence the properties of nanocomposites, such as the fabrication process, the types of additive materials and their perspectives, the degree of melding between two distinct stages, the type of surface tension at the material interface, the relative density of nanoparticles, the characteristics of the

nanoparticles, the nature of the advanced latent period at the material interface, and the size and shape of the nanocomposites.¹⁷(Jeffrey *et al.*, 2005),¹⁸(Jeon *et al.*, 2010).

The literature has described numerous techniques for the synthesis of polymer nanocomposites, including multilayer compounds and all those including carbon nanotubes. The following techniques are primarily used to create polymer nanocomposites.

- In situ polymerization
- Sol-gel process
- Melt intercalation j
- Direct mixing of polymer and fillers
- Melt blending

In general, a relatively recent method of creating nanocomposite materials is melt blending. In this procedure, polymer is melted to create a viscous liquid. The nanoparticles are dispersed into the polymer matrix using hydrodynamic shear frequencies and dispersion at extreme heat. After that, the nanocomposites are produced using either compressive molding or injection molding.⁷(Khan *et al.*, 2016).

In-situ polymerization

It is a method that primarily involves polymerizing the monomer structure that contains the addition. Since the additive is accessible, it would diffuse into the matrix at the time of polymerization. This approach allows for the polymerization of frequently used organic monomers to create composites from renewable components such as cellulose, chitin, starch, and lignin¹⁹(Ates *et al.*, 2020). Low molecular weight dimer solutions readily permeate between layers and produce inflation, which causes nanofillers in mixture solution to rise during in situ polymerization⁷(Khan *et al.*, 2016). The polymerization of monomers derived from renewable sources is another method used in this methodology to synthesize composite materials using renewable resources. Nanostructures like clay, CNTs, and graphene can be added to nanocomposites during the polymerization of terpenes and terpenoids in particular¹⁹(Ates *et al.*, 2020). Either radiation, heat, or an organic initiator is used to polymerize the resultant mixture. After the monomer has been polymerized between interlayers, one of two types of nanocomposites—exfoliated or intercalated—can be created⁷(Khan *et al.*, 2016). An additional

illustration is the creation of nanocomposites using common additives and double-bonded or epoxidized mixtures from vegetable oils. Additive agglomeration is kept to a minimum in composite manufacture using the in-situ polymerization process. As a result, the generated materials have a high degree of homogeneity¹⁹(Ates et al., 2020).

Intercalation method

Typically, the intercalation approach entails dispersing various nanomaterials into the polymer matrix, such as nanoplatelets. Clays (nanomaterials) are widely known for improving bulk qualities like rigidity, contraction, and ignitability when incorporated into polymer matrices. For similar dispersion of surface nanofillers in the polymer matrix, intercalation, a top-down strategy, necessitates surface modification of nanoplatelets⁷(Khan et al., 2016).

Sol-Gel method

The Sol-gel technique is a bottom-up approach that operates on the polar opposite of all the earlier strategies⁷(Khan et al., 2016). The hydrolyzed metal alkoxide and successive hydrolysis are the foundation of the sol-gel method. With this method, ceramic matrices can be used to prepare metal oxide nanoparticles like SiO₂, TiO₂, and ZnO¹⁹(Ates et al., 2020). Sol and gel are the first two steps in a sol-gel relationship. In a monomer solution, solid nanoparticles are colloiddally suspended in a gel, which is a three-dimensional network of connections generated between the phases⁷(Khan et al., 2016). Therefore, it is typically preferred to make inorganic metal oxide additions when making composite materials from clean energy sources. Alkoxides, for example, are pricy and moisture-resistant compounds that are necessary for metal¹⁹ (Ates et al., 2020). Using this method, solid nanoparticles are dispersed in a polymeric solution to generate a colloidal dispersion of colloidal particles (sol), which is then polymerized and hydrolyzed to create a gel that unites the phases⁷(Khan et al., 2016). The use of sol-gel methods and reinforced polymer production techniques to solve the tensile properties concern, which is a key issue with bio-based composites, is still mostly at the intellectual level and is not widely used in the industrial sphere. To improve the mechanical qualities and reduce the time delay in between additive and the matrix phase, an adaptable molecule is specifically bonded to the

surface of the matrix. Future uses of the bonding technique with a solid covalent connection to the functional structure appear to be quite promising¹⁹(Ates et al., 2020).

An array of applications for nanocomposite materials

Membrane technologies are becoming more and more crucial as units of operation for regulating quality of the environment, recovering resources, preventing pollution, producing energy, and monitoring. They are used for a variety of purposes in the purification of wastewater, including the elimination of particles, organic debris, and dehydration⁵(Wiesner et al., 2017). Due to their superior strength and weight compared to their metal equivalents, composite materials have seen a sharp growth in use over the past two decades in a variety of applications. Composite materials are most frequently used in the transportation industry. The following is a discussion of how composites are used in significant industries⁹(Tariq et al., 2021):

- Aerospace Industry
- Marine System
- Structural Application
- Automobile Industry
- Drug Delivery System
- Tissue Engineering

As structural application, alumina which is an electrical insulator widely used for its stiffness. CNTs are seen to contribute resilience to the ceramic particles with superior properties than conventional carbon and fibers, which only add stiffness. CMNCs are being researched for usage in the automobile and aerospace industries, in addition to uses in the energy, transit, defensive performance, sporting goods, and construction industries. Applications in the automotive and aviation industries require SHM capabilities for infrastructure and life safety¹¹(Rathod et al., 2017).

Aerospace system

Aeronautical constructions made of polymer nanocomposites include solar array substrates, thermal shrinkage casing, equipment hatches, aviation interiors, lubricants, and avionics. These materials perform exceptionally well in addition to being lightweight. Constructions used in the aerospace industry are subject to a wide range of circumstances, including variations in temperature and humidity. Jet fuel, deicing liquid, and hydraulic

fluid are also exposed to them. Lightning, UV rays, and 500 mph dust flow must not erode the coatings.¹¹(Rathod *et al.*, 2017). In aerospace applications, CNT nanocomposite technology is the most used variety. The incorporation of slightly elevated polyethylene (HDPE) with reclaimed polyethylene terephthalate (PET) in CNT culminated in a maximum load pressure of 24.9 MPa, which was advantageous for advanced structure design. It comprises of connector chains generated using deformation and adhesion processes²⁰(Bhat *et al.*, 2021). Aerogel wires and cables for power and data cables lower their mass and increase their resilience to fatigue. To reduce cable mass and enhance fatigue resistance, it makes use of carbon nanotube conductors and incredibly light aerogel insulation²¹(Siochi *et al.*, 2015). The susceptibility of CNT and graphene-based nanocomposites to impact damage was higher. Results from nanoplatelets made of alumina and graphene and alumina and CB are also stacked. The depression causes tiny cracks, which cause the fibres to break and become less conductive. Additionally, these nanocomposites demonstrated improved fracture toughness. Thanks to improved microhardness and safety provided by SHM capabilities, alumina/CNT nanocomposites can consequently be employed as building materials for aircraft, spacecraft, and reentry vehicles operating at higher temperatures¹¹(Rathod *et al.*, 2017).

Bio-green Industry

In comparison to petroleum-derived composites, nanocomposites created from bio-renewable resources demonstrate a greener approach, and they are used particularly in the biomedical and commercial food packaging applications. Additionally, these nanocomposites show a great deal of promise for use in a variety of fields, including barrier, sensor, power storage, optoelectronic, automobile, and flame resistance. These organic polymeric frameworks continue to be utilized in numerous sectors. These organic materials have polymers, peptides, synthetic fibers, and complex mixtures as their chemical structures. The most popular structures among protein-based natural polymers include those found in cotton, velvet, gel, keratin, casein, albumin, and fibrin. In addition, because natural polymers are made from plants, they can be recycled. Examples of this include polyhydroxialconates,

tannin, polybutadiene, and polyglutamic acid. These naturally occurring polymeric structures can originate from either plant or animal sources, and the combinations generated with them can be broken down in the soil by bacterial or hydrolytic action¹⁹(Ates *et al.*, 2020).

Drug delivery (Bio-medical Applications)

Pharmaceutical agents can be more reliably delivered into desired locations using formulations designed for drug delivery systems. It is crucial for the drug to be delivered to the target area in order to maximize treatment effectiveness and minimize negative effects. In this respect, nanocomposites in particular and the varieties of them that include bio-renewable elements are appealing, and numerous studies are being conducted on applications for drug administration. In these research, various stimulating elements including temperature, pH, light, etc. are used as drug release mechanisms. Alginate, carrageenan, and pectin are examples of anionic polysaccharides that have been utilized to create N-hydroxyl layered double-hydroxide matrixes which are considered for molecular transfer in biomedical applications.

In tissue engineering, alginate and hyaluronan polysaccharides are combined to generate nanocomposites for bone regeneration. Alginate serves in this construction as a synthetic sponge for tissue engineering applications. As a result, biomimetic nanocomposite materials were created by directly synthesizing apatite crystals into cores on spontaneous alginate strands¹⁹(Ates *et al.*, 2020).

Ecotoxicity of nanocomposites

Natural absorption mechanisms and the impact of environmental variables on bioavailability are both included in ecotoxicity. Nanocomposites seem to provide promising relief and solutions to various problems in different fields. But it is important to mandate and assess the fate of nanocomposites which are released into the environment for various approaches. Nanocomposites once released into the environment undergo various transformations which may cause various ecotoxic effects on soil, land and water²²(Rana *et al.*, 2013). As a result, the fate of these nanocomposites is the subject of an expanding quantity of ecotoxicological studies. Ecotoxicity examines different trophic organism levels with the goal of safeguarding populations

and ecosystems. The ecotoxicity of chemicals have been measured in various microbes, plants, crustaceans, and amphibians using different methods formulated according to the organism and acquaintance circumstances ²³(Nowack and Bucheli, 2007).

Three important factors should be taken into consideration while assessing the ecotoxicity of nanocomposites ²²(Rana *et al.*, 2013).

1. Transport and Transfer: the capacity to transition between different locations
2. Ecotoxicity: Toxic effects to the non-target organism in the particular ecosystem
3. Transformation and Modification: mechanism by which nanocomposites undergo various transformations in contact with the environment.

Marine Ecotoxicity

Various nanocomposites have been brought into application in marine environments. One such example is biofouling. Biofouling seems to be the major problem with the adherence and attachment of various marine micro and macro-organisms to different surfaces which are immersed in sea water for a long period of time ²⁴(Dineshram *et al.*, 2009). In regards to this problem, various antifouling technologies have been developed to overcome the effects caused by biofouling which includes development of various nanocomposites which can be used as an antifouling paint and provide promising results. But the problem arises when the nanocomposite material starts leaching out into the aquatic environment and hindering the marine ecosystem. It's crucial to take a multi-layered strategy while researching aquatic ecotoxicity. In this method, key aspects of the researched materials such as solubility, agglomeration, degradation, and change in aqueous medium are taken into account. The size of the nanoparticles and their stability in the dispersion phase primarily determine the properties of influence. In contrast to protozoa and multicellular species, which have more advanced systems for their absorption and biotransformation, unicellular organisms like bacteria and/or algae are considered to be more resistant to the toxic effect of nanocomposites ²⁵(Bondarenko *et al.* 2013). Nanocomposites used in antifouling technologies causing ecotoxicology effects are discussed

Impact on marine organism

Marine environment comprises various

microorganisms including bacteria, microalgae and diatoms. In the case of diatoms and microalgae, they are believed to be playing a major role in biogeochemical and nutrient cycles. Therefore, any hazardous impacts to these microalgae and diatoms might have a significant consequence for the aquatic ecology, which in return will have an influence on the higher species. Nanocomposites have been used in various surfaces in the form of coating in the marine environment. These nanocomposites stay in the marine environment over a long period of time, undergo various transformations with relevance to the environment and cause ecotoxic effects. Studies on the ecotoxic effects of these nanocomposites should be studied for a long period of time. The study should be chronic rather than being acute.

Microalgae

One fine example for the ecotoxicity of nanocomposites in the aquatic environment is the various nanocomposites being developed as the antifouling agents to compromise the effects caused by the biofouling organisms. Natarajan *et al.*, ²⁶2017 developed antifouling coating using pristine and chitosan/ TiO₂/Ag films in form of nanocomposites. The study was performed against two microalgae *Scenedesmus* sp. and *Chlorella* sp. This nanocomposite caused various toxic effect on the microalgae which includes increased production of lipid peroxidation, increased uptake of nanoparticles by the metabolic system of those microalgae and decrease in their cell viability and biomass ²⁶(Natarajan *et al.*, 2017). On the other side reduced graphene oxide-silver nanocomposites were developed to assess their toxicity against marine microalgae *Chlorella vulgaris*. The toxicity effects of this nanocomposites include decrease in cell viability, reduced photosynthetic activity and severe deformity in the morphological structure which implies the toxic effects of the nanocomposites against various marine microalgal species ²⁷(Nazari *et al.*, 2018).

Diatoms

Diatoms are one of the great primary producers in the marine environment. They are responsible annually for -20% of photosynthetically fixed CO₂ on earth ²⁸(Leblanc *et al.*, 2018). So, it is necessary to assess the toxicity effects of various nanocomposites against diatoms. ZnO – chitosan nanocomposite has been developed

to quantify the antifouling activity against marine diatom *Navicula incerta*. The dissociation behaviour of the nanocomposite highly affects the aquatic ecosystem. ZnO nanoparticle from the nanocomposite were released into the water in the range of 0.001 ppm to 0.009 ppm per week. This nanocomposite coating reduced the viability and affected the metabolic process of this particular diatom²⁹(Al-Naamani *et al.*, 2017).

Environmental micropollutant risk assessment using ecotoxicology

Due to their presence in minute quantities in a variety of environmental matrices and living creatures, micropollutants (MPs) are detected and classified. The levels of MPs at recorded locations in water sources can be used to triangulate the MP values at unknown places, allowing researchers to evaluate the regional variations of the MPs and the risk associated with them. The contamination factor showed that at 15 of the 19 sites, the degree of heavy metal pollution was high and substantial.

In comparison to water analysis, sediment chemical profiling can provide a more comprehensive overview of the possible sources and reservoirs for chemical compounds, particularly those largely associated with the grain sedimentary component (clay and coarse aggregate) and particulates organic carbon. Deposits of sediment are not clearly defined. They are regarded as intricate combinations of gases, dissolved substances, and organic components that come from numerous sources under the direction of physicochemical and biological processes²²(Rana *et al.*, 2013). Pollution builds up over time in river system lakes due to deposits left behind by suspended matter and debris transported along rivers, and these patterns are valid for determining time-integrated abnormalities.

Because of its ability to travel and change in surface debris after prolonged exposure, chromium—a mutagenic, extremely poisonous, and carcinogenic element—has received substantial research. To determine the extent of anthropogenic pollutant accumulation in sediments, the geo-accumulation index is utilised. All sample times revealed pollution, indicating that the main cause of the concentration increase was an increase in temperature rather than an inadvertent release. Significant quantities of manufactured nanoparticles, including those in the surrounding

air and water, have been released into the environment as a result of the development of nanotechnologies.

Ecotoxicity of Nanoparticles

Manufactured nanoparticles in significant quantities have been released into the environment as a result of the development of nanotechnologies¹(Boros *et al.*, 2020). Reactive oxygen species (ROS) generation is a most commonly used parameter to assess the toxicity of various nanoparticles in different microbes. Microbial cells respond to the various stress by building up multiple defense mechanisms that can be reflected in terms of enzymatic activity and transcriptional outputs. Certain nanoparticles (e.g., TiO₂, ZnO, SiO₂, and fullerenes) produce excited electrons when they come into contact with light (photochemically active). These electrons can directly transition to superoxide radicals in the presence of oxygen. In certain circumstances, some organisms can be exposed to both nanomaterials and illumination simultaneously which will result in added up toxicity to the organisms. Ecotoxicity of a particular nanomaterial have been measured at different tropic levels using various model organisms. Standardized study have been developed to determine the exposure of organisms to various nanomaterials and to analyse various parameters for assessing the toxicity effects depending on the exposure period (chronic or acute toxic effects), and various physiological and physical requirements (moderate composition, organism age, etc).

The advantages of microorganisms (majority of them bacteria, but also fungi, protozoa, and algae) include their ubiquity, vast diversity (occupying a range of environments and roles), tiny size (allowing for miniature experiments), and quick production times (permitting rapid tests). In this regard, nanoparticles' mobility is decreased and they are kept from entering the environment when they are embedded in organic or inorganic matrices. For sustainable and safe use of nanomaterials it is better to use it in its nanocomposite form. Utilizing magnetic nanoparticles in the creation of nanoparticles is a complementary strategy to ensure their safety. Magnetic nanoparticles are of great interest to researchers in many different sectors because of their advantageous properties and reactivity to a magnetic flux.

Ecotoxicity of carbon nanotubes

The ecotoxicity of unrefined single-walled carbon nanotubes (SWCNT) as well as double carbon nanotubes to *Danio rerio* was investigated under varying conditions in terms of salinity. In SWCNTs concentrations higher than 120 mg/L, considerable hatching delay was reported in the embryos.³⁰(Cheng *et al.*, 2007). But in case of double-walled carbon nanotubes, only at higher concentration of 240 mg/L delayed hatching were reported, whereas carbon black had no impact. According to a recent study, natural lipid coating on nanotubes makes them more approachable to the marine flea *Daphnia magna*³¹(A. P. Roberts, 2007). Once the marine flea consumes the lipid coated nanotube, the outer lipid layer will be utilised by the flea for their nourishment and the rest of material will choke their digestive tracts and causes various toxicity effects. In aquatic organisms, SWCNTs are less damaging when compared with fullerenes.

Ecotoxicity of Metal nanoparticles

Additionally, metal nanoparticles have antimicrobial properties. The charge at the membrane surface affects a metal nanoparticle's cytotoxicity. Gram positive cells have a thicker peptidoglycan coating than Gram negative cells, making them less susceptible to nanotoxic effects³²(Sinha *et al.*, 2011). Nanotoxicity may be caused by the electrostatic repulsion of nanoparticles with membranes and their aggregation in cytoplasm.

The majority of silver nanoparticle production is done for antiseptic uses, and it is well recognised that these particles have microbiological and apoptotic capabilities, including possible impact on mitochondria and ROS generation³³(You *et al.*, 2012).

Ecotoxicity of Metal Composites

The potential of nanocomposites resides in their multifunctionality, which offers the chance to realize special combinations of features that are impossible to achieve with conventional materials. Depending on the properties of the matrix and the nanophase, numerous distinct forms of nanocomposites can be produced⁷(Khan *et al.*, 2016). Use of polymer-metal nanocomposites may be considered beneficial. Metal nanoparticles in nanocomposites are independent of the polymer used in developing the nanocomposites.

The properties of metal nanoparticles within the polymeric composites may substantially

alter the polymer's surface characteristics due to the emergence of nanoporosity, which accelerates the surface area variability within the nanocomposites, and other structural factors that are essential for their practical applications. Iron nanoparticles, either alone or in conjunction with platinum, are one of the most effective elements (bimetallic particles). However, immobilisation on a solid substrate can improve the durability and stability of the nanoparticles. Ion exchange materials are frequently employed in a variety of water treatment procedures, mostly to remove unwanted or hazardous ionic contaminants. Nanocomposites along with silver nanoparticles can be used to treat the biofouling problem caused in various water treatment plants.

Ecotoxicity of Oxide Nanoparticles

Nanoparticles with magnetic property are of great interest to scientists working in a wide range of disciplines, notably catalyst, bioengineering, and ecological science and technology³⁴(Wu *et al.*, 2008). The use of ferrites is very practical for biomedical applications due to their low toxicity level and their super paramagnetic properties, which is important to note in terms of the materials' safety. The IMS approach makes it simple to create these core/shell metal nanoparticles, and the resulting nanocomposites can be used for water treatment or catalysis. The reduction of seedling growth and root penetration following a 2-hour contact to nanoparticle dispersion in demineralized water has been used to demonstrate the phytotoxicity of Zn and ZnO nanoparticles. Phen-loaded nanoparticles greatly reduced their phytotoxicity and had no negative impacts on the roots of plants³⁵(Yang and Watts, 2005). The authors contend, however, that it is conceivable for phen coupled with nanoparticles to break down in the presence of UV light in the field, and that even phen loaded particles in the environment could have a negative impact on plant growth.

Aquatic cytotoxins and their removal by sorbents made of nanocomposite materials

Access to drinking water is crucial everywhere in the world because water is such a vital component of human life. Nowadays, a number of harmful pollutants are released into water due to urbanization and industrialisation. Human health is seriously threatened by water contamination

from a variety of cytotoxic pollutants, including toxic metal ions, drugs, fertilizers, pigments, and leftovers. As a result, this issue has drawn a lot of recognition from researchers looking into the best methods and technologies for removing dangerous contaminants from water and wastewater

Pollutants and their cytotoxicity

Heavy metal ions

Heavy metal ions are difficult to break down, which increases their toxicity, which might increase underneath the biological proliferation of the food system. Incalculable harm to the human body can result from protracted exposure and accumulation. The toxicity of heavy metal ions to the organism is frequently intricate and all-encompassing; several systems may be harmed simultaneously.

Dyes

Dyes are used in every aspect of rapid industrialization and daily life, however because of a shortage of organic dyes and improvements in dye industry technology, people are relying more and more on synthetic dyes. However, the difficulties caused by the subsequent environmental contamination are ^{36,37}(Hamida *et al.*, 2018; Manzoor and Sharma, 2020) also getting worse.

A wide range of industrial procedures, including acid treatment, nitration, diazotization, reduction, oxidation, and acid (sodium chloride) precipitation, as well as synthetic dye constituents (chromophore groups include aroma formations, nicotiny groups, nitrogen-containing groups, and anthocyanins, among others) are thought to be promising sources of pollution.

Polyfluoroalkyl substances (PFAS)

Perfluorinated compounds (PFC), also known as per- and polyfluoroalkyl substances (PFASs), are a class of artificial, water-soluble organo-fluorine chemicals ^{38,39}(Buck *et al.*, 2011; Ritscher *et al.*, 2018). These compounds include at least one eCnF2ne moiety. PFAS have been manufactured and extensively employed in numerous sectors during the past 60 years. Such contamination often affects a single plant and is isolated.

Nanocomposites adsorbents for the remedy

Nanocomposites have at least one dimension (1 nm 14 109 m) in the nanoscale. A nanocomposite is made up of matrices that might be either organic or inorganic and have a good

compatibility to adsorb substances. Because of their diminutive diameter, active surface, and high density, such materials are good at securing pollutants, but they can also effectively employ the raw materials rather than releasing the harmful payload. ^{40,41}(Makvandi *et al.*, 2020; Zare *et al.*, 2020a, 2020b). This new class of materials was a good replacement for the conventional monolithic and micro composites. In comparison to conventional materials, nanocomposites have better overall adsorption capacities because of their unique properties, including compact size, vast area, surface to volume fraction, ease of access of more adsorption sites for reactant and product interaction, high reactivity, and catalytic prospects. In order to get better outcomes for the sequestration of pollutants from wastewater, nanocomposites are therefore emerging as new options ⁴²(Santhosh *et al.*, 2016). According to the source of the raw ingredients, such as activated carbon derived by pyrolyzing waste material, lignin, chitin, spontaneous clays, etc., bio nanocomposites are further classified broadly into many areas. Another option is to use inorganic polymers to modify nanometal oxides or other nanoparticles ⁴³(Zhang *et al.*, 2019d). Although the creation of unique adsorbent materials has grown significantly, there are still numerous issues with nanocomposites that need to be resolved in order to be used in future applications, such as their stability when exposed to varying pH levels, agglomeration, and ageing.

Genotoxicity studies

The presence of water disinfection by-products (DBPs) in tap water, which come from chlorination or chlorination disinfection procedures, raises the water's mutagenicity and may have negative health impacts. According to recent molecular epidemiology studies, exposure to chlorinated water may cause bladder cancer by activating brominated trihalomethanes by the enzyme GSTT1 and impairing the metabolism of halo acetic acids by a version of the enzyme GSTZ1. Due to the fact that fish were also proved to be excellent markers of mutagenicity, an *in vivo* biological monitoring strategy was chosen ^{44,45}(Rocha *et al.*, 2011; AlSabti and Metcalfe, 1995).

TiO₂ nanoparticles appear to have a strong affinity for activated sludge during the sewage treatment process; as a result, the majority

of these nanomaterials are anticipated to end up in soils through the application of sewage sludge^{46,47}(Johnson *et al.*, 2011; Kiser *et al.*, 2009). The validity of the comet assay and the micronucleus (MN) test, two popular genotoxicity testing methods when used on nanoparticles, was investigated through experiments (NP). Strand breaks (SB) that are caused in cellular DNA are discovered using the comet assay.

Studies revealed that macrophages may not be the most sensitive cell types to the effects of silver nanoparticles, despite the likelihood that they will be among the highest exposed cell types. This suggests that other cell types may need to be considered in the assessment of the biocompatibility of nanomaterials.

CONCLUSION

Human impacts such discharge of industrial effluents, poorly discarded household waste, and soil contamination are the main contributors to surface water contamination and a reduction in water quality. Seasonal changes in natural and anthropogenic processes, such weather and precipitation, which have a consequence on both, such as both, have an impact on the quality of ground water. The study of water on Earth's surface and below its surface, its occurrence and movement, its physical and chemical characteristics, and its interactions with the environment's natural resources and living things are all covered by the science of hydrology. In addition to the fluxes of water itself, many hydrologic problems also concern the transfer of solutes, nutrients, energy, sediment, or pollutants. The ecosystem-harming impacts of heavy metal ions and organic pollutants, as well as their capacity to alter the physical and chemical properties of water, have garnered a lot of attention in recent years. Health and environmental concerns from this pollution are very real. Lead ion (Pb²⁺) and methylene blue (MB) were among the hazardous pollutants that were most closely researched due to their extensive and varied industrial employment in the production of dyeing, printing textiles, lead smelters, oil refining, and battery manufacturing industries. Adsorption, photocatalysis, biological processes, membrane filtration, and ion-exchange have often been employed to remove the dangerous

elements and organic pollutants from water. Several different materials have been developed and used to remove heavy ions and organic contaminants from water. Carbon nanotubes, clay minerals, silica, MXene-based nanocomposites, and metal-organic frameworks are some examples of materials that are frequently employed to adsorb contaminants from aqueous solutions (MOF). However, these high-performance adsorbents were still not widely used due to their poor removal capacity and efficiency. There is hence a need for additional study and development of adsorbents with high heavy metal ion and organic pollutant adsorption capacities and efficiencies. The addition of functional groups and exposure of the adsorbents' outer surfaces offered the best chance of enhancing removal capacity and adsorption rate.

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Conflict of Interest

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