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Toxicology of Nano-Scale Materials Used in Water Treatment

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Abstract: In the last two decades, the use of nanomaterials has increased in food ingredient and packaging, water treatment, pesticides, cosmetics and many other industries. Old habits have begun to change in this process and silver nanoparticles instead of pesticides, carbon nanotubes absorbing pollutants in water treatment, titanium dioxide in smart drugs and cosmetics have become widespread. These nanoparticles, which permeate our lives in all areas, can hang in the air for kilometers and can cause DNA damage by penetrating people, animals and plant cells. Although the magnitude of the risks and the toxic effects are estimated, there are very few studies on this subject yet. Therefore, it is required to reveal the risks and toxic effects of nanomaterials, which are widely used in water treatment, and their effects on human and environmental health were investigated. Thus, the mechanism of action of the investigated nanomaterials was revealed.

Keywords: Water treatment, Nanotechnology, Toxicology

Introduction

As a result of population growth, serious problems such as rapid depletion of existing resources, hunger, inability to access water and health services have emerged worldwide. Producing fast solutions to these problems has become a priority all over the world. The introduction of nano materials, which are seen as one of these solutions, has opened the door to many innovations in the fields of medicine, science and technology, and nano materials have been included in every area of our lives. Its use has become widespread in fields such as sports and sports equipment, cosmetics, biomedical applications, electronic devices, water treatment, new generation drugs, mRNA vaccines, textiles and food (Hurt et al., 2006; Akbarzadeh et al, 2016). In addition to the convenience that nanomaterials bring to life, the magnitude of the risks involved has led to the emergence of the science of nanotoxicology. Nanotoxicology is the study of the toxic effects of nanomaterials by inhalation, contact and ingestion. One of the important factors affecting the toxicity of nanomaterials is the size of nanomaterials, which have a size of less than 100 nm, can accumulate in the body and easily reach more distant areas such as the brain and blood from the areas where they accumulate (Akbarzadeh et al, 2016; Rai et al, 2018).

The fast change and transformation of technology has also caused change and transformation in industries. Therefore, high polluting, toxic, radioactive pollutants, dyestuffs, pharmaceutical chemicals, heavy metals and organic pollutants have changed the pollution profile of wastewater (Madenli et al., 2021). Conventional treatment methods are insufficient in the treatment of such wastewater. For this reason, the use of nanomaterials in water and wastewater treatment has become widespread in recent years. These nanomaterials have been frequently used in treatment methods such as adsorption, filtration, photocatalytic, remediation and disinfection (web 1). Cu, Cr, Cd, Hg, Pb and Ni can be removed from wastewater by using carbon nanotubes in the adsorption process. Organic pollutants can be removed with the use of iron oxide nanomaterials in photocatalysis. In addition, while silver nanoparticles are used in the disinfection of drinking water and wastewater, various organic pollutants such as pesticides, polymers can be treated by photocatalysis using nano TiO2 (Jangid et al., 2021; Madenli et al., 2021; Sadegh & Ali, 2021; Xu et al., 2012). After treatment, the used

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nano silver, nano TiO_2 , nano metaloxides and carbon nanotubes are released to the environment through water and are not considered as a hazardous waste (Rai et al., 2018). However, the negative effects of these materials should be investigated starting from the cellular level and covering the entire ecosystem. The widespread use of nanomaterials facilitates their entry into the living body through skin contact, inhalation, ingestion and injection. The release of significant amounts of carbon nanomaterials into the environment can adversely affect all living things, especially humans (Hurt et al., 2006).

The very small size of nanomaterials and the dangerous mechanism of action caused them to be named "Trojan horse" (Hsiao at al.,2015; Martín-de-Lucía et al., 2017; Park et al., 2010). This nomenclature is proof that scientists are seriously concerned about what they are up against. Before nanomaterials become widespread, proving their reliability should be a priority for scientists. In this study, the ways in which nanomaterials enter the human body through the water and food chain and their mechanism of action were investigated.

Nano Materials Used in Wastewater Treatment

Carbon Nanomaterials and Mechanism of Action

Carbon nano materials, which have many different forms (fullerene, CNT, graphene, etc.), are one of the most popular products used by nanotechnology. It is especially preferred in wastewater treatment to reduce environmental problems. Hazardous substances such as 1,2-dichlorobenzene and dioxin in wastewater are highly carcinogenic and cannot be degraded. These substances accumulate in the living body cause damage. Carbon nanomaterials are preferred as a highly effective absorbent in the removal of these pollutants. This is because carbon nanomaterials have a much higher absorption capacity compared to activated carbon. Because the high surface area of carbon nanomaterials causes a strong interaction with dioxins (Mubarek et al., 2014; Ong et al., 2010; Jangid & Inbaraj 2021).

Different carbon nanomaterials can be used according to the characteristics of the pollutants in wastewater. Multi-walled carbon nanotubes (MWCNT) or single-walled carbon nanotubes (SWCNT) are the most preferred nanomaterials with their cylindrical properties (Lu et al., 2016) in Figure 1.



Figure 1. (Super) structure representations of (a) MWCNTs and (b) SWCNTs.

CNTs form aggregated pores due to the entanglement of thousands of individual tubes sticking together as a result of Van der Waals gravitational forces (Upadhyayula et al., 2009). CNTs are synthesized from graphite using arc discharge, chemical vapor deposition from gas, or laser ablation. In addition to many known pollutants, CNTs exhibit good mechanical strength, high sorption capacity, hydrophilic properties in the removal of some pharmaceutical compounds such as Diclofenac sodium, carbamazepine, which have caused problems in wastewater in recent years (Jangid & Inbaraj 2021). The widespread use of carbon nanomaterials due to these unique properties has accelerated the increase in treated water and its release to the environment. Nanomaterials can be easily dispersed, transported or transformed into water, soil or air environment from the environment in which they are formed. The lack of awareness of the effects of these substances on the environment and living things causes concern among scientists and environmentalists (Werkneh & Rene 2019). Due to their nature and structure, they can easily penetrate living things in the biological environment. Due to these properties, nanomaterials can cause oxidative stress, membrane irregularity, cell wall damage, formation of organic radicals and DNA damage in the absence of light. In addition, functionalized CNTs can be used in medicine as nanoplatforms in cancer therapy and nanocarriers to cross the blood-brain barrier (BBB) for

therapeutic agents to reach the brain. However, negative effects of CNTs on the vascular system are also seen, but their toxicity has not been fully resolved yet (Cao & Luo, 2019).

It is known that carbon nanomaterials penetrate into the cell in two different ways. These are the endocytic pathway and/or passive diffusion (Facciolà et al., 2019) in Figure 2. SWCNTs penetrate the cytoplasm pass through the phospholipid bilayer by passive diffusion. MWCNTs enter the cell using the endocytic pathway and accumulate in the mitochondria (Costa et al., 2016). They can easily cross the blood brain barrier and blood spinal cord barrier, which are selective permeable barriers that protect the central nervous system in the body. This situation may endanger the protective role of the blood-brain barrier, which prevents the entry of pollutants and toxins entering the body through diseases and can expose the person to serious diseases (Facciolà et al., 2019).



Figure 2. Mechanisms of CNTs cellular uptake

Due to the increasing use of masks in recent years, many people have been exposed to CNTs in masks by inhalation. The emerging mask wastes have left to nature in an uncontrolled manner. In the early stages of toxicological research, researchers focused on the effects of CNTs on the respiratory tract because of their similarity to asbestos. They revealed that after inhalation it triggers epithelial cells and macrophages of the respiratory system. As a result of these studies, it has been determined that CNTs cause, genotoxicity, fibrosis, tumor formation, inflammation and apoptosis in the lungs (Facciolà et al., 2019). Exposure to nanomaterials together with air pollution contributes to the progression of autism spectrum disorders, low IQ in children, Parkinson's, Alzheimer's and chronic encephalitis (Costa et al., 2016; Kafa et al., 2016).

Silver Nanomaterials and Mechanism of Action

Silver nanomaterials are zero-valent (Ag^0) silver clusters with a size of 1-100 nm. Owing to its many important features, it is used in the fields of science and technology. With its antimicrobial feature, it appears in the field of medicine, health care products, underwear and shoes, and wet wipes. Thanks to this feature it also serves as a new generation antimicrobial material in water disinfection applications (Zhang et al., 2016). Due to this antimicrobial feature, it has started to be preferred instead of chlorine in water treatment systems and filtration units in hospitals, pools and spas (Esakkimuthu et al., 2014).

Silver nanomaterials reach wastewater and natural water resources as a result of the application and consumption process. In addition, it plays an active role in the removal of E.coli and other pathogens in the treatment processes of wastewater and is released into nature with water at the outlet (Esakkimuthu et al., 2014; Jangid & Inbaraj 2021). Silver nanomaterials cause physical degradation by oxidative stress by disrupting the cellular component (Figure 3). The toxic effects of exposure to silver nanomaterials occur when they act on DNA, rendering phosphorus and sulfur elements unusable. Studies with silver ions and stabilized silver nanoparticles have shown that the toxic effect of silver occurs in bacteria and human mesenchymal stem cells in a certain concentration range (Akbarzadeh et al., 2016). Studies have shown that the toxicity of silver nanoparticles is almost the same in bacteria and humans (Greulich et al., 2012). Again, in studies on mice, it has been observed that silver nanoparticles reduce the viability of macrophage cells, which have a very important place in the immune system (Park et al., 2010).



Figure 3. Antimicrobial effect of silver nanoparticles (Rahman et al., 2019).

Titanium Dioxide Nanomaterials and Mechanism of Action

Titanium dioxide nanomaterials (TiO₂) are shiny due to their high refractive index. In general, they exist in 3 different phases (anatase, rutile and brookite), each of which is different in size. Due to its small size and shine, it has a wide range of applications such as toothpaste, medicine, coating, paper, ink, plastic, food products, cosmetics and textiles. In addition, they are preferred in the preparation of cleaning cloths, car mirrors, window glasses due to their self-cleaning and anti-fogging feature. It has become a very popular nanoparticle due to its easy biosynthesis and cost-effectiveness. It has enormous industrial applications such as wastewater treatment, environmental applications, agriculture, aerospace applications, food industry (Waghmode et al., 2019). TiO₂ nanomaterials serve as photocatalysts for biological treatment of wastewater and removal of pharmaceuticals. Especially non-biodegradable water pollutants can be easily removed from wastewater by photocatalytic degradation (Esakkimuthu et al., 2014). In addition to all these, TiO₂ nanomaterials are used as packaging material for surface water treatment, pesticide removal from groundwater, dye and heavy metal removal from wastewater, and solid phase extraction (Waghmode et al., 2019).

The ecotoxicity of such widely used nanoparticles and their effects on living things are very worrying. The wide application area of TiO_2 nanomaterials increases the exposure rate. TiO_2 nanomaterials, which we frequently encounter in foods with the code E171, can be easily absorbed by intestinal cells. Exposure to nanoparticles can occur through inhalation, skin contact, ingestion, and injection. Studies have shown that exposure to nano TiO_2 in different ways causes damage to important organs (Chang et al., 2013). The effects of ingestion with food were investigated in in vivo experiments and its penetration into enterocytes of rats was confirmed (Jovanović, 2015). In a study conducted on mice, it was reported that orally ingested TiO_2 caused accumulation in liver, spleen, kidney and lung tissue (Wang et al. 2007). The cellular mechanism of action of TiO_2 nanomaterials for vertebrates is shown in Figure 4.



Figure 4. Mechanism of Nano TiO₂ in the cell (Hou et al., 2019)

Oxidative stress is one of the main mechanisms in TiO_2 genotoxicity. In mammals, oxidative stress damages lipids, carbohydrates, proteins, and DNA. Especially, peroxidation of lipids can cause changes in the cell membrane and impair vital functions. This causes the redox state of cells to deteriorate. Toxic effects may occur with the increase of peroxides and free radicals on cell components (Hou et al., 2019). According to the results of the studies, it can be said that TiO_2 toxicity is a public health problem. Due to environmental and occupational exposure from cosmetics, drugs, food and water, risk assessment should be performed and its use should be limited.

Conclusion

The use of nanomaterials, which offer effective solutions in solving environmental problems, is increasing rapidly. Day by day, many new products produced with nano technology are included in our lives. For this reason, nanomaterials will continue to be a popular topic that will keep researchers busy for a long time. The popularity of nanomaterials in water treatment, along with many other fields, has led to an increase in environmental exposure. The alarming consequences of this rapid rise have begun to emerge. Nanomaterials that are not seen as pollutants are transferred to the ecosystem by being released into the soil environment through water. As a result of their unlimited use, it has been revealed that they accumulate in the environments they are transported and turn into more polluting forms with new reactions. It is well known that nanoparticles generate oxidative stress in cells by generating reactive oxygen species and induce toxicity through inflammation. Therefore, their use should be limited by legal means. If this is not done, the emergence of new nano-pollutants that threaten public and environmental health seems inevitable.

Scientific Ethics Declaration

The author declares that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the author.

Acknowledgements or Notes

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