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ORIGINAL ARTICLE

Nanotechnologies and environment: A review of pros and cons

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This review outlines the latest advances in nanomaterials, nanostructures, nanotechnologies and their environmental impact. Environmental restoration is based on the use of physic-chemical methods: adsorption, absorption, chemical reactions, photocatalysis, filtration and technologies that remove contaminants from soil, water and air. New technologies and nanomaterials are now being developed for environmental restoration. Nanomaterials have high surface-to-volume ratio and high reactivity, which makes them suitable for cleaning the environment from heavy metals, dyes, organochlorine and organophosphorus, volatile organic compounds and halogen-containing herbicides. The review examined modern approaches to the classification of nanomaterials, their basic properties, and their scope for the remediation of contaminated soil and water. Despite the wide scope of application, economic and environmental effects, the nanotechnology products possess some toxicity. The review addresses the issues of ecotoxicology and potential risks associated with the use of nanotechnology products, the mechanisms of toxicity of various nanostructures based on their size, shape, concentration and specific biological effects. We supposed that while many studies were effective in the laboratory, the additional research is needed to understand the impact of nanotechnology in real-world scenarios and the processes, which occur with nanomaterials after completing of their task. Therefore, the subsequent studies should determine the state of these materials after their introduction into the environment for recovery, the ways to avoid new contamination caused by them, and development the ways of processing nanomaterials without reducing their activity.

Keywords: Nanotechnologies; Nanomaterials; Environmental remediation; Nanostructures; Pollutants

Introduction

Environmental pollution is a major problem in modern society. New technologies are widely explored in the context of the recovery of pollutants, including solids, heavy metals, pesticides, herbicides, fertilizers, oil spills, toxic gases, organic compounds, industrial effluents and wastewater (Baia et al., 2020). Capture and degradation of pollutants can be problematic due to the complexity of the mixture of compounds, high volatility and low reactivity. New technologies and nanomaterials are being developed to restore the environment (Guerra et al., 2018). Nanotechnology is gained considerable attention due to the unique physical properties of its materials, including increased reactivity and efficiency due to the higher surface-to-volume ratio compared to the volumetric counterparts (Tsekhmistrenko et al., 2018a; Tsekhmistrenko et al., 2018b; Tymoshok et al., 2019; Bityutskyy et al., 2017; Baia et al., 2020; Santhosh et al., 2016).

The surface of nanomaterials can be supplemented with functional groups to influence specific molecules for effective recovery. The deliberate tuning of the size, morphology, porosity and chemical composition of nanomaterials adds useful characteristics for the purification of toxicants and offers significant advantages over conventional methods of pollution control, especially when developing combinations of several materials (composites) and combining the desired properties of each component's efficiency properties, selectivity and stability (Guerra et al., 2017; Guerra et al., 2017a; Shah & Imae, 2016).

Cleaning materials after their using should not pollute the environment, so the application of biodegradable materials does not create waste materials that require removal after treatment and offer a greener and safer alternative to environmental rehabilitation. Capture of specific pollutants, cost-effectiveness, easy synthesis, use of ecological methods of "green" chemistry (Tsekhmistrenko et al., 2019; Tymoshok et al., 2019; Bityutsky et al., 2018; Bityutskyy et al., 2019), non-toxicity, biodegradability, processing and regeneration are major issues for the development of new nanomaterials for environmental restoration (Das et al., 2015; Tsekhmistrenko et al., 2020b). However, despite the advantages, some nanomaterials are unstable under normal conditions and therefore require special production methods, additional manipulations to prevent agglomeration, increase monodispersity and stability can be toxic and form byproducts.

Among the methods of eliminating water pollution (bacteria, pesticides, heavy metals, solvents, and oil), soils (food waste, chlorine compounds, and heavy metals) and air (CO_2, NH_3, carboxylic acids, aldehydes, and NO_x), the following methods are used: absorption, adsorption, chemical reactions, photocatalysis and filtration (Hussain et al., 2015; Low et al., 2017; Azam et al., 2017; Georgakilas et al., 2015; Matin et al., 2019; Song et al., 2016; Mittal et al., 2015; Sun et al., 2015; Gumus et al., 2020).

Literature Review

Nanotechnology: definition, basic properties and classification of nanoparticles

The term nanotechnology (NT) appeared in Richard Feynman's works in 1959, but only after the development of a scanning tunneling microscope (Hulla et al., 2015) in 1981 nanotechnologies were defined as processes describing the fabrication and / or use of nanoscale structures (Santhosh et al., 2016; Das et al., 2015; Brigante et al., 2016; Nakanishi et al., 2015). Advantages of nanomaterials are non-conventional properties and new physicochemical characteristics (Hussain et al., 2015), allowing them to develop their use in health, industry, environmental monitoring, promote advanced materials and produce new products (Santhosh et al., 2016; Das et al., 2015; Brigante et al., 2016; Nakanishi et al., 2015). The manufactured nanomaterials have new physical, chemical, surface and optical electronic properties, solve problems which can't be solved by traditional technologies, and play a role in developing innovative methods for creating new products, materials and chemicals with high productivity and lower energy consumption (Santhosh et al., 2016; Das et al., 2015; Brigante et al., 2016; Nakanishi et al., 2015; Srivastava et al., 2015). The modern expansion of human activity reduces natural resources and creates hazardous waste polluting the environment (NO, SO_2, CO_2, O_3, etc.), colloidal particles and organic compounds, toxic gases that threaten health and environmental safety. Nanotechnology provides a new solution for environmental cleaning (Adeleye et al., 2016) by reducing emissions or preventing the formation of pollutants.

Particles with diameters greater than 100 nm have new properties compared to size-dependent bulk materials. There are several engineering nanomaterials, like carbon nanotubes, nanocomposites, quantum dots, fullerenes, quantum wires and nanofibers (Georgakilas et al., 2015), a wide range of commercial products - metals, ceramics, polymers, smart textiles, cosmetics, sunscreens, electronics, paints, and varnishes, for which the nanomaterials are directed to achieve certain characteristics, and the natural nanoparticles, namely the erosion dust or volcanic eruptions, wood and diesel fuel combustion products (Wagner et al., 2014).

The properties of nanomaterials caused by their high surface-to-volume ratio, which makes them more reactive than volume forms of the same materials (Mukherjee, 2016). Nanomaterials are divided into inorganic, carbon and polymeric for the environmental recovery.

Inorganic materials: features of their structure and methods for environmental restoration

Many studies on pollution removal are devoted to the removal of heavy metals and organochlorine compounds from water due to the fast kinetics and high adsorption capacity of metal and metal oxide nanomaterials (Santhosh et al., 2016). Nanoparticles are flexible for *in situ* and *ex situ* applications in aqueous media (Das et al., 2015). In particular, silver ions nanoparticles (AgNPs) AgNPs / Ag are an effective disinfectant of water against *Escherichia coli* (Baia et al., 2020), and the nanoparticles of titanium oxide (IV) (TiO_2NPs) destroy the *Escherichia coli*, *hepatitis B virus* in soil and remove aromatic hydrocarbons and phenanthrene (da Silva et al., 2016). Titanium (IV) oxide nanoparticles (Sreeja & Shetty, 2016) neutralize *Escherichia coli* and *Staphylococcus aureus* from water, remove 2-chlorophenol, endotoxin and rhodamine B, and titanate nanotubes (Gumus et al., 2020; Okada et al., 2019), and remove gaseous nitrogen oxide.

Silver nanoparticles are known for their significant antibacterial, antifungal and antiviral activity in aquatic environment (Baia L. et al., 2020; Alqahtany et al., 2019). AgNPs less than 10 nm in diameter are highly toxic to *Escherichia coli* and *Pseudomonas aeruginosa*, bind virus glycoproteins, preventing virus binding to host cells, while if larger in diameter (11–23 nm) they exhibit lower activity (Alqahtany et al., 2019). Particle shape is also important, since triangular AgNPs exhibited higher antibacterial effects than Ag-nanorods and Ag-nanospheres (Baia L. et al., 2020).

Nanoparticles of titanium oxide (IV) are used in waste treatment, air purification, self-cleaning of surfaces and as a catalyst for water treatment, as they are characterized by low cost, non-toxicity, semiconductor, photocatalytic, electronic, gas sensitivity and ability to transform energy (Tsekhmistrenko et al., 2019). When activated by light, TiO_2NPs remove organic contaminants from different media and produce hydroxyl radicals and highly reactive oxidants to disinfect fungi, bacteria, viruses and algae (Matin et al., 2019).

Magnetic metal nanoadorbents are easily retained and separated from purified water, for example, iron nanoparticles (FeNPs), hematite nanoparticles and iron oxide after removal of Ni^{2+} (Hashemzadeh et al., 2019; Ebrahim et al., 2016), Cu^{2+} (Poguberović et al., 2016), CO_2^+ (Hashemzadeh et al., 2019) and Cd^{2+} (Ebrahim et al., 2016), as well as biosynthesized iron nanoparticles for the recovery of organochlorine solvents (Guo et al., 2017; Han & Yan, 2016). Nevertheless, their use is problematic because of their aggregation, which affects the reactivity, possible toxicity and cost of the technology.

Zerovalent elemental iron Fe^0 in the shell of Fe (II) and Fe (III) oxides is capable of reducing the chlorine-containing compounds and heavy metals (Hashemzadeh et al., 2019). Their high nanoparticle stability promotes the efficiency, productivity and accelerates the degradation process of pollutants (Sreeja & Shetty, 2016; Zhang et al., 2019; Tamai et al., 2019; Liu et al., 2016).

To reduce the toxicity of chemicals used for the synthesis of nanoparticles (NPs) based on metals and byproducts of decomposition of pollutants, the nanoparticles for the removal of Ni^{2+} and Cu^{2+} (Poguberović et al., 2016) are synthesized using "green" chemistry methods in the presence of plant antioxidants (Poguberović et al., 2016; Han & Yan, 2016; Kocur et al., 2016). The obtained nanoproducts reduce the toxicity of the chemicals and byproducts used, and "green synthesis" reduces the amount of waste (Tsekhmistrenko et al., 2017; Tsekhmistrenko et al., 2018a; Tsekhmistrenko et al., 2018b; Tsekhmistrenko et al., 2019; Tymoshok et al., 2019; Bityutskyy et al., 2017).

To remove Cr^{6+} ions, FeNPs suspension uses herbal extracts of *Camellia sinensis*, *Syzygium aromaticum, Mentha spicata, Punica granatum* juice, and red wine containing polyphenols, which antioxidant effect restores iron ions in aqueous solutions, resulting in the formation of FeNPs (Mystrioti et al., 2016). Various environmental restoration materials used in the field conditions are described (Mackenzie et al., 2016; Kocur et al., 2016; Chowdhury et al., 2015; Jiang et al., 2018). Reported (Poguberović et al., 2016; Han & Yan, 2016) a field study of the effectiveness of emulsified iron nanoparticles for the treatment of groundwater volatile organochlorine compounds (CVOCs).

Adsorbents, mesoporous silica materials in various modifications purify the gas phase from contamination (Wang et al., 2019; Brigante et al., 2016). Mesoporous silicon dioxide functionalized with carboxylic acid removes cationic dyes and heavy metals from wastewater (Tsai et al., 2016). Silica-based materials are capable to remove the organic dyes from wastewater due to the ability of –COOH groups of functionalized mesoporous silica to interact with metal ions, dyes and contaminants (Tsai et al., 2016).

Carbon nanomaterials for environmental restoration

Carbon nanomaterials - fullerenes (convex closed polygons made of three coordinated carbon atoms), nanotubes (allotropic carbon modifications, which are empty cylindrical structure with diameters from several tenth to several tens of nanometers, and lengths from one micrometer to several cms and consist of one or more coiled graphene planes), graphene (a two-dimensional allotropic carbon modification formed by a one carbon atom layer of one atom thick (Reddy & Yaakobovitz, 2019) are used extensively with purpose of purification of pollutants (Azam et al., 2017; Song et al., 2016; Deng et al., 2017; Khare et al., 2016; Mortazavi et al., 2019). Before using carbon nanotubes and graphene to restore the environment, they first treat the surface, activate or functionalize the primary carbon material. The adsorption properties of single-walled and multi-walled carbon nanotubes make them particularly useful for the removal of organic and inorganic contaminants from the air and large volumes of aqueous solution (Azam et al., 2017; Khare et al., 2016; Mortazavi et al., 2019) by photocatalytic methods (Chowdhury et al., 2015; da Silva et al., 2016; Alqahtany et al., 2019).

With high mechanical rigidity (Reddy & Yaakobovitz, 2019), thermal conductivity (Mortazavi et al., 2019), high mobility of charge carriers (Arellano et al., 2019; Ullal et al., 2019), graphene is promising for use in nanotechnology (Wang et al., 2019), because it allows to obtain high-quality samples with high mobility of carriers (Brun et al., 2019). Reported (Wang et al., 2019; Reddy & Yaakobovitz, 2019) on the removal of fluorine from water with primary graphene and of gaseous SOx, H_2, NH_3, heavy metals, pesticides, pharmaceuticals with graphene oxide from aqueous solutions (Song et al., 2016; Deng et al., 2017). Heavy metals are removed from the water using ZnO-graphene/CdS-graphene composite nanoparticles (Zhang et al., 2019; Jiang et al., 2018; Song et al., 2016), and a nanoscale TiO_2-graphene composite has been widely used for removal of benzene gas (Song et al., 2016; Deng et al., 2017; Reddy & Yaakobovitz, 2019; Arellano et al., 2019).

The large adsorption capacity and efficiency of graphene allow it to actively adsorb fluorine (Song et al., 2016; Reddy & Yaakobovitz, 2019), and in the modified state, with reduced aggregation of graphene layers and increased effective surface area, graphene restores a number of toxic compounds (Wang et al., 2019; Reddy & Yaakobovitz, 2019; Mortazavi et al., 2019). In particular, graphene oxide (GO) adsorbs gaseous and aqueous pollutants (SOx, H_2S, NH_3, volatile organic compounds, heavy metals, pesticides, and pharmaceuticals) (Hussain et al., 2015; Wang et al., 2019; Reddy & Yaakobovitz, 2019; Mortazavi et al., 2019).

When using TiO_2-graphene nanocomposites for photocatalytic reduction of benzene in water, a significant effect on the activity of the material causes the ratio of the composite components (Arellano et al., 2019; Georgakilas et al., 2015). The ZnO-graphene and CdS-graphene composites have the purifying properties of water contaminants. The ZnO-graphene composite photocatalytically recovered Cr6+ by 40% faster than pure ZnO (Chowdhury & Balasubramanian, 2014). The optimal content of graphene in the composite for the complete reduction of the content of Cr6+ by 5% was determined, which supports the photoactivity of the composite, the light intensity and the amount of the main component, cadmium sulfide (CdS). Modified graphene with other components expands the list of contaminants that should be decomposed.

Carbon nanotubes (CNTs) are an allotropic modification of carbon, a hollow cylindrical structure from several tenth to several tens of nanometers, and a micrometer to several centimeters long (Azam et al., 2017; Khare et al., 2016; Mortazavi et al., 2019). There are technologies to weave nanotubes into strands of unlimited length (Georgakilas et al., 2015), consisting of one or more twisted-graphene planes.

Currently, carbon nanostructures (CNTs and graphene nanosheets) are widely used to enhance the photocatalytic efficiency of TiO_2, where in the TiO_2-CNT composition electrons are easily transferred through CNTs and delay electron recombination (Low et al., 2017). The conduction band of CNTs lies at a more positive level than TiO_2, so electrons can move from TiO_2 to CNTs.

A significant factor affecting the adsorption capacity of CNTs is the oxygen content and, depending on the synthesis and purification procedure, CNTs may contain the groups –OH, –C = O and –COOH. Chemicals (HNO_3, $KMnO_4$, H2O2, NaOCl, H_2SO_4, KOH, NaOH) are used to oxidize CNTs, which increases the adsorption capacity of Pb_{2+}, Cd_{2+}, Ni_{2+} and Cu_{2+} (Guerra et al., 2018). Activation of the adsorption of cationic dyes by the increasing of pH due to the electrostatic attraction of the surface of CNTs dyes (Ganzoury et al., 2020) and the effect on the ability of the CNTs data to absorb the molecular weight, constant electric dipole moment and critical temperature of gas-sorbate, Az-sorbate, had been reported (Azam et al., 2017; Khare et al., 2016; Mortazavi et al., 2019).

In general, the original carbon nanomaterials without modification are inert to the pollutants and require the modification or coating of reactive materials with appropriate functional groups or charges to improve efficiency.

Polymer based nanomaterials

A higher ratio of surface area to volume of nanomaterials contributes to higher reactivity with concomitant performance improvement, but the occurrence of aggregation, non-specificity and low stability limits the use of nanotechnology products due to lack of functionality. An alternative is to use the base material as a matrix for other materials (Bhardwaj et al., 2019). In particular, amphiphilic polyurethane NPs remove multinuclear aromatic hydrocarbons from soils (Bhardwaj et al., 2019), and polyamidoamine (PAMAM) dendrimers remove heavy metals from wastewater (Arkas et al., 2019). Removal of volatile organic compounds (VOCs) from the gas environment is capable of PDLLA-PEG-modified amine (Guerra et al., 2017a; Guerra et al., 2017) and polyamine-modified cellulose (Guerra et al., 2018). Removal of metal ions, dyes and microorganisms from water by polymer nanocomposites had also been reported (Khare et al., 2016; Mittal et al., 2015; Sun et al., 2015).

Polymers are generally used to identify and remove chemical contaminants (manganese, nitrate, iron, arsenic, heavy metals), gases (CO, SO_2, NOx), organic contaminants (aliphatic and aromatic hydrocarbons, pharmaceuticals, VOCs), biologicals (bacteria, parasites, viruses). Polymeric bases (surfactants, emulsifiers, stabilizing agents, and functionalized surface ligands) are used to enhance stability, overcome the limitations of pure nanoparticles, and to provide desirable properties, increased mechanical strength, thermal stability, and the ability to process in particular.

Amphiphilic Polyurethane Nanoparticles (APUs) are organic nanoparticles with predetermined desirable properties which restore multi-core aromatic hydrocarbons (PAHs) from soils (Bhardwaj et al., 2019). The hydrophilic surface of the nanoparticles promotes mobility in soils, and the hydrophobic inner part is related to the hydrophobic organic pollutants. APU NPs, by removing phenanthrene from the contaminated sand aquifer, showed an increase in affinity for phenanthrene with increasing APU particle aggregation (Bhardwaj et al., 2019).

Polyamidoamine (PAMAM) or dendrimers, as functional groups, contain primary amines, carboxylates, and hydroxamates capable of encapsulating water-soluble cations (Cu^{2+}, Ag^+, Au^+, Fe_2^+, Fe^{3+}, Ni^{2+}, Zn^{2+}, U^{6+}) (Arkas et al., 2019) and they are used as antibacterial / antiviral agents (Arkas et al., 2019). A feature of dendritic nanopolymers is the lower tendency to pass through the pores of ultrafiltration membranes through their lower polydispersity and globular form, which is why they are used to improve the processes of ultrafiltration (UF) and microfiltration (MF) to restore water soluble ions (Arkas et al., 2019).

The use of functionalized biodegradable and non-toxic polymeric nanomaterials for targeted capture of VOCs had been described (Guerra et al., 2017a; Guerra et al., 2017; Guerra et al., 2018). Biodegradability is an important and desirable feature that eliminates problems with the subsequent fate of materials after their use. The incorporation of polyethyleneamine (PEI) functional amino groups on the surface of PLA-PEG polymer nanoparticles allows the capture of specific VOCs containing aldehyde and carboxylic acid functional groups by condensation and acid-base reactions.

Using gas chromatography, amine-functionalized NPs had been shown to reduce the amount of aldehydes and carboxylic acid vapors by 69-75%, even with comparable or more volatile non-target vapors, selective and target capture characteristics (Guerra et al., 2017). The strategy had successfully modified cellulose nanocrystals (CNCs) using PEI to efficiently capture aldehyde VOCs contaminants (Guerra et al., 2018).

Polymers containing NPs of metal and metal oxides are used for environmental restoration (Santhosh et al., 2016), polymers in composites are used as a base, and NPs are responsible for the recovery of contaminants (Santhosh et al., 2016). The use of polymeric nanomaterials for the specific capture of compounds of a gas mixture of non-target contamination had been described (Guerra et al., 2017a).

Polymeric / inorganic hybrid nanomaterials had been studied in terms of adsorption removal of toxic metal ions, dyes, and microorganisms from water and wastewater. Manufactured using sol-gel processes, self-assembly techniques, hybrid materials exhibit high chemical and thermal stability, high capacity, and selective sorption of heavy metals from aqueous media.

Chitosan-based carbon nanofibers (CNFs) had been developed and incorporated into iron oxide nanoparticles with nanocomposite polyvinyl alcohol films (Khare et al., 2016) what effectively adsorb Cr^{6+} from water. Impregnation of SiO_2 nanoparticles in acrylamide hydrogel improves the adsorption capacity of the acrylamide hydrogel monolayer to remove cationic dyes (Mittal et al., 2015).

The main elements of using polymer nanocomposites are biocompatibility and biodegradability. In particular, the green hybrid adsorbent (Sun et al., 2015) removes dyes as a magnetic hydrogel. The ions of Ni^{2+}, CO_2^+, Pb^{2+}, Cd^{2+}, Cu^{2+} and Cr^{2+} were adsorbed same way by the sodium alginate nanogel loaded with tetrasulfonate tetrasodium thiacalisarene and Fe_3O_4 (Lakouraj et al., 2014). Another composition of Fe_3O_4 with magnetic NPs modified by a combination of 3-aminopropyltriethoxysilane and acrylic and crotonic acid copolymers (Rieger et al., 2016) was used to remove Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+} from water. The material, obtained after the introduction of AgNPs in cellulose acetate fibers, has significant antibacterial activity (Rieger et al., 2016). By incorporating AgNP and Ag+ into a mixture of polymethoxybenzyl and poly(1-lactic acid)-co-poly(3-caprolactone)nanofibers, the materials exhibited antimicrobial properties against *Escherichia coli*, *Staphylococcus aureus*, *Aspergillus niger* and *Salmonella enterica* (Meng & Tsuru, 2019). In addition, the dispersion of AgNP (1–70 nm) in polysulfone membranes does not alter the structure of the membrane and reduces the attachment of the *Escherichia coli* suspension to the surface of the immersed membrane by 94% (Meng & Tsuru, 2019). It is clear that polymeric NPs effectively remove multiple pollutants by different mechanisms, playing a critical role in environmental restoration.

Other models of nanoparticles what effectively remove environmental pollution are worth noting. Ag-doped TiO_2 successfully removes 2,4,6-trichlorophenol (Gitrowski et al., 2014), silver-doped TiO_2 nanofibers remove methylene blue dye. Cu / Fe / Ag doped TiO_2 binds nitrate (NO^{3-}) (Tamai et al., 2019). Removal of polycyclic aromatic hydrocarbons (PAH) and Pb^{2+}, Hg^{2+}, Cd^{2+}, Cr_2O7_2– from contaminated waters is facilitated by silica nanoparticles obtained by mixing salicylic acid and hyperbranched polypropyleneimine (Duan et al., 2019). The PAMAM chitosan and dendrimer dendrimer composite separates CO_2 from the gas mixture of CO_2 and N_2 on porous substrates (Duan et al., 2019). Cr^{6+} is removed by a coated carboxymethylcellulose polymer matrix Fe0 (Gumus et al., 2020). Chitosan polymer coated gold (Sadani et al., 2019) and multicellular carbon nanotube (MWCT) (Azam et al., 2017; Khare et al., 2016; Mortazavi et al., 2019) adsorb Zn^{2+}, Cu^{2+} and Th^{4+} from wastewater and industrial water is purified by chitosan / bentonite with polymethacrylic acid.

Application of nanotechnology to solve the modern environmental problems

Nanotechnologies are revolutionizing industry and manufacturing, creating materials used in cosmetics, pharmaceuticals (Bergmann and Machado, 2015), catalytic materials (Hulla et al., 2015) and environmental programs (Santhosh et al., 2016; Das et al., 2015; Brigante et al., 2016; Nakanishi et al., 2015) and lead to increase of investments in nanotechnology research.

Widespread human activity is a major environmental pollution at all levels (Das et al., 2015). Currently, air contains CO, halogenated hydrocarbons, volatile organic compounds and nitrogen oxides, water and soil contain organic and inorganic compounds, the main sources of which are sewage and industrial effluents, used pesticides, fertilizers and oil spills (Das et al., 2015). Some traditional technologies are already being used to eliminate organic and toxic waste through adsorption, biooxidation, and chemical oxidation with the parallel use of nanomaterials in monitoring and purification systems. In particular, liquid-phase nanotechnologies are used to purify water, gas-phase nanotechnologies are used as sensors for gas pollution, and solid-phase nanotechnologies are used to restore soil (Singh and Naveen, 2014). Nanomaterials are perfect adsorbents, catalysts and sensors due to their large specific surface area and high reactivity, some of them are commercialized, such as nanosensors and nano-sized coatings for the prevention of corrosion, nanosensors for the detection of aqueous toxins, nanoscale biosolids, nano-sized biosolids destroys hazardous organic matter indoors, smart particles for environmental monitoring and purification, and nanoparticles as a new photocatalyst for environmental purification (Das et al., 2015).

A large number of nanosystem methods are used for the ecological treatment (Singh and Naveen, 2014) - for photocatalytic oxidation of organic pollutants, reduction and absorption of heavy metals, anions, dechlorination and denitrification, and encapsulation of heavy metals and organic pollutants in water and soil.

Human activity and industrialization change the composition of the atmosphere, affecting chemical, biological and physical factors, introducing into the air carbon monoxide (CO), chlorofluorocarbons (CFC), heavy metals (As, Cr, Pb, Cd, Hg), hydrocarbons, oxides of oxides chemicals (VOCs and dioxins), SO2, sand particles and biological substances (Araújo et al., 2014). Air quality affects the ecosystem of human health, causing various types of deaths (cancer, respiratory and cardiovascular). Created nanomaterials can be used in various industries (Zhang et al., 2016) because of significant monitoring characteristics, improved nanosensors, and reduced pollution by replacing toxic materials with other safe materials. In general, the benefits of nanotechnology in combating air pollution can be divided into categories: recovery and treatment, detection and probing, and pollution prevention (Yadav et al., 2017).

The main uses of nanotechnology for the treatment and reduction of various air pollutants are adsorption by nanoabsorption materials, degradation by nanocatalysis, and filtration / separation by binanofilters. Many problems, including air quality, can be solved or greatly improved with nanoscale adsorbents. Carbon nanostructures are adsorbents with high selectivity, affinity, and capacity due to the average pore diameter, pore volume, surface area, and surface area activity (Yadav et al., 2017). Also the addition of other functional groups with oxygen can provide new active sites for adsorption (Wang et al., 2019), as in nanostructures of carbon, fullerene (0D), carbon nanotubes (1D), graphene (2D), graphite (3D) (Bergmann and Machado, 2015).

Global warming is an air problem that changes land, water sources and climate. Greenhouse gases (GHGs) (IPCC, 2014) – CO_2, CH_4, N_2O and fluorinated gases – are able to stay in the climate for many years. Air pollution can be compensated for and treated by various methods that use nanomaterials as adsorbents (Bergmann and Machado, 2015). Indoor air pollution is given considerable attention as the risk of inhalation of pollutants, in particular VOCs, is higher than in the open air (Salthammer, 2016). Air pollution can be controlled using semiconductor photocatalytic recovery materials (Yadav et al., 2017; Wang et al., 2019). The active surface is an important part of the catalyst where the reaction takes place. As the size of the catalyst decreases, its active surface increases, which leads to increased reaction efficiency (Zhang et al., 2014). Nanotechnology improves particle size and molecular structure of new nanocatalysts with increased surface area, performs rapid and selective chemical transformations with excellent product yield combined with catalyst reduction capability (Ganzoury et al., 2020; Khare et al., 2016; Mortazavi et al., 2019).

Titanium dioxide (TiO_2) nanoparticles with photocatalytic properties are used to make self-cleaning coatings capable of neutralizing atmospheric pollution (nitrogen oxides, VOCs, other pollutants for less toxic species) (Shen et al., 2015). TiO_2 nanoparticles are used as antibacterial drugs whose activity is inversely proportional to the particle size and relates to their ability to produce active carriers that cause active surface species (Low et al., 2017).

New methods of synthesizing metal oxide nanocatalysts can reduce and possibly solve problems with air pollution. Nanofibers of silver, iron, gold and manganese oxide can be used to control the environment for the storage of volatile organic compounds from industrial smoky fuels and have therapeutic effects (Singh and Tandon, 2014), remove carbon monoxide and decompose trichlorethylene (TCE). The ZnO photocatalyst is being developed as a concept (Yadav et al., 2017; Christensen et al., 2015). The bismuth oxybromide microspheres catalyst (BiOBr) of nanoplate microspheres was used to remove NO under the influence of visible light (λ> 420 nm) at 400 ppb, which is a typical concentration for indoor air quality (Christensen et al., 2015).

Another approach to air pollution control is nanostructured membranes with small enough pores to separate pollutants from exhaust and dust (Zhang et al., 2016). Silver nanoparticles and filters from copper nanoparticles are widely used in air filtration technology as antimicrobial materials for the removal of bio aerosols through air conditioning processes (Okada et al., 2019). Removal of health-causing particulate matter (PM) is accomplished by organometallic scaffolds (MOFs), crystalline materials with high porosity, adjustable pore size, and rich functionalities that are expected to capture pollutants (Zhang et al., 2016).

To prevent air pollution, it is necessary to reduce pollution sources and eliminate waste generation. Examples of eco-friendly nanomaterials are biodegradable plastics, specific structure for degradation, non-toxic nanocrystalline composite materials for replacing lithium-graphite electrodes in rechargeable batteries (Yadav et al., 2017), and carbon nanotubes can provide better functionality than conventional cathode-ray tubes containing many toxic metals (Yadav et al., 2017). Nanotechnology enhances air monitoring sensors by detecting several toxic compounds at ppm and ppb levels in different environmental systems (Zhou et al., 2015), and engages in probing (Zaporotskova et al., 2016) for multi-chemical and biological ligands to cover improving the specificity of the sensor and changing the size and shape of the nanoparticles and constructing them from different metals to improve electrical conductivity and sensitivity (Kim et al., 2016). Nanotechnology makes it possible to produce very small "multiplex" sensors, which reduces the cost of analysis and the number of devices used to analyze them, as a carbon nanotube based sensor for determining the sensitivity of gases (NH_3, NO_2 або O_3) (Ye et al., 2015).

Increasing energy demand and the need to reduce greenhouse gas emissions will lead to the use of energy from renewable sources and the conversion of carbon dioxide and water into fuel using solar fuel (Herron et al., 2015). Nanotechnologies had developed several new carbon nanomaterials used to capture CO_2, and nanocatalysts responsible for catalytic conversion of CO_2 and H_2O into fuels (Raj et al., 2017), reduce industrial CO_2 emissions, reduce Earth's warming, and produce additional energy sources. The wide range of nanotechnologies' applications confirms that nanotechnologies also pose a risk of nanoparticles being emitted, which requires an understanding of their mobility, bioavailability and distribution across the food chain, impact on the ecosystem and health (EPA, 2017).

Toxicity of nano-preparations

The development of nanomaterial-based technologies has a growing impact on health. Recycling carbon fiber is costly, energy intensive, and problematic (Moriyama et al., 2019), but its various types did not cause weight loss and did not cause lung fibrosis in experimental animals, indicating no toxicity.

The development of the industry is highly pollute the environment that could be neutralized by nanomaterials (Yang et al., 2019), due to its small particle size, strong regenerative ability, high surface activity and large specific surface area. However, we need to determine whether the nanomaterials themselves can influence the environment and are they fully degradable (Eastlake et al., 2016). A mechanism for the recovery of nanomaterials and measures to reduce the environmental impact of the recovery process are described (Moriyama et al., 2019; Yang et al., 2019; Eastlake et al., 2016).

Traditional soil and water restoration methods are not always efficient and cost-effective and have a secondary pollution problem. The large number of active sites on the surface of nanomaterials makes them suitable for the recovery by sorption of contaminated water and soil (Zhu & Zhou, 2018). Modern cleaning materials include zero-valence metal materials, carbon nanomaterials, metal oxides, semiconductor materials, nanoscale minerals, nanoscale polymers, etc (Liu et al., 2015; Cui et al., 2018). Modified zero-valence nano-iron can restore cadmium contamination. Modification of nanomaterials addresses defects such as easy precipitation in water and soil and difficult recovery, increases the contact area between nanomaterials and sources of pollution, minimizes environmental damage, and enhances electronic transmission between nanomaterials and pollutants (Guo et al., 2016). Different types of nanomaterials are suitable for different objects and reducing mechanisms: nanomaterials based on iron are recovered by redox reactions, coprecipitation and adsorption, nanomaterials based on carbon are recovered due to the Van der Waals force, electrostatic interactions and adsorption complex formation, intermolecular force (Van der Waals force), chemical coordination of bonds, electrostatic interaction.

The purpose of soil and water recovery is to remove or reduce their toxicity, with the restorative effect of nanomaterials related to pH (Liu et al., 2015), time of lightening, concentration of heavy metals (Cui et al., 2018), time of adsorption, temperature (Guo et al., 2014), the number of nanomaterials, the time of addition of nanomaterials, types of pollutants, and other factors (Yang et al., 2019). In general, acidic conditions do not promote the adsorption of heavy metal ions (Cr (VI), Cu(II)) by nanomaterials through the binding of hydrogen sites to adsorption sites and reduce the probability of absorption of metal ions (Yang et al., 2019). The recovery effect of nanomaterials increases with the addition time, the number of nanomaterials, and the rate of adsorption (Yang et al., 2019), however, the adsorption rate gradually slows with increasing time and reaches a fixed value (De Matteis et al., 2016).

Nanomaterials of metals and metal oxides have toxic effects on animals and plants (Tang et al., 2014), in particular nanoscale SiO2 affects the immune system, increasing the aggregation of lymphocytes and macrophages, increasing the size of the spleen and lymph nodes (Tang et al., 2014), disrupts the normal biological functions of macrophages, reducing their number with increasing exposure dose and exposure time (Tsai et al., 2016; Kasaai, 2015; Chan et al., 2017), generates certain toxicity of the immune system (Wang et al., 2016). Nano-TiO_2 in the air damages lung tissues (Okada et al., 2019), performs oxidative degradation on DNA, affects DNA structure and expression, transcription and translation (Sayedena et al., 2019), and polystyrene nanomaterials damage mitochondria and cells membrane (Kik et al., 2020). Nano-ZnO exhibits bacteriocidal action with decreasing particle size (Zhou et al., 2015).

Ag as a disinfectant is one of the traditional means of killing or inactivating bacteria (Santhosh et al., 2016; da Silva et al., 2016; Deshmukh et al., 2019), which is safe at a concentration of <0.1 mg/l (Ebrahim et al., 2016; Adeleye et al., 2016). Silver disinfection depends on concentration, pH, holding time, temperature, presence of ions and pathogens in water (Abebe et al., 2015 ; Vilela et al., 2017). The uncontrolled and overuse of antibiotics and their bacterial resistance can be solved by synergistic combinations of antibiotics with AgNPs (Nadaf & Kanase, 2015). Higher doses should be used to increase the efficacy of AgNPs, leading to kidney, liver (Hamid et al., 2017) and severe toxicity and argyria provoking (Mohamed, 2017; Sreeja & Shetty, 2016), with AgNPs being more toxic. more for aquatic organisms, less for humans and mammals (Mohamed, 2017). This effect is determined by cytotoxicity, genotoxicity, and antiproliferative parameters (Mohamed, 2017), and intracellular silver release is toxic to lung cells (Sreeja & Shetty, 2016, Mohamed, 2017).

It has been shown (De Matteis, 2017; De Matteis & Rinaldi, 2018; Aparna & Karunakaran, 2016; Kiełczykowska et al., 2018), that 36 nm Nano-Se can directly absorb free radicals in vitro and has lower toxicity than selenite or selenomethionine, and all these forms of selenium (Se) have a similar ability to increase selenium levels (Tsekhmistrenko et al., 2020). The size of the nanoparticles plays an important role in their biological activity, however, in Se-deficient cells and Se-deficient organisms, the size effect of Nano-Se on the increase of selenium enzymes and Se in the liver suddenly disappears. It is likely that under element deficiency conditions, the reducibility of selenium uptake mechanisms may be enhanced to support the biosynthesis of selenoenzymes underlying redox homeostasis (Aparna & Karunakaran, 2016). Increased digestibility may outweigh the potential advantage of the small size of Nano-Se, which was observed in selenium replete conditions, eliminating the size effect. Once the selenium enzymes are saturated, the mechanisms of Se uptake are inhibited, and the dimensional effect of Nano-Se on Se accumulation and GST activity is again manifested (Kiełczykowska et al., 2018). The homeostasis of Se accumulation is not so tightly controlled, however, in the liver, the Selenium content was much lower than saturation at almost maximum enzyme activity, confirming the dimensional effect of Nano-Se (De Matteis, 2017; De Matteis & Rinaldi, 2018). Because both GST and low molecular weight selenium compounds accumulated in vivo are important intermediates for the chemoprevention of Se, Nano-Se should be most effective at smaller particle sizes (Aparna & Karunakaran, 2016; Kiełczykowska et al., 2018).

The significant intake of cerium dioxide (CeO_2) nanoparticles dose-dependently provokes the development of liver pathologies (Córdoba-Jover et al., 2019). Renal proximal tubular epithelium, tubular protein accumulation and inflammatory response in the interstitial zones without histologic changes were observed in the kidneys with significant CeO_2 admission (Córdoba-Jover et al., 2019). Despite the good results obtained from the use of CeO_2 nanoparticles in medicine (Del Turco et al., 2019; Estevez et al., 2019; Li et al., 2019), the introduction of tracheal oxide in the liver increases the level of oxide content in the liver, weight loss and changes in blood chemistry. Similar to studies on CeO_2 nanoparticles (Bunderson-Schelvan et al., 2020), titanium dioxide (De Matteis et al., 2019), silicon dioxide (Nazari, 2019; Kasaai, 2015) and copper (Ebrahim et al., 2016), data indicate (Córdoba-Jover et al., 2019) the displacement of CeO2NPs from the lungs into the liver with blood flow. The liver biotransforms toxins and may be the first organ to be exposed to nanoparticles that enter the bloodstream. The same pattern is observed for copper nanoparticles (Ebrahim et al., 2016), carbon tetrachloride and inhalation of anesthetics (Abdel Moneim, 2016). Instillation of CeO_2 nanoparticles damages hepatocytes, releases AlAT and AsAT into the bloodstream and decreases albumin content (Bunderson-Schelvan et al., 2020). Published data (Schwotzer et al., 2017) about toxicity of nano-CeO2 against different pathways of absorption and duration of exposure.

Carbon nanomaterials have an effect on the enrichment of organic compounds. With increasing concentrations of carbon nanotubes, their toxicity to earthworms increased with a decrease in their ability to absorb pyrene (Liang et al., 2020), and in mussel carbon nanotubes damaged the macronucleus and the membrane of muscle cells with increasing degree of damage.

The increasing use of nanoparticles (NPs) in commercial products does not correspond to a comprehensive understanding of their potential harm (De Matteis et al., 2019). There is a need for additional in vitro studies to investigate the effect of the physicochemical properties of NPs on intracellular uptake, intracellular transfer and toxicity. Cell mechanics is a critical indicator of cell health, regulating cell migration, tissue integrity, and differentiation through cytoskeletal remodeling. TiO_2NPs more intensely affected the cellular elasticity of human epithelial colorectal adenocarcinoma cell lines (Caco-2) alveolar basal epithelial human adenocarcinoma cells (A549) compared to SiO_2NPs because they caused significant morphological and morphological changes (De Matteis et al., 2019). TiO2NPs increased elasticity in Caco-2 cells and decreased in A549, demonstrating a correlation between the change in cell elasticity and the toxicity of NPs, which depends on the physicochemical properties of NPs and the specific cell tested.

The widespread use of engineering nanoparticles (ENPs) in commercial products contributes to the dissemination of knowledge about their potential toxicity to humans and the environment (Kumar et al., 2017; Contado, 2015; Combes & Balls, 2019). In vitro and in vivo studies should shed light on the molecular mechanisms of toxicity (Kumar et al., 2017; Contado, 2015). However, the lack of standardized procedures leads to conflicting data and does not understand the interaction between NPs and organisms (Combes & Balls, 2019). Adverse effects of NPs depend on their physicochemical properties, specific test cell or organism (Mu et al., 2014) and on the characteristics of the NP itself (Dinmohammadi et al., 2019; Nymark et al., 2020; Nazari, 2019; Kasaai, 2015). When entered the body through the gastrointestinal tract, lungs and skin (De Matteis, 2017), the SiO2NPs and TiO2NPs affect critical cellular mechanisms (Li et al., 2015), stimulate cytokine release and promote inflammation (Khayal et al., 2019), damage the intestinal microvilli (Faust et al., 2014), induce reactive oxygen species (ROS) production (Tada-Oikawa et al., 2016), inhibit ATP synthesis (De Matteis et al., 2019) induce genotoxicity (Stoccoro et al., 2017; Chan et al., 2017), and interact with cellular mechanics (Septiadi et al., 2018; Flemming et al., 2020; Chaubet et al., 2020).

The proliferation of various ENPs increases knowledge about their biomedical toxicity (Jiang et al., 2018; Liu et al., 2016). In vitro and in vivo studies provide clinical and epidemiological data (Fröhlich, 2018), and cell tests provide an understanding of cellular mechanics that affects apoptosis, differentiation, migration, cancer metastasis and wound healing. Amorphous SiO_2 nanoparticles and crystalline TiO2NPs after incubation with FBS (fetal bovine serum) were larger due to protein crown formation (De Matteis et al., 2019). Amorphous SiO2NPs with a size of 15–20 nm can bind the plasma membrane passively through the lipid bilayer to the cells and translocate into the cytoplasm without visible membrane encapsulation (Tarantini et al., 2015) after the treatment with Caco-2 and A549 cells, which are representative models for the gastrointestinal tract and the respiratory tract (Fröhlich, 2018),. The crystalline form of TiO_2NPs is more chemically reactive (Zhang et al., 2014), more rapidly adsorbs (De Matteis et al., 2016), which is associated with the release of metal ions during degradation of NPs in the intestinal barrier and direct uptake by endocytosis (Gitrowski et al., 2014). NPsTiO_2 localize in the cells cytoplasm and close the nucleus area. TiO_2NPs exhibited the greatest toxicity, provoked extracellular release of the cytoplasmic enzyme lactate dehydrogenase, extensively damaged membranes due to oxidative stress and increased intracellular levels of ROS (De Matteis et al., 2019). The activity of SODs, which binds ROS, was significantly reduced by the introduction of TiO2NPs, probably due to the imbalance of redox reparative systems (De Matteis et al., 2019) and the processes of lipid peroxidation were enhanced by the effects of oxidative stress, as shown by the MDA content after incubation of cells in TiO_2NPs.

This effect reduces membrane fluidity and explains the more intense penetration of TiO_2NPs, intensification of intracellular stress, the formation of ROSs, and the organization of F-actin (Kang et al., 2016). The cytoskeleton is characterized by a set of filaments (actin microfilaments, microtubules and intermediate filaments) organized into a mesh, which affects the mechanical properties and behavior of cells. Any changes in actin filaments cause abnormalities in cell morphology under sub-toxic conditions (Ispanixtlahuatl-Meráz et al., 2018). Protein actin is most commonly associated with SiO2NPs and TiO_2NPs in cell extracts (De Matteis et al., 2019) i.e. these nanoparticles affect its function, cell movement and organelle transport (De Matteis & Rinaldi, 2018). The ability of NPs in vivo to induce changes in the expression of cytoskeleton-related genes (Ispanixtlahuatl-Meráz et al., 2018), cell elasticity changes (Calzado-Martín et al., 2016; Cascione, et al., 2017) were established and, as a result, disease progression (Luo et al., 2016).

Discussion and Conclusion

Various nanomaterials are used to restore the environment. Choosing the best nanomaterial to mitigate or remove a particular pollutant depends on the type of pollutant, the availability of the recovery site, the amount of material required to recover, and the recovered material ability for recycling. Traditional cleaning technologies do not offer the most cost-effective solution for the removal of several common pollutants and are not cost-effective for the removal of pollutants present in low concentrations. Nanomaterials, unlike traditional technologies, can remove pollutants present in low concentrations, their efficiency can be enhanced by particle modification, and how their cost can be reduced by production on an industrial scale and the development of synthesis methods that take into account cheaper raw materials and less energy. In addition, nanotechnology can be reused. The nanotechnologies have advantages and problems of their own use, so their choice should be made in the context of environmental restoration, in spite of the toxic effects on organisms, upon their admission, and possible environmental contamination due to improper use. Nanotechnologies had been studied extensively, but the problems related to recovery have not yet been resolved. Many studies demonstrated effective results in the laboratory, so the additional research is needed to understand the impact of nanotechnology in real-world scenarios and the processes, which occur with nanomaterials after completing their task. Therefore, the subsequent studies should determine the state of these materials after their introduction into environment for recovery, the ways to avoid new contamination, caused by them, and to develop the ways of processing nanomaterials without reducing their activity. Thus, the environmental potential of nanomaterials is fully realized, but the strategies that are suitable for combating environmental pollution are extremely important.

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