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Application of Nanotechnology in Environmental Protection

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Abstract: *Numerous applications of nanochemistry and nanotechnology in electronics, medicine, catalysis, and environmental protection have become popular scientific disciplines in the last decades. Besides the presence of nanomaterials in pharmaceutical products, textiles, food, and packaging, or its applications in the catalysis of traditional organic synthesis at high efficiency, the relationship between nanoscience and environmental protection stands out.*

This relationship has two aspects. One aspect shows numerous possibilities of nanomaterials applications in drinking water treatment, wastewater treatment, gas emissions, and acceleration of anaerobic digestion in biogas production processes from organic waste, together with others. Another aspect is the production of nanomaterials from waste and its contribution to the valorization and elimination of waste that can significantly contribute to the environment.

This chapter will show the tendency of nanochemistry and nanotechnology applications in sensors, catalytic degradations of pollutants, adsorption and filtration, and production of nanomaterials from industrial waste and the potential risks of nanomaterials.

Keywords: Nanomaterials, nanotechnology, environmental protection

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18.1. Introduction

Nanosciences have an impact on various areas of technology due to the rapid development of electronic microscopies that enabled the visualization of nanodimenzional materials (Rodrigues et al. 2021). Nanomaterials have high strength and durability, enhanced catalytic activity, and energy storage potential owing to their excellent intrinsic mechanical properties and electrical conductivity. These properties have enabled applications of nanomaterials in green nanotechnologies, energy storage, and environment protection. High prices and limited resources for nanoparticle (NP) production limit applications of nanomaterials. Nanomaterials are necessary for advances in engineering, medicine, energy storage, and environmental protection. These technologies require funds for large-scale production and implementation of nanomaterials. Thus, the value of nanomaterials in 2022 was about 10.89 billion US dollars, according to the global nanomaterials market size (*Nanomaterials Market Size, Share & Growth Report*). The price of nanomaterials can be reduced by reusing waste materials such as nanoiron oxide synthesis from the mining tailings (Stević et al. 2016; Gotovac Atlagić et al. 2021). Reusing waste for nanomaterials production would reduce pollution. Developing inexpensive methods for nanomaterials production should stimulate the rapid development of nanotechnology.

This chapter will focus on nanomaterials in sensor technologies, catalytic degradation of pollutants, nanomaterials production by the valorization of industrial waste, filtration and adsorption, and potential risks.

18.2. Nanomaterials in Monitoring and Sensor Technologies

Chemical sensors can be electrochemical (amperometry, potentiometry, and voltammetry-based) sensors, photoelectrochemical (PEC) sensors, chemosensors, optical sensors, and mass transducers. Sensing characteristics of any of such materials are highly dependent on a few factors: accumulation potential, time, the concentration of the active material, scanning rate, and obligatory pH. Any of the given factors can disrupt the morphology of the active material, desirably changing its redox properties. Properties of the conducting materials such as graphene or carbon nanotubes, widely studied and applied in sensor technologies could also be modified by different techniques such as adsorption of large polyaromatic molecules, oxidation, complexation with metals such as Zn or Al, and many more techniques (Gotovac et al. 2007; Gotovac al. 2007; Gotovac et al. 2007; Kukobat et al. 2019; Furuse et al. 2023).

In attempts to overcome the robust and demanding instrumental chemical analytical techniques, much attention is given to the PEC techniques development (Shu and Tang 2020). These techniques are mostly relying on nanotechnologies. Contemporary research relies highly on the rapid detection of even the traces of chemical and biological species. To satisfy the necessity for high-performance PEC sensoring, controlled design and synthesis of the photoactive materials are crucial. PEC devices enable the transformation of light into electricity, along with the interconversion of electric with chemical energy, usually explained by the absorption PEC of the protons which have enough energy to induce electron/hole pairs. Photogenerated carriers of charge can produce the signal to the electrolyte, starting the redox reaction and thus energy conversion. Controlably applying these phenomena, it is now possible to harvest energy and develop pollution sensoring and even treatments (Chen et al. 2022). A variety of the nanomaterials used for environmental sensoring technologies can be summarized as given in Fig. 18.1. (Yan et al. 2021).

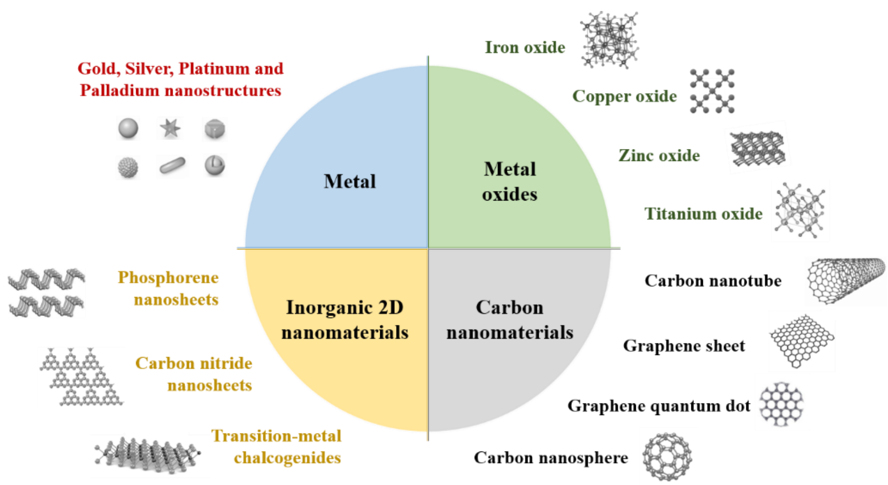


Fig. 18.1. Types of functional electroactive materials used in electrochemical sensing of environmental pollutants. Edited according to the source (Yan et al. 2021)

Сл. 18.1. Врсте функционалних електроактивних материјала који се користе у електрохемијској детекцији загађивача животне средине. Уређено према извору (Yan et al. 2021)

In particular, metal nanostructures produced from Au, Ag, or Pt are most valuable in modifying semiconductors to improve light harvesting and converting ability. On the other hand, metal oxides (TiO_2, ZnO, WO_3, SnO_2, NiO) in combination with chalcogenides (CdS, CdSe, CdTe, Ag_2S, MoS_2, PbS) reach their best utilization possibilities. If nanostructured, metal oxides have a large band gap rendering them not so efficient in photon absorption. However, if combined into the heterostructures with metal chalcogenides, which have a narrow bandgap, the resulting materials gain increased visible light absorption and thus become more applicable in sensor technologies.

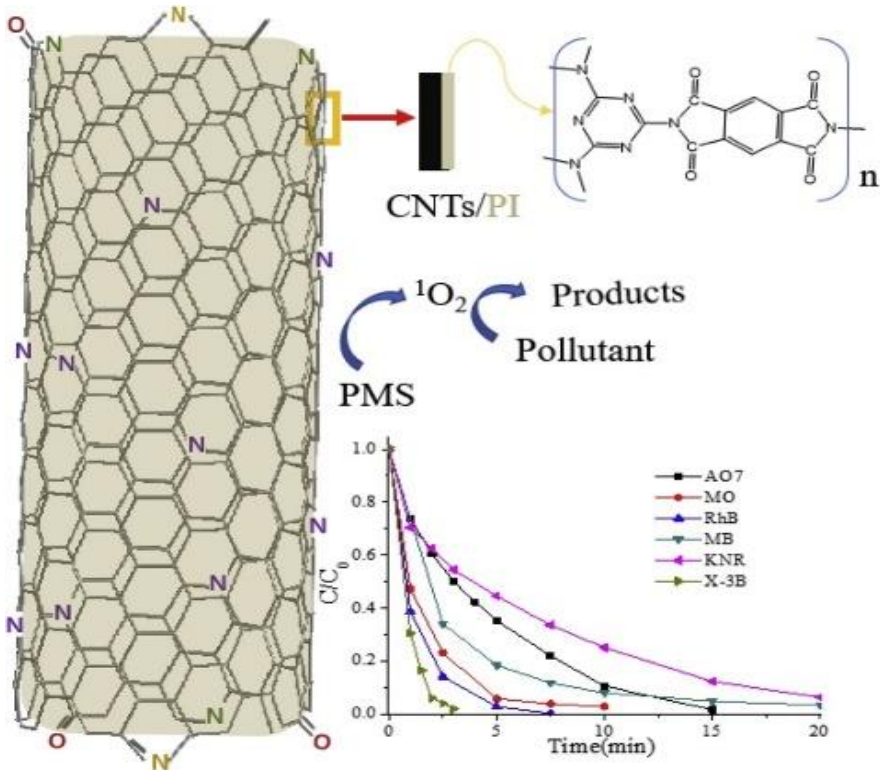
A notable use of environmental sensoring is in pesticide sensing. For example, a PEC sensor in the form of a low-cost electrode with good stability and catalytic effect has been developed for detection of atrazine. Atrazine is one of the cheapest, most available, most efficient herbicides. On the contrary, it has a large negative impact on aquatic ecosystems (Graymore et al. 2001). The developed electrode used tetra-ruthenate porphyrin (TRP) with tetra pyridyl porphyrin (TPyP) coordinated to four Ru (II) complexes in the periphery of the macrocycle, showing electrocatalytic and photoelectrochemical properties. Differential pulse voltammetry (DPV) applied as the measurement technique has given a linear correlation of current response and atrazine concentration in the range of interest (Negut et al. 2020).

Considering the nanosensors in the area of air pollution, common pollutants including toxic gases nitrogen dioxide (NO_2), sulfur dioxide (SO_2), and hydrogen sulfide (H_2S) are still in primary interest. Here, carbon nanotubes as field emission transistors show high sensitivity and a number of prototypes are being developed (Nedelcu 2022). Multifunctionality can be a surplus. For example, recently developed aluminum nitride nanosheets might become efficient simultaneously in detecting SO_2, NO_2, NH_3, and CO_2 gases under a gated electric field (Singh et al. 2020). With ever-increasing urbanization and pollution of the cities, yet at the same time with increasingly demanding workspace safety standards, such multi-sensors will be highly demanded once their efficiency is established.

18.3. Catalytic Degradations of Pollutants by Nanomaterials

Carbon materials such as activated carbon (AC), graphene, reduced graphene oxide (rGO) and carbon nanotubes (CNTs) can be used for catalytic degradation of pollutants due to their excellent properties and reusability (Wei et al. 2020). Recently, CNT/Metal oxide composites have been studied for the treatment of contaminated water. One of the most important applications of this composite is for photocatalytic decontamination of organic pollutants in wastewaters. CNT doped with Fe and Ni (Fe/N-CNT) is an excellent candidate for degradation of refractory organic pollutants in various water matrices, giving excellent performance and stability due to the non-radical pathways (Pham et al. 2021).

New catalytic degradation technology aided with microwave-induced CNTs (MW/CNTs) is efficient for the treatment of organic pollutants in aqueous solutions. MW/CNTs with CNT diameters of 10–20 nm, 20–40 nm and 40–60 nm can catalytically degrade methyl orange (MO), methyl parathion (MP), sodium dodecyl benzene sulfonate (SDBS), bisphenol A (BPA), and methylene blue (MB) in aqueous solutions (Gotovac et al. 2007; Chen et al. 2016). Polyimide-modified carbon nanotubes (PI/CNTs), containing metal-free catalysts are promising for organic contaminant degradation without light irradiation.



Scheme 18.1. Scheme of the polyimide-modified carbon nanotubes induced pollutant degradation with comparative kinetics of AO7 degradation (Wei et al. 2020)

Схема 18.2. Шема разгадње полутаната угљеничним нанотубама модификованим полиимидом са упоредном кинетиком за разградњу АО7 (Wei et al. 2020)

PI/CNTs (Scheme 18.1) provide a promising metal-free catalyst for the degradation of organic pollutants in aqueous solutions, contributing to the development of green materials for sustainable remediation (Wei et al. 2020).

In addition, graphene-based materials have great adsorption capacities due to the presence of oxygen functional groups. The outstanding features of graphene and graphene-based materials have great potential for managing environmental pollution (Tahir et al. 2020).

18.4. Nanomaterials Produced by Valorization of Industrial Waste

In recent years, numerous studies suggest potential solutions for nanomaterials resource availability by pointing out their production from industrial waste, including waste originating from metal production, metal recovery from mining tailings, or e-waste.

Processing industries are generating high amounts of by-products that are rich in diverse metal oxides. Bauxite residue is a by-product from Bayer's process which contains iron oxide, hematite, usually in the highest percentage compared to other components (oxides of Al, Si, Ca, and Ti). Considering nanotechnologies, this material could be used as effective energy storage material, anode material in Li-ion batteries, and other various applications. Production of spherical nanoparticles of red mud 30-50 nm in size can be performed by ball milling for 10 h (Bhattacharya et al. 2019). Obtained nanoparticles have been proven as suitable materials for supercapacitors with relatively high performance compared to conventional materials. As aforementioned, bauxite residue has significant potential as an anode material in Li-ion batteries. Applying magnetic separation, the iron oxide can be extracted from this material and further used in the production of a half-cell that can exhibit excellent stability and a reversible capacity. The fabrication can be further continued with full-cell (with $LiMnO_4$ as cathode material) that exhibit lower reversible capacity and subsequently lower performance compared with iron oxide nanoparticles conventionally synthesized (Suryawanshi et al. 2016). Other potential valorization methods were reviewed along with these for other metal tailings (Gotovac Atlagić et al. 2021).

Zero-valent iron or iron oxide nanoparticles are becoming increasingly useful as the recyclable and completely safe catalysts in the Ficher-Trops and Diels-Alder reactions or, for example, in the growth the carbon nanotubes, as well as in biomedical applications (Gotovac Atlagić and Pavlić 2018). Thus, with ever-increasing demand, methods for their synthesis from yet unrecognized recourses such as mining tailings, which is economical, both energy and resource-wise, are highly desirable. An example is shown in Fig. 18.2. given by present authors in the form of the hematite core-carbon shell nanoparticles synthesized recently from the waste from iron mine sludge (Stević et al. 2016).

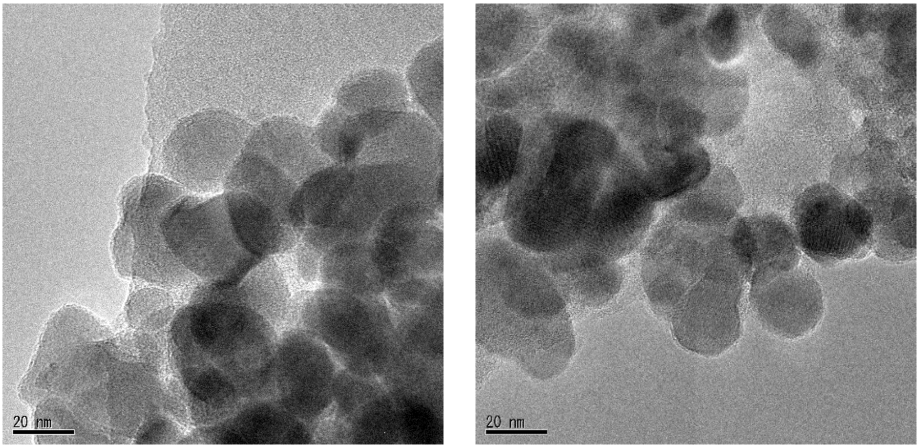


Fig. 18.2. TEM images of hematite nanoparticles synthesized from iron waste applying the microemulsion method (authors' archive, previously non-published micrographs) (Stević et al. 2016)

Сл. 18.2. ТЕМ слике наночестица хематита синтетизоване из отпада жељеза примјеном микроемулзионе методе (архива аутора, раније необјављени микрографи) (Stević et al. 2016)

Metallic nanoparticles can also be obtained by recovering waste metals from other unusual sources. A good example of recycling toxic metal-contaminated sewage sludge is the removal of toxic Cu(II) from contaminated water followed by the production of a Cu-doped carbon electrode that can act as an effective energy storage material (Tan et al. 2019). The applied route for Cu (II) removal can be significant and result in the achievement of 99%.

Another efficient application is the production of electrode material for supercapacitor applications. Waste thermocol sheets and rusted iron wires were used for the production of waste-derived carbon-Fe_3O_4 nanocomposite that showed similar performance to conventional devices and can be practically applied (Vadiyar et al. 2018). Different approaches in the treatment of waste-rusted wires from scarp can result in the production of surfactant-free hematite nanoparticles (Mhamane et al. 2016). After several steps of treatment, the as-synthesized NPs were studied as Li-ion batteries material (with $LiMn_2O_4$ as a cathode). Further testing of performance showed that regardless of this being an efficient recycling method and conversion pathway, this material has significantly lower performance compared with hematite nanoparticles that are conventionally synthesized.

E-waste recycling, so-called "urban mining", is attracting many researchers, considering that information communication technology generates a high quantity of this type of waste that has the potential to be reused in numerous innovative ways. Discarded Zn-Mn batteries can be a resource for the production of nano-zinc oxide (Zhan et al. 2018).

The obtained product is not yet tested for specific applications, however, so far it has shown potential for a successful way of recycling these types of batteries. Furthermore, "green" Si_3N_4 nanowires can be produced using glass and polymer shells (sources of silica and carbon, respectively) from scrap computer monitors (Maroufi et al. 2018). Although further industry scale-up requires additional research and testing, nanowires showed promising hetero-catalyst material properties, i.e. photocatalytic degradation of methylene blue, as presented in the mentioned study.

Water pollution, soil, and waste sludge are one of the most critical issues worldwide and are a priority in all scientific agendas. Green nanotechnology presents a plethora of promising avenues for the treatment and the use of waste as raw materials for nanotechnologies is one of them. Such an approach matches current trends in the valorization of zero-cost, biodegradable, and readily available agro-industrial biowaste to produce green bio-nanocatalysts and bio-nanosorbents for wastewater treatment (Omran and Baek, 2022).

One example related to wastewater, showing potential for biomedical applications is producing specialized fabrics with antimicrobial properties. It considers the synthesis of silver nanoparticles where wastewater (Parkia biglobosa fermented-seed wastewater, PBWW) acts as a bio-reductant or stabilizer for AgNP production (Aguda and Lateef 2021).

A "waste valorization" approach toward converting residues from second-generation (2G) bioethanol production into nanoparticles and nanocomposite films is presented as possible (Rivière et al. 2021). Lignin hydrolysis from 2G bioethanol production was based on fractionation and re-assembly of the nanoscaled components (lignin particles and lignocellulose nanofibrils). If linked, these materials lead to nanocomposite films with low oxygen permeability as well as antioxidant properties.

Surprisingly large is the market for the keratin, natural polymer, which is mainly derived from waste (Fig. 18.3). Europe consumes approximatelly 600,000 tons of keratin per year, mainly in the cosmetics industry but also increasingly in the area of the biomedical applications (Straits Research 2023). This is a very exciting example of the valorisation of the waste, since over 90 million sheeps and over 140 million pigs are slaughted around Europe yearly, producing large amounts of keratin waste (pig hair and wool of lower quality, non-applicable in textile industry).

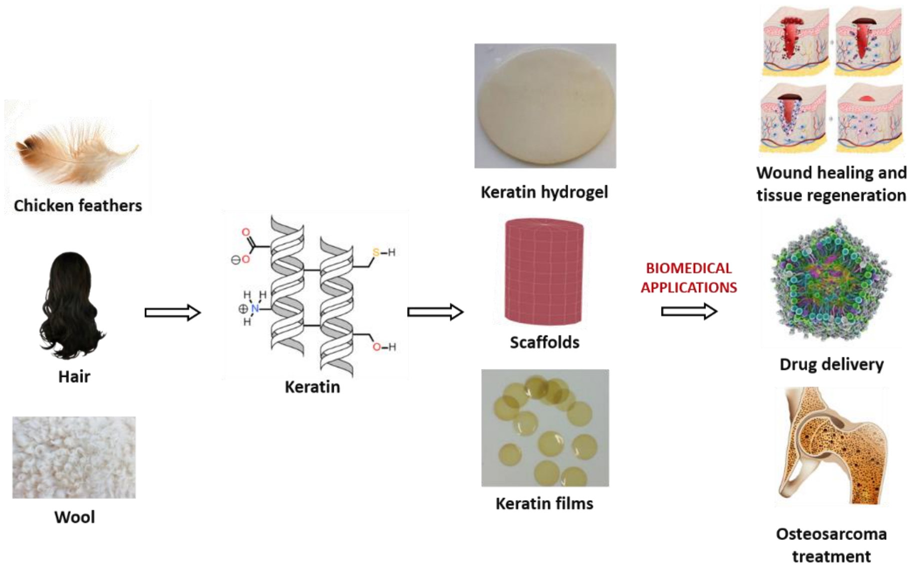


Fig. 18.3. Keratin waste valorisation pathways for biomedical applications (Sharma et al. 2022)
Сл. 18.3. Пут валоризације кератинског отпада у биомедицинске примјене (Sharma et al. 2022)

However, this environmental dimension is matching with present chapter since the application of such regenerated waste keratin in biomedical applications is defined by their nano-dimensional forms, fibers or pearls (Sharma et al. 2022).

18.5. Filtration and Adsorption as Environmental Techniques Involving Nanomaterials

Porous nanomaterials can simply and efficiently adsorb pollutants, transferring the active phase of pollutants from gas or liquid media to the solid adsorbent surface. Carbon-based nanomaterials, owing to their excellent properties in adsorption, advanced oxidation, photocatalysis, and other contaminant removal processes, have been extensively used in environmental pollution control systems (Mazari et al. 2021). Activated porous carbon, such as graphene nanosheets, carbon nanotubes, and biocarbon, have been widely studied for environmental applications in adsorption and catalysis because of their strong adsorption capacity, low production cost, and environmental friendliness. These carbon-based nanomaterials have excellent adsorption performance such as large surface area and porosity, being applicable for molecular separation or adsorption.

Recently, single-wall carbon nanotube (SWCNT) bundles were oxidized at 773 K in an air atmosphere, giving a maximum specific surface area of 1660 m^2 g^{-1} and a total pore volume of 0.6 ml g^{-1} (Furuse et al. 2023). The SWCNT bundles are promising for the adsorption of pollutants, owing to their high porosity.

Metal-organic frameworks (MOFs) are crystalline materials with extremely high porosity with nearly 90% of the free space and a specific surface area of ~6000 m^2 g^{-1} (Zhou et al. 2012). Recently, MOFs have been carbonized, giving carbon-based nanomaterials. MOFs have different metal ions, organic ligands, morphologies, and structures that can be transformed into porous carbon materials of different compositions and functions. MOFs can be modified by controlling the pore size, forming adsorbents and molecular sieves for porous adsorbents for pollutant adsorption. Materials with high surface area and porosity are suitable for the adsorption of pollutants in the form of metal ions or toxic molecules from liquid or gas phases. MOF derived from carbon-based nanomaterials is promising for the potential reduction of metal ions (Wang et al. 2022). Also, these nanomaterials have a high potential for applications in environmental fields (Fig. 18.4) such as sewage treatment and harmful gas adsorption due to the low cost and easy operation (Liu et al. 2022).

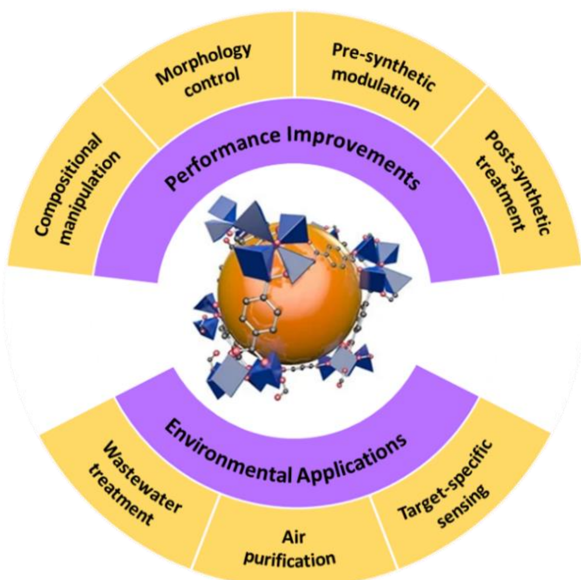


Fig. 18.4. Application of metal-organic framework-derived nanomaterials in environment-related fields (He et al. 2021)

Сл. 18.4. Примјена наноматеријала добијених од метално-органских оквира у областима везаним за животну средину (He et al. 2021)

Graphene oxide (GO) has outstanding chemical and thermal stability, forming layered membranes. Also, GO has exhibited excellent adsorption capacities for heavy metal ions due to its abundance of surface oxygen functional groups including hydroxyl, epoxy, and carboxyl groups (Bagheri et al. 2017). Wang et al. have synthesized a few layers of GO for heavy metal adsorption (Wang et al. 2018). The maximum adsorption capacity of Cd^{2+} and Co^{2+} can reach 106.3 mg g^{-1} and 68.2 mg g^{-1}, respectively. Thus, GO can serve as a membrane and adsorbent for organic compounds and heavy metals.

Activated carbon is a classical material that has been used as an adsorbent for decades. Activated carbon is efficient for the adsorption of small or large organic pollutants. Activated carbon has been widely used for the removal of phenol through adsorption (Fernandez et al. 2003). Modification of activated carbon is efficient for enhanced adsorption of pollutants onto the activated carbon pores (Fig. 18.5).

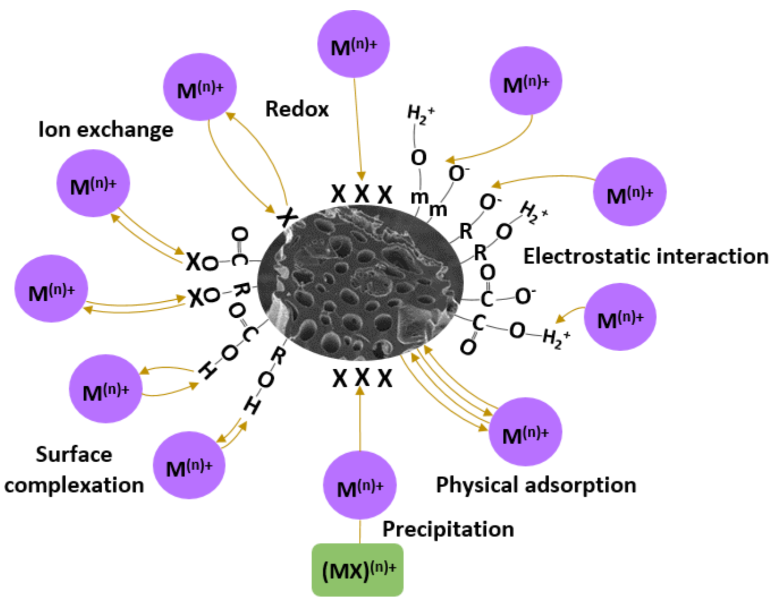


Fig. 18.5. Adsorption mechanisms of toxic metal ions on activated carbon from water solutions. Edited according to the source (Qiu et al. 2021)

Сл. 18.5. Механизми адсорпције токсичних металних јона на активни угаљ из водених раствора. Уређено према извору (Qiu et al. 2021)

Mechanisms of pollutant adsorption by activated carbon include physisorption and chemisorption (Mariana et al. 2021; Qiu et al. 2021). Activated carbon decorated with metal nanoparticles can be efficient for SO_2 conversion into sulfate ions that are easily recoverable (Stanisavljević et al. 2019). Other surface modification can enhance adsorptions of more chemisorption nature such as redox reactions, precipitation, electrostatic reactions of different strength or the surface complexation can take place.

18.6. Genie in the bottle: potential risks of nanomaterials and nanocomposites

The above sections emphasize the ever-emerging and in some cases indispensable applications of nanomaterials in medicine and environmental engineering. However, like in all chemical technologies developed during the past decades after environmental awareness became a norm, the production and application of this group of materials has to be carefully planned and analyzed. Many reports show that nanomaterials can be used to remove different pollutants from wastewater. Self-toxicity of nanomaterials is an emerging issue that should be further analyzed. Graphene-based materials and metal oxides can be toxic at high concentrations (Kobielska et al. 2018; Ding et al. 2022). Furthermore, the toxicity of CNTs depends on their length, surface area, distribution ratio, aggregation degree and concentration (Jones et al. 2019). Also, the single-walled CNTs are less toxic than the double-walled CNTs. They are associated with pulmonary inflammation, oxidative stress, granuloma in the lungs, basic inflammation, apoptosis and fibrosis. The toxicity of TiO_2 depends on its concentration and exposure time (Takahashi et al. 2006). Therefore, research on the effects of nanoparticles on health should be increased in all fields of nanomaterials applications. It is important to investigate/predict the toxicity of any new nanomaterial and propose limitation strategies. A European nano-registry presents a reliable database on quantitative risk assasment of nanomaterials. Based on literature research, a country-specific nano-registers can be compared, thus providing the information on nanomaterial-containing product and defining limitation range (Pavlicek et al. 2021). As different cell lines, culture conditions, and incubation times are often used to assess nanomaterial toxicity, data comparison is not straightforward, particularly to decide whether the observed cytotoxicity is physiologically relevant. Several experimental models (cultured cells, Danio rerio embryos, small mammals, such as mice and rats) are used for *in vivo* toxicity testing. In urban environments, different particles size (including in the nanoscale range) are produced by motor vehicles and other combustion sources. Novel research is focused on assessing their toxic effects, leading to progressively stricter regulations. Experimental findings suggest that fine-sized particles are more harmful (Barhoum et al. 2022). The numerous benefits of nanomaterials applications surpass their potential risks that are mostly predictable and preventable.

Future is most probably going to bring the integral European Union registry of nanomaterials in order to take maximum controle over the environemental faith of the nanomaterials and products containing nanomaterials. This is ever more important with widespread applications of the nanoaditives in food or cosmetics but even more so in products for children. At the time of present publication, such registry is still not obligatory, with only the European Union Observatory for Nanomaterials' (EUON) as an informative data base about existing nanomaterials on the EU market. However, more and more countries are introducing their own national registries on nanomaterials and the corresponding timeline which is continuosuly expanding, is shown on Figure 18.6.

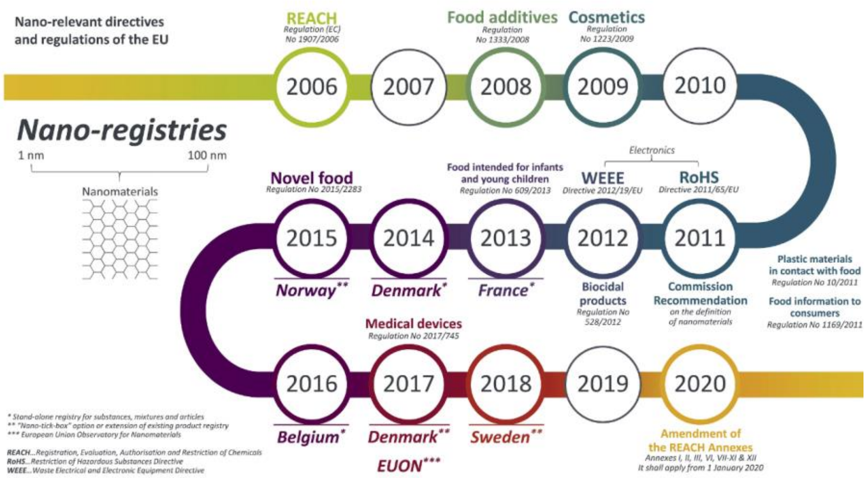


Fig. 18.6. Historical timeline of national nano-registries and EU regulations relevant to nanomaterials (Pavlicek et al. 2021)

Сл. 18.6. Историјски временски оквир националних нано-регистара и регулативе ЕУ релевантне за наноматеријале (Pavlicek et al. 2021)

It can be seen that clearly, much attention is paid to the nanomaterials as additives in food, application of nanomaterials in objects contacting the food, children and infant products as the most important. Denmark is at the present time slightly leading the way in the area of legislation, both respecting the EU recommmendations, but also being the first one to introduce the stand-alone registry of the substance into which the nanomaterials have to be reported. National registries on nanomaterials are reviwed and have shown high degree of reliability. However, the nomenclature and the expressions, as well and sometimes even the parameters followed differ from country to country. Thus, as with all new areas of the applicative sciences in the past, the nanomaterial production and application need to be thorowly examined and followed. It also has to be improved in the future aligning with the newest findings in the biological and medical studies of the influence of nanomaterials on living organisms. Also, in terms of definitions, the nanomaterials continue to be reexamined and not limited to only particles (powdered materils) or 2D and 1D materials but also widened to the "hidden" nanomaterials. Most notably the nano term is not so often used related to the electronics and electrical industries. However, the nano-coatings or printed circuit boards are common in most of these products and their aging with the time and consumtion causes the potential risk during the base material wear-out process. Environmental feith of such layers potentially being released into the environment during the e-waste recycling process is yet to be studied with care and hopefully be introduced into the national and international legislations around the world.

18.7. Conclusions

All the presented examples point out stongly that the role of nanoparticles in numerous environmental technologies is already widespread and, in some cases, even indispensable. However, as with all new technologies throughout the history, risks and sustainability, potential for recycling of these materials has to be always taken into account when choosing the proper technologies. International scientific and expert's communities have to pursue detailed safety and longterm health effects studies before putting new materials or composites into the widespread use. This chapter aims to drawing attention to these emerging materials rapidly contributing to the monitoring and resolution of environmental pollution. Finally, the production of nanometarials from waste or secondary raw materials is an important aspect of circular economy through the green technologies and is certainly going to bring many new and exciting environmental solutions in the future.

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Примјена нанотехнологије у заштити животне средине

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Сажетак

Нанохемија и нанотехнологије, које се примјењују у електроници, медицини, катализи и заштити животне средине, постале су популарне научне дисциплине посљедњих деценија двадесетог и почетком двадесет првог вијека. Осим присуства наноматеријала у фармацеутским производима, текстилу, храни, амбалажи, или њихове примјене у катализовању традиционалних органских синтеза уз много већу ефикасност, уочљива је и веза нанотехнологија и нанохемије са заштитом животне средине. Ова веза је двојака. С једне стране, бројне су могућности за примјену нанотехнологија у пречишћавању вода за пиће, третманима отпадних вода, емисионих гасова, убрзавању анаеробне дигестије у процесима производње биогаса из органског отпада и слично. С друге стране, производња наноматеријала на бази отпада, уз његову валоризацију и елиминацију, може много допринијети заштити човјекове околине.

У овом поглављу назначене су тенденције примјене нанохемије и нанотехнологија у сензорским технологијама, катализама, у адсорпцији и филтрацији и у производњи наноматеријала из индустријског отпада. Расправљано је и о могућим ризицима примјене и производње наноматеријала за очување животне средине.

Кључне ријечи: Наноматеријали, нанотехнологија, заштита животне средине