



Review

# Applications of Environmental Nanotechnologies in Remediation, Wastewater Treatment, Drinking Water Treatment, and Agriculture

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**Abstract:** Today, nanotechnologies (NTs) are well established in both private households and commercial markets. NTs are fully accepted in several sectors, such as medicine and pharmacy, and in industries, such as chemistry, electricity, food production, military, and other commercial branches, due to their unique properties. With regard to the growing demands for environmental resources caused by the still-growing global population, the application of NTs is an extremely important new branch in the environmental sector, delivering several advantages. Our review provides a comprehensive overview of the current developments in environmental remediation, wastewater treatment, drinking water treatment, and agriculture. More specifically, in the section on environmental remediation, we review the application of NTs towards enhanced reductive dechlorination, removal of heavy metals and remediation of oil spills. In the section on wastewater treatment, we highlight developments in the adsorption of heavy metals and persistent substances, advanced photocatalytic degradation of common wastewater pollutants, and improvements in membrane filtration processes. In the section on drinking water treatment, we discuss applications for the enhanced disinfection of pathogens, removal of heavy metals, point-of-use treatments, and the removal of organic matter. In the final section, on agriculture, we provide an overview of precision farming and the current state of the art concerning nanofertilisers, nanopesticides, nanoherbicides, and nano(bio)sensors.

**Keywords:** nanoparticles; remediation; wastewater; drinking water; precision farming



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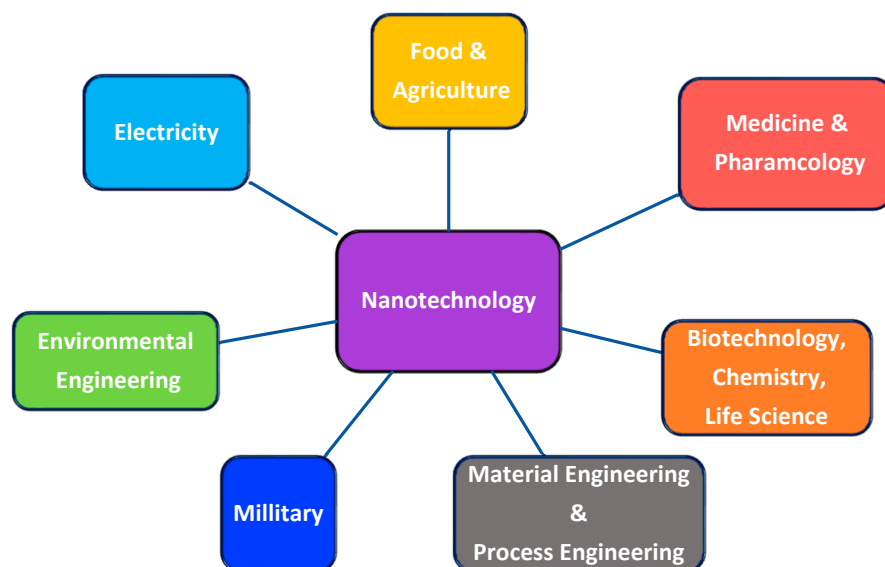


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## 1. Introduction

### 1.1. Historic Development and Applications of Nanotechnology

On the one hand, nanotechnologies (NTs) refer to nanostructure techniques, such as nanolithography and nanomanipulation, but also to nanomaterials (NMs) on the other hand. NMs refer commonly to nanoparticles (NPs), nanotubes, nanofilms, and others. The engineered era of NTs combines different application sectors, including biological, biotechnological, chemical, medical, pharmaceutical, food and agriculture, environmental, electronic, material engineering, and other industrial processing technologies, and other branches (Figure 1). One can say that NMs are just building units at the nanoscale, from small groups of atoms up to macromolecules and complex composed nanoparticles, typically covering the size range between 1 and 100 nm. However, this size range is not sufficient for explaining, for example, why several conventional materials have been replaced by NMs in recent years [1]. The main reasons are because NTs generally provide NMs with versatile functionalities and enhanced reactivity, as well as enhanced selectivity, compared to their bulk counterparts. This is due to higher surface-area-to-volume ratios, higher density, and higher intrinsic reactivity [2,3].



**Figure 1.** Overview of the different application fields of NTs.

The enhanced reactivity often leads to very different chemical properties compared to their bulk materials, such as increased dispersibility and chemical stability [4]. Saleh [5] emphasises that major advantages of nanostructures lead to tuneable chemical, physical, and mechanical properties, as well as enhanced performance compared to their bulkier counterparts. Their different properties can be categorised into electrical, optical, magnetic, mechanical, and thermal properties. Notably, for some NMs, completely different properties have been reported compared to their bulk materials [6].

It was in the late 1950s when Nobel-Prize-winning physicist Richard R. Feynman mentioned during a talk at Caltech (USA) that *“there is plenty of room at the bottom”* [7]. This statement was often cited as incredible with regard to publications focusing on NTs. His concept of nanotechnology became fully operational in 1974 [8]. According to Glenn [9], the term NT was established almost 25 years later by Eric Drexler [10], who described the *“manipulation of atoms and molecules to build structures to complex, atomic specifications”*.

From this historical point of view, Kargozar and Mozafari [11] also emphasised the pioneering developments of both scanning tunnelling microscopy (STM) in 1983 and atomic force microscopy (AFM) [12,13]. Binnig announced in 1985 that he had invented the AFM, and in 1986, he was awarded the Nobel Prize for it. STM and AFM revolutionised both imaging and manipulation of nano-sized objects as a way of demonstrating atomic resolution and reassembling individual atoms’ delivery of novel, unexpected chemical properties [14]. To sum up the long story of historical milestones concerning NTs, it was Feynman who predicted the movement of individual atoms.

Today, NTs are well established in several different sections of the open marketplace. The approaches and applications are still boarding and opening unexpected doors and floors. It is as though NTs were a new built-up skyscraper, of which we have so far not reached the middle. In the early 1990s, the first products were introduced on the market, such as the famous tennis racket with not only an extremely light weight but also high stability. Hence, NMs and their products are attracting more and more attention not only on commercial marketplaces but also from governmental institutions and agencies. Governments in particular have launched institutions, mainly due to environmental issues and health risks, which are becoming more and more of serious concern.

Today, the application range of NTs is extremely wide and comprises commercial sectors (up to 1000 launched products), such as the oil and gas industry, energy transmission industry, and chemical industry, for producing additives in fuels. Other applications include electronics and light-emitting diodes (LEDs) (improving conductivity), the electronic industry, and the military (e.g., uniforms, equipment, bioweapons). Meanwhile, NMs are

also highly relevant in households (e.g., cosmetics, UV sun blockers, stain-resistant clothes, paints), in different areas of biomedicine (e.g., drug delivery agents, biosensors, medical imaging devices), and in the food and agriculture industry, as well as in the environmental sector, including wastewater treatment, drinking water production, soil and groundwater remediation, and air pollution sensors [9,15]. The importance of all of these inventions was underlined in 2016 by the Royal Swedish Academy of Science, which awarded P. Sauvage, Sir Fraser Stoddart, and B. Feringa in the field of chemistry for “the design and synthesis of molecular machines”.

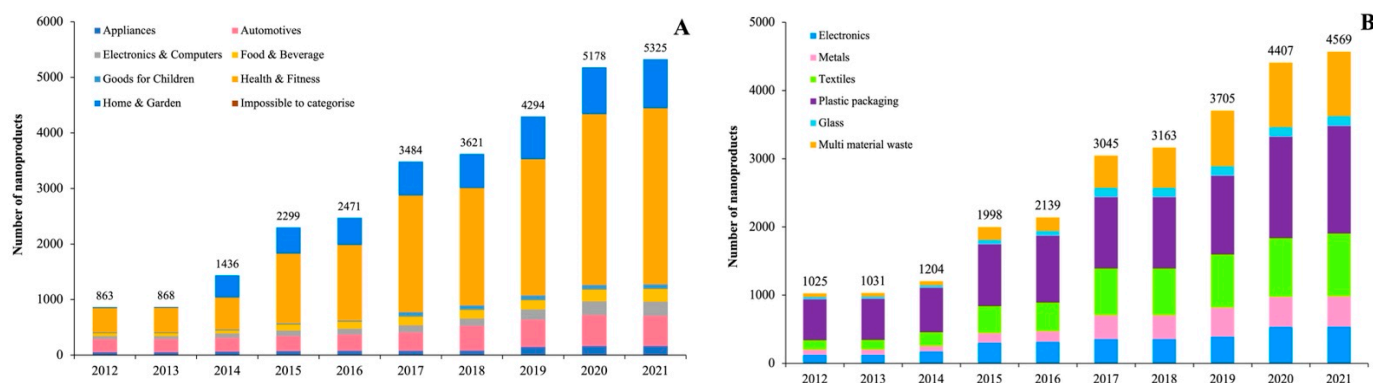
### 1.2. Production Rates and Classification of NMs

A variety of information concerning the global annual production has been published within the past two decades. Bao et al. [16] stated the production of NPs has gone up to 58,000 tonnes per year. Mueller and Nowack [17] reported an annual production rate of nanosilver to be about 500 tonnes per year in 2008. In the current year of 2022, it is assumed that production has dramatically increased. However, it should be noted that this production rate does not include other NMs but mainly NPs. Overall, it is very difficult to obtain comprehensive data on individual and global production rates. Naghdi et al. [18] reported on some more detailed production rates for the annual production of 10 different NMs in Europe, the USA, Australia, and Switzerland. They showed that the production of nanotitanium dioxide (TiO<sub>2</sub>), as well as nanozinc oxide (ZnO) and nanosilicon dioxide (SiO<sub>2</sub>), is the highest globally and averages an annual maximum production rate of 40,000 tonnes, 28,000 tonnes, and 55,000 tonnes, respectively.

According to Sousa and Ribau Teixeira [19], the production rate of nanomaterials in the European Union was around 1,615,000 tonnes in 2016. Giese et al. [20] further estimated, based on these data, an annual growth rate of 5%. Additionally, other scientists estimated similar growth trends in Europe. Most of these products make Europe lead in the production of nanomaterials (up to 50%), followed by the USA (up to 40%) and Asia (up to 10%) [19].

With respect to the total number of products containing nanomaterials, a very detailed overview of the listed nanomaterials has been provided by the “Nanodatabase” webpage (Danish Consumer Council) since 2012. This database was specially developed for nanomaterials by the DTU Environment, the Danish Ecological Council and Danish Consumer Council, initially funded by the European Research Council. On the one hand, this database gives short information and description of various consumer products. On the other hand, the conceptual decision support tool for nanomaterials (NanoRiskCat) recently published by Hansen et al. [21] provides information on the potential of all listed nanomaterials and their exposure to professional end-users, consumers, and the environment. Therefore, each product is assigned a colour code indicating the level of potential exposure or effects.

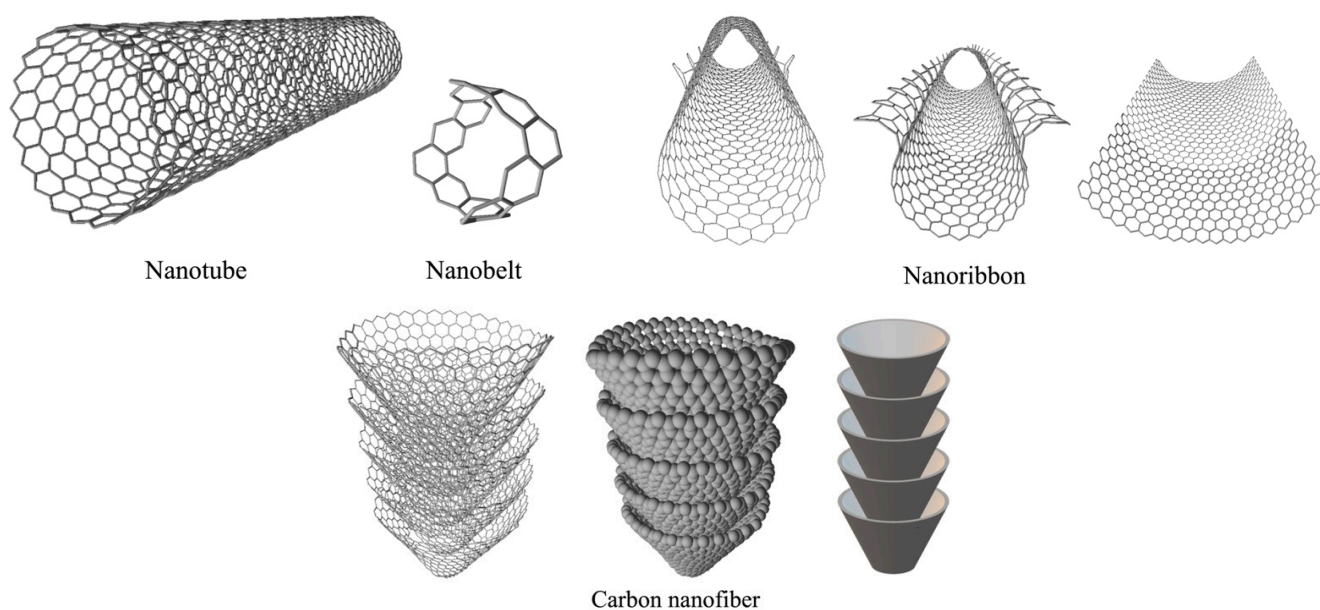
Currently, there are 5325 products of 7 different categories listed in this database (last data retrieval was 7 December 2021). There are actually 162 products listed for different applications, including batteries, heating, cooling and air, kitchen appliances, laundry and clothing care, and 582 products for automotive including exterior, maintenance, accessories, and vehicles. In addition, 261 products have been listed for electronics and computers, including cameras, films, computer hardware, displays, mobile devices, and communication; 227 products for food and beverage, including cooking, food, storage, and supplements. Additionally, 84 products have been listed for goods for children, including toys and basics, 3191 products for health and fitness including clothing, cosmetics, filtration, jewellery, personal care, sporting goods, and sunscreens; while 901 products for home and garden, including cleaning, construction materials, home furnishings, luggage, and paints. In the past nine years, i.e., from 2012 to 2021, products in the categories health and fitness, home, garden, and automotive had the highest production rates (Figure 2A).



**Figure 2.** Overview on NTs-containing products in Europe based on latest data available from the “Nanodatabase” in June 2021 (Copyright Danish Consumer Council, Copenhagen, Denmark, 2012). (A) Number of nanoproducts produced during 2012 and 2021 of seven different categories. (B) Number of nanoproducts in the section of waste materials. Reproduced with permission of Hansen et al. [21].

The section waste materials include different products that are grouped into batteries, cardboards, electronics, glasses, hazardous waste, metals, plastic packaging, textiles, and others, to name a few. In this section, the increased demand and production of commercial nanomaterials is also obvious (Figure 2B). The main group of waste materials listed in the database comprises plastic packing, with a still increasing trend. In 2012, 602 plastic packaging products were registered, which was more than double in 2021, with 1574. Similar trends occurred to nano-based textile products and multi-waste materials.

Besides the differentiation of different production categories, NMs are generally categorised based on their classification. Frankly speaking, NMs can be classified according to their size, shape, and form. Furthermore, their classification greatly depends on the morphology and physicochemical characteristics [22]. Several different terms are often introduced dealing with nanomaterials, which might be misleading for inexperienced scientists and/or newcomers in this research field. Consequently, a clear differentiation is required before discussing more important issues regarding NTs. In particular, nanomaterials comprise not only NPs, which might be the most popular group since silver nanoparticles and iron nanoparticles have conquered the commercial marketplace. Nanomaterials also include nanobelts, nanofibres, nanofilms, nanofluids, nanoribbons, nanorods, nanosphere, nanotubes, nanowires, quantum dots, and hollow spheres. According to Kargozar and Mozafari [11], the classification is further based on their dimension and composition. Thus, one-dimensional (1D) classifications of nanomaterials include, for example, thin nanofilms, nanolayers, and nanosurfaces. Two-dimensional (2D) classifications include, for example, nanowires and graphene sheets (rolled into nanotubes), and three-dimensional (3D) classifications include, for example, NPs, fullerenes, graphite sheets dendrimers, and quantum dots. Examples of common NMs such as nanotubes, nanobelts, nanoribbon, and carbon nanofibres are presented below (Figure 3). Besides classification, nanomaterials can also be categorised into single-phase solids (e.g., crystalline, amorphous particles and layers), multiphase solids (e.g., matrix composites, coated particles), and multiphase systems (e.g., colloids, aerogels, ferrofluids) [11]. Saleh [5] also distinguishes nanomaterials into more specific material-based categories such as metal-based NMs, metal oxide-based NMs, carbon-based NMs, zeolite and silica-based NMs, ceramic NMs, polymeric NMs, lipid-based NMs, and many others. Saleh’s review [5] is highly recommended to readers who are deeply interested in a more detailed description of classifications, categorisations, and properties of NM.



**Figure 3.** Structures of nanotubes, nanobelts, nanoribbon, and carbon nanofibers.

### 1.3. Synthesis of NMs or How to Make a Big Thing Small

Generally, there are three approaches to nanofabrication, i.e., the top-down approach (build in place), the bottom-up approach (self-assembly), and the hybrid approach, which represents a combination of top-down and bottom-up.

The top-down approach basically describes the synthesis of nanomaterials by destructuring the bulk material over powder to nano-sized shaped materials. Different physical methods such as etching, ball milling, grinding/milling, physical vapour deposition (PVD), and several different lithography techniques are applicable [5]. The top-down approach is commonly applied to produce structures with long-range order and for making macroscopic connections. Thus, top-down approaches find broad application in miniaturising current technologies (e.g., microelectronics) but also produce suitable NPs for clothing, sunscreens, or lighter constructive materials needed.

The bottom-up approach describes the self-assembly and molecular patterning by controlling the arrangement atom by atom. This approach is mainly based on chemical techniques such as atomic layer deposition (ALD), molecular layer deposition (MLD), sol-gel nanofabrication, chemical vapour phase deposition, or DNA scaffolding [11]. Bottom-up approaches are commonly applied to produce short-range orders, such as complex molecular devices, but also quantum dots, nanowires, thin films, and derivative or hybrid structures [6]. ALD is a suitable approach to produce inorganic nanomaterials, while MLD is suitable for producing organic nanomaterials.

In recent literature, several descriptions of nanofabrication are found with respect to different top-down and bottom-up approaches. Gregorczyk and Knez [6] also mentioned an approach called the in-between approach, which represents the hybrid approach, as mentioned above. This approach can cover some technical problems existing with top-down and bottom-up approaches [23]. The hybrid approach mainly produces hybrid materials, i.e., the incorporation of organic and inorganic materials, which have become very popular in recent years.

Another way to prepare nanostructures is green synthesis. Often phyto extracts are used as reducing agents to promote the formation and production of different morphologies of different nanoparticles [24–26]. The advantage of using plant extracts leads to the fact that they do not generate harmful by-products [27–29]. Alternatively, microorganisms such as bacteria and fungi can also be used to mediate the fabrication of different nanoparticles [30,31]. Recently, the synthesis of nano-sized  $\text{TiO}_2$  by bacterial strains such as *Bacillus mycoides* and *B. subtilis* was reported [32,33].

Finally, it can be concluded that nanomaterials comprise a large group of nano-based materials applicable in almost every scientific and commercial branch. Additionally, certainly, all these different classified and categorised nanomaterials may deserve a stronger focus during a literature survey. However, this review will henceforth focus on NPs and nanocomposites due to their considerable broad applications in remediation, successful utilisation in wastewater treatment, and drinking water production, as well as in agriculture.

## 2. Use of Nanotechnologies in Environmental Remediation

The application of NTs, or better said predominantly, NPs, is a rising field in environmental remediation approaches. However, before discussing more in detail on many advantages and some disadvantages of NTs for environmental remediation, a short overview of conventional environmental remediation approaches is helpful to fully understand and consider the potential of NTs in this specific environmental sector.

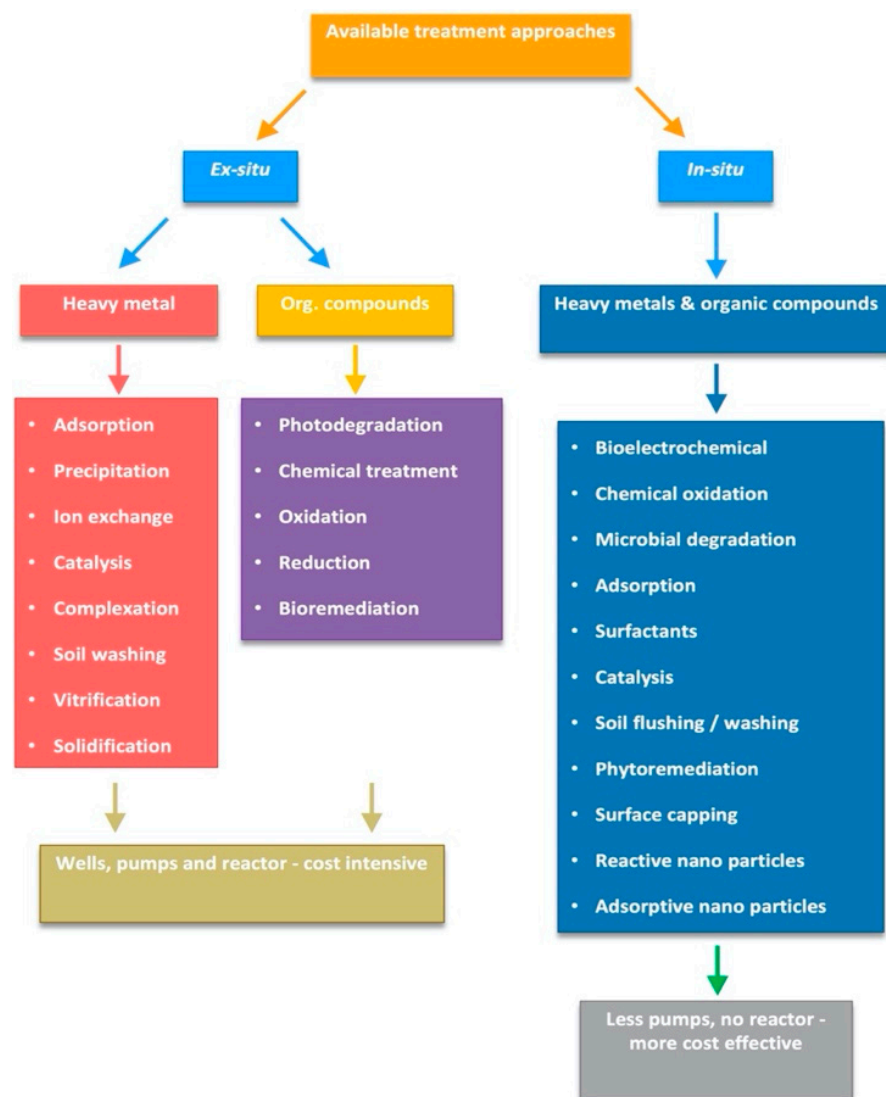
### 2.1. Conventional Environmental Remediation Approaches

Environmental remediation refers to reversing or stopping environmental damages caused by hazardous waste sites. Those environmental pollutions are commonly caused by solvents and other organics, heavy metals (such as lead, chromium, zinc, cadmium, arsenic, iron, mercury, copper), and petroleum products penetrating sediments and soils and finally ending up in groundwater and aquifers. Both public and private companies mainly contribute to those environmental contaminations [34]. For example, high amounts of heavy metals are leached during the mining process. This specific wastewater is not always treated in the right manner prior to its discharge into flowing rivers [35–37]. Thereby, solubilised heavy metals can easily migrate into sediments, soils, and groundwater, serving as hazardous long-term contaminations. Additionally, operational manufacturing plants, chemical industries, and petroleum industries can cause environmental contaminations by releasing organics and solvents through leakage and improper chemical handling. Another source of the hazardous waste site leads to leakage of underground storage tanks. According to Karn et al. [34], up to 80% of hazardous contamination sites refer to groundwater contaminations in the US. They further stated that this is particularly important, considering that more than half of the US population relies on groundwater for drinking.

The costs for remediation, especially for groundwater, are very high. The American Environmental Protection Agency (EPA) estimated in 2004, costs of about \$250 billion for remediation, including construction and post-construction activities, by several clean-up programs only in the US [34]. More recently, Mondal et al. [38] reported that the US EPA has now listed more than 1750 contaminated hazardous waste sites in the US, of which only 417 have been remediated so far. However, hazardous waste sites are not only a common problem in the USA but also globally [39]. Chen and Ye [40], for example, reported that in China, more than 3.3 million hectares are contaminated with increasing trends. Khan et al. [34] stated in their review that globally, about more than 5 million hazardous waste sites are contaminated with toxic elements such as heavy metals and organic compounds from wastewater.

The development of cost-efficient treatment strategies is, therefore, highly encouraged. Commonly, clean-up approaches can be performed either *ex situ* or *in situ* [2]. The choice of a suitable approach depends on the kind of contamination (Figure 4). For example, heavy metal contaminations can be treated *ex situ* by adsorption. This approach is better known as “*pump and treat*”. However, organic contamination can be treated *ex situ* by photodegradation, chemical oxidation, or biodegradation. The *ex-situ* approaches were earlier-developed treatment strategies where contaminated groundwater is pumped to a designed treatment reactor. The treatment can be either physical, chemical, and/or biological. Sometimes, combinations of physical, chemical, and biological treatments are required, making this approach very cost-intensive. In addition, the requirement of several wells and pumps and a very specific reactor design for efficient treatments further

increase the costs. After successful purification, the treated water must be brought back to groundwater, which also requires pumping engines, i.e., high costs for power supply and electricity. For this reason, the development of alternative approaches was necessary. In-situ approaches can be easily performed without exhausting installations of several wells, pumps, and specific treatment reactors. This treatment requires, on the one hand, the delivery of the contamination and, of course, on the other hand, excellent skills on the migration behaviour of the contamination in the groundwater as well as knowledge of specific groundwater parameters regarding the water velocity, water chemistry, water physics, water microbiology, and others. Via wells, for example, the chemical and/or biological treatment process can be either enhanced or stimulated through the injections of liquid and/or gaseous reagents or substrates.



**Figure 4.** Overview of common ex-situ and in-situ treatment approaches for environmental remediation.

Regarding soil and sediment in situ remediation, physical, chemical, and biological methods are also applicable. Physical methods for soil and sediment remediation comprise capping and flushing of hydrophobic organic pollutants (i.e., utilising mixtures of water and surfactants) and thermal treatments for volatile organic contamination (i.e., improving their mobility, volatilisation, and destruction). Chemical methods include adsorption, ion exchange, oxidation, and reduction. Very often, active carbon is applied effectively to reduce both organic and inorganic pollutants in the pore water. Biological methods

commonly use the substrate supply to initiate or enhance biodegradation. Song et al. [41] provided an excellent overview describing these specific approaches in further detail.

## 2.2. Environmental Remediation Applying NTs

In recent years, the application of NTs, particularly NPs for remediation, has become considerably popular. They are mainly beneficial for the rapid transformation and/or detoxification of several long-term contaminations on hazardous waste sites due to their higher intrinsic reactivity. Certainly, one of the most prominent applications of NPs in soil and groundwater remediation leads to surface-modified nanoscale zero-valent iron (nZVI) NPs. The success of nZVI over common reactive iron species is due to its fast kinetics, limited disruption to the environment, non-toxic nature, and cost-effectiveness [34,38,42].

Several studies for different applications of nZVI NPs have been published in recent literature. For example, nZVI was applied to remove chlorinated aliphatic hydrocarbons [43], polylactic acid mixture [44], diesel contamination [45] or heavy metal such as chromium [46] and others. Kheshtzar et al. [47] highlighted the use of nZVI NPs for organic pollutant remediation due to its effective Fenton-like catalyst reaction. In the presence of oxygen, nZVI NPs produce reactive oxygen species, i.e., free radicals degrading organic pollutants [48]. Kheshtzar et al. [47] pointed out that the chemical behaviour of nZVI NPs' participation during remediation is very complex apart from radical-mediated chemical transformation processes. Simultaneous processes such as adsorption, reduction, dissolution, and precipitation can occur easily by applying nZVI.

Regarding the degradation of common organic soil pollutants, He et al. [43] showed in their field assessment that perchloroethylene (PCE) and trichloroethylene (TCE) could be degraded abiotically using nZVI NPs after the injection of 682 L of carboxymethyl-cellulose-stabilised iron NPs. They investigated two different injection loads, i.e.,  $0.2 \text{ g L}^{-1}$  and  $1.0 \text{ g L}^{-1}$ , respectively. They found in both cases maximum abiotic degradation of PCE and TCE within two weeks after injection. They concluded that declined degradation kinetics were a result of exhausting the nZVI NPs' reduction power. Furthermore, they found that the injection boosted biological long-term in situ dechlorination where mZVI served as an excellent hydrogen donor. Luna et al. [49] reported a similar observation with a specifically designed microscale nZVI NP slurry for field application testing in situ PCE degradation. They obtained removal rates between 94% and 100% for chlorinated aliphatic hydrocarbons within one day of injection (initial PCE concentration  $3.5 \text{ mg L}^{-1}$ ). They monitored the aquifer for more than 150 days after the iron slurry injection and found an increasing PCE concentration after 30 days, recovering up to 50% of the initial concentration. This PCE concentration was stable until the end of monitoring, i.e., until day 162. They concluded that the injected iron slurry after three weeks not only showed reduced kinetics but also induced in situ biological dechlorination. Thus, for in situ remediation of chlorinated aliphatic hydrocarbons, abiotic treatment via nZVI NPs promotes and positively stimulates biological long-term in situ degradation in the aquifers. Therefore, the injection intervals and amount of nZVI NPs might be significantly reduced in comparison to conventional iron particles.

Despite these beneficial applications of nZVI NPs, there are also studies investigating the fate of nZVI NPs after injection regarding long-term reactions in more detail. Bennett et al. [50] showed that nZVI loses its mobility over time. They evaluated the in-situ transport of nanoscale nZVI particles with a conservative tracer through push-pull tests and found that NPs lose mobility with time due to the interactions between particles and aquifer sediments. Therefore, their distribution in the aquifer might be limited in some groundwater pores with lower velocities. For this reason, the authors recommended maintaining high groundwater pore velocities during injection to increase advective transport distances (e.g., groundwater circulation wells).

However, the transport and distribution are not the only concerns. Possible chemical transformation processes of nZVI NPs after successful remediation was critically investigated. Commonly, NPs are injected into the aquifer and remain there. So far, only a few



studies investigated the mineralogical transformation of nZVI in groundwater remediation caused by aggregation and oxidation. With a long-term study over 2.5 years, Su et al. [51] demonstrated that nZVI NPs were finally transformed into harmless yellowish lath-like goethite and ferrihydrite-like spherical particles in the top portion of the aquifer. They further concluded that injected nZVI can cause dramatic changes in biochemical parameters of groundwater which can also promote a reductive condition.

In some cases, transformation processes are caused by the aging of nZVI NPs, which can lead to reverse reactions, such as during heavy metal adsorption. In particular, nZVI NPs are also applied for heavy metal removal in soil and groundwater remediation due to their rapid adsorption kinetics. Some concerns arose regarding the release of NPs after successful adsorption over longer periods due to aging. This process is very often caused by oxidation, which can deliver heavy metals to the water. Calderon and Fullana [52] investigated this phenomenon for different heavy metals and showed that after 21 days of contact, cadmium and nickel resuspended for 65% and 27%, respectively. Unintentional oxidation and corrosion of nZVI was caused by the presence of dissolved oxygen, which also led to a decrease in the pH to below 7.5. The decreases in pH can lead to the remobilisation of heavy metals. Thus, the aging of nZVI NPs can decrease the removal efficiency and is a serious problem that must be considered carefully before treating heavy metal contaminations in sediments, soils, and groundwater.

Another important issue that still limits the application of NPs, including nZVI, for soil and groundwater remediation is agglomeration. Most NPs are prone to agglomerate, thereby losing their specific properties dramatically. To overcome this serious problem, nowadays, several NPs are supported with carriers such as active carbon, biochar, alumina, zeolite, and various silicas [53,54].

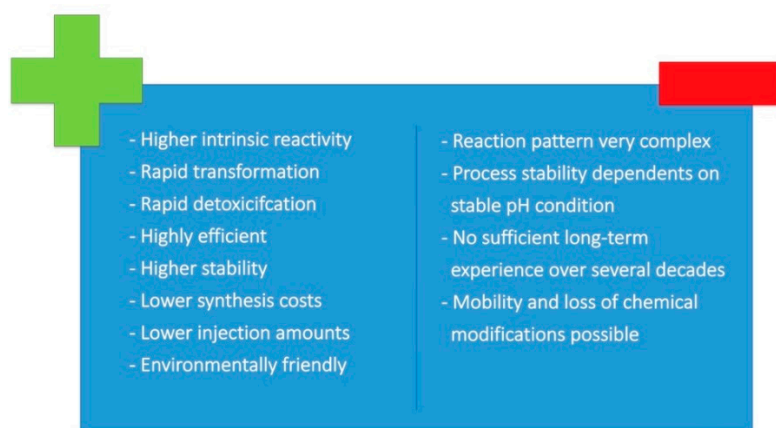
Recently, different nano-based metals stabilised with carriers were investigated for their removal of hexavalent chromium ( $\text{Cr}^{6+}$ ), which is still a serious threat in groundwater remediation. For example, Sathya et al. [55] reported the application of iron oxide NPs loaded with sodium alginate beads to remove hexavalent chromium ( $\text{Cr}^{6+}$ ) from contaminated water. They found that these NPs reduced almost 50%  $\text{Cr}^{6+}$  at pH 7.0 within 15 days, corresponding to an initial concentration of 100 ppm. The removal efficiency was further enhanced to 90%  $\text{Cr}^{6+}$  when the pH was decreased to 2.5. The author concluded that their synthesised NPs were highly efficient, eco-friendly, and required only low costs for synthesis. Studies on field assessment, however, have to be urgently carried out to confirm their potential for remediation. The high removal rates reported were achieved under a standardised condition, i.e., without competing chemical reaction, which often is limiting and/or decreasing the removal efficiency dramatically. Wang et al. [56] reported the development of iron sulphide (FeS) NPs stabilised with carboxymethyl cellulose for enhanced removal of  $\text{Cr}^{6+}$  in contaminated groundwater and saturated soil. They performed different batch and column tests to determine the removal efficiency. In the batch tests, they determined a removal capacity of 1046.1 mg  $\text{Cr}^{6+}$  per gram of FeS NPs and pointed out that the main chemical reaction taking place included adsorption, reduction, and co-precipitation. Furthermore, they found no significant competing adsorptive effects caused by natural organic matter. The high removal capacity was confirmed during column tests where the effluent concentration was still below  $5 \mu\text{g L}^{-1}$  after the elution of 45 column pore volumes through the FeS NPs column bed. Still, field assessments must be carried out to confirm these very promising results.

Apart from stabilised metal-based NPs, bimetallic NPs were also recently reported as promising remediation candidates due to their higher activity towards  $\text{Cr}^{6+}$  adsorption. For example, Ou et al. [57] developed iron/aluminium bimetallic NPs towards  $\text{Cr}^{6+}$ -contaminated groundwater remediation. They determined a removal capacity of 1.47 g $\text{Cr}^{6+}$  per gram of Fe/Al NPs. Like Wang et al. [56], they also identified adsorption, reduction, and precipitation as the main mechanisms in  $\text{Cr}^{6+}$  removal. After adsorption, the reduction in  $\text{Cr}^{6+}$  caused a release of  $\text{OH}^-$  and led to chromium hydroxide precipitation, which then was prevented from further migration in the contaminated aquifer. Bimetallic NPs

can also be used to remediation of toxic dyes, as recently proposed by Gallo et al. [58]. They developed bimetallic silver/iron NPs to remediate bromophenol blue dye from water. Like Ou et al. [57], their developed NPs seem to be very promising in degrading the dye. However, field studies are still missing to confirm their unrestricted application in the aquatic environment.

These few examples demonstrate the broad application range of several NPs products for groundwater and soil remediation. However, remediation does not only focus on clean-up approaches on soils, sediments, and groundwater but also on marine ecosystems such as oceans. Oil spills, for example, are a danger to fragile ecosystems. According to Singh et al. [59], more than 5.7 million tonnes of crude oil were released into oceans over the past four decades. Conventional approaches to clean-up include booms, skimmers, adsorbents, surfactants, dispersants, in situ burning and bioremediation for removal of these contaminants from water can be applied [60]. Nevertheless, these approaches do not always lead to comprehensive oil-water separation. The high adsorption and separation capacity features the utilisation of magnetic NPs, which is commonly the agglomeration of super-paramagnetic NPs. Metals utilised to produce magnetic NPs are commonly iron, nickel, copper, manganese, magnetite, maghemite, mixed ferrites, and others. Novel developments such as materials with super-hydrophobicity and oleophilicity properties were recently tested on oil spills and showed improved surface properties, enhanced biodegradability, non-sinking property, simple recovery, high degree of reusability, eco-friendly nature, and large sorption capacities [61]. Thus, the application of magnetic NPs is an alternative approach to recover oil spills from oil-contaminated water.

To summarise, it can be stated that the application of NPs in remediation is nowadays well established due to the simple application, low cost, and eco-friendly label. However, long-term effects on the environmental behaviour of engineered NMs on sediment, soil, groundwater, and marine water ecosystem is still a big issue of uncertainty, which ought to be not neglected. In view of this, the current review of Qian et al. [62] is highly recommended to interested readers. This review critically summarises the hazardous effects of NMs leading to potential toxicity to terrestrial plants, soil organisms and human health. The main advantages and disadvantages of NPs' application of remediation are summarised below (Figure 5).



**Figure 5.** Summary of the advantages and disadvantages of applying NPs for environmental remediation.

### 3. Application of NTs in Wastewater Treatment

NT and, especially, NPs have also found broad applications in the industrial and municipal wastewater treatment sector. Typical industrial wastewater sources are commonly from the textile industry, leather industry, chemical industry, and medical and pharmaceutical industry. In municipal wastewater treatment, advanced application of NTs is, meanwhile, established via adsorption processes, photocatalytic degradation, and partly by membrane filtration processes. These different applications of NTs in wastewater treatment will be discussed more in detail in the following subchapters.

### 3.1. Adsorption of Heavy Metals as Common Wastewater Pollution

Adsorption is a simple physico-chemical method used to purify harmful wastewaters from heavy metals and/or organic pollutants. In this specific case, surface adsorption onto solid sorbents takes place through electrostatic forces. Those can be caused, for example, by hydroxyl groups and/or other functional groups, resulting in a positively or negatively charged sorbent surface. Depending on the charge of contaminants to be removed, oppositely charged adsorbents are applied. The efficiency of the adsorption is characterised by chemical interactions on the surface of the adsorbents. The main parameters influencing adsorption are pH, temperature, stirring duration (i.e., contact time), initial concentration of the substance to be adsorbed, and the adsorbent dosage. High flexibility in operation and a simple process design (i.e., equipment and set-up) are major advantages, as well as a broad range of target contaminants, especially when activated carbon (AC) is used as an adsorbent. In the case of heavy metal adsorption, adsorbents such as AC or biomaterials can also be generated several times, making this process more cost-effective [63]. Unfortunately, their preferred removal efficiency cannot always be achieved by regeneration.

In conventional adsorption, AC is not only applied due to its versatile and broad application range but also due to simplicity in chemical modification by surface doping, resulting in higher selectivity of specific target contaminations. However, AC produced from coal, and natural materials, such as coconut shells and others, make it still expensive. Common prices, for example, for chromium removal using commercial AC absorbance can range between USD 0.30 kg<sup>-1</sup> and USD 1.37 kg<sup>-1</sup>, providing adsorption capacities between 2.18 g kg<sup>-1</sup> and 15.47 g kg<sup>-1</sup>, respectively. The price can easily increase up to USD 20.00 and even more if higher chromium adsorption capacities up to 50 g kg<sup>-1</sup> are required [64]. Such high prices for adsorbents are by far nonpractical and represent a limiting factor for a further commercial application not only in wastewater treatment.

Thus, low adsorption capacities with respect to relatively high adsorbent costs forced scientists to research and develop alternative adsorbent materials, especially with regard to heavy metals removal [63]. Apart from further developments using AC with several different surface modifications, novel nano-adsorbents have been attracting more and more attention for a couple of years. Due to their higher surface-area-to-volume ratio, nano-adsorbents can exhibit extra accessible adsorption sites, higher reactivity, and stronger affinity towards heavy metals.

Different nanomaterials, such as graphene, fullerenes, nano-metal oxides such as ZnO, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub>, or TiO<sub>2</sub>, and metal organic frameworks (MOFs) were meanwhile developed and showed extraordinary adsorption capacities towards heavy metals such as Cr, arsenic, cadmium, lead, copper, and others. Table 1 summarises the latest outcomes based on heavy metal adsorption experiments under standardised experimental conditions. The findings and new outcomes reported below might not have a direct link to wastewater application yet, but they demonstrate the early-stage developments for applications in this field.

For example, zinc oxide nanoparticles (ZnO NPs) have been investigated to selectively interact with Cr<sup>3+</sup> [65]. In batch experiments, ZnO NPs exhibited very high affinity towards Cr<sup>3+</sup> for an optimum pH range of 3–7 and a very short contact time of 20 min. It is worth mentioning that the author also showed that ZnO NPs selectively adsorbed Cr<sup>3+</sup> from dental wastewater, which contained a mixture of heavy metals, including Ni<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, and Cr<sup>3+</sup>. The strong affinity of ZnO NPs toward Cr<sup>3+</sup> resulted in a maximum adsorption capacity of 88.6 mg g<sup>-1</sup>, which is by far significantly greater than other sorbents, such as AC.

Apart from Cr<sup>3+</sup>, the removal of Cr<sup>6+</sup> has higher priority because its toxicity is over 100 times that of Cr<sup>3+</sup> [66]. In recent years, several researchers reported the development of different nano-based adsorbent materials with improved absorption capacities towards Cr<sup>6+</sup> (Table 1). In particular, Periyasamy et al. [67] reported a biocomposite adsorbent based on nano-graphene oxide for the removal of Cr<sup>6+</sup> from water. They achieved a maximum

adsorption capacity of  $42.64 \text{ mg g}^{-1}$ . They further pointed out that at an acidic pH, the adsorption of  $\text{Cr}^{6+}$  was generally higher, which agrees with other scientific reports that confirmed enhanced adsorption capacities for  $\text{Cr}^{6+}$  at an acidic pH. There are mainly two reasons responsible for this. On the one hand, the pH influences the adsorption surface behaviour, i.e., the acid pH results in an electronic surface charge and protonation of dominating species of functional groups. On the other hand, dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ), which is the dominating ion species of  $\text{Cr}^{6+}$  at an acidic pH, leads to stronger adsorption on protonated surface sites, thus increasing the adsorption capacity. This leads to the fact that for remediation techniques, reduced adsorption capacities have to be taken into account when the treatment is performed at a neutral pH unless advanced adsorbent materials are developed with considerably higher adsorption capacities at a neutral pH.

Periyasamy et al. [67] applied their novel biocomposite nano-graphene oxide to chromium-contaminated groundwater collected from a nearby industrial area and showed that their adsorbent completely removed  $\text{Cr}^{6+}$  from the water at neutral pH. This result is remarkable because it demonstrates the applicability of NPs to groundwater remediation as a suitable alternative to conventional adsorbents at very low dosages. In addition, the authors also stated that regeneration with NaOH was feasible and proposed up to five cycles without any significant loss in the removal efficiency of the biocomposite.

Overall, several novel nano-adsorbents for  $\text{Cr}^{6+}$  removal were recently reported indicating extremely high adsorption capacities. However, most of them were achieved at acidic pH, and readers have to be aware of how to interpret those results reported. For example,  $\text{Cr}^{6+}$  adsorption capacities up to  $970.9 \text{ mg g}^{-1}$  were reported for nitrogen-doped magnetic carbon nanotubes [68]. Nevertheless, a strong acid pH condition is required for this extremely high adsorption capacity; thus, it requires a high acid dosage that might lead to increased treatment costs. It will remain doubtful whether such high adsorption capacities are justified by unfavourable and unpractical treatment conditions regarding remediation and specific wastewater treatment strategies. With regard to wastewater plant operations, environmental issues and legal regulations might be an additional obstacle to applying those nano-adsorbent materials for  $\text{Cr}^{6+}$  removal.

Like chromium, arsenic (As) is also one of the top priority toxic pollutants predominantly removed from wastewater by adsorptive processes. There are several publications available highlighting excellent adsorption capacities based on different nano-adsorbents, especially for arsenate ( $\text{As}^{5+}$ ). In wastewater, As can occur as arsenide ( $\text{As}^{3+}$ ) and/or arsenate ( $\text{As}^{5+}$ ). Both ionic forms are carcinogenic and show toxic effects at trace level concentrations. According to Shan et al. [69], the former is 20–60 times more toxic and difficult to remove. Therefore,  $\text{As}^{3+}$  is often simply oxidised and subsequently adsorbed through electrostatic interactions, surface complexation, and chemical interaction [70]. The choice of the right adsorbent material is, of course, of utmost importance for arsenate adsorption. It is now known that some adsorbents can reduce  $\text{As}^{5+}$  to highly toxic  $\text{As}^{3+}$  which does not often adsorb less on the same adsorbent. Some biochar products and, especially, zero-valent iron were reported as reductive adsorbents for arsenate [71,72]. Wang et al. [70] developed trivalent cerium oxide NPs that exhibit higher affinity towards  $\text{As}^{5+}$  than to  $\text{As}^{3+}$ . They reported a maximum adsorption capacity of  $220 \text{ mg g}^{-1}$  for  $\text{As}^{5+}$ . The authors stated that the adsorption was ultra-strong and thus resulted in irreversible adsorption. Bhaumki et al. [73] reported the development of polyaniline/ $\text{Fe}^0$  composite nanofibres for  $\text{As}^{3+}$  and  $\text{As}^{5+}$  adsorptive removal at neutral pH. The nanocomposite achieved removal rates up to almost 100% from pH 3 to 7 for both  $\text{As}^{3+}$  and  $\text{As}^{5+}$ . Additionally, similar maximum adsorption capacities were achieved (Table 1). Therefore, the authors stated that the developed material might be a promising adsorbent for safe drinking water provision in low-income communities. Hence, those enhanced adsorption capacities can also lead to smaller doses of adsorbents making the approach more environmentally friendly.

Another important heavy metal to be removed from wastewater is cadmium ( $\text{Cd}^{2+}$ ), which originates from the mining industry, pulp and paper industry, dye industry, and many others.  $\text{Cd}^{2+}$  is highly toxic at trace levels and can cause cancer in humans, liver

and blood damage, and other dysfunctions. The reported absorption capacities on novel nano-absorbents are comparably high and range commonly from  $150 \text{ mg g}^{-1}$  to more than  $600 \text{ mg g}^{-1}$ . Sheela and Nayaka [74] reported extraordinarily high adsorption capacities for  $\text{Cd}^{2+}$ . They developed NiO NPs that are applicable from neutral to basic pH range. They stated that  $\text{Cd}^{2+}$  occurs predominantly as a bivalent cation ( $\text{Cd}^{2+}$ ) below pH 8.0. They found that between pH 6–8,  $\text{Cd}^{2+}$  adsorption is a combined process of metal adsorption and precipitation which can lead to high removal rates. They further showed that the adsorption process is predominantly an ion exchange between the cation metal and the  $\text{H}^+$  ions of the sorbents. Therefore, a decrease in the solution pH can occur easily, promoting further adsorption if the pH is within the range of 6 to 8. Generally, higher adsorption capacities can be achieved at higher pH, i.e., above 10. Nevertheless, precipitation might then be the competing process resulting in toxic sludge production to be removed. Thus, it is preferred to perform  $\text{Cd}^{2+}$  adsorption at neutral pH where precipitation does not overwhelm the adsorption process.

With regard to wastewater contamination, lead ( $\text{Pb}^{2+}$ ) also has to be taken into account because this heavy metal often comes along as an impurity from the leather tanning and dyeing industry. Huang et al. [75] pointed out that those wastewaters provide higher complexity due to the coexistence of heavy metals and organic dyes. Like most heavy metals,  $\text{Pb}^{2+}$  also causes carcinogenic effects and is toxic at trace levels.  $\text{Pb}^{2+}$  tends to bioaccumulate and cause blood disease. Thus, efficient removal of  $\text{Pb}^{2+}$  is of utmost importance to protect both human beings and aquatic life. Different treatment technologies were recently proposed, such as precipitation, reverse osmosis, ion exchange, and surface adsorption [76]. However, surface adsorption was often preferred due to high selectivity and producing no secondary pollutants. High  $\text{Pb}^{2+}$  adsorption capacities were recently reported for novel NPs with different modifications. Sheela and Nayaka [74] highlighted an adsorption capacity of  $909 \text{ mg g}^{-1}$  of  $\text{Pb}^{2+}$  on NiO NPs. The authors justified the high selectivity of the novel material based on the metal ion properties. The selectivity of NiO NPs towards  $\text{Pb}^{2+}$  is a result of the metal ion radii, atomic weight, electronegativity, and other parameters. In their experiments, Sheela and Nayaka [74] found that  $\text{Pb}^{2+}$  outcompeted  $\text{Cd}^{2+}$ ; thus, they proposed NiO NPs for the removal of  $\text{Pb}^{2+}$ , preferably, by adsorption. Additionally, Egbosiuba et al. [77] developed and investigated novel NP material and multi-walled carbon nanotubes (MWCNTs) for the enhanced adsorption of several heavy metals, including  $\text{Pb}^{2+}$ . They also compared the adsorption efficiency of MWCNTs-KOH@NiNPs between  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  and found a higher adsorption capacity for  $\text{Pb}^{2+}$ . Like the others, they concluded that the initial pH is a driving factor for successful adsorption. On the one hand, the initial pH influences the deprotonation of the adsorbents, which favours enhanced adsorption in a suitable pH range by reducing the repulsion of metal cations (i.e., electrostatic interactions). In addition, Rezanian et al. [78] proposed a mechanism not only based on electrostatic interaction but also based on metal coordination and complexation which interacts and provide synergetic effects that result in enhanced adsorption and finally increased removal efficiency. Metal coordination and, especially, complexation strongly depend on the pH. The pH also influences the precipitation of metals. In the case of  $\text{Pb}^{2+}$ , the precipitation of hydroxide ( $\text{Pb}(\text{OH})_2$ ) starts above pH 6.0; thus, adsorption is not favoured at pH values higher than 6.0 [75]. For this reason, most developed adsorbents are applied close to pH 6.0. The adsorption capacities reported in most publications range between  $100 \text{ mg g}^{-1}$  and  $500 \text{ mg g}^{-1}$ , with quite short contact times compared to other heavy metals. The successful application of iron oxide magnetic NPs grafted on hyperbranched polyglycerol polymers for the removal of Cu, Ni, and Al from secondary industrial wastewater effluent was recently reported by [79]. Extraordinary adsorption capacities were achieved for all three heavy metals; however, the capacity for Cu was highest and averaged  $700 \text{ mg g}^{-1}$ . The authors stated that organic matter did not negatively affect the adsorption capacity, but the nitrogen content of the wastewater significantly reduced the capacity of the adsorbent. Nevertheless, the developed material was still successfully applied to real wastewater and showed proof for routine application.

Another important heavy metal is copper ( $\text{Cu}^{2+}$ ), which is often discharged from different industrial sources, such as electroplating, paint, metal finishing, mining operation, chemical manufacturing, fertilisers, and the pigment industry, to name a few [80]. Higher doses of  $\text{Cu}^{2+}$  can cause hepatic and renal damage genetic disorder in human beings. Singh et al. [81] stated that the adsorption of  $\text{Cu}^{2+}$  contamination might not be favoured with conventional adsorbents due to disposal problems of metal-loaded adsorbents, high maintenance cost, and difficulties in regeneration. The use of magnetic NPs as promising adsorbents has gained attraction because these adsorbents are better recycled due to the use of external magnetic fields. Thus, magnetic NPs also play an important role in remediating polluted wastewaters. Overall, adsorption capacities were found for magnetic NPs ranging between 15 and  $360 \text{ mg g}^{-1}$ . Most nano-adsorbents were applied at a pH range of 6.0 to 7.0. For most of them, higher pH values might be favoured for deprotonating functional groups at adsorbent surfaces. Many nano-adsorbents, however, are optimised for a pH range between 5.0 and 6.0 since  $\text{Cu}^{2+}$  starts precipitation as  $\text{Cu}(\text{OH})_2$  at a pH higher than 6.0.

To summarise, it is obvious that NPs have great potential to outcompete conventional adsorbents. Nevertheless, Chai et al. [63] critically pointed out that mainly graphene and nano-sized metal oxides are presently favoured as commercial maturity. The authors justified that there is only a small number of studies evidencing the applicability of most nano-adsorbents under real conditions. In many cases, most nano-adsorbents show drastically decreased adsorbent performance. Furthermore, the risk of environmental contamination through leakage during treatment cannot be completely excluded, and their environmental behaviour and path is not completely understood. Those aspects might be considered carefully; however, the novel developments presented here demonstrate a straight trend towards establishing NPs for adsorption purposes in wastewater treatment in the near future.

For readers who are more interested in studying heavy metal adsorption via NPs, the review article of Deshpande et al. [82] is highly recommended. The authors also reviewed the application of nanotechnology in wastewater treatment and underlined numerous articles published for the successful adsorption of heavy metals, such as cadmium, arsenic, uranium, and others.

**Table 1.** Comparison of adsorption capacities of different nanoparticles for different heavy metals.

Target	Adsorbent Material	$q_{\text{max}}$ ( $\text{mg g}^{-1}$ )	Dosage ( $\text{g L}^{-1}$ )	pH	Contact Time	Ref.
$\text{Cr}^{6+}$	GO-HBP-NH <sub>2</sub> -TEPA	300.9	0.2	2.0	360 min	[66]
	n-GO@HTCS biocomposite	43.87	2.0	3.0	50 min	[67]
	Nitrogen doped magnetic carbon nanotubes	970.9	2.5	1.0	<10 min	[68]
	Magnetic iron oxide nanoparticles (m-NIOB)	47.62	5.3	5.0	180 min	[83]
	Ni@N-K-C-900	824.4	1.0	2.0	-	[84]
	Aluminium hydroxide nanoparticles	120.0	1.0	5.0	60 min	[85]
	FeS/chitosan/biochar composite	103.9	0.2	2.0	360 min	[86]
	TA-nano-FeS	381.0	0.1	4.0	120 min	[87]
$\text{As}^{5+}$	Biochar-loaded $\text{Ce}^{3+}$ -enriched ultra-fine ceria NPs	219.8	50	5.0	24 h	[70]
	Nano-scale polyaniline/ $\text{Fe}^0$ composite	227.0	0.1	7.0	60 min	[73]
	$\gamma\text{Fe}_2\text{O}_3$ NP encapsulated microporous silica	248	0.4	2–6	24 h	[88]
	Iron oxide–graphene oxide (GO) nanocomposites	113.0	0.8	-	15 min	[89]
	(S-nZVI@ZSM-5) composite	161.7	1.0	4.0	25 h	[90]
	Zr-MnO <sub>2</sub> @reduced graphene oxide nanocomposite	201.1	1.0	4.0	25 min	[91]
$\text{Cd}^{2+}$	NiO nanoparticles	625.0	0.5	6.0	10 min	[74]
	MWCNTs-KOH@NiNPs	415.3	0.03	5.5	30 min	[77]
	Oxidised starch nanoparticles	151.7	0.05	-	90 min	[92]
	Sulfonate hydroxyapatite NPs—15BDS-HAp	457	2.0	5.0	180 min	[93]

Table 1. Cont.

Target	Adsorbent Material	$q_{\max}$ ( $\text{mg g}^{-1}$ )	Dosage ( $\text{g L}^{-1}$ )	pH	Contact Time	Ref.
$\text{Pb}^{2+}$	NiO nanoparticles	909	0.5	6.0	120 min	[74]
	DTPA chitosan-coated magnetic silica NPs	268.0	1.0	6.0	90 min	[75]
	MWCNTs-KOH@NiNPs	480.0	0.03	5.5	30 min	[77]
	Lanthanum sulphide NP decorated over magnetic graphene oxide	123.5	1.0	5.0	40 min	[78]
	Oxidised starch nanoparticles	182.2	0.05	-	90 min	[92]
$\text{Cu}^{2+}$	Activated carbon/magnetite nanoparticles	23.6	10	-	24 h	[94]
	$\text{Fe}_3\text{O}_4$ - $\text{MnO}_2$ -EDTA magnetic nanoparticles	105.8	0.2	6.0	60 min	[95]
	Graphene oxide sheets with magnetite NPs	16.7	1.0	7.0	24 h	[96]
	Functionalised graphene oxide nanoparticles	357.1	-	6.0–7.0	60 min	[97]
	Hydroxyapatite nanoparticles	70.9	1.25	-	120 min	[98]

### 3.2. Adsorption of Persistent Substances from Wastewater Pollution via NPs

Another typical application of nano-absorbents in wastewater leads to the removal of poly- and perfluoroalkyl substances (PFAS), which are organofluorine compounds [99]. PFAS molecules contain both a hydrophilic functional group (often carboxyl or sulfonic acid groups) and a hydrophobic functional group as a tail which is commonly fluorinated. For this reason, PFAS can easily form hemi-micelle and/or micelle and therefore are classified as anionic surfactants with a very strong electronegativity.

These compounds are often applied as stain guard products for carpets, upholstery, and textile specialised surfactants in the fluoropolymer industry and as important components of fire-fighting foams. PFAS are prominent members of the group of persistent substances and have become major anthropogenic contaminants in the environment in recent years. Hence, their rapid and efficient removal, especially if wastewater is produced, is favoured by adsorption. PFAS adsorption is basically driven by electrostatic attraction, hydrophobic interactions and self-aggregation, as described by Du et al. [100]. In practice, however, it is known that PFAS compounds do not exist alone but are always in a composite of organic substances. The latter may cause competition on adsorption sites depending on the pH value and temperature [101,102]. It is, therefore, difficult to compare different adsorbents with regard to their performance [102]. So far, conventional granulated activated carbon has been used to remove perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) from contaminated waters [102]. The chemical equilibrium, i.e., contact time, is only reached after 72 h, which is a major obstacle because, for the removal of contaminated PFAS wastewaters, only shorter reaction times are economically acceptable. Therefore, nano-absorbents might outcompete conventional adsorbent materials in future not only because of higher removal loads but also due to shorter contact times. Some developments have already been carried out, and removal rates have been investigated. Zhang et al. [99] summarised the important developments of nano-absorbents for PFAS. Most nano-absorbents are nanotubes-based on multi-walled carbon. As mentioned above, the different adsorbent capacities reported by [89] for the different materials are a result of different PFAS used for the experiments, different adsorption surface sizes of the materials, different pH, and contact time. As a consequence, it is very difficult to compare these data. Interestingly, most nano-absorbents follow a pseudo-second-order kinetic model which is different compared with heavy metal adsorption (commonly first-order kinetics). Additionally, as stated above, independent of whether the different novel materials are comparable with each other, all those nano-adsorbents clearly outcompeted conventional adsorbents for the contact time. The shortest contact time for PFOA adsorption was reported by Gong et al. [103] for starch-stabilised  $\text{Fe}_3\text{O}_4$  NPs averaging 30 min. The PFOA adsorption capacity averaged  $62.5 \text{ mg g}^{-1}$  at pH 6.8. Thus, this nano adsorbent does not require extensive pH adjustment and could be easily applied without additional pretreatment. However, one has to bear in mind that competing reactions for adsorption

sites on the adsorbents can dramatically reduce the efficiency of every adsorbent. In this context, Gong et al. [103] also stated that the presence of humic substances inhibited the uptake drastically. Still, nano-adsorbents for PFAS will be a great alternative as adsorbents. However, further progress and research must be carried out to better understand the competing adsorption between PFAS and other organic and/or inorganic compounds commonly present in wastewater.

Another very important application for NPs is the adsorptive removal of dyes from the textile industry and its wastewaters. Several dyes, such as phenol red, congo red (CR), organic dyes, anionic dyes, crystal violet, methylene blue (MB), and others, were recently reported to be successfully removed via NPs such as silver NPs [104], polymer NPs composite of polyaniline-zinc titanate [101], magnesium oxide NPs [105,106], magnetic crosslinked chitosan-glyoxal/ZnO/Fe<sub>3</sub>O<sub>4</sub> NPs [107] and iron oxide NPs [108]. Those dyes are very often removed from wastewater by adsorption processes when other treatment approaches, such as the advanced oxidation process (AOP), are incompatible due to their chemical resistance [109]. Similar to PFAS, a comparison of the adsorption capacities of the different NP adsorbents is difficult due to the different chemical adsorption behaviour of the dyes mentioned and the different adsorbent materials. With regard to environmentally friendly production of NPs, the use of *Eucalyptus* spp. leaf extracts to produce ZnO NPs as a form of green NPs process has been investigated to be very efficient in removing carcinogenic cationic and anionic dyes from wastewater [110]. Examples of these carcinogenic dyes include CR and malachite green (MG). ZnO NPs had a high adsorption capacity of 48.3 mg g<sup>-1</sup> for CR and 169.5 mg g<sup>-1</sup> for MG. Due to their easy regeneration, ZnO NPs are also reusable and strongly compete with conventional adsorbents [110].

The application of NPs in wastewater treatment is not limited only to wastewater from the textile industry. Additionally, petroleum-based pollutants belong to the group of persistent substances and are subject to be removed via nanotechnologies [111]. Wastewater from petroleum processing contains myriad hydrocarbons (HCs) which are free, soluble, and emulsive in nature. These HCs often contain heavy metals and/or solid particles, making them hazardous due to their accumulative potential in human beings and the environment [111]. The authors reviewed treatment technologies for the removal of petroleum-based pollutants in natural ecosystems and wastewater streams. Remarkably, they reviewed 110 carbon nanomaterials as effective adsorbents for petroleum-based pollutants (i.e., organic pollutants such as phenols, BTEX and volatile organic compounds) and summarised their most important performance parameters, including the maximum adsorption capacity. For readers who are interested in more detail, this review is highly recommended.

### 3.3. NPs for the Advanced Photocatalytic Degradation of Wastewater Pollutants

Various technologies have been proposed and studied to remove toxic pollutants from wastewater. These technologies include ion exchange, adsorption processes, membrane processes, and AOP, including photodegradation and photocatalysis.

Photodegradation processes belong to the group of AOP. They are based principally on the use of light radiation as an energy source. The light source for the process may be from ultraviolet lights such as mercury or xenon lamps, LED lamps, or even solar light. When photons from light energy sources are absorbed by molecules, both physical and chemical changes can take place. The photochemical change can either be by direct or indirect means. In direct processes, the photon energy is absorbed by the target pollutant, which then undergoes homolytic cleavage to produce the degradation products (often also called transformation products). In the indirect photochemical process, the photon energy is absorbed by a photosensitive material, which produces species such as radicals that interact with the target molecule to affect the degradation of pollutants. Both indirect and direct photochemical processes involve a series of reductive and oxidative reactions. These processes can be classified as redox reactions. Depending on whether the degradation is initiated by an oxidation reaction or reduction reaction, a photodegradation process may be classified either as an AOP or an advanced reduction process.



Photodegradation processes can be performed either with or without photocatalysts. The latter can be considered a green technology for wastewater treatment because the mechanism can also rely on sunlight irradiation (solar light) to convert toxic pollutants to non-toxic forms.

Basically, the mechanism of photocatalysis is to convert photon energy into chemical energy. Commonly heterogeneous photocatalysis, i.e., between two or more phases, occur where the catalyst is in the solid phase and are mainly semiconductor-based transition metal oxides. The photocatalyst plays an important role in generating a transient state by using photon light energy through absorption and release of the electron-hole pair (leading to radicals) to produce the chemicals (chemical energy) in the form of products. In particular, the adsorbed photon energy results in the excitation of an electron pair in the valence band of the photocatalyst. The valence band is the lowest energy level filled with electrons. If the adsorbed photon energy corresponds to or is greater than the so-called bandgap energy between the valence band and the conduction band (next energy level not filled with electrons), the excited electron pair is transferred to the conduction band (electron acceptor). As a consequence, an electron hole occurs in the valence band at the surface of the catalyst (electron donor). At the conduction band, oxygen reduces and produces superoxide radicals, while at the valence band, the oxidation of water produces hydroxyl radicals. The bandgap energy is characteristic for photocatalysts which are very often semiconductors, as mentioned above. Depending on the bandgap, a defined range of light energy can be adsorbed. Thus, the wider the bandgap, the smaller the range of light energy, i.e., only limited use in the visible light range is possible and high-energy light in the UV light range will be required. In other words, wider bandgaps require more photon energy to excite the electron pair, which can be only generated by UV light photons. Independent of the adsorbed light range, wider bandgaps also often lead to fast recombination, lowering the photocatalytic efficiency. Several surface modifications via doping are investigated to improve the bandgap of semiconductors towards narrow bandgap energy, slow recombination rates, and accelerating interfacial charge transfer. For readers who are more interested in those details, the review of Saputera et al. [112] is highly recommended.

Semiconductor photocatalysts have shown significant efficiency towards organic and inorganic pollutants.  $\text{TiO}_2$  is one of the most commercial and efficient photocatalyst materials used for the degradation of many organic pollutants due to its versatility, easy synthesis, good controllability, and stability.  $\text{TiO}_2$  exhibits a wide band gap (3.2 eV) and adsorbs photons emitted close to the UV range compared to other semiconductor photocatalysts [113]. However, the wide bandgap leads to activation only in the UV region and, therefore, uses less than 5% of solar light [113]. For this reason, the use of  $\text{TiO}_2$  as a photocatalyst activated by sunlight irradiation is not favourable. Based on this drawback, many researchers have focused on the preparation of different structures of  $\text{TiO}_2$ , including nanocomposites, which might also help degrade toxic pollutants in water and wastewater more efficiently.

Javabakth and Mohammadian [114] reported on advanced dye removal of poly azo anionic direct red 80 and azo cationic MB using bentonite/ $\text{TiO}_2$  nano-photocatalyst immobilised with silver NPs under different AOP conditions (3.26 eV) (Table 2). They achieved removal efficiencies up to 77% for the dye direct red 80 and 100% for MB (10 ppm initial concentration) with a load of 0.03 g of the nanocomposite with 0.25% silver content using UV light irradiation. The authors concluded that this surface modification of the nanocomposite resulted in a highly efficient photocatalyst, which is applicable to azo dye wastewater purification. Additionally, Akyüz [115] reported on a synthesised multi-metal oxide containing a  $\text{TiO}_2$  nanocomposite loaded with silver NPs to degrade MB. The author stated that the wide band gap of  $\text{TiO}_2$  was decreased in the presence of transition metal oxides to 2.58 eV, increasing the degradation efficiency. Up to 91% degradation efficiency of 0.3 mM MB (96 mg L<sup>-1</sup>) was achieved within 15 min of treatment. Nevertheless, UV light irradiation was still required to activate the photocatalyst.

Despite novel developments of TiO<sub>2</sub>-based photocatalysts for UV photodegradation, promising developments towards visible-light-mediated photocatalytic degradation have been attracting more and more attention recently. The reason to favour visible light irradiation is that UV treatments require expensive equipment and cause a high energy demand, i.e., high costs. Instead, using visible light which can be emitted by LED lamps or even better solar light for photocatalytic degradation of persistent substances is inexpensive and more environmentally friendly. Furthermore, if recycling those photocatalysts is feasible, this treatment strategy could further enhance and promote wastewater remediation technologies. Some promising examples are introduced more in detail below, and a more comprehensive summary is given in Table 2.

Recently, Cani et al. [116] reported on synthesised doped TiO<sub>2</sub> NPs firmly embedded on the surface of a silica matrix (SiO<sub>2</sub>). They investigated six different grades of TiO<sub>2</sub> doping from 10 to 60 (wt%) on the silica matrix. Overall, they found that these novel photocatalysts showed higher photocatalytic activity towards phenol and rhodamine B under both UV and visible light irradiation. Interestingly, even if the removal efficiency for UV treatment was still higher with TiO<sub>2</sub> NPs embedded with SiO<sub>2</sub> (TiO<sub>2</sub>NP@SiO<sub>2</sub>), both treatments with UV and Vis irradiation resulted in higher removal efficiencies compared to the common NP benchmark P25 TiO<sub>2</sub>, which is remarkable. Despite initial adsorption taking place, the authors demonstrated the highest photocatalytic degradation of both phenol and rhodamine B under visible light by using 10%TiO<sub>2</sub>NP@SiO<sub>2</sub> (3.02 eV; 390 m<sup>2</sup> g<sup>-1</sup>) and under UV light by using 60%TiO<sub>2</sub>NP@SiO<sub>2</sub> (3.13 eV; 295 m<sup>2</sup> g<sup>-1</sup>). The authors concluded that under visible light less doped SiO<sub>2</sub> surface with TiO<sub>2</sub> NP resulted in better adsorption in the visible light range, but the photocatalytic activity was still lower compared to UV light. Nevertheless, the higher sample adsorption on 10%TiO<sub>2</sub>NP@SiO<sub>2</sub> influenced positively the photocatalytic degradation performance.

Additionally, Mousavi and Ghasemi [117] reported on a photoactive black-TiO<sub>2</sub>/CoTiO<sub>3</sub> catalyst to degrade selected organic dyes with significantly increased efficiency under visible light ( $\lambda = 450\text{--}650$  nm; LED light source). They achieved almost 100% degradation efficiency for rhodamine B and MB, as well as for methyl orange and tetracycline, after 60 min under visible light irradiation. They evidenced that all three radical species  $\bullet\text{OH}$ ,  $\bullet\text{O}_2^-$ , and  $h^+$  played a vital role in the degradation process. Furthermore, they highlighted that their nanocomposite was able to be recycled and reused after seven runs of the dyes' degradation.

Even though nanocomposites based on TiO<sub>2</sub> photodegrade organic dyes, other NP materials are also developed as photocatalysts to improve the photodegradation of other organic compounds. Most novel synthesised NPs are doped with metals to achieve better degradation performance. Additionally, for some NPs, such as cobalt (Co) and cobalt oxide (Co<sub>3</sub>O<sub>4</sub>), enhanced photocatalytic activity under solar irradiation was reported with doping on specific surfaces [118]. In more detail, the authors reported solar-mediated photocatalytic degradation of murexide dye and eriochrome black-T dye in wastewater using nanoparticles of Co and Co<sub>3</sub>O<sub>4</sub>, respectively. The achieved removal efficiencies are comparable to those reported by Cani et al. [116] for other organic compounds. However, Co NPs were applied to photocatalytically degraded murexide dye and achieved 43.6% degradation efficiency with an exposure time of 40 min through sunlight irradiation. Co<sub>3</sub>O<sub>4</sub> NPs were applied to photocatalytically degraded eriochrome black-T and achieved 39.4% degradation efficiency with an exposure time of 30 min by sunlight irradiation.

Additional studies reported on the application of photocatalysts to other organic compounds and dyes using visible light. Guo et al. [119] reported that copper phosphide (Cu<sub>3</sub>P) NPs have a bandgap of 2.72 eV to degrade tetracycline as a target antibiotic under visible light. They showed that the synthesised composite with 6% doped Cu<sub>3</sub>P NPs resulted in the highest degradation rates of up to 97% of tetracycline (30 mg L<sup>-1</sup>; 0.25 g L<sup>-1</sup> catalyst; 40 min; visible light irradiation), corresponding to an eight-times higher degradation rate compared to pure hollow tubular carbon nitride without doping. The authors concluded

that the enhanced photocatalytic degradation was not only a result of increased specific surface area but also due to the improved capture ability of incident light.

For readers who are more interested in photocatalytic degradation by nanomaterials, the reviews of Bethi et al. [113] and Kefeni and Mamba [120] are highly recommended. The latter reviewed several ferrite nanoparticles and nanocomposites regarding their use in wastewater treatment and their pollutant removal capacities. Some of the catalysts, such as  $\text{CuFe}_2\text{O}_4 + \text{H}_2\text{O}_2$ , showed very high removal efficiencies for specific dyes. Most of them were still activated by UV light. With ongoing trends and further research, it is expected that novel NPs with or without specific doping will be developed that are mainly activated by visible light (i.e., sunlight), which will lead to more cost-efficient and environmentally friendly photocatalytic treatment of harmful wastewater pollutants.

**Table 2.** Comparison of different nano-photocatalysts for degradation of different dyes.

Treated Compound	Photocatalyst	Bandgap (eV)	$C_{\text{dye}}$ ( $\text{mg L}^{-1}$ )	$C_{\text{cat}}$ ( $\text{g L}^{-1}$ )	Light Source	Time (min)	Efficiency (%)	Ref.
Direct Red 80	Bentonite/TiO <sub>2</sub> /Ag0.25	3.26	10	0.6	UV	120	77	[114]
	NiO/CuO composite	3.80	60	0.05	Sun	60	67	[121]
	Co <sub>3</sub> O <sub>4</sub>	1.85–2.10	10	0.3	Sun	30	78	[122]
Methylene blue	Bentonite/TiO <sub>2</sub> /Ag0.25	3.26	10	0.6	UV	120	100	[114]
	rGO/TiO <sub>2</sub> /CdO/ZnO/Ag	2.58	96	50	UV	15	91	[115]
	B-TiO <sub>2</sub> /CoTiO <sub>3</sub>	2.32/2.40	5	1	Vis	30	98	[117]
	Fe <sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub> /TiO <sub>2</sub>	-	30	0.25	UV	300	100	[123]
	1%Ag-ZnO composite	3.02	10	0.1	Sun	30	98.5	[124]
Methyl Orange	B-TiO <sub>2</sub> /CoTiO <sub>3</sub>	2.32/2.40	5	1	Vis	60	99	[117]
	La <sub>0.7</sub> Sr <sub>1.3</sub> CoO <sub>4</sub> Ruddlesden-popper nanoparticles	2.50	20	5	UV	75	94	[117]
	1%Ag-ZnO composite	3.02	10	0.1	Sun	30	92	[124]
	30%TiO <sub>2</sub> /0.3HZSM-5	-	10	2	UV	150	99.5	[125]
Rhodamine B	B-TiO <sub>2</sub> /CoTiO <sub>3</sub>	2.32/2.40	5	1	Vis	20	99	[117]
	60%TiO <sub>2</sub> NP@SiO <sub>2</sub>	3.13	200	1	UV	180	70	[116]
	60%TiO <sub>2</sub> NP@SiO <sub>2</sub>	3.13	200	1	Vis	180	60	[116]
	Ag <sub>3</sub> PO <sub>4</sub>	2.51	150	0.3	Vis	180	96	[126]
	G-C <sub>3</sub> N <sub>4</sub> /Ag@CoWO <sub>4</sub>	2.30	100	0.1	Sun	120	97	[127]
Phenol	10%TiO <sub>2</sub> NP@SiO <sub>2</sub>	3.02	200	1	UV	180	50	[116]
	10%TiO <sub>2</sub> NP@SiO <sub>2</sub>	3.02	200	1	Vis	180	35	[116]
	TiO <sub>2</sub>	3.20	20	1	UV	450	90	[128]
	Mn <sub>0.6</sub> Zn <sub>0.4</sub> Fe <sub>2</sub> O <sub>4</sub> @Zn <sub>1-x</sub> Mn <sub>x</sub> S	2.57	25	1	Vis	180	99	[129]
Murexide	Co NP	-	50	1.0	Vis	30	43.6	[118]
Eriochrome black-T	Co <sub>3</sub> O <sub>4</sub> NP	-	50	1.0	Vis	30	39.4	[118]
	Potassium zinc hexacyanoferrate nanocubes	-	10	1.5	UV-Vis	120	76	[130]
	Ho(OH) <sub>3</sub> NP	4.14	1	0.04	UV	100	80	[131]
	Nd <sub>2</sub> Zr <sub>2</sub> O <sub>7</sub> NP	3.30	3	0.12	UV	50	84	[132]
	Potassium zinc hexacyanoferrate nanocubes	-	10	1.5	UV-Vis	120	94	[130]
Malachite green	Chitosan/Ce-ZnO composites	2.5	5	0.05	Vis	90	83	[133]
	GP-ZnO-NP	3.41	10	0.2	UV	180	89	[134]
	Diatomite@Ni/NiO	1.71	25	0.2	UV	150	100	[135]

### 3.4. Membrane Filtration—Nanofiltration

Membrane filtration processes in wastewater treatment seem to be mainly focused on the specific branch of nanofiltration (NF) processes when considering the implementation of NTs. Even though the application of NF is not very common in municipal wastewater treatment, there are some relevant applications in industrial wastewater treatment to remove micropollutants and/or other harmful compounds. NF has many benefits over

ultrafiltration (UF) and reverse osmosis (RO). On the one hand, NF provides better rejection properties than UF. On the other hand, NF requires less energy than RO with nearly similar permeate quality [136].

Embedded NPs in nanomembranes and/or the formation of composite membranes have offered new chemical properties and behaviour of a new class of membranes. Thus, novel developments and/or improvements of nanocomposite membranes offer, in most cases, enhanced water purification, increased rejection, and permeate flux. However, their development requires the determination of optimal NP concentration and proper membrane characterisation. Commonly, different microscopic techniques such as transmission electron microscopy, atomic force microscopy, scanning electronic microscopy, and others are used. However, Zeta potential analysis describing membrane charge, X-ray photoelectron spectroscopy (XPS) analysing the surface chemical structure, and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) determining the functional groups present on the surface of the membrane are often required for proper membrane characterisation. Thus, several microscopic analyses combined with XPS, ATR-FTIR and filtration experiments are necessary to determine the optimum performance of membranes. Hence, the development of novel NF membranes coated or blended with NPs is a great challenge and requires very experienced scientists. In this section, we summarise only a few potential applications of the latest developments recently published. All of them are still at the state of science.

Wei et al. [136] summarised current developments of novel thin-film composite (TFC) NF membranes embedded with NPs such as  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and others for NF and UF providing improved water permeability, selectivity, fouling resistance, and separation performance [137–139]. Nevertheless, Wei et al. [136] also pointed out critically that the polymerisation process can be negatively affected by the agglomeration of inorganic NPs such as  $\text{TiO}_2$  during coating. As a consequence, NPs might form uncontrolled membrane structures or cause membrane blockage with declined permeate flux. Therefore, interfacial polymerisation of membranes with NPs is a sensitive and very challenging process for manufacturers. Wei et al. investigated TFC membranes with incorporated laminated  $\text{TiO}_2$  NPs. Like others, they determined an optimum NP concentration by performing nanofiltration experiments. They showed that a  $\text{TiO}_2$  NP concentration higher than 0.3 ( $w/v\%$ ) significantly increases the membrane roughness, which resulted in reduced ion rejection due to agglomeration of NPs. Operating the novel TFC membrane instead, at an optimum concentration of 0.3%, resulted in the enhanced rejection of chloride and sulphate flux.

The successful removal of organic micropollutants and trace contamination such as endocrine-disrupting compounds from real wastewater with NF membranes intercalated with hydrophilic molybdenum disulphide nanosheets was recently reported by Dai et al. [140]. The authors designed novel NF membranes providing hydrophilic surface and nanochannels in the membrane active layer, which enhanced the rejection of tested micropollutants, such as benzylparaben and propylparaben. The authors demonstrated that the novel membrane provided increased water permeability compared with the control membrane and enhanced micropollutant rejection due to suppressed hydrophobic interaction between the membrane surface and hydrophobic endocrine-disrupting compounds. The removal of parabens and other endocrine-disrupting compounds from municipal and industrial wastewater is still a big issue because they can cause adverse effects on human health. Therefore, more developments in their elimination, for example, through advanced NF membranes, is highly welcome and needs to be further progressed.

The development of NF membranes with benzoate ferroxane NPs for the removal of dyes was also reported [141]. Like Wei et al. [136], the authors also determined that increasing blends of NPs into the polymer matrix of the membrane material (polyethersulfone) increased agglomeration which decreased the water flux. Thus, optimal conditions were determined with NP blending ratio up to 0.25 wt%. The novel membrane rejected dyes such as Direct Red and MB by 99% and 98.4%, respectively. Dye removal via NF membranes embedded by hydrophilic graphene quantum dots was also recently reported [142].

According to the authors, synthesised polyvinyl chloride membrane blended with quantum dots resulted in enlarged porosity and improved hydrophobicity, helping to enhance the membrane permeability. The flux could be increased from 69% to 80%, and the rejection of the dye Reactive Blue 19 from wastewater was more than 98%. Nevertheless, these designed membranes are still not state-of-the-art due to their high production costs.

The use of NPs is not only limited to the removal of pollutants from wastewater but also the recovery of important resources, such as phosphorus [143]. Even though phosphorus is an important resource for life, its presence in wastewater poses a serious threat to water quality—namely, eutrophication. However, the use of NF blended with gold NPs can help to separate phosphate in a trivalent form, allowing its mono- and divalent forms to permeate during phosphate recovery [143]. The authors recommended the use of alkaline feed water to obtain high removal rates and optimal membrane permeability. Those NF membrane applications might not be favoured in conventional wastewater treatment but might be interesting treatment approaches for industrial wastewater with higher phosphorus concentrations and legal requirements of P recovery (industrial or agriculture wastewater).

Khalid et al. [144] reported on the development of novel poly(vinyl alcohol) nanofiltration membrane coated with TiO<sub>2</sub> NPs providing enhanced antifouling properties to treat paper and pulp mills wastewater. The NF membrane exhibited excellent removal of dissolved pollutants and microorganisms. Although the authors reported problems in declining flux due to blockage of pores by NPs, the permeate quality outcompeted the permeate quality of conventional NF membranes. Certainly, further research is required to further stabilise this specific membrane type. However, the potential of NP-coated NF membranes demonstrates that NTs also found access to industrial and, in some cases, municipal wastewater treatment. It might be only a question of time until NF implemented with NTs will result in further exciting research outcomes.

#### 4. Applications in Drinking Water Production

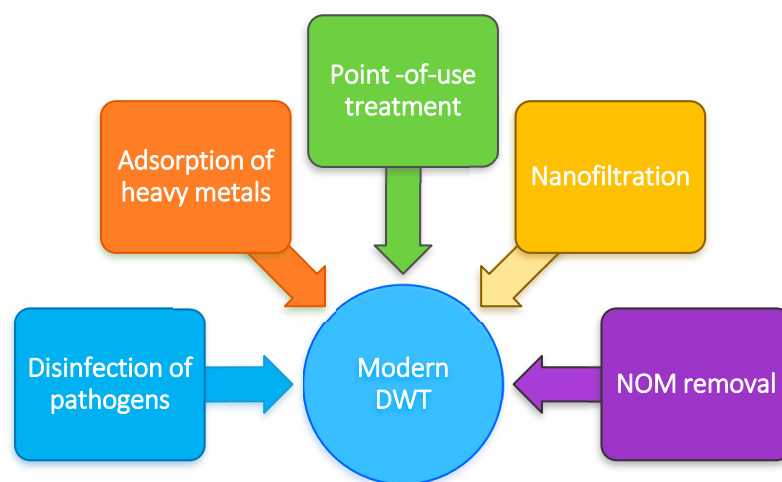
In drinking water treatment, NT has also become an important branch with rising interests and potential to further advance the production process. The application of TiO<sub>2</sub> and Ag has gained importance since the remarkable antimicrobial activity of these metal-based NPs has been demonstrated. However, in comparison to other branches applying NTs, NP-based technologies are still barely applied in the drinking water sector. It is expected that applications of nanomaterial and, especially, NPs will also find further application as advanced drinking water production technologies such as in other sectors (i.e., remediation, wastewater treatment and agriculture-food sector including packaging). In modern drinking water treatment, NT can contribute to the advanced disinfection of pathogens, removal of heavy metals, point-of-use treatments, and the removal of natural organic materials (NOM). Most applications of NP in drinking water treatment led to disinfection technologies, removal of heavy metals mainly via adsorption, nanofiltration, and removal and/or detoxification of organic pollutants (Figure 6).

##### 4.1. Advanced Disinfection through the Application of NPs

The disinfection of viruses, such as adenovirus, norovirus, rotavirus, and hepatitis A, and of bacteria, such as *Escherichia coli*, *Shigella dysenteriae*, *Salmonella typhimurium*, and *Vibrio cholerae*, is attracting attention with regard to more environmentally friendly treatments. Water contamination with viruses and pathogens can occur in both groundwater and surface water and require unrestricted disinfection [145].

Commonly, disinfection in drinking water treatment plants (DWTPs) is carried out conventionally with chlorine, ozone (O<sub>3</sub>), ultraviolet (UV) irradiation, chlorine dioxide (ClO<sub>2</sub>), or chloramines (NH<sub>2</sub>Cl) [146]. Disinfection with chlorine is widespread but has some relevant drawbacks. Overdosing of chlorine can result in typical chlorine odour and taste. However, the main obstacle of chlorine disinfection leads to the release of harmful disinfection by-products when organic compounds are present [147]. According to

Woo et al. [148], some of them have been identified as carcinogenic. Ozonation can overcome most of the problems caused by chlorine disinfection and is, therefore, a powerful tool in drinking water disinfection. Organic compounds are easily oxidised, bivalent iron and manganese are oxidised, no influences in odour and taste occur, and viruses and pathogens are greatly inactivated. Nevertheless, the instability of ozone leads to increased production rates, which also indirectly increases the energy demand and, therefore, the treatment costs. In addition, ozonation can release relevant quantities of aldehydes, carboxylic acids, and other carcinogenic compounds by insufficient oxidation of organic matter (NOM).



**Figure 6.** Contribution of NTs on modern drinking water treatment.

Alternatively, UV irradiation can offer a secure treatment without the production of unintentional by-products. Unfortunately, UV treatment is highly energy demanding which increases treatment costs and, thereby, decreases the eco-friendly image. In recent years, photocatalytic oxidation has become more and more established as cost-efficient and eco-friendly technology for drinking water disinfection.  $\text{TiO}_2$  is one of the widely used catalysts due to its low toxicity and less corrosive effects [149]. The mode of action of  $\text{TiO}_2$  as photocatalyst is the generation of ROS, especially hydroxyl radicals and hydrogen peroxide [145]. However, Liga et al. [145] showed that the inactivation rates of  $\text{TiO}_2$  were often very low against viruses. The efficiency of  $\text{TiO}_2$  can be even more enhanced if Ag NPs are doped on  $\text{TiO}_2$  resulting in increased production rates of hydroxyl radicals which significantly increase the disinfection rates. Liga and colleagues recommended this technology either as a point-of-use application (i.e., decentralised treatment) or as municipal-scale applications.

Applications of Ag NPs were also often reported to be applicable without UV irradiation for drinking water disinfection [150–152]. The main mode of action of Ag NPs is the release of silver ions that can damage the cell membrane through direct contact or damage nucleic acids and other cell compounds. To overcome some relevant drawbacks of Ag NPs in disinfection during drinking water treatment, nanocomposites were recently developed combining some desirable properties (i.e., antimicrobial activity, generation of ROS, no release of toxic by-products). Rai et al. [153] also pointed out reaction kinetics during disinfection for better controlling contact times and Ag NPs for more cost-effective application may preferably be applied in an immobilised form, i.e., nanocomposite. For immobilising Ag NPs, different carriers can be used such as zeolite, silica, or fibreglass, natural macro-porous materials, carbon materials, paper, and polymers of different types. The use of alginate beads to immobilise Ag NPs was also proposed as advanced development for point-of-use drinking water treatment [147]. Some commercial filter systems applying antibacterial disinfection for point-of-use treatment with immobilised Ag NPs are nowadays available such as Lifestraw, Tata Swach, Karofi, or Tupperware [147,154,155].

However, some concerns have been raised that leaching silver ions could impact human health. Therefore, Rodrigues Rosa et al. [156] have investigated the bioaccessibility of colloidal Ag and Ag NPs in drinking water filters and found that Ag NPs were less accessible. The determined hazard quotient was below 1, indicating that no risk is expected. Mpenyana-Monyatsi et al. [157] determined the required material loads and flow rates for a cation resin-silver NP filter system for drinking water disinfection for point-of-use application. They found that already 15 g bed mass was sufficient to provide 15 L of disinfected drinking water daily. The filter system achieved a 100% removal rate of the target microorganisms investigated. Thus, only small bed volumes are required to deliver high water purity and quality. Still, the main drawbacks of Ag NPs application in disinfection of drinking water are aggregation, leaching, and uncertain effects on human health and the environment [18]. Therefore, this application strategy needs to be further improved and more deeply investigated, addressing all issues mentioned above.

#### 4.2. Removal of Heavy Metals from Drinking Water by NPs

Another important application of NPs in DWTP is the removal of heavy metals either by adsorption, ion exchange or membrane filtration. Regarding their implementation, the former seems to be still in its infancy. In general, adsorption of heavy metals is well investigated, and mechanisms and adsorption capacities for many nano-based materials were recently reported (see also Section 3.1). Their application is not restricted to wastewater only, but also most developments seem to be focused on that direction. Overall, fewer developments of NPs seem to be published for drinking water applications. Therefore, we summarise only a few outcomes recently published. Arora [158] reviewed nanomaterials, including NPs, for drinking water treatment and stated that most of them such as ZnO, CuO, TiO<sub>2</sub>, Mn<sub>3</sub>O<sub>4</sub>, and others show excellent adsorption capacities towards arsenic, but their commercial production is still too expensive. This might also be the reason why the adsorptive removal of arsenic impurities is currently not very commercialised through nano-based adsorption columns to treat groundwater and surface water. However, on the one hand, the global drinking water demand is continuously increasing, and on the other hand, secure and simple purification techniques are becoming more and more important. Therefore, further research and novel developments towards nano-based adsorption technologies might also cope with the increased water demand due to their higher adsorption capacities. Pinakidou et al. [159] reported the development of tetravalent manganese ferrihydrite NPs for As(V) removal from drinking water. The author stated that their procedure to polymerise the metal-oxyhydroxyl chains led to more adsorption sites on the NPs and, thereby, enhanced the As uptake. Their adsorption experiments revealed 2.09% to 2.49% adsorption of As. Unfortunately, Pinakidou et al. [159] did not provide the adsorption capacity of their NPs. Other heavy metals such as Pb, Cd, and Ni can be easily adsorbed utilising NPs based on CeO<sub>2</sub>, Fe, or Ag [160]. However, Simeonidis et al. [161] pointed out that in real drinking water application, nano-based adsorption might fail due to several coexisting interferences caused through the specific water chemistry. Regardless, they highlighted the use of magnetite NPs for Cr<sup>6+</sup> removal, achieving adsorption capacity of 2 µg mg<sup>-1</sup> from natural water, and they used low-cost iron sources (FeSO<sub>4</sub> and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>) for producing magnetic NPs and demonstrated that even at a pH higher than 7.5, the initial concentration of 50 µg L<sup>-1</sup> of Cr<sup>6+</sup> was reduced below 10 µg L<sup>-1</sup> within 5 h. They also calculated the cost of producing their NPs and the annual cost for water treatment to each inhabitant if the initial concentration is 50 µg L<sup>-1</sup> Cr<sup>6+</sup> was around 3.5 EUR/kg on a dry basis and 5 EUR/year, respectively.

The advanced adsorption of fluoride from drinking water through magnetic NPs was also recently reported by different scientists all over the world. The contamination of fluoride in drinking water sources can be caused by industries and can increase to up to 5 mg L<sup>-1</sup> [162]. The authors developed core-shell Ce-Ti@Fe<sub>3</sub>O<sub>4</sub> NPs showing high efficiency for fluoride removal with an adsorption capacity of 91 mg g<sup>-1</sup> at pH 7. The authors highlighted that these NPs showed applicability over a wide pH range (from 5

to 11). They compared their adsorption capacities with 18 other developed NPs reported. Only  $\text{Fe}_3\text{O}_4@\text{ZrO}_2$  NPs developed by Riahi et al. [163] showed a higher adsorption capacity, i.e.,  $158.6 \text{ mg g}^{-1}$ . However, this high adsorption capacity was achieved at pH 2.5 while Markeb et al. [162] worked at neutral pH. Even more important, Markeb et al. [162] showed that the absorbent was easy to recover and achieved the quality standards of drinking water during treatment of fluoride-contaminated natural water.

The combination of NPs with membrane technology seems to be more beneficial compared to adsorption processes with immobilised NPs for selective heavy metal removal. Roy et al. [164] reported on nanofiltration (NF) membranes with embedded NPs leading to better performance, higher fouling resistance, featuring antimicrobial properties and in some cases also indicating better ion selectivity. Concerns of increasing costs in membrane fabrication could be prevented using imprinted grafting-form membranes, which are synthesised by inexpensive precursors, lowering the costs significantly. An example for successful implementation of NPs in microfiltration membrane for As(III) removal was recently presented by Luan et al. [165], who achieved removal rates up to 90% in a pH range of 5.0 to 9.0.

The application of nanocomposite membranes and, especially, nanofiltration processes in drinking water production has been well established for more than two decades. Therefore, membrane technology based on nanomembranes for advanced drinking water purification technology is meanwhile commercialised, and higher demand for nanocomposite membranes also reduced production costs. Similar developments might also be expected for the adsorption of heavy metals through NPs with increasing demand for drinking water in future.

#### 4.3. Removal of Organic Compounds from Drinking Water by NTs

Up to now, there are only a few studies focusing on the application of NPs for organic compound removal in drinking water treatment. The removal of NOM is mainly achieved through adsorption followed by photocatalytic degradation, as demonstrated with  $\text{TiO}_2$ -NPs [166]. The authors described both steps more in detail. First, the adsorption of the organic compound takes place, which only reduces the concentration of the pollutant in the media. Without UV irradiation, no degradation occurs. Irradiation initialises the release of ROS and other radicals as above-mentioned. Those carry out the final degradation step of the organic compound, for example, on the surface of  $\text{TiO}_2$ . Unfortunately, UV irradiation can often result in the release of undesirable disinfection by-products also in combination with  $\text{TiO}_2$  NPs if the treatment time is too short. Gora et al. [167,168] proposed the use of linearly engineered  $\text{TiO}_2$  nanomaterials for the removal of those by-products. However, they estimated that the energy demand for a successful removal would require 8 to 36 times more energy than that required for UV/ $\text{H}_2\text{O}_2$  treatment, making this application not compatible for now. Further research might lead to important improvements toward NPs in the removal of NOM in future.

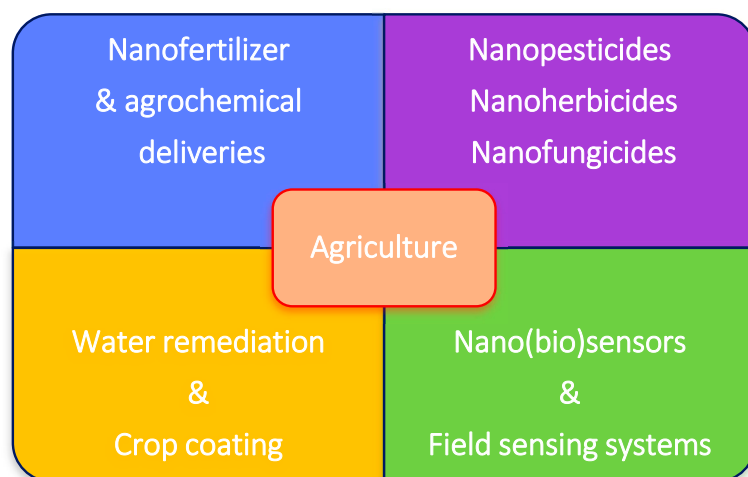
Despite photocatalytic application, Kumari and Gupta [169] recently proposed the use of magnetic nano-absorbents for the removal of aromatic and hydrophobic fractions of NOM from drinking water. They achieved very high removal rates of 98.7% and 91.0% for trihalomethane precursors and trihalomethane, respectively. Further, they demonstrated that the developed magnetic nano-absorbents alum conjugated process was extremely efficient removal, not only for NOM but also turbidity. This simultaneous removal could lead to a single treatment system comprising absorption and reduction of NOM, which could also be realised with low-cost materials. Thus, further research in this area is highly welcome to promote single-stage treatment systems with lower treatment costs and more environmentally friendly benefits.

To summarise, it can be stated that NTs in DWTP are still at an early stage but with very promising outcomes so far. Further promotion to investigate more reaction mechanisms and to assess potential risk (comprising both human and environment) is urgently required to better implement NTs as advanced drinking water treatment technology.



## 5. When Agriculture Meets with NTs

There are some relevant applications and important developments of NTs in the agriculture sector. However, hitherto, it seems that mainly NPs have entered the global market in the past decade. With regard to improving the primary plant and crop production, four main application areas are currently dominating the market, i.e., nanofertilisers, nanopesticides/nanoherbicides, nanobiosensors, and nano-based remediation (for the latter, please see Section 2) (Figure 7).



**Figure 7.** Application possibilities of NTs in agriculture.

According to Parisi et al. [170], there are some very specific reasons for the reserved developments and low benefits in this sector. One major reason for the slow implementation of NTs in agriculture is insufficient and unclear technical benefits, while the investment costs for R&D are still very high. Another major reason is the uncertainty of regulating NTs and non-standardised international levels (i.e., legislative uncertainties). Thus, different assessment and risk analyses in different countries do not promote larger companies to apply similar NTs globally. Regulations on the European market are completely different from those on the American market, which hamper larger industrial organisations and companies investing in these technologies. Parisi et al. [170] pointed out that agro-chemical companies tend to hold and keep broad patents assuring future exploitation in case the global market will be more open for NTs application in this sector. The potential for significantly enhanced agricultural productivity and efficiency with reduced cost and waste is still attracting companies to keep track of novel developments of innovative NTs in the agriculture sector [171].

Despite uncertain regulations, uncertainties of the behaviour and interaction of NMs in living organisms prevent further increases in their application. Still, there are some serious doubts about whether NMs lead to toxic effects on human beings and the environment. Therefore, their application is still limited [172,173]. Up to date, the scientific community has not been able to draw a clear image of the effects on living organisms. These uncertainties lead to further public doubts preventing the acceptance of NMs in agriculture.

Nevertheless, the use of nanofertilisers, nanopesticides/nanoherbicides, and nanobiosensors aim at enhancing fast seed germination, increasing biomass production, improving root–shoot elongation, and advancing precision farming (i.e., maximising crop yield by modelling) [172,174]. Different NMs are used such as metal-based NPs, including Ag, TiO<sub>2</sub>, or ZnO, magnetic NPs, such as manganese oxide (MnO) and iron oxide, or polymeric NPs, such as carbon-based NMs or graphene, and others. In the following sub-chapters, we will focus on the current state-of-the-art concerning nanofertilisers, nanopesticides and nanoherbicides, and nano(bio)sensors for precision farming in more detail.

### 5.1. Nanofertilisers in Agriculture

Nanofertilisers are one of the most promising applications of NTs in agriculture. They comprise nanocapsules, nanoparticles and viral capsids; and are commonly applied to enhance nutrient adsorption by delivering them to specific crop sites [170]. The main reason to further promote the development of nanofertilisers seems to be obvious. Traditional uses of conventional chemical fertilisers lead to high losses due to volatilisation and/or leaching depending on the specific soil characteristics. DeRosa [175] stated that up to 70% of nitrogen-based fertilisers are lost to the environment, either by leaching nitrates, emission of ammonia, or long-term incorporation into soil organic matter. Overall, this can cause nitrogen overloads, therefore highly risking nitrogen-based contamination of soils, sediments, and groundwater, resulting in eutrophication and/or residual contamination.

Another important reason for fertiliser losses is the rapid release of nutrients from fertilisers into the environment once they are emitted. Usman et al. [174] reported nitrogen-based fertiliser losses range between 30 and 60%. Additionally, phosphorus-based losses and potassium-based losses range between 80–90% and 50–70%, respectively [176,177]. Thus, fertilisers with a slow release of their nutrients are a major goal in developing novel fertilisers to improve the accessibility of poorly available nutrients over a long term [178]. This can be achieved by nutrient encapsulation, releasing the nutrients slowly. The reduced nutrient release does not only lead to reduced fertiliser production costs but also results in a more environmentally friendly way of handling available limited resources. Nano-coated urea or hydroxyapatite fertilisers, for example, offer both better-controlled releases of nitrogen and drastically reduced ammonia volatilisation. Usman et al. [174] reported that such nano-based fertilisers could maintain stable release rates of at least four weeks or longer. In India, biodegradable polymeric chitosan nanoparticles have been applied as slow-releasing fertilisers of nitrogen, phosphorus, and potassium [179]. The results were very promising as well as those of kaolin and polymeric biocompatible NPs [180]. The advantage of using polymeric carriers or other encapsulated nanofertilisers leads to rapid adsorption on roots of the plant which prevents leach out and/or run-off. Duhan et al. [181] reviewed very different detailed mechanisms of encapsulated nanofertilisers. They stated that encapsulated nano-silica also prevents crop infections by bacteria and fungi. Other encapsulated nanofertilisers such as silicon-based could increase crop resistance and TiO<sub>2</sub>-based nanofertilisers can be used as additives to increase water retention. Chhipa [182] delivered a very detailed overview of different nanoparticle-based nanofertilisers and their impact on agricultural crops.

Current developments also favour better internal stimuli from the roots to nutrient release, which affect ethylene production in response to nitrogen and/or phosphorus deficiency [174,183]. Concerning the enormous amounts of chemical fertilisers used, novel developments for slow-release nano-based fertilisers stimulating positive crop growth will definitively not only be a fancy future area for ambitious scientists but also address well current debates on growing food demands through continuously worldwide growing populations.

### 5.2. Nanopesticides and Nanoherbicides in Agriculture

The use of conventional pesticides is very well established in modern agriculture, maintaining to a certain extent maximised crop yields. According to Carriger et al. [184], only small amounts of the applied pesticides reach the target pest (less than 1%) that impacts not only the food chain and human health but also negatively impacts the environment. Duhan et al. [181] stated that the worldwide consumption of pesticides is about two million tonnes per year. The main drawback of using conventional pesticides leads to their global hazardous effects on the environment [174]. In contrast, nano-based pesticides show slow degradation and effective pest control over a long time [174,182]. Thus, they can be applied less frequently and in smaller amounts decreasing also environmental damages. Therefore, nanopesticides are also very promising alternatives as they are cheaper and seem to provide reliable control of pests [181].

Like nanofertilisers, nanoformulations also result in reduced application and demand, finally promoting increased crop yield [174]. It should be mentioned that the term nanopesticides refer to pesticide formulation that involves either very small particles of a pesticide's active ingredient or other small engineered structures with useful pesticidal properties, while the term nanoformulation refers to pesticide formulation with potentially greater solubility, mobility, and durability [185,186].

For some nano-based pesticides, significant reduced environmental toxicity was recently reported, such as for the insecticide nano-imidacloprid (IMI) [187], or for nanoformulations of permethrin [188], multi-residue pesticide polyethylene glycol [189], multi-residue insecticide carbofuran and for the organophosphate insecticide acephate [190]. Interestingly, nano-IMI also indicated enhanced photodegradation compared with the conventional formulation of the bulk compound. Nano-acephate showed lower toxicity against non-target organisms. Chhipa [182] also reported very efficient nanoformulation of fungicide, tebuconazole, pesticide, validamycin, diuron, and others.

NMs based on NPs such as Ag [191], iron oxide [192], copper [193], and aluminium [194] were reported as useful pesticides against bacterial, fungal, and viral diseases [195]. The use of encapsulated nanopesticides seems to be most efficient due to its better-controlled and slow release of active ingredients such as nanofertilisers. Thereby, they can deliver more precise site-target activity with higher stability. Encapsulated nanopesticides not only provide these features but also polymeric nano-spheres, nanogels, and nanofibres were developed with similar ingredient action. Some poorly water-soluble pesticides, such as nano-emulsions and nano-dispersions, have been developed to enhance their bioavailability [185].

In agriculture, weed elimination is one of the most challenging and biggest threats. An unintentional high rate of weeds can simply result in declined crop yield. From an economical point of view, the presence of weeds is unpleasant and ought to be minimised as much as possible by using, for example, common herbicides such as glyphosate. However, high amounts of herbicides are required to be utilised, while similar to common pesticides, only minor amounts reach the target. For this reason, nanoherbicides are also very promising in decreasing the effective amounts required, therefore, protecting the environment.

Most nanoherbicides rely on biodegradable polymeric substances encapsulating, for example, common herbicides such as atrazine, ametryn, simazine, and paraquat [174,196]. On the one hand, nanoherbicides provide a longer lifetime. Additionally, on the other hand, they can be easily adsorbed by plants where encapsulates slowly release their active substances. For most of them, increased activity and enhanced plant protection were recognised. Similar observations were reported for nanoemulsion of glyphosate due to increased bioavailability [197]. Overall, there are some very promising scientific articles reporting nano-based herbicides that show more effective activity at lower concentrations as compared to their commercial formulation. Furthermore, the increased activity to reduce inputs leads to significantly reduced soil and groundwater contaminations. However, like nanofertilisers and nanopesticides, the environmental risks are still very uncertain due to the lack of reliable analytical methods and several difficulties measuring NMs in situ. Therefore, some preliminary results on invertebrates might allow judging the potential risks of nanoherbicides [198]. At the moment, it seems that in many cases, nanoherbicides might be more environmentally friendly than their commercialised counter-herbicides.

### 5.3. Nano(bio)sensors for Precision Agriculture

Precision farming is a relatively young scientific discipline, especially with regard to NT implementation. The overall aim of precision farming is to maximise crop yield by minimising inputs (e.g., fertilisers, pesticides, herbicides) through monitoring environmental variables and applying targeted action [181]. Klerx et al. [199] termed precision farming as smart farming and agriculture (digitalisation of conventional farming) to enhance both crop yields and environmental protection.

However, precision farming requires several online data such as fertility, moisture level, temperature, crop growth, diseases, weeds, and others in order to model real-time conditions that support farmers in their decision of action [200,201]. Smart farming requires an excellent understanding of field conditions processed by computers and followed by data analyses, which farmers might not be able to deal with or simply do not accept [199].

Thus, the basic idea of precision farming includes a fusion of computers, sensors, global satellite positioning systems, and remote sensing devices to obtain as much as available online data. They are continuously evaluated by powerful software tools toward maximising crop yields [181]. Precision farming provides a smart solution to local demands which will finally lead to reduced chemical consumption, costs, and environmental damages. It is evident that precision farming is currently a quite futuristic intention but bearing in mind that food demand by 2050 is expected to increase by 70% and meat production will increase by 50%, making the concept of precision farming an important key industry of tomorrow [202,203].

How can NT help to promote further developments in precision farming? Nanosensors are a smart solution to contribute to the development and progression of precision farming. In this context, nanosensors are applied to rapidly detect pathogens and contaminations inhibiting crop growth that would negatively impact crop yield. Acharya & Pal [172] highlighted the application of NTs in electronic devices equipped with nano-based light-emitting diodes that are already applied to determine the chlorophyll status of individual crops indicating their health status. Applications of such devices lead to a significant reduction in pesticides and other agrochemicals because specific crop treatments can then be realised individually and/or locally. Duhan et al. [181] presented a complete bench of different nano(bio)sensors towards precision farming. Nano(bio)-sensors based on inhibition of enzyme reaction or others based on nanogenetics are applied to detect and quantify bacteria, viruses, and pathogens. Additionally, sensors for precise pesticide detection (e.g., organophosphates, methylparathion, chlorpyrifos, and carbufuran) and soil nutrients determination based on sensors of carbon nanotubes or nanoparticles for gases detection (e.g., ammonia, nitrogen oxide, hydrogen sulphide, sulphur dioxide, and volatile organics) can be applied. Antonacci et al. [204] emphasised the fact that nano(bio)sensors have some relevant advantages compared with last generation (bio)sensors. Further, they pointed out that nano(bio)sensors show higher sensitivity, faster response time, ability to mediate fast electron-transfer kinetics (important for enzymatic reactions), higher stability and longer lifetime [205]. Another advantage leads to the fact that nano(bio)sensors are better applicable in complex matrices such as soils with low homogeneity and retained chemicals, increasing analytical background noise.

In future, it is expected that precision farming will also lead to the development of agricultural robots equipped with such nano(bio)sensors. Such robots could help farmers as a “decision support system” by selective robotic weeding. Acharya and Pal [172] called this the ultimate objective of precision agriculture. In addition, plant-specific management such as fertilising a crop or weeding is conceivable. Mali et al. [206] simplified the use of nano(bio)sensors calling it “sensing, detection, and monitoring” of any biochemical and biophysical signal associated with specific stress at the level of a single molecule or cell. Somehow this might sound far-fetched, but according to Feynman (1960), “*there is plenty room at the bottom*”, which we still need to discover, investigate, understand, and apply with respect and responsibility toward next generations.

## 6. Conclusions

The environmental NTs sector is still a young branch compared to other commercialised sectors. However, this sector is starting to become more and more open on the global market. Once governments have defined clear and strict regulations and harmonised international standards, environmental NTs will spread and attract more and more environmental markets. Several NT developments are already successfully applied in environmental remediation due to higher reactivity leading to rapid transformation and/or

detoxification of hazardous waste sites. However, long-term studies will show whether the predicted stability will turn into truth or whether unexpected changes in environmental conditions will have impacts on the application of NPs in environmental remediation.

In wastewater treatment, the potential of rapid pollutant degradation seems not exhausted. Adsorption and chemical degradation of industrial dyes with cytotoxic effects was recently demonstrated. However, it is expected that NTs will also lead to significant development towards the elimination of organic trace pollutants in municipal wastewater treatment. Additional purification stages after biological treatment applying, for example, reactive surfaces doped with catalytic NPs might be one solution for the removal of anthropogenic pollutants.

Similar developments and trends arise in the sector of drinking water treatment. Currently, NTs are mainly applied with regard to the disinfection of pathogens, such as *Escherichia coli*, *Shigella dysenteriae*, *Salmonella typhimurium*, and *Vibrio cholerae*; adsorption of heavy metals; and removal of organic compounds. While application for disinfection is well established, application for heavy metal adsorption and organic compound pollution seems to be still in its infancy. However, it was demonstrated by several scientific groups that novel applications of NMs in drinking water treatment can be more cost-efficient and environmentally friendly compared to conventional treatment techniques. Thus, more acceptance and knowledge dissemination is required to further promote NTs' application in this branch.

In the agricultural sector, the application of NTs focuses mainly on nanofertilisers, nanopesticides/nanoherbicides, and nano(bio)sensors. As previously stated, the development and implementation of NTs in this sector seem to be greatly dependent on international regulations and precise risk assessments. There is a tremendous potential of NT applications in the agricultural sector, especially in the branch of precision farming. Interdisciplinary research is urgently required to progress further developments in this area due to increasing demands in food and other goods. With ongoing development, i.e., increase global populations, humanity will face some relevant challenges ensuring access to sufficient food, drinking water, sanitary service, and health care of high standards. High demands in food production will automatically lead to fostering the implementation of NTs in agriculture due to reduced consumption in terms of fertilisers, pesticides, and others; in terms of water delivery, when necessary; and in terms of optimised crop production according to seasonal changes and others. All these optimisations will hopefully lead to increased crop yields and decreased environmental damages.

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