Environmental Nanotechnologies in Wastewater Treatment

Nanotechnologies (NTs) are nowadays well established on both private households and commercial markets. NTs are fully accepted in several sectors such as medicine and pharmacy, or in industry such as chemistry, electricity, food production, military, and other commercial branches due to their unique properties. With regard to the growing demands on environmental resources caused through still growing worldwide population, application of NTs is an extremely important new branch in the environmental sector delivering several advantages. The entry provides a comprehensive overview on current developments in environmental remediation, wastewater treatment, drinking water treatment and agriculture. More in detail, in the section environmental remediation, the application on NTs towards enhanced reductive dechlorination, removal of heavy metals and remediation of oil spills were reviewed. Developments towards adsorption of heavy metals and persistent substances, advanced photocatalytic degradation of common wastewater pollutants, and improvements in membrane filtration processes were predominantely highlighted. 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.

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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, absorbents such as AC or biomaterials can also be generated several times, making this process more cost-effective [1]. 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^{-1} and USD 1.37 kg^{-1}, providing adsorption capacities between 2.18 g kg^{-1} and 15.47 g kg^{-1}, respectively. The price can easily increase up to USD 20.00 and even more if higher chromium adsorption capacities up to 50 g kg^{-1} are required [2]. 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 [1]. Apart from further developments using AC with several different surface modifications, novel nano-absorbents 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.

Overall, several novel nano-absorbents for 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, Cr^{6+} adsorption capacities up to 970.9 mg g^{-1} were reported for nitrogen-doped magnetic carbon nanotubes [3]. 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 unfavoured 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-absorbent materials for Cr^{6+} removal.

With regard to wastewater contamination, lead (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. [4] pointed out that those wastewaters provide higher complexity due to the coexistence of heavy metals and organic dyes. Like most heavy metals, Pb^{2+} also causes carcinogenic effects and is toxic at trace levels. Pb^{2+} tends to bioaccumulate and cause blood disease. Thus, efficient removal of 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 [5]. However, surface adsorption was often preferred due to high selectivity and producing no secondary pollutants. High Pb^{2+} adsorption capacities were recently reported for novel NPs with different modifications. Sheela and Nayaka [6] highlighted an adsorption capacity of 909 mg g^{-1} of 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 Pb^{2+} is a result of the metal ion radii, atomic weight, electronegativity, and other parameters. In their experiments, Sheela and Nayaka [6] found that Pb^{2+} outcompeted Cd^{2+}; thus, they proposed NiO NPs for the removal of Pb^{2+}, preferably, by adsorption. Additionally, Egbosiuba et al. [7] developed and investigated novel NP material and multi-walled carbon nanotubes (MWCNTs) for the enhanced adsorption of several heavy metals, including Pb^{2+}. They also compared the adsorption efficiency of MWCNTs-KOH@NiNPs between Pb^{2+} and Cd^{2+} and found a higher adsorption capacity for 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, Rezania et al. [8] 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 Pb^{2+}, the precipitation of hydroxide ($Pb(OH)_2$) starts above pH 6.0; thus, adsorption is not favoured at pH values higher than 6.0 [4]. For this reason, most developed adsorbents are applied close to pH 6.0. The adsorption capacities reported in most publications range between 100 mg g^{-1} and 500 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 [9]. Extraordinary adsorption capacities were achieved for all three heavy metals; however, the capacity for Cu was highest and averaged 700 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 (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 [10]. Higher doses of Cu^{2+} can cause hepatic and renal damage genetic disorder in human beings. Singh et al. [11] stated that the adsorption of 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 mg g^{-1}. Most nano-absorbents 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-absorbents, however, are optimised for a pH range between 5.0 and 6.0 since Cu^{2+} starts precipitation as $Cu(OH)_2$ 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. [1] 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-absorbents under real conditions. In many cases, most nano-absorbents show drastically decreased absorbent 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.

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 [12]. 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. [13]. 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 [14][15]. It is, therefore, difficult to compare different adsorbents with regard to their performance [15]. So far, conventional granulated activated carbon has been used to remove perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) from contaminated waters [15]. 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. [12] 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 [16] 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. [17] for starch-stabilised Fe_3O_4 NPs averaging 30 min. The PFOA adsorption capacity averaged 62.5 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. [17] also stated that the presence of humic substances inhibited the uptake drastically. Still, nano-absorbents 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 [18], polymer NPs composite of polyaniline-zinc titanate [14], magnesium oxide NPs [19][20], magnetic crosslinked chitosan-glyoxal/ZnO/Fe$_3$O$_4$ NPs [21] and iron oxide NPs [22]. 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 [23]. 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 [24]. Examples of these carcinogenic dyes include CR and malachite green (MG). ZnO NPs had a high adsorption capacity of 48.3 mg g^{-1} for CR and 169.5 mg g^{-1} for MG. Due to their easy regeneration, ZnO NPs are also reusable and strongly compete with conventional adsorbents [24].

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 [25]. 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 [25]. The researchers 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. 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. [26] is highly recommended.

Semiconductor photocatalysts have shown significant efficiency towards organic and inorganic pollutants. 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. TiO_2 exhibits a wide band gap (3.2 eV) and adsorbs photons emitted close to the UV range compared to other semiconductor photocatalysts [27]. However, the wide bandgap leads to activation only in the UV region and, therefore, uses less than 5% of solar light [27]. For this reason, the use of 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 TiO_2, including nanocomposites, which might also help degrade toxic pollutants in water and wastewater more efficiently.

Despite novel developments of TiO_2-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.

Recently, Cani et al. [28] reported on synthesised doped TiO_2 NPs firmly embedded on the surface of a silica matrix (SiO_2). They investigated six different grades of TiO_2 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_2 NPs embedded with SiO_2 ($TiO_2NP@SiO_2$), both treatments with UV and Vis irradiation resulted in higher removal efficiencies compared to the common NP benchmark P25 TiO_2, 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 $10\%TiO_2NP@SiO_2$ (3.02 eV; 390 m^2 g^{-1}) and under UV light by using $60\%TiO_2NP@SiO_2$ (3.13 eV; 295 m^2 g^{-1}). The authors concluded that under visible light less doped SiO_2 surface with TiO_2 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 $10\%TiO_2NP@SiO_2$ influenced positively the photocatalytic degradation performance.

Additionally, Mousavi and Ghasemi [29] reported on a photoactive black-TiO_2/$CoTiO_3$ catalyst to degrade selected organic dyes with significantly increased efficiency under visible light (λ = 450–650 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 $^\bullet OH$, $^\bullet O_2^-$, 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_2 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_3O_4), enhanced photocatalytic activity under solar irradiation was reported with doping on specific surfaces [30]. 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_3O_4, respectively. The achieved removal efficiencies are comparable to those reported by Cani et al. [28] 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_3O_4 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. [31] reported that copper phosphide (Cu_3P) 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_3P NPs resulted in the highest degradation rates of up to 97% of tetracycline (30 mg L^{-1}; 0.25 g L^{-1} catalyst; 40 min; visible light irradiation), corresponding to an eight-times higher degradation rate compared to pure hollow tubular carbon nitride without doping. The researchers 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.

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 [32].

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, the researchers 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. [32] summarised current developments of novel thin-film composite (TFC) NF membranes embedded with NPs such as TiO_2, Al_2O_3, SiO_2 and others for NF and UF providing improved water permeability, selectivity, fouling resistance, and separation performance [33][34][35]. Nevertheless, Wei et al. [32] also pointed out critically that the polymerisation process can be negatively affected by the agglomeration of inorganic NPs such as 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 TiO_2 NPs. Like others, they determined an optimum NP concentration by performing nanofiltration experiments. They showed that a 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. [36]. 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 [37]. Like Wei et al. [32], 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 [38]. 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 [39]. 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 [40]. 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. [41] reported on the development of novel poly(vinyl alcohol) nanofiltration membrane coated with TiO_2 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.

5. Environmental Risk and Human Health

Nanomaterials revolutionising our modern life through a completely new class of chemical structure with unexpected properties. Apart from many advantageous features, concerns on environmental issues and health risk due to uncertainties of NTs regarding their mobility, reactivity, and potential persistence are nowadays more frequently debated. Risk assessment of nanomaterials has become an important issue on national level and on international level by setting different registration and regulations. In this section, the researchers shortly summarise the current situation of risk assessment of NTs, challenges in forcing strict regulations and potential impacts of NPs on human health and environment.

5.1 Environmental Risk Assessment and Problems in Formulating Strict Regulations

Among several benefits NTs have brought to our modern life so far, high production rates and often unregulated releases of NPs have raised concerns regarding their secured handling. At the beginning of the 21st century, the hype of NT application with several unexpected properties completely overwhelmed the commercial marketplace. Unfortunately, potential risks caused by so-called nanopollution to the environment and finally also to human health were totally underscored and/or neglected. In addition, NT rose up that fast in parallel with scientific innovations that the marketplace was not properly prepared by strict regulations.

One decade later, first concerns regarding environmental impacts have become a serious issue not only due to the debate of climate change within recent years but also due to human health risks. Public awareness on protecting the environment and, thereby, indirectly human health has become a very powerful "pressure tool" also to force companies manufacturing NT products more to be eco-friendly (also seek green nanotechnologies). However, the global debate on environmental impacts, health and safety regarding NMs such as NPs is still an open debate. There are some relevant reasons for this debate. Until the middle of the first decade of the 21st century very little was known about environmental and human health risks due to a lack of serious scientific data availability caused by a lack of powerful analytical methods detecting and determining NPs under standardised conditions. Without reliable scientific data, public policy and governmental regulations and/or laws turned out very slowly [42]. In this context, another important fact was and still is remaining in uncertainty: Standardised approaches by meaning international standards for determining toxicity directly or indirectly caused by NMs as well as eco-toxicity. Furthermore, reliable risk analyses, which must also be implemented in national regulations without reducing the liberty on the open market, are still progressing slowly. Several reviews were published meanwhile regarding risk management and assessment of NTs [43][44].

Despite frameworks and governmental regulations, psychological and sociological aspects should not be neglected. Kamarulzaman et al. [45] has investigated the influence of demographic, psychological and sociological factors on public benefit and risk perceptions of NTs as important instrument for effective formulation of policy addressing public interests. They concluded that effective communication is one major key factor for policy making and ethical NT management. This finding is in great agreement with Kuttschreuter and Hilverda [46].

Much attention has been brought to this issue and frameworks have been created to formulate and propose better policy regulations. Still, this is a running process with further improvements in future for both public and private market. As Friedrich and Schulte [47] pointed out there is demand for implementation of international standards, increased funding for rigorous research determining environmental and human risk and truthful communication with public. Some of these requirements have turned out important aspects such as effects of NPs in the environment and impacts on humans. Others such as promoting international regulation became more complex. Different regulations, especially between the European Union (EU) and the United States (US) demonstrate that this process is still a debate. In particular, the EU follows the precautionary approach considering it as a normative principle prescribing a set of specific regulatory obligations in the context of uncertainty. In contrast, the US does not consider the precautionary approach and follows as Canada, Australia and Japan the traditional model of environmental regulations. Friedrich and Schulte [47] describe the legal differences between US and EU more in detail and pointed out that the debate of regulatory environmental policy is still open. More details on regulations, classification and labelling in the EU is given by Cushen et al. [48].

In short terms, in the EU, chemicals including nanomaterials are covered by the "registration, evaluation, authorisation and restriction of chemicals" (REACH) and "Classification Labelling Packaging" (CLP) regulations. The European Chemicals Agency (ECHA) has launched REACH in 2007 to enhance innovation and competitiveness of the EU chemical industry. All important information on properties and safe handling of chemicals on the market are collected by registration in a central database by ECHA in Helsinki. In 2018, the European Commission decided to implement requirements of NMs in the annex of the REACH regulations which entered into force in the beginning of 2020. The adaptation of the REACH annex allows now systematic risk assessment using the information from the registration dossiers ("Berlin declaration", EU 2018). In 2017, the EU launched the European Union Observatory for nanomaterial (EUON) hosted by ECHA aiming at safety of NMs on the market (also see euon.echa.europa.eu). The EUON offers neutral and reliable information about NMs available on the European market.

As above mentioned, regulations and/or laws turned out very slowly. Meanwhile the EU has covered NMs by regulatory framework within REACH and CLP by meaning that hazardous properties and safety of NMs must be assessable. However, further activities are urgently required. Thus, during the "Berlin Declaration" in 2018, the EU addressed to further progress activities in the field of method adaptation namely the OECD and transversal definition of NMs in all relevant regulatory contexts and others. While legal regulations are progressing that slowly, developments of new products turn out fast and might be registered on markets with less strict regulations due to missing uniform international laws. In the current and next decade, governments are urgently requested to care for reliable risk assessment for both human health and environmental protection. For readers who are more deeply interests in understanding the differences in regulations based on REACH Annex as European approach and national approaches the paper of Pavlicek et al. (2021) is highly recommended. The author provide a more detailed overview on REACH Annex, EUON and national regulation of five European countries namely France, Belgium, Denmark, Sweden and Norway.

5.2 Impacts of NPs on Human Health and Environment

As mentioned earlier, this entry focuses predominately on issues regarding NPs as they are one of the most prominent members of NMs. Despite, they were very often reported dealing not only with advantages and benefits in aquatic remediation and enhanced food production in agriculture but, unfortunately, they also serve as major source of environmental contaminations. Those can occur during aquatic remediation [49], in concentrated sludge and/or discharged effluents caused by wastewater treatment plants [50], or simply through leakage or spill out within NP production, transport, storage, product sale and waste treatment [51]. Therefore, the broad application of NPs has also raised several concerns not only with regard to environmental issues but also with an ethical, health, and safety point of view [52].

The identification of contamination pathways of, especially, NPs penetrating different environmental niches is considerably complex due to several potential unspecific and specific interactions taking place. Thus, the life-cycle of NPs impacting our local and global ecosystems is very extensive. The main obstacle leads to identifying diverse interactions taking place between atmosphere, surface water, soil, sediments and groundwater. Rajput et al. [53] reported about the unsafe disposal of various NPs in massive amounts (several hundred tonnes) to the environment every year. Furthermore, he pointed out clearly that NPs were already detected in atmospheric air, water objects, soils, hydrobionts, algae, fungi, tissues of land plants, tissues of land animals among others [54]. The main environmental risk of NPs is caused by the ionic/dissolved form because they seem to show higher bioavailability and, thereby, promote further inadvertent distribution in different ecosystems. In addition, different chemical species of NPs in the soil can lead to increased distribution in the aquatic environment [55].

Di Sia [56] also summarized those potential problems concerning NPs and pointed out that NPs can be persistent and serve, therefore, as long-term anthropogenic pollutant sources in the environment. Furthermore, several NPs could also have eco-toxicological effects and can finally end up via bioaccumulation in the food chain where they can cause unexpected diseases [57]. In 2007, Friedrich and Schulte [47] already indicated impacts of NPs on human health regarding skin, respiratory tract, blood, lymph, bone marrow, kidney, spleen and heart.

Based on the data available on the Nanodatabase, the three most common potential exposure pathways to human health risks are through direct contact either by dermal, oral and/or inhalation. Since data collection was started in 2012, dermal penetration of NPs such as nano silver (Ag), nano titanium, nano titanium dioxide (TiO$_2$), nano gold (Au) and others is the main potential health risk to human. And the trends are still increasing for all three potential exposure pathways. Currently, there are more than 2056 products on the European market available which can lead to potential dermal exposure and their individual health risks are often uncertain or underscored.

Handy et al. [58] and also Klaine et al. [59] clearly showed that NPs affect organism through disruption of membranes and lead to formation of reactive oxygen species. The latter can then lead to genotoxic responses (e.g. DNA damage, mutation, lethal effects) [60]. More recently, these effects were also demonstrated for NPs such as nano Ag, nano TiO_2, nano ZnO and nano copper oxide (CuO) [61]. The authors showed effects of these NPs resulting in genotoxic, immunotoxic, embryotoxic and molluscicidal effects, as well as behavioural impairments and reproductive toxicity.

Similar results were also published concerning iron oxide NPs often applied in aquatic remediation [62]. The authors stated that iron oxide NP released to environment considerably undergo physical, chemical and biological transformations, such as reduction, oxidation, dissolution, sulfidation, degradation of the surface coating, interaction with macromolecules, homo- and heteroaggregation, photo-oxidation, bio-oxidation and bio-reduction which are very often difficult to control and predict [63]. In addition to these, potential chemical interaction problems are also caused by the size and shape of NPs making them barely detectable at trace levels, therefore, reliable prediction on the environmental behaviour is still a very challenging issue [64].

With regard to plants, some scientists reported that NPs can be taken up and accumulated in edible tissues of crop plants in their original form or as metal [65]. The accumulation of NPs can then cause disorder in physiological plant processes and affect the integrity of cellular and sub-cellular organelles organizations, modify proteins, lipids, and nucleic acids content by generating hydroxyl [52]. Finally, it can be summarised that in recent literature several impacts of NPs on both human and environment have been already identified. Nevertheless, the whole dimension of NPs impacting the environment might never be completely understood until a safe release is established.

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