

Review

An Overview of the Water Remediation Potential of Nanomaterials and Their Ecotoxicological Impacts

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Abstract: Nanomaterials, i.e., those materials which have at least one dimension in the 1–100 nm size range, have produced a new generation of technologies for water purification. This includes nanosized adsorbents, nanomembranes, photocatalysts, etc. On the other hand, their uncontrolled release can potentially endanger biota in various environmental domains such as soil and water systems. In this review, we point out the opportunities created by the use of nanomaterials for water remediation and also the adverse effects of such small potential pollutants on the environment. While there is still a large need to further identify the potential hazards of nanomaterials through extensive lab or even field studies, an overview on the current knowledge about the pros and cons of such systems should be helpful for their better implementation.

Keywords: nanomaterials; water treatment; environmental risks

1. Introduction

Water, a previously plentiful, free resource across the world, has become a rare, costly object over recent decades and currently, water shortage is going to be a challenge for sustainable development of the human community [1,2]. This crisis is dramatically expanding and is regarded a global systemic risk, mainly resulting from urban, agricultural, and industrial pollution. In these areas, water consumption has incremented up to 70% (agriculture), 22% (industry), and 8% (domestic) of the currently available fresh water and, accordingly, an enormous volume of wastewater containing a variety of pollutants has been produced [3]. No doubt, the release of wastewater from commercial and industrial sectors besides untreated domestic sewage and chemical pollutants into fresh water resources is horribly detrimental to both the human community and the ecosystem, including animals and plants. In this regard, the major water contaminants are heavy metal ions, organics (e.g., dyes), and oils that can disqualify any water stream for drinking.

To address the need for water remediation systems, during the past few decades, with the evolution of nanotechnology, a diverse range of new technologies based on nanomaterials has been developed. For instance, as adsorbent systems, nanomaterials offer an extremely large reactive surface area at a low mass, can be produced at a much less cost compared to activated carbon and they can remove pollutants efficiently [2]. In this regard, a plethora of nano-adsorbents in various forms and dimensionalities (D) like nanoparticles (0D), nanofibers and nanotubes (1D), nanosheets (2D), and nanoflowers (3D) has been investigated [2]. In terms of composition, the diversity is indeed extreme and many organic and inorganic nanomaterials have been synthesized that can help purify water streams. The separation mechanism can be based on chemical/physical affinity of the pollutant for the surface of the nanomaterial or through size exclusion of the pollutant by a porous nanomaterial system. In the

latter case, nanomaterials act either as the main building block of the porous separator structure, as seen for nanofibrous microfiltration or ultrafiltration membranes, or as an additive to a polymeric thin film membrane to improve its hydrophilicity and thermomechanical properties. The previously mentioned separation processes such as adsorption or filtration only gather the pollutant molecules in solid form but never entirely “eliminate” or “decompose” them. This issue could be problematic because disposal of the obtained sludge and fouling of the filtration system is challenging [4]. For such reasons, the separation process should be complemented by degradation processes such as photocatalysis, sonocatalysis, and reductive degradation that allow the decomposition of organic pollutants into non-toxic metabolites. Other than environmental remediation, nanomaterials can also be efficiently applied for environmental control and construction of sensors that can detect even trace amounts of water pollutants.

Despite all the beneficial potentials that nanomaterials offer for the sake of water remediation and control, their unwanted and uncontrolled release can harm the environment and health of human beings, animals and plants. While nanomaterials are produced in different dimensionalities and aspect ratios, nanoparticles, i.e., 0D nanomaterials, are indeed the most challenging ones in terms of environmental risks. Originating from anthropogenic and natural sources, nanoparticles have always been present in the environment. Nanoparticles suspended in air are normally regarded as ultrafine particles, while the ones existing in soil and water form colloids [5]. In urban areas, particularly metropolitan areas, the emissions of vehicles fueled with diesel and gasoline as well as stationary combustion sources, generate a large amount of particulate materials of different sizes. In this context, the amount of the manufactured nanoparticles exceeds 36% of the entire particulate number concentrations [6]. Apart from synthetic nanoparticles, naturally formed nanoparticles are also present in the atmosphere, though in a much lower concentration compared to the manufactured ones [5]. In aquatic media, the term “colloid” is generally ascribed to those particles whose size varies in the range of 1 nm to 1 μ m. Aquatic colloids consist of macromolecular organics, including peptides and proteins, humic and fulvic acids, and also colloidal inorganic materials composed of hydrous iron and manganese oxides. The small size, extensive surface area, high surface energy, quantum confinement, and conformational behavior of the colloids enable them to bind to various organic and inorganic contaminants [5]. Lastly, with respect to soils, there is a variety of natural nanoparticles comprising organic matter, clays, iron oxides, and other minerals that are decisive in diverse bio-geochemical processes. The soil colloids encompassing nanoparticles and their impact on soil development (pedogenesis) and soil structure (dispersion and crusting) have been a demanding research topic for decades. In this regard, synthetic nanomaterials and the soil colloids made thereof could drive and ease the transfer process of contaminants in soils [5].

In this review, we introduce potential applications of nanomaterials for water remediation, and on the other hand, discuss the possible routes of their release into different environmental sectors like soils and water bodies and their harmful effects. Search in the “ISI Web of Knowledge” database on the main topics to be discussed in the current review, i.e., “Nanomaterials for Water Treatment” and “Environmental Impacts of Nanomaterials”, provided 222 and 63 relevant articles, respectively, for the 10 year time period starting in 2010 (Figure 1). As seen in this graph, the number of studies on the former topic, that is nanomaterials for water treatment, has increased significantly over time during the past ten years. In contrast, the second topic, that is the environmental impacts of nanomaterials, has been less extensively investigated. This fact suggests the need to dedicate further time and cost investment for the purpose of uncovering the potential impacts and risks of nanomaterials on the environment that have been somewhat overlooked.

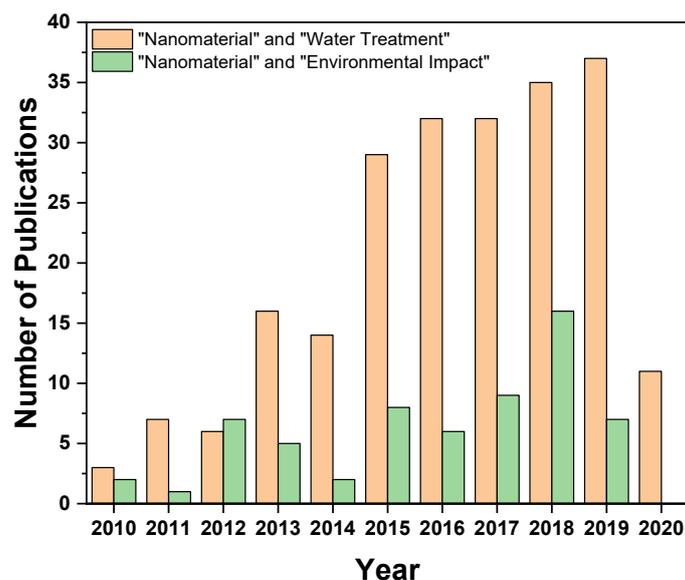


Figure 1. Annual number of publications in the last decade on the main keywords of the current review, according to ISI web of Knowledge (7 April 2020).

2. Nanomaterials for Water Purification

As mentioned earlier, nanomaterials offer several advantages for water treatment and control. This amazing potential stems from their large exposed surface area and functionality that can maximize their interactivity with water pollutants. In this section, we will take a glimpse on some important applications of nanomaterials at the service of water remediation.

2.1. Nanomaterials for Adsorption and Photodecomposition

In the water treatment field, the removal of dye pollutants due to their acute toxicities and carcinogenic nature is of paramount importance. Dyes have a history of thousands of years of application for textiles, paints, pigments, etc. Currently, almost 100,000 types of dyes are produced commercially. In terms of consumption volume, approximately 1.6 million tons of dyes are consumed annually. Thereof, 10–15% are wasted during use [7]. The dye pollutants released from industrial and agricultural wastes are refractory and potentially present carcinogenic effects. Therefore, they must be excluded from water streams through different kinds of traditional treatments, such as activated sludge, chemical coagulation, adsorption, and photocatalytic degradation [8]. Superior to the mentioned techniques, adsorption is relatively effective in the creation of a high quality effluent with no harmful byproducts in an energy/cost efficient manner [9–11]. This approach allows for exclusion of soluble and insoluble organic, inorganic, and biological water contaminants. The diverse merits of adsorption for dye removal are convincing enough to devise sustainable adsorbents that are manufactured on a large scale at low cost and enable fast and efficient dye removal. For this sake, within the course of the past few decades and with the evolution of nanotechnology, a variety of adsorbents of nanoscale size have been scrutinized. Nanomaterials provide an extensive reactive surface area at a low mass and versus activated carbon, i.e., the golden benchmark of adsorbents, they can be produced in a less expensive manner while removing dyestuffs and organic pollutants with a notably less amount [2]. Some examples of dye nano-adsorbents are as follow. Chitosan-coated magnetite (Fe_3O_4) nanoparticles showed a large adsorption capacity for crocein orange G (1883 mg/g) and acid green 25 (1471 mg/g). Interestingly, the adsorbent nanoparticles could be readily recovered by a magnetic field [12]. Based on such a concept, Fe_3O_4 /activated carbon nanoparticles (6–16 nm) that can separate 138 and 166.6 mg/g methylene blue (MB) and brilliant green dyes, respectively, have been developed [13]. Dhananasekaran et al. [14] synthesized α -chitin nanoparticles (<50 nm) from *Penaeus monodon* shell waste and tested their dye (methylene blue (MB), bromophenol blue (BPB), and Coomassie brilliant blue (CBB)) adsorption

efficiency. The nanoparticle adsorbent showed an adsorption efficiency of 95.96–99%, depending on the adsorbent concentration and based on physical adsorption of the dyestuff to the nanoparticles. Other than nanoparticles, nanofibrous adsorbents have also found application in the removal of dye pollutants from water. Such adsorbents are typically made through electrospinning and are superior to nanoparticulate adsorbents due to their easy recovery. As an example for nanofibrous adsorbents, polyethersulfone (PES) electrospun nanofibers containing V_2O_5 nanoparticles have been employed for removal of MB dye pollutant from water [15]. The nanocomposite nanofibers show a low isoelectric point thus at elevated pHs they acquire an extensive highly hydroxylated surface area that facilitates adsorption of cationic MB molecules.

One drawback of adsorption is its inability to completely “eliminate” or “decompose” the dye pollutants. Instead, it solely collects the dye molecules by transferring them to other phases. This feature could be challenging due to the fact that discharge of the dye-related sludge is not straightforward and the adsorbent is rarely reusable [4]. Accordingly, there is a need to complementary degrading treatments such as photocatalysis, sonocatalysis, and reductive degradation that enable decomposition of dye to non-toxic metabolites. In this regard, a variety of advanced oxidation processes (AOPs), provoking release of hydroxyl radicals ($OH\bullet$), have shown a promising potential for decolorization of textile effluents. With unpaired electrons, $OH\bullet$ is drastically reactive and oxidizes recalcitrant organic pollutants [16]. Due to the abundance of low cost, while operative photocatalysts, photocatalysis is indeed of the most researched AOP processes and is considered as a practical degradation process for organic dyes and pesticides. Various semiconductor metal oxide nanoparticles such as ZnO and TiO_2 have shown notable efficiency in the photodecomposition of dye pollutants. For instance, Li et al. [17] developed an oil-in-water Pickering emulsion (PE) stabilized by the presence of TiO_2 particles, wherein the dye containing wastewater and insoluble organic matter were regarded as the water and oil phases, respectively. The TiO_2 particles could offer a large photoactivity effect and notably degrade the dye molecules (Figure 2a). In another relevant study, Kheirabadi et al. [18] synthesized a ternary nanostructure composed of Ag nanoparticle/ZnO nanorod/3-dimensional graphene (3DG) network via a coupled hydrothermal-photodeposition technique. While the 3DG can capture 300 mg/g MB dye by an adsorption process, Ag/ZnO component brings about the possibility of photodecomposition of the dye even under visible light irradiation. The dye removal mechanism of the synthesized adsorbent/photocatalytic system is illustrated in Figure 2b.

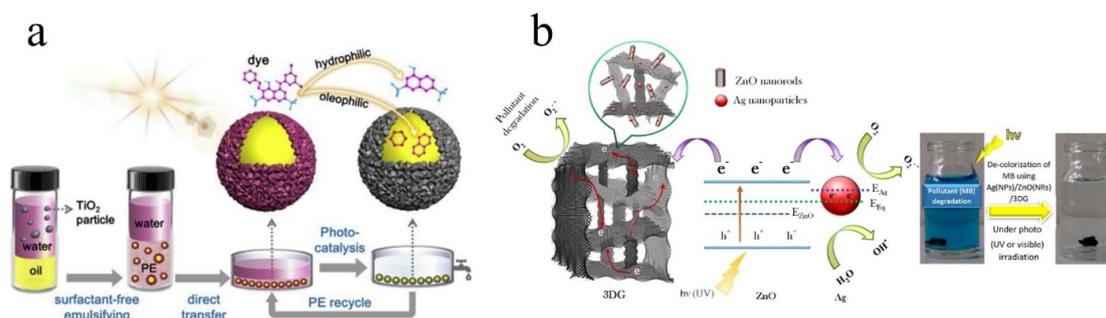


Figure 2. (a) Schematic illustration of an oil/water Pickering emulsion (PE) consisting superhydrophilic TiO_2 particles enabling dye photodecomposition. Reproduced with permission from [17]. Copyright 2019, Elsevier. (b) The dye removal mechanism of an adsorbent/photocatalyst system comprising Ag nanoparticle/ZnO nanorod/3D-graphene hydrogel. Reproduced with permission from [18]. Copyright 2019, Elsevier.

Despite the high potential of semiconductor materials for photodecomposition of various organic pollutants, commercial visible light photocatalysts suffer from poor stability or inefficiency upon irradiation. Addressing such challenges, group II–VI semiconductors whose energy gaps cover the visible light spectral range have been proposed as superior, compatible alternatives [3]. Large aggregation tendency, challenging separation and recovery are the other bottlenecks that have

hampered the broader application of photocatalytic nanoparticles on a large, industrial scale [19,20]. One promising approach to overcome the abovementioned cons could be the nanocomposite strategy. By hybridizing the photocatalytic nanoparticles with polymeric nanofibers, not only is the large availability of the nanoparticles to the neighbouring water medium preserved, but also their intensive agglomeration is hampered and their recovery is facilitated. Nevertheless, due to the different polarity of the photocatalytic nanoparticles and polymeric nanofibers, the hybridization is not straightforward and can lead to clustering of the inorganic nanofillers in the polymer host [21]. In this regard, sol-gel treatment has shown promise in formation of tiny, isolated nanoparticles throughout the polymer nanofiber [22]. Even so, another important concern arises when recalling the possibility of photodecomposition of the encompassing polymer layer induced by the presence of photocatalytic nanoparticles [23]. Figure 3a–d show SEM images of the surface of TiO₂/PVC composite films after UV irradiation for different durations. According to these images, photodegradation of the PVC matrix is initiated from the PVC–TiO₂ interface and results in creation of cavities around TiO₂ particle aggregates that grow and in fact coalesce over time during the irradiation [24]. This behavior is also seen in nanocomposite nanofiber systems. For instance, TiO₂/PES nanofibers undergo photodegradation after exposure to UV irradiation, as reflected in their thermal and mechanical properties (Figure 3e,f, respectively [23]). Induced by UV irradiation, the electron/hole pairs formed in the conduction band (CB) and valence band (VB), respectively, react with O₂ and thereby create various active oxygen species such as O₂^{•−}, ¹O₂, •O₂H, and •OH [24]. In the next step, these active oxygen species start the degradation process and attack the neighbouring polymer chains in the surface and later in the polymer bulk and deeper regions. When the carbon-centered radicals diffuse into the polymer chain, their successive reactions end up with the chain scission with the oxygen incorporation and CO₂ release [24].

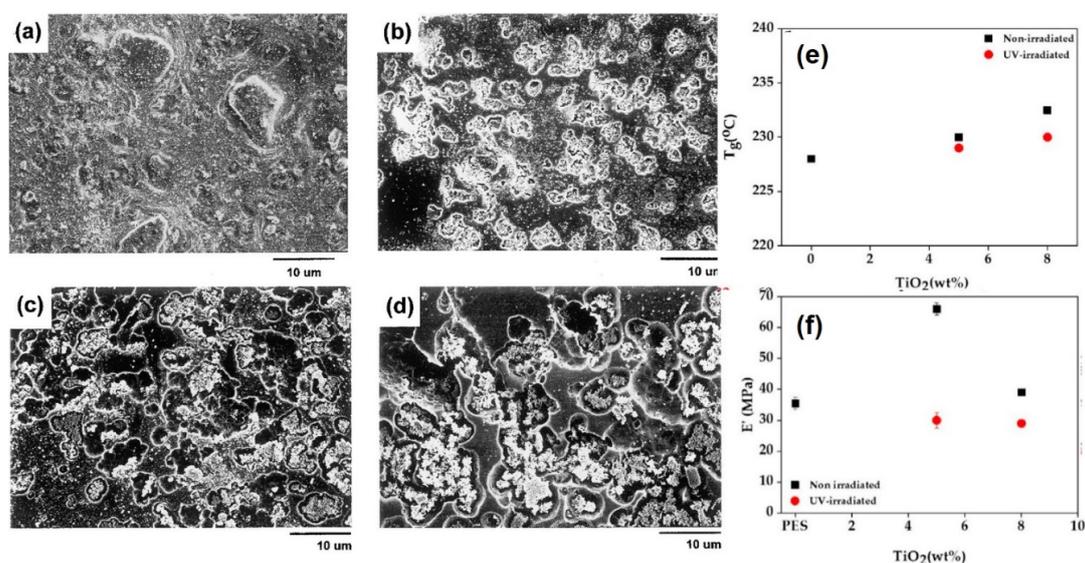


Figure 3. SEM images show the surface morphology of the TiO₂/PVC (1.5 wt.%) composite films after different irradiation times of (a) 0 h; (b) 25 h; (c) 50 h; (d) 100 h. Reproduced with permission from [24]. Copyright 2001, Elsevier. (e) Less notable increment of the glass transition temperature for the UV-irradiated TiO₂/PES nanocomposite nanofibers versus the non-irradiated ones. (f) The dynamic thermomechanical (DMTA) analysis implies that storage modulus for the nanocomposite nanofibers drops upon UV-irradiation. Reproduced with permission from [23]. Copyright the authors 2019, assigned to MDPI under a Creative Commons Attribution (CC BY) license.

2.2. Nanomaterials for Membrane-Based Water Treatment

A membrane is a selective barrier located between two homogenous phases that splits a feed water stream into a retentate and a permeate fraction. The pressure difference between the feed and permeate sides acts as the driving force for the membrane's action and passes water through the

membrane [25]. As a result, based on charge, size, and shape, solutes and particles are discriminated (Figure 4a). The new generation of membrane technologies employ nanomaterials for water treatment.

Nanocomposite membranes comprising a thin polymeric film surface decorated or incorporated with nanofillers are a distinguished class of membranes able to dynamically purify water. Composite materials possess a favorable package of properties that are derived from a combination of encompassing medium's and filler's properties [26–36]. These properties are not restricted to the classic and predefined ones, rather new properties and functionalities arise, especially, when the filler's dimensions lie in the nanoscale. Nanomaterials in different forms and dimensionalities can be used in construction of nanocomposite membranes. Nanoparticles, for instance, have been widely used as nanofillers for mechanical reinforcement or for hydrophilization of polymeric membranes. In this regard, Rodrigues et al. [37] incorporated clay nanoparticles into mixed matrix polysulfone ultrafiltration membranes to improve thermomechanical properties and water permeability of the membrane, while maintaining optimum rejection efficiency. Moreover, the membranes reinforced with clay nanoparticles showed a lower fouling tendency and higher flux recovery when tested with sodium alginate and natural water. One critical concern regarding ultrafiltration (UF) membranes is their biofouling and the presence of bacterial colonies on the surface and thereby clogging the pores and lowering the permeability of the membrane. In this regard, *extracellular polymeric substances* (EPS) are released upon bacterial cell lysis and are adsorbed on the UF membrane and thus reduce the longevity and permeability of the membrane [38,39]. The most promising solution to address the challenge of biofouling of the UF membranes is surface hydrophilization by incorporation of various antifouling agents [40]. In this regard, a diverse range of antifouling agents has been employed in membrane technology, including Ag, Au, Cu, graphene oxide (GO), Zn, and TiO₂ nanoparticles [22,23], and also carbon nanotubes (CNTs) [38]. Despite the significance of industrial production of such nanocomposite membranes for water treatment, their toxicity that could originate from the release of the incorporated nanomaterials during the high pressure difference-driven filtration process should be carefully evaluated to minimize their adverse effects on human health and the environment [41]. The toxicity profile of the nanoparticles embedded in a polymeric matrix could be a function of their size, shape, charge and preparation conditions [38]. Among the nanofillers above mentioned, CNTs are resilient antibacterial agents whose toxic effect is derived from the ions and reactive oxygen species (ROSs) they release and thereby kill bacteria through oxidative stress stimuli [42]. Such a remarkable performance has led to wide application of CNTs in blended UF membranes, for the sake of improvement of filtration performance [43]. As reported in many studies, CNTs optimize water filtration and rejection of salts, nonpolar contaminants, micro- and macro-sized contaminants, and also waste chemical materials [44]. Ayyaru et al. [38] synthesized CNT- and sulphonated CNT (SCNT)-blended UF polyvinylidene fluoride (PVDF) membranes. For the latter group of the membranes, bovine serum albumin (BSA) rejection was 90%. As shown in Figure 4b, flux decline was less notable for the SCNT-PVDF membrane while permeating BSA solution through the membranes, thanks to its improved hydrophilicity. For the CNT- and SCNT-PVDF membranes, the fouling recovery ratio (FRR) was 72.74 and 83.52%, respectively, Figure 4c, implying their optimum antifouling effect arisen from –SO₃H and –OH groups found in SCNT and CNT, respectively. According to Figure 4d, the irreversible fouling value of the nanocomposite membranes, particularly that of SCNT-PVDF, is lower than that of the neat PVDF membrane. This again emphasizes the role of hydrophilicity induced by the presence of the nanofillers on lowering the fouling tendency of the membranes. Although CNTs are potentially versatile additives to membranes and also promising adsorbents for divalent metal ions, dyes, natural organic matters, etc., their relatively high unit cost is a limiting factor for their widespread practical use [3]. Moreover, the existence of metal catalysts in raw CNTs might induce a toxic effect. In contrast, chemically functionalized CNTs have not been shown yet to be toxic [45]. Accordingly, practical applicability of CNTs as adsorbents or inclusions in membranes for water treatment is tightly associated with finding cost effective production methods for CNTs and minimizing their toxicity effect by development of safer alternatives such as carbon nanocrystals (CNCs) [3].

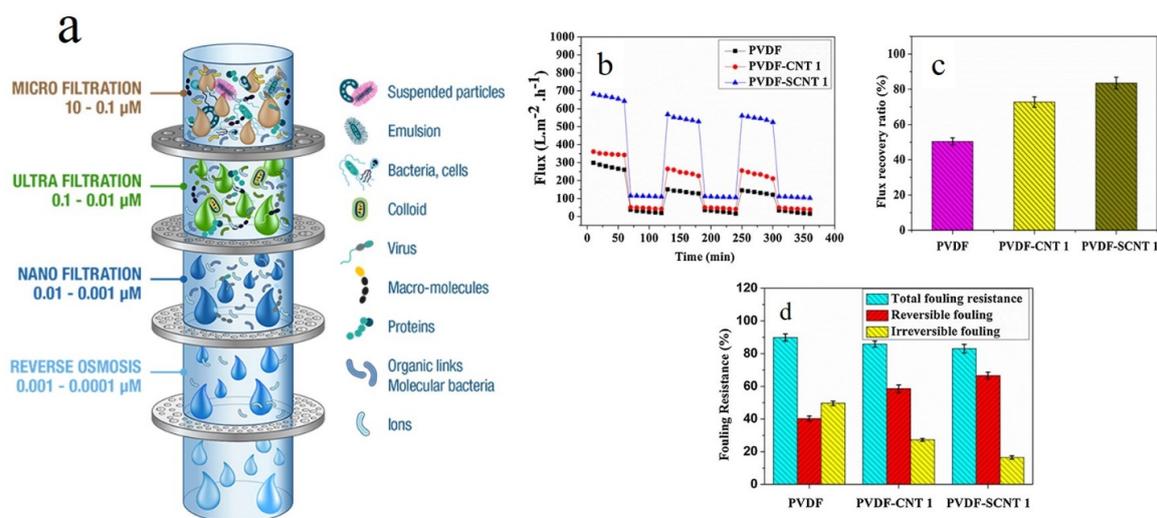


Figure 4. (a) Schematic shows diverse membrane filtration processes including reverse osmosis, nanofiltration, ultrafiltration, microfiltration, and particle filtration. Other than the reverse osmosis membranes whose structure is almost dense and non-porous, the rest are different in terms of the average pore size (the image was obtained from www.muchmorewater.com). Antifouling properties of CNT/PVDF UF membranes represented in cycle filtration (b), water recovery flux (c), and fouling resistance (d). Reproduced with permission from [38]. Copyright 2019, Elsevier.

Other than film-like membranes widely used for ultrafiltration and nanofiltration, electrospun nanofibrous membranes have also been developed for size exclusion of contaminants. Such nanostructured membranes possess a large porosity and an interconnected porous structure with microscale pore sizes. While the high porosity assures notable permeability to gas and liquid streams, the interconnected pores enhance fouling resistance. Such features lead to low energy consumption for the membrane process. Moreover, extensive available surface area and flexibility in surface functionality optimize the adsorptive nature and selectivity of the nanofibrous membranes. The constituting nanofibers could be as neat, chemically functionalized, nanocomposite, and even biofunctionalized [46–50]. For instance, a PES electrospun nanofiber mat overlaid on a poly(ethylene terephthalate) (PET) non-woven was evaluated as a membrane for liquid filtration and removal of micro- and submicron sized polystyrene (PS) particles from water [51]. Despite a high initial flux, upon increase of the feed pressure, the nanofibrous membrane's porosity declines and thereby the water flux drops. Therefore, while the nanofibrous membrane shows a high potential for pre-treatment of water e.g., as a microfiltration (MF) membrane, it should be mechanically reinforced and hydrophilized to raise water permeability and flux. To meet such objectives, PES nanofibers were stabilized and hydrophilized by incorporation of ZrO_2 [52] and TiO_2 [22] nanoparticles. Nanofibrous membranes can also be used for UF, i.e., a particular liquid filtration process separating a variety of pollutants, such as viruses, emulsions, proteins and colloids that are as small as 1–100 nm. For this sake, a nanofibrous membrane needs to possess a surface pore size less than 0.1 μm that alongside a high surface area potentially render them prone to rapid fouling and notable flux decline. To address this concern, a nanofibrous membrane is coated with a thin film and makes up a thin film composite (TFC) membrane [53]. Such a concept has shown applicability for forward osmosis (FO) membranes, as well [54].

Self-sustained hydrophilic nanofiber supports have been investigated for construction of the TFC FO membranes [55]. With a particular scaffold-like structure, the nanofiber support optimally lowers the internal concentration polarization (ICP) and raises water flux. To address the challenge of biofouling, the nanofibers could be equipped with antimicrobial properties, as well. For this sake, antibacterial nanoparticles e.g., Ag nanoparticles can be incorporated within the nanofibers. This strategy has been previously applied for various applications with respect to wound dressings [56] and water filtration [57]. For FO water treatment, Pan et al. [55] synthesized a TFC FO membrane

based on an antibiofouling Ag nanoparticle-incorporated nanofibrous support layer, that could offer an improved water flux and reduce biofouling and ICP, Figure 5a–e. The as-formed FO membrane provides a remarkable bactericidal effect for *E. coli* (96%) and *S. aureus* (92%), thanks to release of Ag⁺-species into the solution.

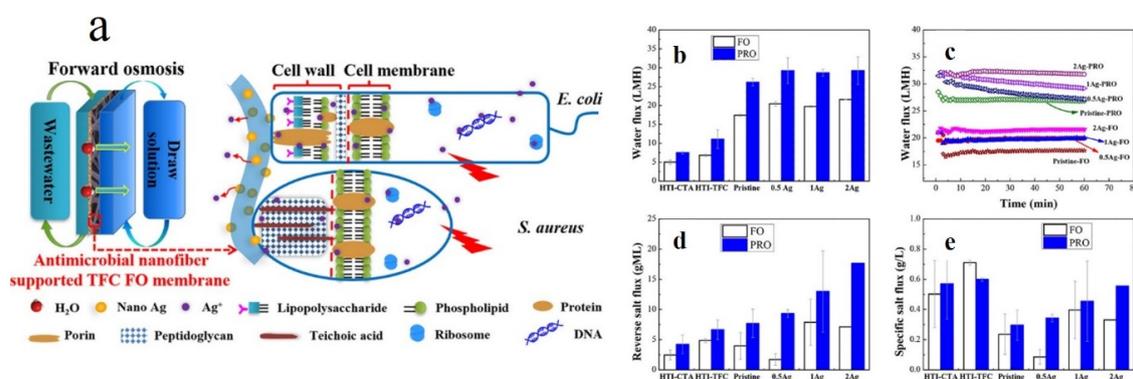


Figure 5. (a) Schematic illustration of the structure of the antimicrobial nanofiber supported TFC FO membrane (Ag/PAN-thin film nanocomposite (TFN)) (left) and the antibacterial action of the Ag nanoparticles incorporated in the nanofibers that damage DNA and membranes of the bacteria (right). (b) Water flux of the Ag/PAN-TFN versus that of commercial FO membranes and (c) water flux trend of the Ag/PAN-TFN FO membranes over time (in the FO and PRO modes). (d) Reverse salt flux and (e) specific salt flux of the Ag/PAN-TFN membrane compared to those of commercial FO membranes (in the FO and PRO modes). Note that the experiments were performed using 0.5 M NaCl as draw solution and DI water as feed solution; In the FO and PRO mode, the active layer face feed and draw solution, respectively. Reproduced with permission from [55]. Copyright 2019, American Chemical Society.

As shown in Figure 5a, the Ag ions are able to (quasi)covalently bond with thiols, phosphates, and organic amines available in proteins, lipopolysaccharide, and phospholipid of the cell membrane, and cell wall, thereby damaging them. Moreover, some ions could pass through the cell wall and adversely influence ribosomal subunit proteins and enzymes [58] and disrupt DNA's structure, leading to cell death. Other than the bactericidal activity, the hydrophilic, porous nanofibrous support allows for a superior water flux compared to commercial FO membranes (HTI-CTA and HTI-TFC) in two modes of FO and pressure-retarded osmosis (PRO, Figure 5b). The water flux remains steady over time in the FO mode, whereas it declines in the PRO mode due to dilution of the draw solution, leading to a lower osmotic pressure difference (Figure 5c). Regardless of the operation mode, the nanocomposite membranes show an increased reverse salt flux versus the commercial FO membranes (Figure 5d). In contrast, as shown in Figure 5e, the nanocomposite membranes exhibit a much less specific reverse salt flux, implying their higher selectivity and efficiency for a FO process.

Graphene, i.e., a 2D, 1-atom-thick planar sheet of sp^2 bonded carbon atoms, possesses remarkable physical, mechanical, thermal and optical properties [59]. In relation to water remediation, graphene's atomic thickness can potentially guarantee a high fluid permeability (that is significantly larger than that of typical nanofiltration (NF) membranes) and therefore lower energy consumption and inexpensive operation. Moreover, the 2D nanochannels forming between stacked graphene sheets or the nanopores available in a single graphene layer enable size-selective transport and purification of water streams (Figure 6a) [60]. The graphene that has been employed for development of water desalination membranes can be in different forms, such as pristine graphene, graphene oxide (GO) and reduced GO (rGO). Also, structurally graphene membranes can be constructed either as single layers or as stacked, multilayer forms. Monolayer graphene membranes with intrinsic pores have been studied for NF purpose experimentally as well as theoretically via simulation. For instance, O'Hern et al. [61] mounted a monolayer of chemical vapor deposition (CVD) graphene onto a porous polycarbonate substrate and thereby fabricated a graphene composite membrane with an active filtration area of

25 mm². The graphene monolayer contained intrinsic nanopores as small as 1–15 nm that could contribute to the size-selective passage of molecules such as KCl, tetramethylammonium chloride, Allura Red AC (496 Da dye) and tetramethylrhodamine dextran (70 kDa), through the membrane made thereof. While KCl and tetramethylammonium chloride permeated through the graphene membrane, the diffusion of tetramethylrhodamine dextran was hampered. Despite the feasibility of selective molecular transport through the monolayer graphene membrane, selectivity is not controllable thanks to arbitrary sizes and locations of the intrinsic pores. Conclusively, formation of graphene layers with a large number of nanopores with adjusted, near monodisperse sizes and chemistries is a sophisticated objective that must be targeted in the new generation of graphene membranes.

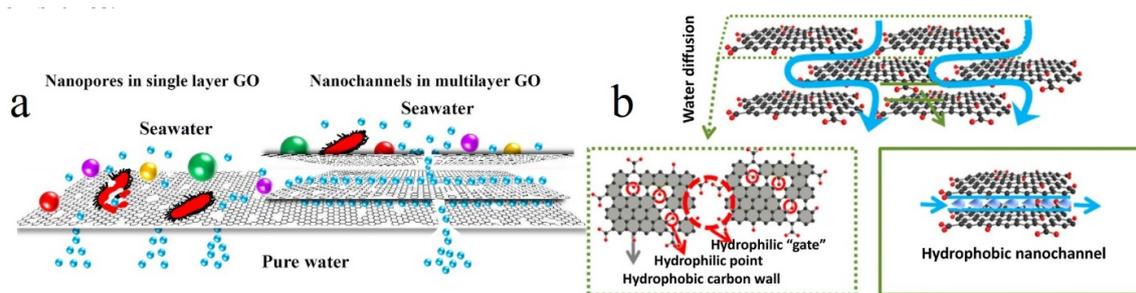


Figure 6. (a) Schematic illustration of the water purification mechanism for a single layer graphene membrane containing nanopores of tailored size and a multilayer graphene membrane comprising stacked GO sheets. Reproduced with permission [62]. Copyright 2018, Elsevier. (b) Schematic depicts the nanochannels forming between adjacent GO sheets that comprise hydrophobic and hydrophilic zones facilitating water flow and removal of tiny water pollutants. Reproduced with permission from [63]. Copyright 2016, American Chemical Society.

Despite various advantages of the monolayer graphene membranes for nanofiltration and even water desalination, large scale production of nanoporous graphene is indeed challenging and a single layer graphene is not robust enough to withstand the usual filtration pressures. In contrast, multi-layered GO membranes can be produced in a scalable manner and survive under large applied pressures. The nanochannels formed between the stacked GO nanosheets decorated with various polar functional groups allow water permeate through the membrane [64]. Induced by the notable slip length of water within the interlayer channels, the stacked GO inhibits passage of the solute particles. Figure 6b schematically shows how water molecules get into the hydrophilic zones and slip through the hydrophobic nanochannels. With respect to selectivity, because of hydration, the interlayer spacing of the GO nanosheets rises to 0.9 nm upon their immersion in ionic solutions. This structural change enables permeation of K⁺ and Na⁺ ions, and disqualifies the membrane for desalination purposes [65].

Despite the promising potential of graphene membranes for water purification, their release into water and thereby the environment is a concern that should be taken into account. In this regard, there are several reviews in the literature that widely discuss the fate, transformation, and toxicological impacts of such nanomaterials in the environment [66–68]. However, there is still a need to realistic, long term determination of the environmental implications of graphene nanomaterials. These precise ecotoxicological and life-cycle analyses enable us to better judge pros and cons of graphene nanomaterials and to find out how we can employ the safest ones with the least health and environmental concerns.

As highlighted so far, there are many promising achievements in relation to employment of nanomaterials for water treatment. Some of the recent developments (as of 2019) in this field are tabulated in Table 1. Many nanoadsorbents and nanomembranes are currently in development stage for the sake of large-scale production and industrialization. Given the fact that the water recycling is regarded an important aspect of sustainable development in the human communities, particularly when recalling the expanding water shortage crisis across the world, significance of realizing advanced water treatment technologies using nanomaterials is further stressed. However, this tiny functional

building blocks could be also problematic and harmful in terms of sustainability, if released into the environment in an uncontrolled manner. In the next section, we review how they would be scattered in different media of water and soil and how they influence the biota living in such systems.

Table 1. Some examples of recent studies (as of 2019) on nanomaterials for water treatment.

Composition	Structure	Water Pollutant	Removal Mechanism	Nanomaterial Role	Ref
Cu NP/CNT/PVDF	Nanocomposite film	arsenic	Dynamic adsorption and oxidation	As oxidizer and adsorbent	[69]
Co doped ZrO ₂	Nanoparticle	MO dye	Visible light photodegradation	As photocatalyst	[70]
NiO	Nanoparticle	ciprofloxacin	Adsorption	As adsorbent	[71]
Fe ₃ O ₄ NP/AC	Nanocomposite particle	MO and RhB dye	Adsorption	To enable magnetic recovery and to raise adsorption capacity	[72]
Fe ₃ O ₄ @MIL-100(Fe)	Nanocomposite MOF	diclofenac sodium (DCF)	Adsorption and photodegradation	Magnetic recovery	[73]
Fe _x Co _{3-x} O ₄	Nanoparticle	CR dye	Adsorption	To offer adsorption activity with easy magnetic recovery	[74]
ZnO-ZnFe ₂ O ₄	Nanofiber	CR dye	Adsorption	To raise adsorption efficiency	[75]
Ag-ZnO/PANI	Nanocomposite film	BG dye	Adsorption	To raise adsorption efficiency	[76]
ZnS NP/PES	Film membrane	Humic acid	Filtration assisted by the antifoulant NPs	As antifouling agent	[77]
ZnO/KGM-PVA	Nanofiber membrane	MO dye	Visible light Photodegradation	To induce photocatalytic and antibacterial activity	[78]
Boehmite NP/EPVC	Nanocomposite Film membrane	BSA	Ultrafiltration	To improve hydrophilicity and water flux	[79]
Ag NP/wood	Nanocomposite Film membrane	MB dye	physical adsorption and catalytic degradation	Dye adsorption and antibacterial activity	[80]
(3-aminopropyl-triethoxysilane) APTES-Fe ₃ O ₄ NP/PES	Nanocomposite Film membrane	arsenic	Adsorption	Heavy metal ion adsorption	[81]
PEI/PD/Ag NP	Nanocomposite Film membrane	BSA/HA/Oil	Ultrafiltration	As anti-fouling and anti-biofouling agent	[82]
Carbon dioxide plasma treated PVDF	Nanofiber membrane	CV dye and iron oxide NPs	size exclusion and adsorption	Ionic selectivity	[83]
Bentonite NP/PA	Nanocomposite Film membrane	NaCl	Reverse osmosis	To raise water permeability	[84]
PVA/PAN	Nanofiber membrane	Nanoparticles and Cr (VI) and Cd (II) ions	Adsorption and microfiltration	PVA nanofibers as the mechanical support and PAN nanofibers for selective adsorption of the ions	[85]
Clay NP/mixed matrix PS	Nanocomposite Film membrane	PEG and sodium alginate	Ultrafiltration	To improve antifouling properties, membrane thermal/ mechanical resistance and permeability with minimal loss in rejection	[37]
Clay NP/mixed matrix PS	Nanocomposite Film membrane	PEG and sodium alginate	Ultrafiltration	To improve antifouling properties, membrane thermal/ mechanical resistance and permeability with minimal loss in rejection	[37]
CS NP&Ag-CS NP/polyphenylsulfone	Nanocomposite Hollow fiber membrane	Reactive black dye	Adsorption	To improve porosity, dye rejection efficiency, hydrophilicity, and antifouling property	[86]

NP: nanoparticle; CNT: carbon nanotube; PVDF: polyvinylidene fluoride; Co: cobalt; MO: methyl orange; AC: activated carbon; RhB: Rhodamine B; MOF: metal-organic framework; CR: congo red; PANI: polyaniline; BG: brilliant green; AB: acid blue; AY: acid dye; PES: polyether sulfone; KGM: Konjac glucomannan; PVA: polyvinylalcohol; EPVC: emulsion polyvinyl chloride; BSA: bovine serum albumin; MB: methylene blue; PEI: poly(ether imide); PD: polydopamine; HA: humic acid; CV: crystal violet; PA: polyamide; PAN: polyacrylonitrile; PS: polysulfone; PEG: polyethylene glycol; CS: chitosan.

3. Ecotoxicology of Nanomaterials

As an inevitable result, with extensive use in water treatment, nanomaterials can be released into soils and water bodies, thereby threatening the quality of life of humans, animals, and plants (Figure 7a). In the case of uncontrolled release, they are accumulated and as suspended solids contaminate food and drinking water. Their final destiny strongly depends on their properties as well as the characteristics of the environment they are released into. Consequently, a variety of adverse ecotoxicological impacts can take place on microorganisms, plants, invertebrates, and fish. In the case of human, no significant risk from such nanomaterials has been reported, though the relevant studies performed so far are insufficient [87]. It is extremely necessary to research on the potentially hazardous effects of the nanomaterials on ecosystem and human health. This will encompass quantitative and qualitative assessment of such nanomaterials in different segments of the environment and determination of the likely consequences on the health of various species living in that segment. Accordingly, the research must be directed towards identification and testing of the environmental fate and transport, and ecotoxicology and toxicology of the nanomaterials.

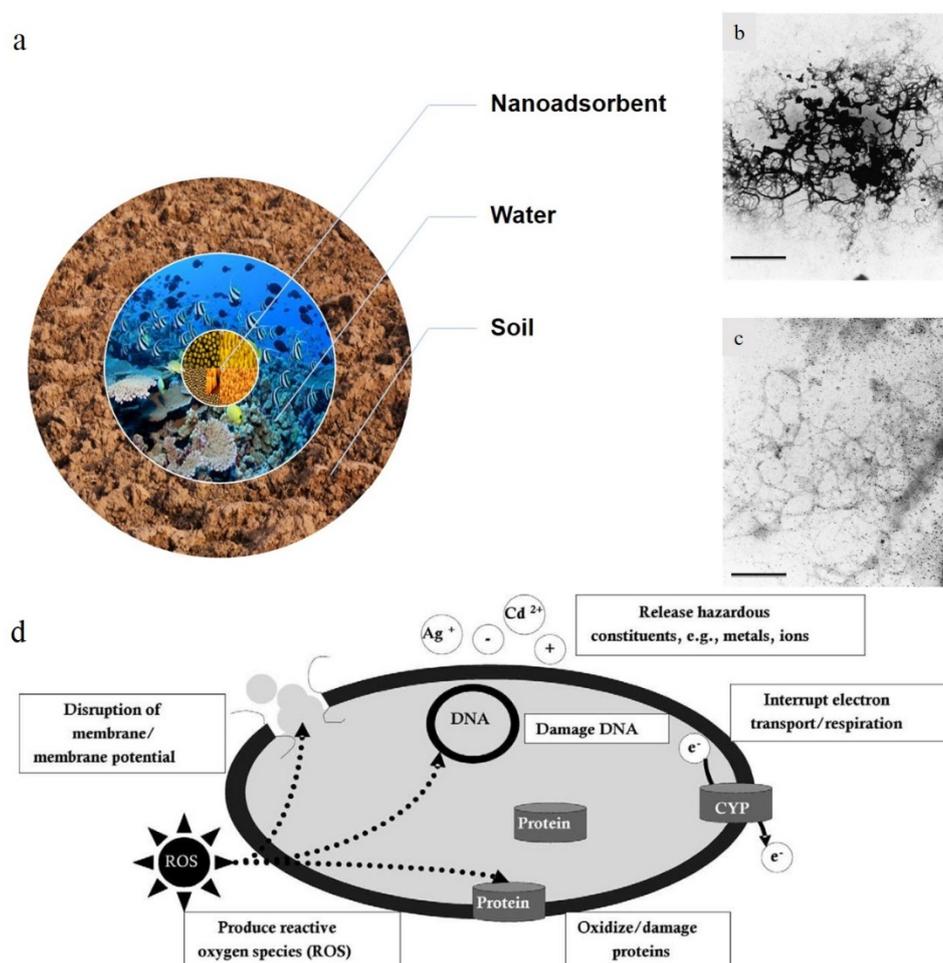


Figure 7. (a) The cycle of release of nanomaterials into environment from water to soil and vice versa. (b) The aquatic colloid comprising hydrous iron oxide aggregates and organic fibrils (scale bar = 1 μm). (c) The aquatic colloid made form silver stain on organic fibrils along with the polysaccharide fibrils possibly decorated with hydrous iron oxides (scale bar = 200 nm). (d) The likely cytotoxicity mechanisms of nanomaterials exerted on bacteria. CYP = cytochrome P. Reproduced with permission from [5]. Copyright 2009, John Wiley and Sons.

Among nanomaterials, carbon and metal oxide ones (e.g., TiO_2) are hardly biodegradable and persist in the environment [88,89]. It is anticipated that many of such insoluble nanomaterials would aggregate (as homo- or heteroaggregation) in the ecosystem and eventually settle out [90,91] and be subjected to various species as sediments. With respect to the soluble nanomaterials, the dissolution rate and solubility are determining in their fate. The release of toxic ions and generation of reactive oxygen species (ROS) are considered as the main toxicological pathways for metal/metal oxide nanomaterials, thereby threatening the life quality of aquatic and terrestrial creatures [5,92,93].

3.1. Nanomaterials in Aquatic Systems

As a general rule, the nanomaterials released into the environment interact with different substances available in that medium and thereby experience aggregation, dissolution, sedimentation, and transformation [94]. In 2010 it was reported that from 8 to 28% of the released nanomaterials are accommodated in soil, while between 4 and 7% in water [95]. These statistics are associated with the higher potential of soil (i.e., its constituents) and its interaction level with the liberated nanomaterials.

The nanomaterials are released into different ecosystems including the aquatic ones either intentionally or unintentionally. While the nanomaterial can be on purpose added to address the available contamination in the groundwater [96], they can also originate from the atmospheric emissions and solid/liquid waste streams delivered from factories, for instance. Furthermore, the nanoparticles present in paints, textile, and health care products, e.g., sunscreens and cosmetics, can potentially be released into the environment. As an example, thanks to desirable bactericidal ability, Ag nanoparticles are commonly employed in the consumer products (e.g., to inactivate the odor-causing bacteria in socks). However, their release into water streams can kill also useful bacteria that exclude ammonia from wastewater treatment systems [97]. Metal oxide nanoparticles, such as TiO_2 , ZnO and CeO_2 , are also extensively utilized in diverse products (e.g., sunscreens, paints, coatings, catalysts) and can reach water systems in different ways. The released nanoparticles are settled on soil and surface water systems, and in case of proper surface treatment they remain un-aggregated and float on the water. The nanoparticles that are deposited on the land, contaminate soil, transit through the surface, reach the ground water and in the course of this travel affect the existing biota. Wind and rainwater stream also displace the nanoparticles available in the solid wastes, wastewater effluents, direct or uncontrolled emissions into water bodies. Though accidental release of the nanomaterials can be strictly controlled within the production units, likely spillage during transportation to the consuming units is indeed challenging [5].

The majority of released nanoparticles aggregate as soon as hydrated, thereby being sediment in different rates. The extent of aggregation depends on the nanoparticle's surface charge and charge magnitude, and likely coverage of the nanoparticle's surface by mono- and divalent cations, by natural organic matter (NOM) or other organic molecules. In fact, such features determine the prevail of attractive and repulsive forces, thereby governing the nanoparticles' aggregation or their sticking to other surfaces [89] e.g., aquatic colloids.

Aquatic colloids, according to the definition established by the International Union of Pure and Applied Chemistry (IUPAC), are the materials whose dimension(s) are below $1\ \mu\text{m}$. Accordingly, aquatic colloids encompass (natural) nanoparticles, i.e., the materials with a minimum of two dimensions larger than 1 and smaller than 100 nm. In terms of composition, aquatic colloids are composed of organic (mainly humic substances and protein and polysaccharide fibrils) and inorganic fractions (e.g., metal oxides of Fe, Mn, and Al, and silicon oxide) and also microorganisms including viruses and bacteria (Figure 7b,c). It is very likely that nanoparticles (nanomaterials) interact with the aquatic colloids and thereby aggregate and sediment. This means that fate of the nanoparticle can be dominated by characteristics and concentration of aquatic colloids. For instance, it is reported that in estuarine and marine waters, density of aquatic colloids is notably low, on the other hand, concentration of nanoparticle is also low due to the high aggregation tendency and thus increased sedimentation rate at the aqueous systems with high ionic strengths [5]. It is worthy to note that the concentration of the

nanoparticles commonly found in natural waters including those made of Ag and oxides of Ti, Ce, and Zn could range from 1 to 10 µg/L, and cumulatively, this concentration can reach 100 µg/L [5]. With respect to the interaction between the aquatic colloid and nanoparticles, humic substances coat the surface of the nanoparticle [98] and stabilize their surface charge, thereby minimizing the chance of aggregation [99], as shown for CNTs, for instance [100]. On the other hand, the fibrils raise this possibility via bridging mechanisms [101]. The main factors or properties of the nanoparticles that significantly influence their behavior in natural water systems are: chemical composition, mass, particle density, surface area, size distribution, surface charge, surface contamination (the likely shell and capping agents), and stability and solubility of the nanoparticle [5].

Given that industrial discharges are mostly exposed to marine environments, and the freshwater streams and coastal runoff end up to seas, this medium and its contamination is of utmost importance. The sea environment has a high ionic strength, is typically alkaline, and contains a diverse range of NOMs as well as colloids whose type and concentration depends on the location (coastal zone versus oceanic one). This medium can potentially be contaminated by the nanoparticles that are released via atmospheric deposition and/or coastal runoffs. The physicochemical properties of water such as temperature, salinity, and type of NOM varies by depth and affects the aggregation and colloid formation [102]. Similar to freshwater systems, the formed aggregates of the nanoparticulate contaminants precipitate slowly down to the ocean floor. In this route, they may stop at the interface of cold and warm streams or even be recycled by the existing biota. In either cases of complete sedimentation on the ocean floor or getting stuck in the mentioned interface, the living species corresponding to the zones might be affected. Additionally, the nanoparticles could be suspended and trapped in the surface microlayer of oceans and thereby impose risks to the birds, mammals and the species living in the microlayer [103].

The uptake of nanoparticles by living organisms can induce toxicity effects through different mechanisms. Nanoparticles can find a way into the cells by penetration through cell membranes, endocytosis as well as adhesion [104–106]. As soon as the nanoparticle is accommodated in the cell, it starts to damage the natural functions in different ways such as destruction of membrane structure or potential, proteins oxidation, genotoxicity, blockage of energy transduction, and generation of ROS and toxic substances [5]. Such mechanisms are illustrated schematically in Figure 7d. For instance, graphene is toxic to bacteria and damages the membrane and raises the oxidative stress level. In the graphene family, GO shows the most notable antibacterial activity, followed by rGO and graphite [107].

3.2. Nanomaterials in Terrestrial Systems

Given the large availability of a reactive sink, that can lead to overestimation of the exerted dose to the biota relative to the real one, soil is notably distinct from fresh and marine waters. In a similar manner, soil can be contaminated with nanomaterials intentionally (for the purpose of remediation, fertilizing, etc. e.g.) or unintentionally (by uncontrolled spills in the course of production and transport, e.g.) [5,108]. Regardless of the application aim, they can affect the biota present or dealing with soil.

Upon contacting soil, nanomaterials are physicochemically adsorbed to the soil particles' surface through hydrophobic interactions, hydrogen bonding, electrostatic interactions, etc. Induced by the presence of organics, they could experience chemical transformations. Additionally, nanomaterials can penetrate into the pores of macroparticles and stay there for a long time [109]. The behavior of nanomaterials i.e., their retention or mobility, in soil is dependent on several factors including soil texture, pH, humic acid, and chemistry of soil, surface coating and nanomaterial size, and pore water velocity. Particularly, pH and humic acid of soil determine the aggregation and colloidal stability of nanomaterials in soil [110].

Soil is a medium that accommodates diverse species such as microorganisms, plants and nematodes. These soil inhabitants are crucial in the cycle of nutrients, decomposition of materials, and nitrogen fixation [110]. Therefore, any damage to such important ecosystem elements can have non-compensable consequences on the life quality and nature.

Microorganisms are vital for performance and health of soil, taking into account their role in modulation of the organics' turnover and the cycle of mineral nutrients. They also play a crucial role in the physical characteristics of soil, thereby influencing water maintaining potential and the tendency of compaction or erosion. Accordingly, any undesired effect on microorganism community from the released nanomaterials could indirectly affect soil's quality and function. A diverse range of nanomaterials including fullerenes (C_{60} and nC_{60}) [111], 3-aminopropyl/silica, palladium, dodecanethiol/gold and copper nanoparticles [112] have been challenged with respect to their effect on soil's microbial community. In this regard, specifically, the factors such as soil respiration, microbial biomass, phospholipid fatty acid quantity, methyl ester of fatty acids, enzymatic activities, colony forming unit and DNA profile of bacterial community have been analyzed. While the above cited reports imply no toxicity of the mentioned nanomaterials, there are other studies such as that of Johansen et al. [113] on nC_{60} that explicitly demonstrate a notable decline in bacteria density of the soils exposed to this kind of nanomaterial. Nogueira et al. [108] also showed that the bacterial communities in soil samples treated with gold nanorods, TiO_2 nanoparticles, the polymeric nanomaterials composed of carboxymethyl-cellulose (CMC), the hydrophobically modified CMC (HM-CMC), the hydrophobically modified polyethylglycol (HM-PEG), and the vesicles of sodium dodecyl sulphate/didodecyl dimethylammonium bromide (SDS/DDAB) are notably influenced by their toxicity effects. According to Rodrigues et al.'s study [114], bacteria can survive when exposed to SWCNTs, while fungal microbiota are unable to recover after the exposure. In another study, it was shown that FeO and Ag nanoparticles can decrease fungal biomass [115]. In contrast, quantum dots and super paramagnetic nanoparticles impose no notable toxicity to *Fusarium oxysporum* [116]. In general, the nitrifying bacteria are more vulnerable to nanomaterials' toxic effects compared to the bacteria with nitrogen fixing and denitrifying ability [110]. In the case of the ammonia oxidizing bacteria, several nanomaterials such as TiO_2 nanoparticles have shown a toxicity effect [117].

Plants are the other main species that are influenced by the presence of nanomaterials in the soil. Several kinds of nanomaterials have shown the ability to diffuse into plants via their roots, translocation, biotransformation, and spread in different forms across their structure, thereby impacting on photosynthesis, growth and regeneration abilities [118,119]. The resulting perturbation of the physiological functions impacts on seed germination, seedling growth, higher ROS production, damage to cell walls, and changes in proteins, carbohydrates, lipids, pigments, and hormones [120]. In this regard, metal oxide nanomaterials have been widely used as fertilizers for agriculture [121]. These nanoparticles account for a major number of the nanoparticle contaminants in soil including: Al_2O_3 , TiO_2 , CeO_2 , ZnO, CuO and ZrO_2 . The other important nanocontaminants are carbon fiber, SiO_2 and Ag nanoparticles, as well as carbon black [122]. Of the aforementioned metal oxide nanoparticles, ZnO and CeO_2 are especially detrimental for the plants [121]. As shown by Priester et al. [123] soybean (*Glycine max*) is vulnerable to high amounts of CeO_2 nanoparticles in soil, as witnessed by large ROS production, lipid peroxidation, visible stains (Figure 8a,b), and also declined total chlorophyll amounts. Compared to the leaves exposed to ZnO nanoparticles, the ones treated with CeO_2 nanoparticles show a higher percentage of visible damages, Figure 8c,d.

Feizi et al. [124] examined the effect of TiO_2 nanoparticles in different concentrations of 0, 5, 20, 40, 60 and 80 $mg.L^{-1}$, on the fennel seed germination. According to their results, after 2 weeks of seed incubation with TiO_2 nanoparticles (60 $mg.L^{-1}$), there was an increase in the total germination percentage. Other reports also show a rise in seed germination for tomato and rice when exposed to SiO_2 nanoparticles [125] and CNTs [126], respectively. It is worthy to note that concentration of the nanomaterial is an influential factor on the plant reaction and various plants might react differently to a single specific nanomaterial. It is imaginable that nanomaterial undergoes transformation within the plant and the resulting product can potentially impose a further risk or even be beneficial for the plant growth [110]. Other than the impacts on the growth process of plants, nanomaterials can affect and raise the generation of ROS in a plant. The high concentration of ROS can engender protein oxidation,

DNA and cell membrane destruction, lipid peroxidation, electrolyte leakage, etc., thereby inducing oxidative damage and eventually cell death [127].

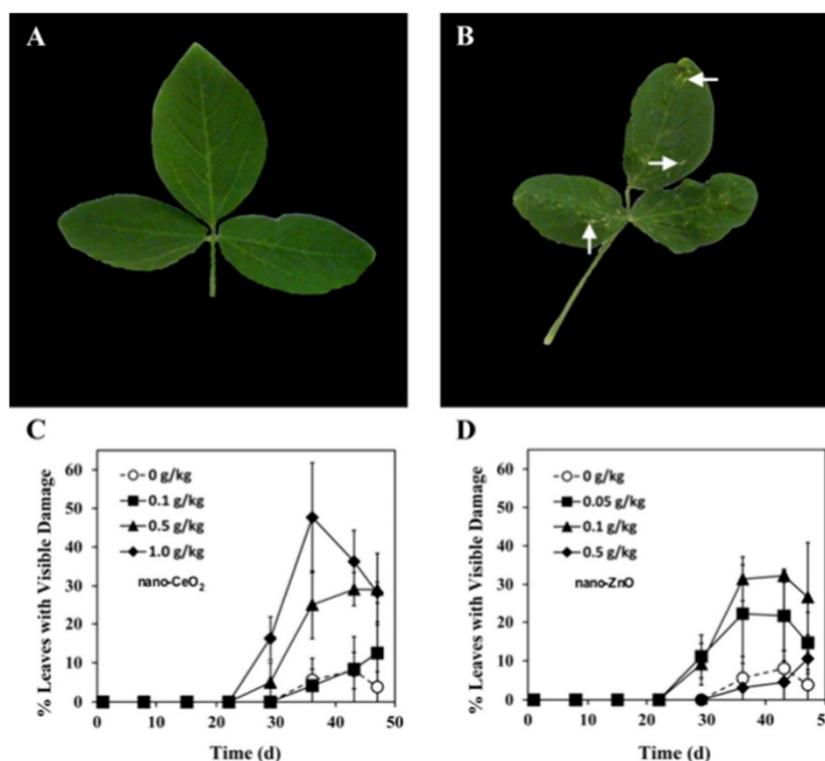


Figure 8. Camera images of soybean leaves without (a) and with (b) exposure to CeO₂ nanoparticles. The percentage of the leaves whose damage is recognized visually after exposure to (c) CeO₂ and (d) ZnO nanoparticles. Reproduced with permission from [123]. Copyright 2017, Elsevier.

One important point that must be kept in mind is that nanomaterials are normally transformed from origin i.e., the fabrication facility to destination. Thus, the results obtained in the studies based on pure nanomaterials could be not applicable to the realistic situations. Also, environmental factors such as pH, surface charge, ionic strength, surface coating, (UV) light irradiation, humic acids, inorganic ligands, mono- and divalent cations, affect the toxicity of nanomaterials in their destination [110]. With respect to the inclusion of nanoparticles into the terrestrial systems and their consequences, there are several reviews [110,128–131].

4. Conclusions and Future Outlook

Nanomaterials are favorable candidate materials for water remediation and control and an exciting prospect for their integration into point-of-use systems, and also in absolute removal of the current and emerging inorganic and organic pollutants from water is foreseen. They can be used in construction of nanoadsorbents that effectively capture polar and non-polar pollutants from water depending on their surface functionality. In this regard, the extensive surface area offered by nanomaterials is decisive and maximizes the adsorption efficiency. In case, the used nanomaterial is a photocatalyst, adsorption is extended to photodecomposition. Accordingly, the stuck organic pollutant is degraded into harmless byproducts and the adsorbent's surface becomes ready for a next round of adsorption/photodecomposition process. As another opportunity originated from nanomaterials, membrane nanostructures can be mentioned. Nanomaterials can be exploited as building blocks of a porous separator, as seen in electrospun nanofibrous membranes or single/few layer graphene membranes. Additionally, they can be used as additives to conventional thin film polymeric membranes for ultrafiltration to reduce fouling tendency and to raise thermomechanical

properties. Despite such merits of nanomaterials in filtration and water treatment industry, there are a variety of bottlenecks that must be properly addressed:

- (1) *Solar light driven photocatalysis*: With respect to photocatalysis-based water treatment, it is of paramount importance to avoid hole-electron recombination in the photocatalyst and also shift the light responsiveness from the UV to the visible solar light range. The latter goal guarantees a lower energy consumption and wider applicability of photocatalysis for water purification. Research has begun to develop a new generation of solar light responsive doped photocatalysts that assure versatility and energy efficiency of photocatalytic nanoadsorbents.
- (2) *Aggregation and poor recovery*: One important disadvantage regarding the nanoparticulate adsorbents is their aggregation tendency and challenging recovery. In this regard, one optimum solution is deposition of nanoparticles on nanostructured substrates e.g., nanofibers. This hybridization reduces the aggregation tendency and eases recovery of the nanoparticles, while preserving their high exposure to the external water medium.
- (3) *Photodegradation of polymer hosts*: Many nanomaterials in different forms such as nanoparticles, nanotubes, nanofibers, and nanosheets are typically used as coupled with a polymer substrate or host. In case of applying photocatalytic, aggressive nanomaterials, the chance of photodegradation of the encapsulating polymer is considerable. To address this problem, inclusion of photostabilizers could be a main strategy.
- (4) *Unwanted release of nanomaterials during the water treatment process*: Nanomaterials employed in the construction of micro-, ultra-, and nanofiltration membranes can be released into water streams when the membrane is subjected to harsh water streams and their complicated stress patterns. Therefore, primarily stabilization of nanoparticles on/in the membrane structure should be taken into account and secondly, innocuous materials should be employed that impose less hazardous effects on biota.
- (5) *Long term, realistic testing of novel generation of nanostructured membranes*: Nanomaterials in higher dimensionalities such as 1D nanofibers and the 2D graphene family have also been studied for the development of membranes. Electrospun nanofibers have shown a promising potential in size exclusion and also adsorption of water pollutants. Thanks to their tunable pore size, high porosity and interconnected porous structure they can guarantee a less energy consuming water treatment process. That is why they have found large applicability for building up advanced ultra- and nanofiltration membranes as a porous, robust support for the overlaying selective layer. However, no industrial utility has been reported for nanofibrous membranes. This could arise from the available gaps with respect to reliable testing of such membranes. Nanofibrous membranes must be challenged in long term, and under realistic conditions with real wastewater models and also be exposed to various complicated mechanical stress patterns. Typically, the relevant research experiments done at the lab scale consider only one type of pollutant and ignore co-existence of other dye, ionic, or organic pollutants, as seen in real wastewater, which compete for a limited number of available active/binding sites. Such a perspective was previously taken into account for activated carbon as a commercial adsorbent, and led to its commercialization. Graphene membranes are also a fascinating group of advanced nanomembranes that have shown amazing potentials, particularly with respect to water permeability, while offering an ionic selectivity comparable to classic NF and ideally RO membranes. Nevertheless, their properties have been mainly theoretically validated rather than experimentally and there is still a large gap ahead till realistic employment of such membranes.
- (6) *Large scale and economical production of nanostructured membranes and adsorbents*: This issue is under extensive investigation. In fact, technical difficulties with respect to scale-up and integration of nanomaterials into a relevant technology, cost effectiveness, and energy-related issue are all hindering concerns that have slowed the marketing trend of such products. For instance, TiO₂ nanoparticles and CNTs are among the most widely studied nanomaterials for adsorption of dyes. However, they are toxic and produced in a costly manner involving high temperature

and pressure. The former nano-adsorbent needs UV irradiation to photodecompose the dye pollutants that adds to the expenses of the treatment. In fact, it is highly necessary to produce large amounts of such nanomaterials at justifiable costs for water treatments, specific to different categories of wastewaters.

- (7) *Environmental hazards*: This concern will persist in the future. This stems from the reality that many environmental and biological consequences of nanomaterials should be identified in the long term. Short term studies have shown that several nanomaterials are safe to human being, plants and animals. But, there is no certainty about their long term safety. For this reason, establishment of nanomaterial based water treatment systems should be followed with sufficient precautions. Technologically, it is also vital to secure such systems so that the release of nanomaterials into environment would be minimized.

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