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► To cite this version:

Didier Robert, Paul Henri Alle, Nicolas Keller, Marie-Antoinette Dzuila, Patricia Garcia-Muñoz. Challenges and opportunities for microplastics and nanoplastics removal from industrial wastewater. Current Developments in Biotechnology and Bioengineering, Elsevier, pp.425-446, 2022, 10.1016/B978-0-323-99908-3.00009-9. hal-03795524

HAL Id: hal-03795524 https://hal.science/hal-03795524

Submitted on 4 Oct 2022

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Challenges and opportunities for microplastics and nanoplastics removal from industrial wastewater

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Abstract

Microplastics (MPs) and nanoplastics (NPs) are ecotoxicological threats because they are able to accumulate and transport toxic metals, persistent organic pollutants or pharmaceuticals products. Consequently, NP pollution is also a public health problem. MP and NP particles arise into surface water bodies and sea water through two major routes: 1) by the transport in the marine environment as synthetic microbeads or microparticles (for example, incorporated into cosmetic products, or during the washing of synthetic clothes) and 2) by the fragmentation of large plastic debris into MPs and NPs, through ultraviolet (UV) photodegradation, biodegradation, mechanical and chemical degradation processes (secondary microplastics). Even if, interest of the scientific community in environmental pollution caused by MP and NP started at the beginning of the 21st century, the research works for reducing and/or removing

them in water is very recent. The objective of this chapter is to present the main methods of treatment or removal of MPs and NPs from water, as well as the processes under development.

Keywords: nanoplastic, microplastic, wastewater treatment processes, photocatalysis, WWTPs, AOPs.

1. Introduction

Globally, over 300 million tons of plastics are produced every year, with about 13 million tons being released into rivers and oceans (Foerster, 2017), and 250 million tons predicted to cumulate by 2025 (Jambeck et al., 2015). Depending on their utilization, plastic products may have a service life of 1 to more than 50 years. Thus, the release of micro- and nano-sized plastic waste in marine and freshwater bodies (Schirinzi, et al., 2017) and its potential impact on aquatic life (Kögel, et al., 2020) have recently become a major concern. In a recent report published by the European Commission in 2017, microplastics (MPs) most commonly defined as man-made plastic items smaller than 5 mm, are of particular concern for marine and inland aquatic environments. Nanoplastics (NPs) have still not been precisely defined, but we may consider that they represent plastic particles smaller than one micrometer.

MPs and NPs are an ecotoxicological threat because they are able to accumulate and transport toxic metals, persistent organic pollutants, pharmaceuticals, and personal care products (Atugoda et al., 2021, Arienzo et al., 2021). NP pollution is also a public health problem (Jian et al., 2020, Sana et al., 2020). In fact, the human body is daily subjected to NPs exposure for instance via food and drinking water which contain MPs and NPs. Also, MPs particles might be involved in immune or neurodegenerative illnesses. What are the consequences of such pollution for the environment, and for human and animal health? Due to their small size close to the size of macromolecules and natural proteins, NPs are highly bioavailable and may cross physiological barriers, leading to translocation in tissues, oxidative stress and cytotoxicity. Furthermore, their persistent nature allows their concentration in organisms, contributing to severe inflammation, and increasing the risk of cancer (Prata et al., 2020). Also, MP particles might be involved in immune or neurodegenerative illnesses (Prüst et al., 2020; Kannan et al., 2021). Additionally, NPs may release chemicals, such as organic plastic additives (OPAs) present in their formulation, or various environmental pollutants (heavy metals, persistent

organic pollutants (POPs)) (Menéndez-Pedriza et al., 2020). They can also act as a support for microbial biofilms and pathogens (Prata et al., 2020; Wang et al., 2021). According to Paul et al. (2020), MPs and NPs can reach the human body amongst others via the oral route. Oral ingestion is followed by a number of steps that influence the particles and therefore, their interactions, like the contact with digestive fluids, the contact to intestinal cells, uptake and transport in the intestine and liver, and excretion.

Small plastic particles arise into surface water bodies and sea water through two major routes, as follows, with further undergoing degradation from the macro- to the micro- and nano-scale size:

1. Transport in the marine environment as synthetic microbeads, incorporated into cosmetic and personal care products such as shampoos and scrubs. Transport occurs via landfill leachates or wastewater treatment plant effluents connected to surface waters running into the sea. Moreover, synthetic clothes are primary and secondary sources of MPs. Their fragmentation during washing leads to a discharge of large quantities of MPs and NPs in wastewater treatment plants (WWTPs). Approximately 35% of worldwide oceans primary MPs may come from synthetic textile laundry (Boucher and Friot, 2017).

2. Fragmentation of large plastic debris into MPs and NPs, through ultraviolet (UV) photodegradation, biodegradation, mechanical and chemical degradation processes (secondary MPs) (Andrady et al., 2011).

Interest of the scientific community in environmental pollution caused by MPs and NPs started at the beginning of the 21st century. Presence of MPs in water environments, such as rivers, lakes and oceans has been well identified and studied. MPs and NPs have been detected in freshwaters around the world (Eriksen et al., 2013 and Wang et al., 2018), including polar regions (Mishra et al., 2021). However, as mentioned by Estahbanati et al. (2021) in their review, interest of the scientific community in technologies for reducing and/or removing MPs and NPs in water is very recent. Especially, the first studies for NPs removal have been published less than 5 years ago, and publications on MPs and NPs removal increased twice between 2019 and 2020 (Establanati et al., 2021).

Removing all MPs and NPs present in oceans appears unrealistic and impossible. However, limiting their discharges in the environment is possible, by acting upstream on municipal WWTPs, for example. Currently, plastic materials are primarily removed by skimming and settling, sedimentation, bar screening, flotation, grease and grit removal, coagulation-flocculation, aeration and clarification, biofilm/activated sludge, chemical oxidation, membrane separation, chlorination, biological treatment, disinfection, and filtration processes (Okoffo et al., 2019). Nonetheless, the smallest plastic debris ranging between 20 to 100 nm (i.e. NPs) could circumvent all treatment stages, with being released in the environment (Cesa et al., 2017). Up to date, no large-scale study has been carried out on the release of NPs in surface water, mainly because NPs are difficult to detect and quantify. Many studies suggest that despite their upgrade, WWTPs still represent one possible way of daily MPs and NPs release in the environment (Enfrin et al., 2019).

Processes occurring in WWTPs can be classified into two categories: separation (coagulation-flocculation, membrane separation...), and degradation processes (photo-oxidation, biological treatment...). They are also considered as preliminary, primary, secondary and tertiary treatment steps. Estimated MPs flow are reported in Figure 18.1 (Sun et al., 2018), showing the removal efficiency of MPs at the different treatment steps.

INSERT FIGURE 18.1 HERE

Lyare et al. (2020) analyzed the results of 21 studies reporting MPs concentrations at the WWTPs outlet. Average removal efficiencies of 88% and 94% were estimated for WWTPs

comprising preliminary/primary plus secondary treatments, and preliminary/primary plus secondary and tertiary treatments, respectively. Although these installations are not designed for removing this type of emerging pollutants, most of MPs seem to have been retained by WWTPs. But, even though the overall removal efficiency is high, the residual amount of MPs in the WWTP outlet (~10% of MPs in the influent wastewater) represents a significant release of MPs in the aquatic environment, considering the large effluent volumes involved. Moreover, NPs could not be quantified in those studies, because current analytical techniques employed for estimating MPs are not adapted to NPs detection and quantification (Gigault et al., 2021).

2. Preliminary and primary treatment steps

Preliminary and primary treatments are the first WWTP steps. They allow the removal of materials such as bottles, wood pieces, floatables, grit and grease that may impair or counteract downstream processes (Metcalf et al., 2014). They consist of coarse and fine screening, grit and grease removal, skimming and primary settlement (sedimentation), and allow the removal of plastic particles larger than 5 mm, and of 50% –98% MPs (Gies et al., 2018; Gundogdu et al., 2018). However, these performances depend on several factors such as MPs and NPs concentrations, shapes (fibers, spheres, etc.) and formulation (polymer or copolymer type, additives, toxicity, etc.).

Coagulation and flocculation (primary treatment) using low-cost aluminum or iron-based coagulants, are essential steps of the drinking water as well as wastewater treatment process (Bratby, 2006). Depending on the water pH, pollutants surface charge and concentration, flocs are quickly formed and settle at the bottom of the sedimentation tank. However, the process efficiency decreases with high concentrations of MPs or NPs in the effluent because negatively charged MPs and NPs interact with some iron or aluminum salts, thus requiring higher

concentrations of coagulants. Since water MPs and NPs concentrations remain unknown and difficult to estimate, MPs/NPs are a limiting factor for coagulation processes. Whereas MPs surface is neutral or negatively charged (due to surface weathering and oxidation), these particles can adsorb on metal hydroxides (Fe(OH)₃ or Al(OH)₃) produced during coagulation, or act as ligands (Enfrin et al., 2019), leading to larger and more stable aggregates which can precipitate. Moreover, MPs size controls the coagulation efficiency. Thus, MPs ranging between 30 and 100 nm were almost completely removed, while 10-30 nm particles were only removed at 50% (Shahi et al., 2020). It also appears that the coagulation process was 25% more efficient with Al^{3+} than with Fe^{2+} for removing 0.1–5 mm MPs (Ma et al., 2019b), and even improved by 60% with the addition of anionic surfactant.

Once coagulation allowed charge neutralization between particles and colloids, flocculants are added to promote particle aggregation through various mechanisms which are highly dependent on the flocculant type, the nature of the material to be aggregated, and the flocculation medium conditions (Figure 18.2). Polyacrylamides and their derivatives are the most common flocculants. After coagulation/flocculation steps, solid-liquid separation is carried out to obtain clarified water and sludge (initial colloidal particles + flocs), before moving on to the next step which is the secondary treatment step. At this level, the sludge contains a large part of MPs.

INSERT FIGURE 18.2 HERE

3. Secondary treatment steps

The secondary treatment steps are classically a biological treatment process. According to Jeong et al. (2016) this treatment removes a part of MPs which were not eliminated during the primary treatment step, through MPs entrapment in solid flocs, sedimentation in secondary clarifiers, or even ingestion by microorganisms, e.g., protozoa or metazoan. Sun et al. (2019)

have shown that this treatment can remove until to 36% of MPs from the primary treatment effluent. According to Carr et al. (2016), MPs contact time is crucial for their removal. In fact, the longer the contact time, the more the biofilm will develop on MPs surface, modifying their surface properties, and therefore impacting positively the treatment. This secondary treatment removed more fragment particles than fibers (Figure 18.3) (Lares et al., 2018).

INSERT FIGURE 18.3 HERE

This was supported by studies showing that the relative abundance of MPs fragments decreased while that of fibers increased after the secondary treatment (Talvitie et al., 2015). As, large MP particles can be further removed during the secondary treatment, they concentration in the secondary effluent is lower. Studies showed that MPs with size >300 mm only account for 8% after secondary treatment (Talvitie et al., 2016, Mintenig et al., 2017) However, several studies on this subject conclude that a tertiary treatment step is necessary for effective MPs removal from wastewater (Estabbanati et al., 2021).

4. Tertiary treatment steps

MPs and NPs removal from water is only partial with primary and secondary treatment steps. Not only do microparticles remain from the primary effluent, but new, much smaller plastic particles (NPs) are formed during processing. Indeed, according to Enfrin et al. (2019), NPs/MPs travelling through WWTPs processes face varying shear forces induced by mixing or pumping which can break NPs/MPs into smaller particles increasing the number of toxic NPs released in water. There is a lack of knowledge regarding interactions between NPs/MPs and WWTPs processes, especially on NPs generation through MPs fragmentation. Tertiary treatment steps include the following processes: membrane filtration such as reverse osmosis, rapid granular filtration, disc filtration, dissolved air flotation and other processes (Booth et al., 2020).

4.1. Rapid Sand filtration

Rapid sand filtration/RSF (or Rapid granular filtration/RGF) allows catching suspended solids from wastewater either by mechanical straining or by physical adsorption through three layers comprising anthracite grains, silica sand and gravel (Figure 18.4) (Enfrin et al., 2019; Scholz, 2016). The main disadvantage of RSF is that the first top layers get clogged quickly, requiring a regular backwash.

INSERT FIGURE 18.4 HERE

On the other hand, once MPs have reached the silica bed, they interact with SiO₂ through surface hydroxyl sites formed as a result of weathering, which can be an advantage because a large part of MPs/NPs is retained by RSF (Figure 18.4). It is also a drawback because the filter regeneration is more difficult after NPs/MPs adsorption. This process can be effective in stopping MPs, but their removal efficiency is strongly dependent on the particle size as well as on the polymer nature. Zhang et al. (2020) have shown that MPs and NPs particles having a size below 1 μ m were more easily retained on the filter than MPs having a size between 10 and 20 μ m.

4.2. Disc and membranes filtrations

Disc filtration is based on physical retention in the filters with formation of a mud cake. Simon et al. (2019) evaluated the performance of disc filters that retain MPs from treated wastewater. They showed that the disc filter retained 89.7% of particles, and 75.6% of their mass. However, the presence in the filtrate, of an unexpectedly large number of MPs whose size substantially exceeded the pore size of the disc filter suggested that particles could either bypass or pass through the filter mesh, somewhat diminishing the filter performance.

Membrane separation is one of the most widely applied technologies for the treatment of drinking water and wastewater. This process has the advantages of stable effluent quality and simple operation. Depending on the type of membrane it can efficiently remove/separate organic pollutants, bacteria, suspended solids, multivalent ions and by-products, and at the same time, reduce the hardness of water. Membranes can act as physical barriers for MPs. As explained by Baker et al. (2012), as MPs size is of the same order of magnitude than membrane pore size, a large part of MPs should therefore be removed through membrane separation. For example, Ziajahromi et al. (2017) investigated the fate of MPs in WWTPs in Sydney. Their results showed that after ultrafiltration and reverse osmosis, primary treated effluents contained only 1.515% MPs particles/L (Figure 18. 5).

INSERT FIGURE 18.5 HERE

As indicate by Enfrin et al. (2020), one challenge of membrane filtration utilization is membrane fouling which reduces the throughput. Small MPs and NPs could impose a more intense fouling effect than big ones because they cause complete to intermediate pore blocking. Dynamic membrane filtration and sequential membrane filtration which might be news solutions for reducing membrane fouling, and their associated maintenance cost and energy input.

Membrane bioreactor (MBR) is a type of wastewater treatment technology combining membrane separation process with conventional activated sludge (CAS) treatment process. Since the membrane pore size should be below 0.1µm, MBR can effectively produce a high-quality clarified effluent. The MBR process has received more and more attention because of its advantages such as high removal efficiency for pollutants, space saving, and reduced sludge production. According to Li et al. (2020), the MBR system could effectively treat MPs contaminated surface waters with removing almost all MPs. Most MPs were retained in the biofilm carrier side of the MBR system (Figure 18.6).

INSERT FIGURE 18.6 HERE

However, the presence of MPs even at low concentrations (10 particles/L) caused fouling of the membrane, requiring regular physical cleaning and reducing the membrane service life. This study has shown that most MPs caused irreversible membrane fouling (Li et al., 2020).

However, that despite utilizing modern technologies, WWTPs are still a potential pathway to release MPs in the large volumes of effluent discharged daily into the environment (Kalcíkov et al., 2017), as shown by the data on the removal efficiency of MPs from WWTPs in Table 18.1 (Hamidian et 2021). It is therefore essential to develop new efficient technologies for removing MPs and NPs from water. These processes must be destructive and not extractive in order to avoid shifting the pollutants to another type of ultimate treatment.

INSERT TABLE 18.1 HERE

5. Advanced treatments and novel solutions to remove MPs and NPs from wastewater

In the first part of this chapter, we saw that currently, plastic materials are primarily removed by skimming and settling, sedimentation, bar screening, flotation, grease and grit removal, coagulation-flocculation, aeration and clarification, biofilm/activated sludge, membrane separation, biological treatment and filtration processes. Nonetheless, the studies indicated that the smallest plastic debris varying from 20 to 100 nm could circumvent all treatment stages (encompassing tertiary treatment) and thus, were released in the environment (Cesa et al., 2017). Up to date, no large-scale study has been carried out on the release of plastic NPs (size less than 1 μ m) in surface water, mainly because they are difficult to detect and quantify. Many studies suggest that despite their upgrade, WWTPs still represent one possible way of daily MPs and NPs release in the environment (Enfrin et al., 2019). As described above, MPs and NPs disrupt the operation of conventional wastewater treatment processes (rapid sand filtration, membrane filtration, etc.) and unlike MPs, NPs are almost completely released into natural environments. Moreover, the main drawback of most conventional processes is that these treatments are non-destructive and just transfer NPs pollution somewhere else (on filters or adsorbents). For example, coagulation/flocculation or electrocoagulation processes produce large volumes of sludge containing high MPs and NPs concentrations (Padervand et al., 2020). The development of environment friendly degradation and mineralization processes is therefore necessary to remove MPs and especially NPs present in drinking water or in wastewater. However, all studies on catalytic, photocatalytic, and electrochemical degradation of MPs and NPs have been performed at laboratory scale, and further research is necessary to evaluate the challenges associated with scaling-up (Estabbanati et al., 2021).

5.1. Advanced oxidation processes

While efficient NPs removal technologies remain underdeveloped, advanced oxidation processes (AOPs) represent attractive technologies for NPs degradation (Zhao et al., 2007, Talvitie et al., 2017, Allé et al., 2021). Use of AOPs for environmental applications, have been precisely defined by Glaze et al. (1987) as water treatment processes performed at room temperature and atmospheric pressure, based on the *in-situ* generation of a powerful oxidizing agent, such as hydroxyl radicals (OH°), at a sufficient concentration to effectively decontaminate waters. These AOPs are efficient technologies for water treatment in terms of organic micropollutant degradation. During the last 30 years, multiple studies compared the efficiencies of the main AOPs (Comninellis et al., 2008, Babuponnusami et al., 2012, Oturan et., 2014). However, most of them were focused on the degradation of organic molecules (pesticides, dyes, drugs, etc.) and their by-products (Rizzo et al., 2018, Wols et al., 2012, Brillas, 2020).

Advanced oxidation for environmental treatment (AOPs) refers to those oxidative processes that generate highly oxidizing species under moderate conditions, for the destruction and ultimate mineralization of targeted contaminants. Amongst oxidative treatments developed for destroying organic contaminants in natural waters and wastewaters, a few of them focused on MPs degradation. In 2010, Feng et al. (2010) demonstrated that a homogeneous *photo-assisted Fenton* reaction was able to mediate the mineralization of polystyrene materials containing sulfonate decorations (Figure 18.7).

INSERT FIGURE 18.7 HERE

Fenton and photo-assisted Fenton processes consist of the *in-situ* generation of hydroxyl radicals using H₂O₂ in the presence of iron salt catalysts. This strategy of photo-assisted Fenton degradation and mineralization might also be applicable to advanced oxidative treatment of other synthetic polymers. For instance, Miao et al. (2020) have shown an electro-Fenton like (EF-like) technology for degrading polyvinyl chloride (PVC), based on a TiO₂/graphite (TiO₂/C) cathode. It exhibited a good performance for PVC degradation via simultaneous cathodic reduction dechlorination and hydroxyl radical oxidation (Figure 18.8).

INSERT FIGURE 18.8 HERE

Heterogeneous photocatalysis is considered as an environmentally friendly process able to degrade organic pollutants into water, CO₂ and mineral acids. It is based on the interaction of a semiconductor such as TiO₂ with a pollutant and light. When the semiconductor absorbs light with $E \ge Eg$, the electrons (e⁻) located in the valence band are transferred into the conduction band, leaving behind a positive hole (h⁺). Both species react with H₂O, OH⁻ and O₂ adsorbed on the surface of the semiconductor, with generating reactive oxygen species such as hydroxyl (OH^o) and superoxide (O₂^{o-}) radicals (Nakata and Fujishima, 2012) (Figure 18.9).

INSERT FIGURE 18.9 HERE

Few works have been performed on plastics removal by heterogeneous photocatalysis. Most of them considered polymeric films such as Polyvinylchloride (PVC) (Horikoshi et al., 1998), Low Density PolyEthylene (LDPE) (Tofa et al., 2019) and Polystyrene (PS) (Shang et al., 2003). In the scientific literature few examples only concerned the photocatalytic removal of polymer nanoparticles. For instance, Wang et al. (2019) used a photocatalytic TiO₂-based micromotor (Au@mag@TiO₂, mag = Ni, Fe) for the elimination of NPs from washing powders, toothpastes and face cleansing creams.

Titanium dioxide is not the only semiconductor that has been used for the photocatalytic degradation of HDPE. Jiang et al. (2021) synthesized a hydroxy-rich ultrathin bismuth oxychloride (BiOCl-X) photocatalyst. They showed that BiOCl-X has a strong potential for photocatalytic degradation of MPs, with a 24 times higher plastics mass loss than for BiOCl nanosheets (Figure 18.10). Moreover, from the degradation mechanism of HDPE, they demonstrated the influence of surface hydroxyl groups on the MPs photodegradation. This work could be useful for designing controllable hydroxy-rich photocatalysts with applications in MPs degradation.

INSERT FIGURE 18. 10 HERE

In another study, Tofa et al. (2019) successfully demonstrated the degradation of MP fragments, LDPE films in water using visible light excited heterogeneous ZnO photocatalysts. Photocatalytic LDPE oxidation led to the formation of low molecular weight compounds like hydroperoxides, peroxides, carbonyl and unsaturated groups, resulting in increased brittleness along with wrinkles, cracks and cavities on the LDPE surface. The authors have shown that the catalyst surface area was found to be crucial for enhancing the LDPE degradation. More recently, Nabi et al. (2020) proposed the efficient degradation and complete mineralization of PE and PS nanospheres (between 700 nm and 5mm) by a film of TiO₂ nanoparticles under UV light irradiation. They studied the degradation mechanism by *in-situ* DRIFTS and mass

spectrometer, showing the generation of hydroxyl, carbonyl, and carbon-hydrogen groups, which demonstrates PS photodegradation. Ariza-Tarazona et al. (2019) have conducted the photocatalytic degradation of HDPE MPs extracted from a commercially available facial scrub using N-TiO₂.

In their recent work, Allé et al. (2021) studied the feasibility of NPs degradation by photocatalysis with TiO₂-P25/ β -SiC foams under UV-A. Unlike previous work, they used very small polymer particles (between 100 and 500 nm) and determined the influence of various parameters (i.e., flowrate, pH and light intensity) on the photocatalytic degradation of calibrated polymethylmethacrylate (PMMA) and polystyrene (PS) nanoparticles. The first results are very positive, because they showed that it is possible to mineralize PMMA and PS nanobeads (NBs) by UV-A photocatalysis. After 7 hours irradiation, 50% of an aqueous suspension loaded with PMMA NBs (TOC = 12 mg/l) has been mineralized by working at an irradiance of 112 W/m², with a flowrate of 10 mL/min and at initial pH value of 6.3 in a flow-through mode. They also compared the reactivity of the two polymers and observed that PMMA degrades faster than PS, probably because of the more easily breakable ester function (Figure 18.11).

INSERT FIGURE 18.11 HERE

5.2. Other processes

Catalytic oxidation: Recently, Kang et al. (2019) studied the degradation of cosmetic MPs by the means of a catalytic activation of peroxymonosulfate to generate reactive radicals from carbon hybrids. Thanks to the synergistic effect of nitrogen doping, transition metal (Mn) encapsulation, and robust helical structure, the catalytic performance and stability of Mn@NCNTs has been considerably increased for MPs degradation, with a significant reduced activation energy. However, the complete mineralization of MPs was not achieved.

Nevertheless, according to the authors, the toxicity evaluation with *C. vulgaris* showed that MPs degradation intermediates were considered to be without hazard for microorganisms and could serve as nutrients for waterborne algae.

Electrochemical oxidation: In recent studies, electro-oxidation (EO) showed a good efficiency for the degradation of persistent pollutants, such as pesticides, dyes, pharmaceuticals, and petrochemicals (see for example, the work of Wang et al., 2021). Electrochemical oxidation is divided into anodic oxidation and indirect cathode oxidation, and the most common method is anodic oxidation (AO), referring to the direct oxidation of organic pollutants on the anode surface through charge transfer, or indirect oxidation of pollutants by •OH or reagents. Recently, Kiendrebeogo et al. (2021) showed that electro-oxidation using a Boron-doped diamond anode is a feasible technology for the treatment of water contaminated with MPs. They obtained a strong degradation of mono-dispersed suspension of PS microbeads ($89 \pm 8\%$), using Na₂SO₄ (0.03 M) as supporting electrolyte and a current intensity of 9A during 6 h electrolysis. As MPs and NPs react with OH° radicals during the process, the oxidation of PS microbeads occurs through the same mechanism as for photocatalytic degradation. In another study, a real washing machine effluent was treated by electro-oxidation (EO) in a pre-pilot plant scale electrochemical flow reactor, using active (Ti/Pt) or non-active (boron doped diamond (BDD)) anodes and Ti cathode (Duran et al., 2018). The authors showed the effect of anode material and of the applied current density on the removal of the organic matter, in terms of chemical oxygen demand (COD) during the electrochemical oxidation.

Magnetic extraction: Grbic et al. (2019) developed a method that magnetically extracts plastics, taking advantage of their hydrophobic surface to magnetize them. They developed hydrophobic Fe nanoparticles that bind to plastic, allowing magnetic recovery. According to the authors, it possible to recover the main families of MP from seawater (polyethylene (PE), polyethylene terephthalate (PET), polystyrene (PS), polyurethane (PU), polyvinyl chloride (PVC), and

polypropylene (PP)). For example, they recovered 92% of 10–20 μ m PE and PS beads, and 93% of >1 mm MPs from seawater.

Another alternative separation approach proposed by Misra et al. (2019) consist in the preparation of composites based on polyoxometalate ionic liquid (POM-IL) adsorbed onto magnetic microporous core–shell Fe₂O₃/SiO₂ particles, giving a magnetic POM-supported ionic liquid phase. They used commercial colloidal solutions of spherical PS beads (diameter 1 μ m and 10 μ m) as models of environmentally persistent MPs. PS particle removal was quantified using dynamic light scattering. After 24 h treatment of solutions of 1 μ m and 10 μ m PS beads (c = 1g / L), the extraction rate was 100%.

Moreover, Tang et al. (2021) synthesized magnetic carbon nanotubes (M - CNTs) as adsorbates to remove MPs. Tests performed with suspensions of PE, PET, and polyamide (PA) showed a successful extraction of MPs from the water after adsorption on M-CNTs (Figure 18.12).

INSERT FIGURE 18.12 HERE

However, magnetic extraction of MPs and NPs from wastewater is unsuccessful for MPs and NPs removal, but allows their extraction and storage before degradation using an additional treatment step.

Removal by Metal–organic frameworks (MOFs): Metal-organic frameworks are organicinorganic hybrid crystalline porous materials that consist of a regular array of positively charged metal ions surrounded by organic 'linker' molecules. Metal ions form nodes that bind the arms of the linkers together to form a repeating cage-like structure. Due to this hollow structure, MOFs have an extraordinarily large internal surface area (until 7800 m²/g). Developed since 1990s, they can be used for gas storage, separation, catalysis, sensing and contaminant removal. Chen et al. (2020), have prepared a series of Zr-MOFs-based foam materials through a unique acetone-assisted method with various functional groups (UiO-66-X, X ¹/₄ H, NH₂, OH, Br and NO₂). These MOFs have been used in efficient MPs removal that is suitable for various types or concentrations of simulated microplastics suspensions. The best (UiO-66-OH@MF-3) effectively removed MPs with an efficiency up to 95.5 % and can maintain high efficiency through recycling (10 cycles) (Figure 18.13).

INSERT FIGURE 18.13 HERE

Table 18.2 and Table 18.3 reported the recent works respectively on the separation treatment processes and advanced treatment processes for the removal of MPs and NPs in waters. This confirms that studies and research concerning separation processes are more numerous and more efficient even if the micro- and nanoplastics are not degraded. While works on advanced treatment processes are recent and in full development.

INSERT TABLES 18.2 AND 18.3 HERE

6. Conclusions and perspectives

Plastics are known for their stability and durability, and very few of them are said to be "biodegradable". Once they end up as waste in the environment, they remain there for many years, mostly in the form of MPs and NPs. All surface waters (rivers, seas, oceans, etc.) are affected by this pollution. Consequently, MPs are found in drinking water including tap and bottled water. Plastics removal from the entire ocean is impossible, but MPs discharge in the ocean can be limited with WWTPs. However, research on MPs removal in wastewater and drinking water treatment processes is still relatively scarce. This chapter listed and discussed the main methods of treatment or removal of MPs and NPs from wastewater, as well as the processes under development. This list can be complemented by other treatments such as biological and biodegradability processes. All these methods can be classified into two categories: separation methods (membrane filtration, flocculation, magnetic processes, etc.) and degradation methods (catalysis, photocatalysis, electro-oxidation, etc.).

Currently, separation technologies are the most studied, and they are more efficient than destruction processes. Most of these technologies achieve performances greater than 90% (disc filtration, rapid granular filtration, coagulation, etc.) while degradation processes show yields between 50 and 90% (heterogeneous catalysis and photocatalysis). However, separation technologies will no longer be viable in the long term, as they will face problems of waste management, storage and disposal. Destruction processes will be preferred in the future, but only if the scientific community improves their efficiency, and develops economically viable technologies.

Current treatment technologies need to be optimized for limiting MPs concentration and ensuring global treatment process performances. In particular, it is necessary to monitor and quantify nanoplastics which are produced at each treatment stage of WWTPs. But this requires the development of simple and rapid techniques for measuring and characterizing NPs in water, which is another challenge to overcome.

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Figure 18.1: Estimated MPs flow in primary, secondary and tertiary treatment step (Sun et al.

2018)



Figure 18.2: Illustration of the hypothetic flocculation mechanisms occurring among negatively charged particles and cationic polyeletrolytes: (A) charge neutralization, (B) patching and (C) bridging (Magalhães et al. 2020)

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Figure 18.3. The proportion of different types (fibers, fragments, spheres) of microplastics in different stages of the WW TP and a nearby lake (Lares et al. 2018)



Figure 18.4: Interaction between nano/microplastics and rapid sand filtration processes (Enfrin

et al. 2019)



Figure 18.5: Number of microplastic particles per liter in the final effluent of each wastewater treatment plant according to their shape (Ziajahromi et al. 2017).







Figure 18.7: 1. Photoassisted Fenton treatment of PS and CS (Sulfonated)-PS beads: (a)
changes in dissolved organic carbon content of the degradation mixtures during the treatment;
(b-e) SEM images of the CS-PS beads at different time intervals (t from 0 min to 60 min) of the photoassisted Fenton degradation (Feng et al. 2010).



Figure 18.8: The proposed electro-Fenton degradation process for PVC microplastics (Miao et al. 2020).



Figure 18.9: General mechanism of TiO₂ photocatalysis



Figure 18.10: SEM image of the original PE-S (a) and the photodegraded PE-S by BiOCl-1 at 1 h (rough and porous) (b), 5 h (broken) (c), and 10 h (Shatter) (d) (Jiang et al. 2020)



Figure 18.11: Comparison of photocatalytic mineralization of NBs-PMMA and NBs-PS1/PS2 (Flow rate: 10 mL/min, pH: 6,2)



Figure 18.12: Effect of M–CNTs dosage on MPs removal (pH = 7.0 ± 0.1 , MPs dosage 5 g·L–1, contact time 300 min, 25 °C). (Tang et al. 2021).



Figure 18.13: The removal efficiency of UiO-66-X@MF (X ¹/₄ X ¹/₄ H, NH2, OH, Br and NO2) (left). The removal efficiency of UiO-66-OH@MF-3 for different microplastics types (right). (adapted from Chen et al. 2020)

Table 18.1: Reported microplastics removal efficiency of different WWTPs around the World(Adapted from Hamidian et al., 2021)

Country	Microplastic	Type of WWTP	% Removal	Reference
Canada	Fibers	Primary sedimentation	92.84	Gies et al., 2018
	MP particles	and scum removal	88.40	
	MPs	_	84	
	MPs	Secondary tratment	98	
Italy		Primary grease and sedimentation process	84	Magni et al., 2019
	MPs	Tertiary	55.5	
Finland		Primary clarifier	98.85	Lares et al., 2018
		Secondary: membrane permeate	60	-
China	MPs	Aerated grit chamber	60	Yang et al., 2019
Scotland		Grit and grease	44.59	Murphy et al.,
		Primary settling tanks	33.75	2016
China	Microfibers	Coarse and fine grid, aerated grit chamber, and primary settlement tank	40.70	Liu et al., 2019
	MPs	Secondary	16.60	-
		Tertiary	7.1	-
Australia	MPs	Primary	98.7	Ziajahromi et al., 2017
		Primary and secondary	66	
		Primary, secondary and tertiary	87.27	-
Korea	MPs	Primary	98.70	Hidayaturrahman et al., 2019
		Secondary	54.7	
		Tertiary: ozone	89.9	
		Tertiary: membrane disc- filter	79.4	
		Tertiary: rapid sand filtration	73.8	
Finland	MPs	Tertiary: disc filtration	40	

	Tertiary: rapid sand	97.1	Talvitie et al.,
	filtration		2017
	Tertiary: dissolved air	95	
	flotation		
	Tertiary: membrane	99.9	
	bioreactor		

Table 18.2: Recent works on the separation treatment processes for the removal of MPs and NPs in waters.

Treatment	MPs/NPs type	Analytical	Results	References
process	and size	methods		
Filtration, centrifugation, coagulation	PET (<400 nm)	-Turbidity -Size distribution analysis	-Filtration with 0.22 μ m filter: 92 \pm 3% removal - Centrifugation with 10,000 rpm for 10 min: 99 \pm 1% removal -Flocculation for 10 min: 77 \pm 15% removal	Murray and Ormeci, 2020
Dynamic membrane	1.65–516 µm	-Laser diffraction particle size analysis - Turbidity	-Turbidity reduced from 195 NTU to ≤1 NTU after 20 min	Li et al., 2018
MBR Disc filtration Rapid granular filtration Dissolved air flotation	PES, PE, PS, PP, PA, polyurethane, polyvinyl chloride (PVC), polyacrylamide, polyacrylate, alkyd resin, polyphenylene oxides, and ethylene-vinyl acetates (>300 μm, 100–300 μm, and 20– 100 μm)	-Stereo microscopy with an integrated HD camera	Elimination of 99.9% of MPs Elimination of 40–98.5% of MPs Elimination of 97% of MPs Elimination of 95% of MPs	Talvitie et al., 2017
Disc filtration	PE, PS, and PVC	FPA-µFTIR	Elimination of 89.7% (based on numbers) or 75.6% (based on weight) of MPs	Simon et al., 2019
Membrane bioreactor	PES, PE, polyamide, PP (0.25 and 5.0 mm)	-Optical microscopy -FTIR -Raman	-Elimination of 98.3% of MPs	Lares et al., 2018

	PE and PES (<500 μm)	-SEM -FTIR	Elimination of 75.61% of MPs	Zhou et al., 2020
Coagulation	PE (15 μm), rayon (8.7 or 20.6 μm), and PES (17.5–50.6 μm	-Zeta potential -Turbidity	Finial turbidity <1.0 NTU	Skaf et al., 2020
Flocculation	PS (0.05–0.1 μm)	-UV-vis spectrophotometer - Zeta potential - SEM	Elimination ≥90%	Chen et al., 2020
Coagulation and flocculation	PE (15 and 140 μm), PS (140 μm), PES	Quartz crystal microbalance with dissipation monitoring (QCM-D)	-PES removal: 97% - PE removal: 99% - PS removal: 84%	Lapointe et al., 2020
Electrocoagulation	PE (300–355 μm)	-TSS analysis -Counting fluorescent particles	-Elimination ≥90% -Optimal elimination of 99.24%	Perren et al., 2018

Table 18.3: Recent works on the advanced treatment processes for the removal of MPs and NPs in waters.

Treatment	MPs/NPs	Analytical	Results	References
process	type and size	methods		
	-PE film (50 µm thickness)	-Digital microscopy -Dynamic mechanical analysis -FTIR	-30% increase of viscoelastic properties	Tofa et al., 2019
Photocatalysis	-PE (500 μm)	-SEM -Optical microscopy -ATR-FTIR -Mass loss analysis	-Mass reduction: 3% after 10 h	Ariza- Tarazona et al., 2019
	-PS (0.1-05 mm) -PMMA (0.14 mm)	-TOC -Py-GC-MS	-Mineralisation > 80%	Allé et al., 2020
		-COD analysis -TOC analysis -Spectrophotometry	-88.9% COD reduction in 6 h	Duran et al., 2018
Electrooxidatior	-PS (25 μm)	-Weight analysis -granulometric analysis -COD analysis -TOC analysis -SEM	-Elimination of 89 ± 8% of MPs	Kiendrebeogo et al., 2021