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Fate of micro- and nanoplastics in water bodies: A critical review of current challenges, the next generation of advanced treatment techniques and removal mechanisms with a special focus on stormwater

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ABSTRACT

Micro- and nanoplastics (MNPs) are a growing source of pollution from natural and plastic fibers to non-fiber particles in water matrices. The current review highlights the detection, pathways, measurements and fate of MNPs. Besides, it addresses various treatment technologies, the next generation of MNPs degradation and their removal mechanisms from water bodies especially stormwater. The removal efficiency of MNPs decreases with decreasing particle size, as smaller particles were able to pass more easily through the tertiary sand filter or membrane filter. NPs exhibited lower removal efficiency compared to MPs. Conventional methods for treating stormwater including bioretention filters and constructed wetlands are inadequate in removing MNPs effectively. Some novel methods, such as egg protein derived ultra-lightweight hybrid monolithic aerogel, rely solely on gravity and do not require water, demonstrating up to 100 % removal of microplastics from seawater. This method could also be applied to stormwater treatment. This is superior to membrane technologies including UF and MF, which operates with a substantial energy input and excess water. Integrated treatment systems that combine different technologies can overcome the limitations of individual methods. Furthermore, the core mechanisms involved in eliminating MPs/NPs via biofilm consist of electrostatic surface attachment, hydrophobic interaction, absorption onto the biofilm layer, intermolecular repulsion, and electrostatic interaction between MPs/NPs and the membrane surface.

1. Introduction

Massive amounts of plastic are being discarded into the environment, resulting in contamination of microplastic across the planet, from the Mount Everest's summit to the depth of oceans. People already consume these microplastics through food, water and even by breathing in. They have been discovered in the feces of both babies and grow-ups with a higher amount in babies' feces [1,2]. The earliest studies showed personal-care products, plastic pellets, discarded bottles, car tires, and synthetic clothing fibers as various sources of microplastics, which can be ingested over 100,000 particles by people through air, water, salt, and seafood [3]. Therefore, inhalation, ingestion dermal absorption are pathways for MNPs to enter the human body, which can lead to health problems [4,5]. Fig. 1 illustrates how microplastics can enter the body of individuals.

The National Oceanic and Atmospheric Administration (NOAA) defines microplastics as tiny particles of artificial polymers, with a diameter of <5 mm, that are resistant to (bio) degradation [6]. In contrast, nanoplastic (nanospheres, nanowires/nanotubes, and nanofilms) is characterized as particles with even smaller dimensions, ranging between 1 and 100. Based on their origin, MP and NP are divided into two classes, primary and secondary plastic [7]. The first category consists of

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tiny fragments of specially manufactured plastic, such as hand and facial cleansers, shower gels, toothpaste, industrial scrubbers, and plastic micro-nanospheres. The latter category refers to small pieces of plastic that result from the breakdown of larger plastic waste, both at sea and on land. The most commonly found plastic materials in these waste products are polypropylene (PP), polyethylene (PE), Polystyrene (PS), polyvinyl-chloride (PVC), polycarbonate (PC), polyamides (PA) Polyester (PES), and polyethylene terephthalate (PET). These are reversible thermoplastic polymers, highly recyclable materials that can be heated, cooled, and shaped repeatedly [8].

Also, treated sewage effluent, sewage sludge [9], agricultural soil [10], leachate of active and closed landfills [11], organic fertilizer including fermentation of biowaste and composting [12], are the key sources of MNPs. Microplastic-containing waters are used for cultivation of crops, and microorganisms are continuously degrading the plastics in soils. Therefore, humans ingest MNPs via crops, food products, meat, and water. According to a study [13], the source of microplastics in the atmosphere in megacities are textile, architectural coating and weathered plastic products, and coasting additive with the most polymer types of PET (51 %) and EP (19 %). The presence of microplastics in animal and human feces has provided evidence of consuming plastic particles through directly ingesting or food and drinks [14]. In a study, 22 blood samples of anonymous donors were analyzed. PET plastic was found in 50 % samples, approximately 68 % samples contained polystyrene, while polyethylene was in a quarter of blood samples, which are commonly used in drinks bottles, packaging products and plastic carrier bags, respectively. The result showed that the particles are transported through the body and can limit the ability of oxygen transportation by red blood cells. Furthermore, MPs have been found in the pregnant woman's placentas and can pass into the heart, brain and foetuse's organs [1]. In a study, 75 % of 34 breast milk samples of healthy mothers contained MPs but there was no correlation between mothers' consumption of food, drink in plastic packaging or seafood and the presence of microplastics in breast milk. This result suggested that human exposure of MPs is inevitable and needs larger studies to identify risk factors [15]. Microplastics might be found in over 50 % of the human's stool. According to a study's report, the most number of plastics were polypropylene and polyethylene terephthalate [16]. The smallest particles of MNPs can enter the bloodstream and lymphatic system, and may be able to reach the liver. The presence of MNPs in the gut may hinder the immune response of the digestive system, or it could aid in the spread of harmful substances and pathogens. The sources of MNPs found in stool samples are currently unknown [14], However, there is a correlation between the concentration of fecal microplastics and the severity of inflammatory bowel disease (IBD), indicating that exposure to microplastics may be linked to the disease process, or that IBD exacerbates the retention of microplastics. Based on this research, MPs concentration in fecal samples of IBD patients were 41.8 items/g dm in comparing to the healthy people's fecal samples with 28.0 items/g dm [17].

Nowadays, wastewater treatment plants (WWTPs) retain 98 % of MPs, but they do not retain MPs that are smaller than 20 μm and NPs as well. As a result, WWTPs are considered to be a significant contributor to plastic pollution in wastewater effluents [18]. WWTPs involve four main processes: preliminary treatment, primary treatment, secondary treatment, and tertiary treatment, which is also known as final or advanced treatment [19]. Preliminary processing is frequently necessary to safeguard machinery and improve the effectiveness of subsequent processing procedures. The initial phase involves the elimination of large suspended organic solids, however, the liquid waste produced still contains a significant quantity of suspended organic material, with MP removal efficiency of around 25 %. While the secondary phase is more effective, it can decrease MP levels by 75 % [20]. The use of tertiary treatment, although not always common, can achieve a removal efficiency of 98 %, resulting in an effluent that is nearly as clean as drinking water. However, the limited use of tertiary treatments in wastewater treatment plants, along with the large volume of treated wastewater needed to produce water of varying quality, leads to the presence of plastic in the effluent. It is essential to implement advanced technologies for final stage wastewater treatment in order to prevent contamination of effluent by plastics [19].

In this review, an analysis of the documents in this field has been carried out to highlight the growing interest of the scientific community towards the problems of plastic pollution as well as to demonstrate the still insufficient knowledge and experience in the removal of plastic from water bodies, with specific emphasis on storm water treatment. Current challenges and the next generation of advanced treatment techniques to micro and nano plastics, as well as the mechanisms involved in their removal, have been documented and thoroughly analyzed.

2. Potential human health implications of MNPs in the body

Plasticizers can easily migrate from plastics and have negative effects on living organisms. Some of these additives are lipophilic and can enter cell membranes, where they can disrupt important biochemical reactions. This can lead to a range of concerns, including behavioral and

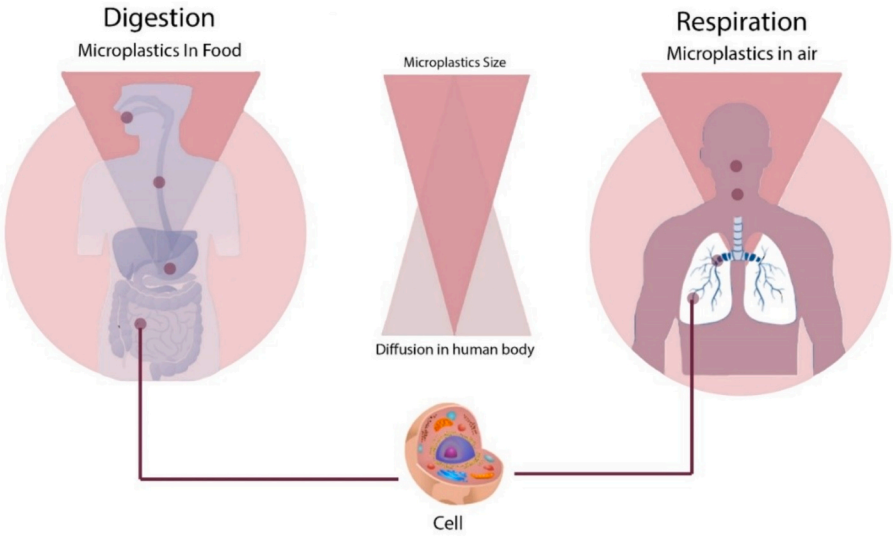

Fig. 1. Pathways for MNPs to enter the human body.

reproductive problems. NPs are a greater threat to living organisms compared to MPs because of their smaller size. Plasticizers are known to have the ability to penetrate cell membranes, and this is also true for NPs. Plasticizers and NPs have the potential to accumulate in any part of an organism. Recent research has shown that small latex particles that are <50 nm in size can accumulate in a species of Japanese fish, including in testes, liver, blood, and brain. These particles can decrease survival rates of fish fetus, as well [21]. The most concerning finding is that these particles can breach the blood-brain barrier of Japanese rice fish, which poses severe health risks to all animals, including humans. Studies also indicate that NPs can lead to changes in behavior, physiology, and metabolism in fish, such as crucian carp. While these studies have largely examined the impact of NPs on marine organisms, it is expected that any terrestrial organisms living near or in water sources will face similar problems when exposed to these particles [22]. While NPs can cause brain damage through crossing the blood-brain barrier in fish [23], they can pass the placental barrier via passive diffusion [24]. MNPs have potential adverse effects on immune system [25]. Humans are exposure to NPs at a low concentration for a long time, maybe whole lifetime. Due to the difficulty in detecting NPs, their effects are not widely understood. What indicated by in vitro and in vivo investigations are absorbing MNPs into human body, accumulation in the intestinal lumen and excreted some of them through feces. Studies on animals showed that distributed nanoparticles in intestinal lumen can be penetrated the intestinal barriers and then blood vessels for example, alveolus, a blood-air barrier in lung, can be a vital organ where NPs penetrate blood-circulating system [26]. Due to the small size and adverse effects of microplastics on water bodies, aquatic life, animals and human health and, the bioaccumulation by organisms, they are of today's particular concern [27]. NPs can introduce chemical additives into body and cause adverse human health effects, for example, disturbing membranes of the small intestine's cell. Owing to having long-range transport potential, MNPs can function as vectors to various contaminants through their sorbent surfaces [28,29]. By Bioaccumulation and biomagnification concepts, it can be understood how pollutants transport within food chains. To net uptake of microplastics or nanoplastics from the environment through any exposure and from any source like water, residue and food, is the definition of bioaccumulation. Bioaccumulation means to uptake contaminants by organisms in a huge mount than normal capacity [30]. Cytotoxic effects on cells of human brain and carrying various contaminants for example antibiotics are other diverse effects on human health [31]. MPs can obtain from fecal samples of adults and infants whereas infants may be more exposed to MPs due to using toys and food stuffs frequently, for example, 16.200,000 microplastic particles can be released from infant feeding bottles per litter [32]. Although finding different types of MPs shows that they are generated from various sources, the most frequently detected MPs in fecal samples were polyethylene terephthalate and polyamide [31]. The size and shape of plastics partially have an important effect on toxicological impact of plastic pollution for example, nanomaterials. Small particles have a great potential to internalize and translocate through tissues of living organisms. In addition, plastic additives, which applied for enhancing polymer performance but are not chemically bound, can straightforwardly leach from particles and pose a risk to human health and the environment. Furthermore, commonly used polymers can adsorb and transport other environmental pollutants and pathogens to living organisms, known as the Trojan horse effect [33,34].

Multiple studies conducted in laboratory settings and on living organisms have demonstrated that MNPs can have significant negative effects on the human body. These impacts can be included physical stress and damage, cell death, inflammation, oxidative stress, and immune responses [35,36]. MPs can easily carry contaminants such as hydrophobic materials and heavy metals [37,38]. Inhaled MNPs can have multiple adverse effects on the respiratory epithelium and pose a potential risk to respiratory health. Exposure to various sizes of MNPs can lead to a reduction on cell viability, cell cycle arrest, activation of inflammatory gene transcription, and alter protein expression related to cell cycle and pro-apoptosis. Major decrease in cell proliferation, significant modifications in cell morphology and uptake are other consequences of MNPs. Although the negative disorders indicate toxicological implications for human cells, healthy respiratory cells can adapt to low levels of repeated MNPs exposure [39,40]. To uptake of NPs is significantly affected by the particle's size [41]. MNPs are capable to enter the gut directly and accumulate in the intestine. Therefore, animals consumed as a whole can be identified as a source of MNPs for human consumption. In addition, microplastic consumption food chain can influence the microbial communities in host's intestines [4]. Nanoparticles have the ability to enter the capillary blood system and circulate throughout the entire body. They can also accumulate in tissues and cells, leading to metabolic disorders and inflammation. Smaller NPs (44 nm) compared to larger counterpart (44 nm) are more efficient at accumulating in cells and inducing cytokine upregulation. Furthermore, MPs with size of 750 and 1500 nm are blocked by the skin [42].

3. Occurrence, detection and measurement of microplastics and nano plastics

3.1. Occurrence of MNPs

Plastics have been produced since the 19th century. In the several previous decades, the production of plastic in the world grew up from 15 million tons to over 3 billion tons annually with a plastic production estimation of 33 billion tons in 2050 [43,44]. Plastics are made from chemical interactions with some toxic additives for more strength and flexibility. According to a study, over 10,000 unique chemicals has been used in plastics which 2400 caused potential concerns. Up to 88 % of additives can leach into surrounding environment; water, air, food or even body tissues [29]. As plastics are exposed to different environmental phenomena such as wind, water, sunlight, friction and living things, they are converted into small segments called microplastics. If MPs is fragmented into smaller size of 1–100 um, NPs are produced [45,46]. Microplastics, are defined as approximately five (≤5) millimeters across plastics [5]. Both MNPs originate mostly from initial plastic waste and secondary subsidiary products as their sources in the environment. Mainly, industrial and domestic cleaning products such as nanomedicines, nanosensors and care products are initial plastic wastes and secondary subsidiary products are included disintegrated plastics driven by physio-chemical or microbial operations [26,47–49]. Microplastics can originate from both aquatic and land environments. Aquatic-based MPs are formed through natural processes such as weathering, photolysis, and microbial decomposition in the environment, while land-based MPs can infiltrate the environment through urban runoff and sewage treatment plant effluents [50]. Disposable products such as bottles, coffee cups, straws, bags and cutlery are identified as a main source of plastics [51]. During the COVID-19 pandemic, there was an excessive use of polyester and polypropylene face masks [52]. Numerous research studies have demonstrated that MNPs can enter the human food chain through different pathways, including animals consuming them in their natural habitats, contamination during food production processes, and leaching from plastic packaging used for food and beverages. To date, MNPs particles have been found in various food and drink products, including honey, beer, salt, sugar, fish, shrimps, and bivalves [53]. According to a research study, the presence of MPs in the respiratory system is linked to smoking, invasive examination, and other factors. These findings can provide a connection between exposure to MPs and both personal smoking habits and invasive examination of the trachea. In addition, MPs can enter the respiratory system through inhalation and may be expelled from the body through sputum [54]. According to a review study, 46 types of polymeric materials were identified in human samples with the priority of polypropylene (PP) (87 %), polyethylene terephthalate (PET)

(82.6 %), polyethylene (PE) (73.9 %), polyamide (nylon) (PA) and polystyrene (PS) (60.9 %), and polyurethane (PU) and polyvinyl chloride (PVC) (56.5 %) [55]. While, in another study with determining the presence of MPs in rainwater pipelines in China, the most found polymer types were PE, PP, PET, PVC and PS, respectively. The results showed that urban rainwater pipelines are the place to migration of land-based MPs to freshwater, and the accumulation of MPs in stormwater pipe sediments was a significant contributor to MPs in freshwater area.

Wibowo et al. [57] found that 50 % of participant's stool samples who lived in a coastal region, were MP positive with a large amount of polyethylene. The study concludes that wastewater treatment plants (WWTPs) are a significant source of MPs in the aquatic environment, posing a threat to both humans and ecosystems. However, there is a lack of standardization in sample collection and characterization methods. FTIR and Raman techniques are currently the best options for identifying MPs in WWTP samples. The most prevalent polymers found in WWTPs are polystyrene, polyethylene, polyethylene terephthalate, polyamide, and polypropylene, with fibers being the most commonly detected shape. The removal rate of MPs depends on their size, shape, density, and other factors like bacterial fouling and retention time. The eliminated MPs are restored in the waste sludge generated in WWTPs, which could be a potential source of MPs in surface waters. MPs have adverse impacts on aquatic organisms, and they can also act as a carrier for pathogenic and bacterial taxa assemblages and antibiotic resistance genes. The study also highlights the sub-lethal impacts of widely used plastic additives on fish and aquatic invertebrates [58].

MPs, a type of microplastic, are transported by wind and can persist in the atmosphere for extended periods due to their small size and low density. They are found in road dust, sea spray, and agricultural soil dust. An estimated 1.21 tons of suspended atmospheric MPs are transported annually from terrestrial sources to the marine environment. MPs have been found in remote areas, suggesting long-range transport from urban and industrial centers. Evidence from the open ocean suggests MPs accumulate in the ocean surface microlayer and are injected into the atmosphere through sea spray aerosol formation [59–63].

According to recent studies, MPs are present in the atmosphere of crowded places like Shanghai, Dongguan, and Paris. Public health is also affected by MPs; specifically, depending on the particle size, plastic fibers may affect human respiratory systems because only particles smaller than 10 μm are inhaled. Additionally, MPs in the air may act as carriers of other pollutants that are in the atmosphere and are adsorbed on their surfaces. MPs have been found in inland waters, estuary waters, coastal sediments, and even living things. MP atmospheric transport has gained attention recently as a potential vector for MP deposition in aquatic or terrestrial ecosystems. Even though it is known that the continent provides 80 % of the fibers observed in maritime habitats, the specific portion that comes from air sources remains unidentified [64].

3.2. Detection and measurement

MNPs can accumulate in lakes and rivers, which act as a major sink for these pollutants. These water bodies receive run-off from surrounding urban and rural areas, as well as discharges from wastewater treatment plants and stormwater drains, which can contain macro-, micro-, and nanoplastics. The presence of these plastics in rivers and their tributaries can then result in their transport to larger freshwater bodies such as lakes, ponds, and wetlands, and eventually to the ocean. These plastics can be carried by river currents and end up on banks and shorelines that are distant from where they were originally contaminated [22]. For example, sediment and surface water are measured mainly as the environmental matrices for evaluating MPs because of distributing in costal sediments from some countries with a concentration up to 5000 particles per kilogram [65]. A study described a novel and efficient method for detecting and quantifying MPs in water using flow cytometry following flotation, UV irradiation, and filtration. The proposed method accurate analysis of MPs in various water sources. The method was validated in parallel with the standard method of visual inspection with optical microscopy. It is leading to non-significant differences in the quantification of microbeads. The analytical procedure that was developed has several benefits. It enables the automated quantification of MPs pollution in both mass/volume and counts in water. This makes it ideal for real-time monitoring in various settings such as wastewater treatment plants, rivers, and drinking water [66]. The main methods for detecting MNPs in human biological samples were predominantly μ-Raman, μ-FT-IR, LDIR, Py –GCMS and LC-MS/MS, respectively [55,67].

3.3. Micro- and nanoplastics in urban and highway stormwater

Nowadays identification of plastic debris in urban waters has become a significant concern due to their direct and indirect environmental and human health effects. Among these debris microplastics (MPs, 100 nm - 5 mm) and nano plastics (NPs, <100 nm) are considered the most intractable ones as the result of their specific characteristics and consequently difficult control and removal. Although the MPs and NPs may be the same in origin and composition, NPs have their own distinct characteristics in analytical challenges, transport properties, interactions with pollutants, and their removal and environmental fate due to their small size [42].

3.4. Fate of MPs in storm waters

Stormwater runoff is considered one of the most important ways of plastic particles interring the water bodies as the result of high concentrations of MPs (0.009 to 3862 particles/L) and the only pathway carrying special kinds of rubbery particles such as tire and road wear particles along with other contaminants. According to reports, MPs are the most frequent type of plastic waste in aquatic ecosystems, and high concentrations of MPs have been measured in stormwater ponds and sediments derived from stormwaters [68].

MPs in urban water systems tend to stay more stable and deposited in sediments without aggregation due to their larger size. It is evidenced that 200 nm-sized MPs are more stable and do not aggregate compared to 5 nm NPs. On the other hand, MPs undergo more physicochemical degradation and aging processes that lead to an increase in surface area and functional groups, which reinforce the interaction with surrounding microbial matrix and contaminants and consequent hetero-aggregates. Removal of MPs in wastewater treatment plants has been studied widely and suggested that 94–99 % of MPs are removed through primary, secondary, and tertiary units [42].

3.5. Fate of NPs in storm waters

NPs due to their light and small size obey Brownian motion that limits their vertical transport, which results in their suspension in urban waters. Although it was mentioned that NPs tend to be dispersed in water matrixes, they are more likely to aggregate with surrounding substances in comparison with MPs based on their size, surface properties, and surrounding chemicals/colloids. The degradation and aging processes are less effective on NPs due to their size. However, to date, no study provides a definite NPs removal efficiency in WWTPs and scientific data about the particles smaller than 1 μm are still unclear and limited; tertiary units might have a large contribution to NPs removal from urban waters [42,69].

Since the thermal analytical methods are not affected by particle size, Xu et al. investigated the mass concentration of NPs in WWTPs by Py-GC/MS coupled with a developed ultrafiltration-based method to concentrate and detect trace NPs. Based on the results this method was feasible for the identification of sub-MPs and NPs in complex wastewater matrixes, however the resulted mass concentrations in this study are not comparable with results of other studies on the particle number. In the case of small particle size, even though with high number of particles,

the detected mass can be very low. On the other hand, results of quantitative methods my encounter with overestimation due to the fragmentation of particles as a result of physical and chemical processes in WWTPs. The removal efficiency decreased as the particle size decreased, as smaller particles were able to pass through the tertiary sand filter or membrane filter more easily. NPs exhibited lower removal efficiency compared to MPs with larger particle sizes [69]. Despite various data indicating the presence of NPs in water bodies, there is still limited understanding of the levels and behavior of NPs when compared to MPs, particularly in urban water systems [70].

Domestic wastewater contains high concentrations of M/NPs as a result of laundry activities and the use of personal care products such as exfoliants and toothpaste: a 1.6 g of toothpaste can contain >4000 microbeads. Effluents from wastewater treatment plants are another source for plastic particles retained in wastewater after treatment and those that are removed end up in the sludge that eventually enters the environment as a consequence of sludge application or wastewater irrigation. Urban areas are considered as primary source and one of the focal points of plastic emissions to the environment. Atmospheric deposition and urban runoffs with an imperative role for the latter one are other transmission ways of plastic particles into the aquatic environments. It is estimated that 40 % of MPs entering the European rivers resulted from urban runoff. On the other hand, littering and attrition of tire and road surfaces could be a major contributor to MPs transmission to receiving waters [22,70–73].

Rainfall and storm events are recognized as hot moments of transportation of contaminants between land and waterways as based on the studies the rainfall intensity and the concentration of MPs in urban runoffs was positively correlated [73–77]. As shown in Fig. 2, the consequent water fellow on urban surfaces including catchment and road runoff convey MPs from land to water bodies through drainage systems, and stormwater retention structures such as constructed wetlands, bioretention systems, and stormwater retention ponds [71–73].

Based on recent studies, MP contamination during rainfall and storms increased dramatically and rain and snowmelt waters are considered to be the main contributors to polluting urban water systems and migration of MPs to freshwater reservoirs, especially in arid regions. A Seven-fold and a 14-fold increase in MPs concentration were observed on the coast of California and surface water in mersian bay respectively after rainfall and subsequent flooding [71–73,75,76]. So stormwater runoffs are considered as important pathway for transferring MPs to water bodies and stormwater control measures (SCMs) that are constructed to reduce runoffs act as sink and sources of MPs as retain them for a period of time [73,78]. This hypothesis has been proved by high concentration of MPs reported in urban runoffs, SCMs, and rainwater pipelines and drainage systems in different areas (Table 1).

Table 1 is a brief report of studies that investigated the occurrence and identification of MPs in mentioned urban water systems in different regions. The total concentrations of MPs in urban runoff globally range from 0 to 8580 particles/L which is strikingly higher than that of in wastewater effluents that shows the importance of urban runoffs in the transportation and retention of MPs [71,73,93,97]. The concentration and characterization of MPs pollution in stormwater reported in different studies vary in the different location and depends on parameters such as land use, characteristics of the MP particles, and local environments such as the portion of pervious surfaces, and rain intensity [71,97,98]. So the direct comparison between the results of MPs identification and characterization studies in storm waters is difficult due to the different approaches in sampling, identification techniques, cut-off particle size, and sampling locations [71,72,75,97,99,100]. On the other hand in some studies, the MP concentration is likely to be underestimated as a result of the sampling method such as the mesh size of nets used for sampling [75,100].

MPs entering the urban storm waters are from different kinds and sources such as atmospheric deposition, municipal and industrial sewage, littering and attrition of plastic products, and tire and road wear particles (TRWP) with the most contribution of the latter one [71,72,74,75,98,99]. Road and traffic-related microplastics are considered significant sources of microplastics transmitted to the environment [71,72,99]. Since stormwater retention structures sustain urban runoff for a period of time and reduce the flow velocity which results in consequent sequestration and reduction of MPs downstream, some studies investigated the abundance and characteristics of MPs at the entrance, inside, and outlet of these structures to evaluate their efficiency in the removal of MPs [93,97,101].

Currently, there is not much research on the presence and detection of NPs in urban stormwaters, but it is important to note that they often exist alongside MPs. The identification of microplastic particles also

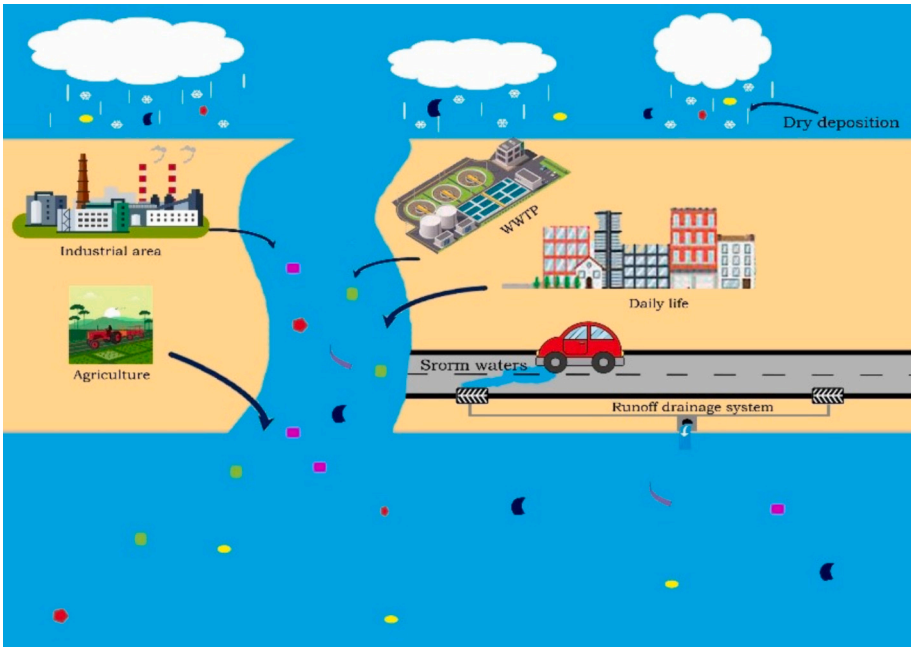

Fig. 2. The routes by which microplastics are dispersed into the environment.

Table 1
Micro- and nanoplastic concentrations and characteristics in different sampling sites.

Sapling site	MP concentration (particles/L)		Size (μm)	Morphology	Type of polymer	Region	Reference
	Mean	Min–max					
Urban run off	1.9	1.2–3.0	<5000	Fibers, fragments, filament, granules, foam, others	–	Iran	[79]
	–	3.0–129	25–5000		PE, PP, PS, others	France	[74]
	35	24–60	–	Fibers	–	France	[80]
	15	2.3–29	125–5000	Fibers, films, fragments, foams, bundles, others	PP, PE, PVC, PTFE, Nylon, PA, PU, PET others	Ontario, Canada	[81]
	8.3	1.1–25	125–5000	Fibers, fragments, others	PE, PET, PP, cellulose acetate, copolymers	California, USA	[72]
	167	13–366	25–5000	Fibers, fragments, films, granules	PE, PS, PA, PET, PP	Tijuana, Mexico	[82]
	186.5	81–292	10–5000	Fibers, flakes	AS, EVA, PEPD, PEP, PET, PS, PE, PP	Tokyo, Japan	[83]
Drainage systems	Entrance 9.5	2.0–22	37–5000	Fragments, fibers, granules, films	PE, PP, PET, PVC, PS	Wuhan, China.	[76]
	Entrance 8.3	–	–	Microdebris[a]	PP, PE, PET, PU, others		[84]
	Inside –	1500–6000	20–5000	–	TBMPs	Gothenburg, Sweden	[85]
	Inside 581	98–1485	20–5000	–	–	Gothenburg, Sweden	[86]
	Inside 88	18–139	25–5000	Fibers, fragments, films, granules	PE, PS, PA, PET, PP	Tijuana, Mexico	[86]
	Outlet 4.6	1.4–6.8	54–1000	Fibers, fragments, pellets, others	PE, PP, nylon 6/6, others	Hong Kong	[87]
	Outlet 289	12–2054	25–5000	Fibers, fragments, films, granules	PE, PS, PA, PET, PP	Tijuana, Mexico	[82]
	Outlet 0.3	–	250–2000	Fragments, films, granules	COPOLY, PET, PE, PS, PP	New Jersey, USA	[88]
	Outlet –	0.4–0.6	500–2000	Fragments, pellets, sheets	PE, PS, others	New Jersey, USA	[88]
Stormwater control and retention structures	Entrance 24	–	–	Microdebris[a]	PP, PE, PET, PU, others		[84]
	Entrance 29	8.0–66	90–5000	–	PE and PP	Espoo, Finland	
	Entrance 1212	42–8580	20–100	–	PP, EVA, EPDM, SBR others	Sundsvall, Sweden	[90]
	Entrance 196	0.4–1624	100–300	Fibers, fragments, granules, others	–	Sundsvall, Sweden	[91]
	Entrance 3.0	0.3–23	300–5000	Fibers, fragments, granules, others	–	Sundsvall, Sweden	[91]
	Entrance 186	–	106–5000	Fibers, rubber, films, fragments	PET, PU, PE	Canada	[92]
	Entrance 1.9	–	125–5000	Fibers, fragments, others	PET, rubber, PE, acrylic, PU	California, USA	[72]
	Entrance 1.6	0.4–3.2	125–5000	Fibers, fragments, others	Anthropogenic microparticles	California, USA	[93]
	Entrance 0.9	–	25–5000	Fragments, fibers	Poly(styrene-coethylacrylate), PP, nylon, PET, PE	Australia	
	Inside 6.0	0.5–23	10–2000	–	PVC, PS, PP, PE, PET, others	Denmark	[95]
	Inside 270	–	10–500	Fragments, fibers, others	PP, PET, PS, PA, PE, others	Denmark	[96]
	Outlet 4.2	–	–	Microdebris[a]	PP, PE, PET, PU, others		[84]
	Outlet 1.9		90–5000	–	–	Espoo, Finland	
	Outlet 82	0–240	20–100	–	PP, EVA, EPDM, others	Sundsvall, Sweden	[90]
	Outlet 6.2	0–39	100–300	Fibers, fragments, granules, others	–	Sundsvall, Sweden	[91]
	Outlet 0.3	0–1.7	300–5000	Fibers, fragments, granules, others	–	Sundsvall, Sweden	[91]
	Outlet 31	–	106–5000	Fibers, rubber, films, fragments	PET, PU, PE, acrylic	Canada	[92]
	Outlet 0.1	–	125–5000	Fibers, fragments	PET, PE, acrylic, polyacrylamide	California, USA	[72]
	Outlet 0.8	–	250–2000	Fragments, films, granules	COPOLY, ABS, PE, PP, PS	New Jersey, USA	[88]
	Outlet 4.0	–	25–5000	Fragments, fibers	Poly(styrene-coethylacrylate), PP, nylon	Australia	

[a] Any marine debris between 0.1 μm and <5 mm.

represents the existence of NPs in urban water systems [100].Therefore these results highlighted the importance of mitigation strategies against the conveyance of MNPs pollution through stormwaters into the water bodies and their efficiency in controlling MPs pollution to achieve a plastic-free urban water goal [71,75,99].

4. Various treatment approaches against micro- and nanoplastics from stormwater

In recent years, various approaches from chemical and electrochemical to physical and biological have been developed to remove micro/nano plastics (MNPs) from types of wastewaters including stormwater as shown in Fig. 3. Different factors such as plastic particles size, concentration, hydrophobicity, and type of functional groups can

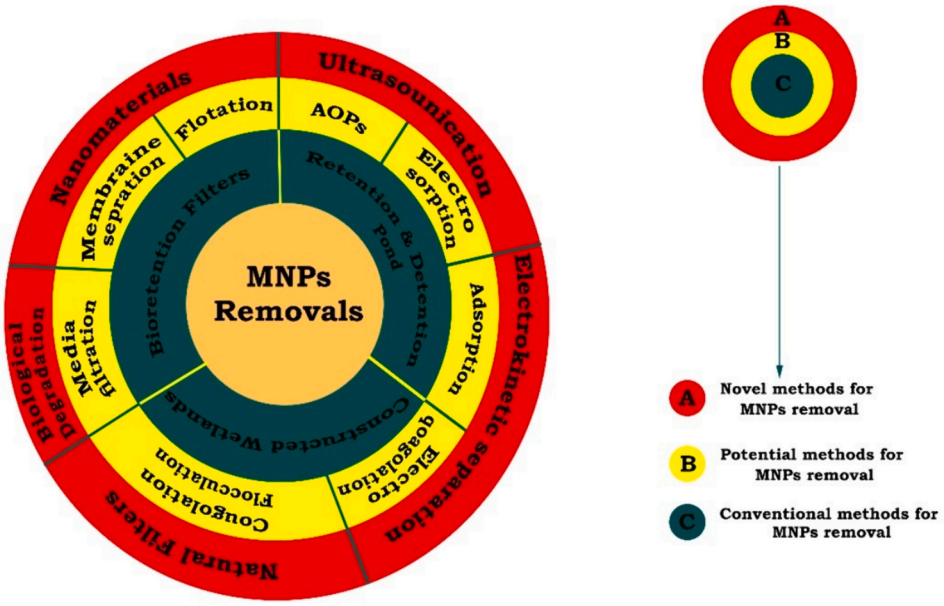

Fig. 3. Three strategies namely conventional, potential, and novel for effective micro- and nanoplastics removal from stormwater.

be effective in choosing the right method for removal of MNPs. Some of these techniques are preliminary, primary, and secondary treatments which can remove >80 % of MPs, while to reach >98 % removal efficiency tertiary treatments such as membrane separation processes and advanced oxidation processes must be applied [102–104]. In this review paper, most of the methods of MNPs removal is reviewed.

4.1. Conventional treatment methods

In most of rainfalls, stormwater combines with sewage and causes combined sewer overflow (CSO). Although combined sewer systems are predominant for treatment, some methods including retention and detention ponds, bioretention filters and constructed wetlands can separate stormwater from sewage to minimize CSO [105]. These removal methods are commonly used methods to separate only MPs from stormwater discharge.

4.1.1. Retention and detention ponds

Stormwater retention ponds as a sustainable technology to manage stormwater remove pollutants from soluble to particulate materials by allowing them to settle for days to weeks. Soluble materials can be removed with sorption and degradation as main processes, while particulate pollutants such as MPs and NPs are removed through sedimentation and deposition as dominant mechanisms [95,106]. Stormwater drainage systems are important sink for MPs and transferring them from terrestrial to marine environments [107]. In some drainage systems, stormwater is conveyed with domestic, agriculture, and industrial wastewater and in some cases, it is conveyed through separate pipe. Combined drainage systems are the most common systems to convey stormwater [105].

Not many studies have investigated removal effect of retention ponds on MPs in stormwater. In a study, Brooks et al. [108] investigated water and bottom sediment samples from six stormwater ponds to know effect of different factors on concentration and behaviors of MPs. Microplastic concentrations in water and sediment sample were 0.0–0.0555 particles/m^3 and 2.5–203.0 particles/kg dry weight, respectively. More regular-shaped plastics found in sediment sample that show more tendency of these particles to settle first [108]. Lutz et al. [107] collected their samples from five stormwater drainage systems with some differences in factors such as land uses, area, and characteristics of sediments. Results of μ-FTIR showed polyethylene (PE) and polypropylene (PP) as dominant polymers in fiber shapes. A mean concentration of MPs was 664 particles/Kg. They estimated 760 particles/Kg microplastic concentration in urban drain and 245 particles/Kg for agricultural drain based on a Generalized Linear Mixed Model [106]. In another study, MPs in urban and highway stormwater were analyzed by Liu et al. [97]. They collected samples from sediment of seven stormwater ponds from highway, residential, industrial, and commerce areas. Based on the result, the highest concentration of microplastic was in industrial and commerce areas and the lowest concentration of microplastic was in highway and residential areas. Polypropylene (PP), polystyrene (PS), polyester (PES), polyethylene (PE), and polyvinylchloride (PVC) were dominant polymers in stormwater. Also, the largest MPs particles were in residential area stormwater sample [97].

Rasmussen et al. assessed the effectiveness of stormwater ponds in retaining microplastics for the first time. The results demonstrated that the four ponds under investigation held microplastics fairly effectively, either to levels comparable to or higher than those usually observed for suspended particles. Lighter-than-water microplastics were also held rather effectively (77–95 %), despite the fact that they would float in quiescent water on their own. These naturally floating particles, however, were retained less effectively than microplastics that are heavier than water (97–99 %). Heavy-than-water car tire material was removed from stormwater ponds in three out of four, but the retention efficiency of microplastics varies depending on the polymer type. This suggests that the mechanisms removing lighter-than-water and heavier-than-water microplastics may not be identical. The slow settling in quiescent water dominates, leading to slower settling of heavier-than-water microplastics [109]. In another study, Jonsson and Ockerman determined the removal efficiency of two ponds using the MP concentrations at the entrance and outflow. They discovered that the efficiencies varied between 73 and 100 % for MPs larger than 300 μm and between 90 and 98 % for MPs smaller than 300 μm [110]. Vogelsang et al. investigated MPs larger than 50 μm, however they found that removing total suspended solids (TSS) could be used as an alternative for MP removal because tire wear particles accounted for >78 % of TSS in road runoff [111]. MPs smaller than 50 μm have also been recorded in several investigations, so it is probable that TSS removal overestimates MP removal; still, MP removal is comparable to TSS removal [112]. Thus, Vogelsang et al.'s results are probably true for MP particles larger than

50 μm. Wet ponds were shown to have a 75 % TSS removal effectiveness based on data from 315 facilities. The final effluent concentration was 11.7 mg/L, which is marginally less than the values found for MPs by Olesen et al. [96]. Although more research is needed to assess the efficiency, detention reservoirs, also known as dry ponds, demonstrated a great potential for MP removal. The lack of data on MP treatment by pond size makes it difficult to conduct correlation analysis between efficiency performance, volume, and surface area. Larger ponds, however, should have longer retention periods, which will allow for more possibilities for particles to settle [113].

4.1.2. Bioretention filters

Bioretention cells that are depression places composed of engineered porous media, mulch, and vegetation are a type of low impact development system. They are composed from two layers, vegetation at the top layer and the media filter in the substrate. Substrate layer is a mixing of sand, organic matter, and small sized soil. To reach better performance of substrate such as better hydraulic conductivity, water retention capacity, and sorption capacity some chemical materials like zeolite, fly ash, vermiculite, biosorbents, and biochar can be added to the conditional media. Selection of bioretention materials depends on hydrological and pollution characteristics of stormwater, local vegetation, soil media and substrates. While bioretention systems ability to remove dissolved matters is various, they are effective in removal of suspended materials by physical separation strategies [92,105,114]. Based on previous studies, various materials in stormwater such as total suspended solids (TSS), particulate metals and phosphorus, MPs can be removed through bioretention cells [90,115]. Bioretention cells with unique benefits such as improving runoff quality, biodiversity improvement, runoff volume management, are installed in many countries of the world as an efficient option. Despite the potential benefits of filtration systems for removing pollutants from stormwater, their development has been hindered by a lack of research. Additionally, there are some disadvantages in their design that need to be addressed, such as choosing the right vegetation for a specific location, selecting the appropriate substrate for the desired pollutant removal purpose, and ignoring the impact of weather conditions. Until these issues are addressed, it is difficult to conclude that filtration is always the best option for stormwater treatment [114].

Bioretention cells can remove wide range of micropollutants from 20 to >100 μm. In a study, Lange et al. investigated removal of MPs from highway stormwater with gross pollutant-bioretention and a non-vegetated sand filter to show bioretention system ability to remove 20 to 100 μm sized MPs. Polypropylene (PP), Ethylene Propylene (EP), Diene (EPDM) rubber and Ethylene-vinyl acetate (EVA) were the dominant polymers in stormwater with a median concentration of 230 particles/L. The results showed better performance of bioretention system than the non-vegetated sand filter for removing 20 to 200 μm MPs. In addition, there was no significant removal of MPs in the gross pollutant trap [90]. These findings supported those of Kuoppamäki et al. [116], indicating that vegetation is advantageous for the removal of MP from bioretention systems. In the summer event, vegetation improved stormwater retention. One approach to demonstrate how roots create preferred paths for water and related compounds is to look at the concentrated concentration of MPs along root channels. Other particles and related materials accumulated along root channels, where MPs were carried deeper in the soil than in nonvegetated systems, because MPs were transported by water along these channels. Biofilters have been found to effectively remove microplastics, as they do with total suspended solids (TSS), indicating their efficiency in this regard. Developing strategies to keep MPs out of water bodies is crucial because of their slow degradation and consequent persistence in the environment. In another study, Smyth et al., evaluated a bioretention cell performance with a construction made from covered media filter with vegetation to remove MPs from urban runoff. In urban runoff, MPs in the atmosphere are a source of pollution. The media filter was combination of sand (62 %), silt and clay (38 %). Based on Fig. 4, they could successfully capture 84 % of MPs with 106–5000 μm size through the bioretention cell. Their investigation revealed the performance of vegetated stormwater infiltration system as an effective system for trapping MPs from urban runoff [92].

In some studies, rain gardens were used for removing MPs. Rain gardens consisting of engineered soil, mulch, organic matter, and native vegetation can act as a bioretention cells to remove chemical materials, nutrients, metals, and MPs [72]. Werbowski et al. [72] investigated stormwater runoff from 12 watersheds contained anthropogenic microparticles and MPs with 1.1 to 24.6 particles/L concentrations. They showed concentration of MPs in stormwater is much higher than wastewater treatment plant effluent and stormwater mitigation should be given more attention. 85 % of all particles in all samples were fibers and black rubbery fragments. 100 % of black rubbery fragments and 96 % of anthropogenic debris removed through rain garden [72]. It is proposed that variations in filter size, drainage areas, or material can be the cause of the variations in removal efficiency. The better removal performance of the filter media utilized by Werbowski et al. [72] and Gilbreath et al. [93] was probably due to the fact that it included 70 % more sand than the filter media utilized in earlier research.

While bioretention and filtration have been shown to be effective in removing larger MPs >100 μm (μm), their effectiveness in removing smaller MPs is less well understood. Since MPs smaller than 100 μm are commonly found in the environment, it is important to investigate the ability of these treatment systems to remove them. Adsorption, the process by which MPs attach to the surface of other materials, may play a role in MP removal. However, the potential environmental consequences of plant adsorption, such as toxicological effects and changes in ecosystem function, need to be further investigated, which should also be investigated in future studies [105].

4.1.3. Constructed wetlands

Constructed wetlands by using wetland vegetation, soils are natural treatment systems that allow settling pollutions such as suspended solids and pathogens. These wetlands, receive MPs from different sources and can be as an important sink for them [117,118]. Distribution of MPs in wetlands depends on soil and vegetation characteristics [119].

In recent years, constructed wetlands as a secondary/tertiary low-cost treatment method have been used for urban and rural wastewater treatment plants. Constructed wetlands are popular stormwater and wastewater treatment plants in all over the world. There are two horizontal and vertical configurations of constructed wetlands that their performance has been investigated in some studies. For instance, Chen et al. studied removal of MPs in different shapes and sizes by two configurations of surface flow constructed wetlands (SF-CWs) and horizontal subsurface flow constructed wetlands (HSF-CWs). Result of their study showed 100 % removal by (HSF-CWs) and 81.63 % removal by

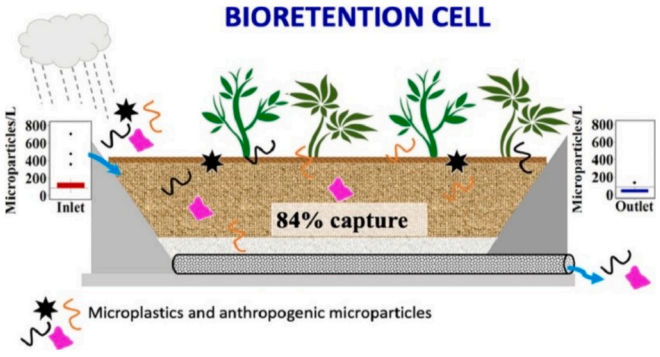

Fig. 4. Trapping microplastics from urban stormwater through a bioretention cell.
(Reproduce with permission from ref. [92].)

(SF-CWs) [119]. Also, Wang et al. [118] employed horizontal subsurface flow constructed wetlands (CWs) to remove MPs from secondary effluents and they reached 88 % removal efficiency. They collected macroinvertebrates from constructed wetlands and investigated their potential for MPs distribution in the wetland. Macroinvertebrates like bristle worms, snails, and beetle larvae, which occur in high numbers in CWs, can ingest MPs with content of 166,200 MPs/Kg. Macroinvertebrates caused a significant reduction of 88 % MPs from 6.45 to 0.77 MP/L [118]. This high removal rates of MPs in CWs may Be due to the presence of other compounds such as organic matter with hydrophobic interactions [120]. In summary, microorganisms play a vital role in the degradation of MPs, and environmental and abiotic factors can affect the rate and efficiency of biodegradation. Stormwater ponds and wetlands are effective in removing MPs through sedimentation and ecological interactions, respectively. However, Vogelsang et al. estimated lower removal efficiency of MPs as 55 % for constructed wetlands, with an effluent concentration of 14.1 mg/L [121].

Long et al. [122] investigated removal efficiency of horizontal subsurface flow constructed wetlands (HSSFCWs) to remove MPs from two rural wastewater treatment plants (WWTPs). The result showed 26.59 % removal efficiency for rural WWTP1 and 10.61 % for rural WWTP2 [122]. Another type of wetland is floating wetland that is constructed from recycled PET plastic bottles, but there is a concern about releasing material of this wetland to the environment. In a study performance of a stormwater floating treatment wetland was investigated. They compered MPs concentration in water and sediment in inlet and outlet of the floating wetland. The result showed 15 to 38 % rubber carbon filled particles as dominant microplastic in the sediment that is most probably derived from car tires. The results showed tires can be as main source of microplastic pollution in stormwater and road runoff. Also, they did not detect any microplastic originate from the constructed floating wetland's material [122]. Urban wetlands are important for stormwater management because they can reduce pollutants and MPs before entering receiving water. Townsend et al. investigated correlation between pollution and different urban lands. MPs were in all samples with 46 particles/Kg of dry sediment concentration. Major type of microplastic in all samples were plastic fragments with 68.5 % of all MPs. Fragment abundance had a higher proportion in urban wetlands with higher industrial densities than urban wetlands with higher residential densities [123].

Despite the limited number of studies on the ability of ponds and wetlands to remove MPs, those that have been conducted have shown high removal efficiencies as mentioned previously. Therefore, future studies on wetlands and stormwater retention ponds should focus on evaluating the long-term performance of these systems in removing MPs. Some research indicates that wetlands have the ability to capture and retain MPs, serving as a storage for these pollutants [98,124], but there are also concerns that wetlands may release MPs into the environment. This is because artificial wetlands are often constructed using plastic materials, such as PET [123]. However, a recent study by Ziajahromi et al. investigated a wetland constructed using PET. They did not detect any PET in the samples they collected. Based on this finding, the authors concluded that wetlands are not a source of MPs. They also recommended investigating older wetlands to determine whether MPs are released when wetlands deteriorate over time.

4.2. Potential treatment methods

Conventional treatment methods have been used in many studies to remove MPs from stormwater; however, other removal techniques of such micropollutants that have been used for other types of wastewaters have the potential to remove both MPs and NPs from stormwater and should be investigated in future studies. Some studies investigated these techniques are mentioned in Table 2.

4.2.1. Coagulation/flocculation

These processes are most applicable technologies for pollutant removal in water treatment plants. In the coagulation process, the addition of coagulants destabilizes and aggregates suspended MPs particles, which then interact to form huge flocs, which ultimately cause their separation from water matrix [103,125]. Different coagulants can remove MPs in different ways, however dominant mechanism for all of them is charge neutralization, adsorption, and sweep flocculation [125]. Based on Table 2, Al-based salts and Fe-based salts as coagulants are frequently used during coagulation [126–128]. However, the use of Al-based coagulants may result in residual aluminum in the treated water, which could have a negative impact on human health [129]. Also, these salts can be coupled with other materials to improve coagulation performance. In a study, alum coagulant coupled with polyamine-coated (PC) sand to compare its performance with conventional alum for removing MPs. The result showed increasing alum concentration >30 mg/L can cause a sharp decrease in removal of MPs. By adding PC sand, alum concentration was reduced by 50 % and as a result MPs removal enhanced by 26.8 % [130]. In some studies, coagulants have been used with flocculants [127,130]. By adding flocculants, which are typically long polymeric molecules that link together smaller flocs of material, the flocculation process can optionally be improved [131].

In a study, Monira et al. investigated the effect of alum, PAM coagulants and their combination for the removal of low-density polyethylene (LDPE), high-density polyethylene (HDPE) and polypropylene MPs from synthesized stormwater. As shown in Fig. 5a, a small efficiency rate was observed even in high alum dose (150 mg/L), respectively 11 % of LDPE, 10 % of HDPE and 13 % of PP, respectively. A slight increase to 12 % LDPE, 15 % HDPE and 19 % PP was found by adding 80 mg/L PAM (Fig. 5b). The reason for the decrease in removal efficiency is attributed to the fact that a high dosage of PAM could reduce the hydrophobicity of MP. High MPs removal efficiency were obtained by using combination of alum and PAM coagulants. This is because large flocs were formed by attraction between positively charged alum and negatively charged PAM. These large flocs can remove the higher amount of MPs duo to their large adsorption surface area. 15 mg/L of anionic PAM and 150 mg/L of alum were optimum dosages to reach the highest MPs removal efficiency of 60 % LDPE, 54 % HDPE and 79 % PP, respectively. In conclusion, the removal efficiency of MP was not significant using standalone alum or PAM coagulants, because of small floc size and less attraction surface of MPs [132].

Additionally, coagulation can be utilized as a pretreatment technique for processes like membrane. In order to remove polyethylene MPs, Ma et al. evaluated that how well ultrafiltration membrane performed with and without the use of coagulants prior to membrane separation operation. They used Al-based and Fe-based salts for coagulation of PE particles. Removal efficiency was decreased with high dosage of coagulant salts. In the next stage, they used poly acrylamide (PAM) to improve PE removal efficiency. The removal efficiency was little affected by changes in the water's ionic strength or turbidity level. The removal effectiveness of PE improved with the alteration of floc characteristics brought on by solution pH or PAM, particularly with anionic PAM with high dosage of Al-based salts. Due to the small pore size UF membrane, PE particles were totally removed during the ultrafiltration process. On the other hand, some membrane fouling was caused after coagulation with Al-based salts at a conventional dose because of the big PE particle size. As a result of forming thick cake layer with increasing coagulant dosage, membrane fouling steadily got worse. However, the Al-based floc cake layer became more heterogeneous with increasing PE particle size, which resulted in less severe membrane fouling [13,129]. Zhang et al. [133] found that combining magnetic nanoparticles such as Fe_3O_4 with magnesium hydroxide enhances the removal efficiency of MPs. The researchers noted that magnetic magnesium hydroxide coagulant (MMHC) demonstrated a notably high removal efficiency of up to 87 %. This may be due to the clustered structure of bubble particles in MMHC, which increased the collision rate between particles in water

Table 2
Potential treatment methods for MNPs removal.

Method		Wastewater	Plastic types	MNPs size	Functional materials and condition	Separation performance	Ref.
Chemical and electrochemical methods	Coagulation	Synthesized wastewater	PMMA MPs, PS NPs	MPs 5–30 μm, NPs 0.1–0.4 μm	Polymeric Al-Fe bimetallic coagulants	Al:Fe best ratio: 9:4	[128]
	Coagulation	Synthesized wastewater	PS NPs	50–1000 nm	PAC and PAM coagulants	Optimal removal efficiency: 98.5 %	[183]
	Coagulation	Drinking water treatment plants	PVC MPs	<50 μm	Ferric and aluminum sulfate coagulants	Optimal removal efficiency: 80 %	[126]
	Coagulation	Synthesized stormwater	LDPE, HDPE, PP	<5000 μm	Alum, PAM coagulants, pH 3–5	LDPE 92 %, HDPE 84 %, PP 96 %	[132]
	Coagulation/ flocculation	Wastewater treatment plant	PS	<10 μm	Ferric chloride, polyaluminum chloride, polyamine coagulants, pH 6.5–7.3	99.4 %	[127]
	Coagulation/ flocculation	Synthesized wastewater	PS MPs	3–4 nm	Lysozyme amyloid fibrils as natural bio-flocculant	98.2 %	[184]
	Electrocoagulation	Synthesized and real wastewater	PE MPs	25–1500 μm	Aluminum electrodes pH 4–7	Synthesized wastewater 99 % Real wastewater 96.5 %	[138]
	Electrocoagulation	Synthesized wastewater	PE, PMMA, CA, PP	>50 μm	Aluminum and iron electrodes, Electrolyte concentration: 0.05 M pH: 7.2, applied voltage density: 10 V anode: Al	PE 93.2 %, PMMA 91.7 %, CA 98.2 %, PP 98.4 %	[139]
	Electrocoagulation/ adsorption	Domestic sewage treatment plant	PE, PP, AC, PS, PES, PTFE, AKD	20–50 μm	Aluminum electrodes 800 kg of GAC	Electrocoagulation: 90 % GAC adsorption: 92.8 %	[140]
	Adsorption by magnetic materials	Synthesized aqueous solution	PS NPs	80 nm	Modified fly ash with Fe ions as a magnetic adsorbent pH 5–7	Adsorption capacity: 82.8–89.9 mg/g	[40]
	Adsorption by magnetic materials	Kitchen waste	PE, PET, PA MPs	48 μm	Magnetic carbon nanotubes	Adsorption capacities: PE 1650 mg/g, PET 1400 mg/g, PA 1100 mg/g Removal efficiency: 80 %	[148]
	Adsorption	Ultrapure water and surface water	PS NPs	91 nm	GAC adsorbent	Adsorption capacity in ultrapure water: 2.20 mg/g Adsorption capacity in surface water: 6.33 mg/g	[142]
	Adsorption	Synthesized aqueous solution	PS MPs	1 μm	ZIF-67 adsorbent as a metal-organic framework	Adsorption capacity: 11.6 mg/g The highest adsorption rate: 92.1 %	[147]
	Adsorption	Synthesized aqueous solution	TSS, Phosphorus, PS NPs	20 nm	Iron grafted cellulose fibers as an adsorbent	Removal efficiency: TSS (81 %), NPs (71 %)	[145]
	Adsorption	Synthesized aqueous solution	PS NPs	50–70 nm	Chromium-based metal-organic framework	Adsorption capacity: 800 mg/g Removal efficiency: 96 %	[146]
	Adsorption by renewable biomaterials	Synthesized aqueous solution	Neat PE, carboxylate-modified PE, amine-modified PE	1 μm	Chitin and graphene oxide in sponge structure	Adsorption capacity: neat PE 89.8 %, carboxylate-modified PE 72.4 %, amine-modified PE 88.9 %	[143]
	Adsorption by renewable adsorbent	Synthesized aqueous solution	PMMA, PVC, PVAc NPs	50–137 nm	Surface modified cellulose fibers (PEI@CE)	Removal efficiency: >98 %	[144]
	Electroadsorption	Synthesized aqueous solution	PS NPs	40 nm	Two typical pharmaceuticals and personal care products: CIP and BPA	Adsorption capacity: 4.92–8.71 mg/g	[150]
	Electro-Fenton-like oxidation	Synthesized aqueous solution	PVC MPs	–	TiO_2/graphite (cathode), temperature: 100 °C, operation time: 6 h	Dechlorination efficiency: 75 %	[151]
	Thermal Fenton oxidation	Synthesized aqueous solution	UHMWPE, LDPE, HDPE, PS, PVC, PP, PET	–	$FeSO_4{\cdot}7H_2O$; H_2O_2, temperature: 140 °C, operation time: 16 h	Mineralization efficiency: 75.6 %	[185]
	UV/persulfate oxidation	Synthesized aqueous solution	PVC	–	Persulfate, UV light, operation time: 35 h	58.495 ± 6.090 mg/L Cl^- release	[152]
Physical methods	Froth flotation	Synthesized aqueous solution	PET, PS	Powders: <74 μm Particles: 125–500 μm Tablets: 4000–5000 μm	Air bubbles, K^+, Na^+, Ca^{2+}, Al^{3+}, HA	100 % removal efficiency under aeration volume: 5.4 mL/min and other dosage: 28 mg/L	[161]
	Flotation	Deionized water, river water, influent of wastewater treatment plant	PS without surface coating, PMMA coated with carboxyl functional group	5 μm	Coagulative colloidal gas aphrons (CCGAs)	Removal efficiency: <94 % PS particles	[164]

(*continued on next page*)

Table 2 (*continued*)

Method		Wastewater	Plastic types	MNPs size	Functional materials and condition	Separation performance	Ref.
	Media filters	Wastewater treatment plants	PE, PA	Granular PE: 10 μm, fibrous PA: 100 μm	1. Modified aluminosilicate filter media by cationic surfactant 2. Rapid sand filter (RSF)	Removal efficiency by modified filter: >96 % Removal efficiency by RSF: 63 %	[169]
	Media filter	Wastewater	Different types of MPs	>10 μm	Disc filter	Removal efficiency: 89.7 %	[186]
	Membrane/media filters	municipal wastewater treatment plants	Different types of MPs	>20 μm	1. MBR 2. Rapid sand filter 3. Disc filter	Removal efficiency by MBR: 99.9 % Removal efficiency by RSF: 97 % Removal efficiency by Disc: 40–98.5 %	[18]
	Membrane/media filter	Urban wastewater treatment plant	Fibers, films, fragments, beads	210 μm	1. MBR 2. Rapid sand filtration	Removal efficiency by MBR: 79.01 % Removal efficiency by RSF: 75.49 %	[167]
	Membrane	Synthesized aqueous solution	PA, PS	20–300 μm	PC, CA and PTFE membranes with 5 μm pore size	Removal efficiencies: >94 %	[187]
	Membrane	Synthesized aqueous solution	PE	<5000 μm	PVDF Ultrafiltration membrane	Removal efficiencies: 100 %	[129]
	Membrane	Synthesized wastewater	Diatomite	1.65–516 μm	Dynamic mesh membrane	Removal efficiency: >99 %	[180]
	Membrane	Municipal WWTP	PET, PS	>20 μm	MBR	Removal efficiency: >99.4 %	[188]
	Membrane	Raw water	PS	0.1, 1, 10, 18 μm	PVDF hollow fiber Ultrafiltration membrane	Removal efficiency: >99.4 %	[171]
	Membrane	Influent leachate samples	PE, PES, PP, PA, EPM, PVAC	1000–5000 μm, 500 μm, 1000 μm, <500 μm	1. Ultrafiltration membrane 2. MBR	Removal efficiencies by UF: 75 % Removal efficiency by MBR: 50 %	[189]

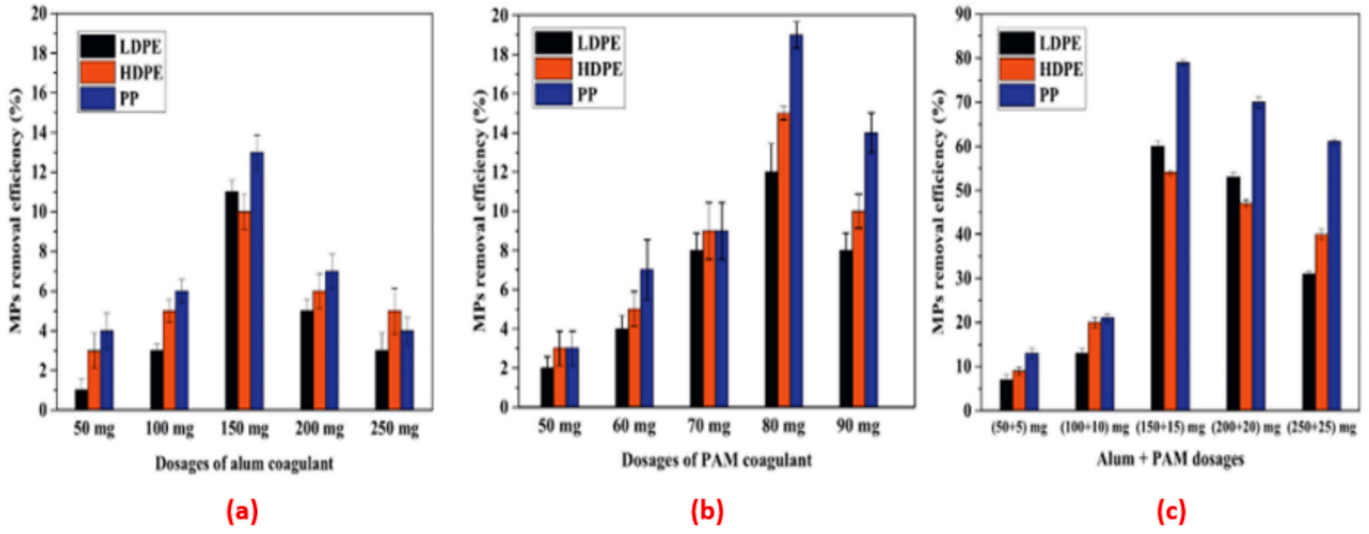

Fig. 5. Effect of different dosages of a) alum coagulant b) PAM coagulant and c) alum and PAM coagulants on LDPE, HDPE, and PP removal. Experimental conditions: temperature 22 ± 1 °C, solution pH 7 [132].

during the coagulation process. Consequently, this resulted in the formation of uniform and dense flocs, contributing to the higher removal rate. While these coagulants are effective in laboratory settings for removing MPs, their potential environmental impact at a larger scale remains unexplored. It is important to consider that the benefits and drawbacks of the process may differ based on the type of ions used to create coagulants. For example, one potential drawback of using coagulants (such as liquid bittern for MMHC) is the increase in sludge volume (e.g. precipitation of $Mg(OH)_2$), which can raise environmental concerns when discharged [134,135]. However, there is currently a lack of research on the specific environmental effects of using coagulants in removing MPs. Therefore, more research is needed to evaluate the effectiveness of inorganic coagulants for different types of MPs. Additionally, while they are effective, the cost of inorganic coagulants may restrict their widespread use, highlighting the necessity for further research on their cost-efficiency. Due to their unique surface characteristics, small dimensions, large specific surface area, low density, and high hydrophobicity, MPs pose a greater challenge for removal during coagulation treatment when compared to other types of particulate pollutants [136].

4.2.2. Electrocoagulation (EC)

In contrast to the chemical coagulation requires the external addition of coagulants, electrochemical coagulation (EC) produces coagulants directly in situ using metal electrodes. As a result, there is no danger of secondary contamination and significantly less sludge generation, and the coagulation process is easy automation [125]. Numerous initiatives have been undertaken to enhance the efficiency of electrocoagulation processes through the improvement of electrode materials, electrolyte, current density, and characteristics of MNPs [137]. Elkhatib et al. investigated EC method for removal of polyester MPs from two synthetic and real wastewaters. Based on the obtained results, 2.88 mA/cm^2 current density and an initial pH of 4 were optimum conditions to reach the lowest operational cost. In this condition, the removal efficiency of PS MP was 99 % in synthesized solution, while this rate was 96.5 % for real wastewater with 92.2 % of COD and 88.8 % of thermotolerant coliform removal [138]. In another study, influencing factors on removal of MPs by EC was investigated by Shen et al. They evaluated the removal effectiveness of four polymethylmethacrylate (PMMA), cellulose acetate (CA), PE, and PP MPs in granular and fiber form under different pH, voltage densities, electrolyte concentrations, and using aluminum and iron electrodes. Based on the results, aluminum anodes performed better than iron ones, and fiber MPs were more effectively eliminated than granular ones. In the pH range of 3 to 10, 82 % of the four MPs could be removed at their best rates. Additionally, increasing the applied voltage density and electrolyte concentration had a favorable effect on the MPs removal rate [139]. Similar to coagulation, EC can be used to boost the removal rate of other procedures by pretreating pollutants. Kim and Park used EC as an effective pretreatment process before using granular activated carbon (GAC) as an adsorption and tertiary process. The result showed 90 % of MPs were transformed into separate flocs by centrifugation after 30 min of EC with aluminum electrodes and as a result GAC could be used to successfully remove these flocs [140].

As mentioned above, EC involves the use of metal electrodes that release ions to serve as a coagulant, destabilizing suspended particles and aiding in the formation of flocs. These flocs can attract MPs, leading to simultaneous charge neutralization. Additionally, electrostatic interactions assist in the removal of NPs, as negatively charged NPs can adhere to the positively charged anode. The effectiveness of NP adsorption depends on the specific capacity of the electrode, and optimization of process parameters such as electrode material, distance, and current density can further improve efficiency. This method offers advantages such as minimal sludge production, low capital cost, low energy consumption, and high efficiency. However, there are limitations to using EC for MNPs removal, including the need for anode replacement, high conductivity requirements, concerns about residual metal ions, and anode passivation. Despite its reduced chemical consumption and ease of operation, the configuration and design of the electrode pose challenges [141].

4.2.3. Adsorption

It is another chemical technique to remove MNPs with <10 μm size from different aqueous solutions. Factors such as porosity and surface functional group of adsorbents, pH and other operating conditions are influencing factors on adsorption efficiency [103,137]. Based on Table 2, Metal-organic frameworks, cellulose fibers, carbon-based and magnetic adsorbents are new adsorbents for removal of MNPs.

Activated carbons are the most frequently used type of carbon-based adsorbents due to their large surface area, porous structure, and demonstrated effectiveness in removing organic and inorganic contaminants from drinking water and wastewaters. Arenas et al. used granular activated carbon to adsorb polystyrene NPs from a natural lake and ultrapure water. Based on the results, 90 % removal efficiency was found in the natural lake at 20 mg/L concentration of NPs which was three times higher than that in ultrapure water due to the presence of dissolved organic matter (DOM) in the natural lake. PS surface charge can be modified through divalent ion presence and as a result the adsorption of PS-DOM complexes and aggregation of PS NPs will be possible [142]. In another study, MPs removal studied by a renewable biomaterial formed from chitin sponge and graphene oxide (ChGO). These renewable materials have excellent characteristics such as reusability, biocompatibility and biodegradability. In this study, the ChGO as a renewable adsorbent showed removal rate of MPs near 90 % after three adsorption-desorption cycles [143].

Adsorbents derived from cellulose-based materials are another type of renewable adsorbents. In a study, surface modified cellulose fibers by polyethylenimine (PEI@CE fibers) were used for removal of polymer nanoparticles and revealed >98 % removal efficiency during 30 min [144]. In a recent study by Lapointe et al., iron grafted cellulose fibers were constructed to remove conventional and new pollutants from wastewater treatment systems. They synthesized Fe-fibers to increase the amount of positively charged iron (hydr)oxides grafted onto cellulose in order to increase the adsorption capacity for negatively charged pollutants like phosphorus. The fibers significantly enhanced floc size and allowed settling by screening technology. In comparison with conventional treatment, removal of total suspended solids improved from 22 % to 81 % through fiber-based treatment. NPs removal rose considerably from 20 to 71 % after combination of fibers with a coagulant (alum) and a flocculant (polyacrylamide). Another important result was reusability of fibers more than five times with >95 % removal efficiency and operational cost reduction [145].

Metal-organic frameworks (MOFs) are made by assembling metal ions and organic ligands. They are porous and crystalline materials with high porosity, tunable structure, and rich functionality that can be used in a variety of applications, and including removing NPs [146]. Zeolitic imidazolate frameworks (ZIF) are among these materials and have many benefits because of a high adsorption capacity, large surface area, and a stable structure. In a study, ZIF-67 as a novel metal organic framework showed 92.1 % removal rate of PS MPs. Operating conditions such as pH, PS MPs solution concentration, and temperature were effective parameters in achieving optimal conditions. Hydrogen bond interactions, π-π stacking, and electrostatic interactions were dominant mechanism in adsorption of PS MPs on the ZIF-67 [147]. In a study that recently has been done by Esfahani et al., chromium-based metal-organic framework (Cr-MOF/MIL-101) was used to remove PS NPs. Their result showed 96 % removal efficiency of NPs with 0.8 mg/Kg maximum adsorption capacity [146].

Magnetic adsorbent are new types of adsorbents and their mechanism is based on binding magnetic carrier media to MNPs in order to magnetize them. Having a better separation capacity is dependent on the particle size and magnetic carrier media density of MNPs. Magnetic adsorbents are more effective in collecting larger polymers than smaller plastics. Also, a larger magnetic carrier media density can lead to improved separation efficiency because of more collisions between MPs. Additionally, a high ion concentration can reduce the magnetic particles' electrostatic repulsion, which encourages the binding of magnetic particles to MPs [102,103]. Different materials can be used as a magnetic adsorbent such as magnetic carbon nanotubes [148], nano-Fe_3O_4 [149], and modified fly ash with Fe ions [40]. Tang et al. synthesized magnetic carbon nanotubes (M-CNTs) for the first time and tested it for removal of PE, polyethylene terephthalate (PET), polyamide (PA) MPs from kitchen wastewater. Under acidic conditions, it was shown that PA MPs with a positive charge increased their electrostatic repulsion with M-CNTs, but the hydrophobic effect of PE/PET and M-CNTs was reduced as a result of the creation of acidic oxygen-containing groups on the carbon nanotubes' surface. Also, this magnetic adsorbent showed reusability capacity and 80 % MPs removal efficiency after four times recycling [148].

Adsorption has the potential to achieve high levels of MNPs removal, targeting both large and small particles. The adsorbent material effectively attracts and eliminates MNPs from water, making it suitable for various water sources and MNPs types. Different adsorbent materials, such as activated carbon, zeolites, and specific polymers, can be utilized

to tailor the process to specific water treatment needs. Additionally, these materials can also remove other water pollutants, contributing to overall water quality improvement. In some instances, adsorbent materials can be regenerated and reused, reducing operational costs and environmental impact. However, the finite adsorption capacity of the material may require replacement or regeneration, leading to increased operational and maintenance costs. The selectivity of adsorption may necessitate the use of multiple materials or pre-treatment processes to enhance MNPs removal efficiency, which is a major disadvantage in the use of adsorbents. The cost of adsorbent materials can vary, impacting the overall cost-effectiveness of the process. Proper disposal methods for used adsorbents containing captured MNPs should be implemented in future studies to prevent environmental contamination.

4.2.4. Electrosorption

This method as an electrochemical process has been recently used for separation of NPs by an electric field. The two-electrode makes it possible to remove NPs from the electrolyte, particularly the aged-NPS spheres. Due to the negatively charged nature of the aged-NPS and NPS spheres, the anode counterpart can remove more microscopic plastic particles from the solution [137]. In a study, Xiong et al. used electrosorption technology for the first time to remove NPs from solutions. They synthesized PS NPs with 40 nm diameter and used electrosorption with a capacity of 0.707 g nano-polystyrene/g AC and 0.322 g aged-nano-polystyrene/g AC. Their finding implied that adsorption under an electric field is likely a viable tertiary treatment method for removal of NPs in aqueous environments [150]. Modification of surface charges of MNPs, construction of porous electrodes to have a large surface area, optimization of electrode distance and electrolyte are important factors that must be modified to optimize the use of electrosorption in the future [137].

4.2.5. Advanced oxidation processes

The method of chemical oxidation is based on either mineralization or the breakdown of MPs into tiny molecules. Limited studies have focused on mineralization of MPs. Miao et al. [151] suggested that under heating conditions, PVC microplastics could obtain electrons directly from TiO_2/C cathode, initiating dechlorination via cathodic reduction. Simultaneously, PVC microplastics could be oxidized by OH radicals, forming oxy-organics containing oxygen groups like C═O and O—H. These species could further oxidize by •OH radicals to form smaller fragments such as alcohols, carboxylic acids, and esters. Eventually, partial mineralization of these substances to CO_2 and H_2O could occur. In an optimum condition, after 6 h of potentiostatic electrolysis at −0.7 V vs. Ag/AgCl, the dechlorination efficiency of PVC reached 75 %. Ouyang et al. [152] indicated strong oxidation capacity for free radicals, inducing non-selective mineralization or decomposition of microplastics, given sufficient operational conditions. The result demonstrated the PVC MPs can be effectively broken down using a UV/persulfate technique, with a dichlorination rate of 58.495 ± 6.090 mg/L Cl in about 35 h of treatment. Nabi et al. [153] investigated the photocatalytic degradation of PS microspheres and PE over TiO_2 nanoparticle films under UV light irradiation. They observed complete of PS and PE in 12 h and 36 h respectively with CO_2 identified as the primary end product. The activation of TiO_2 by UV light creates electron-hole pairs, initiating two pathways: the valence band pathway, where positive holes oxidize organics and generate hydroxyl radicals, and the conduction band pathway, where electrons react with oxygen to form radicals that degrade pollutants, including microplastics.

Ozonation, Fenton reaction-based and photocatalyst technologies are currently used in advanced oxidation methods (AOPs) for the removal of MPs. Hydroxyl, chloride, and sulfate radicals have been widely used as reactive oxygen species (ROS), for the mineralization of different kinds of organic contaminants by oxidizing them, because of their potential for turning organic contaminants into safe byproducts [137,154]. Ozone is an oxidant that mainly targets functional groups with many electrons such amines, double bonds, and activated aromatic rings to produce •OH radicals. Based on previous studies, ozonation can be more effective than chlorination for degradation of PS NPs. Also, ozonation can be as an effective tertiary treatment [137]. Ozonation can be integrated with other processes such as UV [155] or hydrogen peroxide [156]. In both integrated methods, an increase in carbonyl groups leads to a decrease in hydrophobicity and as result more degradation of PS NPs. Also, •OH radicals can be produced by Fenton reaction-based that is high efficiency and nontoxicity process [154]. The degrading performance of MNPs has been improved by Fenton reaction-based integrated approaches, such as the electro-Fenton like system, bio-photo-Fenton system, and thermal Fenton system [137].

AOPs are considered as environmentally friendly due to their minimal impact on the environment and their effectiveness in eliminating a wide range of organic pollutants. Given that plastics fall under the category of organic pollutants, AOPs could be utilized in addressing environments polluted by MNPs. However, the use of AOPs is linked to high operational costs as they necessitate the use of costly chemicals and/or energy input [157]. There are several limitations to the degradation of MNPs by AOPs. Compared to other AOPs, conventional Fenton is less effective at degrading MNPs. Smaller MPs, including microfibers (MFs), actually increase in abundance after ozonation. Laboratory studies often use longer UV exposure times than what is required for treatment at full-scale. Furthermore, oxidized MPs have less interaction with hydrophobic micropollutants. It should be mentioned that the use of ozonation in treatment plants has led to increased fragmentation of MPs, including MFs, resulting in the generation of new MPs. It is important to pay more attention to the toxicity effects of intermediates, and standardize the methods of analysis for MNPs in stormwater in order to effectively compare studies [158].

4.2.6. Flotation

It is based on the hydrophilic/hydrophobic interaction between bubbles and MNPs surfaces. Surface characteristics of bubbles and MNPs, and solution chemistry are effective factors on interaction between bubbles and MNPs. Based on some studies, bubbles can be modified by some surface functionalized agents such as PDADMAC and cetyltrimethylammonium bromide (CTAB) that by charging the microbubbles (MBs), increases the charge attraction and sweeping between MPs and MBs [159]. Also, there are several modifications that can be made to MNPs' surfaces, such as surface oxidation, surface functionalization by coating, and magnetization, to improve flotation performance [160]. Additionally, flotation efficiency can be influenced by aquatic solution properties such as pH solution, presence of different metal ions, and dissolved organic matter [161].

Colloidal gas aphrons (CGAs) is a typical microbubble that can be coated with a coagulant or a flocculant. Coagulant or flocculant-coated colloidal gas aphrons (CCGAs) as an attractive modified microbubble due to its large surface area, good transportation of bubbles, and high air capacity properties has been used in some studies [162,163]. In a study, Zhang et al. used CCGAs microbubbles to remove MP with 5 μm and dissolved organic matter simultaneously. They used Carboxyl-modified poly-(methyl methacrylate) and unsurface-coated polystyrene as MPs. Result of their study showed 94 % removal of PS MPs and less removal of PMMA because of competition of humic acid (HA) polyanions, which competed with the negatively-charged PMMA to receive CCGAs. Also, in river or influent of wastewater treatment plant, MPs were removed completely, while DOM was removed incompletely due to the free DOM or the DOM-coated MPs by complexation interaction [164]. Feilin and Mingwei have developed a new method for removing MPs from rivers using a positively charged carrier in an air flotation system. Initially, the air was ionized and then introduced into a reactor after the electrons are neutralized. The four most commonly found polymers, including polyethylene (PE), polystyrene, polyvinyl chloride, and fiber mixture from clothing washing machines, are crushed and added as pollutants to river water and tap water samples to study the removal capabilities of the

small-scale facility. The results of the experiments showed that the method was effective and achieves a removal efficiency of over 90 % for all four polymer samples within 2 min. PE was the easiest type of MPs to remove from river water, and particles larger than 200 μm were efficiently removed. The results indicated that this proposed method shows promise in addressing the MPs issue in rivers due to its short retention time, high removal efficiency, lack of chemical additives, and ability to handle various types of polymers [165]. However, in another study [166] the dissolved air flotation (DAF) utilized to eliminate PE particles without coagulation, resulting in low efficiency (25 % to 30 %). Therefore, it is essential to incorporate coagulation and flocculation processes to achieve high efficiency in removing MPs. Since MPs have low density and float in water, using the DAF method instead of sedimentation in the final stage of coagulation process can potentially achieve sufficient efficiency with a lower coagulant dose. Further research is needed to assess whether DAF could be a promising standalone method or if it should be combined with post-treatment processes.

4.2.7. Media filtration

In most of media filtrations, sand filtration and activated carbon are used as media filter. Shape and size of MNPs are important factors for selecting media filters. The study found that membrane bio reactor (MBR) and rapid sand filtration (RSF) were effective in removing MPs, with a higher removal rate for particulate-shaped MPs (98.83 % and 95.53 %) compared to those in fiber form (57.65 % and 53.83 %) in MBR and RSF separations, respectively [167]. Based on previous studies, RSF is effective media filtration for big-sized particles (>10 μm), while granular activated carbon showed 56.8–60.9 % removal efficiency for MPs smaller than 10 μm and 73.7–98.5 % separation efficiency for MPs in size 1–5 μm [103].

Wang et al., employed biochar as a low-priced material for integration with sand filters for removal of uniformly graded microplastic spheres. They used four types of biochar including C300, C400, C500, and hardwood. Based on Fig. 6a–b initial concentration of MPs dropped considerably after filtration with the biochar, apart from the silica sand filter. Among the four types, C500 and C300 biochars provide the highest and the lowest removal efficiency, respectively. As shown in Fig. 6c, all types of biochar filter showed >95 % removal and immobilization of microplastic spheres with 10 μm diameter which was larger than the sand removal efficiency (60–80 %). Also, biochar C500 showed 100 % removal efficiency and 0 % MP releasing. These results introduced biochar as a potential material with high capacity for improving sand filters efficiency to remove MPs in WWTPs [168].

Recently, some novel filters such as surfactant-modified aluminosilicate filter media have been evaluated elimination of MNPs. Shen et al., evaluated tertiary sewage treatment of MPs in WWTPs through modified aluminosilicate filter for the first time. They used granular PE MPs with 10 μm size and fibrous PA with 100 μm size. The modified filter showed removal efficiency >96 % for both PE and PA MPs, while this percentage was 63 % for rapid sand filter [169].

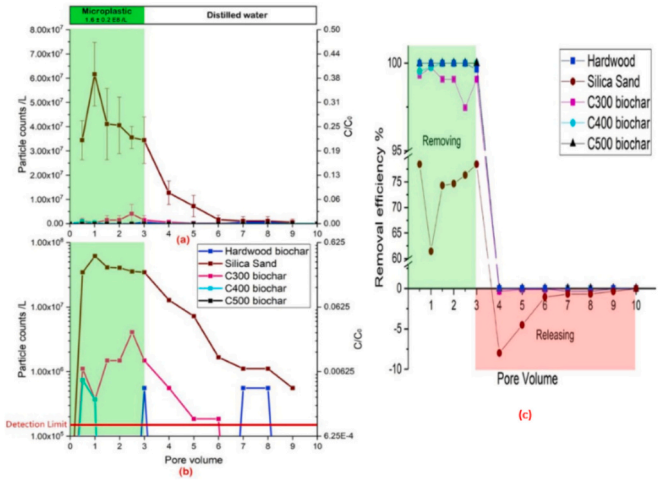

Fig. 6. a, b) Concentrations of microplastic particles measured in the effluent and c) the removal efficiency of microplastic spheres at different pore volumes [168].

4.2.8. Membrane separation

Membrane separation technologies have recently been introduced for the separation of MNPs. Removal of MNPs is based on electrostatic interaction and hydrophobic-hydrophobic interaction between surface of MNPs and membranes [170]. Based on Table 2, MBR, Ultrafiltration (UF), and dynamic (DA) membranes are the most widely used membranes for removal of MNPs. UF membranes are mainly efficient in the removal of NPs because their pore size falls within the same range (0.005–0.1 μm) [137]. In some studies, UF membranes showed removal efficiency >99 % [129,171]. MBR as another effective membrane process which is combination of membrane separation (such as UF) and biological treatment processes has been showed high potential for removal of MPs along with other advanced method technologies [18,167]. Talvitie et al. treated four samples of different municipal wastewater treatment plants with MBR and media filters. They used MBR for treating primary effluent and disc filter, rapid sand filtration, DAF to treat secondary effluent. In their study, MBR showed 99.9 % removal efficiency of MPs with 6.9 to 0.005 MPs/L concentration [18].

The results of Lin et al.'s study [172] showed that membrane fouling during secondary effluent nanofiltration was exacerbated by the accumulation of substances similar to proteins, polysaccharides, and humic acids on the membranes, which resulted in the worsening of membrane fouling by MPs. MPs may make the membrane flow fall worse over the course of the secondary effluent's 50-day filtering. In about 19 days, MPs caused a more noticeable decrease in membrane flux from 33.1 LHM to 8.2 LHM, but without MPs, the decrease was less pronounced to 10.8 LHM. This suggests that MPs in secondary effluent can significantly worsen short-term nanofiltration membrane fouling. Filtering the SE without MPs, the flux stabilised at around 7.8–9.0 LHM after 40 days of operation. The flux curve was almost horizontal over the course of the last ten days of filtration. The dynamic equilibrium between the foulant deposition on the membrane surface and their spalling under the cross-flow shearing force was identified as the cause of this occurrence [173]. Nevertheless, it was discovered that the membrane flux steadily decreased to 6.6 LHM when MPs were added to the secondary effluent, indicating that the flow was scarcely maintained constant throughout long-term nanofiltration. Thus, during the nanofiltration of secondary effluent, MPs may exacerbate both short- and long-term membrane fouling at the same time. On the other hand, the buildup of MPs during the filtration process may have an impact on membrane fouling development both directly and indirectly [174]. MPs have the potential to contribute significantly to membrane fouling. While some MPs with hole sizes smaller than membrane pores can form dense cake layers on the membrane surface by aggregating with other organic contaminants, the remaining MPs can block membrane pores directly [13]. Furthermore, some MPs with high shape irregularity can lead to a loose and porous morphology, which can reduce membrane fouling by breaking down the compact structure of fouling layers [175]. It is suggested that the size connection between MPs and membrane pores determines the particular mechanisms of membrane fouling that MPs directly control. Conversely, MPs can affect bacterial metabolism and microbial activity by offering microbes hazardous or abundant homes, which can result in varied levels of extracellular polymeric material secretion and fouling potential [176]. Lin et al. found that MPs constantly worsen membrane fouling over the course of filtration time, as seen by the membrane flux behaviors. This is most likely caused by the MPs' inherent tendency to accumulate in nanofiltration systems and their ability to increase the release of metabolites. Consequently, this causes the secondary effluent's quality to decline [172].

A study investigated the impact of coagulation with polyethylene (PE) on ultrafiltration (UF) performance. The researchers found that membrane fouling decreased as the dosage of coagulant increased. This was attributed to the increased porosity of the floc cake layer due to the presence of PE particles, particularly large ones. The presence of larger PE particles had a positive effect on membrane fouling, reducing the decrease in membrane flux. For example, in the presence of large-particle-size PE ($2 < d < 5$ mm), the membrane flux decreased by only 10 % after coagulation with 0.2 mmol/L PAM and 2 mmol/L $FeCl_3{\cdot}6H_2O$ [129]. However, this behavior may not be a general rule but can depend on several factors, including the specific membrane process and the characteristics of the plastic particles (such as their chemical composition, size, and shape). To maintain flux rates, control membrane fouling, minimize cleaning frequency, and prolong the lifespan of RO equipment, a pretreatment stage is typically required. Common pretreatment methods involve the use of chemicals such as coagulants, antiscalants, oxidizing agents, and disinfectants [177]. Other strategies for mitigation membrane fouling include cleaning, surface modification, and the use of novel membrane materials [178]. Nowadays, combining UF pretreatment with RO has been shown to achieve stable performance in terms of water quality and flux in desalination process. There is a growing trend towards the application of combined RO-UF plants for desalination at an industrial [179].

Recently, Dynamic membranes (DMs) have attracted many attentions because of their low-cost, saving energy, removal of non-degradable plastics, and reusability. These membranes are gravity driven membranes that their mechanism is based on trapping MPs in the cake layer formed on the large pore mesh surface [103,180]. The previous analysis suggested that MPs particles might cause a linear increase in cake layer thickness as transmembrane pressure increased [180]. However, membrane fouling which is the main operational challenge can diminish the productivity of the membrane and its technological and economic viability [181]. Some studies have been conducted to reduce membrane fouling when they used for MPs removal. Li et al., evaluated elimination of MPs by an ultrafiltration membrane and the effect of different factors on the UF membrane fouling. They used different sizes of MPs and their result showed the most sever fouling through MPs with average 1 μm size. Also, there was a positive correlation between trans membrane pressure (TMP) and loading of MPs. They used aluminum-based flocs (Al-flocs) to improve removal of MPs and these flocs led to formation of loose cake layer on the membrane surface and as a result TMP reduced by 85 % in Al-flocs dosage of 26 mM. Application of module rotation or helical rotation can further enhance this filtration. They concluded that cake layer can be easily reduced due to the shear stress and turbulent flow [171].

Fouling is a significant factor that limits the widespread use of membranes, as it leads to a reduction in membrane flux and an increased need for cleaning chemicals. When membranes are cleaned with chemical agents after fouling, it can result in damage to the membrane structure and a shorter service life. Membrane fouling occurs when contaminants in the feed water block the pores on the surface and internal structure of the membrane, leading to the accumulation of contaminants and the formation of a cake layer. This phenomenon happens when contaminants smaller than the membrane pore size are adsorbed in the pores, causing them to narrow and clog, while larger contaminants accumulate on the membrane surface, forming a cake layer. The challenges in removing MNPs using membranes currently involve issues such as membrane contamination, the possibility of MPs being released from polymeric membranes into water/wastewater, and the potential for MNPs to pass through even dense membranes like RO. It is important to study the conditions that lead to the release of MNPs from polymeric membranes into water/wastewater and their passage through the membranes [182]. Future research should prioritize the development of membranes with anti-fouling and self-cleaning properties to minimize membrane fouling caused by MPs.

4.3. Novel treatment methods

Recently, new techniques for the degradation of MNPs from various aquatic environments have been developed. These techniques include the use of natural materials such as food products (natural filters), biological materials such as microorganisms (biological degradation), electrocatalytic and photoelectrocatalytic micro and nanomaterials (electrochemical degradation), radical-based catalysis (ultrasonication), and electric field generators such as triboelectric nanogenerators (electrokinetic separation), which will be covered in the following.

4.3.1. Natural filters

Using natural materials, such food products, as filters to remove MNPs is one option because they have advantages in terms of sustainability and environmental friendliness. For this purpose, researchers have used proteinaceous materials found in nature that have covalent networks of 1D carbon-nanofiber (CF) structure and hierarchical porosity, as well as good mechanical behavior, high surface areas, and thermal, electrical, and electrochemical conductivities [190–193]. In recent study has been done by Ozden et al., egg-white (EW) proteins were used to produce an ultralightweight G-CF aerogel for MNPs from seawater and aqueous environments. They could create a filter with an integrated structure from 1D-carbon nanofiber (CF) and sheets of 2D-graphitic carbon (G) with unique characteristics such as high surface area, low densities, and better mechanical performance. They used their synthesized filter for desalination and water purification aims and the results showed 98.2 % removal of ionic impurities and 99.9 % MNPs capturing. Moreover, the findings demonstrated this filtration technique uses only gravity and wastes no water, in contrast to membrane, which operates with a substantial energy input and excess water. Furthermore, the results showed that this filtration method relies solely on gravity and does not waste any water, unlike membrane filtration, which requires a significant amount of energy input and results in excess water usage [194].

4.3.2. Biological degradation

There are few studies on using biological materials such as microorganisms to degrade MNPs. Recently, scientists have used environmental microbes for this aim. Bacteria have a natural tendency to congregate and attach to surfaces. These sticky bacteria can create multicellular biofilms on the surface of MPs using their own exopolymeric matrix, which frequently had changed diversity, metabolism, and function. This ability makes microbe nets on the MPs surfaces that can easily collect MPs from polluted sources [195–198]. Additionally, easy plastic recovery from bioaggregation may encourage recycling of recovered plastics rather than using landfills or incineration [199].

Microalga is another microorganism that is used to remove MNPs from aquatic environments. Microalgae are photoautotrophic organisms, unlike bacteria and fungi that can also grow mixotrophically in a variety of environments, including fresh water, marine, wastewater, soil, and wet surfaces. Microalgae have a far better ability for the removal of pesticides, medicines, heavy metals, ions, than terrestrial plants. They also have a lot higher biomass yield. Microalgae remove pollutants through a variety of techniques, including immobilization, adsorption, accumulation, and then intracellular conversion to useful chemicals. For removing MNPs, particles attach to algal surfaces or absorb into algal cells to filter them out of the water body and eventually destroy them from the polluted biomass with downstream process. MNP-microalgal cell interactions may improve a number of crucial aspects for potential microalgal harvesting and/or desired macromolecule accumulation [200,201]. According to one theory, under MNP stress, microalgal biomass can collect lipids and carbohydrates, enabling the conversion of the biomass into biodiesel and bioethanol, respectively. The use of microalgae as biofuel feedstocks provides a cost-effective and environmentally beneficial alternative to burning fossil fuels [202–204].

4.3.3. Electrochemical degradation

Photocatalytic (PC), electrocatalytic (EC) and photoelectrocatalytic (PEC) Catalytic degradation of MNPs particles by micromotors and nanomaterials are current effective emerging approaches due to the high reactivity of nanomaterials. Various nanomaterials include organic molecule-based and inorganic nanomaterials can be used as catalytic nanomaterials. The most widely used nanomaterials for this aim are cadmium-based NMs [205], carbon-based NMs (such as graphene [206], graphene oxide (GO) [207], reduced graphene oxide (RGO) [208], and carbon nanotubes (CNTS) [209]), transition metal oxide NMs (such as TiO_2, ZnO [210], Cu_xO-based NMs [211], nickel [212], and niobium-based oxide NMs [213]), and other NMs (such as Bismuth oxychloride (BiOCl) [214] and Ni_2P [215], etc.). ZnO and TiO_2 are the catalysts that are most frequently used because they have a satisfactory MNPs decomposition efficiency. These nanomaterials as effective materials and a potential can be used for degradation of MNPs in the stormwater [216].

Photocatalytic self-propelled micromotors are another type of photocatalytic materials, which their performance is based on their phoretic interaction [217]. Wang et al., produced TiO_2 based micromotor (Au@mag@TiO_2, mag = Ni, Fe) that was applicable in both peroxide and water environment under UV beam. Also, they assembled chains of micromotors through an external magnetic field to remove peroxide free microplastics [218].

4.3.4. Electrokinetic separation

Another novel effective method to remove MNPs from stormwater can be electric field generators such as triboelectric nanogenerators (TENGs) that extract particles from wastewater by electrophoretic force based on their zeta potential. This method can be effective for removal of sub-microscale nanoparticles in wastewaters. TENGs can be effective as a power source for different applications such as batteries, water splitting, and environmental monitoring because electrical power generation from TENGs can convert various forms of ambient mechanical energy into electricity [219–221]. TENGs are effective for generating a strong electric field that can be utilized for electrophoresis without the need for complex circuits. This is due to their ability to produce high voltage and their low output current, making them relatively safe for aquatic organisms. In a study, Jung et al. compered performance of two configuration of TENG including three-dimensional porous-pyramid polydimethylsiloxane and flat film-based. The power output of a TENG made from a three-dimensional porous-pyramid polydimethylsiloxane was three times greater than that of a TENG made from a flat film. Additionally, the rate at which it could be removed was 5.6 times faster than the flat film-based TENG. It was discovered by measuring the area that the particles adhering to the electrode covered that the output voltage and operating time of the TENG had a considerable impact on the removal of particles. It is effectively established that a TENG-driven self-powered electrophoretic system can remove sub-micron nanoparticles of polystyrene, CdSe/CdZnS, ZnO, and SiO_2 [222]. Table 3 summarizes advantages and limitations of the treatment strategies for removal of MNPs.

5. Mechanisms involved in micro- and nanoplastics removal/degradation

Different techniques are employed to remove and degrade MNPs, utilizing a variety of mechanisms including charge neutralization, adsorption, sweep flocculation, hydrolysis, electrostatic interaction, adhesion, physical filtration, advanced oxidation processes (such as oxidation, chlorination, and photooxidation), biodeterioration, biofragmentation, assimilation, and mineralization. Table 4 shows the comprehensive overview of these techniques and their respective major removal mechanisms.

Table 3
Advantages and limitations of the treatment methods for removal of MNPs.

Treatment methods	Advantages	Disadvantages	
Coagulation/ flocculation	Simple operation; Cost effective; Pretreatment for membrane filtration; Versatility of coagulants.	Residual aluminum concerns; Limited standalone effectiveness.	[129]
Electrocoagulation	In-situ coagulant generation reducing the need for external chemical additions and minimizing the risk of secondary contamination; Lower sludge production, Ease of automation, High removal efficiency,	High operational costs, Complexity of optimization of parameters, Handling and disposal of generated sludge, Potential release of metals in treated water	[141]
Adsorption	High porosity and surface Area, Tunable structure and functionality, choice of renewable biomaterial with high removal efficiency	Cost and synthesis complexity, Sensitivity to pH and temperature:	[142]
Electrosorption	Effective removal of NPs, high adsorption capacities (for e.g. 0.707 g nano-polystyrene/g AC), viable tertiary treatment method for removal of NPs	Complex optimization, Energy consumption.	[150]
Advanced oxidation processes	Effective degradation, Integration with other processes, Effective as a tertiary treatment step.	Operational costs, Potential formation of harmful byproducts or secondary pollutants that require additional treatment steps, Methods like UV activation can be energy-intensive, pH sensitivity, handling of reagents	[102]
Flotation	The large surface area of microbubbles, especially CCGAs, enhances interaction with MPs, boosting removal efficiency. Modified microbubbles can also remove MPs and dissolved organic matter (DOM) simultaneously.	Competitive interactions between HA polyanions and negatively-charged MPs reduce removal efficiency Surface modification of MBs and MNPs is costly, and agents like CTAB and PDADMAC may introduce harmful chemicals.	[159,160]
Media filtration	High removal efficiency for microplastics and nanoparticles, Potential for regeneration and reuse, Potential for Innovation: Novel filters like surfactant-modified aluminosilicate filter media showcase ongoing innovation in filtration technology, offering promising solutions	Higher initial cost, may require significant resources for production, regeneration, or replacement, impacting overall sustainability and cost-effectiveness, may require pre-treatment or additional filtration steps for optimal performance	[167]

(continued on next page)

Table 3 (*continued*)

Treatment methods	Advantages	Disadvantages	
	for enhanced pollutant removal.		
Membrane separation	UF, MBR, and DMs over 99 % removal efficiencies for MNPs, driven by gravity, offering cost-effective and reusable solutions, aided by techniques such as module rotation to mitigate fouling and enhance longevity.	Membrane fouling, Efficiency is influenced by particle size and transmembrane pressure, requires precise control for process efficiency, MBR sustain substantial setup and maintenance costs.	[180]

5.1. Charge neutralization, adsorption, sweep flocculation and hydrolysis

Different coagulants can remove MNPs in different ways, however dominant mechanism for all of them is charge neutralization, adsorption, and sweep flocculation. Charge neutralization involved the neutralizing MPs original negative charge by adsorption of hydrolysates of metal coagulants, such as PAC and $FeCl_3$ and causing particle destabilization. In adsorption, coagulants like PAC produce positively charged monomers or clusters adsorb surrounding particles, including MPs, leading to the formation of flocs that eventually settle. Wherein the hydrolysis products of coagulants neutralize the negatively charged particles. While the hydrolysis process does have a positive effect on the coagulation performance, it is not particularly strong. Additionally, the hydrolysis of coagulants contributes to the coagulation process by generating hydrolysis products that interact with MPs. Chemical bonds are formed between MPs and coagulants, indicating a chemisorption process. Overall, the removal mechanism of MPs involves a combination of charge neutralization, adsorption, and the hydrolysis process of coagulants [223]. Peydayesh et al. [184] investigated the removal of negatively charged polystyrene particles to test the effectiveness of amyloid fibrils (novel bio-flocculant) in removing MPs from water. The removal mechanism involved coagulation-flocculation induced by electrostatic interactions between the amyloid fibrils and the negatively charged polystyrene particles. The positively charged amyloid fibrils neutralized the negative charges on the particles, causing them to destabilize and coagulate to form larger flocs that could be easily removed from the water. The flocs were then allowed to sediment, which resulted in the removal of the MPs from the water.

Monira et al. [132] conducted research on the elimination of MPs from synthetic stormwater using a mixture of coagulants. It was found that a combination of alum and polyacrylamide (PAM) was more effective in removing MPs than using a standalone coagulant. This was achieved through charge neutralization and hydrophobic interaction between the coagulant flocs and MPs. As shown in Fig. 7, the mechanism of MP removal using coagulation-flocculation, positively charged alum or PAM coagulants strongly react with negatively charged MPs which leads to destabilized by neutral charge as the main mechanism. This is because the strong hydrophilic interactions between negatively charged MPs and the positively charged coagulants will form a large floc to attract a significant amount of MP particles by intermolecular or Van der Waals attraction to finally settle or be trapped. Although charge neutralization is the dominant factor, the critical role of surface morphology and surface area in removal mechanisms should not be overlooked.

The study conducted by Wang et al. [224] examines the removal mechanisms of MNPs using polymeric Al-Fe bimetallic coagulants. It was observed that the removal of MPs was more effective than NPs due to the ability of MPs to overcome water's surface tension and settle rapidly. Coagulants with higher Fe content demonstrated better MP removal by enhancing sweep flocculation and settling of Fe hydroxides on MPs' surfaces. The denser Al element facilitated the adsorption of Al clusters onto flocs through electrostatic interactions. Conversely, NPs exhibited three modes of removal: binding with hydroxides, aggregation into larger agglomerates, and adsorption onto floc surfaces. Charge neutralization played a crucial role in NP removal. The addition of Fe promoted MP removal but inhibited NP removal, and the dosage of coagulant affected turbidity removal and zeta potential. The major removal mechanism for coagulation process for MNP removal involves sweep flocculation and charge neutralization, respectively, with the dominant mechanism depending on Fe content and particle size (Fig. 8).

Shen et al. [139] investigated the removal of MPs by using electrocoagulation (EC), which involves using an electrical current to dissolve metal anodes (Al or Fe) and form Al^{3+} and Fe^{3+} ions in water. These ions then react with OH- ions generated at the cathode to form various hydroxides, including $Al(OH)_3$ and γ-FeOOH precipitates. The Al^{3+} ions have a long retention time in water and can polymerize to form a network of nuclear polymers, which can remove MPs by adsorption or net catching and sweeping. The addition of sulfate in water can promote the connection of more network polymers.

Electrostatic adsorption as shown in the following reactions:

$$AlOH^{2+} + 2MPs - \rightarrow AlOH^{2+} - 2MPs - \quad (1)$$

$$Al(OH)^{+2} + MPs - \rightarrow Al(OH)^{+2} - MPs^{-} \quad (2)$$

$$Al3(OH)5 + 4 + 5MPs - \rightarrow Al_3(OH)5 + 4 - 5MPs^{-} \quad (3)$$

The positively charged hydroxide ions can adsorb negatively charged ion MPs, and the addition of anionic surfactants can enhance this effect. However, the production of microbubbles from the hydrogen evolution reaction at the cathode can disrupt the formation of flocculants. Thus, the MPs undergo flocculation and charge neutralization at the same time during EC.

5.2. Electrostatic interaction, surface complexion, adhesion, and physical filtration

Several studies have investigated the use of adsorption as a method for removing polystyrene nanoparticles (PSNPs) from water. Modak et al. [146] found that chromium-based metal-organic frameworks (Cr-MOFs) were effective in adsorbing PSNPs, with a maximum adsorption of over 96 % occurring at pH 5, primarily through electrostatic interactions. Meanwhile, Arenas et al. [142] evaluated the use of granular activated carbon (GAC) for removing polystyrene NPs and found that electrostatic interactions were also the main adsorption mechanism in ultrapure water.

Singh et al. [225] highlighted that the major removal mechanisms for NPs using iron-modified biochar sorption are surface complexation and electrostatic attraction (Fig. 9). The observation from their experiments includes the lack of significant impact from ionic strength or interfering ions on NPs sorption, minimal impact on NPs removal with changes in solution pH, despite a drastic variation in the zeta potential of the composites suggested the mechanism beyond electrostatic attraction are involved in the removal process. In FTIR analysis the disappearance of the COO— peak, the generation of FeOOH stretching, and a shift in the Fe—O band were observed in the composite after sorbing NPs confirm the involvement of surface complexation, as NPs were found to form complexes with hydroxyl and COO— groups of biochar. Additionally, the π-π conjugation and hydrophobicity also plays important role in interaction mechanism between the NPs and composites. Overall, adsorption offers a gentle and effective method for removing polystyrene NPs from water with low energy consumption and negligible by-products [217].

Wang et al. [159] investigated the removal mechanism of MPs using dissolved air flotation (DAF). They found that by modifying the DAF process, the adhesion between MPs and microbubbles (MBs) could be

Table 4
The summary of the various techniques for degradation of MPs/NPs from aquatic systems along with major removal mechanism.

Technique	Major removal mechanism	Type of microplastics	Key notes	Ref.
Chemical coagulation	Charge neutralization and hydrophobic interaction	Low-density polyethylene (LDPE), high-density polyethylene (HDPE) and polypropylene (PP)	Doubling the dosage of alginic and humic acid to 40 mg/L significantly enhanced removal efficiencies: LDPE (92 %), HDPE (84 %), and PP (96 %), as weathering effects on microplastics fostered stronger interactions with flocs, altering their physical and chemical properties.	[132]
	Charge neutralization & Hydrolysis process	Polystyrene (PS) Polyethylene (PE)	Increasing PAC dosage enhanced MP removal by promoting coagulation into larger flocs, surpassing the effectiveness of $FeCl_3$ and exhibiting stronger charge neutralization, particularly in the PAC-PE system. The impact of hydrolysis products in both PS and PE systems outweighs that of the hydrolysis process itself, emphasizing their significant role in coagulation.	[223]
Electrocoagulation	Flocculation & charge neutralization at the same time	Two granular microplastics (polyethylene, PE; polymethylmethacrylate, PMMA) and two fibrous microplastics (cellulose acetate (CA) from cigarette butts; PP from disposable surgical masks)	Highly polymerized aluminum flocculant efficiently captures and sweeps MPs through netting, surpassing the removal capacity of iron flocs.	[139]
Bioretention system	Physical Filtration	Rubber, Bitumen and other microplastic	>70 % removal of rubber, bitumen, and microplastics in the 100–300 μm size fraction was achieved by the treatment train, with the filter cells playing a major role.	[91]
Biodegradation	Biodeterioration, Bio fragmentation, Assimilation, Agglomeration, Biosorption, and Mineralization	–	For low biodegradable microplastics such as PP, PE, PS, and PVC, pyrolysis is commonly used to break down these plastics into fatty alcohols and alkenes. For relatively low biodegradable microplastics like PET, surface-modifying enzymes and esterases such as cutinases, lipases, and PETases have been used to hydrolyze PET. Highly crystalline microplastics can be made bioavailable to microbes through sustained thermal hydrolysis, commonly found in industrial composting plants.	[231] [230]
AOP	Ozonation (Surface oxidation of polymer)	Polyethylene	Ozone-generated reactive oxygen species cause surface oxidation of PE microplastic particles in water, resulting in the formation of functional groups and crosslinking through Norrish type I reactions, enhancing their reactivity.	[237]
	Chlorination (Breakdown of C—C bond of main chain of polymer)	Polystyrene	Nano-sized polystyrene plastics demonstrate resistance to chlorination (4.2 % MW degradation and 3.0 % mineralization).	[238]
	Fenton Process (Two-stage degradation process involving chain stretching and oxidation, which resulted in the formation of carbonyl groups and decreased crystallinity of the microplastics).	Polyethylene	95.9 % weight loss in 16 h and 75.6 % mineralization efficiency in 12 h. The pivotal chain stretching stage significantly enhances subsequent chain cleavage and Fenton oxidation, optimizing the treatment efficacy.	[185]
	Photodegradation (ROS mediated photo transformation)	Polystyrene	ROS quenchers effectively inhibit ROS-mediated photoaging of PS-MP, preventing surface roughness increase and particle size decrease, demonstrating the pivotal role of ROS in PS-MP phototransformation.	[239]
	Photocatalytic degradation (Semiconductor material (N–TiO2) to produce electron-hole pairs that react with oxygen species to degrade microplastic)	High-density polyethylene (HDPE) and low-density polyethylene (LDPE)	Smaller MPs contributed to higher degradation, while film-shaped MPs yielded lower degradation due to suboptimal illumination and oxygenation of the reaction medium.	[240]
	Phoretic interaction and shovelling/ pushing interactions	Polystyrene	67 % of clearage efficiency. Enhance clearance efficiency by incorporating a small amount of peroxide. The shovelling interactions works efficiently independent of the fuel in dilute peroxide solution and water.	[218]
Phytoremediation	Translocation, absorption/adhesion	Polyethylene	The rapid adhesion of MP/NP to *Lemna minor* is likely attributed to the plant's surface stickiness and electrostatic interaction with the biomass, facilitating agglomeration on roots and fronds.	[235]
Adsorption	Electrostatic interaction between nanoplastic and metal organic framework	Polystyrene	A 96 % removal efficiency was achieved using the pseudo-first-order model, primarily driven by electrostatic interaction between PSNPs and Cr-MOF.	[146]

(*continued on next page*)

Table 4 (*continued*)

Technique	Major removal mechanism	Type of microplastics	Key notes	Ref.
	Physical adsorption and monolayer coverage	Polystyrene	Electrostatic attraction facilitates effective adsorption, with higher PS NP removal in acidic systems compared to alkaline systems.	[223]
Sorption	Electrostatic interaction and surface complexion and ion exchange	Polystyrene	Iron modified biochar @ 550 °C (FB-550) exhibited higher removal efficiency for 1000 nm amine, with a capacity of 290.20 mg/g. Significant variations in zeta potential indicated the likelihood of surface complexation processes occurring during sorption.	[225]
Adsorption to algal cells	Complexation/agglomeration behavior and cellular attachment and adsorption	Polystyrene	Adsorption of nanoparticles onto the cell wall of *P. subcapitata* was stronger for neutral and positively charged particles compared to negatively charged ones. Increase in water hardness leads to stronger attachment of PS-COOH particles to algal cells. This is because the charges on the particle surfaces and cell walls change, making them less likely to repel each other. Calcium ions can also help bridge the particles and cell walls together.	[241]

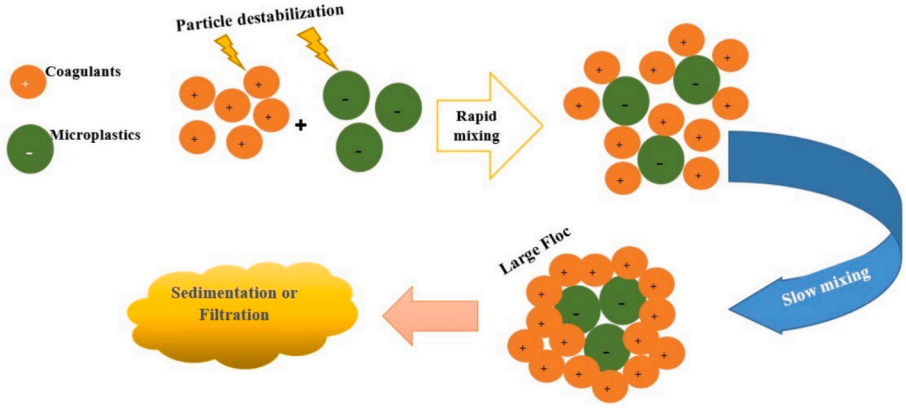

Fig. 7. Charge neutralization as the dominant mechanism involved in the abatement of MP. (Modified after Monira et al. [132].)

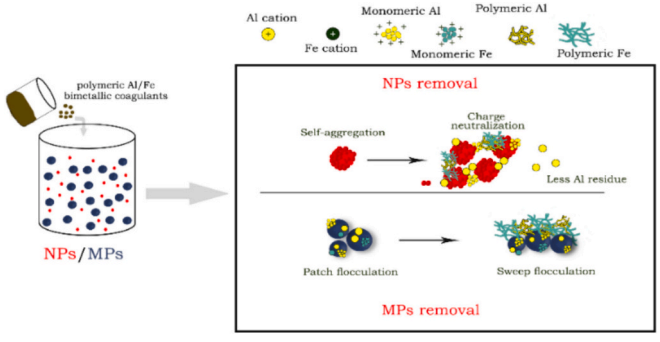

Fig. 8. MNP removal mechanisms using polymeric Al-Fe bimetallic coagulants. Modified after (Efficiency and mechanism of micro- and nano-plastic removal with polymeric Al-Fe bimetallic coagulants: Role of Fe addition).

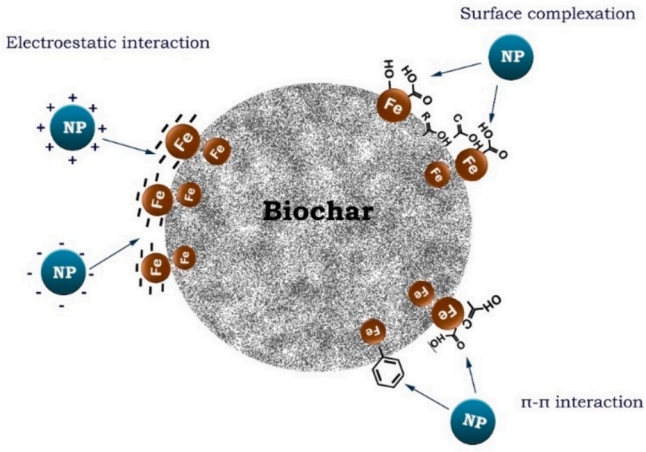

Fig. 9. Schematic of surface complexation and electrostatic attraction as the major removal mechanisms for NPs using iron-modified biochar. (Modified after Singh et al. [225].)

improved, leading to enhanced removal efficiency. In conventional DAF, MPs remained separate in the water, but the addition of surface modifiers, such as CTAB and PDADMAC, facilitated adhesion. CTAB increased the number of smaller-sized MBs and improved electrical attraction, resulting in the formation of small flocs consisting mainly of individual MPs. On the other hand, PDADMAC, with its long molecular chain and greater hydrophilicity, acted as a bridge between MPs and MBs, forming larger flocs and increasing the effective volume of modified MBs (Fig. 10). The study highlighted that adhesion, along with electrical attraction and other mechanisms, played a crucial role in the removal of MPs using modified DAF techniques.

Bioretention systems have been used to effectively remove MPs from

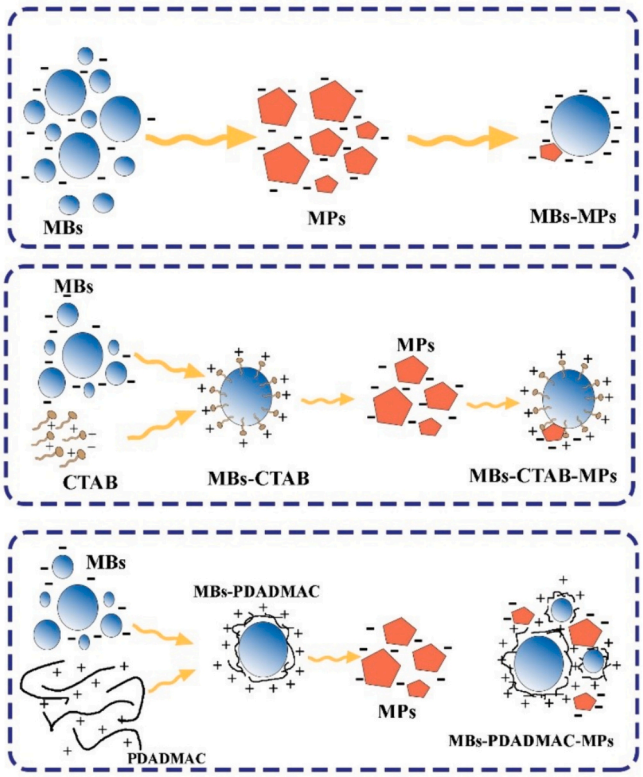

Fig. 10. Removal mechanism of MPs using modified dissolved air flotation by addition of surface modifiers namely CTAB and PDADMAC.
(Modified after Wang et al. [159].)

stormwater, with physical filtration being the most effective mechanism [105]. In comparison, gravitational settling is less effective due to the low sedimentation rates of MPs. While the vegetated biofilter and sand filter were efficient at removing MPs, the gross pollutant trap (GPT) was not effective due to the difficulty in removing these particles through gravity-based processes. The size of MPs can affect their retention, with MPs in the 100–300 μm size range being effectively retained by the bioretention systems. However, microfibers, due to their small widths, may have been underestimated in concentrations [91]. In addition, due to exposure to the sun and mechanical stress, there is a growing number of tiny particles in the environment, may have affected their correct sieved size ranges. The underdrain slot size of the bioretention cell can also affect particle retention, and the potential development of biofilm and sediment build-up on the underdrain slots can further reduce the entry point size for MPs and microfibers to the bioretention cell outlet [92].

Wang et al. [168] conducted an experimental study on using biochar in sand filter systems to enhance the removal of MPs in wastewater treatment plants. They observed MPs immobilization by three particle interaction modes: 'Stuck', 'Trapped', and 'Entangled'. Biochar acted as a sieve, retaining smaller particles in its porous structure. It could trap particles in honeycomb and loofah-like structures and entangle MPs. Additionally, MPs could become entangled with flaky biochar particles due to Van der Waals forces and electrostatic interactions. Biochar outperformed silica sand in immobilizing MPs, with C500 biochar showing the best performance. ESEM microscopy confirmed the three immobilization mechanisms in biochar but only 'Stuck' in sand filters (Fig. 11).

5.3. Hydrophobic interactions, sorption, and trap-release

Bioinspired molecules or biomaterials are engineered materials that

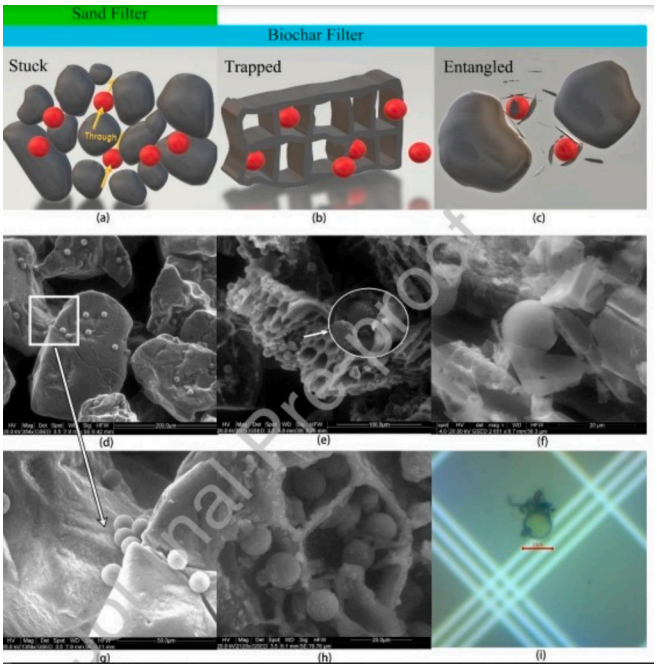

Fig. 11. Three ways in which microplastics can be immobilized: "Stuck" (a); "Trapped" (b); "Entangled" (c) corresponding ESEM images – sand filter (d, g); biochar filter (e, f, g) and optical microscope image (i).
(Reproduce with permission from [168].)

interact with living systems to control certain processes. They are particularly important in the removal of hydrophobic microplastic particles. Bioinspired molecules have advantages due to their combination of organic and inorganic building blocks. The organic unit acts as a spacer and reactive site, while the inorganic unit serves as a cross-linker. Functionalized hybrid materials that incorporate both organic and inorganic elements possess unique characteristics. The concept for removing hydrophobic pollutants involves three synthesis steps: creating an inclusion unit (IU) which serve as bioinspired component, a capture unit (CU) with preorganization and target bonding ability, and combining them to form an inclusion compound (IC) (Fig. 12) [217]. This compound is then used to trap hydrophobic MPs, which can be easily separated and isolated using a cost-effective method like a sand trap. The complexation of hydrophobic pollutants is driven by hydrophobic and van der Waals interactions, with water displacement and

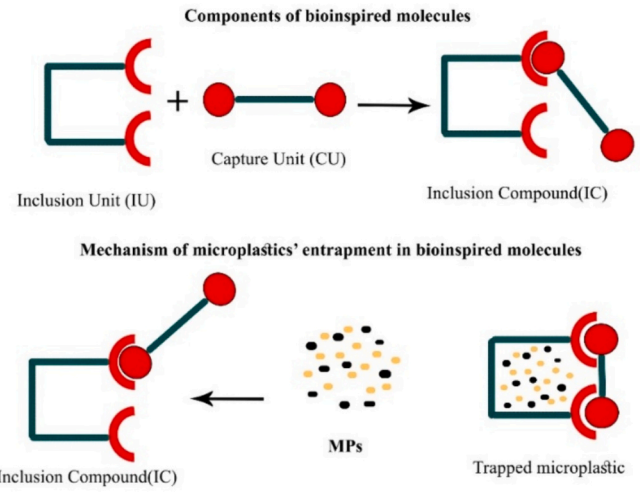

Fig. 12. Mechanism of microplastics' entrapment with bioinspired molecules.
(Modified after [217].)

formation of new hydrogen bonds playing a role [226,227].

Biofilm degradation of MPs is a four-stage process. In the first stage the microorganisms (bacteria, fungi, prokaryotes) aggregate on the microplastic surface, altering its properties. In the second stage, additives and monomers are leached from the MPs. The third stage involves biologically derived enzymes or free radicals attacking the MPs and their additives, resulting in embrittlement and loss of mechanical stability. The fourth stage is characterized by water penetration and microbial filaments entering the polymer matrix, leading to MP degradation by microorganisms. The second stage is considered critical as additives hinder the degradation of MPs until they are leached [228]. The core mechanisms involved in the removal of MPs/NPs through biofilm includes electrostatic surface adsorption, hydrophobic interaction, sorption onto the biofilm layer, intermolecular repulsion, and electrostatic interplay between MPs/NPs and the membrane surface [170]. Liu et al. [199] have developed a remarkable bacterial biofilm with a "trap-release mechanism" to tackle microplastic pollution. The biofilm, using exopolymeric substances (EPS) and controlled by the signaling molecule *c*-di-GMP, efficiently aggregates microplastics for easy removal. By reducing *c*-di-GMP levels, the biofilm disperses and releases trapped microplastics. The engineered strain shows increased microplastic accumulation and can aggregate low-density microplastics, aiding their sinking and removal in bioreactors. Additionally, the biofilm incorporates a release mechanism that activates enzymatic activity to degrade the biofilm matrix and release microplastics for convenient recovery. This innovative approach holds promise for effectively accumulating and separating microplastics for their subsequent removal.

5.4. Translocation, absorption, and adhesion

Microorganisms play a crucial role in degrading MPs through several steps, including biodeterioration, bio-fragmentation, assimilation, and mineralization, with enzymatic activity being a significant factor [229,230]. Microbial enzymes like esterases, lipases, and peroxides aid in the hydrophilicity enhancement of MPs, and environmental conditions like temperature, pH, salinity, and oxygen level, as well as abiotic factors like UV radiation and photo-oxidation, can influence the rate and efficiency of biodegradation [231]. The end products of plastic degradation are CO_2, H_2O, and CH_4, which can serve as carbon and energy sources for microorganisms, making them suitable for bioremediation purposes [232]. Stormwater ponds, including detention and retention ponds, are effective in removing MPs by allowing them to settle in sediments, which act as a sink for MPs [96,105]. Wetlands, on the other hand, offer the added benefit of vegetation, which helps remove pollutants through ecological interactions [105].

Phytoremediation using hyperaccumulator plants is an environmentally friendly technology that can be employed for the removal of MNPs. In wetland systems, both emergent and submerged macrophytes have been shown to be effective in settling NPs due to their unique morphological characteristics that reduce flow velocity or turbulence, facilitating nanoparticle remediation [233]. Removal mechanisms of MNPs by these plants include translocation, absorption, and adhesion to their surface [234]. Recent studies have shown that aquatic plants, such as the floating macrophyte *Lemna minor*, can rapidly adhere to polyethylene MPs in aquatic environments due to the surface stickiness of the plant. The electrostatic interaction between MNPs and plant biomass may also contribute to their agglomeration on plant surfaces [235]. Similarly, *Fucus vesiculosus* has been shown to trap fluorescent PS MPs, reducing their bioavailability in marine environments [236].

6. Conclusion and future directions

With the increase in plastic production and consumption worldwide, pollution caused by MNPs is having negative impacts on human health, the environment, and ecosystems. It is crucial to have a fundamental understanding of treatment methods to eliminate MNPs from various environmental sources. This article provides a comprehensive overview of detection, measurement, pathway, various treatment technologies to remove MNPs in stormwater. In the same vein, the following challenges and recommendations must be addressed for future studies:

- One significant challenge lies in the inadequacy of conventional stormwater treatment methods, such as bioretention filters and constructed wetlands, in effectively removing MNPs. Addressing this gap requires the exploration of emerging approaches like photocatalytic, electrocatalytic, and photoelectrocatalytic degradation using nanomaterials to enhance MNPs removal efficiency.
- Macroinvertebrates such as bristle worms, snails, beetle larvae, and other species commonly found in constructed wetlands exhibit a tendency to ingest microplastics (MPs), suggesting their potential contribution to the dispersion of MPs within these aquatic habitats.
- Rapid sand filters (RSFs) are better at removing particles larger than 10 μm compared to granular activated carbon. On the other hand, modified filters have shown improved performance in removing MPs compared to RSFs, the effectiveness of innovative filters, such as those using surfactant-modified aluminosilicate filter media, should be tested for their ability to remove NPs from stormwater.
- Membrane as a potential treatment method for MNPs suffers from fouling that reduces flux as well as life span of membrane. Although it is a significant limitation of membrane application, it is important to note that MNPs can be removed through adsorption onto the fouling layer. Therefore, the positive and negative effects of fouling need to be assessed.
- Effective methods for high degradation of polyvinyl chloride (PVC) have been observed through the simultaneous oxidation of hydroxyl radicals (•OH) and cathodic dechlorination using integrated Fenton reaction-based techniques, such as electro-Fenton technology with a TiO_2/graphite cathode. Such efficient combined processes could also be investigated for the removal of NPs from stormwater.
- The core mechanisms involved in the removal of MPs/NPs through biofilm includes electrostatic surface adsorption, hydrophobic interaction, sorption onto the biofilm layer, intermolecular repulsion, and electrostatic interplay between MPs/NPs and the membrane surface.
- Most research has focused on microplastics, while very few studies have investigated nanoplastics. This lack of research is primarily due to the challenges of sampling and analyzing environmental nanoplastics, therefore it should be considered in future studies.
- It is challenging to achieve a high level of MNPs removal with just a single treatment method. To overcome this challenge, integrated treatment systems can be utilized to effectively remove MNPs by addressing the limitations of individual technologies.
- Most laboratory studies on MNPs have concentrated on their concentration in water bodies and various treatment strategies, rather than on their toxic impacts. Therefore, more studies on environmentally relevant concentrations of MNPs are required to better understand their potential toxicity effects on organisms and humans.

CRediT authorship contribution statement

Milad Mousazadehgavan: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Resources, Project administration, Methodology, Funding acquisition, Data curation, Conceptualization. **Sara Khademi:** Writing – review & editing, Writing – original draft, Methodology, Data curation. **Alireza Motovalibashi Naeini:** Software, Writing – original draft, Formal analysis, Writing – review & editing. **Icen Yoosefdoost:** Writing – review & editing, Writing – original draft, Investigation. **Vishakha Vashisht:** Writing – original draft, Data curation. **Marjan Hashemi:** Writing – original draft, Methodology. **Massoumeh Manouchehri:** Writing – original draft, Investigation. **Khalid Hashim:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors declare that the data supporting the findings of this study are available within the manuscript.

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