Jordanian Journal of Engineering and Chemical Industries

Print ISSN: 2616 - 9584 Online ISSN: 2617 - 720X

Removal of Micro/Nano-Plastics from Water by Flotation Technology: A Review

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Abstract

Microplastics (MPs) and nanoplastics (NPs) are brand-new types of persistent contaminants that have lately emerged in the ecosystems owing to the extensive use of plastic items in our daily lives. It has been recognized that these contaminants have many hazardous implications on the environment and on the human health. This has set off alarm bells worldwide to find effective solutions in order to reduce the discharge of MPs and NPs into the environment. Flotation technology is a promising solution to reduce the contents of MPs/NPs in wastewater streams prior to their discharge into the surface water. This review summarizes the risks of MPs and NPs to human health and ecosystems and describes the principles of flotation technology. Furthermore, advances in flotation technology to improve the removal efficiency of MPs and NPs from water are reviewed. Current challenges and future remarks on the flotation technology in removing MPs/NPs from water are also highlighted

Paper type: Research paper

Keywords: Microplastics, nanoplastics, flotation, water treatment.

Citation: Eskhan, A.,“ Removal of Micro/Nano-Plastics from Water by Flotation Technology: A Review”, Jordanian Journal of Engineering and Chemical Industries,Vol. 8, No.1, pp: 60-73 (2025).

1. Introduction

Plastic materials have venously emerged into our daily life replacing most of the materials that were in use and exhibiting intriguing properties in various applications. This has raised concerns pertaining to their potential harm to humans and nature. Once plastic is in the environment, it can take 100 to 1000 years or more to decompose, based on environmental conditions (EPA.gov). Plastics can potentially undergo fragmentation processes due to various environmental factors such as UV radiation, pH, salinity and temperature. These processes will produce small pieces of plastics called microplastics (MPs), and even much smaller pieces known as nanopalstics (NPs) (Dimassi *et al.* , 2022). The MPs and NPs are prevalent in the environment and can easily enter the food chain creating risks to human health (Yee, Hii et al. 2021). MPs and NPs have been recognized mainly as marine pollutants with hundreds of thousands of metric tons estimated to be floating in marine ecosystems.

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Received 18 Dec 2024
Revised: 18 Feb 2025
Accepted 1 Mar 2025.

Jordanian Journal of Engineering and Chemical Industries (JJECI), Vol.8, No.1, 2025, pp: 60-73

However, recent studies have also revealed that MPs and NPs permeate freshwater bodies and various terrestrial environments (Amobonye *et al.* 2021). In addition, daily human activities such as laundry processes and personal care products have been found to be major sources of MPs and NPs that enter wastewater streams through domestic discharge (Talukdar *et al.* 2024). Therefore, removing MPs and NPs from water and/or wastewater has been an active research field over the past few years.

Numerous water remediation methods have been applied for the removal of MPs and NPs from water. Examples of these methods encompass adsorption, coagulation, flotation, membrane separation, magnetic separation, biodegradation and oxidation. Some studies have compared the performance of diverse treatment units in the removal of MPs. For instance, one study investigated the performance of three different methods in a drinking water treatment plant and found that 57.8 % of MPs were separated by a powdered activated carbon adsorption unit, 48.3 % by a multimedia filter, while 49.3 % of MPs were removed by a coagulation, flocculation, followed by a sedimentation unit (Al Omari *et al.* 2024). Although water treatment methods such as adsorption and magnetic separation are efficient, they produce secondary pollutants that need further treatment (Gao *et al.* 2022). Similarly, biodegradation suffers from low efficiency (Gao *et al.* 2022) and often takes a long time (Khoiriyah *et al.* 2024). Coagulation process requires a large consumption of reagents, which increases cost and environmental concerns (Pawak *et al.* 2023). In addition, although membrane separation processes are promising, the tendency of membranes to foul makes their replacement inevitable and limits their widespread use. Furthermore, membranes can only retain MPs and NPs that are larger than their pores. Unlike these methods, the flotation process only produces collapsible foams containing the target MPs and NPs. Other advantages of the flotation technique include high selectivity to pollutants, low operating costs, high pollutant removal efficiency and reduced detention time (Rubio *et al.* 2002).

In this review, the particular use of flotation technology in the removal of MPs/NPs from water is reviewed. The various definitions given for MPs and NPs in the literature are summarized. The environmental and health effects of MPs and NPs are briefly described, highlighting the urgent need to find effective solutions to address this environmental issue. Flotation technology and its applications in water and wastewater treatment processes are outlined. Moreover, the main strategies adopted in flotation technology to improve the removal efficiency of MPs and NPs from water are discussed. The challenges and future trends of flotation technology in removing MPs/NPs from water are also remarked.

2. What are MPs and NPs?

The development of the first totally synthetic plastic, Bakelite, in 1907 had revolutionized the polymers and plastics industry through introducing various types of polymers and plastics into our daily life (Olatunji 2024). The polymer and plastic materials are proven to be superior to other materials as a result of their low cost, lightweight, low electrical and thermal conductivity, transparency, resilience, ease of processing, durability and resistance to corrosion (Shrivastava 2018). These factors contributed to their widespread distribution in a broad range of applications from food packaging to medical and technical applications. However, over the years these materials have raised global environmental concerns due to their prevalence in marine and freshwater ecosystems. The natural environmental conditions within these systems, especially ocean wave dynamics, solar radiation, erosion and interactions with ship vessels and organisms, cause plastic products to gradually degrade and fragment into plastic debris commonly known as MPs, a new type of contaminants in water (Frias *et al.* 2019). Numerous definitions have been given to the term “microplastic” (Frias *et al.* 2019) along the years by researchers, with a recent one introduced by GESAMP, which stands for the Group of Experts on the Scientific Aspects of Marine Environmental Protection, who defined MPs as: 'plastic particles that are less than 5 mm in diameter, which include particles in the nano-size range (1 nm)' (GESAMP 2015, GESAMP 2016). Other researchers have subdivided the materials in this range to MPs (>100 nm and < 5 mm) and NPs (< 100 nm) (Nguyen *et al.* 2019, Dimassi *et al.* 2022). While this terminology is still under debate in the literature, some researchers have adopted a size limit of 1 micron to differentiate between MPs and NPs (Hartmann *et al.* 2019), based on their colloidal behavior such as high aggregation tendency owing to their high surface-to-volume ratio, Brownian motion and the ability to penetrate cell membranes (George *et al.* 2021).

MPs are usually classified according to their source of origin into primary MPs and secondary MPs (Auta *et al.* 2017). The primary MPs are microplastics that are fabricated for certain industrial or domestic applications to be of a microscopic size. They include plastic particles used in facial cleansers, toothpaste, cosmetics like shower gels, deodorant, make-up foundation, mascara, shaving cream, baby products, bubble bath lotions, hair coloring, nail polish, insect repellents and sunscreen, others include synthetic clothing, abrasives found in cleaning products, drilling fluids, and air-blasting media. The secondary MPs, in comparison, are the smaller particles that arise from the fragmentation of larger plastic debris over time when they are subjected to a combination of physical, chemical and biological processes reducing their structural integrity until they end up as MPs (Auta *et al.* 2017).

MPs and NPs are of various origins and transport through different routes in the environment. Thereby, MPs exist in different shapes such as films, spheres, fibers and foams (Yuan *et al.* 2022). Most manufactured plastics are made from petroleum-derived products, including low/high-density polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), polystyrene (PS), and polyvinyl chloride (PVC), etc. (Hu *et al.* 2022). Annually, more than eight million tons of plastics emerge into the oceans, and over 60% of floating debris in the surface waters was found to be plastics in 2015. It has been reported that PE represents the largest proportion (23%) of all available plastics in marine environments, followed by polyester, polyamide and acrylic (PP&A) (20%), PP (13%) and PS (4%) (Hu *et al.* 2022). In addition, MPs have been detected in rivers, lakes, groundwater, tap water, and wastewater. The main polymer components of MPs in freshwater have been specified as PE, PP, PS, and PET, constituting 70% of the total (Li *et al.* 2020). The major source of MPs in freshwater systems are effluents from wastewater treatment plants (WWTPs). Most of MPs from the influents are separated and retained in sludge, which is usually reused as land fillers and in land-based applications resulting in the transmission of MPs across the environmental systems (Hu *et al.* 2022). For instance, a significant source of primary MPs in terrestrial environments is sewage sludge from WWTPs that contain synthetic fibers or sedimented MPs from personal care or household products (Horton *et al.* 2017). Additionally, the presence of MPs and NPs in the sewage sludge, which mainly consists of solid wastes separated from wastewater through sedimentation, has an adverse effect on the anaerobic digestion of sludge as MPs are great carriers of poisonous substances such as antibiotics and organic contaminants. Thus, it negatively impacts methane production (Zhang *et al.* 2020).

3. Environmental and health impacts of MPs and NPs

The environmental impacts of MPs and NPs can be classified into physical, chemical and biological impacts (Li *et al.* 2018). The physical impacts mainly include entanglement and ingestion. After ingestion, the chemical and biological impacts can be seen in toxicity transfer to humans and living organisms through numerous pathways and mechanisms. MPs serve as carriers of different toxins such as additives used in the production of plastics or calcitrant pollutants via sorption processes in water (Li *et al.* 2018). Moreover, MPs have demonstrated the ability to attach to aquatic organisms. However, the ecotoxicological effects are not yet fully understood (Kalčíková 2023).

The hazard assessment of MPs has shown that their risk is linked to three primary factors: (a) exposure pathways, including seawater (surface water and water column), sediment and air, (b) the exposure levels to MPs, and (c) the potential hazard of MPs (physical, biological, and chemical toxicity) (Yuan *et al.* 2022). The primary route of human exposure to MPs has been specified as ingestion (via contaminated drinking water or accumulation in the food chain), inhalation, and dermal penetration (Sun *et al.* 2023). Small plastic particles (< 150 μm) can be ingested by organisms, travel through the intestinal wall and reach lymph nodes and other organs. It can be absorbed by biota tissues, organs, and even cells, leading to negative effects on human health. MPs may pose several toxicity concerns, including acute and chronic toxicity, carcinogenicity, and developmental toxicity. In addition, NPs resulted from the breakdown of large plastics may cause chronic toxicity, genotoxicity, and developmental toxicity (Yuan *et al.* 2022). MPs also provoke oxidative stress, perturb metabolism, interfere with gut microflora and gastrointestinal functions, increase the risk of cancer, cause liver toxicity, disrupt immune systems, and deteriorate reproductive health (Mamun *et al.* 2023, Tang *et al.* 2024).

4. Flotation as a technology in water and wastewater treatment

Flotation is a complicated process that incorporates fundamental hydrodynamics with many primary physicochemical steps (bubble-particle interaction forces, particle-particle interaction forces, etc.) (Peleka *et al.* 2016). The process of flotation comprises four main steps: generation of bubbles, contact between the gas bubble and the contaminant of interest (particle, oil droplet, metal ion, etc.) that is dissolved/suspended in water, attachment of the contaminant of interest to the bubble, and lifting of the bubble/contaminant of interest combination to the surface where the floated materials are skimmed off. The flotation technology relies on the differential density between the bubbles to which the contaminants (such as small solid particles or oil droplets) attach and the water (Shammas *et al.* 2010). Flotation technology initially began in the field of mineral ores processing and as such has long been used in solid/solid separation applications utilizing stable froths to selectively separate various minerals from each other. Years later, applications of flotation in wastewater and domestic sewage treatment have evolved (Rubio *et al.* 2002).

Flotation technology has been extensively used for the separation and concentration of aqueous suspensions of various minerals, coal, precipitates, inorganic wastes, and even microorganisms and proteins. Plastics flotation has also been developed to separate plastics from solid wastes or to separate plastic waste particles from mixtures utilizing the differences in the surface energy of different plastics or through selective hydrophobization or hydrophilization of plastic surfaces via chemical reagents and physical processing such as plasma treatment, microwave treatment or gamma flotation (Nguyen 2007, Wang *et al.* 2019). For example, the authors in one study modified plastics with sodium hydroxide and dibutyl sebacate (DBS) which is used as a wetting agent to separate PET from four kinds of mixed plastic packaging wastes for recycling purpose (Guo *et al.* 2016). Flotation technology has been highlighted to be a promising method when compared to other water and wastewater treatment technologies. In one study, when dissolved air flotation (DAF) and direct filtration were compared, similar removal percentages of total organic carbon (TOC), disinfection by products (DBP) precursors, and iron and manganese were obtained for both processes. In a second study, the authors investigated the removal of MPs from effluents using different advanced final-stage treatment technologies. The study included membrane bioreactor (MBR) that treats primary effluent as well as other different tertiary treatment technologies (discfilter, rapid sand filtration and DAF) that treat secondary effluent. Their results revealed that the MBR removed 99.9% of MPs in the treatment, rapid sand filter removed 97%, DAF removed 95% and discfilter removed 40-98.5% of the MPs during the treatment (Ferguson *et al.* 1995).

Various flotation technologies have been developed over the years depending on the method used to produce the gas bubbles (usually air) including electrolytic flotation/electroflotation (EF), induced or dispersed air flotation (IAF), DAF, and colloidal gas aphrons-based flotation (CGA) (Prakash *et al.* 2018). In the EF technology, the basis of microbubble's generation is the electrolysis of conducting aqueous solutions while simultaneously producing gas bubbles (hydrogen and oxygen) at both electrodes **Figure 1.** Applications of this technology include the separation of light colloidal systems such as emulsified oil, ions, dyes and fibers from water. The bubble size produced in the EF technology is in the range of 15-80 µm (Prakash *et al.* 2018) Since bubble generation in EF does not cause turbulence, this technology is also promising for the separation of fragile flocs (Nguyen 2007).

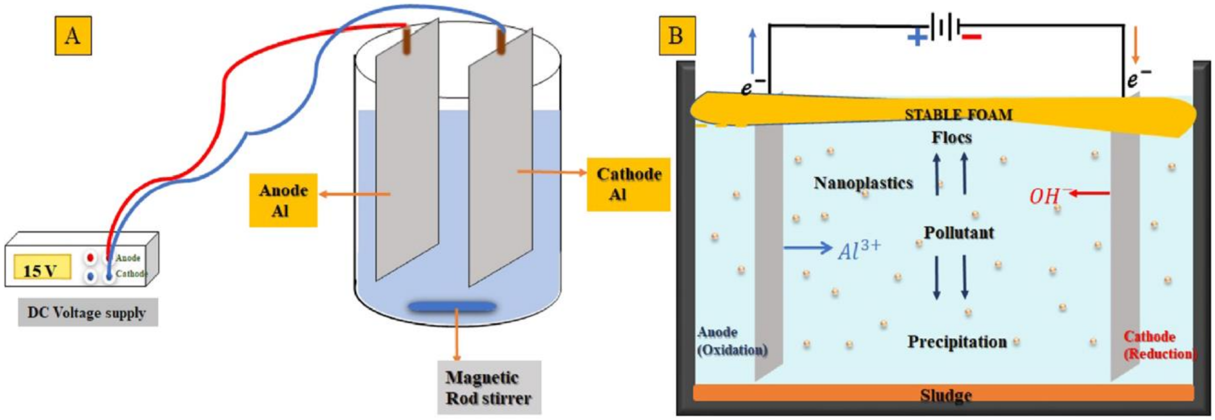

Fig. 1. Schematic diagram of an EF flotation unit: a) experimental setup, b) removal mechanism of NPs by the EF process. Reprinted with permission from (Pawak *et al.* 2023).

In comparison, in the IAF technology, bubbles are formed mechanically by coupling a high-speed mechanical agitator with an air injection system. The introduced gas and the liquid are completely mixed and then passed through a disperser outside the impeller, after which bubbles with a diameter range of 700-1500 µm are formed. The IAF is mainly used in the mineral processing field. It is also employed in the petrochemical industry to separate oil from water (Zouboulis, Matis et al. 1992, Rubio, Souza et al. 2002). On the other hand, in the DAF technology **Figure 2**) the water is supersaturated with air at pressures higher than the atmospheric pressure. The supersaturated water is then pumped through needle-valves or special orifices producing tiny bubbles (microbubbles) with diameter in the range of 20-100 µm (Edzwald 2010). The DAF technology mainly (Hubbe *et al.* 2016).

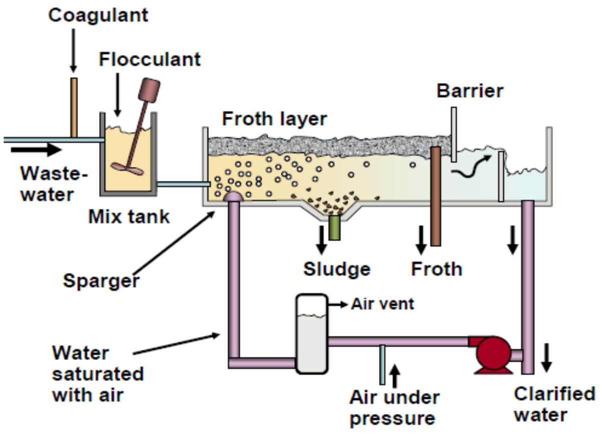

Fig. 2. A schematic diagram of a dissolved air flotation (DAF) unit. Reprinted with permission from (Hubbe et al. 2016).

finds applications in water and wastewater treatment (Zouboulis, Matis et al. 1992). It can be used to separate different contaminants from water such as particles, droplets or microorganisms in the size range of 10 to 100 µm (Prakash, Majumder et al. 2018).

Finally, in the CGA technology, CGAs are used, which are dispersions of gases in liquids generated using a venturi generator that introduces a gas into a surfactant solution that circulates in a high velocity, and low pressure region (Rubio, Souza et al. 2002). The CGAs are gas bubbles surrounded by thin multiple soapy shells (**Figure 3**) (Sebba 1985). They have a large interfacial area and a high stability so that they can be moved by a pump like water without breaking down. They also have the same charge as the surfactants used to produce them. The CGA flotation technology can produce extremely stable microbubbles (10-100 µm) using a stirrer which rotates at around 8000 rpm. The CGA technology can be used to separate fine particles with a diameter range of 4-20 µm (Prakash, Majumder et al. 2018)

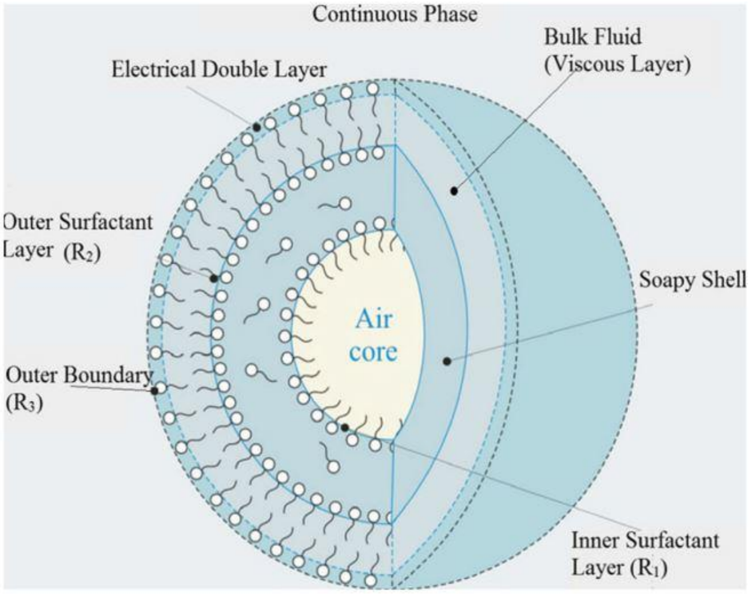

Fig. 3. Schematic of a colloidal gas aphron (CGA). Reprinted with permission from (Sebba 1985).

Froth flotation is also a term that is commonly encountered in literature. It is a commonly used process in the mineral processing industry where particles of interest are separated from the liquid phase based on their hydrophobicity. Whilst hydrophobic particles adhere to air bubbles and move to the surface to form a froth that can be scraped off, hydrophilic ones stay in the liquid phase (Crawford and Quinn 2017). Froth flotation is also applied for the selective separation of target plastics from plastic waste mixtures either by flotation or by sinking (Kökkılıç, Mohammadi-Jam et al. 2022). Although the term froth flotation is typically used for applications of selective separation of certain types of plastic particles from solid mixtures, it has sometimes been used interchangeably to refer to the conventional flotation process used in water treatment.

A variety of surfactant types are used in the flotation process. Collectors, for example, are used to increase the hydrophobicity of the particles to promote their flotation. Depressants reduce the hydrophobicity of impurities to prevent their flotation. In contrast, frothers are preferentially adsorbed at the gas-liquid interface in order to increase froth stability which is a critical factor for increasing materials recovery by flotation (Pawliszak, Bradshaw-Hajek et al. 2024).

5. Removal of MPs from water by flotation

Various technologies have been applied to remove the harmful MPs from water (Gao *et al.* 2022, Alrbaihat *et al.* 2023) including magnetic separation (Shi *et al.* 2022), adsorption (Sun *et al.* 2021), membrane filtration (Pizzichetti *et al.* 2021), catalytic degradation (Uheida *et al.* 2021), coagulation (Gao *et al.* 2023), and bioremediation (Tang *et al.* 2022). Flotation is another technology that has demonstrated an excellent potential in MPs removal from water (Zhang *et al.* 2021, Ahmed *et al.* 2024). It is utilized as one of the general steps in the primary treatment stage of wastewater. In some purification plants, flotation is implemented after primary sedimentation process (Zhang *et al.* 2020). However, there may be differences between different treatment plants based on the specific purpose. The density of plastics usually ranges between 0.83-1.58 g/cm3. Thus, 'flotation' as a density-based approach, has a great potential in the separation of plastic materials. This is because the flocs that contain trapped gas bubbles have a lower bulk density than that of water and hence can be skimmed off from the solution surface as they float (Zhang *et al.* 2021). The factors that determine the average density of the bubble-particle aggregate include the size distribution of bubbles, the surface fraction of the particle covered with bubbles, the density and size of the particle as well as the surface area of the particle (Wang *et al.* 2015). Other studies combined between flotation and other separation methods. For example, the authors in one study designed a mini-hydrocyclone to separate MPs from water through injected microbubbles. The authors attributed this air flotation-induced increase in the hydrocyclone efficiency, which ranged from 5 % to 15 %, mainly to the lower density of MPs-bubble agglomerates (Yuan *et al.* 2022).

Previous studies have demonstrated that the overall MPs removal efficiencies of WWTPs without using tertiary treatment were above 88% while increased to over 97% with tertiary treatment (Sun *et al.* 2019). The primary treatment plays the major role in removing MPs (Zhang *et al.* 2020). Comparatively, secondary treatment which is typically comprised of biological treatment is not expected to eliminate MPs due to their low biodegradability. However, the extracellular polymer substances (EPS) secreted by microorganisms can catch the MPs. In addition, sludge can act as a mesh to capture the MPs in the water when it is present in high concentrations (Zhang *et al.* 2020). Obviously, MPs larger than 300 μm can easily be removed by WWTPs processes. However, MPs smaller than 300 μm including the NPs will be of particular concern to the surface water bodies which receive the treated water from WWTPs (Pramanik *et al.* 2021). The following sections overview the main sustainable strategies that have been implemented in flotation technologies to enhance the removal percentage of MPs and NPs from water.

5.1. Modifying microbubbles/MPs to enhance the flotation efficiency

The selectivity of the flotation process is based on surface forces. According to the extended Derjaguin-Landau-Verwey-Overbeek (XDLVO) theory, the interaction forces between bubbles and particles in water can be described as a summation of electrical double layer forces, van der Waals forces and hydrophobic forces (Yoon *et al.* 1996, De Somer *et al.* 2024). In general, air gas bubbles in distilled water and in aqueous solutions are negatively charged (Han *et al.* 1998, Bueno-Tokunaga *et al.* 2015). However, the gas bubbles can be conditioned using surfactants. Conditioning with strong electrolyte surfactants will modify the charge of the bubble making it positively charged in the presence of a cationic surfactant while keeping it negatively charged in the presence of an anionic surfactant (Laskowski *et al.* 1989). In conventional flotation, oppositely charged particles and bubbles attract each other forming bubble-particle aggregates, which is a prerequisite for flotation. However, the particles should be hydrophobic enough to tear the wetting films between the particles and bubbles creating three-phase contact lines. Otherwise, the particles, especially the large ones, can be easily detached from the bubble surface (Yoon 2000, Waters *et al.* 2008). The inherent hydrophobicity of MPs/NPs and the interplaying attractive hydrophobic forces between gas bubbles and MPs would facilitate their attachment to the inherently hydrophobic air bubbles (Gochin *et al.* 1983). To additionally improve the collection efficiency of gas bubbles, modifications of the surface properties of microbubbles and/or MPs have been shown to be of paramount importance as they can alter their hydrophobicity and electrostatic forces. For instance, modification of microbubbles with a positively charged surfactant (CTAB-modified Posi-DAF) resulted in attractive electrostatic forces and improved the removal of MPs compared to unmodified microbubbles (Wang *et al.* 2021). Another study proposed a mechanism depending on electrostatic force-induced aggregation and flotation to reduce MP pollution in rivers (Feilin *et al.* 2022). The air used as a flotation carrier was first ionized, and then dispersed into a circumfluent reactor after the electrons were offset. Their experimental results showed that the process occurred rapidly in 2 min with a maximum removal efficiency (particle number based) of over 90% for the four samples (PE, PS, PVC and fiber mixture from the fiber washing machine) (Feilin *et al.* 2022). The authors highlighted the advantages of this process which included short hydraulic retention time, high removal efficiency, no need to add chemicals and robustness to polymer types. In another study the authors have generated CGAs using an eco-friendly natural surfactant solution and used it to remove MPs such as PET, PS, PP and PE from real water matrix i.e. deionized water, seawater, river water, wastewater and leachate (Priyanka *et al.* 2022). Furthermore, the repulsive electrostatic forces between MPs and microbubbles can be minimized by changing their surface charges. This can be made possible by altering the solution pH and/or solution chemistry or ionic strength. Manipulation of solution pH (zeta potential of particles) to minimize the particles' surface charge and thus minimize the repulsion with the negatively charged bubbles (Waters *et al.* 2008), or by reducing the solution pH of particles below their point of zero charge (Lu *et al.* 2018).

In real life, MPs are prone to natural environments, forming aged MPs, giving rise to their increased hydrophilicity that most likely stems from surface oxidation and accumulation or deposition of aqueous species such as humic substances and clay minerals on MPs (Jiang *et al.* 2022, Jiang *et al.* 2023). Therefore, the addition of surfactants might become essential to restore MPs' hydrophobicity and enhance the flotation efficiency. For example, a study has shown that modification of aged MPs with an anionic surfactant (NaOL) exhibited a higher flotation removal efficiency than modification with the cationic dodecyl trimethyl ammonium chloride (DTAC) due to the better enhanced hydrophobicity of MPs (Jiang *et al.* 2023). Another study has used microbubble flotation to remove MPs, specially microplastic fibers (MFs) that are released during laundry processes, as well as surfactants, which are major components of commercial detergents and common pollutants from laundry wastewater (LW) (Zhao *et al.* 2024). Their results demonstrated that under optimal conditions, more than 98 wt % of MPs/MFs and more than 95 wt % of surfactants were removed from LW. Other studies have used coagulant or flocculant-coated microbubbles to further improve the flotation performance of MPs. For instance, a study has used an ecofriendly EF flotation process without surfactants to remove polystyrene NPs (PSNPs) from synthetic wastewater. Under optimized conditions, nearly 95 % of PS NPs removal efficiency was achieved. The authors speculated that the suggested method is favored since a foam layer on the surface of the reactor is formed when NPs and coagulants are mixed, enabling removal by a simple scraping process (Pawak *et al.* 2023). In another study, the authors have used polyaluminum chloride (PACl)-modified CGAs (CCGAs) to remove MPs (~5 µm PS) from water in the presence of dissolved organic matter (DOM) (Zhang *et al.* 2021). A recent study has reported an enhanced removal of ~100 nm PSNPs using chitosan-modified air flotation from 3.1 % to 96.7 %. The authors demonstrated that the removal mechanisms of PSNPs included electrostatic attraction, improving hydrophobicity and bridging adsorption (Xu *et al.* 2024).

5.2. Reducing bubble size and/or increasing MPs size to enhance the flotation efficiency

A wide range of experimental studies have indicated that flotation of particles is a size-dependent process. In minerals flotation for example, a particle size range of 15-150 µm has been reported to work best, while recovery of fine and coarse particles outside that range has been shown to be problematic (Farrokhpay *et al.* 2021). The low flotation of coarse particles has been attributed to the detachment of particles from the bubbles under high turbulent conditions that increases as the hydrophobicity of the particle surface decreases (Jameson 2010, Farrokhpay *et al.* 2017). Conversely, lower flotation of fine particles is due to less collision between particles and bubbles as these particles follow the streamlines of the fluid around the rising bubbles because of their small inertial force and do not collide with the bubbles (Yoon *et al.* 1989, Farrokhpay *et al.* 2021).

The flotation process involves three critical steps or microprocesses: particle-bubble collision, attachment, and detachment. Particle-bubble collision models show that the probability of collision increases with increasing particle size and decreasing bubble size. For reviews of the collision models, please see (Dai *et al.* 2000, Tao 2005). Since the probability of fine particles colliding with bubbles is low, it is difficult for them to be captured by bubbles, especially large bubbles (Tao 2005). All of the collision efficiency or probability models have predicted that collision efficiency increases with particle size at a fixed bubble size. The flotation or collection efficiency, in the case of stable particle/bubble aggregate, is the product of collision efficiency and attachment efficiency.

Different attachment probability models have been also derived in the literature for particle recovery by flotation applications. A study has derived an expression for the attachment probability by measuring the time a particle takes to slide along the bubble surface after collision (Yoon *et al.* 1989). In their model, they assumed that the bubble-particle adhesion occurs when the sliding time is equal to or greater than the induction time **Figure 4** (see section 5.2), which differs according to the particle hydrophobicity. In their study, the attachment probability was found to be a function of particle size, bubble size and induction time. Their model and other models have indicated that attachment efficiency increases as particle size decreases and it also increases with decreasing bubble size until the bubble size becomes too small (Tao 2005). These opposing trends between collision efficiency and attachment efficiency as described above are the reason for the maximum plateau observed in flotation recovery with particle size, in agreement with experimental observations (Crawford *et al.* 1988). A typical recovery versus particle size curve is like the well-recognized elephant curve **Figure 5** that shows a maximum recovery in the middle and a decrease in flotation performance for fine and coarse particles (Farrokhpay *et al.* 2021). Some efforts have been made to expand the particle size range applicable to flotation (Kohmuench *et al.* 2018, Mankosa *et al.* 2018).

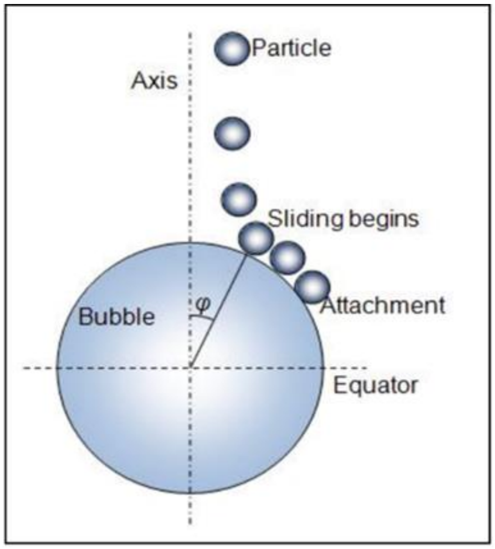

Fig. 4. A schematic representation of a particle sliding over a gas bubble surface. Reprinted with permission from (Verrelli *et al.* 2012).

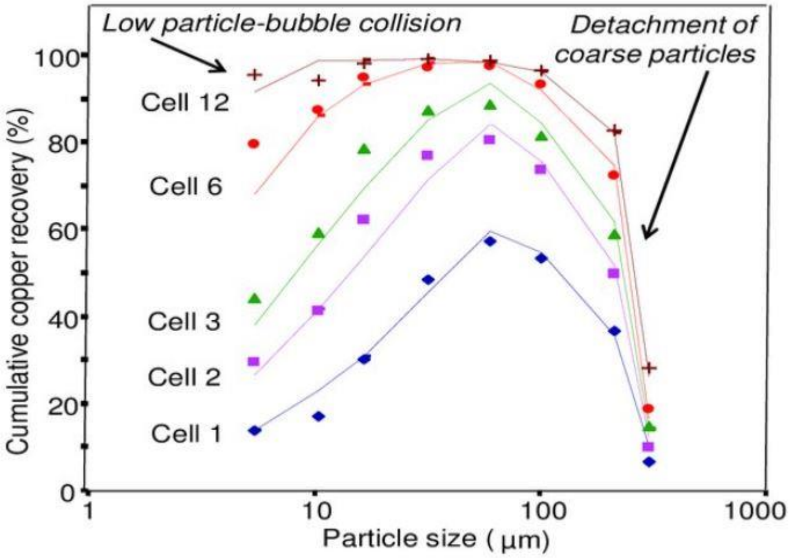

Fig. 5. A typical flotation recovery as a function of particle size. Reprinted with permission from (Ralston *et al.* 2007).

A more complex flotation of fine particles results from their larger surface area compared with coarse particles, consequently, they require more surfactants and reagents. They also tend to be more influenced by surface coatings, perhaps due to their large surface area, making them reactive and more influenced by the chemistry of the water and ions in the solution. In addition, fine particles increase foam stability (Farrokhpay, Filippov et al. 2021). To overcome the low flotation of fine particles, different strategies have been proposed in the literature based on increasing the particle size by selective aggregation, reducing the bubble size using nano- or picobubbles, or by using reactor-separator type flotation cells that foster stronger particle-bubble (Farrokhpay, Filippov et al. 2021)

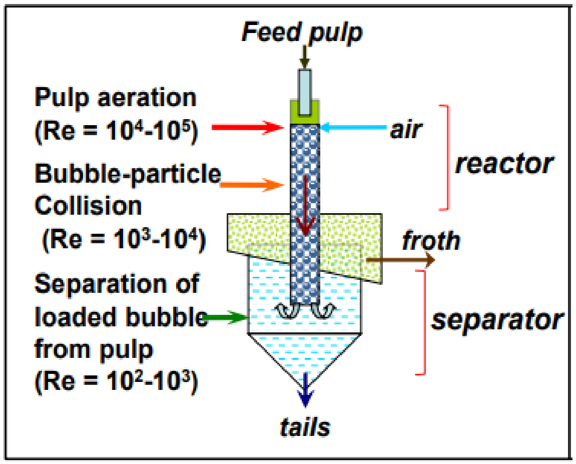

Fig. 6. A schematic diagram of a flotation cell of type reactor-separator. Re is the Reynolds number. Reprinted with permission from (Fornasiero and Filippov 2017).

Plastic materials are generally grouped into three subcategories depending on their particle size: macroplastics (> 5 mm), MPs (>100 nm and < 5 mm) and NPs (< 100 nm) (Nguyen, Claveau-Mallet et al. 2019, Dimassi, Hahladakis et al. 2022). MPs and NPs are considered the most harmful to humans and organisms, especially in marine environments (Dimassi, Hahladakis et al. 2022). MPs and NPs are also challenging to separate from water systems. NPs, in particular, remain dispersed in water systems for a long time due to the dominance of Brownian motion over sedimentation and buoyancy, making vertical transport of individual NPs small compared to MPs composed of the same material, which can lead to analytical difficulties and pose further limitations on density separation methods like flotation (Gigault, El Hadri et al. 2021, Chen, Shi et al. 2023). Therefore, flotation is usually considered to be incompatible with the ultrafine particles of plastics due to the low buoyancy force, and since surface fouling can significantly alter the ultrafine particle density (Nguyen, Claveau-Mallet et al. 2019). Another concern of plastic flotation particularly in recycling applications is the difficulty of recovering small particles from the air-liquid (foam) interface.

Clearly, plastics can be separated at much larger sizes compared with mineral ores due to their lower density (Wang, Wang et al. 2015). In other words, the maximum particle size capable of floating for plastics is larger than that for ores. The size of floatable plastic particles is normally one or two order of magnitude larger than that of the ore. There are a number of studies in the literature that have investigated the effect of particle size of MPs and/or NPs on the flotation efficiency. In one study, the authors have investigated the influence of particle size range on flotation (4-5 mm, 3-4 mm, 2-3 mm, 1-2 mm, 0.5-1 mm, 0.125-0.5 mm, 0.074-0.125 mm, and < 0.074 mm) and reported that large PS and PET particles resulted in increased flotation rate and higher flotation recovery compared to smaller sized particles at the same bubble density (Zhang, Jiang et al. 2021) **Figure 7**. In that study, an aeration device was used to generate carrier bubbles. The authors attributed the higher removal of PET MPs to its higher density, which results in higher collision and adhesion probabilities than PS MPs. In addition, the removal efficiency varied with the initial concentration of MPs where it was more difficult to remove MPs from more concentrated solutions than diluted ones. However, it is worth mentioning that studying the effect of particle size on flotation while fixing the bubble density, bubble size and the initial MPs/NPs concentration (e.g., in unit of g/L) will lead to comparisons between feed samples of different particle numbers that are dispersed in the solution. This would thus lead to different probabilities of collisions between bubbles and particles which depend also on the relative number of bubbles relative to the number of particles.

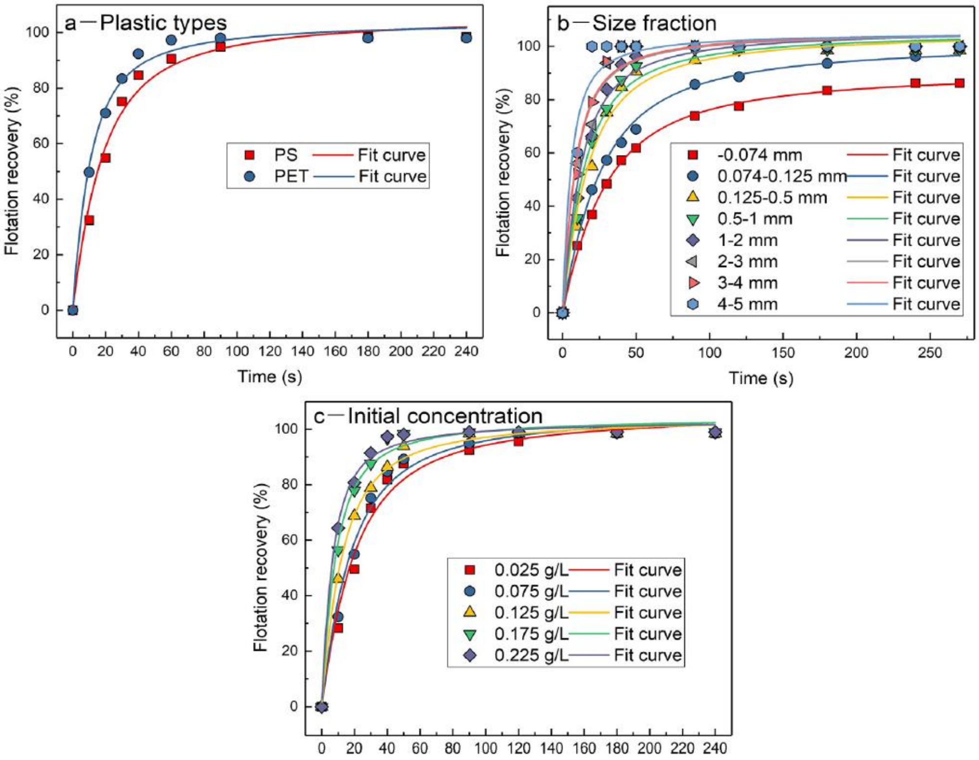

Fig. 7. The flotation removal of PS MPs with different plastic types (a), size fraction (b), and PS MPs initial concentration (c). Reprinted with permission from (Zhang *et al.* 2021).

In a second study, smaller particles (MPs/NPs) of the size of (1.88, 1.14 and 0.74 µm) were tested . The authors of that study found that larger particles had lower removal efficiency and attributed this to the greater weight of larger MPs, which need a larger amount of bubble carriers to float (Pramanik, Pramanik et al. 2021). In that study, air was bubbled into the flotation cell through a porous substance of pore size of 16-40 µm.

When a particle is attached to a bubble and a stable aggregate of the particle and bubble forms, lifting of the aggregate should follow to accomplish the flotation process (Tao 2005). The aggregate stability depends on factors such as reagents and particle geometry. As previously mentioned, the success of a flotation process not only depends on the aggregate stability, but other factors, such as induction time, collision probability and attachment probability, are also crucial (Warjito, Harinaldi et al. 2016). The induction time is defined as the minimum duration of close contact between the bubble and the particle in order to achieve attachment (Verrelli, Koh et al. 2012). During close contact between the particle and the bubble, the following events should occur: 1) thinning of the liquid film intervening between the particle and the bubble and its rupture after reaching a critical thickness, and 2) expansion of the three-phase contact line to form a wetting perimeter. The sum of these two events is the induction time, which must be less than the contact time for flotation to occur (Crawford and Ralston 1988). However, the second event takes negligible time compared to the first one. Therefore, the induction time mainly refers to the time required for the film thinning and drainage process, which is measured by the hydrodynamics of the system (Yoon and Luttrell 1989). If a particle is hydrophobic enough, the liquid film between the bubble and the particle thins and eventually ruptures due to the attractive (hydrophobic) surface forces. This is followed by the establishment of the three-phase line of contact (Tao 2005). A study, for instance, has shown that aggregate stability and induction time relied on particle size. Small particles (38-106 µm) exhibited long induction time and ability to rupture the liquid film forming a three-phase contact line. In comparison, big particles (150-300 µm) showed short induction time, and an inability to attach to bubbles easily. The authors ascribed this to the apparent gravity force affecting the interaction between particles and bubbles (Warjito, Harinaldi et al. 2016).

As fine particles are harder to separate with flotation processes, many efforts have been conducted to increase the size of fine particles through agglomeration/aggregation processes. For instance, a study has used an agglomeration-flotation technique using kerosene as a bridging liquid to increase the size of MPs particles and make them floatable (Julapong, Ekasin et al. 2022). Their results showed that adding 1 mL of kerosene to 1500 mL of water improved the floatability of high-density MPs to 96-99%. While the floatability of lower density MPs (SG < 1) didn't change. In another study, the authors have used Al-based and Fe-based coagulants in a DAF cell to remove

PE MPs (or the formed flocs of PE) from greywater, which is one of the most common types of MPs present in greywater (Esfandiari and Mowla 2021). A reduction in PE MPs of 96.10 % and 70.56 % was observed for Al- and Fe-based coagulants, respectively.
Several models have shown that the detachment rate of the particle from the bubble surface increases with increasing bubble and particle sizes. Therefore, using small bubbles increases the probability of collision and adhesion and decreases the probability of detachment. However, larger bubbles would provide enough levitation for the aggregates of bubbles and coarse particles (Tao 2005). The bubble size depends on various factors such as the frother, collector, slurry properties such as temperature and pH, mechanical energy input and air flow rate. As discussed above, the probability of bubble-particle collision can be improved greatly when using smaller bubbles. Nanobubbles (NBs), also called picobubbles (PBs), refer to little bubbles mostly smaller than a few hundred nanometers. More generally, NBs are approximately two orders of magnitude smaller than microbubbles (Tao, Fan et al. 2010). It is well documented that using nanobubbles (NBs) or picobubbles (PBs) along with conventional-sized bubbles (air bubbles can be up to 1.5 mm in diameter) shows a remarkably promising potential in mineral flotation (Tao, Fan et al. 2006, Pourkarimi, Rezai et al. 2017). Such ultrafine bubbles have been generated using different methods including hydrodynamic cavitation, electrolysis, temperature change and power ultrasonic (Xiong and Peng 2015, Nazari, Hassanzadeh et al. 2022). In fact, the flotation or rising velocity or buoyancy force of NBs/PBs is relatively low. However, NBs/PBs adsorb to the particle surface and act as a conditioner or a second collector (surfactant), thus they can aggregate fine particles and improve their flotation **Figure 8**. In a study, the authors have demonstrated that the number and size of NBs attached to the particle surface increases with increasing surface hydrophobicity of particles (Zhang, Cai et al. 2024). NBs can also promote the attachment of coarse particles to the traditional-sized bubbles leading to the growth of large bubbles and an increase in their number (Rosa and Rubio 2018). In other words, they enhance particle-particle and bubble-particle interactions through NBs bridging (Zhang, Cai et al. 2024). NBs have been found to expand the lower and upper particle size limits for successful flotation of coal (Fan, Tao et al. 2013), phosphate (Fan and Tao 2008), and iron ore, etc. (Ahmadi, Khodadadi et al. 2014). Another advantage of using NBs/PBs is the reduced consumption of collectors/frothers (Fan and Tao 2008, Ahmadi, Khodadadi et al. 2014). For a review of the properties and recent advances of NBs in the applications of various water treatment processes, please see (Jia, Farid et al. 2023).

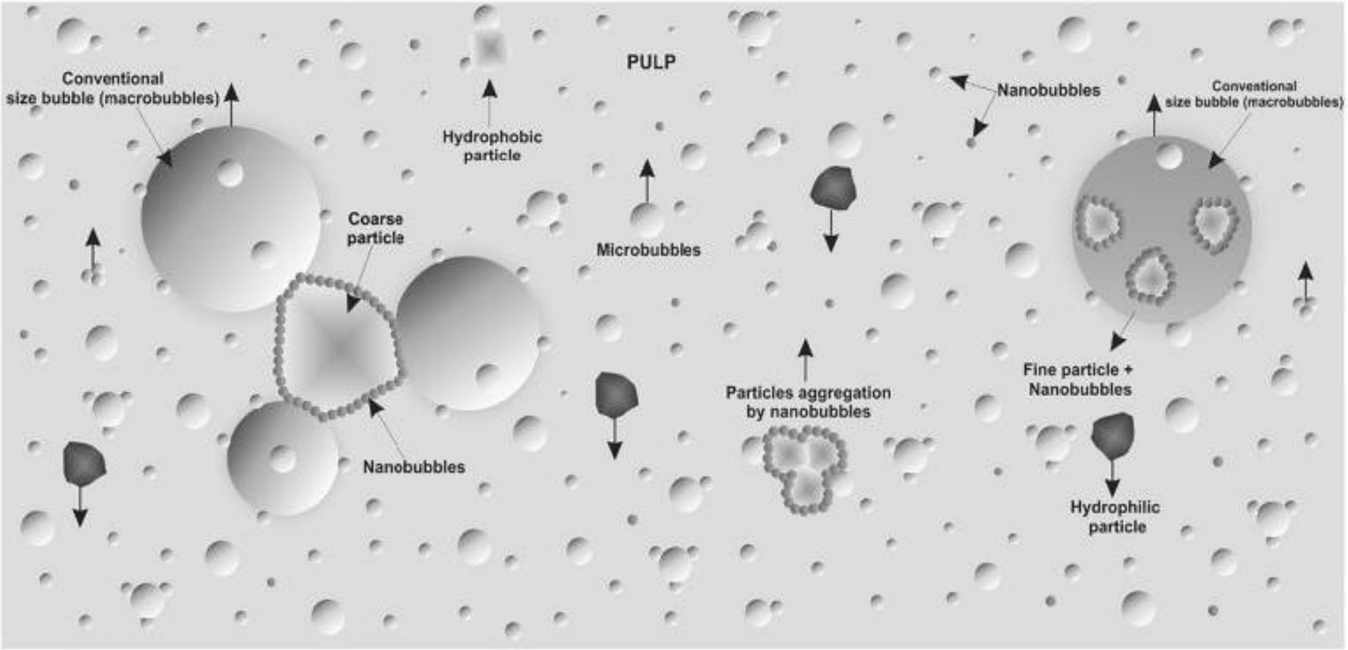

Fig. 8. A schematic representation of the mechanisms involved in the enhanced flotation using nanobubbles (NBs). Reprinted with permission from (Rosa *et al.* 2018).

NBs have been tested for the removal of MPs/NPs from water. For instance, a study also used a mixture of micro-nanobubbles (MNBs) and demonstrated that the enrichment efficiency of MPs increased with flotation time until it reached a maximum value. Their study revealed that the concentration of detergent could be reduced in domestic laundry sewage because the detergent was also adsorbed on the surface of MNBs and could be collected along with MPs (Wang *et al.* 2022). Similarly, another study has used a NB-enhanced flotation process to increase the removal efficiency of regular and irregular MPs from wastewater (**Figure 9**) (Jia *et al.* 2024). The authors demonstrated that the proposed process outperformed the conventional flotation process by promoting the interactions between bubbles and MPs, increasing removal rates of MPs and providing an overall efficiency increase of up to 17 % for different particle sizes.Another study has investigated the factors affecting the process of continuous separation of MPs from water using ultrafine bubbles (microbubbles/NBs). Their results revealed a decrease in the separation of MPs from water with increasing initial concentrations of MPs and an improvement in separation with increasing separation time (Poolwong *et al.* 2023). In addition, a different study has recently applied nanobubble (NB) flotation technology using a commercial NB generator that produces air NBs with an average size of 128.81 nm and found an improvement in the removal of MPs < 100 μm in size, particularly small MPs (< 50 μm) compared with their removal using the traditional DAF (Kharraz *et al.* 2024). The authors attributed their findings to multiple reasons: First, enhancing the probability of bubble-particle collisions, in particular for fine particles, due to the tiny size and high concentration of NBs, second, enhancing the probability of bubble-particle attachment due to the reduction in the bubble size which results in a decrease in the bubble rise velocity extending the sliding time, and third, facilitating hydrophobic interactions due to the hydrophobic nature of NBs, which may dominate over the hydrodynamic repulsive force that is more typical with large bubbles promoting the coalescence of NBs and thus increasing the flotation efficiency.

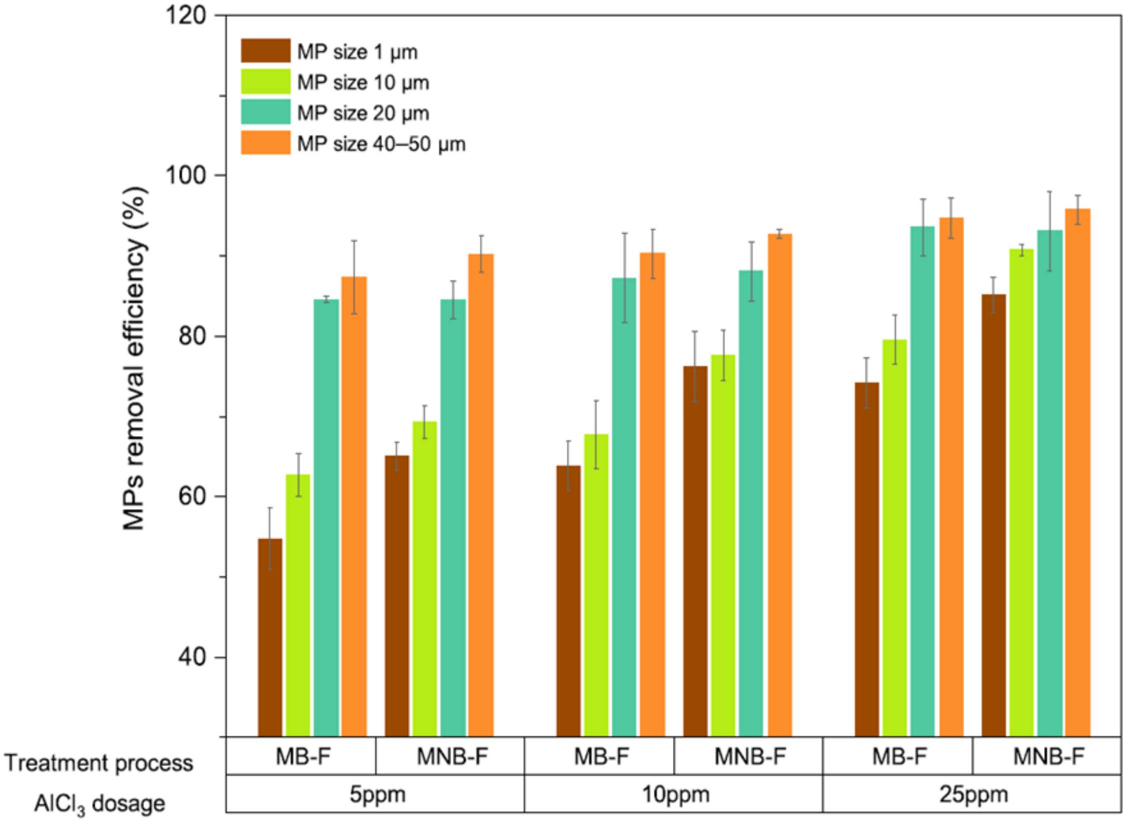

Fig. 9. The removal efficiency of MPs by microbubble flotation (MB-F) and combined microbubble with NBs flotation (MNB-F) showing comparison of the removal efficiency of MPs with different sizes (1-50 μm) and at different doses of coagulant by MB-F and MNB-F. Reprinted with permission from (Jia *et al.* 2024).

6. Current challenges and future directions of flotation technology in the removal of MPs/NPs

One of the challenges in removing MPs/NPs from water via flotation technology is the diversity of plastics that make up the MPs/NPs, which have different densities and shapes, as well as, the wide range of sizes in which they exist. For example, more than 30 types of plastic polymers have been identified in the influents and effluents of WWTPs (Sun, Dai et al. 2019). This will make the flotation a more complex process to optimize and operate. Likewise, the typically detected range of MPs size is from 1.6 to 5000 μm in the influents and effluents of WWTPs (Van Do, Le et al. 2022). It should be noted that the lower range limit will depend on the extraction method used to separate the MPs from water. Another concern is the high cost resulted from the use of reagents such as surfactants, frothers and coagulants that would limit large-scale applications. Flotation of high-density plastic materials might require higher air flow rates meaning higher energy consumption. Moreover, there are limitations related to the analysis techniques used for measuring the plastic contents in water. Real samples contain particles of different sizes spanning a wide range in the nano and microscales which usually exceeds the standard measuring ranges of commercial instruments. Environmental samples may also contain non-plastic particles of comparable size which will affect the accuracy of the analyses (Surette, Mitrano et al. 2023). In addition, some extraction and/or processing methods of samples to be analyzed, such as filtration methods, would exclude small particles that pass through the filter pores from the analysis (Surette, Mitrano et al. 2023). NPs are known to have higher toxicological effects than larger particles and hence methods that allow nanoscale resolution are required for their analysis. Therefore, to comprehensively analyze real samples containing MPs/NPs of diverse properties such as size, shape, polymer type, additives, aging state of MPs/NPs, a range of analytical methods will be needed (Ivleva 2021).

It is also well recognized that particle floatability is applicable only over a certain size range. It may not be easy to determine process parameters that suit the entire particle size range in real samples. Thus, ultrafine and coarse plastic particles may require additional adjustments in flotation process parameters such as altering the bubble size and/or the particle size to make them either larger or smaller. Additionally, the inherent hydrophobic nature of plastic materials is in favor of their attachment to the hydrophobic gas bubbles. However, these particles are prone to fouling or aging in nature which might alter their properties such as hydrophobicity, surface charge, shape and density lowering their floatability.

The use of flotation technology to remove MPs/NPs from water is still in its preliminary stages and a limited number of scale-up studies have been conducted up to the present. More efforts should be directed toward optimizing the process to be suitable for the complex nature of real waters. In addition, the use of multi-stage flotation where each stage uses a specified bubble size range would eliminate the need for plastic particle size adjustment which is usually accomplished through the addition of chemical reagents such as flocculants/coagulants. A greener alternative would rely on the use of eco-friendly and natural surfactants or coagulants which are made from renewable resources and are cheaper, nontoxic, and biodegradable.

Acknowledgments

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

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