Chapter

Perspective Chapter: Role of Nanobubbles Technology in Wastewater Treatments

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Abstract

Bulk nanobubble technologies, developed over the last decade, represent an environmentally friendly innovation in water treatment. Nanobubbles (< 200 nm) exhibit unique properties due to their colloidal behavior and negative surface charge. They are affected by Brownian motion, which enables them to remain stable in aqueous systems for several days, leading to a new approach for liquid-gas and solid-gas contact systems. Their main characteristics include exceptional stability, long residence times, large specific surface area, high gas transfer efficiency, strong interfacial potential, enhanced adhesion, and the ability to generate free radicals. These features make nanobubbles highly promising for enhancing conventional water and wastewater treatments, improving the overall efficiency of wastewater treatment plants. Main applications include flotation processes, aerobic biological technologies such as activated sludge, biological activated carbon, or membrane bioreactors, and ozone-based oxidation treatments. The generation of active free radicals that oxidize organic compounds facilitates pollutant degradation. Nanobubbles improve the efficiency of individual treatment processes, reduce operating costs and chemical consumption, and, in summary, may extend the limits of existing wastewater treatment plants. This chapter explores the fundamental properties and technological applications of nanobubbles in wastewater treatment, highlighting their potential to remove macro- and micro pollutants while improving overall process sustainability.

Keywords: nanobubbles, nanotechnology, wastewater treatment plant, nano-ozonation, nano-flotation, nano-aeration, emerging contaminants

1. Introduction

Ensuring safe and high-quality water is a global priority, as freshwater scarcity and pollution continue to intensify due to rapid urbanization and industrial expansion. Traditional water treatment technologies, although effective at removing macropollutants, struggle to fully address the challenges posed by micropollutants such as emerging contaminants (ECs). These pollutants, including pharmaceuticals, pesticides, chlorinated hydrocarbons, and persistent organic matter, among others, are often resistant to conventional physical, chemical, and biological treatments, remaining in the final effluents of wastewater treatment plants (WWTPs), leading to risks of secondary pollution [1, 2]. **Figure 1** summarizes the typical performance of conventional treatments and indicates the extent to which each process can remove ECs.

To extend the efficiency of urban WWTPs, the EU has updated the urban wastewater treatment legislation with the new Directive EU 2024/3019. It mandates quaternary treatments for removing micropollutants in plants serving more than 150,000 population equivalent. This requires the integration of advanced, ad-hoc technologies into existing treatment trains to enhance and complement conventional equipment.

In this context, nanobubble (NB) technology has recently emerged as a promising upgrade for a wide variety of treatments. NBs present unique physicochemical properties, particularly at gas-liquid interfaces, which enable improvements in processes where contact efficiency and mass transfer are critical. The next section explores these properties in detail, highlighting how NBs can enhance current technologies such as flotation, biological treatments, or advanced oxidation, among others.

On the other hand, NB production depends on scalable, energy-efficient technologies such as hydrodynamic cavitation (using devices like Venturi injectors), fluidic oscillation, microporous materials, and ultrasonic irradiation [3–6]. At the industrial scale, production focuses on optimizing generator design, operational parameters, and process control to ensure consistent NB size, stability, and concentration, broadening their applicability. Moreover, recent advances highlight the use of microporous materials to passively produce NBs with tunable gas composition, reducing energy costs compared to traditional mechanical aeration or ultrasound [7].

This chapter aims to explore the fundamental properties and technological applications of nanobubbles (NBs) in wastewater treatment, highlighting their potential to enhance pollutant removal efficiency, energy performance, and process sustainability. The methodology follows the steps described in **Figure 2**. First, a precise search on Web of Science (WoS) was conducted by selecting two main topics: "nanobubble" and "water treatment," including their potential related synonyms like "bulk-nanobubbles" or "wastewater treatment," among others.

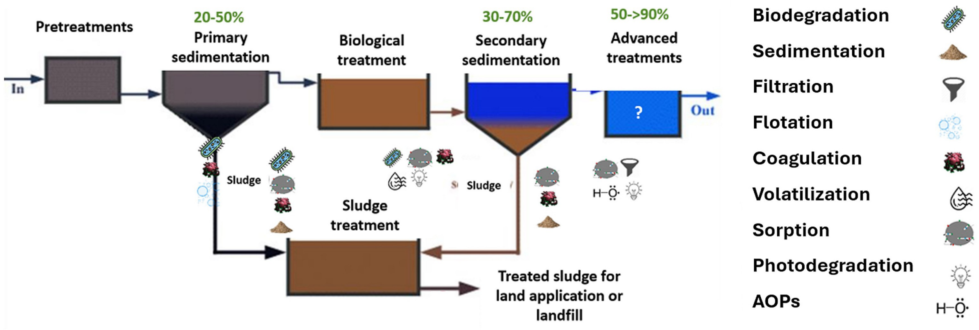

Figure 1.
Potential removal of ECs in a conventional WWTP.

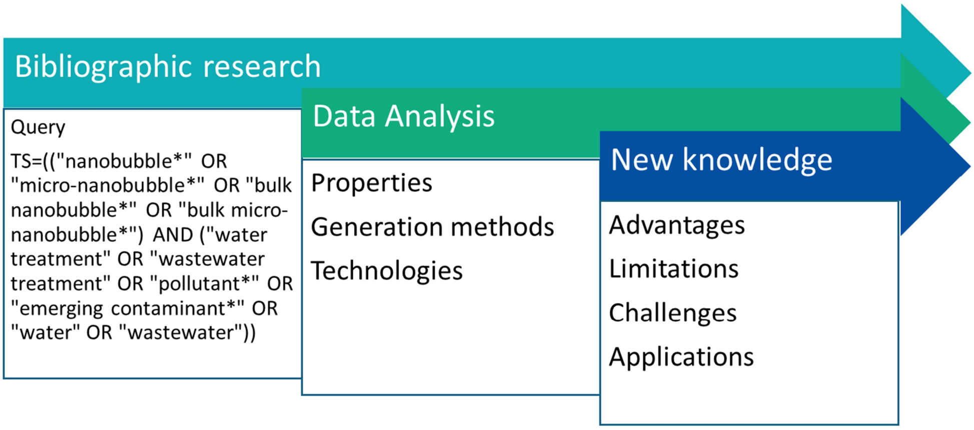

Figure 2.
Methodology for the bibliographic search.

Once the bibliometric parameters were selected, the obtained data were analyzed and categorized into three main topics: nanobubbles' physicochemical properties, generation methods, and effects on water technologies. Finally, a critical analysis of the papers provided key information about nanobubble properties and applications, considering advantages, current limitations, and further challenges.

2. Properties, advantages, and limitations of nanobubbles

NBs, typically defined as gas-filled cavities smaller than 1 μm, exhibit extraordinarily long lifetimes in water, high surface charge (zeta potential), large specific surface area, and enhanced gas transfer efficiency compared to microbubbles (MBs) or conventional aeration systems [8, 9]. Unlike ordinary bubbles, which rapidly rise and burst at the liquid surface, NBs remain stable for days or even weeks. This stability prolongs their interaction with dissolved and colloidal pollutants, as well as microbial communities [10, 11]. NBs are generally classified into two types: surface NBs and bulk NBs [12]. Surface NBs remain attached to liquid–solid interfaces, whereas bulk NBs are spherical nanobubbles dispersed within the liquid phase [13]. In water treatment applications, bulk NBs are the predominant type [12]. **Figure 3** shows a summary of the unique properties of bulk NBs compared to MBs.

As bubble size becomes smaller, the rising velocity decreases (up to 10^6 times lower compared to MBs), and surface tension increases. The outer layer of NBs tends to be negatively charged, depending on the pH and the surrounding chemical environment. This charge is quantified through zeta potential, which can reach – 50 mV under neutral or alkaline pH. As a result, repulsive forces between NBs prevent coalescence and confer remarkable stability and negligible buoyancy. Consequently, NBs remain suspended in water for extended periods (days) without rising quickly to the surface, contributing to their superior performance in pollutant removal and gas-transfer efficiency [14, 15].

At the same time, decreasing the bubble size increases the interfacial surface area, one of the most significant advantages of NBs. The enlarged surface enhances

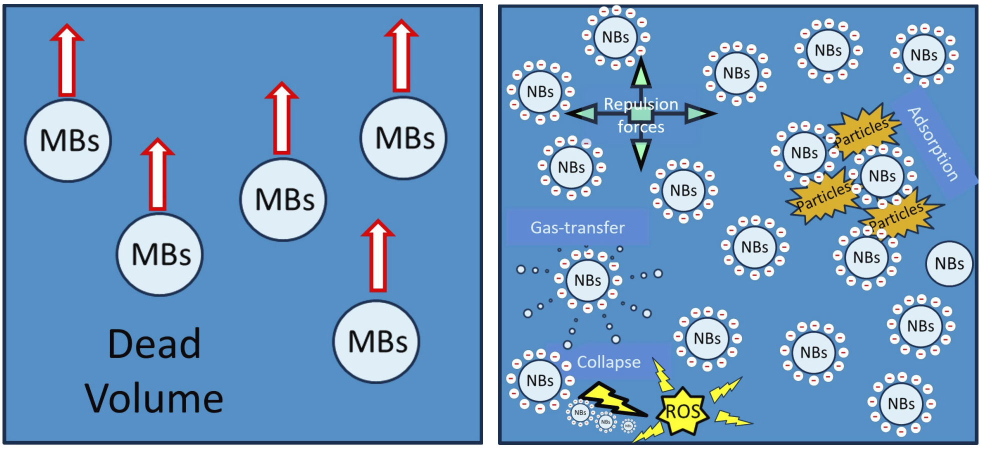

Figure 3.
Properties of microbubbles (MBs) compared to nanobubbles (NBs).

adsorption on suspended and colloidal contaminants. Combined with electrostatic forces, it accelerates the aggregation of oppositely charged particles in the water matrix. This improvement in adsorption kinetics increases removal efficiency and can be effectively combined with biological treatment processes. The convergence of adsorption, biodegradation, and NB-enhanced processes offers a powerful and environmentally friendly strategy for upgrading water treatment. Furthermore, NBs can improve flotation processes by reducing the chemical oxygen demand, turbidity, total solids, and cationic demand of the wastewater [15, 16].

The expanded surface area also facilitates more efficient mass transfer compared to traditional systems, such as aerators in WWTPs [17, 18]. Studies have shown that the volumetric mass transfer coefficient (k_La) and gas utilization efficiency can be more than doubled when NBs are used instead of larger bubbles [15, 17, 18]. These improvements translate into doubling the dissolved oxygen in biological reactors with the same supply, leading to improvements in process efficiency.

In case of collapse, NBs can generate reactive oxygen species (ROS), such as hydroxyl radicals (·OH) or superoxide anions ($O_2{\cdot}^-$), depending on several factors like the chemical species present in the water matrix or the pH, among others. This phenomenon is attributed to the extreme temperature and pressure reached in localized hot spots during bubble implosion (up to 5 GPa, depending on the gas type). Under such conditions, the high concentration of ions accumulated in the disappearing interface does not have enough time to dissolve, releasing the chemical energy required to form ROS. The type of ROS formed depends on the chemical species present in the water. When NBs interact with oxidants such as ozone or hydrogen peroxide, additional radicals are produced, enhancing oxidative degradation [19, 20].

By simultaneously improving oxygen transfer, accelerating adsorption kinetics, and facilitating oxidative degradation, NBs offer synergistic effects that align with the growing demand for sustainable technologies capable of addressing complex mixtures of organic pollutants in municipal and industrial wastewater.

Beyond their physicochemical properties, NBs provide several operational and environmental advantages that make them a promising innovation in water treatment.

Advantages	Limitations
High gas transfer efficiency and enhanced oxygen dissolution	High energy consumption during NB generation
Large specific surface area, improving adsorption and mass transfer	Equipment cost and maintenance requirements
Long-term stability in aqueous systems	Difficulties in scaling up while maintaining bubble stability
Ability to generate reactive oxygen species (ROS) for the oxidation of pollutants	Sensitivity to water chemistry (pH, ionic strength, multivalent cations)
Enhanced coagulation/flocculation and particle aggregation	Lack of standardized measurement and monitoring protocols
Enhanced flotation	Determination of optimal micro/nano ratio
Improved oxygen availability for biological treatment processes	Limited understanding of ROS formation and NB–microorganism interactions
Potential for micropollutant removal	Potential disturbance of microbial community balance
Reduced chemical use and improved process efficiency in pilot-scale applications	Lack of long-term, full-scale validation and economic assessment

Table 1.
Advantages and limitations of nanobubble technologies.

However, despite these advantages, several limitations still hinder the large-scale application of NB technologies. The high energy demand and equipment costs associated with NB generation remain significant barriers to full-scale implementation. Maintaining bubble stability and consistent performance under variable water conditions also poses technical challenges. In addition, the lack of standardized characterization methods and cost-effective monitoring tools limits accurate evaluation of NB behavior and performance. At the biological level, potential alterations in microbial community structure and the limited understanding of long-term impacts require further research. **Table 1** presents a summary of the main advantages and limitations of NB technologies.

3. Technical applications

The different properties of NBs justify that they act through several mechanisms for the removal of pollutants by different technologies, depending on how they interact with the particle, colloid, and dissolved pollutant, as shown in **Figure 4**. The following sections provide a detailed description of the specific applications and benefits of NBs in flocculation, flotation, biological treatments, adsorption, and advanced oxidation processes.

3.1 Flocculation processes

Flocculation is involved in the separation stages of many industrial processes. It improves sedimentation, flotation, filtration, and other separation operations. Some of these processes, such as flotation, can be directly improved by using NBs, but the

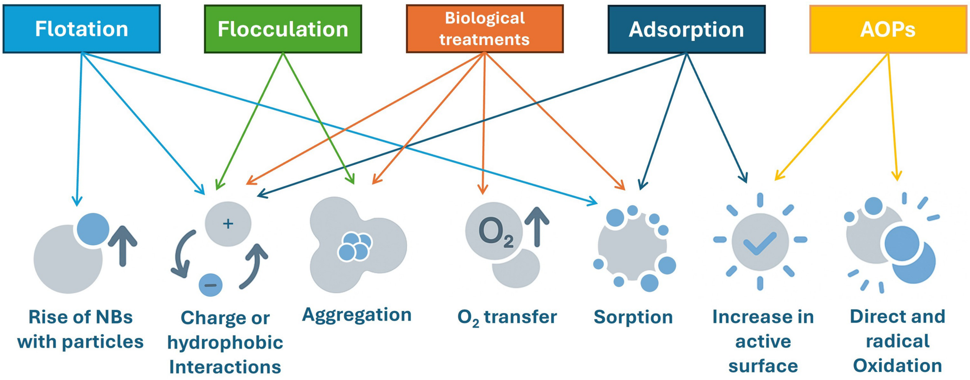

Figure 4.
Main mechanisms of nanobubble interactions in different water treatment technologies.

negative charge of the NBs promotes interactions that also favors flocculation. Therefore, there is a synergistic effect in the separation process due to the use of coagulants/flocculants and the presence of NBs.

Most of the studies on the effect of NBs on particle interactions are in the framework of mineral suspensions and water treatment. Flocculation of coal, kaolin, clay, and calcite, for example, has been improved by NB additions. Most of the particles in these studies were hydrophobic or had hydrophobic parts. For example, kaolin with plate-like morphology has hydrophobic edges, and NBs promote the interaction between edges, leading to a gel-like flocculated suspension [21, 22].

NBs are mainly adsorbed on the hydrophobic particle surfaces [23], although they can also be adsorbed on hydrophilic particles [24, 25]. This adsorption is driven by the interactions described in the DLVO (Derjaguin–Landau–Verwey–Overbeek) theory and by hydrophobic forces [26]. Therefore, electrostatic repulsion and van der Waals attraction forces define the interaction energy profile between the bubble and the solid-liquid interface. These forces determine the system's stability and the likelihood of effective attachment, depending on the physicochemical conditions of the surrounding medium.

The adsorption of NBs onto particle surfaces has mainly four consequences:

- The apparent volume of the particle increases, which promotes its interaction with other particles through orthokinetic flocculation in forced convection systems [27].

- The area of the solid-liquid interface decreases, this reduces the stability of colloidal suspensions [28].

- The NBs covering neighboring particles can interact before the distance between surfaces is small enough to cause significant repulsive forces. This is called long-term forces, and they allow the formation of capillary bridges between particles [21, 29].

- The zeta potential of the suspension is altered in the presence of NBs, which affects stability. This fact has been observed in kaolin suspensions, where NBs neutralized the zeta potential and reduced the stability of fine particles [24].

In summary, the presence of NBs in a suspension may induce the flocculation of particles, improving the efficiency of the process. The main mechanism explaining the improvement is the enhancement of long-term forces or hydrophobic forces due to the hydrophobic interactions, forming capillary bridges between adsorbed NBs on the particle surface [24, 28, 29]. The stability of capillary bridges is related to the charge density of the NB. High charge density decreases bridge stability, which affects floc stability [29]. Since the addition of cationic surfactants and flocculants affects the charge density of NBs, some studies have been carried out with this kind of additive. Wang et al. proved a synergic effect between sodium oleate and NBs in calcite flocculation because of both the decrease in zeta potential and NB size, and the stability increase [30]. Later, Dutta et al. proved and explained this fact while working with different surfactants and salts [29]. Some authors have studied the effect of NBs on the flocculation of kaolin [24, 27] and fine coal [28] induced by polyacrylamide. The studies showed a clear improvement in flocculant efficiency due to the NBs, and in the case of fine coal, some aggregation was driven by NBs before adding the flocculant. These results evidence the possibility of using NBs to improve flocculation efficiency, especially in the case of mineral particles.

3.2 Flotation processes

Flotation is a well-known separation process that uses gas bubbles as carriers to transport suspended particles to the liquid surface [31, 32]. Considering the NBs' properties described above, flotation performance can be significantly enhanced through the following mechanisms:

- Surface modification: Nanobubbles (NBs) adsorb onto particle surfaces, altering surface energy and increasing hydrophobicity. This facilitates stronger particle-bubble interactions and improves separation efficiency [33].

- Heterocoagulation: NBs present a high negative zeta potential, which favors electrostatic interactions with positively charged particles. This leads to heterocoagulation and destabilization of colloidal matter, promoting particle aggregation and separation [6].

- Nucleation sites: NBs serve as nucleation centers for dissolved gases. In the case of a pressure drop or agitation, they expand, forming MBs and improving the probability of particle–bubble collisions [34].

- Bubble–particle attachment efficiency: Due to their nanoscale size, NBs can spread across particle surfaces, reduce induction time, and increase attachment efficiency. During particle–bubble interactions, the presence of surface NBs on particles leads to wetting film rupture at larger thicknesses compared to systems lacking surface NBs. This effect is particularly beneficial for removing micro-sized particles that would be hard to separate using conventional flotation [32, 35].

Flotation with NBs has been successfully applied to more efficiently remove contaminants such as organic matter, metal ions, oils, dyes, minerals, and fine powders [15, 35]. Efficiency depends strongly on bubble size, surface charge, and the contaminant properties. Smaller bubbles lead to higher collection efficiency and improved separation. Han et al. demonstrated that separation efficiency is proportional to the product of the collection efficiency and the number of bubbles present [36].

Several innovations highlight these benefits. Terasaka developed a spiral-flow bubble generator that successfully removed fine carbon particles [37]. Nazari et al. demonstrated that NBs increased the flotation recovery of coarse particles (>100 μm) by 14% (from 53% to 67%) through upgraded bubble–particle attachment and a reduced Reynolds number [38]. Similarly, Calgaroto et al. showed that combining NBs (200–720 nm) with large bubbles (400–800 μm) enhanced the capture of fine and ultrafine quartz particles (<8–74 μm) due to their slower rising velocity and entrainment effect [39].

High removal efficiency was also achieved in oily wastewater [40], where column flotation using NBs with fine bubbles reduced oil content to less than 5 mg/L [16]. Other advances include a T-tube flotation device that decreased oil concentrations on offshore platforms from 38 to 12 g/m^3, while spiral-flow bubble generators recovered 90% of iron oxide fines within 60 minutes [18].

3.2.1 Dissolved air flotation

Dissolved air flotation (DAF) process is the most established fine-bubble-based technology. It produces MBs (20–100 μm) by depressurizing air-saturated water, improving contaminant removal compared to conventional systems [41]. NBs can further enhance DAF through several mechanisms:

- Seeding effect: NBs act as seeds that expand into MBs during decompression, producing a stable and uniform bubble size distribution [6].

- Improved bubble–particle collision: The increased bubble number concentration provided by NBs raises the collision probability between bubbles and particles, including those in the submicron range [34].

- Electrostatic interactions: The negative surface charge of NBs promotes attachment to cationic contaminants, thereby increasing bubble–particle interactions [33].

- Localized ROS generation: In some cases, the collapse of oxygen or ozone NBs generates radicals, such as •OH, which degrade organic contaminants. Hence, hydrophobicity and flotation efficiency are enhanced [42].

Some DAF applications include the removal of oil, metal ions, dyes, and fine particulates. There are studies that report higher efficiency, reduced chemical demand, and shorter flocculation times [41]. For instance, Calgaroto et al. achieved 80% removal of amine pollutants using DAF with NBs [39], while Etchepare et al. achieved > 99% removal of Fe^{3+} and 66–91% removal of $Fe(OH)_3$ colloids [6]. Similarly, Xiao et al. further demonstrated that the presence of NBs inhibits precipitation and increases flotation efficiency, from < 20% to 90% when treating styryl phosphoric acid-Pb particles to recover organic phosphine [33]. Other authors report > 99% oil removal in oil–water separation systems [34]. NB-based flotation is also particularly effective in removing algal cells and emulsified hydrocarbons that are otherwise difficult to treat using conventional DAF [33].

Mixtures of micro and nanobubbles (MNBs) exhibit improved bubble persistence, increasing the reliability and robustness of DAF processes under variable matrix conditions [42]. Hence, clarification is improved, leading to reduced dosages of coagulants and flocculants [32]. Overall, the evidence highlights the powerful role of NBs in enhancing flocculation, pollutant attachment, and mass transfer rates in flotation and DAF processes, turning them into a promising technology for water and wastewater treatment.

3.3 Biological treatments

3.3.1 Aeration

The efficiency of biological wastewater treatment is deeply influenced by the availability of dissolved oxygen to sustain microbial metabolism. Conventional aeration using microbubbles (MBs) is often limited by rapid bubble rise, low oxygen solubility, and high energy consumption. Nanobubbles (NBs) may overcome these limitations due to their specific properties (small size, high surface-to-volume ratio, negligible buoyancy, etc.), allowing them to remain in the water matrix for longer periods. Therefore, oxygen transfer efficiency can nearly double when NBs are used as the aeration medium [43, 44]. It has been reported that dissolved oxygen concentrations increase from 2 to 4.5 mg/L, offering more effective oxygen enrichment for microbial communities in biological systems [43].

Unlike coarse or fine bubbles that break once they have reached the water surface, NBs dissolve gradually until gas equilibrium is achieved. Tekile et al. observed that NBs maintained high dissolved oxygen concentrations long after their formation, providing a more uniform oxygen distribution in the water matrix [44]. This prevents oxygen-depleted “dead zones,” which are common in conventional activated sludge and sequencing batch reactors.

The long persistence of NBs ensures that oxygen is delivered more efficiently and uniformly, maintaining and stimulating aerobic microbial metabolism across the entire matrix [43]. In addition, this also enhances the breakdown of pollutants. Several studies highlight the benefits of NBs for microbial activity and pollutant removal. In pilot-scale biological reactors, NB aeration improved the degradation of organic matter, measured as chemical oxygen demand (COD), the nitrification of ammonium (NH_4^+-N), and even the removal of total phosphorus [45]. Additionally, different authors have reported that NB aeration also reduces sludge production through enhanced cell lysis and improved microbial utilization of organic matter [43, 45].

Energy consumption in wastewater treatment is mainly caused by aeration, which accounts for up to 50–70% of the total energy demand. Since nanobubbles (NBs) increase oxygen transfer efficiency, the air supply required to achieve the same dissolved oxygen levels is reduced. Pilot studies and field applications report reductions of 30–40% in aeration energy consumption while maintaining or even improving effluent quality [43]. Furthermore, the generation of sludge is also reduced, and considering that sludge management represents approximately 60% of operational costs in biological treatment, this is a significant advantage due to the lower biomass production.

3.3.2 Biological activated carbon processes

Biological activated carbon (BAC) filtration is a hybrid technology in which biological degradation and adsorption act simultaneously to remove contaminants from water. Activated carbon (AC) is a well-known material that has been used to capture a wide range of contaminants, such as heavy metals, soluble dyes, hydrocarbons, or phenols, among others [46]. Its porous structure and large internal surface area make it a highly effective material with high removal yields. However, adsorption is inherently limited by saturation, after which the process stops unless the AC undergoes regeneration. In BAC systems, biofilms develop on the carbon's surface and within its pores through bacteriological growth on the adsorbed organic matter. This phenomenon facilitates continuous regeneration of the AC without interrupting the process or requiring investment in external regeneration systems. Hence, the dual mechanism of biodegradation and adsorption forms the core strength of BAC filters. The integration of bulk NBs into BAC systems enhances, on the one hand, the biodegradation and adsorption processes and, on the other, the regeneration of the AC.

One of the principal challenges in BAC processes is oxygen transfer. Bacterial metabolism within the active carbon pores depends on how much dissolved oxygen is present. Since these sites are difficult to reach by an external gas input, conventional aeration systems, whether mechanical diffusers or surface aerators, are energy-intensive and inefficient in terms of mass transfer. Nevertheless, NBs may overcome this limitation by supplying high oxygen dissolution rates of up to twice the conventional value. In addition, their negligible buoyancy permits them to remain suspended for long periods, resulting in continuous diffusion of oxygen. Furthermore, their small size of less than 1 μm allows them to reach smaller mesopores. Consequently, this not only enables microbial growth within the AC but also accelerates their metabolism, resulting in the removal of more biodegradable contaminants [17, 47, 48].

From an operational perspective, the combination of NBs in BAC processes could also lead to energy and sustainability benefits, since NB aeration can reduce energy consumption by up to 80% [47]. These savings could make the process more economically suitable for large-scale WWTPs. Furthermore, since NBs can be formed from different gases like oxygen, ozone, or even carbon dioxide, their application may be designed to meet specific treatment goals, whether promoting biodegradation, enhancing oxidation, or improving adsorption.

Furthermore, the ability of NBs to collapse and generate ROS introduces an oxidative pathway that complements both adsorption and biodegradation. Hydroxyl radicals are non-selective and can attack a wide range of recalcitrant pollutants, including those that resist microbial attack. Considering that BAC affects biodegradable matter, the addition of NBs could expand its scope to more recalcitrant contaminants. For instance, ozone NBs have been shown to increase BAC yield by transforming hydrophobic fluorophores into more biodegradable products [49]. Similarly, NB-based AOPs can synergistically decrease toxic species' concentration before adsorption, leading to less biofilm stress and an extension of the filter life.

The active role of NBs in BAC systems also connects to broader adsorption applications. In traditional granular activated carbon (GAC) or powdered activated carbon (PAC) processes, saturation is a limiting factor. NBs can accelerate adsorption rates and upgrade desorption efficiency while lowering the cost of adsorbent regeneration. Their high surface energy and mobility allow them to act as carriers of pollutants toward adsorption sites, while maintaining aerobic conditions that avoid biofouling. Furthermore, the presence of NBs can affect the physicochemical properties of adsorbent surfaces and contaminants, increasing hydrophobic interactions and enhancing adsorption efficiency for compounds that otherwise display low affinity.

3.4 Advanced oxidation processes

3.4.1 General perspective and · OH generation

Advanced oxidation processes (AOPs) are treatment technologies that *in situ* generate highly reactive radicals, such as · OH, to degrade recalcitrant contaminants in water. These processes aim to mineralize recalcitrant pollutants, which are resistant to conventional treatments, often resulting in less toxic byproducts that improve their biodegradability.

The generation of · OH in micro and nanobubbles (NBs) depends on physicochemical and operational conditions. Key parameters include gas composition, bubble size, pH, temperature, dissolved oxidants, pressure, and external stimuli such as ultrasound or UV irradiation [50].

Bubble size plays a fundamental role in · OH generation. Small bubbles (<200 nm) exhibit higher internal pressures due to the Young–Laplace effect, which leads to gas supersaturation and bubble-collapse processes capable of generating · OH radicals [14]. The probability of these interactions occurring increases due to the bubble stability and slow rising velocity, which extend their residence time in the water matrix [15]. In contrast, larger bubbles rise quickly and generate fewer radicals due to lower internal pressure and shorter lifetimes.

The composition of the bubbled gas is one of the key parameters that affect · OH formation. Oxygen NBs tend to produce more · OH than air or inert gases because dissolved oxygen directly takes part in radical formation reactions [16]. Ozone NBs are particularly effective, as O_3 decomposition leads to the secondary formation of · OH through chain reactions. Hydrogen nanobubbles, although less common, exhibit unique redox chemistry that may influence ROS dynamics [51].

pH is another determining factor that influences · OH generation, which is favored under acidic conditions because lower pH enhances the redox potential of oxidants and minimizes radical recombination, thereby increasing the oxidative degradation capacity. Conversely, alkaline conditions often lead to the scavenging of · OH by hydroxide ions and to the formation of less reactive species such as hydroperoxide anions (HO_2^-), resulting in reduced oxidation efficiency. Nevertheless, pH also governs the surface properties of NBs. Under alkaline conditions, NBs acquire a stronger negative surface charge, reflected in a more negative zeta potential. This enhanced electrostatic repulsion stabilizes the NBs, prolonging their lifetime, increasing the coexistence of oxidants and pollutants in the aqueous phase, and, on the other hand, influencing their interactions with cationic charged contaminants [14]. Moreover, the decomposition of oxidants such as ozone and hydrogen peroxide into · OH is accelerated at higher pH values [52]. Conversely, in acidic environments, NBs exhibit reduced stability and diminished ROS yields. Nevertheless, these assumptions must be considered carefully since external factors influence them too. For instance, it has been proven that the generation of · OH can be increased by the decomposition of oxygen molecules and protons. Hence, more acidic conditions and/or high oxygen concentrations might also lead to the generation of · OH.

Temperature affects reaction constants and NBs' stability. High temperatures can reduce stability, leading to bubble collapse, but they also enhance reaction kinetics, promoting · OH generation [53]. Dissolved oxygen concentration is crucial because it provides the source for ROS. Hence, high dissolved oxygen concentration in the form of NBs enhances ROS production and vice versa [20].

Cavitation caused by pressure changes promotes · OH generation. Under high pressure, followed by rapid depressurization, NBs collapse, forming localized hot spots with extreme temperature ($\approx 10^3$ K) and pressure (≈ 5 GPa) during several picoseconds [54]. Saturation pressure during dissolved air flotation or similar processes is directly correlated with · OH concentration [6]. Optimal pressures ensure continuous NB generation without destabilizing the system.

External energy inputs further enhance · OH production. Ultrasound has been reported as a promoter of · OH production. Acoustic cavitation increases bubble collapse intensity, raising both the frequency and magnitude of radical formation [55]. UV irradiation also enhances radical production, especially when combined with oxygen or ozone NBs, by initiating photolysis reactions that yield · OH [56].

Oxidants such as ozone and hydrogen peroxide highly induce · OH production when they are present with the NBs. Ozone NBs react to form · OH in alkaline water, while hydrogen peroxide undergoes homolytic cleavage under UV or catalytic activation [52]. The introduction of catalytic reactions, such as Fenton-like (Fe^{2+}) or photocatalytic pathways (TiO_2), can further accelerate these processes [57].

Water matrix chemistry must also be considered. Certain ionic species severely affect radical generation, acting as catalysts or inhibitors. High levels of carbonate scavenge · OH, decreasing effective radical concentrations [58]. Nevertheless, transition metals may catalyze secondary radical reactions, increasing · OH formation. Thus, water chemistry must be carefully considered in practical applications. Overall, a good characterization of the water matrix that is being studied, combined with a thorough understanding of the interaction of these parameters, is key to optimizing the application of NBs.

3.4.2 Ozone-based processes

In conventional ozonation, O_3 suffers from a high self-decomposition rate during the transition from the gas to the liquid phase. This leads to low solubility (≤ 10 mg/L) in water under neutral pH and room temperature, requiring higher O_3 dosages. Moreover, its short half-life and limited mass transfer coefficient further restrict its efficiency. NBs offer a promising alternative by overcoming these limitations. Their high stability, prolonged residence time, and large interfacial area significantly enhance O_3 solubility and mass transfer in aqueous solutions, thereby extending the oxidative activity of O_3 and its derived ROS. As a result, high concentrations of NBs generate ROS-rich microdomains, where pollutants are more likely to encounter oxidative species, accelerating degradation rates of refractory organic pollutants such as pharmaceuticals and surfactants [42, 59].

The enhanced performance of NB-assisted ozonation can be attributed to several mechanisms. First, the large interfacial area of NBs improves the dissolution of oxidizing gases, which is especially beneficial in ozonation and peroxone (O_3/H_2O_2) systems, where higher solubility directly translates into increased $\cdot OH$ generation [59]. Second, the strong negative zeta potential of NBs facilitates electron transfer reactions that accelerate the decomposition of ozone and hydrogen peroxide into ROS [59].

Experimental studies confirm the effectiveness of NB ozonation, reporting more than 80–90% removal of dyes (e.g., methylene blue, reactive black 5) and pharmaceuticals (e.g., tetracycline, carbamazepine). Compared with conventional ozonation, NB-based systems achieve faster degradation kinetics and higher mineralization (TOC removal) [59]. As a result, lower dosages of ozone, hydrogen peroxide, or persulfate are needed to achieve equivalent pollutant degradation [42]. Furthermore, coupling NB ozonation with external stimuli such as UV light, TiO_2 photocatalysis, or Fe^{2+}/Fe^{3+} catalysts produces greater ROS yields due to higher gas solubility and prolonged oxidant lifetime [42].

It is also important to highlight that controlled and sustained ROS production enables more mineralization of pollutants and fewer toxic intermediates than bulk ozonation [59]. In addition, ROS generated by collapsing NBs can inactivate viruses, bacteria, and biofilms, providing a dual advantage of pollutant oxidation and microbial disinfection [42]. Despite these advances, the exact mechanisms of O_3 transport and interfacial reactions during NB-assisted oxidation remain insufficiently understood, warranting further research [50].

3.4.3 Other AOPs processes

NBs hold significant potential to enhance a wide range of AOPs beyond the conventional ozone- or peroxide-based systems. Their application in emerging catalytic pathways, such as peracetic acid, sodium percarbonate, photoelectrocatalysis, and electro-Fenton oxidation, remains largely unexplored. Investigating the potential synergistic effects of NBs in these systems, particularly regarding ROS generation, improved gas–liquid mass transfer, and catalyst activation, could open new avenues for more efficient contaminant degradation [50].

3.5 Adsorption processes

As explained in the previous section on BAC, NB-based technology also influences adsorption mechanisms. NBs significantly enhance adsorption processes in water treatment by increasing adsorption rates, capacities, and pollutant-adsorbent interactions. Their effectiveness depends on water chemistry, adsorbent type, and pollutant properties, making them a promising and cost-effective tool for advanced water purification. A summary of the main mechanisms through which NBs upgrade adsorption is provided below:

- Adsorption rate and capacity: the presence of NBs accelerates the adsorption rate and can substantially increase the adsorption capacity of adsorbents such as biochar or AC. For instance, NBs enhanced the adsorption capacities by up to an order of magnitude compared to conventional methods in the removal of heavy metals and dyes when compared with conventional systems [60–62].

- Pollutant-adsorbent interactions: NBs facilitate closer contact between pollutants and adsorbent surfaces, often forming pollutant–NB colloids that are more readily captured by adsorbents. This mechanism is especially effective for hydrophobic or surface-active contaminants such as polyfluoroalkyl substances (PFAS) and boron [62–64].

- pH and ionic strength sensitivity: NB performance is strongly affected by pH and ionic strength. Low pH values and ionic strengths stabilize NBs and enhance adsorption, while the presence of multivalent cations (e.g., Fe^{3+}) can further increase removal efficiency [62, 64].

- Surface charge and electrostatic effects: NBs can modify the surface charge of species present in the matrix, creating electrostatic interactions that favor adsorption, especially for charged pollutants and functionalized adsorbents such as chitosan-modified carbon [60, 62–64].

Luo et al. showed that the addition of NBs enhances the interfacial interactions of carbon-based adsorbents with conventional PFAS, improving adsorption efficiency across a range of pH values and ion concentrations [64]. Accordingly, Liu et al. demonstrated that perfluoroalkyl acids were more effectively adsorbed onto GAC modified with chitosan when NBs were added, thanks to the improvement in mass transfer and reduced diffusion resistance [63].

Experimental comparisons between adsorption with and without NBs highlight their benefits. Kouvalakidou et al. reported higher pollutant removal and faster kinetics in batch adsorption experiments using NBs [60]. Kyzas et al. observed that, while AC adsorption capacity for lead ions remained similar, adsorption kinetics were dramatically accelerated, up to 366% faster, with NBs [65]. This increase may be a result of electrostatic interactions at the NBs' interface, which attract charged molecules and drive their penetration into the pores of the adsorbent. Such improvements prove that NBs can reduce the equilibrium time for adsorption, promoting faster removal rates and improving the adsorption–regeneration cycles in industrial filters. In practical terms, larger volumes of water can be treated before saturation or breakthrough occurs, increasing operational efficiency.

NBs also enhance adsorption by stabilizing suspensions and changing surface properties. For instance, Ma et al. showed that ion adsorption onto NBs contributes to their stability, indirectly affecting colloidal interactions with adsorbents [66]. This stabilizing effect, coupled with improved dispersion, promotes the adsorption of complex contaminants such as nanoplastics, as reported by Arenas et al. and Ighalo et al. [67, 68].

Apart from upgraded kinetics, NBs can affect water chemistry to promote adsorption. Cerrón-Calle et al. showed that CO_2 NBs changed interfacial reactivity, creating favorable conditions for these processes [69]. Accordingly, Takahashi et al. showed that ROS formation from NBs could enhance oxidative pretreatment, indirectly favoring adsorption yield by reacting large organics into more easily adsorbable species [70].

Compared with traditional adsorption, which is often limited by diffusion and pore accessibility, NBs enhance surface contact, promote turbulence at the microscale, and modify surface charges. Collectively, these mechanisms result in higher adsorption capacities, faster kinetics, and improved operational efficiency. These findings suggest that NB integration can overcome conventional limitations, making adsorption processes more efficient, sustainable, and versatile in addressing ECs.

4. Challenges

4.1 High energy demand for generation

Producing NBs requires specialized equipment, and the choice of generation method strongly influences energy consumption, bubble size, and bubble stability. Common approaches include ultrasound or hydrodynamic cavitation, pressurized dissolution, jet dispersion systems, electrochemical methods, and high-speed shearing impellers. However, many of these processes are energy-intensive. For instance, electro-chemical generation suffers from high energy consumption and low efficiency [71, 72]. Similarly, high-speed shearing impeller systems generate large quantities of NBs but require high power input and often produce unstable bubble sizes [17]. In contrast, devices such as Venturi injectors can improve efficiency, but their energy balance depends heavily on generator design, operational conditions, and scale [72, 73].

Since energy consumption is one of the main barriers to the large-scale application of NBs, strategies to reduce electrical demand during their preparation and optimize operating conditions for NB-assisted technologies must be prioritized. Whole-life cost calculations and energy balance analyses are essential to assess the feasibility of different generation technologies. Furthermore, exploring in situ NB formation during AOPs – such as bubbles produced in plasma oxidation or heterogeneous photocatalytic oxidation – offers an opportunity to reduce external energy input while enhancing ROS yields [50].

4.2 Capital and operational costs

NB generators are typically more complex and expensive than traditional aerators. Diffusion plate systems, though relatively simple to operate, require high-cost devices with micropores that are easily clogged, which include extra maintenance costs [71]. Jet dispersion methods avoid vibrations but still present operational complexity at scale [72]. Consequently, traditional aeration is cheaper and more robust compared to NB generators, which involve higher capital investment and the risk of fouling or scaling, thereby increasing lifecycle costs.

4.3 Scaling challenges

Although the benefits of NBs are well-documented at laboratory and pilot scales, achieving uniform and stable generation at full scale remains difficult. It has been proven that mechanical and chemical methods yield bubbles across a wide distribution, ranging from tens of nanometers to tens of micrometers, complicating consistent application [8, 72]. The absence of a scientific consensus on the stable generation and persistence mechanisms of NBs further hinders large-scale deployment [54]. Some of the main challenges regarding scaling include reactor hydrodynamics, mixing efficiency, and uniform bubble distribution [74].

4.4 Potential interference of ROS with microbial communities

Depending on several factors described above, NBs can produce ROS such as $\cdot$OH, singlet oxygen ($^1O_2$), or superoxide (O_2^-) when they collapse. Nevertheless, results may vary across studies. Some reports indicate significant disinfection and contaminant degradation related to ROS, while others detect negligible ROS activity under similar conditions [19, 75]. This uncertainty makes process control difficult. Excessive ROS levels could damage beneficial bacteria or extracellular enzymes, unbalancing the biological treatment ecosystem [76].

NBs can double dissolved oxygen levels and, under certain conditions in the water matrix, generate ROS. This may benefit aerobic processes, but such conditions may also disturb or inhibit strict microbial species developed in anoxic/anaerobic zones of biological reactors [47]. Alterations in microbial ecology, such as biofilm structural changes or shifts in dominant populations, could negatively impact processes like denitrification or biological phosphorus removal [77]. Therefore, the long-term stability of biofilms under continuous NB exposure must be assessed.

Despite the promising findings regarding NBs combined with biological and adsorption processes, the interaction mechanisms between them and organic contaminants remain incompletely understood. While ionic attraction and interfacial effects explain enhanced kinetics in heavy metal adsorption, organic molecules are structurally more complex and may interact differently with bubble surfaces. For instance, aromatic compounds or hydrophobic dyes may benefit more from increased surface hydrophobicity induced by NBs, while polar compounds may rely on electrostatic attractions. Understanding these dynamics is essential to optimize the global process.

4.5 Sensitivity to water chemistry

The stability and performance of NBs are deeply influenced by water chemistry, including pH, ionic strength, and the presence of chemical species such as surfactants and organic matter. Studies have shown that higher ionic strength and natural organic matter can destabilize NBs, accelerating their collapse and reducing their persistence [78]. This implies that complex water matrices, which contain diverse ions and organic contaminants, may not retain NBs long enough to achieve the expected benefits. Furthermore, changes in zeta potential, depending on gas type and water chemistry, directly influence NBs' stability and their interactions with pollutants [9, 79].

Further research is needed to systematically assess the effects of inorganic species and dissolved organic matter on NB properties, pollutant degradation efficiency, and the formation of potential by-products. Considering the full treatment cycle, it is also critical to evaluate risks associated with undesirable reaction products. For example, in NB-assisted ozonation, high bromide concentrations may lead to bromate (BrO_3^-) formation, posing regulatory and health concerns [50]. Developing strategies to predict and mitigate these risks will be essential for the safe and sustainable application of NB technologies in water and wastewater treatment.

4.6 Measurement and monitoring difficulties

Developing standard methods to precisely control the physicochemical properties of NBs is critical for advancing their application in water treatment. Achieving consistent regulation of parameters such as bubble size and concentration will improve the reproducibility of treatment outcomes and enable broader implementation. To this end, optimizing generation methods and establishing international standards are essential steps. A major challenge is that NBs are typically smaller than the optical resolution of conventional plant instrumentation, making their detection and monitoring difficult. Their characterization often requires advanced tools such as nanoparticle tracking analysis, dynamic light scattering, or zeta potential analyzers [9]. However, these instruments are not commonly available in municipal or industrial plants, limiting the operator's ability to confirm NB presence and stability in real time. Consequently, routine process monitoring and optimization are challenging, underscoring the need for cost-effective, accessible, and standardized monitoring technologies.

5. Conclusions and future prospects

NBs offer significant advantages in water and wastewater treatment due to their enhanced gas transfer efficiency, longer interaction with pollutants, and ability to generate ROS under specific conditions. Their effectiveness in improving flocculation, flotation, aeration in biological treatments, AOPs, and adsorption processes has been demonstrated at both laboratory and pilot scales. Nevertheless, several limitations still hinder their large-scale application. High energy consumption, equipment costs, and the complexity of maintaining stable and consistent performance during scale-up remain critical barriers. Moreover, uncertainties regarding ROS generation mechanisms, the influence of water chemistry on bubble stability, and the lack of cost-effective monitoring technologies complicate operational control. In the case of biological systems, potential long-term disturbances of microbial community balance cannot be underestimated.

Overall, this chapter concludes that NB technologies represent a highly promising yet still emerging approach for sustainable water and wastewater treatment. Future research should focus on optimizing generator design, reducing energy demand, and improving real-time monitoring tools to achieve stable, scalable, and economically viable implementation. Advancing the understanding of NB–microorganism and NB–contaminant interactions will be essential to maximize treatment performance and ensure process stability in biological systems. Importantly, the potential of nanobubbles for the direct removal and degradation of micropollutants remains largely unexplored and deserves systematic investigation. Furthermore, integrating NBs into hybrid systems that combine advanced oxidation, adsorption, and biological processes could yield transformative improvements in both micropollutant removal and circular water management. Finally, the establishment of standardized testing protocols, operational guidelines, and life-cycle assessments will be key to ensuring the safe, efficient, and sustainable deployment of NB-based technologies at full scale.

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Conflict of Interest

The authors declare no conflict of interest.

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