

THE INCREASING CONTRIBUTION OF MICRO/NANO BUBBLE USAGE IN INDUSTRIAL PURIFICATION PROCESSES

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Abstract

Froth flotation is a proven and widely used method for fine particle separation in mineral processing and water treatment, but process efficiency decreases rapidly as particle size decreases. The separation of ultrafine particles, typically smaller than 10 μm , presents a significant technical challenge for mineral processing plants and environmental remediation efforts. Although various approaches can be considered (such as design, collector type, etc.), in recent years, the use of surface micro/nanobubbles in flotation has been recognized as an effective approach to increase removal efficiency and recovery. Compared to traditional macrobubble flotation processes, the unique surface and volume properties of micro/nanobubbles significantly enhance separation and treatment performance. Beyond ultrafine particle removal, dissolved air flotation systems are now being applied as a treatment and recovery methods in many sectors, including the food, pharmaceutical, paper, and chemical industries. This review provides a comprehensive overview of the current status by briefly outlining the fundamentals and applications of micro/nanobubble flotation.

Key words: Water treatment, Dissolved air flotation, Sustainable water management, Micro/nanobubble.

1. Introduction

Sustainable water management and reliable access to water resources are undoubtedly one of the most important complexities of recent years. Pollution resulting from increasing world population, climate change, and increased consumption coupled with increased agricultural/industrial practices pose serious challenges in water management. As a result, sustainable water management and control of water pollution are becoming increasingly importance. Although many water treatment methods, including sedimentation, adsorption, advanced biological treatment, nano-based and membrane technologies have been developed and successfully applied to reduce environmental impacts and water consumption, the current use of these methods is still far from the desired results depending on the pollution sources, energy dependencies and socio-economic characteristics of the countries.

Pollutants mainly classify as physical, chemical or biological sources according to their form in water and they are kept under control by treatment/cleaning methods compatible with their forms [1]. For example,

dissolved and suspended inorganic substances such as metals, inorganic fertilizer, sulfides, ammonia/nitrides can be given as examples for physical form, while, mineral oil, paints, surfactants, phenol, pesticides, bacteria, viruses and molds can be given as an examples of the most common organic and biological substances (Fig. 1).

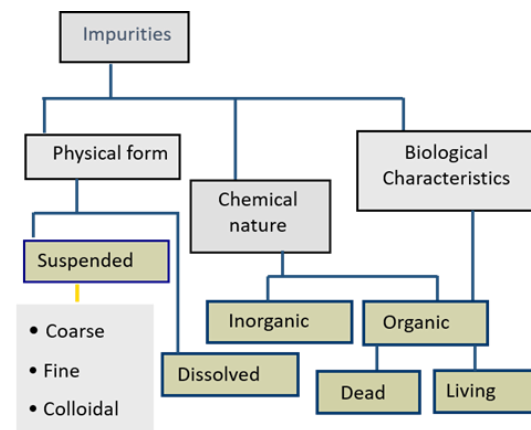


Figure 1 Classification of impurities according to their physical form [1]

In applications, treatment methods are used alone or in combination with each other, in the early stages of the process or at the end, in a series of separation stages such as second and third stage separators. The choice of treatment processes for any particular application

depends on the quality of received effluent, type of pollutant, required quality of the treated water and the economic resources available to pay both capital operating cost [2, 3]. The methods which have been currently use are summarized in Fig. 2.

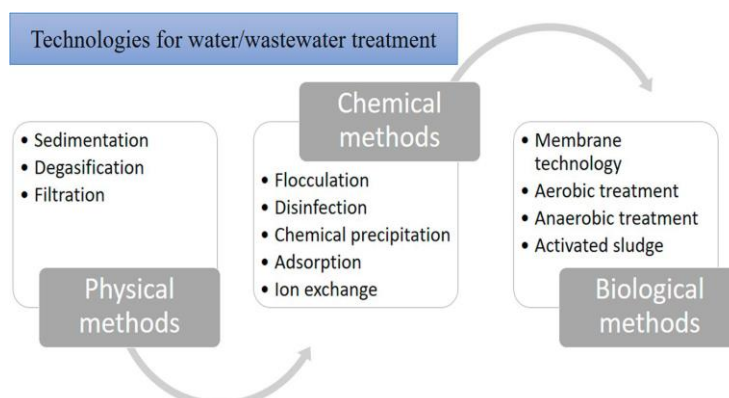


Figure 2 The methods used for water and wastewater treatment [1]

Mining and metallurgical operations are one of the areas that must be monitored with great care in terms of pollution sources. These applications inevitably generate large volumes of process water contaminated with fine particles, chemicals, metal ions, oils and others. The traditional method for heavy metal removal from these sources has been sedimentation-sedimentation followed

by thickening or filtering of the sludge. However, the method presents several limitations such as sedimentation, chemical instability of precipitated slurry of sediments and large volumes that are difficult to filter, which has led researchers to seek different methods such as flotation. The advantages of DAF over sedimentation are summarized in Table 1.

Table 1 Advantages of DAF over Sedimentation

Advantages of DAF	Sedimentation
Ability to working less solids content (weight/weight basis) (%)	Mainly suited to work at raw waters with high-density suspended solids
Higher hydraulic loading rates	Comparatively lower hydraulic rates
Workability at low-density floc (coagulation) with high recovery (TOC)	High recovery generally for high density flocks
Allows lower coagulant dosages resulting in smaller chemical storage and lesser sludge	Comparatively higher coagulant dosages
Improved algae removal and cold water performance, good to excellent removal of harmful pathogens such as Cryptosporidium and Giardia	Less sensitive to algae removal
Less post-processing requirement if a skimmer used	Requires post-processing

Flotation actually is a widely used method in mineral processing and beneficiation to effectively separate mineral particles. The method based on the binding of hydrophobic or conditioned particulate matter to gas bubbles and the introduction of gas bubbles as a transport medium was first developed for the separation

of minerals in the mining industry and was adapted for fiber separation in the 1930s by the paper industry [4]. Since then, the process has been continuously developed; in the early 1960s, it was first used for drinking water treatment outside of mineral processing. Based on the bubble formation mechanisms, it can be divided into

three categories: dispersion, dissolved air, and electroflotation. Among these applications, dissolved air flotation (DAF) is a continuously growing option in the treatment of paper mill and refinery wastewater, tertiary treatment of municipal water, recycled paper deinking, wastewater recovery and drinking water treatment. The general application of DAF for the cleaning of metal contaminants is adsorptive colloid flotation, in which hydroxides, insoluble salts or complexes with surfactants are used, or is a carrier flotation using particles have high surface area and suitable for flotation such as mineral particles, polymeric resins, activated carbon [5, 6]. Recently Kyzas et al [7] stated that in 2021, there were over 90 water treatment installations operating in the U.K. utilizing the DAF process and around the world it has been reported that there were 37 works in Finland, 26 in Australia, 26 in South Africa, 20 in the United States, etc.

2. Dissolved air flotation (DAF)

2.1. Brief History

Flotation method has been accepted as an important mineral beneficiation method in mining industry since 1860. The process still keeps their importance specially to perform selective mineral separation at large scale. Besides the mineral processing applications, it was first adapted in the environmental industry on the separation of fiber in 1924. Although its introduction into practice dates back to relatively earlier years, the widespread use of dissolved air flotation in water and wastewater treatment, particularly in South Africa and Europe, has been since the 1960s [8, 9, 10]. The first DAF plant for drinking water treatment was built in Finland in 1965 and by 1988, 34 plants were in operation [11].

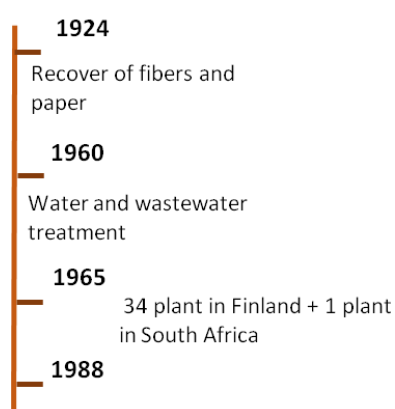


Figure 3 The methods used for water and wastewater treatment

At about the same time, in the United Kingdom, the first full-scale water treatment plant using the DAF process was commissioned in 1976 at the Glendye Treatment Works of Grampian District Council, Scotland. This initiative resulted in the development of more than 90 additional DAF facilities over the next 25 years. Typical design for DAF plants in the UK was based on flocculation times typical of sedimentation, while surface loading rates were higher than the norm for Scandinavian DAF plants, up to 12 m/h [12].

The use of DAF in USA and elsewhere is relatively recent compared to Europe. The first treatment plant based on the Krofta design was commissioned in 1982, and a total of five treatment plants were constructed by 1990. The first tap water treatment plant using DAF was commissioned in 1993. This plant used conservative design parameters based on previous achievements, such as three flocculation stages, total flocculation retention times of 20 minutes, and DAF loading rates of 6 m/hr. Although conservative parameters were used in this first application, in the following years the development of new design parameters such as high efficiency of modern equipment, new designs, low sludge formation and high productivity have allowed the use of DAF in more and more facilities around the world. For example, a large-scale (75 Ml/day) high-rate DAF plant in Manaus, Brazil in 2002 can be given an example of increased process capacity [12].

In recent years, the integration of microbubble (MB) and nanobubble (NB) technologies into treatment processes has increased the interest in flotation methods in particular. The advantages of its bubble structure and media properties make DAF a reliable and preferred method for wastewater treatment beyond mineral processing applications. Today, it finds numerous applications in the treatment of liquids with varying properties, from drinking water to wastewater and industrial water. In these applications, the treatment efficiency of DAF has encouraged the integration of hybrid technologies that have yielded positive results in pollutant removal. In addition to fine solid particle removal, it has also met environmental discharge standards such as turbidity, color, Total Suspended Solids (TSS), Chemical Oxygen Demand (COD), and Biochemical Oxygen Demand (BOD). It can also be applied in the removal of oil, grease, and antibiotic removal from the pharmaceutical industry wastewater. Statistical data on the number DAF documents obtained from Scopus data in the last 10 years and their distribution according to their application areas are given

in Fig. 4. It is clearly indicated the remarkable increase on the number of DAF research in recent years. Beyond the increasing number of research and publications, forecasts for the potential use of DAF systems in the

global water treatment industry indicate a growing trend. DAF Systems market size was valued at USD 2.4 billion in 2024 and is projected to reach USD 3.8 billion by 2033 at an increasing annual growth rate (CAGR) [13].

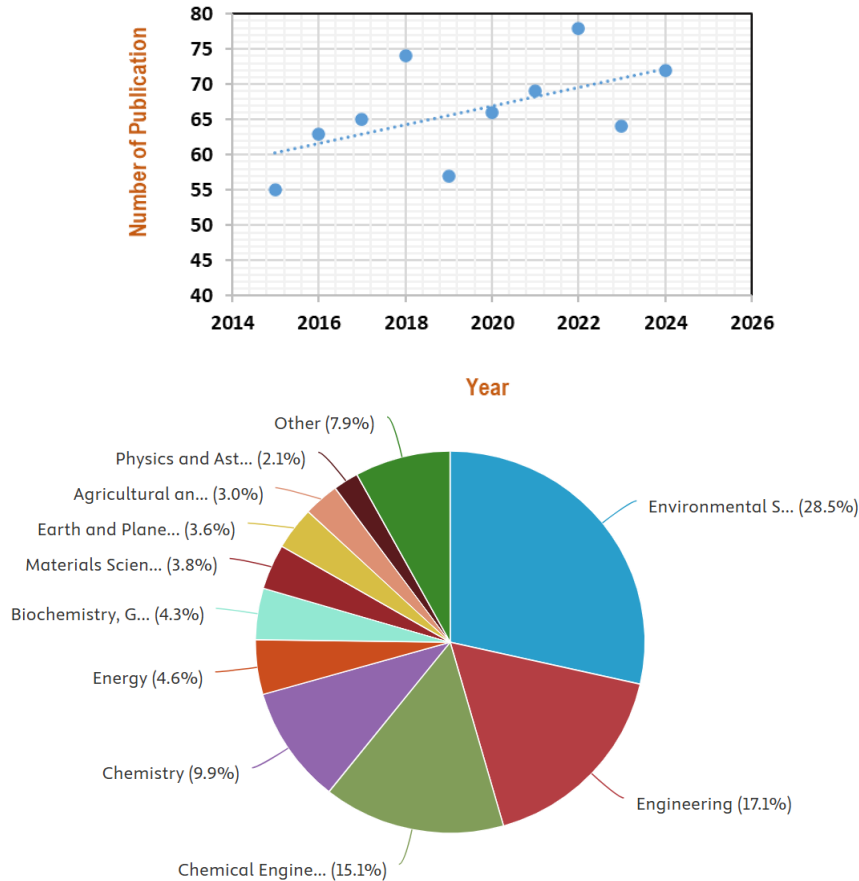


Figure 4 Number of documents on DAF over last 10 years and their subjected areas from Scopus data (<https://www.scopus.com/sources>)

2.2. Contribution of Micro/Nanobubbles on Process Efficiency

Future expectations for today's wastewater treatment technologies largely focus on processing efficiency and economic benefits. In this context, selectivity, short processing times, high efficiency, process simplicity/economics, and environmental compatibility are driving interest in new modifications and new techniques for existing processes. Air is one of the most fundamental components of the gas-liquid flows used in water and wastewater treatment. Air addition helps reduce treatment plant size, shorten operating times,

reduce operating costs, and simultaneously increase treatment efficiency. Compared to other applications, flotation is an excellent example of a well-established technology that has yielded positive results in many applications. Operating costs are low, and the technology is robust. In addition to its high fine particle separation efficiency, separation efficiencies range from 90% to 99%, despite low algae density and the size difference between algae and microbubbles.

In flotation processes, the general assumption is that the smaller the bubble diameter, the greater the likelihood of bubble-particle interactions (collisions and adhesion). Bubble stability is another factor that significantly affects

removal efficiency. Low rise velocity and dispersive electrostatic repulsion increase dispersion. Micro- and nanobubbles generally form a dense cloud characterized by a large total surface area, low rise velocity, long residence time, and high gas-liquid transfer rate. Although small bubbles contain the same air volume as large bubbles, their large number results in a significant increase in the total bubble surface area available for oxygen transfer. However, in micro- and nanobubble flotation applications, longer-than-necessary froth zone passages can be encountered as a limiting factor for efficiency (e.g., algae). In this context, one suggestion is to increase froth flotation efficiency by combining micro- and nanobubbles with macrobubbles [14, 15].

Generally, nanobubbles can be generated using three main categories of generators: gas with liquid flow,

gas without liquid flow, and low-power generators. The main methods used in these applications include pressurized aeration and dissolved air, electrolysis, ultrasonic cavitation, photocatalysis, solvent exchange, temperature difference method, Venturi tube preparation method, vortex-type micro-nanobubble generator, and membrane method. The most commonly used techniques are summarized in Table 2. More information on bubble generation can be found in a recent study by Chang et al. [16]. For the, micro-nanobubble generators, one of the key factors in choosing the method is the amount of power used for bubble generation. The higher the power used, the costlier the system becomes and the more heat is generated. In many cases, excess heat causes rapid bubble implosion, significantly reducing removal efficiency.

Table 2 Most commonly used techniques for micro/nanobubble production

Preparation Method	Most effective factors	Bubble type	Description	Target
Pressurized aeration and dissolved air	Value of air pressure.	Microbubbles, micro–nanobubbles	Dissolve air in a slurry under high pressure and then releasing after depressurization.	Removal of suspended solids, oils, and greases.
Electrolysis (Electroflotation)	Current densities and voltage windows is crucial for effective performance.	micro–nanobubbles	The primary driving force of the Faradaic reaction is the electrolysis of water at both electrodes (O ₂ anode, H ₂ cathode).	Removal of range of contaminants such as oils and low-density suspended particles.
Ultrasonic cavitation	Air flow rate, air pressure, frother concentration.	Microbubbles nanobubbles	Generation of tensile stress and negative pressure in liquid, followed by the escape and release of air from the liquid. The cohesive energy of water molecules between solid and water, the decrease in water pressure with increasing flow velocity, and the sedimentation of dissolved air in the form of air nuclei or nanobubbles.	Mainly fine particle removal.
Hydraulic cavitation				

2.3. Principle of DAF

DAF is a solid-liquid separation process based on the production of microbubbles as a result of the pressure effect and the transfer of solids to the liquid surface by binding of solid particles to fine air bubbles. In this sequential operation series, water is first saturated with high-pressure air, usually between 3 and 6 atm. The

saturated water is then forced to flow through needle valves, and bubbles (10-100 µm in diameter) are produced immediately downstream of the constriction, and finally, solids are separated by bubble-particle binding [17]. The mechanism of application of dissolved air flotation is based on the theory of reversible chemical reactors and Henry's law, which governs the dissolution of gases in aqueous solutions as a function of pressure [18].

In principle, two factors, bubble formation and bubble-particle interaction, have a direct effect on the working mechanism of DAF. For bubble formation, the first process is the nucleation process that begins when pressurized water and air are released from the nozzle, while the second step is the transfer of excess air in the saturated water to the flotation tank in gas form. Although in this step the bubbles begin to increase in size due to coalescence and decrease in

hydrostatic pressure as they rise from the flotation tank, the air volume remains constant. Bubble-Particle attachment performed by collision or precipitation of air on the solid surface, bubble entrapment in a floc structure, and bubbles being absorbed in a floc structure while the floc is forming. Adhesion or collision, entrapment, and absorption are the sequential mechanisms in bubble-particle bonding (Fig. 5).

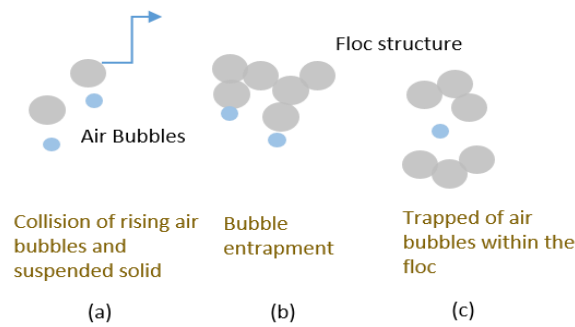


Figure 5 Bubble particle attachment

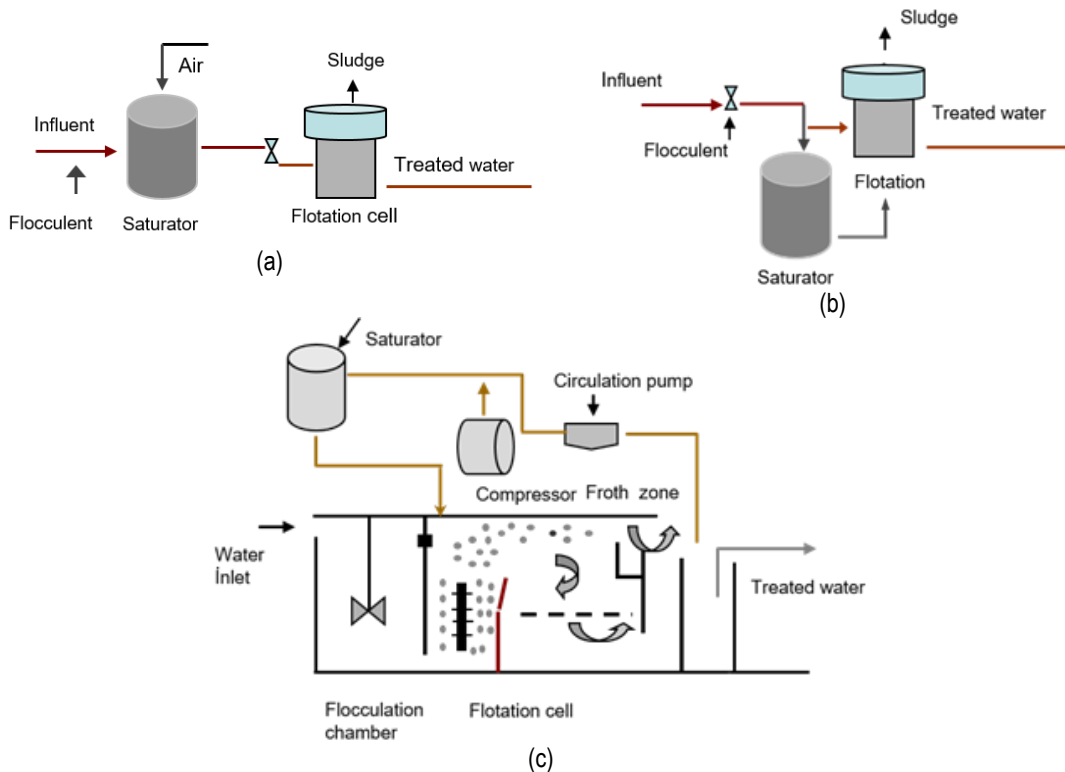


Figure 6 Split flow operational modes (a), recycle flow (b) and rectangular flotation tank with recycle flow system (c) [22]

DAF is mostly applied alone for mineral enrichment processes, while it is used together with coagulation/flocculation for clarification and wastewater cleaning processes. Such usage of coagulation and flocculation pretreatment steps ensures improvement in the efficiency of the bubble-particle capture during flotation. In order to achieve good agglomeration between the particle and the bubble, the particle must be destabilized. However, the particle must meet two most important conditions: neutral charge and hydrophobic surface. Under these conditions, the bonding between the particle and the bubble is very strong, resulting in successful flotation. The coagulation process, which results in the formation of a fluid, low particle charge, and hydrophobic particle surface, requires appropriate dosage and pH value. In order to achieve good agglomeration between the particle and the bubble, the particle must be destabilized. However, the particle must meet two most important conditions: neutral charge and hydrophobic surface. Under these conditions, the bonding between the particle and the bubble is very strong, resulting in successful flotation. The coagulation process, which results in the formation of liquid, low particle load and hydrophobic particle surface, requires appropriate dosage and pH value. In potable water treatment, the flocculation-flotation-filtration process chain is a common concept. The importance of flocculation in these sequences is obvious because of its direct effect on flotation performance and subsequently on filter design and performance. Dissolved

air flotation is used in many industrial applications not only as an alternative to sedimentation plants, but also as a clarification method to improve filtration [19-22] (Fig. 6a to c).

2.4. Comparisons and application advantages

The main application advantages of DAF compared to sedimentation and the comparison of DAF with other flotation methods are given in Table 2 and Table 3, respectively. Although the energy costs required to generate microbubbles for DAF are high, compact structure and the high surface loading rate offer the opportunity for lower equipment and construction costs compared to sedimentation. This advantage is also valid when compared to high rate floc blanket, sand ballast or plate settlers. One of the main drivers for the use of DAF is the lower life cycle cost compared to a conventional sedimentation settler, especially for mechanical dewatering and limited land use requirements.

Compared to dispersed air flotation, DAF has the advantage of producing small bubbles (μm), which is the most interesting feature of the flotation process for use in clarification or water treatment processes. Because the smaller the bubble size, the larger the bubble-particle interface contact area and) higher the process efficiency (Table 3). Large bubbles produce turbulent flows that can disrupt the upper sludge layer. In addition, small solid particles have a greater tendency to adhere to small air bubbles.

Table 3 Comparison of flotation methods for mineral beneficiation and water treatment

Advantages	Froth flotation of minerals	Water treatment
Ability to produce micro-bubbles	600 - 2000 μm	30 - 100 μm (DAF) 100 - 600 μm (jet/columns)
Ability to working less solids content (weight/weight basis) (%)	25 - 40	<4 (DAF) 10 - 30 (jet/columns)
Workability on fine Particle size to float	10 - 150 μm	1 - 50 μm (not flocculated) and 1 - 5 mm flocs (with polymers)
Less bubbles rising velocity (m/h)	250 - 800 (appx)	0.7 - 30 (DAF) 30 - 1000 (jet/columns)
More number of bubbles (cm^3)	$9 \cdot 10^3 - 2 \cdot 10^2$	$6 \cdot 10^8 - 2 \cdot 10^6$ (DAF) $2 \cdot 10^6 - 9 \cdot 10^3$ (jet/columns)
Increased bubbles surface area (cm^2/cm^3)	100 - 30	4000 - 600 (DAF) 600 - 100 (jet/columns)

There are three kinds of pressures dissolved in air flotation that can be used: full-flow, spilt-flow, and recycle flow pressure flotation. Recycle flow: The influent flows

into the flocculation or flotation tank if flocculation process is not required. A portion of the treated influent is recycled, pressurized, saturated with air, and released to

the flotation tank. This type of flow is applied to influents that need coagulation and flocculation. It is a common type of flow, and it is used more often than other types.

In a recent review published by Ali et al. [23], it was noted that three factors: air pressure, recycle ratio and air-solid ratio affect the performance of DAF and the efficiency of this process. The authors suggested that the treatment performance can be greatly increased by applying the DAF process under optimum conditions before especially for biological treatment.

3. Applications

In most cases, DAF is an alternative process to sedimentation for the removing of suspended solid

particles, metallic ions, microorganism, and macromolecules. The technique offers several advantages, including better final water quality, rapid startup, higher rates of operation, and thicker sludge. Additionally, DAF systems need less space compared with normal clarifiers, and due to their modular components, they allow easy installation and setup. Rather than the unit operation, an application of DAF as an integrated with sorption or membrane processes has also recognized as an efficient and quite promising method especially for the removal of metal ions from waste/surface water [24-26].

A summary presentation of the application areas and advantages other than the bubble structure/mechanism compared to traditional treatment methods is given in Table 4.

Table 4 A brief presentation of the application areas and advantages over traditional treatment methods

Advantages of DAF	Disadvantages of DAF	Application areas
Compact design, high loading rates, small flocculation tanks, Low detention time, process flexibility through air loading	Not suitable for raw waters containing high concentrations of suspended solids.	Treatment of production sector wastewaters such as: metalworking industry, personnel care product, seafood industry, paper mill, meat industry, oil refineries and metal plating industry
High quality effluent generally less than 0.5 NTU.	Sensitivity to variable weather conditions such as snow and rain, need for protection.	Mineral beneficiation Cleaning of flotation enrichment wastewaters
Excellent removal ability for Cryptosporidium and Giardia	Although the cost of bubble generation is high, the lifecycle cost is lower than a traditional sedimentation settler, especially if there is a shortage of available land for the facility and mechanical dewatering of solids is required.	Landfill leachate treatment
Low taste and odor for short processing times.	Integrated application usually requires pre-treatment for applications while some applications also need post-processing.	Urban Drinking / waste water treatment

Heavy metal removal based on precipitation of metal hydroxides and subsequent thickening or filtration of the sludge is one of the traditional methods used for many years. However, this method has some limitations, such as incomplete precipitation, chemical instability of the precipitates and formation of large volumes of sludge difficult to filter. As an overcome these limitations it was reported that DAF method can be considered as a primary alternative separation technique for the treatment

of heavy metals (Ni, Cr, and Cu) from metal finishing process water by SEPA [27]. The results confirmed that DAF is more effective than sedimentation. Another study on the use of DAF for the removal of metal ions from solutions was reported by Rubio and Tessele, 1997 [28]. In this study, Zn, Cu and Ni were successfully removed from the solution by carrier flotation where the small-sized zeolite particles (as sorbent) and Fe(OH)₃ precipitates (co precipitant) were used as carrier. Results confirmed that

nearly 98% of the heavy metals removed could be obtained. The separation of arsenic from aqueous solution can also be given another example to the combined application of DAF for water treatment [29]. A pilot scale tests were showed that arsenic has been removed about 99% recovery by this method.

Not only an alternative to sedimentation, several laboratory and pilot scale applications confirmed that DAF can be considered as an ideal alternative treatment options for the clarification of paper mill and refinery wastewaters, treatment of municipal waters, recycled paper de-inking, wastewater reclamation and recently in drinking water clarification to improve filtration as secondary or tertiary stages. A research study conducted by Bourgeois et al. [30] on the treatment of drinking water residuals showed that DAF can be used effectively for the separation of solids of lower density. Pennsylvania-US, city of Waco and Atkins-North Saluda water treatment plants are the examples of a system that installed as pilot scale, which confirmed that it could efficiently remove algae, Giardia/Cryptosporidium and iron /manganese ions provided with low turbidity, exceeded filter run times and high sludge solids for dewatering. The South San Joaquin Irrigation District, CA-US can also be given as an example for the treatment of raw water having high TOC, color and algae by DAF. The pilot study verified that a combination of DAF and membrane technologies without employing polymer was a winning solution for the treatment plant [31]. A recent study published by Kurama et al. [22], showed that DAF can be evaluated as an alternative method for the removal of ammonium (NH_4) ions from surface water. Natural zeolite, clinoptilolite samples with fine particle size ($<10 \mu\text{m}$) were used as carrier material during flotation tests. The tests results revealed that test loaded with 5 mg/L ammonium resulted in a residual ammonium concentration of $<0.5 \text{ mg/L}$ with corresponding turbidity values of treated water ($<10 \text{ NTU}$).

A number of studies in the literature have shown that coagulation with ferric and an aluminum metal salt combined with DAF is an effective method for the treatment of oily wastewater with a removal performance of over 90% [32–35]. Apart from these known salts, there are many studies in the literature focused on the use of more environmentally friendly and low-cost adsorbents. Among the alternative adsorbents, one of the most interesting materials is organoclay (OC). The term organoclay describes clay minerals, mostly belonging to the illite group, modified with quaternary ammonium cations. The usability of organoclay integrated with DAF

was investigated in a relatively recent study by Younker and Walsh [36]. In this study, the treatment capacity of the integrated process was compared with the individual unit processes of FeCl_3 coagulation and organoclay adsorption followed by DAF. In experiments three different treatment configurations, ferric chloride coagulation-DAF (FeCl_3 -DAF), organoclay adsorption-DAF (OC-DAF) and integrated adsorption-coagulation-DAF (OC- FeCl_3 -DAF) were tested. It was reported that coagulation performed with organoclay is very effective for dispersed oil removal even at relatively low FeCl_3 doses but its efficiency is highly dependent on the OC dose and mixing time. The results of the OC- FeCl_3 -DAF integrated treatment shown that the reduction of oil and grease concentration to below 30 mg/L is possible. Increasing the FeCl_3 dose from 10 to 50 mg/L significantly ($p < 0.05$) improved oil and grease removals in the integrated trials. Therefore, the authors concluded that coagulation, rather than adsorption, was the main mechanism for dispersed oil removal in the integrated treatment process.

A study on reducing algae load for drinking water applications was conducted by Jung et al. [37], using the DAF technique and reported that DAF had a sufficient effect because algae were characterized by their buoyancy, low cell density, small size and negative surface charge. These results support the previous study by Teixeira and Rosa reporting that the DAF technique was more effective than sedimentation for the treatment of algae-rich water. However, in both studies, the dose and type of coagulant, coagulation, flocculation and DAF operating conditions were the main parameters for removing bacterial cells [38]. Another study supporting the potential of DAF in the treatment of oily wastewater was reported by Yu et al. [39]. The results noted that DAF could remove 90% of oil and 92.5% of chemical oxygen demand (COD) in the treatment of oily wastewater.

Another interesting research result on the application of DAF was reported by Ortiz-Oliveros et al. [40], for the treatment of radioactive liquid wastes originating from the nuclear industry. In this study, it was emphasized that the DAF process supported by a coagulant/flocculent system consisting of a modified cationic polyamine and a light cationic polyacrylamide is a viable alternative for the treatment of oily wastewater contaminated with radionuclides produced in nuclear power plants.

An example of the possible contributions of DAF use in production processes can be given for the paper industry. The paper industry is one of the largest sectors

in terms of water consumption in the production process. Therefore, under strict environmental legislation, reducing both production costs and water use makes water management important for this sector. Closed systems, which minimize fresh water usage in terms of water management, are the most preferred methods. However, the increasing concentration of suspended, colloidal and dissolved substances with different properties in the reused water during production processes, causing unwanted blockages in purification and circulation systems, and the negative effects of impurities included in the production process and incompletely purified water on product quality is important problems that need to be eliminated. The most appropriate approach to eliminate these problems is coagulation/flocculation and DAF application. For this process, it is clear that the appropriate use of flocculation reagents before the flotation process is one of the factors that determine the treatment performance. In this context, the study conducted by Miranda et al. [41], investigating the charge density of cationic (C-PAM)/anionic polyacrylamide (A-PAM) with a coagulant in single and double treatments and the removal of dissolved and colloidal material with DAF is important in terms of its contribution to practical use. The results showed that for single systems, good results can be achieved with both low and high charge C-PAMs (1.0 and 3.0–3.5 meq/g), while for double systems, high charge C-PAMs (3.0–3.5 meq/g) and A-PAMs (1.5 meq/g) are the most efficient options.

For many metalworking industries, water use is an essential part of the system. Water is intentionally added to cool, lubricate or prevent rust in the contact area between the machining tools and the work piece. This water needs to be cleaned for storage after use. Traditional physical and chemical techniques are usually used for this purpose and usually have single or multiple stages depending on the final purpose. This situation creates difficult conditions to control for many plants. A study focusing on the usability of DAF as an alternative to conventional treatment methods was recently proposed by Amin et al. [42]. In this study, the final treatment of industrial wastewater contaminated with metalworking fluids was carried out using a chemically added dissolved air flotation (CA-DAF) unit followed by a photo-Fenton process. The authors noted that this hybrid approach revealed removal efficiencies of 99.85% and 98.9% for COD and TPH in the optimized photo-Fenton process as pH 3, FeSO₄: 100 mg/L, and H₂O₂: 17.8 g/L. In addition, the cost analysis for energy (6 kWh) and chemicals

(0.01818 kg FeSO₄ and 17.15 kg H₂O₂) consumed for the proposed process was calculated as approximately \$26 per m³ DAF waste. These results indicated by the authors that the CA-DAF unit followed by photo-Fenton is an effective and practical method for the treatment of metalworking wastewater. An example of possible proposal for the use of DAF integrated with biological treatment systems was presented by Özgün et al. [43] for a multistage sewage treatment scheme coming from different production lines in the confectionery industry, producing approximately 170,000 m³ of wastewater per year. The wastewater treatment system consisted of a conventional activated sludge system with screens, equalization tanks, dissolved air flotation, anaerobic expanded granular sludge bed reactor (EGSB) and sludge treatment line. The research results proved that COD in an anaerobic reactor reached 88%, while the use of an anaerobic reactor led to a 95% reduction in COD. These results are encouraging for the use of anaerobic technology as a pretreatment before conventional oxygen treatment. Another interesting application was reported by Li et al. [44] This study used the flocculation-flotation method for wastewater pretreatment to investigate the removal rate of organic pollutants in reconstituted tobacco wastewater used in papermaking. Research has shown that under optimal conditions, the operating cost of wastewater pretreatment using the flocculation-flotation method is 2.72 yuan per ton.

Apart from the water industry mentioned above, an interesting application for DAF usage in mining industry has recently been released by Santos et al. [45]. In this work, a wastewater treatment using DAF, associated with coagulation and flocculation, has been investigated to develop an alternative process for the reuse of the water from tailings dams of an industrial apatite flotation unit. The recycling water had the following characteristics: 288 NTU for turbidity, 2.25 mg/L for fluoride, 35 mg/L for calcium, 15 mg/L for magnesium, and 33 mg/L for phosphate (P). Results have shown that the use of recycling water after the wastewater treatment resultant a good performance of apatite flotation, leading to recovery (80.5%) and grade (31.2%) of P₂O₅ highest than minimum acceptable in this industry. More recently the DAF process was evaluating to test its efficiency for the treatment of coal industry wastewater in order to reuse water in the beneficiation plant by Cuoto et al., [46]. It was proposed that possible to obtain good turbidity removal efficiencies (up to 98%) using low concentrations of coagulant (50 mg/L) and flocculant (0.5 mg/L). In experiments air saturation pressure in the saturator

vessel was 4.5 bar (450 kPa). The flow of air-saturated liquid was controlled according to the recycle ratio of 30%. The results emphasized that the possibility of using the DAF as an alternative technique for treating wastewater from coal mining, allowing the reuse of water in the plant. It was noted that the iron chloride coagulant was more effective in conjunction with the previous addition of the flocculating agent into the air saturation tank, making it possible to obtain high removal efficiencies of corrected turbidity (above 98%) with small coagulant dosages (50 mg / L) and Nalco flocculent (0.5 mg/ L).

As mentioned earlier, one of the most significant challenges we face today is water scarcity, undoubtedly a consequence of increasing urbanization and climate change. This necessitates sustainable water management. The high efficiency of modern equipment, innovative designs, low sludge formation, high productivity, and low implementation costs make DAF an important alternative method for expanding its use in green technology [47].

Beyond advances in processing techniques, rapid advances in computer science over the past decade have led to a significant expansion of available data and the increased application of machine learning and artificial intelligence methods in a variety of fields, from everyday life to advanced scientific applications. These developments, impacting areas such as voice and facial recognition, autonomous vehicles, spam filtering, and social media platforms, clearly demonstrate the potential positive impact of these technologies on many production processes on a global scale. In this context, an increase in the number of research studies proposing potential solutions using machine-generated and artificial intelligence techniques to address the complexities encountered in mineral beneficiation processes is also observed. These models offer successful solutions for optimizing many critical application parameters that affect the efficiency of flotation processes. In a paper published by Maia et al. [48], a specialized device for microscopic image capture was used to investigate the effects of water velocity on floc size distribution and overall color and turbidity removal efficiency for DAF. Analyses conducted for laboratory and pilot plant sizes indicated that the application could yield positive results. A recent study by Galas and Litwin [49], analyzed the relationship between the stability of the flotation process and the efficiency of Machine Learning (ML) algorithms based on flotation foam images. The results demonstrate that estimating foam content using an ML

algorithm based on foam surface images is feasible and successful. In another study, Bendaouia et al. [50], proposed a novel approach based on a Convolutional Long Short-Term Memory (ConvLSTM) neural network for real-time monitoring of chemical composition gradients in flotation foam. This model aims to better understand the dynamic behavior of the foam surface during flotation processes by effectively extracting spatial and temporal patterns from video data. The authors report this model as an accurate and reliable model. Information on application examples covering research on determining/controlling flotation variables (grades and recoveries, purity, particle properties and hydrodynamic conditions) using various machine learning and deep learning methods can be found in recent reviews [51, 52].

4. Conclusions

The high efficiency of modern equipment, new designs, low sludge formation, high productivity, and low application costs are the main drivers for the extended use of DAF in the field of green technology. However, the process faces some challenges, such as being unsuitable for raw waters with high concentrations of suspended solids, limitations due to flotation freezing – which leads to the sedimentation of previously floated solids under certain weather conditions – and relatively high costs compared to simple sedimentation. Nevertheless, it is expected to become more widespread as increasing optimization with artificial intelligence allows for close monitoring of the flotation process and prediction of characteristic bubble parameters such as shape, size and rise speed.

Note

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POVEĆAN DOPRINOS UPOTREBE MIKRO/NANO MEHURIĆA U INDUSTRIJSKIM PROCESIMA PREČIŠĆAVANJA

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Izvod

Flotacijska koncentracija je dokazana i široko rasprostranjena metoda za izdvajanje sitnih čestica u pripremi mineralnih sirovina i tretmanu voda, ali se efikasnost procesa brzo smanjuje sa opadanjem veličine čestica. Koncentracija ultrafinih čestica, tipično manjih od 10 μm , predstavlja značajan tehnički izazov za postrojenja za pripremu mineralnih sirovina i prilikom remedijacije životne sredine. Iako se mogu razmatrati različiti pristupi za rešavanje ovog problema (kao što su projektovanje postrojenja, vrsta kolektora, itd.), poslednjih godina, upotreba površinskih mikro/nano mehurića u flotaciji je prepoznata kao efikasan pristup za povećanje efikasnosti koncentracije i iskorišćenja. U poređenju sa tradicionalnim procesima flotacije makro mehurićima, jedinstvena površinska i zapreminska svojstva mikro/nano mehurića značajno poboljšavaju razdvajanje i performanse procesa prerade. Pored uklanjanja ultrafinih čestica, postrojenja za flotaciju rastvorenim vazduhom se sada primenjuju kao metode tretmana i rekuperacije u mnogim sektorima, uključujući prehrambenu, farmaceutsku, industriju papira i hemijsku industriju. Ovaj pregledni rad pruža sveobuhvatan osvrt na trenutno stanje ukratko izlažući osnove i primene flotacije mikro/nano mehurićima.

Ključne reči: Tretman voda, flotacija rastvorenim vazduhom, održivo upravljanje vodama, mikro/nano mehurići.
