

INTERFACE SCIENCE AND TECHNOLOGY

Advanced Low-Cost Separation Techniques in Interface Science

Edited by
George Z. Kyzas
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Advanced Low-Cost Separation Techniques in Interface Science

Interface Science and Technology

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Chapter 2

Flotation: recent innovations in an interesting and effective separation process

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1. Introduction

The importance of flotation, as a separation process, to the economy of the whole industrial world is considered to be enormous. Without this process, many familiar metals and inorganic raw materials would be exceedingly scarce and costly because the high-grade ores that could be processed by simple physical and mechanical methods have long since been used up. It is believed [1] that the historian Herodotus, in ancient Greece, is probably the first person who described a process similar to flotation in the 5th century B.C. for the separation of gold particles from sand using fatty substances. Later, in the 15th century A.D., the Arabs used resins for the selective separation of azurite from gangue. These are considered to be the historical roots of flotation.

Let us also give a reference to Bohemians, using a basket for wet sieving a pulverized ore, in perhaps the first published book in the area (*De Re Metallica*), in 1556 by Saxonian Georgius Agricola written in Latin; this is the beginning of the development of the mining and metallurgical sciences. Since then of course much time has passed with significant technical advances, which of course cannot be covered in a few lines. The increasingly complex mineralogy and lower grade of many current ore reserves have forced technology to evolve rapidly in the decades to treat these materials economically.

Various types of the flotation process exist, being tested at different scale and hence, the respective terminology, i.e., ion, precipitate, adsorbing colloid, froth, foam, sorptive, biosorptive flotation, and so on. While here, in the

aforementioned list, due to the different (air or gas) bubble generation methods available, there should be included dispersed air, electrolytic, and dissolved air flotation (termed DAF). The latter usually requires previous flocculation, as it was examined in-depth in a recent review [2]. In the case of fine particles, their agglomeration may lead to greater capture efficiency. An overview of the effects of particles on bubble surfaces was published [3].

Fig. 2.1 illustrates graphically and in brief our group's history and contribution in the area. As “chemicals,” one may include collectors, surfactants, dispersants, modifiers, and as “feed it could be oil and grease, plastics or inks (for paper recycling), etc. This scheme was inspired from a schematic representation of separation methods based on surface activity and wettability, by Fuerstenau [4]. The concept of unit operations, overtime, and subsequent concepts in chemical technology have evolved into a unified field of separation processes [5].

Certain significant activities in flotation research have been recently described, with main focus in the contribution of physical chemistry to flotation, such as zeta-potential measurements, contact angle, etc. [6]. There has been phenomenal progress in flotation chemistry and chemicals—both in design and manufacture; there are also many new concepts and tools on which we can capitalize [7]. Mineral, metal values, and by-products can be recovered by flotation separation. The economic aspect of the recovery of useful valuable minerals (such as gold), contributing to recycling meanwhile with environmental technology and wastewater treatment, was enlightened, for instance, of gold from arsenic-rich auriferous pyrite concentrates [8].

Furthermore, selective separation of pyrite from arsenopyrite in an auriferous bulk flotation concentrate, stockpiled in the mine area (in Stratoni Halkidiki, Greece), was found to be possible under carefully controlled flotation conditions; the latter could be beneficial to the gold recovering process. The removal of arsenic-bearing minerals from concentrates is becoming more important as environmental laws become ever stricter with regard to smelter emissions [9].

Nevertheless, to be fair, different extraordinary (even bizarre) flotation applications have been published: oil contaminated sand particles were noticed to self-assemble in order to form granular shells around air bubbles [10]. The

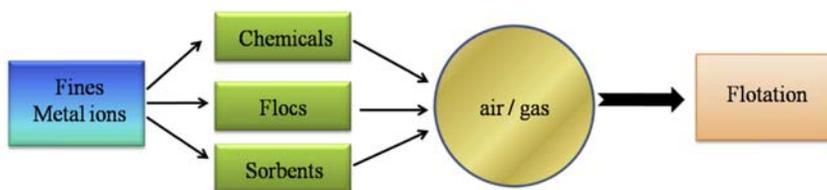


FIGURE 2.1 Scheme illustrating the experienced flotation techniques in the Laboratory.

most engineering application for the molecular self-assembly of sulfhydryl compounds on solid surfaces was elsewhere said to be froth flotation [11]. This idea was also forwarded by AFM measurements [12].

On the other hand, nowadays, flotation has been linked with sustainability; as for instance, in relation to deinking plants of the paper industry [13]; to the sulfidic mine tailings (among the largest mining wastes on Earth) that are prone to produce acid mine drainage [14]; and to the harvesting of algal biofuels [15], as for instance, harvesting imposes a major constraint in microalgal downstream processes (and production of various high value products). The possibility of reprocessing fine to ultrafine material from a tailing heap of an historic gravity separation circuit in Germany, by conventional flotation and by applying an oil-assisted agglomeration flotation approach, was investigated [16].

1.1 Background

Mineral particle attachment to air bubbles is the basis of the froth flotation process. A three-phase system is created, by various mechanisms, in which the following three interfacial tensions exert governing effects: (1) the gas–solid tension, (2) the solid–liquid tension, and (3) the gas–liquid tension, i.e., flotation being a quite unique (“peculiar”) separation technique or the encyclopedia of colloid science, as it was called by Nguyen and Schulze [17].

The former tensions determine together the contact angle concept introduced by the Young equation at the point of conjunction of the three phases [18]. The larger the contact angle, the greater the tendency of the bubbles to adhere with the particles. The fractional flotation efficiency, i.e., the fraction of particles contained at the fluid volume that are scavenged by the bubble, which will be permanently attached to the bubble is the product of the collision efficiency and the attachment efficiency. The influence of different flotation variables on the speed of adhesion between particles and bubbles was presented [19].

Regarding the physicochemical aspect of the bubble–particle collision process, two models are usually considered important: the electrostatic model (according to it the energy for the coupling of the particle with the bubble is due to electrostatic attraction between the particle and an interfacial surface carrying opposite charge) and the hydrophobic model (according to it the particles become hydrophobic after the adsorption of the surfactant and this allows their adhesion with the bubbles) [20].

Furthermore, there are three mechanisms mainly by which bubbles can assist the suspended solids in raising them to the surface: (1) adhesion of a gas bubble to a suspended or solid phase, (2) trapping of a gas bubble in a floc structure as the gas bubble rises, and (3) adsorption of gas bubbles in a floc structure, as the floc structure is formed [21].

Whether or not a colliding particle sticks to a bubble is a question of which surface forces come into play, when the aqueous film between the two has thinned sufficiently. It was shown that if a solid is hydrophobic (defined as forming a finite contact angle), very thin water films spontaneously rupture and shrink into a series of droplets, leaving dry areas between them [22]. These films must be subject to a negative disjoining pressure, devoted possibly to electrostatic attraction where the solid–liquid and gas–liquid interfaces carry electrical double layer of opposite sign.

Nevertheless, extremely small particles will be carried along the streamlines and will not make a close encounter with a bubble, unless they cross the streamlines by executing Brownian motion (diffusion) [23]. Only when the process of particle detachment is well understood and modeled, minerals recovery using the flotation process can be modulated to achieve a high efficiency by suitably changing the operating parameters [24].

It was proposed—a NATO Advanced Study Institute in Cornwall, UK (with an ominous title)—that the fine particle recovery may be enhanced by using fine bubbles generated by the (then) unconventional techniques [25]. It was elsewhere observed that by decreasing the bubble diameters the possibility of collision is increased; a narrowly sized sample of very hydrophobic particles was used in these experiments [26].

The hydrodynamic performance of very fine gas required for dissolved air (pressure) flotation, which is produced by dissolving air in water under pressure and subsequent flushing to normal pressure through a nozzle, was studied [27]. The results clarified the effects of dissolved pressure, liquid flow rate, and nozzle geometry, and empirical equations were obtained for the number of generated bubbles.

In general, it is known that, after the formation of bubbles, they tend to coalesce [28]; coalescence is the phenomenon where bubbles grow in diameter by feeding on small bubbles. Hence, bubbles coalesce when two bubbles collide and form a single one. There are three main factors that favor this: (1) the presence of bubbles having nonuniform diameters, where the larger bubbles gobble up the smaller by collision; (2) violent agitation tends to coalesce bubbles; (3) the presence of a large surface in contact with the bubble–liquid surface. The large surfaces serve as deposition points for the microbubbles, where coalescence can readily take place. Also, as the bubbles move toward the surface of the solution, they collide with each other; therefore, it is quite possible for coalescence to occur.

These phenomena, however, can be inhibited with the addition of surfactants because they (1) are adsorbed on the bubble surfaces during the flotation process, having their polar groups oriented toward the liquid. The surfactants are hydrated and eventually the bubbles are surrounded with a hydrated layer. This layer stabilizes the surface of the bubbles by forming a wet hymenion and thus prevents adhesion and reduces the coalescence potential by protecting the bubbles from rupturing. (2) They allow better adhesion of the bubbles to the

particles, ions, and solution constituents, thus permitting their effective transfer to the surface of the solution [29].

The importance of bubble charge in its effect on the rate of flotation of small particles was also investigated. In a single species pulp, i.e., an emulsion of oil in water, it could be possible to maximize the flotation rate by controlling the pH value of the emulsion, for example, to give essentially zero charge on the particle and perhaps on the bubbles [30]. In this case, the flotation rate would be maximum for the following two reasons: The electrostatic repulsion between bubbles and particles would be minimum. The conditions would also lead to coagulation of the oil droplets in order to form larger aggregates whose rate would be enhanced. Gas bubbles generally are reported to be negatively charged in pure water and in solutions of inorganic electrolytes [31].

The collision between a bubble and a particle is, therefore, the result of a combination of the interception phenomenon (finite particle size) and the tendency of particles to deviate from fluid streamlines (due to their velocity up and/or their inertia); the dependence of the attachment efficiency on the bubble diameter is not a general feature but depends on the particular conditions, for example, the particle density. A composite expression for the flotation frequency (frequency of successful bubble–particle collisions) in a combined gravitational and turbulent flow field was derived [32]. Flotation is, as mentioned, a complicated process combining many elementary physico-chemical steps also with fundamental hydrodynamics.

Its modeling is certainly important to understand the process, as well as it is a necessary tool for equipment design and optimization. Flotation units, as the chemical reactors, are distinguished as cells of ideal and nonideal flow; the superiority of countercurrent contact flow was particularly highlighted [33]. Flotation efficiency is generally expected to be a function of the residence time distribution. The stimulus–response technique is often used, where the tracer (a dye, electrolyte, etc.) input is usually of a pulse or step function. In an investigation of electroflotation hydrodynamics, a theoretical multiparameter model (by Levenspiel) was applied, consisting of interconnected dead water, back mix and plug flow regions, with bypass, recycle, and cross flow through and around these regions.

2. ROLE of particles—separation applications

2.1 Minerals

Agitated flotation cells are widely used in the mineral processing industry for separating, recovering, and concentrating valuable particulate material from undesired gangue. Their performance is lowered, however, when part of the particulate system consists of fines, with particle diameters typically in the range from 30 to 100 μm . For example, it was observed difficult to float fine

particles because of the reduction of middle particles (of wolframite) as carriers and the poor collision and attachment between fine particles and air bubbles; a new kinetic model was proposed [34].

As an alternative to agitated cells, bubble columns—used in chemical engineering practice as chemical reactors—were proposed for the treatment of fine particle systems. Flotation columns, as they came to be known, were “invented” back in the 1960s in Canada [35]. The main feature that differentiates the column from the mechanical flotation cell (of Denver type) is wash water, added at the top of the froth. It was thought to be beneficial to overall column performance since it helps clean the froth from any entrained gangue, while at the same time preventing water from the pulp flowing into the concentrate. In this way, it was hoped that certain cleaning flotation stages could be gained.

Let us note that the perhaps insistence here on mineral processing is only due to the fact that most of the available literature on flotation is from this area, where the process was originated and being widely practiced. The effect of particle size on flotation recovery is significant; it was shown that there exists a certain size range in which optimum results may be obtained in mineral processing. This range varies with the mineral properties such as density, liberation, and so on, but was said to be of the order of 10–100 μm [36].

Regulating the oxidation state of pyrite (FeS_2) and arsenopyrite (FeAsS), by the addition of an oxidation or reduction chemical agent and due to the application of a short-chain xanthate as collector (such as potassium ethyl xanthate, KEX), was the key to selective separation of the two sulfide minerals, pyrite and arsenopyrite [37]. Strong oxidizing agents can depress previously floated arsenopyrite. Various reagents were examined separately as modifiers and among them were sodium metabisulfite, hydrazinium sulfate, and magnesia mixture. The laboratory experiments were carried out in a modified Hallimond tube, assisted by zeta-potential measurements and, in certain cases, by contact angle measurements.

This conventional bench-scale flotation cell provides a fast, convenient, and low-cost method, based on small samples (around 2 g), usually of pure minerals and also artificial mixtures, for determining the general conditions under which minerals may be rendered floatable—often in the absence of a frother (to collect the concentrate in the side tube) [38]. This idea was later further modified in the lab replacing the diaphragm, in order to conduct dissolved air or electroflotation tests—see Section 3.

Pyrite concentrates sometimes contain considerable amounts of arsenic. Since they are usually used for the production of sulfuric acid, this is undesirable from the environmental point of view. However, gold is often associated with arsenopyrite, often exhibiting a direct relationship between Au content and As grade. There is, therefore, some scope for concentrating arsenopyrite since the ore itself is otherwise of little value (see Fig. 2.2). Note

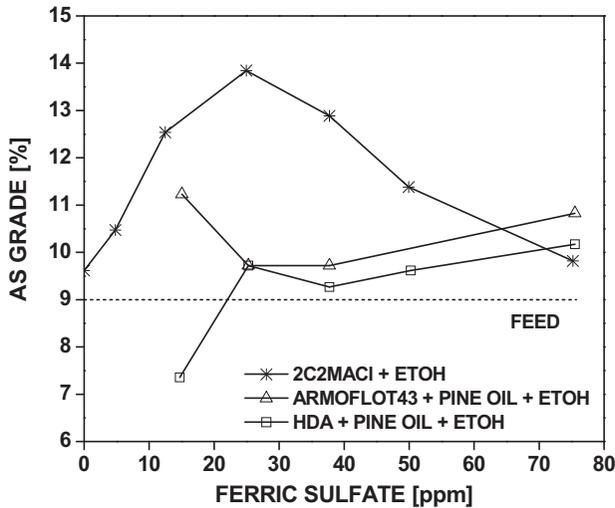


FIGURE 2.2 Effect of $\text{Fe}_2(\text{SO}_4)_3$, added as conditioner, on grade and recovery of arsenopyrite in column flotation. Reprinted with permission; copyright Pergamon Press P. Mavros, K.A. Kydros, K.A. Matis, *Arsenopyrite enrichment by column flotation*, *Miner. Eng.* 6 (12) (1993) 1265–1277.

that previous work on pyrites usually concentrated on the problem of floating pyrite [40].

In the aforementioned figure (shown as example), the following conditions were applied: (1) collector [2-coco 2-methyl ammonium chloride] 42 mg/L, frother (EtOH) 0.15% (v/v), superficial liquid velocity $u_L = 1.02$ cm/s, superficial gas velocity $u_G = 0.65$ cm/s, superficial wash water velocity $u_w = 0.53$ cm/s; (2) hexadecylamine, 45 mg/L; pine oil, 50 mg/L; EtOH, 0.025%; $u_L = 0.84$ cm/s; $u_G = 0.72$ cm/s; $u_w = 0.66$ cm/s; (3) Armoflot 43, 50 mg/L; pine oil, 50 mg/L; EtOH, 0.025%; $u_L = 0.84$ cm/s; $u_G = 0.71$ cm/s; $u_w = 0.66$ cm/s [39]. The pyrite (with a relatively important Au content of 21 g/ton) was a xanthate-floated concentrate. The presence of xanthates, however, might cause problems in the subsequent cyanidation of pyrites when recovering their Au value, which perhaps justified the need to find alternative collectors. In general, the amines exhibited a behavior similar to that of the xanthates (O-alkyl dithiocarbonates). The benefit of the amine was in its lower consumption, as compared with the xanthate systems.

The arsenic content of the pyrite was approximately 9% (from an initial 3.5% of the mixed sulfide ore). The material was sieved and the $-75 \mu\text{m}$ fraction was used for the laboratory-scale cylindrical column experiments. The effect on metallurgical characteristics of the flotation concentrate of varying the amount of ferric sulfate added to the pulp was studied; three collectors were used and their performance was compared (in Fig. 2.2). Both hexadecylamine and Armoflot 43 (manufactured by Akzo) exhibited an increased

recovery but a very low enrichment, whereas 2-coco 2-methyl ammonium chloride (Arquad-2C) showed a considerable enrichment; a compromise had to be made, therefore, between a high-grade and a low recovery.

Electroflotation (electrolytic flotation) is an unconventional separation process owing its name to the bubbles generation method it uses, i.e., electrolysis of the aqueous medium. In the bottom of the microcell, the two horizontal electrodes were made from stainless steel, the upper one being perforated. The current density applied was 300 A m^{-2} . It was observed that with lime used to control pH, different behavior was observed (see Fig. 2.3). Pyrite, with permanganate (a known depressant) also as modifier, remained activated from pH 5.0 to 8.0 at 80% recovery, while it was depressed at the pH range from 9.0 to 12.0. A conditioning of 30 min was applied in the presence of modifier alone and further 15 min after the addition of xanthate. The pure mineral sample, previously hand collected, crushed, and pulverized in the laboratory, was separated by wet sieving to the -45 to $+25 \mu\text{m}$ particle size range.

Pyrite due to its very heterogeneous surface, consisting of a mosaic of anodic and cathodic areas, presents a strong electrocatalytic activity in the anodic oxidation of xanthate to dixanthogen. It is also possible that the presence of the electric field, during electroflotation, affected the reactions taking place. In order to explain this difference in flotation behavior thermodynamic calculations for the system Fe-EX- H_2O have been done [41]. It was concluded that electroflotation was capable of removing fine pyrite particles

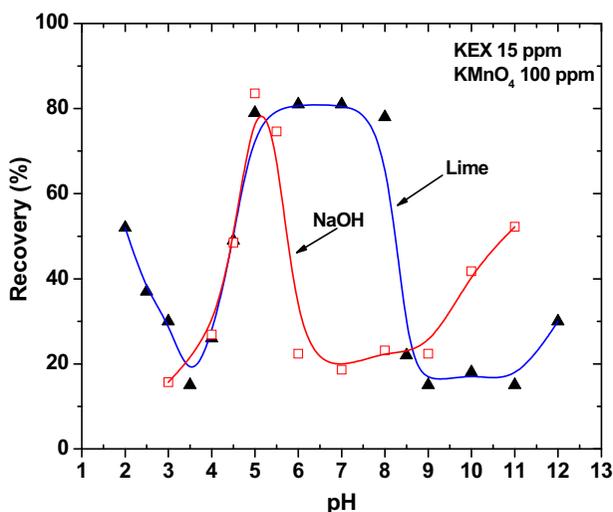


FIGURE 2.3 Electroflotation of pyrite: effect of the pH and regulators, lime, or sodium hydroxide. Reprinted with permission; copyright Society of Chemical Industry K.A.Kydros, G.P. Gallios, K.A. Matis, *Electrolytic flotation of pyrite*, *J. Appl. Chem. Biotechnol.* 59 (1994) 223–232.

from a dilute dispersion, under controlled conditions. Nevertheless, dispersed air and electroflotation presented apparent differences for the same application.

The size of the gas bubbles produced was of the order of 50 μm , in diameter [21]. Similar measurements were later carried out at Newcastle, Australia [42]; where it was also noted that a feature of electroflotation is the ability to create very fine bubbles, which are known to improve flotation performance of fine particles.

In fact, the two electrodes of a horizontal electrodes set, usually applied in electroflotation, could be separated by a cation exchange membrane, as only one of the produced gases is often necessary [43]. In the lower part/separated electrode, an electrolyte was circulated to remove the created gas, and in the meantime, increase the conductivity; hence having power savings (as the electric field is built up between the electrodes through the use of the suspension conductivity). Attention should be paid in this case to anode corrosion, mainly by the chloride ion (i.e., seawater).

Microorganisms have a tremendous influence on their environment through the transfer of energy, charge, and materials across a complex biotic mineral–solution interface; the biomodification of mineral surfaces involves the complex action of microorganism on the mineral surface [44]. Mixed cationic/anionic surfactants are also generating increasing attention as effective collectors during the flotation of valuable minerals (i.e., muscovite, feldspar, and spodumene ores); the depression mechanisms on gangue minerals, such as quartz, were focused [45].

2.2 Wastewaters

There is, in general, a “feeling” that a gap exists between froth (dispersed air) flotation and DAF; may be even for historical reasons, and this was the sub-theme of the United Engineering Foundation Conference on Flotation (organized by Profs. R.W. Smith and J. Rubio, held in Tahoe City, California, 2001). The aforementioned feeling perhaps originates from the separate areas of flotation application or in other words, the completely separate traditions and of course, the seldom interaction among them. But, mainly we may say, it comes from the different aims in these two fields:

- i) selective separation or not,
- ii) difference in particles concentration and/or size,
- iii) use or nonuse of collectors and other chemical reagents (modifiers, frothers) for environmental reasons, etc.; may be, the idea of collectorless flotation, if possible, is worthwhile.
- iv) From an economic point of view, the things are completely different: as mineral processing is obviously economically attractive, while no one “really” wants to pay (at least too much) to treat the effluents.

Certainly, the process originated from mineral processing; hence, a lot has been learned from this scientific area, being almost the encyclopedia of flotation for the beginners.

According to the drinking water fact sheet of WHO (updated July 2017), 884 million people lack even a basic drinking water service, and at least 2 billion people use a drinking water source contaminated with feces, i.e., clean potable water is not self-evident. It has been well established nowadays that dissolved heavy metals escaping into the environment pose a serious health hazard, hence justifying perhaps the scope of our research.

DAF is known as an effective solid–liquid separation process used in water treatment as an alternative to sedimentation [46]; the experience in the area of the Water Research Center, UK, including relative costs, was described. Refineries commonly use the methods of DAF and/or dispersed air flotation to remove free and emulsified oil from refinery wastewater. Two waste streams from an oil refinery wastewater treatment system, float from a DAF unit (DAF sludge), and waste-activated sludge were investigated to determine toxicity and biogas production potential for anaerobic digestion through batch testing [47]. It is known for long time now that (dissolved air) flotation is effective for activated sludge plants, both for clarification and thickening [48].

A computational fluid dynamics (CFD) model incorporating flotation kinetic expressions was developed to simulate the performance of flotation tanks utilized in water and wastewater treatment plants [32]. The focus was on tanks that operate without any external means of flow mixing (impeller, etc.), such as the DAF tanks. The flotation kinetic concepts such as collision, attachment, and detachment efficiencies were employed first time in CFD studies by Koh and coworkers [49]. Elsewhere, it was argued that with the recent advances in nanotechnology, environmental and health consequences of nanomaterial disposal merit close attention [50].

The two main bubble generation techniques were examined: DAF is quite different from the dispersed air flotation [51]. In DAF processes, microbubbles of 10–80 μm in size were said to be generated [52]. The trend in the development of DAF technology for potable water was to move to very thick microbubble beds with high flow rates—even advertised as the third-generation technology; a flow rate of more than 60 m/h was given, where flotation operation was approaching turbulent flow conditions. A compact (downstream filtration being in the same basin) so-called reflation plant with hydraulic flocculation was built, for instance, for Tampere Finland water and sewerage works in 1997 (by the company OY Rictor AB). One of the advantages of flotation was its speed, hence its ability to operate inside a factory, due to cold weather conditions.

The formation of macrobubbles, undesirable in DAF, was found closely to connect with the mechanisms operating in the depressurization zone [53]. The geometry of the nozzles had generally a strong influence on obtaining microbubbles: the greater the conic divergence angle, the smaller the bubbles

and the more restricted the size distribution; as the distance from the expansion zone was increasing, bursting and coalescence occurred simultaneously. Water coming out of the nozzle has the aspect of a milky cloud of bubbles. The influence of bubble size on the fluid dynamic behavior in a DAF tank was examined in another study [54].

The process was applied, for instance, to cadmium ion (10^{-4} M) removal, as presented in Fig. 2.4A, following the mechanism of precipitate flotation as hydroxide at pH 10–11 by surfactant sodium dodecylsulfate, as collector 2×10^{-4} M (in presence of 0.1% v/v ethanol, as frother). Cadmium is a highly toxic and rather ubiquitous metal in its distribution throughout the world. These experiments were run in parallel and under the same conditions: Dispersed-1: airflow rate $600 \text{ cm}^3 \text{ min}^{-1}$ for a retention time of 10 min, in a column of 34-mm diameter and 0.4 L content; air was entering the porous diaphragm with an excess pressure of ~ 1 atm. Dispersed-2: airflow rate $200 \text{ cm}^3 \text{ min}^{-1}$ for a retention time of 4 min. While in DAF (unit purchased from Aztec Environmental Control Ltd.), a 10% recycle ratio was used, with 1 L content initially. A photograph was previously shown with detailed information of our laboratory arrangement, of a typical continuous flow flotation rig [57].

So, the removal of cadmium (initially up to 10 mg L^{-1}) was near 100%, while the remaining concentration in the solution after flotation was less than 0.10 mg L^{-1} . The parameters that determine the optimum flotation conditions, except the pH, appeared not to be very critical. Flotation was concluded as an effective method that deserves perhaps more attention as an alternative treatment to other conventional methods, especially concerning dilute metal ion solutions, even in hydrometallurgical processes. Later, the flotation of cadmium ion was reseen, using this time potassium ethyl xanthate as

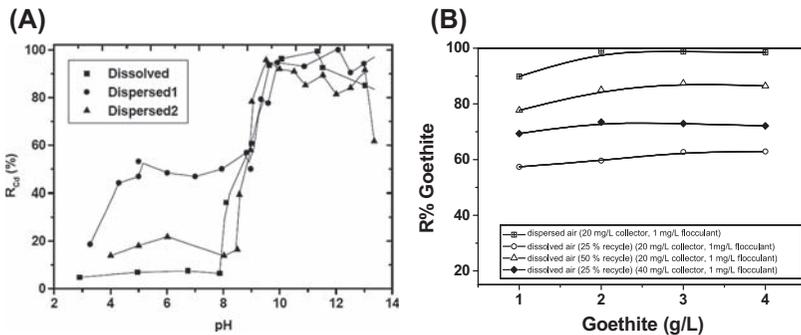


FIGURE 2.4 (A) Comparison of flotation techniques for cadmium ion removal: influence of solution pH. (B) Comparison of dispersed air with dissolved air flotation, for Cr(VI) removal on goethite. Presented in the 34th International Conference on Mining and Metallurgy, Bor, Serbia [55]. (A) Reprinted with permission; copyright IAWQ A.I. Zoubouls, K.A. Matis, *Removal of cadmium from dilute solutions by flotation*, *Water Sci. Technol.* 31 (3–4) (1995) 315–326.

precipitating agent [58]. The collectorless flotation of copper ion was earlier investigated by dissolved air, precipitated upstream as colloidal CuS [59].

The need for fresh sources of drinking water is becoming more and more urgent worldwide, including certainly many areas and/or countries across the Mediterranean Sea. Reverse osmosis membranes, on the other hand, are known to be very sensitive to foulants as colloids, inorganic scale, and biofouling; so, pretreatment (i.e., by flotation, among other) of their seawater feed is often a key step [60]. The economics is the usual worry in desalting water production [61].

2.2.1 Adsorbents

Carrier flotation (ultraflotation or “piggy-back” flotation) constitutes a technique to improve the flotability of fines; the known example of commercial application is that of anatase impurity being removed from kaolin clay by flotation using coarse calcite particles as an auxiliary mineral (the carrier) [62]. Adding an adsorbent (like powdered activated carbon) into the coagulation process is an emerging treatment solution for targeting hard-to-remove dissolved organic compounds from both drinking water and industrial wastewater [63]. The experimental tests were performed on synthetic oily wastewater.

Fig. 2.4B extends the aforementioned comparison between the two flotation techniques for the separation of metal-loaded goethite (1 g/L), at pH 4, following the mechanism of sorptive flotation. The advantage of dispersed air was obvious in this case; exactly similar results were obtained for the flotation of zinc-loaded goethite. The existing conditions applied were dodecylamine (20 mg/L) as collector, flocculant magnaflow 919 (1 mg/L); dissolved air: flocculation time = 5 min at 60 rpm—5 min at 300 rpm; the recycle was the main parameter studied (at least 20% was necessary); dispersed air: flocculation time = 5 min 350 rpm—5 min 700 rpm, air = 425 cm³/min. Meanwhile, the chromium(VI) removals were near 100% (from 50 mg/L initial concentration). The nanocrystalline sorbent, i.e., goethite, was previously synthesized [64] and had been tested as heavy metals (i.e., cadmium and pentavalent arsenic) adsorbent [65]. Other typical inorganic adsorbents satisfactory for heavy metals removal are certainly zeolites [66].

Perhaps, a special case of sorptive flotation constitutes the technique known as adsorbing colloid flotation (i.e., a type of carrier flotation), which involves the removal of the solute from the aqueous solution by adsorption on, coprecipitation with, or even occlusion in a carrier floc, produced by adding ferric or aluminum salts. A second stage involves the combination of flocs into larger aggregates, which are then floated with the help of an appropriate surfactant.

Bentonite and kaolinite clays were elsewhere published for the sorptive flotation removal of radioisotopes of europium [58] and pyrite for As(V) [67]. As well as, results were presented on the removal of Fe³⁺ ions, as precipitates

and nanoparticles of $\text{Fe}(\text{OH})_3$ by nanobubbles (generated at 2.5 bar, after their separation from microbubbles) and by DAF [68]. In parallel, the use of nanoparticles has attracted widespread interest for effectively removing pollutants (and in this treatment flotation was also included); so, carbon nanotubes were used for nickel ion [69] and silica nanoparticles for a dye [70].

2.2.2 Biosorbents

The ability of microorganisms to remove metal ions is a known phenomenon; biosorption was termed the process that makes use of dead biomass (contrary to bioaccumulation), coming usually from fermentation wastes or by-products. Metal recovery or removal from solution may involve various pathways [71]. A comparison of the various treatment processes for metal-laden wastewaters was published, among others, by Eccles [72] giving their characteristics and disadvantages when applied to dilute aqueous solution. May be the difficulty in biomass separation (harvesting) was advocated as one of the disadvantages of biosorption, and for this reason, flotation has been thoroughly examined in our lab.

A comparison of the floatability of various types of biomass has been carried out, over the whole pH range (presented as Fig. 2.5A). Four types of biomass were evaluated: *Streptomyces rimosus* (an actinomyces bacterium from tetracycline production), *Penicillium chrysogenum* (fungi used for antibiotics), *Saccharomyces carlsbergensis* (yeast for beer production), and grape stalks (a by-product of the winery industry). Improved biomass flotation recoveries were observed, some reaching almost 100%. These biomasses were tried as biosorbent for a synthetic aqueous mixture of metals in deionized water containing the following metals (in mmol dm^{-3}): Zn 0.765, Cu 0.157, Ni 0.034, Ca 2.49, and Na 4.35. The concentrations were selected as being representative of those commonly found in industrial wastewaters, whereas Ca and Na were also added to simulate the usual hardness of most metal-laden wastewaters.

Fig. 2.5B presents a conceptual flow diagram showing recycle routes of a total process (investigated under an EU environmental research program): the second cycle represents the applied flotation (or may be, sedimentation) separation. The solids are diverted to a filtration unit where they became immobilized as a filter cake [74]. The elution step regenerated the biomass for subsequent biosorption steps and also, greatly concentrated the cadmium in the eluate, with respect to the original wastewater. A rotating cathode cell was used downstream for metal recovery [75], resulting in cadmium powder and cadmium-depleted electrolyte, which is recycled as the eluant. The bacterial cell surfaces are known to be anionic due to the presence of ionized groups in the various cell wall polymers. This was also the reason that a cationic surfactant, such as cetyl-trimethyl ammonium bromide, was applied during

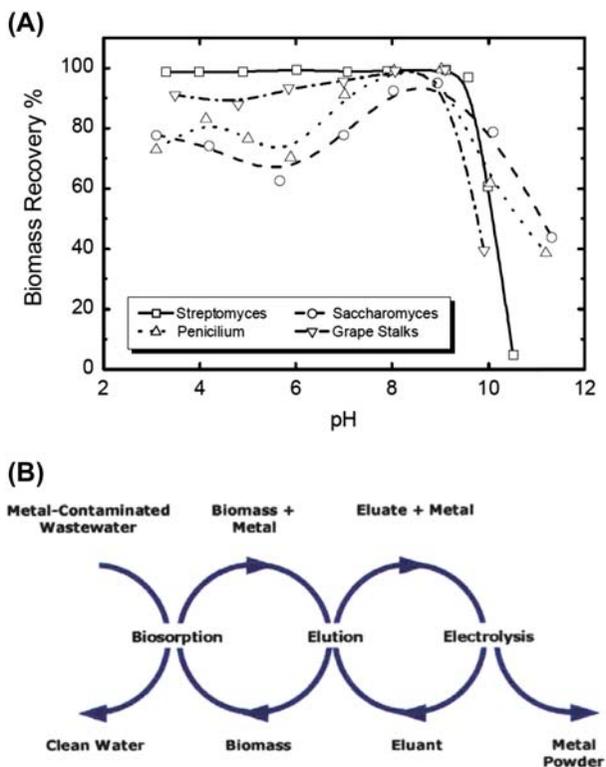


FIGURE 2.5 (A) A comparison of various biosorbent types, showing the obtained floatability, as a function of pH change. (B) An illustrative conceptual flow diagram showing recycle routes for a total process. (A) Reprinted with permission; copyright Wiley D. Zamboulis, E.N. Peleka, N.K. Lazaridis, K.A. Matis, *Metal ion separation and recovery from environmental sources using various flotation and sorption techniques*, *J. Appl. Chem. Biotechnol.* 86 (3) (2011) 335–344; (B) Reprinted with permission; copyright Elsevier T.J. Butter, L.M. Evison, I.C. Hancock, F.S. Holland, K.A. Matis, A. Philipson, A.I. Sheikh, A.I. Zouboulis, *The removal and recovery of cadmium from dilute aqueous solutions by biosorption and electrolysis at laboratory scale*, *Water Res.* 32 (1998) 400–406.

flotation. The presence of the heavy metals in the solution was also found to alter the electrokinetic properties of biomass.

The polluted aqueous system and the pretreated biomass were contacted countercurrently [76]. A two-stage countercurrent scheme was selected with one parallel of elution, based on extensive pilot plant studies; this scheme has similarities to a previously published activated carbon system for the separation of liquid contaminants. An advantage of the proposed process is that its basic unit processes are rather conventional and widely applied in the field. Multiple cycles of biosorption/flotation/elution were also examined with this system, applying appropriate elution between the treatment cycles of the

flotation concentrate (i.e., the separated metal-loaded biomass). It was observed that supplementary addition of a surfactant during the third cycle was necessary, otherwise biomass flotation substantially dropped, as flotation is based on surface activity. The following mixture of common metals was examined in the laboratory as a simulated approach of industrial wastewaters: Cd 1.5, Zn 7.5, and Cu 30 mg/L. The used biosorbent was a large-scale fermentation waste from a pharmaceutical industry (with trade name Mycan).

Microbubbles, generated by a fluidic oscillator, were applied for the recovery of yeast cells from their growth medium using the bioflocculant, chitosan [77]; bubble size affects recovery efficiency in a different way. To decontaminate heavy metal-containing wastewater, a microbial biotechnology was developed by using the synergy between *sulfate-reducing* bacteria, *Bacillus cereus* and *Camellia oleifera* cake [78]; flotation has been led into this system for increasing the efficiency as well. Another work aimed to compare a biosorption method and a coagulation–DAF method (found preferable) as inexpensive and effective means of eliminating hexavalent chromium from industrial wastewater [79]; process optimization was carried out using an artificial neural network.

Researching on cadmium ion removal onto sewage sludge biomass, it was observed that electroflotation (in order to separate or concentrate the loaded biosorbent) was capable to operate even without the presence of surfactants (i.e., collectorless), giving promising results using 10 min as retention time, a small ethanol concentration as a convenient frothing agent (easily biodegradable), and applying at least 130 A/m² as current density [80]. In the absence of biomass, only ~25% of the metal was possible to be removed.

Today, there is a tendency for combined and more compact processes as, for example, membrane bioreactors (MBRs) [81]. The main limitation to the faster development of this process was attributed to membrane fouling [82]. Various hybrid systems that include membrane separation processes have been presented in literature in recent years, except the known MBR: so, a hybrid distillation–reverse osmosis system was published [83], a hybrid distillation–membrane pervaporation system [84] and also, a hybrid membrane–ozonation system [85]. A new hybrid process for cleaning wastewater combining membrane microfiltration and flotation was investigated in our lab [86].

3. Role of bubbles

3.1 The hybrid cell

The hybrid process combined the advantages of both membrane separation and flotation: the flotation cell removed a large proportion of suspended solid particles, while the membrane module produced a clean water permeate effluent. The proof of concept for the combined hybrid separation process was

investigated using an aqueous suspension of ultrafine zeolite particles (from Ineos Silicas), and the main application was the treatment of heavy metal wastewaters. Air bubbling is one of the techniques used to limit membrane fouling, among the large number of techniques that have been used.

Certain limitations were imposed on the examined parameters, e.g., airflow, membranes type, and position, etc. The laboratory arrangement for the hybrid cell consisted of a mixing tank, peristaltic pump, thermometer, the flotation column with membrane microfiltration (shown in Fig. 2.6A),

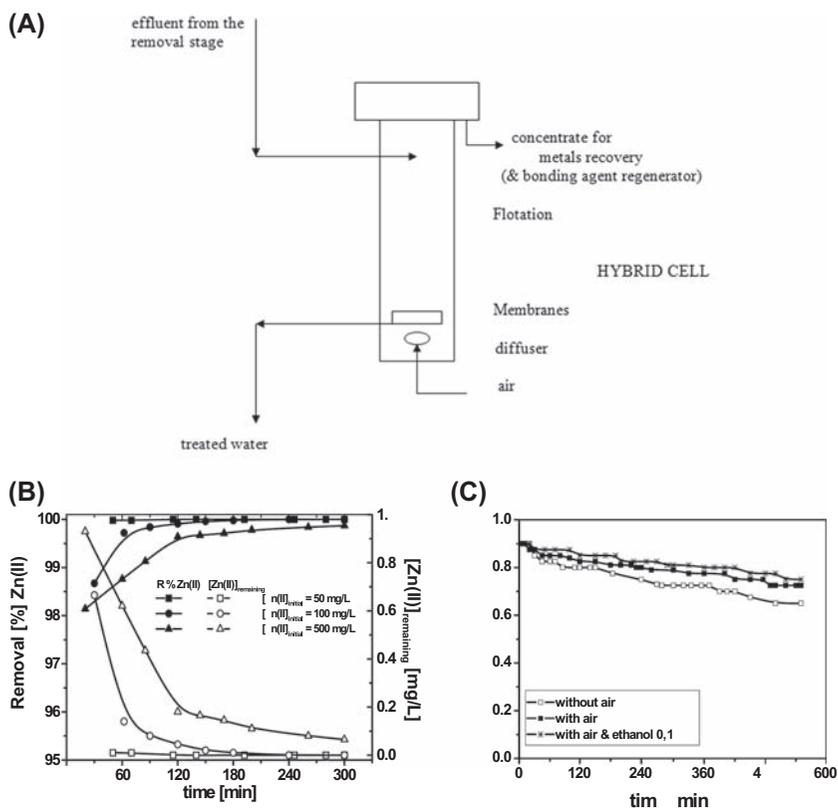


FIGURE 2.6 (A) Scheme of the innovative hybrid cell idea. (B) Obtained zinc removals in the retentate by the flotation-microfiltration cell; results expressed in two ways during precipitate flotation. (C) Effect of ethanol presence on membranes operation with metal-loaded zeolites: transmembrane pressure against time of operation. (B) Reprinted with permission; copyright Taylor and Francis E.N. Peleka, N.K. Lazaridis, P. Mavros, K.A. Matis, A new hybrid flotation-microfiltration cell, *Separ. Sci. Technol.* 41 (2006a) 3229–3243; (C) Reprinted with permission; copyright Elsevier K.A.Matis, E.N. Peleka, D. Zamboulis, T. Erwe, V. Mavrov, Air sparging during the solid/liquid separation by microfiltration: application of flotation, *Separ. Purif. Technol.* 40 (2004) 1–7.

manometer, air flow meter, nonreturn valve, slide valve, foam collection tank, and permeate collection tank. The microfiltration module, inserted inside the flotation column, consisted of a twin set of parallel, double-sided ceramic membranes, with a flat sheet multichannel geometry, having a mean pore size of 0.3 μm , a total surface area of 0.021 m^2 , hydrophilic surface properties, and an expected pure water flow rate of ~ 2 L/h.

Fig. 2.6B presents an example of a similar work without a sorbent applied, highlighting also the successful contribution of precipitate flotation with the hybrid cell; metal precipitation of dissolved zinc as hydroxide was conducted by pH adjustment, at the pH value of 9. When varying the feed, i.e., metal, from 50 to 500 mg/L and hence, varying the zinc precipitate concentration, the membrane permeabilities were reduced increasing the concentration. When plotting as remaining metal in solution, with the higher feed concentration used, the obtained results are not as good (although the removals were over 99.5%). A comparison was also given, in the form of a table, of the above process with the one when zeolite was used (i.e., sorptive flotation) [86]. Advantage of the former was that less solids were present inside the hybrid cell and so the pressure drops were much lower.

With the latter system [87], it was found that the finer the air bubbles used, the lower the transmembrane pressure (TMP) through the membranes. Fig. 2.6C shows the influence of ethanol (as frother) on TMP, with 4 g/L loaded zeolites, the air sparger was porous diaphragm Schott D4; the corresponding figures for permeabilities were presented, too. It was obvious that the results were still improved when the frother was used, as higher TMP was noticed, as expected. The efficiency of flotation, as found macroscopically, meanwhile was shown to have as outcome more than 90% of solids to be floated, those escaping the membranes (see below the economics aspect).

During these experimental series of continuous flow separation, all the collected samples showed, due to the membranes filtration, 100% zeolites recovery; hence, efficient solid–liquid separation, while the metal removal depended just on the amount of used sorbent. At the end of this program, the idea was tested, with a hybrid rig constructed (by UPT Saarbrücken, Germany), on-site at the Assarel-Medet open pit copper mine effluent near Panagyurishte, Bulgaria. Dispersed air flotation was indeed capable for a preliminary solids recovery of the order of 90%, with the Cu content in the froth concentrate approaching 6%. It was found in this pilot-scale study that the residual heavy metal (Cu, Mn, Fe, and Pb) concentrations in the membranes permeate were below 0.05 mg L^{-1} [88,89].

3.2 Further discussion

Further to the information given above (due to overlapping), from an older work Fig. 2.7A is here presented; the attachment efficiency expresses the

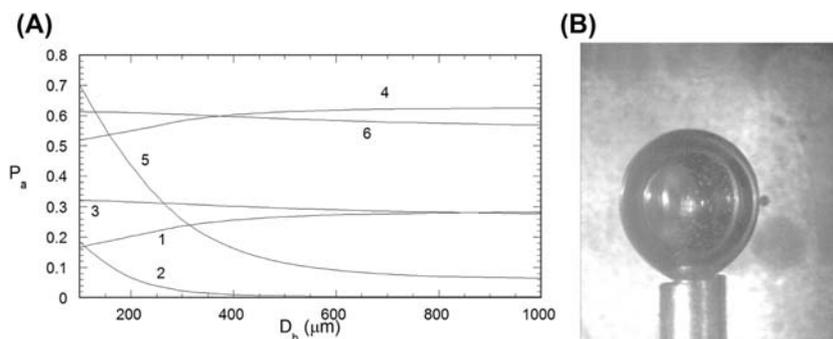


FIGURE 2.7 (A) Theoretical attachment efficiency, P_a , versus bubble diameter, D_b : (1) model (i), induction time $t_{\text{ind}} = 0.1$ s, particle size $D_p = 10$ μm ; (2) model (iii), $t_{\text{ind}} = 0.1$ s, $D_p = 10$ μm ; (3) model (ii), parameter $h_r = 1.98$, $D_p = 10$ μm ; (4) model (i), $t_{\text{ind}} = 0.02$ s, $D_p = 30$ μm ; (5) model (iii), $t_{\text{ind}} = 0.02$ s, $D_p = 30$ μm ; (6) model (ii), $h_r = 1.45$, $D_p = 30$ μm . (B) Photograph of particles on a bubble; kindly offered from the flotation research of my good colleague Prof. Thodoris Karapantsios and coworkers, in the Lab. (A) Reprinted with permission; copyright Elsevier M. Kostoglou, T.D. Karapantsios, K.A. Matis, *Modeling local flotation frequency in a turbulent flow field*, *Adv. Colloid Interface Sci.* 122 (2007) 79–91.

probability of the collided particle to drain the thin liquid film and eventually aggregate with the bubble. Where, model (1) is a modification of the classical Yoon-Luttrell [26] approach by King [90]; model (2) was developed by Bloom and Heindel [91]; and model (3) was developed by Nguyen [92]. In the second model, the induction time t_{ind} (i.e., a parameter which collectively includes all physicochemical interactions between a bubble and a particle) has been replaced by another parameter h_r . This is the ratio of the initial thickness at the moment of collision of the bubble–particle liquid film to its thickness at the moment of disruption and formation of a particle–bubble aggregate. It is a purely empirical parameter and must be obtained (like t_{ind}) from experiments or empirical relations.

Obviously, $P_{a,\text{iii}}$ (for the third case) decreased as bubble size increases due to reasons mentioned. The efficiencies for the two other methods, however, showed a smaller variation (in opposite directions), but it was sure that the two methods cannot be assumed to be equivalent. Hence, it is apparent from the above figure that both the particle and the bubble size are of significance and affect the process and its separation results. On the other hand, the naive conclusion is perhaps that there should be some care as to what model is to be applied (and to the relative assumptions made). For bubble and particle diameters in the ranges 100–1000 μm and 2–40 μm , respectively, the new expression incorporated most appraised earlier existing theories which, however, have a limited extent of validity and to which the new expression can degenerate as particular asymptotic cases [32].

The single bubble—single particle interactions of interest to flotation applications were later investigated with a developed experimental device [93]. Two separate high-speed cameras were employed to monitor the bubble surface from two different Cartesian directions allowing thus a 3D perspective of particles trajectories and collisions with the bubble (see Fig. 2.7B). A single bubble was kept at a fixed position and the suspension of particles moved against it; the bubble was created at the tip of a vertical capillary tube of external diameter of 600 μm . The experiments in this work were performed using spherical hydrophobic particles (polystyrene cross-linked with divinylbenzene) (Micropore Technologies Ltd.) with an average diameter of 330 μm , $\rho = 1050 \text{ kg/m}^3$.

Understanding the limits of fine particle flotation is the key to their selective separation [94]. The low flotation rate and recovery of hydrophobic fine particles ($<20 \mu\text{m}$) is mainly due to their low collision efficiency with bubbles, which may be overcome with decreasing the bubble size; other influences investigated in this review were the particle aggregation, particle induction time, the action of surface and capillary forces on fine particle—bubble capture, and different flow conditions. Various bubble—particle collision and attachment efficiency models have been reviewed, and the factors influencing collision and attachment efficiencies were extensively discussed. Finally, Table 2.1 summarizes other recent literature publications on this area that are worth mentioning.

4. Reports on process costs

A techno-economic study was also conducted for the aforementioned hybrid cell (see, for example, Fig. 2.8), applying the software tool SuperPro Designer (from Intelligen). The study showed that the capital investment of the plant would be of the order of US\$ 0.92M (2003 prices). The operating costs are about \$ 1.76M per year. The processing rate is $68.83 \times 10^6 \text{ kg/year}$ of influent and the unit processing cost is 0.0256 \$/MT of influent; detailed tables were published. The total revenues from water recycling and reuse are \$ 68,800 per annum. It is noted that this only accounted for the environmental costs and did not consider any credit due to copper recovery. The cost of the combined process was not the mere addition of the individual processes costs: the required membrane surface, which is a major cost factor, is lower in the hybrid process since flotation removed the majority of solid particles, and therefore a smaller membrane area is required to yield the same permeate [106].

In Table 2.2, a brief account is given on costs from selected (from the very few available) papers in the recent literature; noting that the general trend, at least according to our opinion, is to avoid giving an idea on costs, but meanwhile speaking on low-cost effective processes. Finally, in an extensive review [112], a discussion on electroflotation costs can be traced, including some comparison with relative processes for effluent treatment.

TABLE 2.1 Selected papers on the role of particle/bubble size.

Brief flotation details/application	References
Fine particle capture and aggregation of the quartz ultrafines by nanobubbles were the main mechanisms responsible for higher recoveries; nanobubbles enhanced the contact angle of quartz.	[95]
Bubble diameter, bubble velocity, and turbulence suggested to be the key factors involved in particle–bubble interactions. The collision efficiency of ultrafine particles (1–10 μm) was generally improved with bubbles of finer sizes, e.g., $D_b = 0.08$ cm.	[96]
The effect of surfactants on bubble properties was examined in turbulent conditions, with the primary aim to identify the relationship between the size-scale surface properties leading to the decrease in bubble size.	[97]
The addition of frother to a synthetic sea salt reduced the measured bubble size, at certain mechanical conditions; in flotation, bubble size is a function of both coalescence and breakup phenomena.	[98]
Considering poorly modeled flotation systems and operation experience, a combined feed forward– and feedback-based control scheme of reagent dosage was presented to implement tracking for probability density function of the desired bubble size.	[99]
The effect of the addition of submicron silica particles of intermediate hydrophobicity was examined on the foaminess and gas dispersive properties of nonionic surfactants; the results indicated that this addition increased the gas holdup.	[100]
Nanomaterials were used that did not contribute to the flotation efficiency at shallow froth (i.e., 15 mm, in a Denver machine); contrary to this, nanosized Fe_2O_3 and Al_2O_3 provided a significant increase in barite recovery (7%–11%), at deep froth (35 mm).	[101]
A theory of combined microflotation was proposed to describe the kinetics of fine particles flotation, utilizing small quantities of fine bubbles in combination with coarse bubbles. Fine bubbles played the role of flotation carriers.	[102]
The effect of frothers on the degree of entrainment is important for selective flotation, and the mechanism of this was studied with gangue-only batch flotation tests, performed using fully liberated quartz.	[103]
A higher air fraction was shown to be needed at higher loading rates in DAF, to achieve the same removal efficiency. Model predictions, in the presence of stratified flow in the tank, showed that an optimum bubble size was present, which increased with an increase in particle size.	[104]

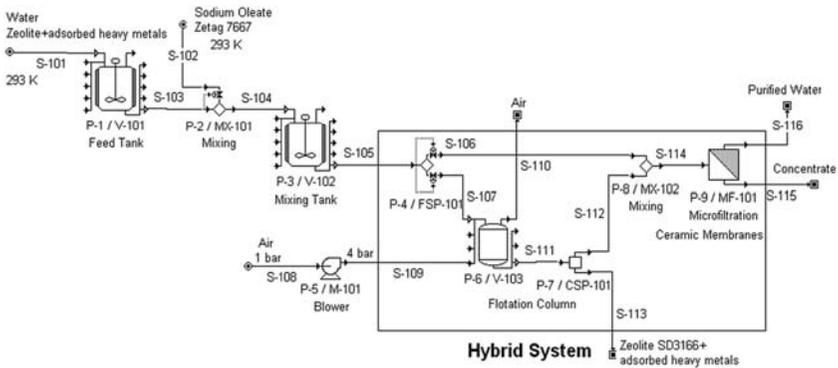


FIGURE 2.8 Technical economical flowsheet analysis of the hybrid process. *Reprinted with permission; copyright Elsevier Matis K.A., N.K. Lazaridis, A.I. Zouboulis, G.P. Gallios, V. Mavrov, A hybrid flotation-microfiltration process for metal ions recovery, J. Membr. Sci. 247 (2005) 29–35.*

5. Summary and conclusions

Flotation constitutes a scientifically interest (and perhaps, difficult) separation process, as we very often face a three-phase G/L/S system. The particles size to be floated should be rather small, so that they can be levitated by the bubbles produced, by different methods: dispersed air or froth, dissolved air, and electroflotation; a comparison was included. Fine particles usually present a (separation) problem in chemical industry and raw materials processing, often as by-products. Sustainability in this field is of significance, with emphasis given to recycling, because the need for fresh sources of drinking water is becoming urgent worldwide.

Some significant examples were presented in this work (see also Fig. 2.1), with satisfactory separation results, concerning heavy metal ions removal from aqueous solution, such as cadmium, zinc, and hexavalent chromium. Certainly, the process originated from mineral processing; i.e., the given reference to the further reprocessing of an arsenic-rich, gold-bearing pyrite concentrate by column flotation. This selective separation is of interest when, for instance, gold is associated selectively with one of the constituents; hence, contributing to recycling. The role and type also of bubbles, including their respective size, were discussed. The difference between wastewater treatment and mineral processing was highlighted.

Among the various available separation techniques, particularly the following were reviewed in some extent: the application upstream of sorbents (as zeolite, goethite, biosorbents, etc.) and of a combined flotation-microfiltration cell. Also, there were given hereby cost information for certain flotation techniques: DAF chemical dosage, solid waste remediation, flotation cell (as far as energy efficiency is concerned), posttreatment for DAF, electroflotation, and hybrid units.

TABLE 2.2 Some literature reports on relative costs of flotation applications.

Process and economics information	References
Work was carried out on a typical steel industry, in selection of the optimum amount of chemicals dosage used in a dissolved air flotation (DAF) unit to remove oil and grease; neural models were developed. The amount of alum required was ~ 104 kg/day-shift and of polyelectrolyte 1 kg/day-shift.	[107]
The distribution of turbulence was investigated in a mechanical (conventional) 3 m^3 flotation cell, considering the power number as a useful hydrodynamic indicator. Flotation was said not to be a particularly energy-intensive process.	[108]
Three soils polluted by municipal solid waste (MSW) incineration residues and containing various concentrations of Cu, Pb, Sb, Sn, and Zn were treated using magnetism, gravity separation (jig and shaking tables), and flotation/leaching. The estimated costs of the process, including direct and indirect costs, varied from \$82 to \$88 per ton of treated soil, depending on the proportion of MSW incineration residues mixed with the soil.	[109]
A sequential treatment of olive mill wastewater, comprising a DAF pretreatment and nanofiltration was published; involving operation costs of approximately $2.56\text{--}3.08 \text{ €/m}^3$ (depending on the working plan schedule and volume reduction factor) and requiring a footprint of approximately 52 m^2 to treat 1000 m^3 of olive mill wastewater.	[110]
Posttreatment of industrial wastewater polluted by metalworking fluids was performed using the photo-Fenton process, in following of the chemical addition-dissolved air flotation unit. The cost analysis of this process for the consumed energy (6 kWh) and chemicals (0.01818 kg FeSO_4 and 17.15 kg H_2O_2) was estimated at approximately 26 \$ per 1 m^3 of DAF effluent.	[111]

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References

- [1] V.A. Glembotskii, V.I. Klassen, I.N. Plaksin, Flotation, Primary Sources, 1972. New York.
- [2] E.A. Deliyanni, G.Z. Kyzas, K.A. Matis, Various flotation techniques for metal ions removal, *J. Mol. Liq.* 225 (2017) 260–264.
- [3] G. Bournival, S. Ata, E.J. Wanless, The role of particles in multiphase processes: particles on bubble surfaces, *Adv. Colloid Interface Sci.* 225 (2015) 114–133.

- [4] D.W. Fuerstenau, Fine particle flotation, in: P. Somasundaran (Ed.), *Fine Particles Processing*, SME-AIME, New York, 1980, pp. 669–705.
- [5] E.N. Peleka, K.A. Matis, Water separation processes and sustainability, *Ind. Eng. Chem. Res.* 50 (2) (2011) 421–430.
- [6] G.Z. Kyzas, E.A. Deliyanni, K.A. Matis, Research activities related to flotation process, *Trends Green Chem.* 1 (2015) 1–8.
- [7] D.R. Nagaraj, R.S. Farinato, Evolution of flotation chemistry and chemicals: a century of innovations and the lingering challenges, *Miner. Eng.* 96–97 (2016) 2–14.
- [8] G.Z. Kyzas, K.A. Matis, Methods of arsenic wastes recycling: focus on flotation, *J. Mol. Liq.* 214 (2016a) 37–45.
- [9] G. Long, Y. Peng, D. Bradshaw, Flotation separation of copper sulphides from arsenic minerals at Rosebery copper concentrator, *Miner. Eng.* 66–68 (2014) 207–214.
- [10] B. Tansel, D. Boglaienko, Self assembly, mobilization, and flotation of crude oil contaminated sand particles as granular shells on gas bubbles in water, *Sci. Total Environ.* 574 (2017) 437–442.
- [11] G. Liu, J. Xiao, J. Liu, X. Qu, Q. Liu, H. Zeng, X. Yang, L. Xie, H. Zhong, Q. Liu, Z. Xu, In situ probing the self-assembly of 3-hexyl-4-amino-1,2,4-triazole-5-thione on chalcopyrite surfaces, *Colloids Surf. A* 511 (2016) 285–293.
- [12] J. Wang, R.-H. Yoon, J. Morris, AFM surface force measurements conducted between gold surfaces treated in xanthate solutions, *Int. J. Miner. Process.* 122 (2013) 13–21.
- [13] M. Ahola, K. Villforth, S. Schabel, Process modelling in deinking plants: forecasting recycled pulp quality and resource efficiency, *Intl. Paperworld 2016* (2016) 26–35.
- [14] B. Dold, Evolution of acid mine drainage formation in sulphidic mine tailings, *Minerals* 4 (2014) 621–641.
- [15] C.A. Laamanen, G.M. Ross, J.A. Scott, Flotation harvesting of microalgae, *Renew. Sustain. Energy Rev.* 58 (2016) 75–86.
- [16] T. Leistner, M. Embrechts, T. Leibner, S.C. Chelgani, I. Osbahr, R. Möckel, U.A. Peuker, M. Rundolph, A study of the reprocessing of fine and ultrafine cassiterite from gravity tailing residues by using various flotation techniques, *Miner. Eng.* 96–97 (2016) 94–98.
- [17] A.V. Nguyen, H.J. Schulze, *Colloidal Science of Flotation*, Marcel Dekker, New York, 2004.
- [18] J. Leja, *Surface Chemistry of Froth Flotation*, Plenum Press, New York, 1982.
- [19] V.I. Klassen, V.A. Mokrushov, *An Introduction to the Theory of Flotation*, Butterworths, London, 1963, p. 43.
- [20] A.N. Clark, D.J. Wilson, *Foam Flotation – Theory and Applications*, Marcel Dekker, New York, 1983.
- [21] [a] K.A. Matis, P. Mavros, (i) Recovery of metals by ion flotation from dilute aqueous solutions, *Separ. Purif. Methods* 20 (1) (1991) 1–48;
[b] K.A. Matis, P. Mavros, Foam/froth flotation: Part II. Removal of particulate matter, *Separ. Purif. Methods* (1991) 163–198.
- [22] H.J. Schulze, Elements of physically-based modeling of the flotation process, in: P. Mavros, K.A. Matis (Eds.), *Innovations in Flotation Technology*, Kluwer Academic, Dordrecht, 1992, pp. 171–180.
- [23] B.V. Derjaguin, S.S. Dukhin, N.N. Rulyov, Kinetic theory of flotation of small particles, *Surf. Colloid Sci.* 13 (1984) 71–113.
- [24] G. Wang, A.V. Nguyen, S. Mitra, J.B. Joshi, G.J. Jameson, G.M. Evans, A review of the mechanisms of bubble-particle detachment in froth flotation, *Separ. Purif. Technol.* 170 (2016a) 155–172.

- [25] K.A. Matis, G.P. Gallios, Dissolved-air and electrolytic flotation, in: B.A. Wills, R.W. Barley (Eds.), *Mineral Processing at a Crossroads*, Martinus Nijhoff, Dordrecht, 1986, pp. 37–70.
- [26] R.H. Yoon, G.H. Luttrell, The effect of bubble size on fine particle flotation, *Miner. Process. Extr. Metall. Rev.* 5 (1989) 101–122.
- [27] T. Takahashi, I. Miyahara, H. Mochizuki, Fundamental studies of bubble formation in dissolved-air pressure flotation, *J. Chem. Eng. Jpn.* 12 (4) (1979) 275–280.
- [28] K.A. Matis, A.I. Zouboulis, The role of bubble/particle size, in: K.A. Matis (Ed.), *Flotation Science and Engineering*, Marcel Dekker, New York, 1995, pp. 63–87.
- [29] E. Valdes-Krieg, C.J. King, H.H. Sephton, Removal of surfactants and particulate matter from sea water desalination blowdown brines by foam fractionation, *Desalination* 16 (1975) 39–53.
- [30] Y. Sato, Y. Murakami, T. Hirose, H. Yamamoto, Y. Urgan, Removal of emulsified oil particles by dissolved-air flotation, *J. Chem. Eng. Jpn.* 12 (1979) 454–459.
- [31] S. Usui, H. Sasaki, Zeta-potential measurements of bubbles in aqueous solutions, *J. Colloid Interface Sci.* 65 (1978) 36–45.
- [32] M. Kostoglou, T.D. Karapantsios, K.A. Matis, Modeling local flotation frequency in a turbulent flow field, *Adv. Colloid Interface Sci.* 122 (2007) 79–91.
- [33] E.N. Peleka, K.A. Matis, Hydrodynamic aspects of flotation separation, *Open Chem.* 14 (2016) 132–139.
- [34] G. Ai, X. Yang, X. Li, Flotation characteristics and flotation kinetics of fine wolframite, *Powder Technol.* 305 (2017) 377–381.
- [35] D.A. Wheeler, Column flotation: the original column, in: S.H. Castro, J. Alvarez (Eds.), *Froth Flotation, Proc. 2nd Latin-American Congr.*, Concepción, Chile, Elsevier, Amsterdam, 1988, pp. 17–40.
- [36] W.J. Trahar, L.J. Warren, The floatability of very fine particles – a review, *Int. J. Miner. Process.* 3 (1976) 103–131.
- [37] G.P. Gallios, K.A. Kydros, K.A. Matis, Electrokinetic behaviour of sulphide minerals: a contribution to the chemistry of flotation, in: G.P. Gallios, K.A. Matis (Eds.), *Mineral Processing and the Environment*, Kluwer Academic Publishers, Dordrecht, 1998, pp. 25–42.
- [38] K.A. Matis, G.P. Gallios, K.A. Kydros, Separation of fines by flotation techniques, *Sep. Technol.* 3 (1993) 76–90.
- [39] P. Mavros, K.A. Kydros, K.A. Matis, Arsenopyrite enrichment by column flotation, *Miner. Eng.* 6 (12) (1993) 1265–1277.
- [40] G.W. Poling, M.J.V. Beattie, Selective depression in complex sulphide flotation, in: M.H. Jones, J.T. Woodcock, I.M.M. Australasian (Eds.), *Principles of Mineral Flotation – the Wark Symposium*, 1984, p. 137.
- [41] K.A. Kydros, G.P. Gallios, K.A. Matis, Electrolytic flotation of pyrite, *J. Appl. Chem. Biotechnol.* 59 (1994) 223–232.
- [42] MdS.K.A. Sarkar, G.M. Evans, S.W. Donne, Bubble size measurement in electroflotation, *Miner. Eng.* 23 (2010) 1058–1065.
- [43] G.Z. Kyzas, K.A. Matis, Electroflotation process: a review, *J. Mol. Liq.* 220 (2016b) 657–664.
- [44] K.H. Rao, A. Vilinka, I.V. Chernyshova, Minerals bioprocessing: R&D needs in mineral beneficiation, *Hydrometallurgy* 104 (2010) 465–470.

- [45] L. Wang, R. Liu, Y. Hu, J. Liu, W. Sun, Adsorption behavior of mixed cationic/anionic surfactants and their depression mechanism on the flotation of quartz, *Powder Technol.* 302 (2016b) 15–20.
- [46] T.F. Zabel, Flotation in water treatment, in: P. Mavros, K.A. Matis (Eds.), *Innovations in Flotation Technology*, Kluwer Academic, Dordrecht, 1992, pp. 431–454.
- [47] L. Haak, R. Roy, K. Pagilla, Toxicity and biogas production potential of refinery waste sludge for anaerobic digestion, *Chemosphere* 144 (2016) 1170–1176.
- [48] J. Bratby, G.v.R. Marais, Flotation, in: D.B. Purchas (Ed.), *Solid/Liquid Separation Equipment Scale-Up*, Uplands Press, Croydon, 1977, p. 155.
- [49] P.T.L. Koh, M.P. Schwarz, CFD modeling of bubble-particle attachments in a flotation cell, in: *Proc. Centenary Flotation Symp.*; Brisbane, Australia, June, 2005, pp. 201–207.
- [50] M. Zhang, P. Guiraud, Elimination of TiO₂ nanoparticles with the assist of humic acid: influence of agglomeration in the dissolved air flotation process, *J. Hazard Mater.* 260 (2013) 122–130.
- [51] K.A. Matis, N.K. Lazaridis, Flotation techniques in water technology for metals recovery: dispersed-air vs. dissolved-air flotation, *J. Min. Metall. A* 38 (2002) 1–27.
- [52] IWA, in: *Proc. 4th Intl. Conf. Flotation in Water and Waste Water Treatment*, Finnish Water and Wastewater Works Assoc., Helsinki, 2000.
- [53] M. Ponasse, V. Dupre, Y. Aurelle, A. Secq, Bubble formation by water release in nozzle – II. Influence of various parameters on bubble size, *Water Res.* 32 (1998) 2498–2506.
- [54] A. Chen, Z. Wang, J. Yang, Influence of bubble size on the fluid dynamic behavior of a DAF tank: a 3D numerical investigation, *Colloids Surf., A* 495 (2016) 200–207.
- [55] K.A. Matis, A.I. Zouboulis, N.K. Lazaridis, Dispersed-air vs. dissolved-air flotation: a comparison applied to metal-loaded goethite, in: *Proc. 34th Int'l. Conf. Mining and Metallurgy*, Organized by Univ. Belgrade, Techn. Fac. Bor Serbia, 30 Sept.-3 Oct., 2002, pp. 240–246.
- [56] A.I. Zouboulis, K.A. Matis, Removal of cadmium from dilute solutions by flotation, *Water Sci. Technol.* 31 (3–4) (1995) 315–326.
- [57] A.I. Zouboulis, K.A. Matis, Removal of metal ions from dilute solutions by sorptive flotation, *Crit. Rev. Environ. Sci. Technol.* 27 (3) (1997) 195–235.
- [58] M.R. Mahmoud, N.K. Lazaridis, K.A. Matis, Study of flotation conditions for cadmium(II) removal from aqueous solutions, *Process Saf. Environ. Protect.* 94 (2015) 203–211.
- [59] N.K. Lazaridis, K.A. Matis, G.A. Stalidis, P. Mavros, Dissolved-air flotation of metal ions, *Separ. Sci. Technol.* 27 (1992) 1743–1758.
- [60] E.N. Peleka, K.A. Matis, Application of flotation as a pretreatment process during desalination, *Desalination* 222 (2008) 1–8.
- [61] M.A. Darwish, H.K. Abdulrahim, A.S. Hassan, A.O. Sharif, Needed seawater reverse osmosis pilot plant in Qatar, *Desalin. Wat. Treatment* 57 (2016) 3793–3819.
- [62] Y.H.C. Wang, P. Somasundaran, A study of carrier flotation of clay, in: P. Somasundaran (Ed.), *Fine Particles Processing*, SME/AIME, New York, 1980, pp. 1112–1128.
- [63] J.M. Younker, M.E. Walsh, Effect of adsorbent addition on floc formation and clarification, *Water Res.* 98 (2016) 1–8.
- [64] D.N. Bakoyannakis, E.A. Deliyanni, A.I. Zouboulis, K.A. Matis, L. Nalbandian, T. Kehagias, Akaganeite and goethite-type nanocrystals: synthesis and characterization, *Microporous Mesoporous Mater.* 59 (2003) 35–42.
- [65] K.A. Matis, D. Zamboulis, A.I. Zouboulis, N.K. Lazaridis, Goethite mineral as a sorbent for heavy metals, in: P. Misaelides, F. Macašek, T.J. Pinnavaia, C. Colella (Eds.), *Natural*

- Microporous Materials in Environmental Technology, Kluwer Academic Publishers, The Netherlands, 1999, pp. 425–433.
- [66] A.I. Zouboulis, D. Zamboulis, K.A. Matis, Foam flotation of zeolites: application on zinc ion removal, *Separ. Sci. Technol.* 26 (3) (1991) 355–365.
- [67] G. Bulut, Ü. Yenial, E. Emiroğlu, A.A. Sirkeci, Arsenic removal from aqueous solution using pyrite, *J. Clean. Prod.* 84 (2014) 526–532.
- [68] R. Etchepare, A. Azevedo, S. Calgaroto, J. Rubio, Removal of ferric hydroxide by flotation with micro and nanobubbles, *Separ. Purif. Technol.* 184 (2017) 347–353.
- [69] M.H. Dehgani, B. Karimi, A. Rafiepour, Continuous removal of toxic nickel from industrial wastewater by flotation-adsorption with multi-walled carbon nanotubes: kinetic and adsorption isotherms, *Desalination Wat. Treatment* 71 (2017) 107–115.
- [70] N. Hu, W. Liu, L. Ding, Z. Wu, H. Yin, D. Huang, H. Li, L. Jin, H. Zheng, Removal of methylene blue from its aqueous solution by froth flotation: hydrophobic silica nanoparticle as a collector, *J. Nanoparticle Res.* 19 (2) (2017) article no. 46.
- [71] M.N. Hughes, R.K. Poole, *Metals and Microorganisms*, Chapman and Hall, London, 1989, pp. 328–395.
- [72] H. Eccles, Treatment of metal-contaminated wastes: why select a biological process? *Trends Biotechnol.* 17 (1999) 462–465.
- [73] D. Zamboulis, E.N. Peleka, N.K. Lazaridis, K.A. Matis, Metal ion separation and recovery from environmental sources using various flotation and sorption techniques, *J. Appl. Chem. Biotechnol.* 86 (3) (2011) 335–344.
- [74] T.J. Butter, L.M. Evison, I.C. Hancock, F.S. Holland, K.A. Matis, A. Philipson, A.I. Sheikh, A.I. Zouboulis, The removal and recovery of cadmium from dilute aqueous solutions by biosorption and electrolysis at laboratory scale, *Water Res.* 32 (1998) 400–406.
- [75] F.S. Holland, The development of the Eco-Cell process, *Chem. Ind.* 1 (1978) 453–456.
- [76] A.I. Zouboulis, N.K. Lazaridis, K.A. Matis, Removal of toxic metal ions from aqueous systems by biosorptive flotation, *J. Appl. Chem. Biotechnol.* 77 (2002) 958–964.
- [77] H. Hanotu, E. Karunakaran, H. Bandulasena, C. Biggs, W.B. Zimmerman, Harvesting and dewatering yeast by microflotation, *Biochem. Eng. J.* 82 (2014) 174–182.
- [78] M. Wu, J. Liang, J. Tang, G. Li, S. Shan, Z. Guo, L. Deng, Decontamination of multiple heavy metals-containing effluents through microbial biotechnology, *J. Hazard Mater.* 337 (2017) 189–197.
- [79] A. Esmaili, E. Hejazi, Y. Vasseghian, Comparison study of biosorption and coagulation/air flotation methods for chromium removal from wastewater: experiments and neural network modeling, *RSC Adv.* 5 (111) (2015) 91776–91784.
- [80] A.I. Zouboulis, K.A. Matis, Cadmium ion removal by electroflotation onto sewage sludge biomass, *Int. J. Environ. Waste Manag.* 9 (3/4) (2012) 245–256.
- [81] I. Chang, S. Judd, Air sparging of a submerged MBR for municipal wastewater treatment, *Process Biochem.* 37 (2002) 915–920.
- [82] T. Ueda, K. Hata, Y. Kikuoka, O. Seino, Effects of aeration on suction pressure in a submerged membrane bioreactor, *Water Res.* 31 (1997) 489–494.
- [83] E. Essam, A. Mahmoud, E. Sadeq, E. Ahmad, Performance evaluation of two RO membrane configurations in a MSF/RO hybrid system, *Desalination* 128 (2000) 231–245.
- [84] A.M. Eliceche, M.C. Daviou, P.M. Hoch, I.O. Uribe, Optimisation of azeotropic distillation columns combined with pervaporation membranes, *Comput. Chem. Eng.* 26 (2002) 563–573.

- [85] B. Schlichter, V. Mavrov, H. Chmiel, Study of a hybrid process combining ozonation and membrane filtration-filtration of model solutions, *Desalination* 156 (2003) 257–265.
- [86] E.N. Peleka, N.K. Lazaridis, P. Mavros, K.A. Matis, A new hybrid flotation-microfiltration cell, *Separ. Sci. Technol.* 41 (2006a) 3229–3243.
- [87] K.A. Matis, E.N. Peleka, D. Zamboulis, T. Erwe, V. Mavrov, Air sparging during the solid/liquid separation by microfiltration: application of flotation, *Separ. Purif. Technol.* 40 (2004) 1–7.
- [88] N.K. Lazaridis, E.N. Peleka, T.D. Karapantsios, K.A. Matis, Copper recovery from effluents by various separation techniques, *Hydrometallurgy* 74 (2004) 149–156.
- [89] V. Nenov, N.K. Lazaridis, C. Blöcher, B. Bonev, K.A. Matis, Metal recovery from a copper mine effluent by a hybrid process, *Chem. Eng. Process* 47 (2008) 596–602.
- [90] R.P. King, *Modeling and Simulation of Mineral Processing Systems*, Butterworth-Heinemann, London, 2001.
- [91] F. Bloom, T.J. Heindel, A theoretical model of flotation deinking efficiency, *J. Colloid Interface Sci.* 190 (1997) 182–197.
- [92] A.V. Nguyen, Hydrodynamics of liquid flows around air bubbles in flotation: a review, *Int. J. Miner. Process.* 56 (1999) 165–205.
- [93] Z. Brabcová, T. Karapantsios, M. Kostoglou, P. Basařová, K. Matis, Bubble–particle collision interaction in flotation systems, *Colloids Surf. A* 473 (2015) 95–103.
- [94] T. Miettinen, J. Ralston, D. Fornasiero, The limits of fine particle flotation, *Miner. Eng.* 23 (2010) 420–437.
- [95] S. Calgaroto, A. Azevedo, J. Rubio, Flotation of quartz particles assisted by nanobubbles, *Int. J. Miner. Process.* 137 (2015) 64–70.
- [96] A. Hassanzadeh, B.V. Hassas, S. Kouachi, Z. Brabcova, M.S. Çelik, *Colloids Surf. A* 498 (2016) 258–267.
- [97] Z. Jávör, N. Schreithofer, K. Heiskanen, Multi-scale analysis of the effect of surfactants on bubble properties, *Miner. Eng.* 99 (2016) 170–178.
- [98] J.M. Sovechles, M.R. Lepage, B. Johnson, K.E. Waters, Effect of gas rate and impeller speed on bubble size in frother-electrolyte solutions, *Miner. Eng.* 99 (2016) 133–141.
- [99] J. Zhu, W. Gui, J. Liu, H. Xu, C. Yang, Combined fuzzy based feed forward and bubble size distribution based feedback control for reagent dosage in copper roughing process, *J. Process Control* 39 (2016) 50–63.
- [100] G. Bournival, Z. Du, S. Ata, G.J. Jameson, Foaming and gas dispersion properties of non-ionic frothers in the presence of hydrophobized submicron particles, *Int. J. Miner. Process.* 133 (2014) 123–1131.
- [101] E.C. Cilek, S. Karaca, Effect of nanoparticles on froth stability and bubble size distribution in flotation, *Int. J. Miner. Process.* 138 (2015) 6–14.
- [102] N.N. Rulyov, Combined microflotation of fine minerals: theory and experiment, *Miner. Proc. Extractive Metal. C* 125 (2016) 81–85.
- [103] L. Wang, Y. Peng, K. Runge, The mechanism responsible for the effect of frothers on the degree of entrainment in laboratory batch flotation, *Miner. Eng.* 100 (2017) 124–131.
- [104] B. Lakghomi, Y. Lawryshyn, R. Hofmann, A model of particle removal in a dissolved air flotation tank: importance of stratified flow and bubble size, *Water Res.* 63 (2015) 262–272.
- [105] K.A. Matis, N.K. Lazaridis, A.I. Zouboulis, G.P. Gallios, V. Mavrov, A hybrid flotation-microfiltration process for metal ions recovery, *J. Membr. Sci.* 247 (2005) 29–35.
- [106] E.N. Peleka, M.M. Fanidou, P.P. Mavros, K.A. Matis, A hybrid flotation-microfiltration cell for S/L separation: operational characteristics, *Desalination* 194 (2006b) 135–145.

- [107] R. Wadhvani, B. Mohanty, S. Khanam, Optimization of the amount of chemical dosage to improve the performance of dissolved air flotation unit, *Separ. Sci. Technol.* 50 (2015) 1038–1049.
- [108] E. Tabosa, K. Runge, P. Holtham, K. Duffy, Improving flotation energy efficiency by optimizing cell hydrodynamics, *Miner. Eng.* 96–97 (2016) 194–202.
- [109] P. Jobin, L. Coudert, V. Taillard, J.-F. Blais, G. Mercier, Remediation of inorganic contaminants and polycyclic aromatic hydrocarbons from soils polluted by municipal solid waste incineration residues, *Environ. Technol.* 37 (2016) 1983–1995.
- [110] S. Sanches, M.C. Fraga, N.A. Silva, P. Nunes, J.G. Crespo, V.J. Pereira, Pilot scale nanofiltration treatment of olive mill wastewater: a technical and economical evaluation, *Environ. Sci. Pollut. Res.* 24 (2017) 3506–3518.
- [111] M.M. Amin, M.M.G. Mofrad, H. Pourzamani, S.M. Sebaradar, K. Ebrahim, Treatment of industrial wastewater contaminated with recalcitrant metal working fluids by the photo-Fenton process as post-treatment for DAF, *J. Ind. Eng. Chem.* 45 (2017) 412–420.
- [112] K.A. Matis, E.N. Peleka, Alternative flotation techniques for wastewater treatment: focus on electroflotation, *Separ. Sci. Technol.* 45 (2010) 2465–2474.

Advanced Low-Cost Separation Techniques in Interface Science

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