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Review

Flotation of Biological Materials

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Abstract: Flotation constitutes a gravity separation process, which originated from the minerals processing field. However, it has, nowadays, found several other applications, as for example in the wastewater treatment field. Concerning the necessary bubble generation method, typically dispersed-air or dissolved-air flotation was mainly used. Various types of biological materials were tested and floated efficiently, such as bacteria, fungi, yeasts, activated sludge, grape stalks, *etc*. Innovative processes have been studied in our Laboratory, particularly for metal ions removal, involving the initial abstraction of heavy metal ions onto a sorbent (including a biosorbent): in the first, the application of a flotation stage followed for the efficient downstream separation of metal-laden particles. The ability of microorganisms to remove metal ions from dilute aqueous solutions (as most wastewaters are) is a well-known property. The second separation process, also applied effectively, was a new hybrid cell of microfiltration combined with flotation. Sustainability in this field and its significance for the chemical and process industry is commented.

Keywords: solid/liquid separation; bubbles; microorganisms; float; foam

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1. Introduction

The importance of the flotation 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 [1]. Thus, flotation initially originated from the field of mineral processing, usually termed froth flotation. As, for many years, various particulate solids besides minerals have been extracted from water by using this effective gravity separation method that is based on the idea of applying rising gas bubbles as the transport medium. The attachment of bubbles to particles transfers the solids from the body of water to the surface. As opposed to settling, flotation is a solid-liquid separation technique that is applied to particles whose density is lower or has been made lower than the liquid they are in. These flotation applications include mainly the treatment of water and wastewater. Today, for example, applications of flotation exist in paper manufacturing for deinking and waste paper recycling, emulsified oil from various industrial wastewaters, and the separation of used plastics.

The typical classification of flotation is, according to the method used for the generation of bubbles, in the following two main and broad categories:

(a) dispersed-air flotation (including electroflotation), and
(b) dissolved-air flotation (just the initials are often used, as DAF).

Between the flotation techniques different scopes are often encountered, such as the eventual selectivity (or not) obtained during the separation process (especially important for the separation of minerals from ores), the differences in the used initial particles concentration (varying from very high to very low), the possible use (or not) of surfactants (collectors), as well as of other chemical reagents (e.g., modifiers, frothers, *etc*.) due to operational or environmental reasons, *etc*. From the economic point of view, the options seem to be also completely different, as the application of flotation in mineral processing is obviously economically attractive, whereas the application of flotation for the treatment of effluents is considered mainly to create higher costs for the overall production process.

Ion flotation involves the removal of (usually) surface-inactive metal ions (cations or anions) from aqueous solutions by the addition of specific reagents and by the subsequent passage of gas bubbles through these solutions. The surfactant is usually an organic compound of hydrophobic and hydrophilic character, carrying opposite charge to that of the metal ion to be removed. As a result of this procedure, on the surface of solution and within the froth structure appears an agglomerate of fine solid particles (insoluble precipitates), containing the surfactant as a chemical constituent. This permits the separation of dissolved and dilute ionic species within a small concentrated volume, usually less than 5%, as compared with the original volume of solution, of collapsed foam. The surfactants are generally recoverable from the floated product and can be reused, whereas the resulting clarified water may be also recycled. The increase of initial surfactants concentrations, at least to stoichiometric ratios with the respective metal ions to be removed, may lead to the preliminary precipitation of ion-surfactant floatable product, even before air is passed. This means that the system is not a solution anymore, but rather a solid/liquid dispersion—*i.e*., precipitate flotation [2].

On the other hand, the method of sorptive flotation involves the preliminary abstraction or scavenging of metal ions using appropriate sorbents, which already exist at the fine or ultrafine particle-size range. Therefore, further size reduction is not needed, before the application. Due to fine particulate nature, these sorbents were preferably applied in continuous stirred-tank reactor type equipment offering high kinetic rates, and not in typical column arrangements. In this case, the

sorption process should be followed by the application of an appropriate separation method, such as flotation, in order to remove/separate the metal-loaded sorbent particles from the treated and cleaned solution. As a final result, a foam concentrate is produced, in addition to an underflow stream, which is purified water suitable for recycling [3]. Adsorbing colloid flotation was termed the method involving the removal of a solute (dissolved constituent) by the adsorption on, co-precipitation with, or occlusion into a carrier floc.

2. The Separation Process Applied to the Area

The first time we actually met in the biblography this separation application to biological materials was by Gaudin [4], a leader in the area of mineral processing, who examined (in a noteworthy book) the flotation of *Escherichia coli*, *Bacillus cereus*, *B. subtilis*, *Bacillus megaterium,* and *Serrata marcescens*. Microorganisms have found increasing use in minerals engineering; some of the applications, such as biologically assisted leaching of sulfide ores and biooxidation of refractory sulfide gold ores, are established commercial processes [5]. In addition, Edzwald [6] presented in London his work on DAF—during an International Symposium to mark the retirement of K.J. Ives. Table 1 [7–35] shows certain literature facts worth mentioning. Recently, certain reviews on this scientific area were published by our lab—*i.e.*, [36–38].

Table 1. Brief historical literature background of the scientific area.

Flotation details	Reference
Bacterial cells	[7]
B. cereus, application to microbiology	[8]
Bacteria and materials causing organic color	[9]
Six species of bacteria (among other)	[10]
Algae and activated sludge	[11]
Saccharomyces carlsbergensis from culture broth	[12]
Proteins, produced by yeast, fractionated	[13]
Recovery of proteins, proteolytic enzymes	[14]
Streptomyces pilosus after lead accumulation	[15]
Yeast foam flotation	[16]
Iron-oxidizing bacterium, mineral flotation	[17]
Waste activated sludge	[18]
Biosurfactants as collectors	[19]
Mycobacterium phlei, hematite	[20]
Biodegradable polymer flotation	[21]
Silica-induced protein *E. coli* and quartz	[22]
Algae separation	[23]
Flotation in seawater desalination	[24]
Tributyltin-based paints elimination	[25]
Acid mine drainage high-rate flotation	[26]
Serratia marcescens, flotation of iron ore	[27]
NOM removal by coagulation	[28]
EPS in bioflotation	[29]

Table 1. *Cont.*

Flotation details	Reference
Acidithiobacillus ferrooxidans to replace NaCN	[30]
Phanerochaete chrysosporium decompose pyrites	[31]
Phosphate-dolomite separation, two bacteria	[32]
Electroflotation sludge thickening	[33]
Rhodococcus opacus, apatite/quartz	[34]
Microorganism as collector for hematite	[35]

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 [39]. The manner in which bacteria affect the surface reactivity and the mechanism of bacteria adsorption has been unknown and accumulation of the primary data in this area was started. The bioflotation and bioflocculation concern the mineral response to the bacterium presence, which is essentially an interplay between microorganism and the physicochemical properties of the surface, such as the atomic and electronic structures, the net charge/potential, the acid-base properties, and the wettability of the surface.

Biological treatment is regarded as the best method in terms of cost input (chemical consumption and refill, handling of sludge and equipment maintenance) and water quality (in terms of COD level) produced. The aforementioned was investigated for laundry wastes [40]. The performance of a poultry slaughterhouse wastewater treatment plant and the operating strategies that were applied have been elsewhere examined [41]; the plant consisted of dissolved air flotation, anaerobic ponds and a facultative pond. The generation of stable foam on the surface of aerated reactors is a common feature of activated sludge systems and its control was studied including the microbial ecology of foaming [42]. Finally, dissolved ozone flotation was seen as a more efficient technique than the conventional mechanical diffuser system to achieve discharge limits, by reducing pollutants from municipal wastewater [43].

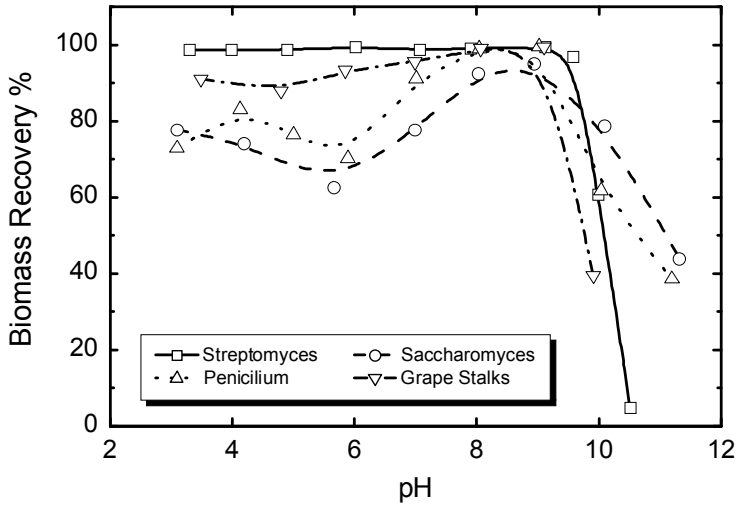
3. Floatability of Biological Materials

A comparison of the floatability of various types of biomass was conducted over the whole pH range and is shown in Figure 1. 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%. Hence, biomass separation by flotation is possible and the optimum conditions have been found for the different systems examined. It was also observed for the same system that the optimum pH value for biosorption is not necessarily the same as that for flotation [44]. Several biological systems are known to explore the presence of microorganisms and their ability to adsorb and bind toxic metals from liquid or solid wastes.

Focusing on hydrophobicity of biological systems is required, among others, when the scope of investigation is the eventual immobilization of microorganisms on a suitable substrate, as for example in the case of biosorption process, when applied in columns. But the hydrophobicity of biomass forms

the significant parameter that has to be examined for the identification and finding of the appropriate conditions, leading to an effective separation by the application of flotation (being actually a three phases, solid-air-aqueous, complex system). The hydrophobicity of bacteria cells is mainly due to the properties of cell wall (*i.e.*, the biosorption sites), which strongly depend on the presence of various polysaccharides, proteins and lipids that form a biopolymer surface layer, whose properties can be affected with the changing of growth conditions.

Figure 1. A comparison of various biosorbent types, showing the obtained floatability in the laboratory (by dispersed-air flotation), as a function of pH change. Reprinted with permission; copyright Wiley, 2011 [44].



Toxic metals exist of course in the effluents of many industrial operations and the impact of chemical speciation was stressed during various flotation applications for metal separation from the effluent [45]. Thermodynamic equilibrium diagrams and software packages were employed to interpret the removal mechanism involved. In the precipitate flotation of lead in the form of insoluble hydroxides, by simply regulating the solution pH and by the addition of (cationic surfactant) dodecylamine, the obtained successful removal of lead ion was correlated to the theoretically expected precipitation of lead hydroxide at the pH value of 10 [46].

4. Contact Angle

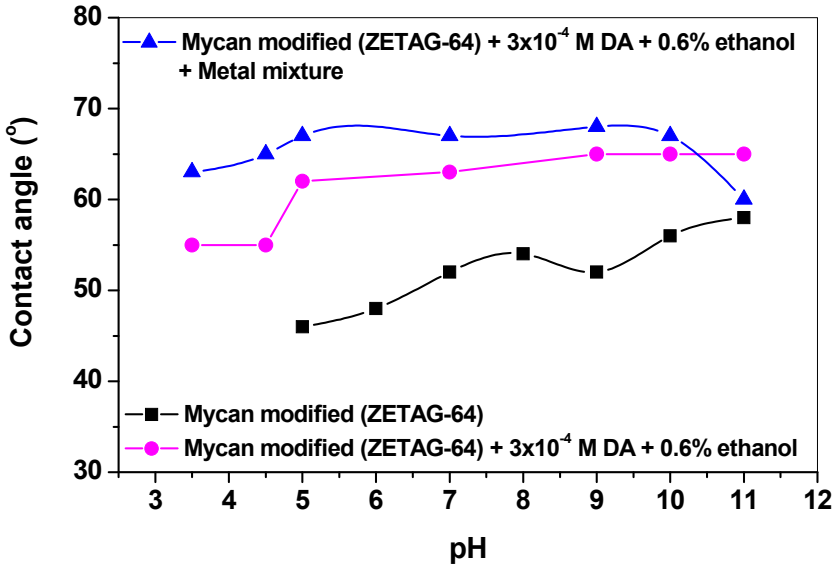
Hydrophobicity was indirectly measured, often by: (i) contact angle measurements (mentioning that the greater the contact angle, the more hydrophobic the system is); and (ii) surface tension measurements of biological systems (noting that greater surface tension values mean better wetting ability of the medium). Hydrophobicity in a solid/liquid/gas system, as flotation is, is certainly a complex phenomenon and a result of different interactions; in this way, the measurement of contact angle becomes significant.

The correlation between contact angle, adsorption density, zeta-potential and flotation recovery is typically used in fundamental studies of mineral processing, for instance for the system of dodecylamine-quartz [47]; where the pH of maximum recovery, contact angle and zeta-potential was shown to correspond to the pH at which precipitation and adsorption of dodecylamine collector

occurred. In addition, magnesite contact angle measurements and the recovery by sodium oleate *versus* the solution pH were presented, during a North Atlantic Treated Organization (NATO) Advanced Study Institute (ASI), held in Halkidiki, Greece [48]. Contact angle measurements usually serve as a measure of the hydrophobicity of mineral surfaces, although this—as far as flotation is concerned—was disputed.

Figure 2 presents the respective results for the examined system. The contact angle measurements correlated quite well with the floatability of biomass, as both curves at pH values around 11 started to decrease [49]. The major factors that affect the hydrophobicity of microorganisms are the following: the type of microorganisms, their growth rate, the growth conditions (composition of substrates, type of used carbon source, temperature, *etc*.), the pH and ionic strength of medium, the growth phase of the microorganisms (e.g., static or logarithmic), the specific time of taking the measurement (aging effect), the presence of other polycations, the aeration, and the presence of oxygen.

Figure 2. Contact angle measurements of modified biomass as influenced by the solution pH (in presence also of collector and metals mixture). Reprinted with permission; copyright Elsevier, 2009 [49].



5. Surface Tension

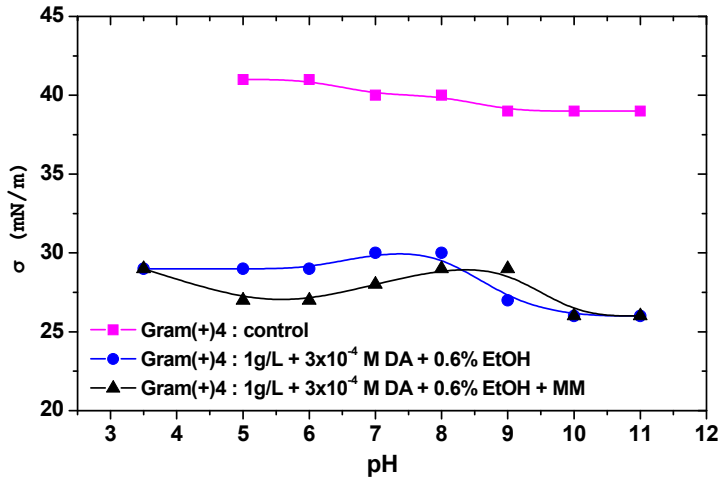
Liquid/vapor surface tension control was applied to regulate flotation [50]. Surface chemistry issues, such as surface tension, zeta-potential (see also below), *etc*., are incorporated in several treatment methods, such as the adsorption of specific chemical agents (collectors) to enhance process efficiency, the change of hydrophobicity of a solid particle for the purpose of separation, that is, by the application of flotation. Especially, the concept of critical surface tension for the examination of wetting effects proved to be important to improve selective flotation.

The influence of different physicochemical properties on flotation efficiency is known from the relevant previously published work in the minerals enrichment field; similar effects (positive or negative) can be expected also on metal biosorption. Among the major parameters affecting flotation is the surface tension, being largely affected by the surfactant concentration; respective results, for example, are presented in Figure 3. These results could be correlated well with data of contact

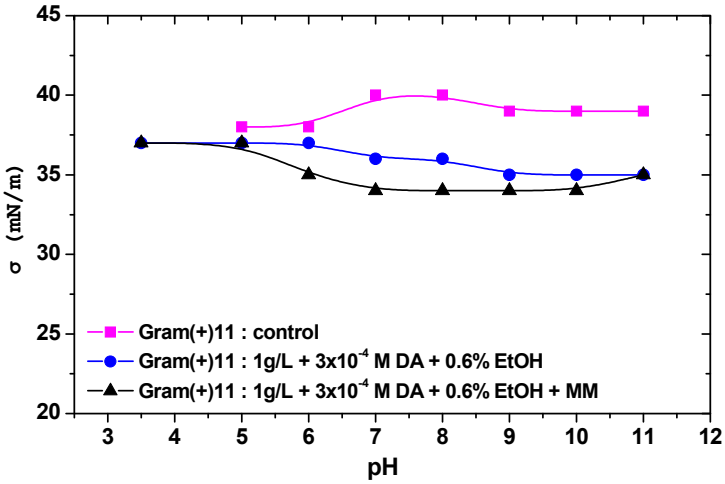
angles [51]. It was concluded in the paper that the conducted work, including contact angle, surface tension and zeta-potential measurements and examining the main parameters affecting the hydrophobicity of micro-organisms (and, hence, their eventual floatability), in parallel with typical metal sorption and separation experiments, could integrate the studied process, providing useful options to the removal mechanism(s) that can be also applied for operational improvements, or for design reasons.

It has to be noted, however, that this is a combined effect, also due to the simultaneous presence of frother, because the flotation collector (in that case: dodecylamine) was added as ethanolic solution to improve solubility. Surface tension is also a measure of the wetting ability of the medium. Additionally, the addition of ethanol results in the decrease of air bubble size, and, hence, can stabilize the produced froth.

Figure 3. Values of surface tension of Gram-positive microorganisms in presence and absence of dodecylamine and cadmium. Reprinted with permission; copyright Inderscience, 2010 [51]. (**a**) Figure for Gram(+)4; (**b**) Figure for Gram(+)11; (**c**) Figure for Gram(+)16.

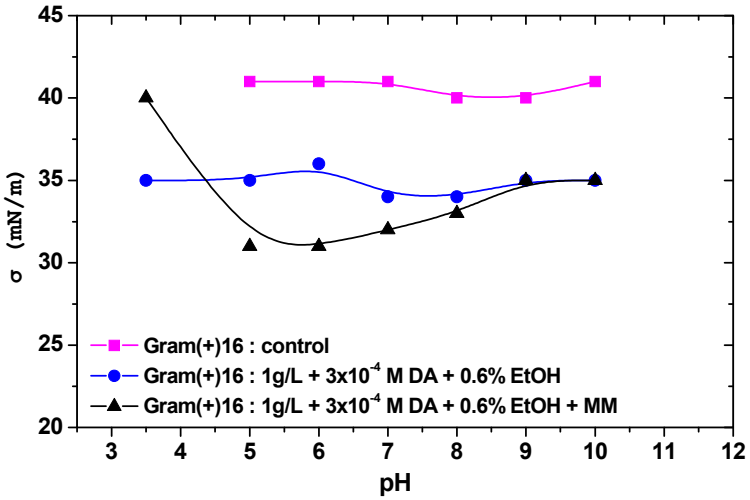


(**a**)



(**b**)

Figure 3. *Cont.*



(**c**)

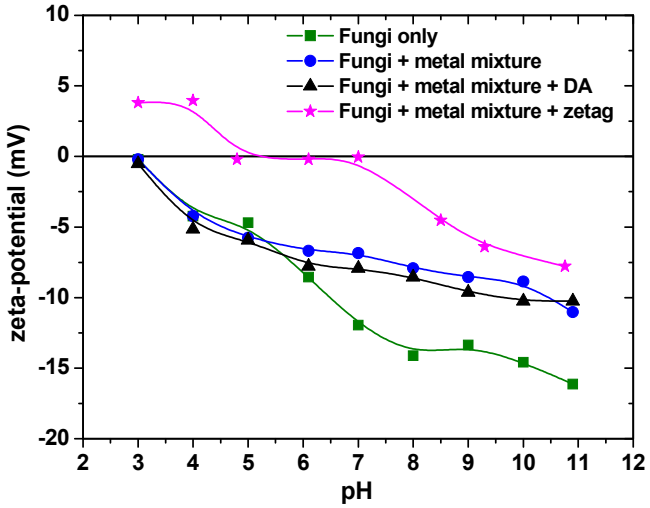
6. Zeta-Potential

The electrokinetic measurements may provide useful indications on flotation, being usually followed by floatability experiments. Perhaps the best application of this work has been to sulfide minerals [52]. It was concluded that electrochemistry is the basis to explain the mechanisms of pyrites flotation and even to control the process. Pyrite (*i.e.*, iron sulphide mineral), was found to act as an efficient Cr(VI) reducing agent, and the resulted hydroxo-Cr(III) species were found to be precipitated and removed onto the pyrite particles. The process mechanism was also examined by zeta-potential measurements and speciation studies [53].

The main chemical groups of biomass surfaces that are capable of participating in sorption and chelation of a number of bivalent metal cations are polar or anionic in nature, such as hydroxyl, sulfhydryl, carboxyl and phosphate groups, as well as nitrogen-containing (amino) groups. Such groups will contribute to the zeta-potential of the surface. The measured zeta-potential values for the biomass samples are presented in Figure 4. Negative gradually decreasing values over the whole of the studied pH range (3–11.5) were observed; similar behaviour was previously observed for other biosorption systems [54]. The point of zero charge was determined for *Streptomyces* and fungal biomass to be around pH 3, while for yeast it occurred at a lower pH value.

The presence of metals, as well as of dodecylamine, was found to change the zeta-potentials towards less negative values. Surface charge neutralization and reversal towards positive values was also observed when a cationic polyelectrolyte was added. The proper flocculation of biomass, which will in part depend on surface zeta-potential, will assist its subsequent flotation separation. Conventional separation techniques, under similar experimental conditions (to those described in the publication), were examined for comparative purposes, namely centrifugation, filtration, and ion flotation.

Figure 4. Electrokinetic measurements of biomass as a function of solution pH (in presence and absence of the metals mixture, dodecylamine and cationic polyelectrolyte) for Penicillium. Reprinted with permission; copyright Wiley, 1999 [54].



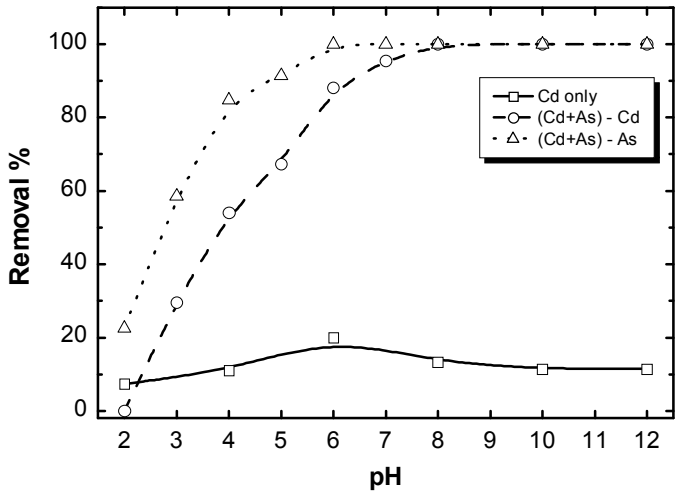
7. Flotation Techniques

Several variations of flotation were proposed, especially for the recovery of fine mineral particles (*i.e.*, having diameter below 0.045 mm); the background and performance of some of these techniques were reviewed and the associated problems were discussed [2]. An extension of the older carrier flotation mineral process led to the development of a novel process termed "biosorptive flotation", which generally is a technique capable of scavenging metal ions from dilute aqueous solutions, by using appropriate biosorbent materials. The ability of microorganisms to abstract metal ions from water (usually termed as bioaccumulation or biosorption, depending on whether the microorganisms are living or not, respectively) is an already well-known and extensively studied treatment process. The integrated approach has been examined [55]. The influences of the presence of a filter aid with biomass, and of applying a quaternary ammonium surfactant were also investigated [56].

The common flotation methods of bubble generation have been compared in detail and any differences between them examined [57]. Further, it was considered that there is a gap between the fundamental considerations of froth (mainly dispersed-air) and of dissolved-air flotation and their respective application areas, which seldom can interact.

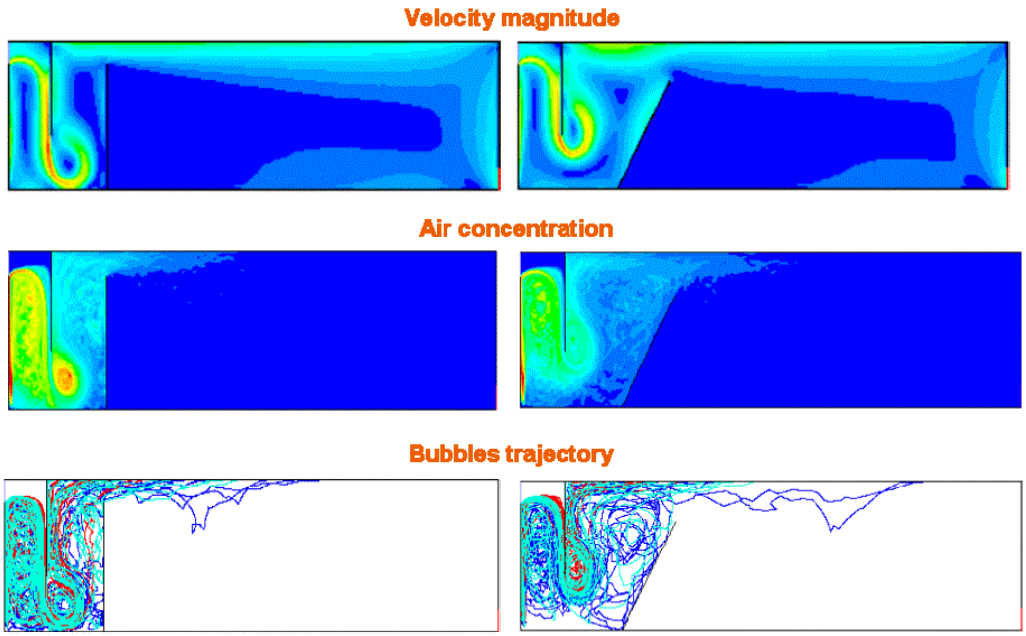
Electroflotation (or electrolytic flotation) offers certain advantages over other flotation techniques of dispersed-air or dissolved-air [58].The results were improved, when alternative aluminum alloy electrodes were used (see Figure 5), instead of the previous ones that consisted of pure aluminum; sufficient biomass separation (around 90%) was possible, approximately from the pH value 7. This result was found by applying smaller flotation time (10 min) and even at the lower current density (65 A/m^2). The two curves of cadmium biosorption on biomass and of floated (Cd-loaded) biomass almost coincide with the studied pH variation. In addition, in the same figure the substantially lower removal of Cd ions, but without the presence of biomass (simply by the influence of pH), is indicated [59].

Figure 5. Electroflotation of cadmium ion, using activated-sludge biomass: effect of solution pH. Reprinted with permission; copyright Inderscience, 2012 [59].



During an electroflotation study of pyrite, in order to explain the observed difference in flotation behavior, thermodynamic calculations for the system Fe-EX-H,O have been done and pe-pH predominance diagrams for iron and xanthate species were presented [60]. Dispersed-air was then compared to electrolytic flotation for this case; although hydrophobicity of the particles assisted both techniques, electrolytic flotation also worked well in hydrophilic, moderately flocculated particulates.

Figure 6. Dissolved-air flotation studied by computational fluid dynamics (CFD): impact of inclined internal baffle on the separation process. Reprinted with permission; copyright Inderscience, 2007 [60].



Recent systematic theoretical analyses clearly depicted the various hydrodynamic and physicochemical parameters that dictate flotation performance The application of CFD codes to simulate large-scale flotation processes offers distinct advantages in investigating the relative significance of various design

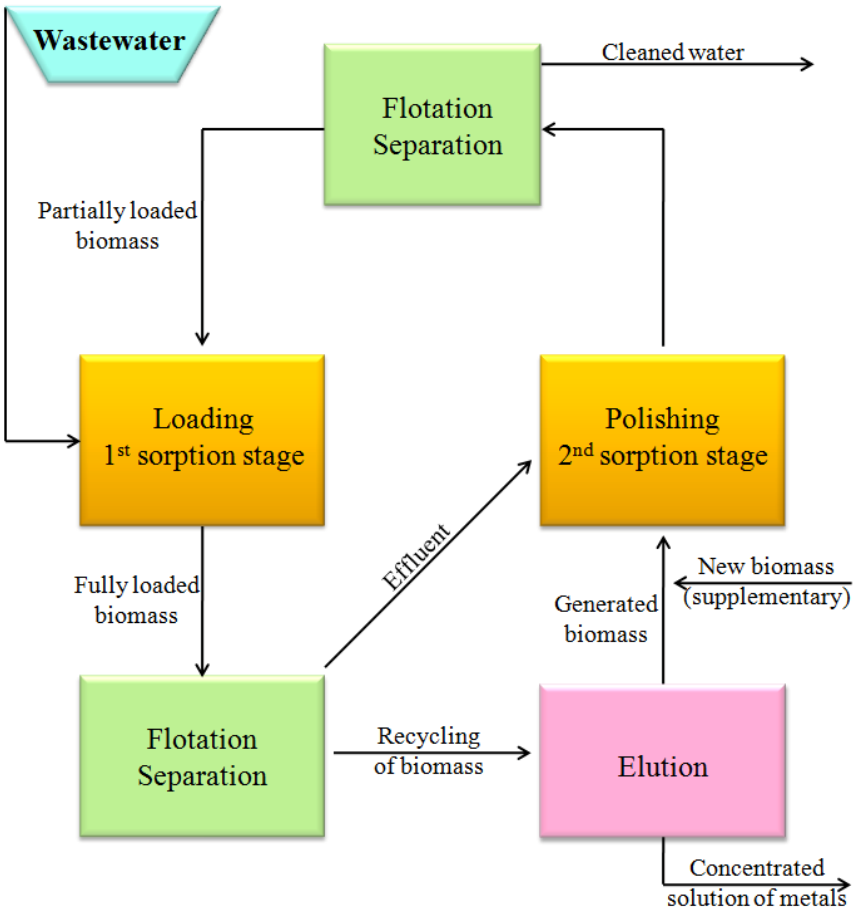
and operating parameters (Figure 6). Testing different multiphase and turbulence models in CFD simulations (the code FLUENT 6.1 was used) was a valuable tool for appraising the operation of an ill-functioning DAF tank. Regarding the employed turbulence models (the *standard k*-ω and *standard k*-ε models), they produced comparable results in terms of the water velocity and air volume fraction but predicted considerably different bubble/particles aggregates recoveries. This is an indication that it is rather the local features of bubble/particles encounters (probability of bubble/particle collisions and collision rate) and not the macroscopic phase distributions in the tank that determines the flotation rate.

During the last decade, several investigators have employed numerical simulations to examine large-scale hydrodynamic aspects of flotation processes. Owing to the large computational burden, most of them refer to two-phase (gas-liquid) systems and a 2D-structure grid and only a few attempts were made with three coexisting phases (gas-liquid-solid) [61].

8. Sustainable Chemistry

A review of sustainability and its significance for the chemical and process industry was presented [62]. The complexity issues in the ecological aspects of chemical engineering were elsewhere discussed [63]. Water pollution is a fact in many developing countries; the United Nations warns further that the world's use of water is not sustainable [64]. The need for fresh sources of drinking water is becoming urgent worldwide.

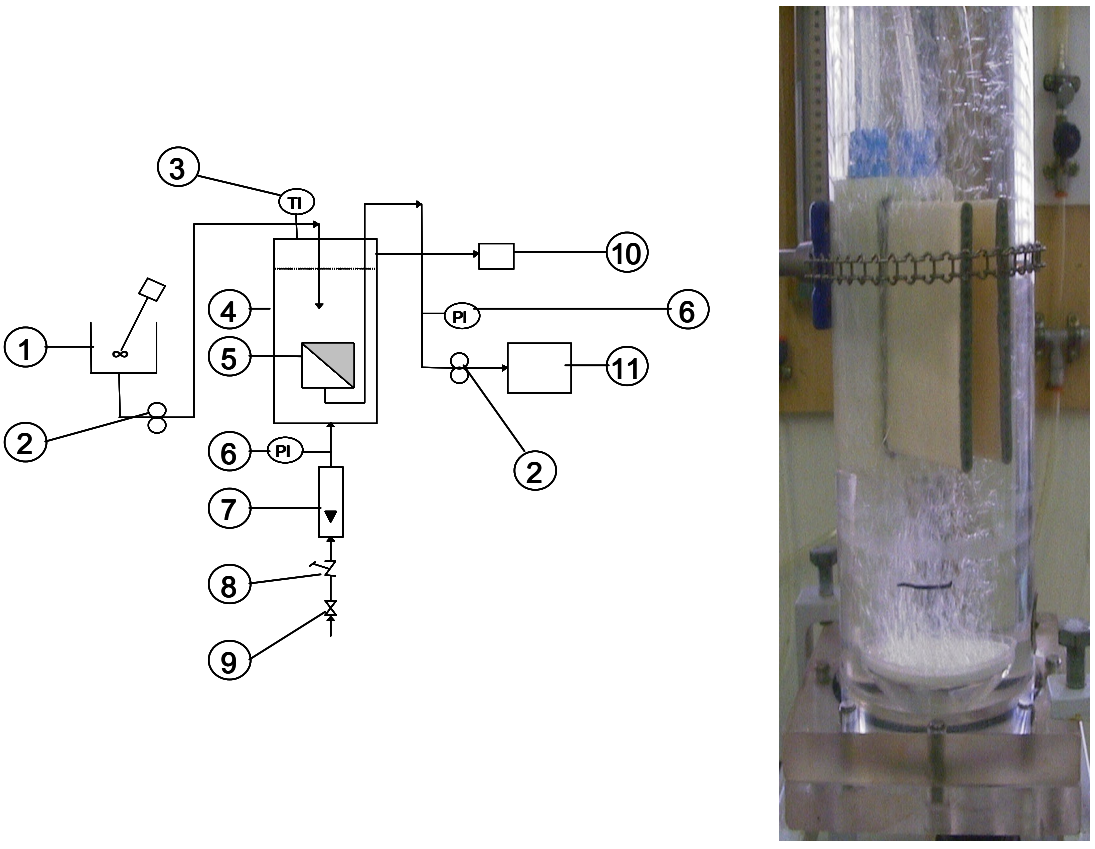
Figure 7. Flowsheet of the proposed two-stage countercurrent biosorptive flotation process. Reprinted with permission; copyright Wiley, 2002 [55].



As far as the flowsheet configuration is concerned for biosorptive flotation, a two-stage counter-current scheme was selected, consisting of a leading and then a polishing biosorption steps, whereas the elution stage was following in the end, closing the recycle loop. The partially loaded (initially fresh or eluted) biomass was guided counter-currently from the polishing to the leading biosorption stage, where the raw wastewater feed was introduced, following the reverse route, *i.e.*, from the leading to the polishing treatment stage (Figure 7). The application of electrolysis, using a rotating cathode cell as the final stage, in order to recover the metal in the form of powder was also proposed; the cadmium-depleted electrolyte to be recycled as the eluant [65].

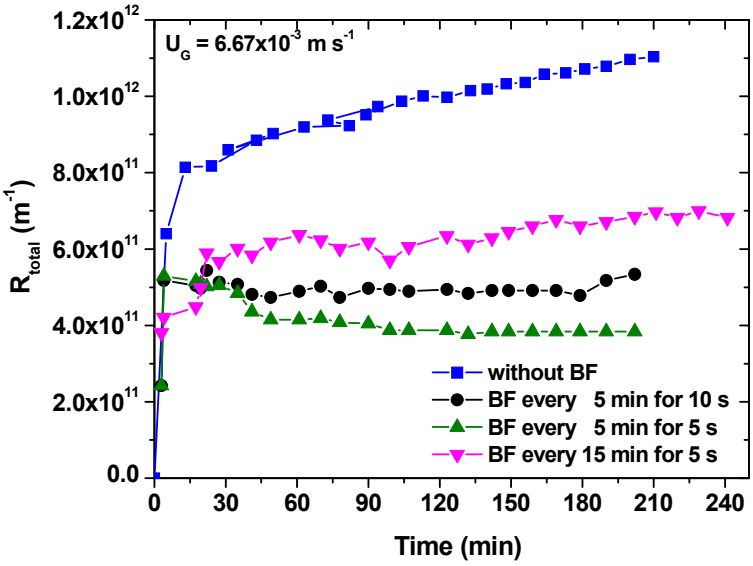
Membrane filtration technologies are increasingly used for S/L separation purposes in water and wastewater treatment plants. A new hybrid cell of microfiltration combined with flotation, applied effectively downstream for the same aim, has been also studied in depth (see Figure 8) [66]; as, today, there is a tendency for combined and more compact processes.

Figure 8. Scheme of the experimental hybrid cell rig (1, mixing tank; 2, peristaltic pump; 3, thermometer; 4, flotation column; 5, membrane microfilter; 6, manometer; 7, air flowmeter; 8, non-return valve; 9, slide valve; 10, foam collection tank; 11, permeate collection tank), including a photograph of the cell. Reprinted with permission; copyright Elsevier, 2004 [66].



Typical selected results, while membrane backflushing testing, are presented in Figure 9; for *Saccharomyces* yeast removing zinc ion [67]. As the unit also needs periodic backflushing for efficient operation. Flotation removed effectively a major part of the biomass particles, responsible for membrane fouling.

Figure 9. Experiments with the hybrid flotation cell and biosorbents: effect of frequency and duration on total resistance. Reprinted with permission; copyright Taylor and Francis, 2009 [67].



A large number of techniques have been used today to limit the membranes fouling and among them, certainly is air bubbling constituting also the transport medium in flotation, as applied in wastewater treatment. Meanwhile, dispersed-air flotation is suitable as a pretreatment stage for microfiltration. Ceramic flat-sheet membrane modules were used in the Laboratory for this scope, of multi-channel geometry, inserted inside a typical flotation cell, as shown. A cost estimation analysis was also done for a typical plant flowsheet, achieving also energy savings.

The proof of the concept for this hybrid separation process was investigated using an aqueous suspension of fine and ultra fine particles (synthetic adsorbents, ion exchangers). The feasibility of the combined process was investigated *in situ* in the successful recovery of metal cations (*i.e.*, copper) from a Bulgarian mine effluent [68].

9. Concluding Remarks

It was said that there was an urgent need for developing basic knowledge that would underpin biotechnological innovations in the natural resource (re)processing technologies that deliver competitive solutions. New economy activities are in fact surprisingly dependent on traditional raw materials. Chemistry, of course, was one of the foundations of the wealth and growth of the European economy during the 20th century based on an ever-improving understanding of interactions on a molecular level to enable increasingly sophisticated manipulation of the physical world.

Certainly, much time passed and meanwhile, noteworthy studies published since the question by Ross Smith and his team existing in the perhaps "peculiar" title—*i.e.*, future technology or laboratory curiosity [69]. An attempt was made to show some of the promise of microorganisms in mineral bioprocessing, being the main application of the flotation technique. That microorganisms, both living and dead, and products derived from the organisms, can function as flotation agents and flocculation agents is abundantly clear. They can modify the surfaces (of minerals). They can function as flotation

collectors and as flotation depressants and activators. In many cases they or their products can function as specific flocculation agents. Problems that must be solved before such microorganisms or products from the organisms can be used in commercial operations include culturing the organisms at a cheap cost and reduction in dosages required for various separations. These tasks are formidable. However, the concept of using such natural materials in place of various chemical reagents that may be toxic is very attractive.

Thousand tons of residual biomass are produced each year from fermentation industries and also from biological wastewater treatment plants; hence, it could be considered as a candidate source for suitable biosorbents. The waste biomass often contains poorly biodegradable biopolymers (cellulose, chitin, glucans, *etc*.) that make it a quite poor fertilizer for agricultural use. Apart from microorganisms having low density, certain are of branched filamentous type, such as the *Actinomycetes*, being ideal for flotation separation. A common feature in biotechnology is of course the presence of suspended particles, living or disrupted microorganisms, which are difficult or time-consuming to remove by filtration and on the other hand, centrifugation is apparently more expensive. The biomass flotation recoveries observed were some reaching almost 100%.

It was also illustrated that it has been possible to prevent microfiltration membranes fouling by gas sparging; which prevents solid particles from depositing on the surface of the membranes or from entering and blocking the membrane pores. The same bubble stream was used in an innovative hybrid cell to remove the solid particles from the dispersion, by flotation into the froth layer. This apparently results in the membranes being subjected to only a part of the initial feed concentration of solid particles.

It is hoped that this research has contributed, even by a little, towards sustainability.

Conflicts of Interest

The authors declare no conflict of interest.

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