

Review

# Flotation in Water and Wastewater Treatment

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**Abstract:** Flotation constitutes a separation process that originated from mineral processing. Nowadays, wider applications have been found and compared to flotation for water and wastewater treatment. Stress in the present review paper was mainly applied to heavy metal ions recovery by flotation and the respective mechanism followed, being either ion, precipitate, or sorptive flotation. In the latter case, the use of adsorbents is included (such as powdered activated carbon, zeolites, and goethite), as well as various biosorbents. The flotation of the following metals was reviewed: copper, zinc, nickel, lead, iron, chromium, arsenic, gold, and others. The bubble generation method could be applied for typical dispersed-air flotation column, electroflotation, or dissolved-air flotation; the latter being the most appropriate established technique in water treatment. The role of particle size (for example, studying flotation of salt-type mineral fines) was also examined.

**Keywords:** separation; dispersed-air flotation; metals; particles; biomass

## 1. Introduction

Flotation is known as a separation process, based on the introduction of gas bubbles as the transport medium. Suspended particulate matter, being hydrophobic or conditioned to be so, is then attach to the bubbles and moves toward the water solution surface—i.e., contrary to the direction of gravity [1,2]. Different bubble generation methods exist, belonging either to the broad class of dispersed-air flotation (or froth, in mineral processing) techniques, in which electroflotation is often included, or dissolved-air flotation (DAF) that is based on Henry's law [3,4]. Traditionally, the flotation process and the relative scientific information, that is used to investigate and explain the separation mechanism involved, came from the field of mineral processing [5]. However, the process has found different interesting applications, including the use upstream of sorbent materials, parts of chemicals, such as collectors, frothers, modifiers, etc.

The knowledge of chemistry can help in flotation separation, as evidenced by various examples. For instance, a wide variety of heavy metal bearing waste streams require treatment, so due to their solubilities and mobilities, toxic metals could cause significant damage to the environment [6–8].

The removal of microplastics (defined as plastic particles <5 mm) from effluent was investigated in four municipal wastewater treatment plants, utilizing different advanced final stage treatment technologies, including flotation [9]. A coagulation-flotation method (using an anionic surfactant and a cationic polyelectrolyte) was designed for the rapid removal of tetracycline antibiotics from water [10]. The latter are broad-spectrum antibiotics commonly used in livestock farming and often prescribed for human therapy. Also, petroleum refining, and maybe unavoidably, generates large volumes of oily wastewater. The development status of relevant treatment methods was summarized [11]. Oily wastewater constitutes a typical application for flotation (perhaps for density reasons). Pollutants

removal by (dissolved-air) flotation was analyzed at combined sewer overflows, which usually contain sewage and rainwater [12]. These are thought to be the main cause of eutrophication and algae occurrence in lakes.

Various types of biological materials were also reported to be efficiently floated, such as bacteria, fungi, yeasts, activated sludge, and grape stalks [13]. Given the aforementioned, the scope of the present paper is to review the floatation process in-depth, including updating the current literature in the area of wastewater treatment. The importance of flotation, as a separation process, to the economy of the whole industrial world, is considered to be enormous. Sustainability issues in this area have been recently expressed [14,15].

## 2. Flotation of Metal Ions

Ion flotation involves the removal of surface-inactive ions from aqueous solutions by adding surfactants or collectors, usually with an ion having a charge opposite to that of the metal ion to be removed [16,17]. Collectors are a type of surfactant that increase the natural hydrophobicity of the surface, increasing the separability of the hydrophobic and hydrophilic particles. As the respective concentrations are raised, this may lead to precipitation of the ion-surfactant floatable product before air is passed. This means that it is no longer a solution, but rather a dispersion (i.e., precipitate flotation) [18]. The method of ion flotation was employed to remove metal ions from solutions containing low concentrations of heavy metal, which may be produced from any industrial process: the metal working, semiconductor, metal industries, and mine water [19,20]. The results changed (some ions presented better results) when a Denver flotation cell was used. This can be attributed to the different hydrodynamic conditions existing in the cell [21].

Ion flotation was elsewhere carried out to investigate the effective factors and kinetics of Zn(II) ion removal from wastewater [22]. The optimum conditions were determined at first by experiments that were conducted in a Hallimond tube. The same group also studied ion flotation of nickel ions [23]. This removal was evaluated based on various parameters including the chemical interactions, water entrainment in the froth phase, separation mechanism, and the Ni(II) removal rate. In an older notable publication [24], the hydrolytic behavior of a metal (i.e., zinc) was related to its removal by foaming. The results demonstrated that precipitate flotation at a pH above 8, where zinc is no longer an insoluble hydroxide, was a more efficient removal process than the foam separation of soluble metal species.

The typical laboratory arrangement, as shown in Figure 1, usually includes the following parts: a conditioning/feed tank with a mechanical mixer, a peristaltic pump, liquid rotameters, the flotation column with a weir (on the top), a foam collection tank, an air compressor connected through a needle valve, washing trap and air flowmeter, a porous diaphragm at the bottom of the cell, a mercury U-tube manometer and effluent tank, a pH meter, and a chemical dosing pump. For hydrodynamic reasons, counter-current operation is preferable [25].

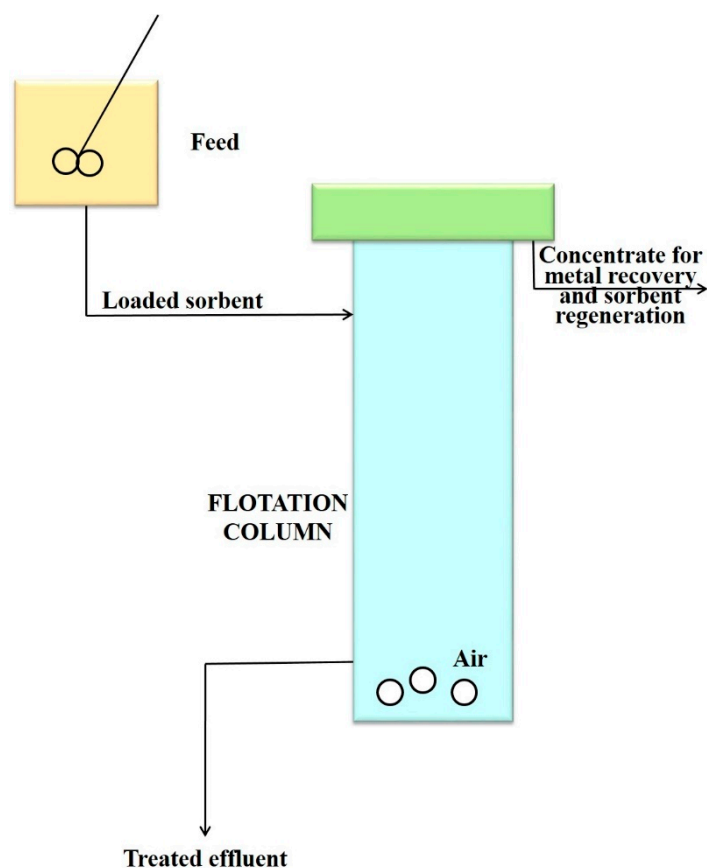


Figure 1. Scheme of a counter-current dispersed-air flotation rig.

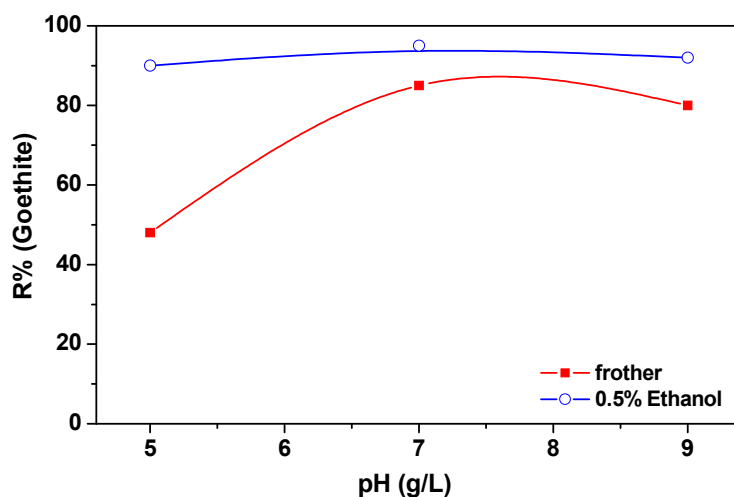
### 3. Adsorbents and Flotation

The removal of soluble ionic species, such as toxic metal cations or oxyanions, from dilute aqueous solutions (as most wastewaters are) has been extensively investigated in the laboratory (with batch-scale and continuous mode experiments) by applying what was termed as the sorptive flotation technique. This method involves the preliminary abstraction or scavenging of metal ions using proper “sorbents”, which exist at the fine or ultrafine particle-size range, followed by a subsequent flotation stage for the separation of metal-loaded sorbent particles from the treated (cleaned) solution [16,17]. Sorption, by definition, is a general term describing the attachment of charged species (like toxic metal ions) from a solution to a co-existing solid surface [26]. Sorption kinetics maybe controlled by several independent processes that can act in series or in parallel.

Other researchers [27] combined this technique with palm oil mill effluent in order to reduce the respective Chemical Oxygen Demand (COD), and having modified natural bentonite as the adsorbent. Cosmetics wastewater samples were also effectively treated by dissolved-air flotation, assisted by coagulation—i.e., with  $\text{Al}_2(\text{SO}_4)_3$  [28]. The use of nanoparticles as adsorbents attracted widespread interest because they have a large surface area-to-volume ratio and the capability for functionalization with different molecules. Silica nanoparticles were tried for this scope to recover trace copper ions [29]. The possibility to determine hydrophobic properties of (mineral) surfaces in water using the concept of colloidal probe atomic force microscopy was introduced [30]. The latter may be useful during flotation research in the investigation of the so-called hydrophobic effect or the occurrence of small gas layers on hydrophobic surfaces.

Figure 2 presents, as an example, the application of goethite to remove pentavalent arsenic oxyanion; the simultaneous addition of the frother improved the loaded sorbent floatability, realising savings in the respective consumption of collector, with cetyltrimethyl-ammonium bromide being

a typical cationic surfactant. The use of a frother in dispersed-air flotation led to the production of finer bubbles due to lowering the surface tension of the solution; its secondary action was to further stabilize the foam layer. Of course, the impact of nanostructures on the properties of high surface area materials is a field of increasing importance to understand, so inorganic materials for diverse technological applications can be created and improved. Synthesized material was used in two forms in the laboratory: in fine powder of nanocrystals and grains (for packed-bed column experiments).

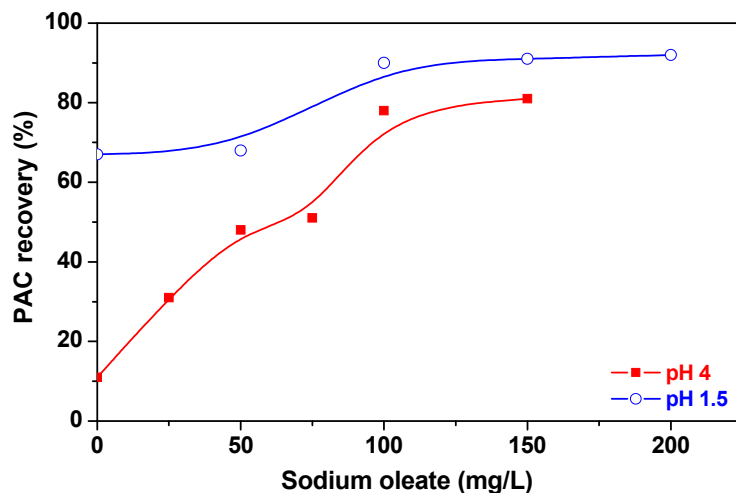


**Figure 2.** Recovery due to flotation of synthetic goethite particles with As(V): effect on the separation of ethanol addition as a frother, 0.5 g/L goethite, in presence of 25 mg/L CTMA-Br (cetyltrimethylammonium bromide). Reprinted with permission [31]. Copyright Elsevier, 1997.

Arsenic and its compounds are highly toxic, necessitating effective removal from effluents and occasionally from water supplies of underground origin [32]. Iron-based compounds, like goethite, have often been used as a suitable bonding agent for heavy metals, perhaps one of their advantages is the capability to remove both cations and anions—as presented below. A number of surface complexation approaches were developed, such as the Constant Capacitance, Stern, Diffuse Double Layer, and Triple Layer Models, the fundamental concepts upon which all these are based remain more or less the same [33]. The application of the program PHREEQC (of the U.S. Geological Survey) was found to be a helpful tool for sorption calculations [34].

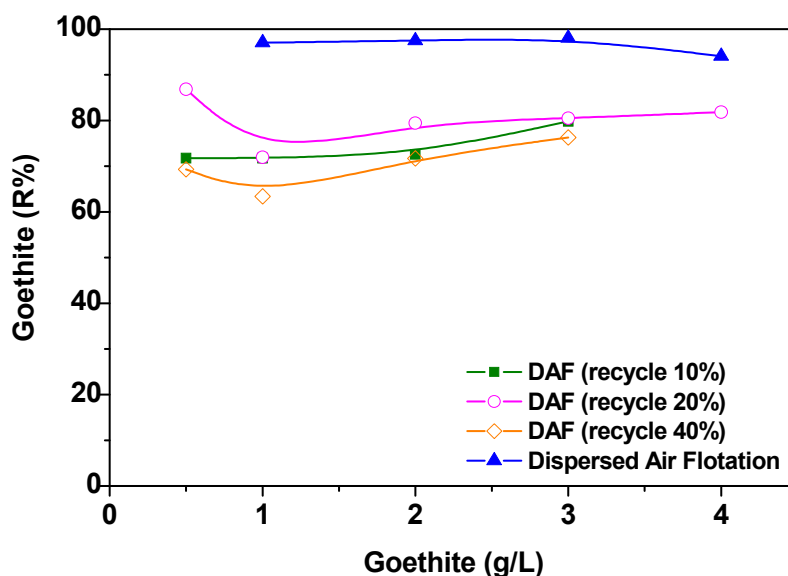
Activated carbons are among the effective adsorbents because of their excellent sorption capacity, and their microporous nature is generally well suited to many applications; although their use has been often prohibited mainly due to their relatively high cost, low selectivity, and regeneration problems [35]. Thiourea ( $\text{CS}(\text{NH}_2)_2$ ), on the other hand, presents an alternative lixiviant to cyanide, applied in acidic media for gold recovery. This process offers certain advantages. Noting that the dissolution of gold in acid thiourea solutions is a rather complex process, involving the formation of a soluble, cationic gold-thiourea complex, and the oxidation of thiourea itself through intermediate products. The application of an external oxidant, such as  $\text{Fe}^{3+}$  or  $\text{H}_2\text{O}_2$ , seems to be essential. A Freundlich-type sorption isotherm was found to fit the bench-scale laboratory results, using a commercial powdered activated carbon. Typical adsorption models were discussed.

As a flotation surfactant, anionic sodium oleate was here tested as seen in Figure 3 for example. The promising recoveries obtained were further studied by means of electrokinetic measurements. It was confirmed that gold always followed activated carbon in the flotation concentrate. Motivation for this work was the possible application of the process in gold leach solutions, for instance, after heap leaching. The impact of chemical speciation was stressed during various flotation applications for metal separation from the effluent. The Mineql+ computer program (Environmental Research Software) was used for the construction of thermodynamic equilibrium diagrams for the examined systems.



**Figure 3.** Floatability tests of 0.5 g/L powdered activated carbon (PAC), loaded with gold from thiourea solution: influence of collector concentration at two different pH (gold = 20 mg/L; TU = 400 mg/L (thiourea); and ethanol = 0.5 v/v; flotation contact time 5 min). Reprinted with permission by [36] Copyright Elsevier, 1994.

A comparison between dispersed-air (by a gas diffuser) and dissolved-air flotation was attempted, as shown in Figure 4, for the same separation and under comparable conditions. In the dispersed-air flotation cell, the flow conditions were more intensive in the complex solid/liquid/air system, as a greater number of larger air bubbles existed, resulting in higher mixing increasing sorption removal. In DAF processes, micro-bubbles of approximately 10–80  $\mu\text{m}$  in size are generated. The bubble size may be varied not only by using another diffuser or perhaps by the application of a frother, but also by another generation technique, i.e., electrolytically.

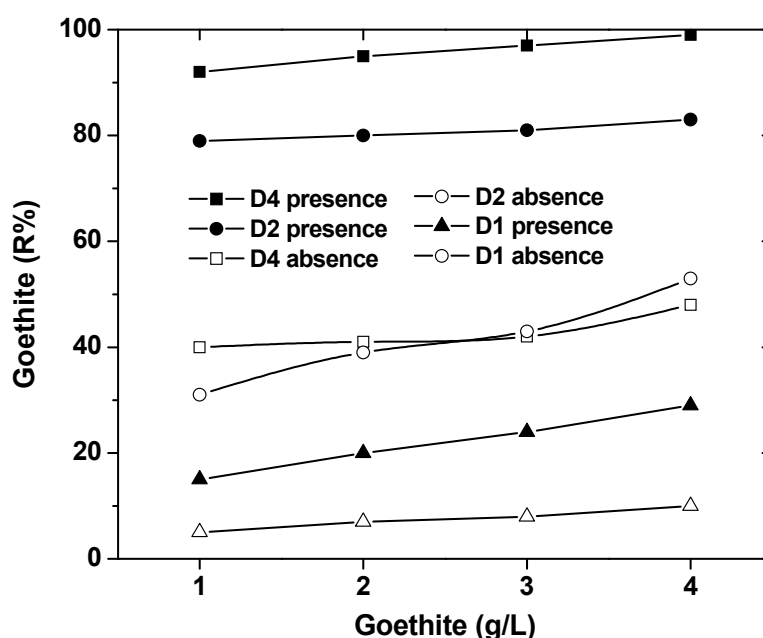


**Figure 4.** Comparison of dispersed-air with dissolved-air flotation for Zn(II) removal (collector: 200 mg/L sodium dodecyl sulfate (SDS) + 0.17% ethanol, flocculant: Zetag 87.4 mg/L); dissolved air: flocculation time = 5 min, 60 rpm–5 min 300 rpm–dispersed air: flocculation time = 5 min 350 rpm–5 min 700 rpm, air = 425  $\text{cm}^3/\text{min}$ ) [37].

The sorptive flotation process was here repeated for zinc. Considering that zinc hydroxide is generated at the alkaline region, the experiments have been conducted at a pH of 7. An anionic

collector (sodium dodecyl sulphate) was selected for performing the experiments, since the surface charge of the loaded material was positive. Dispersed-air flotation has considerable air volume (around 1000 times more than used in DAF), speed, and power to float a large amount of heavy solids, whereas dissolved-air flotation seems to be suitable for delicate particulate matter. Generally, both flotation techniques gave good flotation recoveries. Nevertheless, the dispersed-air flotation looks preferable, hence the number of bubbles (i.e., air volume) is more important than bubbles size. Notably, a 40% recycle for DAF is rather unrealistic as this flotation technique works usually according to the idea of a chemical reactor with recycle [16].

A flocculant was also required, particularly for DAF. Meanwhile, the metals removals were near 100%. In dispersed-air flotation, the finer the bubble size (obtained by changing in the cell the used porous diffuser), the better the results; as was apparent from a respective comparison—see for example in Figure 5. An approximate bubble size of 0.79–0.83 mm was calculated for the D4 diffuser, with pore diameter 10–16  $\mu\text{m}$  (being the lower). The size of bubble released is a function of the pore diameter of the opening, liquid density, and surface tension. Bubble-particle collection and attachment efficiencies increase with decreasing bubble size.

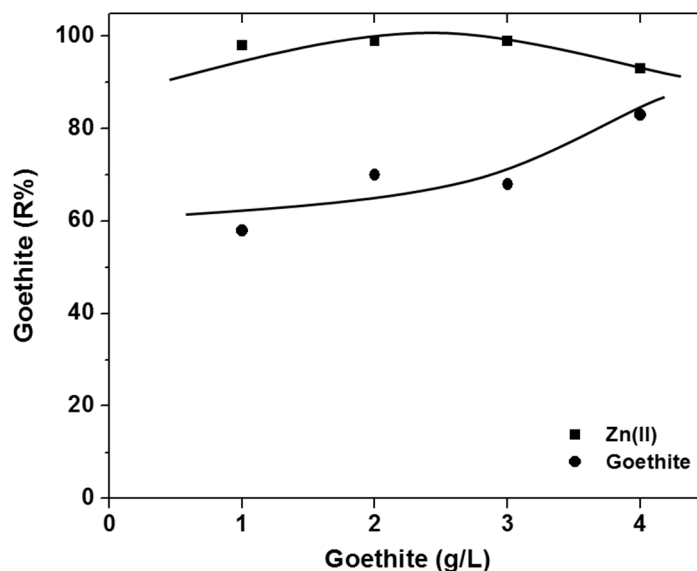


**Figure 5.** Removal of goethite by flotation in presence and absence of flocculant for different air diffusers (Schott fritted glass), loading zinc: [goethite] = 1 g/L, [Zn] = 50 mg/L, pH = 7.0, [SDS, sodium dodecyl sulfate] = 200 mg/L, [Zetag 87] = 4 mg/L. Reprinted with permission by Ecomed [38].

Goethite,  $\alpha\text{-Fe(III)}$  hydroxy-oxide, is a ubiquitous mineral and the most stable iron oxide in soil environments. It can be prepared in the laboratory by mixing Fe(III) nitrate with ammonium carbonate added as the precipitating agent dropwise, under vigorous mechanical stirring. The preparation of ferric ion gel was performed in a round bottom flask in a thermostat at 25  $^{\circ}\text{C}$  [39]. The procedure stopped when the pH of the suspension reached  $8.0 \pm 0.1$ . The precipitate was dialyzed until no nitrates were detected in the bulk and then freeze-dried. The characteristics of goethite adsorbents were measured by powder X-ray diffraction (XRD), nitrogen adsorption-desorption isotherms, infrared (IR) spectra, Scanning Electron Microscopy (SEM), and Transmission Electron Micrographs (TEM).

The simulation of this process was also examined using the computer program ExtendSim (Imagine That Inc., San Jose, USA), as shown in Figure 6. Simulation is known to be a method for predicting the course and results of certain actions (tests), to understand why observed events occur, to identify the problem area before implementation, to explore the effects of modifications conducted,

to confirm that all variables are known, and to evaluate ideas and explore inefficiencies. Sorption modelling was also investigated by surface complexation, in order to describe the process or even predict the outcome for the expected rate [40].



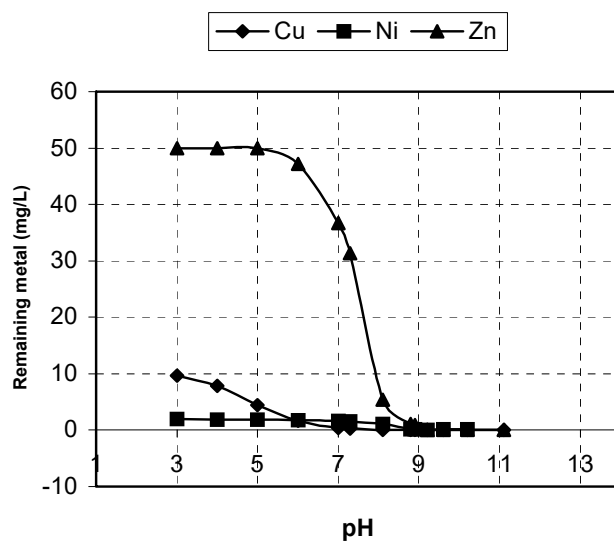
**Figure 6.** Simulation (by the Extend programme) of zinc sorption by goethite; without ionic strength, with flocculant, collector 200 mg/L, pH 7 [41].

#### 4. Biosorption and Flotation

Dissolved-air flotation was reported to be particularly effective in treating reservoir water supplies containing algae, natural color, or natural organic matter, and with low mineral turbidity, being more efficient than sedimentation. Furthermore, it is more efficient in removing *Giardia* cysts and *Cryptosporidium* oocysts [42]. The fundamental developed models, which provide a basis for understanding the process and optimizing and integrating it into water treatment plants, were reviewed and discussed extensively. The removal of nutrients by *Scenedesmus* sp. in a high-rate algal pond and subsequent algal separation by coagulation-flocculation or flotation with ozone to recover biomolecules, was elsewhere evaluated [43].

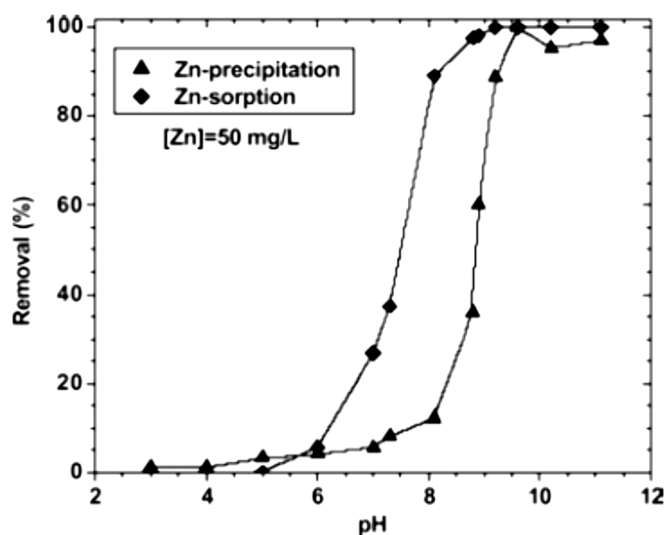
Various processes are suitable for reclamation of heavy metals, and among them, biosorption constitutes an alternative. The ability of microorganisms to remove metal ions from solution is a well-known phenomenon [16,17]. Applications of biosorption make use of dead biomass, which does not require nutrients and can be exposed to highly toxic environments. Biosorption is based upon several mechanisms, the most important being physical adsorption, ion exchange, surface complexation, and surface precipitation. On biomass surfaces, several chemical groups may be present, which could attract and subsequently sequester metals from the surrounding aqueous environment.

The biosorption of toxic metals, commonly found in many industrial wastewaters, from an aqueous mixture was investigated in the laboratory in a continuous stirred-tank reactor (CSTR) configuration, as shown in Figure 7. A theoretical speciation study showed that, in this aqueous mixture of metals, copper (is the first metal that) precipitates as hydroxide at a pH of about 5.9, followed by zinc at pH 7.3, and then by nickel at pH 7.8; calcium did not precipitate at the range investigated. Industrial filamentous biomasses of different origin have been examined as effective sorbents. Here, it was a large-scale fermentation waste from a pharmaceutical industry (with trade name Mycan). Free suspended biomass particles were used in the form received from the industry; however, in this case, efficient solid-liquid separation downstream may be a common problem and so flotation was applied.



**Figure 7.** Effect of pH on biosorption from aqueous multi-metals solution in batch by modified *Penicillium chrysogenum* fungal biomass (1.14 kg dry wt/m<sup>3</sup>; the mixture contained as nitrate salts Zn: 0.765, Cu: 0.157, Ni:  $3.408 \times 10^{-2}$ , Ca: 2.495 and Na: 4.348 mmol/dm<sup>3</sup>; the initial volume to be treated was 500 mL and the contact time 15 min). Reprinted with permission by Telford [44].

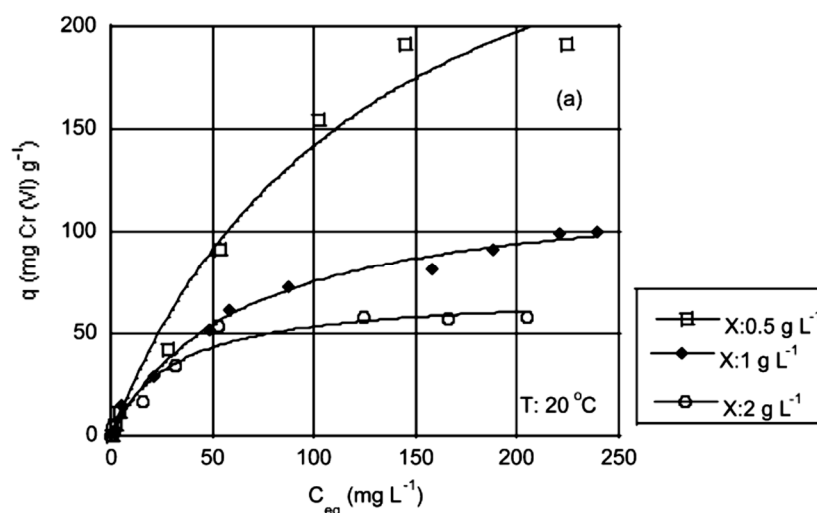
Conventional separation techniques, under similar experimental conditions to those described above, were examined for comparative purposes, such as that displayed in Figure 8. The pH-front seems to have been moved toward the left, to lower pH values. The advantage of the examined process is that its basic unit processes are rather conventional and widely used in the field. From extensive test work in the lab, it was concluded that the combined biosorptive flotation was a viable and effective separation process for the aqueous system (mixture of metal ions) under investigation, no matter the sort of biosorbent applied. A two-stage countercurrent scheme was finally selected with one parallel of elution, based on the studies, flotation has been included following each respective biosorption stage [16,17].



**Figure 8.** Comparative evaluation of zinc (50 mg/L) biosorption and precipitation removals, both followed by flotation; the aqueous solution containing a mixture of metals. Reprinted with permission by Interscience Enterprises [45].

Sorption kinetics may be controlled by several independent processes that can act in series or in parallel. These processes fall into one of the following general categories: (1) bulk diffusion, (2) external mass transfer (film diffusion), (3) chemical reaction (chemisorption), and (4) intraparticle diffusion. Various arguments were raised concerning the kinetics of biosorption and mainly regarding the influence of temperature, rate-determining step(s), specific surface area and nature of biomasses, type of isotherm followed, and maximum loading capacity. The obtained kinetic information may have significant practical value for technological applications, since kinetic modeling successfully replaces time and material consuming experiments, necessary for process equipment design [46].

A study of biosorption by using *Aeromonas caviae* as dead biomass followed. This microorganism is often present in groundwaters and exhibits a particular tolerance towards heavy metals. Non-living biomass of *A. caviae* presented sufficient biosorption capacity both for Cr(VI) oxyanions and cadmium cations, in comparison with other types (sources) of biosorbent materials. Experimental adsorption isotherms of chromate anions here, found with different biomass concentrations and constant temperature, are presented for example in Figure 9. The pH value was kept constant for all experimental runs. We were tempted to argue, following extensive work on kinetics, that the biosorption of metal ions is perhaps more correctly described by more than one model, as it is often the case with sorption in wastewater treatment.

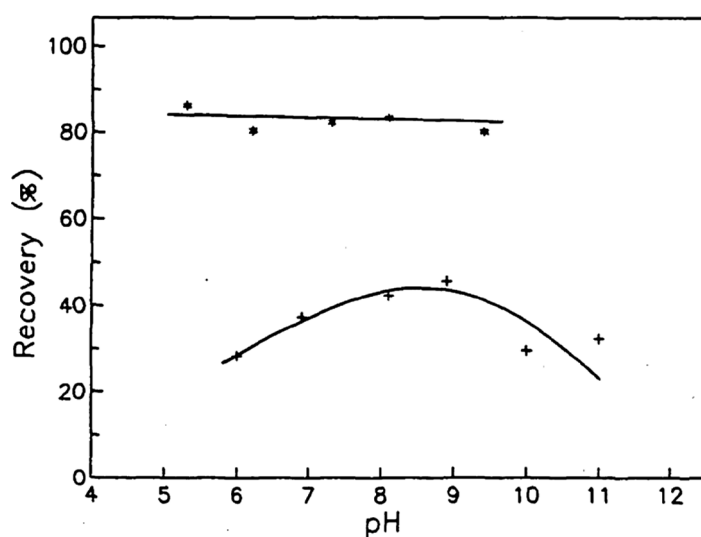


**Figure 9.** Equilibrium biosorption experiments of chromates, at pH 2.5, for different biomass (*Aeromonascaviae*) concentrations,  $X$ ; the solid lines represent the best fit of the Langmuir model to the measured data. Reprinted with permission by American Chemical Society [47].

## 5. Electroflotation

The importance of nanobubbles is known and particularly their applications and potential in mineral processing [48]. This interest was attributed to the peculiarities of their physical, chemical, and physicochemical properties. The electroflotation by only hydrogen bubbles of ultrafine silica particles was investigated, achieving recoveries greater than 85% [49]. The feasibility of employing an electroflotation-oxidation process for the harvesting of green microalgae and treatment of residual pollutants in coke effluent was published [50]. Electroflotation, or perhaps correctly, electrolytic flotation (as electricity is used in other flotation techniques, i.e., for the impeller), owes its name to the bubbles generation method it uses: electrolysis of the aqueous medium.

The adsorption of fatty acids on mineral fine particles was examined. Electroflotation, previously applied to chromium effluents, was tested in this case; Figure 10 presents an example of using magnesite ( $MgCO_3$ ). The presence of a modifier (here, sodium hexametaphosphate) could almost diminish the process, from the over 80% recorded in its absence.



**Figure 10.** Electrolytic flotation of magnesite fine particles by a commercial tall oil (40 mg/L); in presence (+ symbols) and absence (\*) of 200 mg/L sodium hexametaphosphate modifier. Reprinted with permission by Taylor and Francis [51].

It may be recognized that, compared to other flotation techniques, electroflotation has a greater energy cost required for electrolysis. However, often in many cases, this cost is depreciated by: (1) reduction in collector consumption, or perhaps even work collectorless; (2) greater flotation rate; (c) better quality of concentrate; (d) possibility of complete use of raw materials or effective recycling (including by-products recovery); and (e) use of this technique for cases to which the other processes could not be applied successfully. Certainly, a long time ago (in 1940), Soviet scientists proposed that fines can be collected more effectively by finer bubbles [52].

In general, this technique was said to be suitable for small-scale applications, as far as economics are concerned [53]. The running cost of electroflotation is largely a function of the conductivity of the aqueous solution. The idea of applying alternative types of electrodes was also discussed, such as bipolar or separated by an ion exchange membrane (as only one of the created, by the electrolysis, gases is usually necessary for flotation), and sacrificial ones, i.e., aluminum, to assist in coagulation.

A comparison of electrolytic flotation with dissolved-air flotation of dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) fine particles is provided in another work [54]. In this case, quite similar behavior was observed, while greater differences were taken in other comparisons, not shown here. Increasing the modifier (depressant) addition dissolved-air flotation was becoming more effective, noting that the case of salt-type minerals will be further discussed in the following chapter. It was also noticed that in the areas of high results by electroflotation, a flocculation of particles in the concentrate was apparent because of the so-called electrochemical effect. A modified Hallimond tube was used for these tests, with parallel perforated electrodes in the bottom instead of the porous plate [54].

A flotation unit is fundamentally a form of reaction vessel, with a separation occurring instead of a chemical reaction. Consequently, a detailed knowledge of the flow characteristics involved in a particular tank may be expected to comprise an important feature of its design. The hydrodynamics of flotation separation has been reported, as the efficiency is expected to be a function of the residence time distribution [25]. The advantages of different operation modes in continuous flow have also been discussed. A relative investigation for the case of an electroflotation column was undertaken. The stimulus-response technique was used in this experimentation, and the tracer input signal was an electrolyte, having the form of a step function. Assuming that the flow regime was composed of various flow types, a theoretical multi-parameter model was applied, known from Levenspiel [55], and from this, the relevant parameters were calculated.

It was found that the plug flow region was about the same for both operation modes, countercurrent and co-current, in relation to the bubbles rising, which was arranged by varying the inlet port of the feed near the top of the tank or at the bottom near the electrodes, respectively. As might be expected, differences were noticed in the mixed flow and dead-water regions, whereas no by-pass was found. In the countercurrent flow, there was more back mix flow (~87.7%); whereas in the co-current operation, a stagnant region appeared (~6.7%).

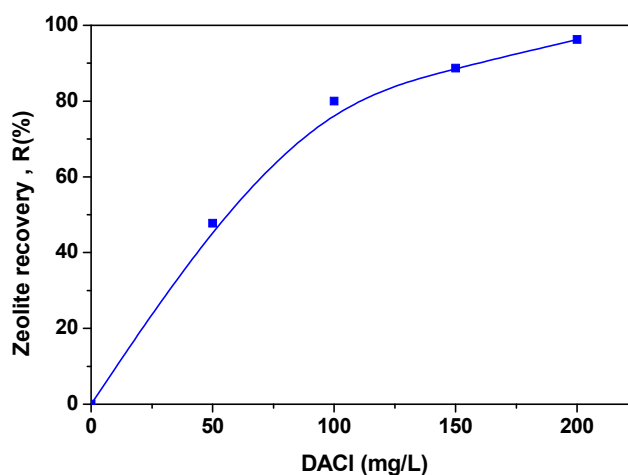
Certain advantages of this technique were discussed, focusing mainly on process development [56]. The basic requirement for the electrodes is to evolve very fine bubbles by electrolysis of the influent fluid; to accomplish this in practice, a number of criteria must be satisfied. The bubbles (both hydrogen and oxygen) were found to have a mean diameter of around 50  $\mu\text{m}$ . A direct measurement method was used with a specific camera applied (in the mid-1970s), constructed for earlier investigations in solvent extraction. Surprisingly, the bubble size decreased with increased current densities and at the same time, the number of bubbles increased. Although fine bubbles will improve certain aspects of the process, no general conclusion may be drawn as to whether or not the use of fine bubbles will improve the overall results of any flotation system.

## 6. Flotation of Fine Particles

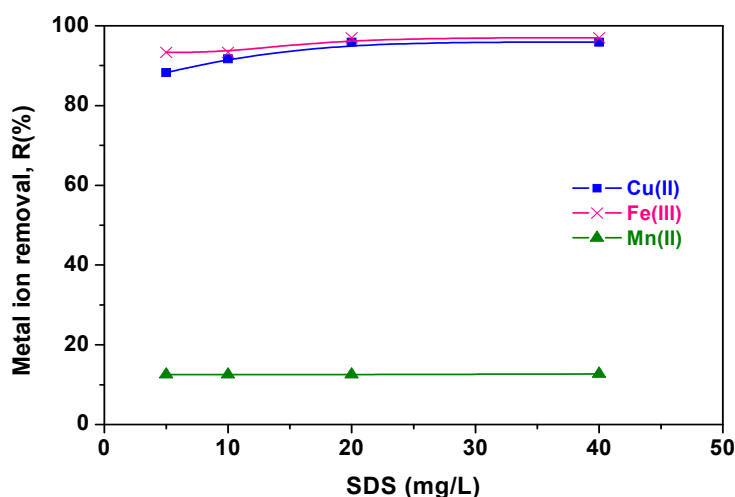
Air bubbling or sparging, under appropriate conditions, is one of the techniques among others (cross-flow liquid velocity, the use of baffles, back flushing, trans-membrane pressure pulsing, and some more.) used to limit membrane fouling. It could be used as the transport means for flotation, as an efficient separation method applied in water and wastewater treatment. An innovative idea thoroughly investigated was the integration of both processes in the same tank [57]. Assuming that flotation achieves a solids recovery of about at least 90%, which is typical, this can be advantageous to a MF/UF filtration unit (even a separate one), obviously limiting membrane fouling.

The significance of this investigation, used to separate fine loaded sorbents and metal precipitates, became apparent from the on-site application of the process to the Bulgarian Assarel copper mine effluent. The isoelectric point of copper hydroxide is at pH 9.5; hence, having positive surface charge at lower solution pH explains the application of a typical anionic surfactant as sodium dodecyl-sulphate to collect the particles during flotation. A cationic surfactant, such as dodecylamine chloride (DACl), was used for the (type 4A) zeolite, applied as the metal sorbents, as proved by zeta-potential measurements [58]. Due to speciation, in this effluent, copper was expected to precipitate following ferric iron. The selectivity during flotation followed the order of metal precipitation (Figures 11 and 12). So, if the goal is obtaining a purer froth concentrate, a further (initial) stage of iron removal could be possible at pH 4.5. In the hybrid process studied, specially designed at the Department of Process Technology, Saarland University, submerged microfiltration modules were integrated into the flotation cell (D4 sparger for dispersed-air), with multi-channel flat-sheet ceramic membranes.

However, certain limitations were imposed on the examined parameters (i.e., airflow, etc.) by the decision to work with a hybrid process, and by the apparatus design (the position of the membranes). For example, it was not possible to use horizontal membranes. It was also published that air slugs improve membrane efficiency; slugs, though, are not suitable for flotation. Therefore, the conditions of air bubbling should be also appropriate for flotation. Other important effects could be expected from the treated wastewater itself: solution pH, ionic strength, and the existence of other (organic) substances besides the metal ions [16,17].



**Figure 11.** Assarel mine mixture in a hybrid unit: second-stage separation by flotation of loaded (with metal cations) zeolites as a function of collector (dodecylamine chloride) concentration. Reprinted with permission by Elsevier [57].



**Figure 12.** Assarel mine mixture in a hybrid unit: 1st stage experiments for copper recovery by precipitate flotation, at pH 6.5 with collector sodium dodecyl sulphate. Reprinted with permission by Elsevier [57].

A method based on dissolved-air flotation of treating a metalworking industry effluent composed of water, cutting fluid, and graphite was developed. The graphite was distributed in the form of very small particles emulsified in water and distributed in both phases [59]. Notably, lubrication and cooling media are quite stable water-oil mixtures (due to emulsifiers), being elsewhere treated by electroflotation [56]. An innovative flotation cell from Australia, the Jameson cell, gave interesting solutions in the recovery of fine coal, metallic minerals, and wastewater treatment [60]. Also, a centrifugal flotation technique was developed in the USA. It has been well established that the flotation process efficiency decreases significantly when the size of floated particles falls below 25  $\mu\text{m}$ ; recent studies showed that this challenging problem could be resolved by also using microbubbles in the flotation process [61]. Research on the mechanisms of particle-bubble interactions provided valuable information on how to improve the flotation of fine and coarse particles with novel flotation machines [62].

Understanding the limits of fine particle flotation is the key to the selective separation of fine mineral particles [63]. Among the rather limited papers on electroflotation, work on pyrite and other

minerals such as cassiterite, manganese, and diamonds is notable; the changes in the composition and properties of collectors that occur during the process were also discussed.

The existence of very fine particles is well known to present difficulties in flotation [16,17]. These can be created even during mixing or conditioning, and during size reduction operations (crushing, pulverizing, etc., in mineral processing). Of course, as the particle size is reduced, two characteristics begin to dominate: the specific surface becomes large and the mass of the particle becomes very small. Certain phenomena such as low flotation rate, high reagent consumption, and rapid oxidation affect the recovery. Other phenomena (such as fine particle entrainment and non-specific collector adsorption) affect the grade that is of importance in conventional beneficiation, where we are generally attempting to achieve selective separation. However, there are some phenomena affecting both flotation recovery and grade, such as froth or foam stabilization and higher dissolution.

If, on the other hand, the bubble size is reduced in proportion to the particle size, the rate of collision remains unchanged. The latter possibly indicates that flotation with fine bubbles would recover effectively fine particles; although the above thinking forms perhaps an oversimplification [64]. This was in fact the reason why both electroflotation and dissolved-air flotation (being two techniques producing fine bubbles) have been investigated extensively in our lab, and were both applied to fine mineral particles. With the same reasoning, another effort made was to increase the size of the particles (to be separated), for instance, by flocculation. A similar conclusion was reached, empirically in the beginning, in wastewater treatment, where normally the particles to be removed are fine (less than 20  $\mu\text{m}$ ).

The two mineral particles examined, although of the same type (i.e., salt-type minerals), did not behave similarly during flotation [65]. Dolomite, which was mineralogically crystalline, was the more amenable to processing, giving high flotation recoveries in the fine size range ( $-45 + 15 \mu\text{m}$  fraction); the presence of modifying reagents significantly depressed its floatability. Nevertheless, the magnesite tested was of crypto-crystalline nature, being friable. Due to the solubility of salt-type minerals, the aforementioned constituted a serious problem for flotation, as selectivity was required.

## 7. Conclusions

Hence, there are certain similarities between the fields of dispersed-air flotation and dissolved-air flotation (as there are also differences, i.e., from an economic point of view). It has even been argued that a gap exists between these two areas, perhaps due to the separate tradition and the seldom interaction among the researchers [44]. Nevertheless, much of the theoretical and practical development of flotation in wastewater engineering was based on the previously advanced experience on mineral processing, as far as the process of flotation is concerned. It is thought that many advances can be gained in the near future, as we are currently increasingly worried about sustainability and the need for drinking water sources is becoming urgent worldwide. It was shown that flotation may significantly contribute in this scope, for the purification and clarification of water, and to the effective separation of various pollutants (including the examined metal ions) before toxic substances enter our food chain.

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