Water Separation Processes and Sustainability

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The concept of unit operations, over time, and subsequent concepts in chemical technology have evolved into a unified field of separation processes. Sustainability in this field and its significance for the chemical and process industry will be commented, because the need for fresh sources of drinking water is becoming urgent worldwide. The biosorption of metal ions via residual biomass will be specifically examined in this review paper, as a separation technique. It has been recognized that the increased application of ion exchange and also membrane processes for producing potable water necessitates the use of advanced technologies as well as combinations of these. Therefore, a new hybrid cell of microfiltration combined with flotation will be also described in the present and applied effectively downstream for the same purpose (i.e., metals removal). Flotation is a separation process originated from minerals processing.

Introduction

The concept of unit operations embodies many different methods of separating mixtures and represents a major advance in chemical technology. Over time, those and subsequent concepts have evolved into a unified field of separation processes.[1] According to King, there are several major gains in understanding, insight, capability, and efficiency that come from viewing separation processes as a unified field. Separations have always had their place in analytical chemistry, as any student of qualitative or quantitative analysis knows. New dimensions in separations chemistry, analysis, and processing arose with the development of gas and liquid chromatography. Another important general area of separations with roots in chemistry is membrane-based separations. The latter received a boost with the development of the Loeb−Sourirajan asymmetric cellulose acetate membrane for purification of seawater and brackish waters, and with the development of macroporous membranes with relatively uniform pores.

Chemistry, of course, was one of the foundations of the wealth and growth of the 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. European Technology Platforms (ETPs) focus on strategic issues where achieving future growth, competitiveness, and sustainability depends on major technological advances; one of these ETPs is the one for sustainable chemistry.[2]

A review of sustainability and its significance for the chemical and process industry has been presented elsewhere.[3] Until now, it has been difficult to find useful sustainability criteria and ready-to-use guidance tools for the design of products, processes, and production systems. Fortunately, over the past decade, a range of practices and disciplines have appeared, transforming the way in which traditional disciplines are conceived. The complexity issues in the ecological aspects of chemical engineering have been discussed elsewhere.[4] Environmental sustainability is a stand to stay within forecasted limits in the resources and renewability capacity of the Earth.

Water pollution, however, is perhaps a fact in many developing countries. More than 300 million people in China, for example, did not have access to safe drinking water;[5] their water is contaminated by industry, and farmers in dozens of villages died prematurely. Industrial plants have been working only overnight, so that it does not upset local government officials, who often resisted addressing the problem, because the solution may entail shutting down manufacturing facilities that provide jobs and tax revenues. Many places exist, even termed as “cancer villages” in the article, where the incidence of cancer is well over twice the national average.

For centuries, water has been a manufacturing tool that industry has taken for granted, because it is inexpensive and plentiful. But population growth, globalization, and climate change are shepherding in a new water-constrained era. Good, clean water just cannot be replaced—and it is becoming harder to come by. For big industrial companies (for example, Dow Chemical and General Electric in the United States), water presents both an operational challenge and an opportunity for growth.[6] As manufacturers, they must manage their physical operations in a way that conserves and reuses water. As suppliers to other manufacturers, they are investing in new technologies to take advantage of the evolving demand for water treatment chemicals, services, and equipment.

The United Nations (UN) warns that the world’s use of water is not sustainable. Globally, agriculture claims 70% of the world’s supply of fresh water, leaving little for industry. The big pressure on water supplies in the future will come from irrigation for food crops. Spending on water technologies can create cost savings elsewhere in the business mix. In the 1990s, the industry started shifting toward a new type of system—membrane bioreactor for wastewater recycling—because of material advances and cost reductions. In the United States, the cost for a year of water treatment can be up to \$250 million for the pulp and paper industry and \$350 million for the pharmaceutical industry.

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 and seawater desalination could be a solution. The scope should be an environmentally acceptable project that is one which fulfills the requirements of sustainable development. The plant costs and other factors are important, but these can be integrated into environmental considerations. Perhaps an effort that is worth mentioning is the use of renewable energies in seawater

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Table 1. Characteristics and Differences between Bioremoval Processes[a]

feature	biosorption	bioaccumulation
metal affinity	high, under favorable conditions	toxicity will affect metal uptake by living cells; however, in some instances, high metal accumulation occurs
rate of metal uptake	usually rapid, a few seconds for outer cell wall accumulation	usually slower than biosorption
selectivity	variety of ligands involved; hence, poor	better than biosorption, but less than some chemical technologies
temperature tolerance	within a modest range	inhibited by low temperatures
versatility	metal uptake may be affected by anions or other molecules; the extent of metal uptake is usually pH-dependent	requires an energy source; dependent on plasma membrane ATP-ase activity; frequently accompanied by an efflux of another metal

[a] Data taken from ref 21.

desalination, especially for remote areas. Flotation has been also used for pretreatment in seawater desalination.[7]

Reverse osmosis (RO) membranes, extensively used in desalination plants, are very sensitive to foulants such as colloids, inorganic scale, and biofilm development. Furthermore, with an open seawater intake of the plant, the membranes are sensitive to other types of pollution: algae, precipitated metal, organic matter, hydrocarbons, particles, turbidity, etc. An efficient pretreatment has to control the flux of each pollutant. Hence, the pretreatment should be designed to face the worst water quality, providing a constant and good RO feedwater quality.

For some time now, it has been recognized that the increased application of ion exchange and membrane processes for producing drinking water from qualitatively poor sources of raw water, such as brackish water and seawater, necessitates the use of advanced mechanical and chemical technologies, as well as combinations of these; in this way, the use of flocculation, precipitation, sedimentation, and flotation have been studied as pretreatment stages. According to the roadmap from the Institution of Chemical Engineers (IChemE), membranes are in fact steadily increasing their applications in water treatment and research is showing innovative ways of using them; however, they still must compete with the very robust methods developed over the last century.[8] Of course, there is a need to develop existing, and implement new, water and wastewater treatment processes that enable low-cost, low-energy-intensive, and low-environmental-impact purification to standards appropriate to end use from both traditional and poorer source waters.

The food-chain pyramid, on the other hand, receives metals through man's activities. On top of the pyramid, man receives preconcentrated metal toxicity. There are also cases of nonanthropogenic pollution, the best known is perhaps that of arsenic in underground wellwater in Bangladesh and eastern India, affecting almost 70 million people. However, it has been known that microorganisms are able to remove metals from waste or process solutions. The microbial biosorption of metals has attracted the interest of scientists as a treatment method, especially during the last two decades.[9,10] Although the biological treatments are a removal process for some organic compounds, their products of biodegradation may also be hazardous.[11]

Bioprocesses

The various mechanisms involved in biosorption were discussed, including the effects of critical parameters. Many low-cost biosorbents have been investigated in recent years, including brown algae.[12] The passive removal of toxic heavy metals by inexpensive biomaterials requires that the substrate displays high metal uptake and selectivity, as well as suitable mechanical properties for applied remediation scenarios. Hydrophobic bacteria strains, such as *Rhodococcus opacus*, have been also tried.[13] The process has been recently reviewed in a book.[14] Generally, metal recovery or removal from solution may involve the following pathways:

(1) The binding of metal cations to cell surfaces, or within the cell wall, where microprecipitation may enhance uptake.

(2) Translocation of the metal into the cell, possibly by active (metabolic energy dependent) transport; the active uptake or concentration of metal by living microbial cells is often termed bioaccumulation.

(3) The formation of metal-containing precipitates, by reaction with extracellular polymers or microbially produced anions such as sulfide or phosphate.

(4) The volatilization of the metal by biotransformation (see Hughes and Poole[15]).

Biosorption is usually considered to be the attachment of adsorbates (e.g., of dissolved metal ions) onto a nonliving biomass surface (being usually bacteria, algae, or fungi) or onto a material containing natural biopolymers acting as biosorbents (e.g., chitin). According to Volesky,[16] there are at least three major points to consider when choosing the metal for biosorption studies to focus on: metal toxicity (direct health threat); metal costs (recovery interests); and how representative the metal may be, in terms of its behavior (scientific studies). There are two trends for the development of the biosorption process for metal removal: one is to use hybrid technology for pollutants removal, especially using living cells; another trend is to develop the commercial biosorbents using immobilization technology and to improve the process including regeneration/reuse, making the biosorbents similar to a form of ion-exchange resin, as well as to exploit the market with great endeavors.[17]

The comparison of biosorptive techniques by different scientists showed biosorption by dead cells to be superior.[18-20] Microorganisms have a high surface-area-to-volume ratio, because of their small size; therefore, they can provide a large contact interface, which would interact with metals from the surrounding environment. Microbial metal accumulation has received much attention during recent years, because of the potential use of microorganisms for treatment of metal-polluted water or wastewater streams.[20] The ability of several microorganisms, isolated from metal-polluted soils to biosorb and remove toxic metals from aqueous solutions was showed. Perhaps an interesting question—"why select a biological process"—was asked by Eccles in the title of his publication.[21] Table 1 presents the two techniques. Comparative costs for biosorptive processes with ion exchange and chemical precipitation are also given.

More or less similar curves were obtained with different biomasses and various metals.[22] It is stressed that biosorptive treatments do not necessarily need to replace existing methodologies but may act as polishing systems to processes that are not completely efficient, thus complementing them. In the long

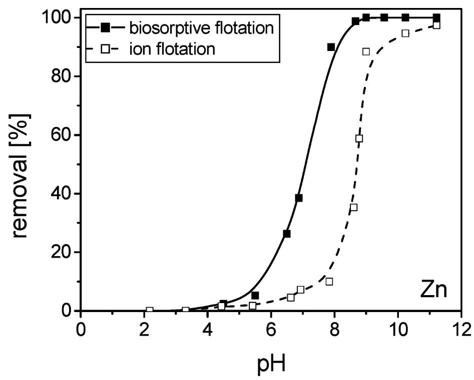

Figure 1. Removal of heavy-metal ions from an aqueous mixture by biosorption (with flotation followed downstream) or ion flotation (due to precipitation): a comparison of the two techniques is shown (in ion flotation, dodecylamine in ethanolic solution was used as a surfactant; for the removal of zinc, for instance, the effect of solution pH is presented). Results have been modified from earlier work.[10]

term, source separation offers the more-sustainable solution to the entire wastewater problem, also including the organic micropollutants.[23]

Thousands of tons of residual ("waste") biomass are produced every year from fermentation industries and from biological wastewater treatment plants. Their disposal might be a problematic issue. Hence, the possible reuse of biomass for the treatment of metal-laden wastewaters, eventually followed by its regeneration, could offer an alternative solution to this important disposal issue. The laboratory experiments consisted of two stages of biosorptive flotation; flotation applied effectively downstream for solid/liquid separation.[10]

From a comparison between biosorption and other metal separation methods, such as filtration, centrifugation, etc., it was found that, in terms of the removal efficiency and applicability at lower (acidic) pH values, the former was favored. In these conventional processes, the metal cations removal is mainly due to their precipitation as hydroxides, due to pH alteration toward alkaline values.

Figure 1 presents the case with precipitate flotation (of the so-called "first kind") or perhaps, ion flotation, where, here, the term is used in its broad sense. Note that ion flotation involves the removal of surface-inactive ions from aqueous solutions by adding surfactants or collectors and the subsequent passage of gas bubbles through the solutions; the surfactant is usually an ion having a charge opposite to that of the metal ion to be removed (termed "colligend"). As a result of this flotation procedure, a fine solid particle containing the surfactant as a chemical constituent appears on the surface. This permits the separation and concentration of the ionic species in a small volume of collapsed foam. The surfactants are generally recoverable from the product (sublate) and may be recycled as also the clean water. Raising the respective concentrations may lead to precipitation of the ion-surfactant floatable product, before air is passed. This means that it is not a solution anymore, but rather is a dispersion.

In the aforementioned figure, note that biosorption moves the pH front to the left, and the same results are also observed with copper and nickel, in the presence of Ca^{2+} and Na^{+} ions (usual co-existing cations in related systems). As effective biosorbents, bacteria (*Streptomyces rimosus*), fungi (*Penicillium chrysogenum*), and yeasts (*Saccharomyces carlsbergensis* and *Saccharomyces cerevisiae*) were applied. Selectivity was observed, particularly for the removal of copper.[10]

The use of low-cost sorbents, such as natural materials and agricultural or industrial waste products, as a replacement for currently costly methods of removing heavy metals from solution has been reviewed; the usual point of reference is activated carbon.[24,25] The examined novel process (called biosorptive flotation) is closely related to the older adsorbing colloid flotation method, which involves the removal of solutes by adsorption on, or precipitation with appropriate carrier particles or flocs, depending on the specifically applied experimental conditions; the loading sorbents are subsequently separated by the application of flotation, usually with the aid of surface active agents/surfactants. Two pilot-plant studies were performed at the University of Newcastle upon Tyne, U.K. (for respective European Union research programmes) to investigate the potential of microorganisms to remove toxic metals from liquid wastes.

Figures 2 and 3 present such a comparison for Cr(VI) and Cd ions.[26,27] Similar results are shown, and, in some cases, even the biosorbents worked better than their inorganic alternatives (pyrite, goethite, akaganèite, hydroxyapatite). That which is noted, in the figures, as nonliving biomass was coming from selected gram-positive *Actinomycetes* strains. The respective comparison certainly was not very easy, because of the varying experimental conditions.

Aeromonas caviae is a gram-negative bacterium isolated from water wells; however, little attention seems to have been given to its resistance to heavy metals. The cultivation of the microorganism is a relatively simple procedure, while the cultivation medium can be obtained without excessive cost. Among the most important aspects that must be evaluated in a biosorption study is the selection of a suitable microorganism, capable of sequestering large amounts of heavy metals from wastewaters. A possible preliminary test, which may be used to perform this selection, is the surface titration of biomass. The obtained favorable biosorption results, in terms of capacity and rate, of the examined metal ion onto the biomass demonstrated a potential for technological treatment of metal waste streams by such an inexpensive waste material (suitable both for cations and oxyanions).

Classical adsorption models, such as the Langmuir and Freundlich models, have been used extensively to describe the equilibrium established between adsorbed metal ions on the biomass and metal ions remaining in solution at a constant temperature. Analysis of the equilibrium data is important for developing an equation that can be used for design purposes. Nevertheless, often biosoption is not allowed to reach equilibrium.

In another review,[28] the thermodynamics of the process was discussed, including also typical biosorption isotherms and their understanding. Some interesting concerns about biosorption research and application were reported, including the fact that the process cannot be readily assumed to be an elementary reaction, because of the complexity of the biosorbent surface.

A kinetics study was also reported for a thoroughly examined system (for the removal of cadmium and chromates by the same biomass); however, the conducted analysis has been rather incapable of providing strong evidence in favor of any of the examined mechanisms, since several diverse kinetic models were successful in fitting the experimental data.[29] These models include the following: a Ritchie second-order chemical reaction and a finite volume diffusion, which, by themselves, may effectively describe the largest part of the process; alternatively, an external surface enhancement dominating the very beginning of the process, followed by external film diffusion. One is tempted to argue that biosorption may be more correctly described by more than one model, as is often the case with the sorption of metal ions. Sorption kinetics can be controlled

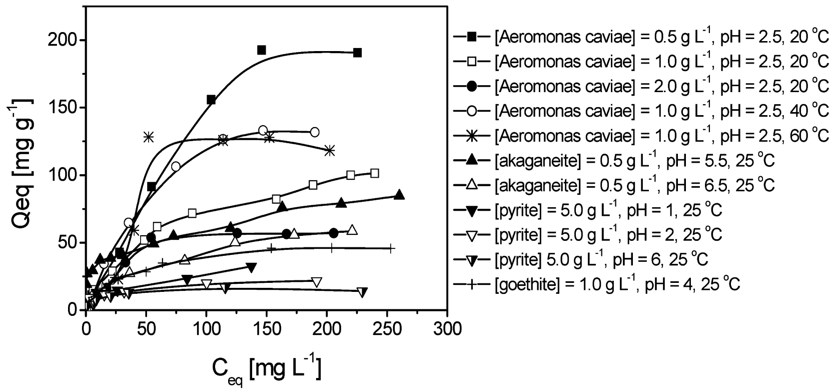

Figure 2. Comparison of the sorption isotherms of chromates for different sorbent types of inorganic or biomass origin (and different experimental conditions).[26] The quantity of adsorbed metal oxyanion on the sorbent is shown at equilibrium with the concentration of metal ions remaining in solution at a constant temperature.

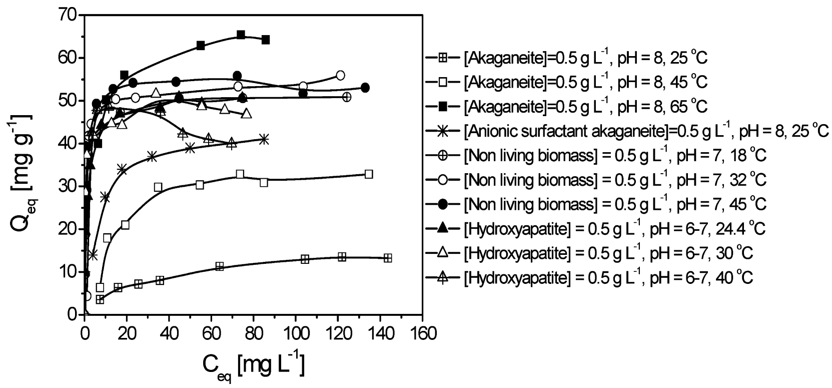

Figure 3. Comparison of the sorption isotherms of cadmium for different sorbent types of inorganic or biomass origin (and different experimental conditions).[27] The quantity of adsorbed metal oxyanion on the sorbent is shown at equilibrium with the concentration of metal ions remaining in solution at a constant temperature.

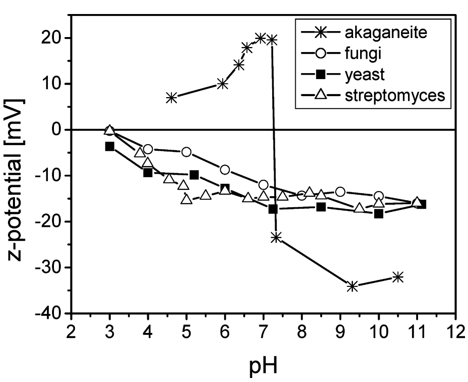

Figure 4. Zeta-potential measurements of metal-laden sorbent (as stated) against the solution pH: a comparison of biosorbents with an inorganic sorbent.[10,30]

by several independent processes that can act in series or in parallel, such as the following: (i) bulk diffusion, (ii) external mass transfer (film diffusion), (iii) chemical reaction (chemisorption), and (iv) intraparticle diffusion.

The impact of chemical aqueous speciation during the various mentioned applications, which were examined for the removal/separation of metals from aqueous solutions, should be stressed. Depending the applied conditions, the process mechanism could be varying. Figure 4 shows the relation of ζ-potential of the sorbents with the solution pH.[10,30] Negative gradually decreasing values over the entire studied pH range were observed for biosorbents. The main chemical groups of biomass surfaces that are capable of participating in sorption and chelation of several bivalent metal cations are polar or anionic in nature, such as hydroxyl, sulphydryl, carboxyl, and phosphate groups, as well as nitrogen-containing (amino) groups. Such groups will contribute to the zeta potential of the surface.

The electrokinetic measurements were performed using a microelectrophoretic apparatus, and expressed as zeta-potential values. Iron-based bonding materials have been widely used as adsorbents. Akaganèite (β-FeO(OH)), which is an innovative inorganic sorbent studied in depth at Aristotle University of Thessaloniki (AUTh), is given here for comparison;[30] some of the reasons for selecting the iron-based bonding materials were that they are inexpensive, they are easily synthesized, and they present low risks for adding a further pollutant to the system.

The emerging applications of biotechnology, particularly in the production and processing of chemicals, for sustainable development have been reviewed.[31] Environmental and economic benefits that biotechnology can offer in manufacturing, monitoring, and waste management were highlighted. Treatment of municipal wastewater by activated sludge method was perhaps the first major use of biotechnology in bioremediation applications. These authors had no doubt that biotechnology is set to transform industrial production to a basis that is more compatible with the biosphere.

The provision of bioprocessing-related courses for continuous professional development has been recently proposed by IChemE.[8] Such a course was introduced in the curriculum of our department eight years ago, for the last-semester students

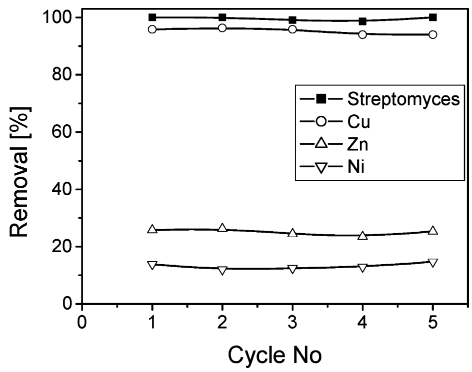

Figure 5. Multiple-cycle operation of biosorptive flotation (a combined two-stage process) batchwise from an aqueous mixture of metals: % removal of metal ions and recovery of loaded biomass, in five cycles tried. (Reproduced, with kind permission, from ref 35. Copyright 2003, Elsevier, Amsterdam, The Netherlands.)

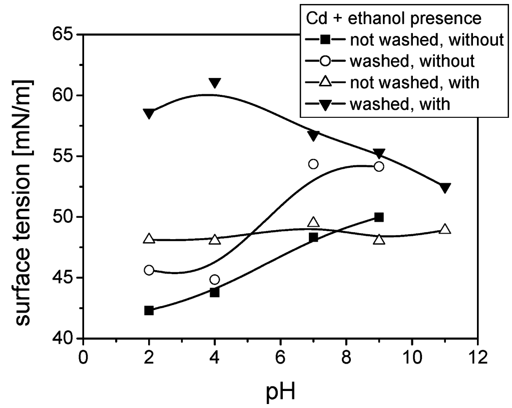

Figure 6. Surface tension measurements during biosorption of *Streptomyces clavuligerus* biomass (1 g/L), removing cadmium (1×10^{-4} M) against the solution pH. (Reproduced, with kind permission, from ref 37. Copyright 1994, Wiley, New York.)

of the optional (from the existing four) division of Biochemistry—Biotechnology and Foods.

Flotation

A brief outline of the pioneering events in the development of flotation technology, which originated in Broken Hill, Australia, at the start of the 1900s, was presented in the Centenary of Flotation Symposium by Clark et al.32a In the same meeting, Carissimi and Rubio discussed a new in-line flocculation-rapid flotation device to remove aerated aggregates.[32b] It is abundantly clear that micro-organisms, both living and dead, and products derived from the organisms, can function as flotation agents and flocculation agents; in many cases, specifically, they can modify the surfaces of minerals and function as flotation collectors, depressants, or activators.[33] These authors were wondering about whether all of this constitutes a future technology or laboratory curiosity.

The importance of the flotation process to the economy of the entire 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. So, flotation initially originated from the field of mineral processing (usually termed froth flotation). Since, for many years, various particulate solids (besides minerals) have been extracted from water using this effective gravity separation method, which is based on the idea of applying rising gas bubbles as the transport medium; the attachment of bubbles to particles transfer the solids from the body of water to the surface. According to the specific technique used for the generation of the necessary bubbles, two broad categories of this process exist: (i) dispersed-air flotation (including electroflotation), and (ii) dissolved-air flotation (which is often abbreviated as DAF).[34]

Multiple-cycle operation was experienced, as shown in Figure 5. Sodium sulfate-modified *Streptomyces rimosus* was applied at pH 7, with the addition of a dodecylamine surfactant in the first and third cycles; loaded biomass flotation recovery and metals removal are presented. Between the cycles, elution of the flotation concentrate (i.e., separated metals-loaded biomass) was involved by a mixture of sodium sulfate and citrate. No difference in the biosorption of the three metals was obtained, while, in the cycle in which a flotation collector was not applied, a slight decrease of flotation recovery (being ~100%) was observed.[35] The effect of increased biomass amount was also examined, because it was apparent that, at neutral pH values, higher additions were required, to improve the separation of zinc and nickel. The increase of air flow rate applied during flotation was determined to improve the results somehow. The concept of using natural materials, such as micro-organisms, in place of various chemical reagents that may be toxic, looked attractive; biosorptive flotation was concluded to be a viable and effective separation process for the aqueous system (mixture of metal ions) under investigation, regardless of the type of biosorbent that was applied.

Surfactants are surface-active compounds, as we know, capable of reducing surface and interfacial tension at the interfaces between liquids, solids, and gases, thereby allowing them to mix or disperse readily as emulsions in water or other liquids. The enormous market demand for surfactants is currently met by numerous synthetic, mainly petroleum-based, chemical surfactants. These compounds are usually toxic to the environment and most of them nonbiodegradable; therefore, they may bioaccumulate, whereas their production processes and byproduct can be environmentally hazardous. Tightening regulations and increasing awareness for the need to protect ecosystems have effectively resulted in increased interest for the use of biosurfactants, considered as possible alternatives.[36]

Surface chemistry issues, such as surface tension, zeta potential, 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, etc. (see Figures 6 and 7).[37,22] Surface phenomena, such as surface tension, as well as zeta potential and contact angle, have been rather seldom examined for the case of effective removal of toxic metals from aqueous solutions.

Hydrophobicity in a solid—liquid—gas system, as flotation is, is certainly a complex phenomenon and a result of different interactions: chemical, bonding, specific properties of solid/liquid and solid/liquid/air interfaces, solid crystal structure, reactions of solid surface in water, etc. The measurements of contact angle, surface tension, and zeta potential (under similar conditions), examining the main parameters affecting the hydrophobicity of microorganisms 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 the operational improvements or for design reasons.

It is known that flotation is based on surface activity. A substance (molecular, colloid, or particulate in size) that is not

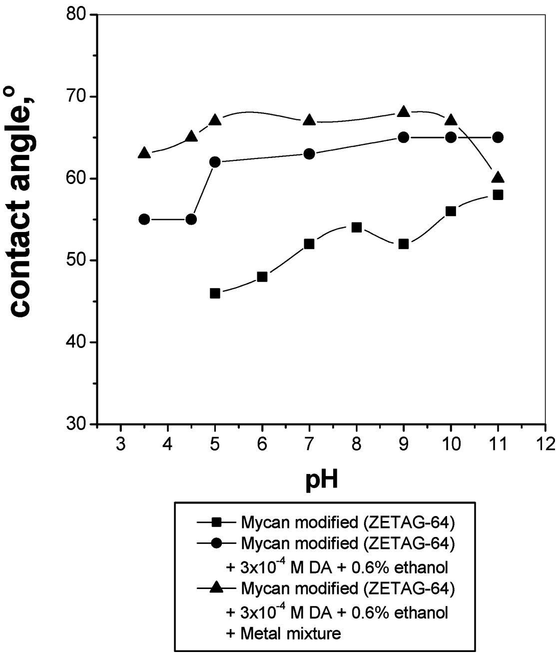

Figure 7. Contact angle measurements of modified biomass, as influenced by the solution pH, also in the presence of dodecylamine collector and a mixture of metals (metal ions concentrations: Zn, 50 mg/L; Cu, 10 mg/L; Ni, 2 mg/L; Ca, 100 mg/L; and Na, 100 mg/L). (Reproduced, with kind permission, from ref 22. Copyright 2009, Elsevier, Amsterdam, The Netherlands.)

surface-active itself may be made effectively surface-active through a union with or adherence to a surfactant. For this reason, the surface tension measurements (during biosorption) were made, in an attempt to collect information on the entire process. With washed *Streptomyces clavuligerus* in the acidic pH region (Figure 6), up to neutral pH, the addition of cadmium and ethanol in solution increased the surface tension, up to ~60 mN/m (possibly the area of successful flotation).[37] Nevertheless, it is possible that certain microorganisms may be naturally hydrophobic, possibly because of the existence at the cell walls of groups such as fatty acids. Thus, they may be floatable even without a collector, at least under specific conditions. The operating running costs, if the process were commercialized, would thereby be considerably decreased.

Figure 7 presents the respective laboratory results of the contact angle measurements for the examined system; the biosorbent used was *Penicillium chrysogenum* (with the tradename Mycan) in an aqueous mixture of heavy metals, aiming at the simulation of commonly found toxic metals in industrial wastewaters. The contact angle measurements correlated quite well with the floatability of biomass, as both curves at pH ~11 started to decrease. The contact angles for the unmodified biomass (data not shown) were comparatively low (25°−33°). The addition of flotation surfactant to the modified biomass (either via the addition of Na_2SO_4 solution or via a cationic polyelectrolyte solution of Zetag-64) was determined to increase the contact angle; that is, with the addition of 5% dodecylamine, higher contact angles (54−62°) were obtained, which is a fact that is associated with the increase in biomass hydrophobicity.[22]

Filamentous fungi are commonly used in fermentation industries to produce several commercial products/metabolites, such as enzymes, flavorings, or antibiotics, as well as industrial byproducts, which are able to remove several heavy metals, mostly via chelation. The main chemical groups on a biomass surface, taking part in biosorption, are the electronegative groups (e.g., hydroxyl or sulphydryl), the anionic groups (e.g., carboxyl or phosphate), and the nitrogen-containing groups (e.g., amino). Fungi can accumulate metal and radionuclide species via the implementation of several physicochemical and biological mechanisms, including the extracellular binding by metabolites and biopolymers, the binding to specific polypeptides, as well as the metabolism-dependent accumulation.

Membrane filtration techniques as well as flotation, including electroflotation, allow one to achieve high-performance, low-reagents-consumption treatment of heavy-metal-containing wastewaters, as found in Russia.[38] Electroflotation is an unconventional separation process; its name comes from the bubble generation method it uses (i.e. electrolysis of the aqueous medium).[34] It has been shown that the bubble size plays an important role in the flotation recovery of fine particles. Fine particles float better with small bubbles, because, as the bubble size decreases, the probability of particle−bubble collision (and, hence, flotation) increases.

Microfiltration

One of the most serious problems encountered in membrane separation processes is fouling during their use. Membrane fouling is the result of the accumulation of rejected particles on the top surface of the membrane (external fouling), or the deposition and adsorption of small particles at the pore entrances or within the internal pore of the membrane (internal fouling). Many researchers have tried to overcome this obstacle, using turbulence promoters, corrugated membrane surfaces, pulsate flow, vortex generation,[39] feed-pretreatment,[40] surface modification of membrane,[41] and gas sparging.[42,43] Polyelectrolytes were used in membrane processes to modify their operation for optimum treatment.[44]

The introduction of gas/liquid two-phase flow has been shown to enhance the performance of some membrane process applications significantly.[39] This paper reviewed the state of the art of the above technique and, in particular, it focused on the use of gas bubbles and slugs in microfiltration and ultrafiltration with flow inside tubes and fibers, across flat sheets, and outside fibers. Another study focused on gas bubbling in ultrafiltration hollow fibers to prevent a particulate deposit.[42] On the basis of experimental results for clay suspensions, an analysis of the influence of the two-phase flow parameters on the cake characteristics (porosity, thickness, and specific resistance) was then introduced and allowed to demonstrate that the notion of cake deposit is no longer available with a gas/liquid flow.

An innovative hybrid cell was investigated that combines the advantages of both flotation and membrane separation, while overcoming their limitations and having, as an outcome, clean water from an industrial wastewater. A large number of techniques have been used today to limit the membrane 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. The hybrid cell used in the laboratory in this work consisted of a cylindrical flotation column made of plexiglass (internal diameter = 100 mm) and a flat ceramic porous gas sparger having a diameter of 60 mm (with an average porosity of 40−100 μm), placed above the flat bottom of the column; the membranes were positioned 60 mm above the gas sparger.

Ceramic flat-sheet membrane modules of multichannel geometry were used, inserted inside a typical flotation cell and combining flotation with microfiltration by submerged membranes.[45] The Institute of Environmentally Compatible Process

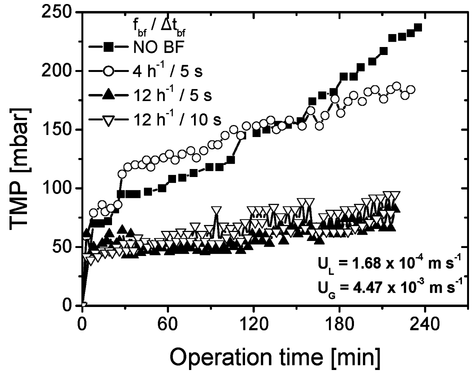

Figure 8. Effect of backflushing (BF) frequency and duration on transmembrane pressure (TMP) versus the operation time of the hybrid flotation−microfiltration cell (ultrafine solid particles removed: zinc-loaded zeolites) at specific feed and air superficial velocities; as far as the zinc cations are concerned, almost total removal was always achieved.[45]

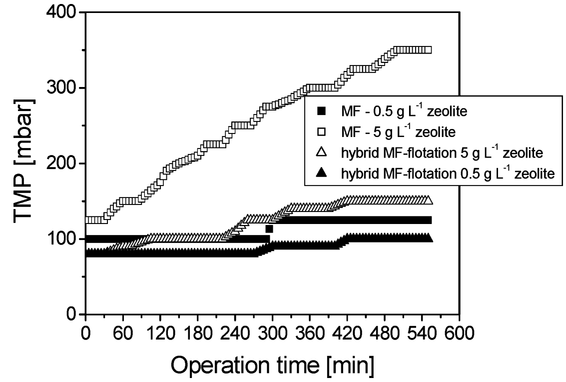

Figure 9. Study of the effect of solids concentration: transmembrane pressure (TMP) versus operation time. Data used involves the previous work with the metal-loaded zeolites, at different suspension concentrations; a flashback and a comparison that does (and does not) apply flotation in the hybrid system (i.e., microfiltration alone).

Technology (upt), at the University of Saarland (Saarbrücken, Germany), gratefully provided the membranes.

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

The effectiveness of the hybrid process was examined with two goals in mind: (i) to remove any undesirable dissolved or even suspended constituents from the aqueous effluent, and/or (ii) to recover a stream of water clean enough for potential reuse.[46] The studied processes clearly were dependent primarily on the nature, characteristics, and efficiency of the applied metals or bonding agents. For example, the particle size distribution of the bonding agents, their concentration, and the surface charge determine the effectivenessof flotation. The combined process was applied to (1) the removal of zinc using solid particles (zeolite) as adsorbents by sorptive flotation, (2) the removal of chromates using ferric flocs by adsorbing colloid flotation, while (3) at the same time, obtaining a stream of clean water.

Backflushing (BF) is an in situ method for removing particles that have collected in the pores and/or on the surface of the membrane, using a periodic reversal of the transmembrane flow: the permeate is periodically forced in the reverse direction through the membrane, thereby lifting off the cake layer and, to some extent, cleaning the membrane pores and the surface. The cake that is lifted would normally be resuspended in the cell. Figure 8 presents selected results for membrane BF frequencies every 5 min (f_{BF} = 12 h^{-1}) or 15 min (f_{BF} = 4 h^{-1}) and for BF durations of 5 or 10 s. A backflush duration of 5 s at f_{BF} = 12 h^{-1} was determined to be satisfactory, giving low transmembrane pressure (TMP) drops and high permeability values. When the BF duration was doubled, the TMP evolution deteriorated.[45] The periodic backflushing generally resulted in an improvement of the hybrid cell performance. The process was finally tested for metal (copper) recovery, being applied to a real industrial wastewater at the Bulgarian Assarel-Medet open pit copper mine and minerals processing plant (located near Panagyurishte), with promising results. The recovery of Cu ions from simulated and real wastewaters from the mine was initially investigated in the laboratory. The separation process employed was flotation, which was applied in three different mechanisms: (i) ion flotation using xanthates, (ii) precipitate flotation generating copper hydroxide, and (iii) sorptive flotation using zeolites as sorbent material.

It is interesting to examine a comparison on the influence of solids, presented in Figure 9, between the simple microfiltration and the hybrid process with a supply difference by a factor of 10. Apparently, membrane fouling and, hence, efficient operation would be expected to be a function of their loading with solid particles. As it is clearly shown, the effect of increasing the input concentration had only little influence in the case of the hybrid cell. The hybrid process investigated in this case to remove phosphates was using an aqueous suspension of iron colloidal particles produced in situ. As far as the phosphates are concerned, their almost-total removal was always achieved for the iron concentration and pH values tested in those experiments.

The results were quite promising and were certified later, when a biosorbent, *Saccharomyces cerevisiae*, was also applied.[47] Yeast has been used by humans for over 6000 years for a variety of applications and it is presently one of the most important commercial micro-organisms. Figure 10 shows a comparison between microfiltration and the hybrid process for two varying superficial air velocities. However, when the latter was increased beyond a certain limit, flotation was not working at an optimum level and the results for the two modes were quite comparable (i.e., the difference was diminished). Lower permeabilities were observed in biomass systems (both simple microfiltration and hybrid flotation−microfiltration systems), possibly because of the nature of the particles and the filtration mechanism.[47] This was the outcome of the comparison with the previous referred cases of zinc removal using zeolites (of type 4A with an ion exchange capacity of 6 mequiv/g and a particle size of 3 μm) for metal bonding and the hybrid sorptive flotation−microfiltration system for the S/L separation, and metal precipitation as a hydroxide (with pH adjustment) and the hybrid precipitate flotation−microfiltration for the S/L separation.

Surfactants have been added for the purpose of improving the system performance substantially. This resulted in a longer membrane operation time with less-frequent membrane cleaning. Sorption of Zn^{2+} by brewer's yeast was very rapid, attaining equilibrium within 30 min. The separation of biomass by flotation was examined at a natural pH value (6.0−6.5), by applying different concentrations of cetyl-trimethyl-ammonium

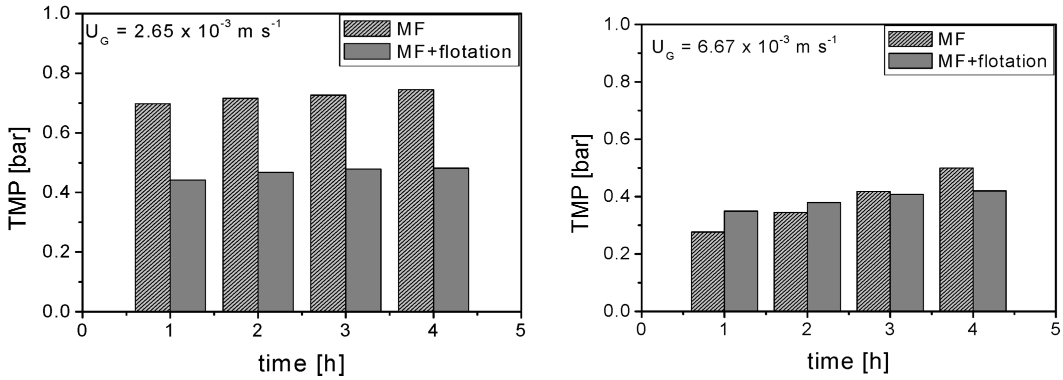

Figure 10. Comparison between microfiltration and hybrid cell, when applying biosorbents for zinc ion removal in the hybrid unit, compared to microfiltration alone: transmembrane pressure (TMP) versus operation time at two superficial air velocities ($U_G = 2.65 \times 10^{-3}$ m/s (left) and 6.67×10^{-3} m/s (right)).[47]

bromide (CTAB) as a collector and Zetag 63 as a flocculant. It was observed that the obtained recoveries of solids were higher in the case of CTAB: using a recovery of 20 mg/L, the flotation recovery was in the order of 95%; the rest of the metal-loaded biomass was kept by the membrane. As far as the Zn^{2+} ions are concerned, their almost-total removal was always observed for the tested experimental conditions (feed concentration = 50 mg/L).

From the economic data, the hybrid system seemed to have lower capital cost and lower operating costs. Furthermore, flotation following microfiltration was calculated to require larger membranes.[45] Technical−economical flowsheet analysis of (a) the flotation process, (b) membrane microfiltration, and (c) the combined hybrid process was conducted (using the software tool SuperPro Designer of Intelligen).

Discussion and Concluding Remarks

"New" economic activities are, in fact, surprisingly dependent on traditional raw materials. All electronic appliances use copper and require electrical power to make them work; this is power that may well be generated by coal and transmitted by aluminum and copper wires and cables. A home personal computer (PC) typically contains ∼30 mineral ingredients. The central idea of the new economy is that the generation and exploitation of knowledge are beginning to play an ever-increasing part in the creation of wealth.[48]

In one paper,[49] how sustainability is interpreted both theoretically and in practice for the primary extraction industries was investigated. Two contrasting perspectives can be adopted: one states that continued extraction of nonrenewable resources is a necessary part of sustainable development, while the other states that extraction of these resources must be greatly reduced or even eliminated. As shown in Figure 11, concerns in all three lobes must be addressed for sustainable development to occur, represented by the shaded area where all three lobes intersect. There is now a burgeoning amount of literature that examines sustainable development in the context of minerals and mining, most of which is concerned with sustainability at global and national scales.

The SingSpring plant (a subsidiary of Hyflux company) clinched the Distinction Award, Desalination Plant of the Year 2006. After passing through filter screens, the seawater is pumped to a dissolved-air flotation/filtration unit to clarify and pretreat it before undergoing reverse osmosis. Therefore, contaminants such as oil, grease, and suspended solids are removed in the pretreatment process, where flotation is assisted by coagulation. High-rate flotation applied in seawater pretreatment was examined, following a hydraulic optimization of the

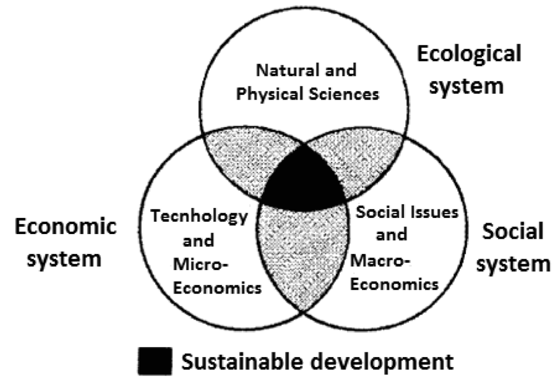

Figure 11. Aspects of sustainable development.[49] Concerns in all three shown lobes must be addressed for sustainable development to occur. (The need for sources of drinking water is becoming urgent.) (Reproduced, with kind permission, from ref 49. Copyright 1999, Elsevier)

flotation cell, to face variable- and bad-quality surface seawater and was determined to be an efficient tool.[50] The raw water silt density index (SDI) values were both permanently very high and with wide fluctuations, mainly during storm events. The preliminary treatment by dissolved-air flotation was reported to allow good removal of turbidity, suspended solids, and hydrocarbons.

This company also built a desalination facility in Antofagasta, Chile's second-largest copper producer; in the pretreatment line upstream from the RO membranes, this facility had stages of screening and grit removal with a fast flotation system. The Antofagasta facility, which takes raw water from the Pacific Ocean, was designed to produce 45 000 m^3 of process water for the mine daily, which is located in a desert area 2800 m above sea level.

Engineering considerations are central in decisions concerning the commercial future of biosorption, and a practical solution is needed for certain problems, such as the efficient separation of metal-loaded biomass. Unfortunately, compared to the basic research of biosorption, today, the application of biosorption technology rather falls behind and there is some journey ahead. Flotation, as opposed to settling, is a solid−liquid separation method that is applied to particles, whose overall density is lower, or has been made lower, than that of the surrounding (aqueous) solution. The dispersed-air flotation technique, which has been examined in the present investigation, uses aeration by bubbles, produced through fine pore diffusers.

Flotation constitutes a process capable of removing finely suspended matter whose size ranges from the particle size of pulverized mineral fines, down even to chemical ions. It has been established that flotation (which is rarely achieved without the presence of surfactants, i.e., collectorless) was promising for the effective separation of metal-laden biosorbents from the decontaminated (clarified) solution and it can be suitably applied for cases, when the sorbent material is used as a suspension in the liquid (e.g., in a continuous stirred tank reactor type).

The goal of the present research projects was also to avoid the main disadvantages of conventional processes for the removal of toxic metals from industrial wastewater by developing new technologies, new separation materials, and new hybrid processes for the reuse of water and metals. Environmental problems are gradually becoming more important, and public interest toward them is growing. It is known that many specific industrial wastewater streams with large flows contain toxic metals (in concentrations up to 500 mg/L) that must be removed prior to water recycling, indirect discharge into the sewage system, or direct discharge into surface waters. Some examples of these industries are the rinsing water in metalworking enterprises and the rinsing water in the semiconductor industry.

In today's economy, chemical and process engineering must respond to the changing needs of the chemical processes and related industries, to satisfy both the increasing market requirements for specific end-use properties of the product required by the customer, and the social, raw-material and energy-savings, and environmental constraints of the industrial-scale process.[51] Developing sustainable supplies of metals will rely on smart product design and more-efficient recycling.[52] Metals have limits in the same way that water and crude oil do.

According to the vision for 2025 and beyond of the ETP for Sustainable Chemistry, better use of chemistry and biotechnology will enable increased eco-efficiency of the industry.[2] An effective framework for innovation in these scientific areas will strengthen its excellent skills base.

In conclusion, membrane filtration technologies are increasingly used for solid−liquid separation purposes in conventional water and wastewater treatment plants. One of the major problems encountered during their operation is fouling by solid particles, which causes a gradual degradation in process efficiency. In this work, it was illustrated that it is possible to prevent 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 bubble stream may be used at the same time 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. The combination of the two processes into a hybrid cell, with the membrane module submerged inside the flotation cell, also achieves energy savings, since no additional energy (beyond that needed for flotation) was necessary for countering the fouling of the membranes.

It is well-known that many metal ions precipitate out by simple pH adjustment; in contrast, others form soluble oxyanions in the aqueous solutions. The latter, as well as low concentrations of metals in general (even following a preliminary treatment), can be separated and recovered by some sort of sorption, applying (or forming in situ) an appropriate bonding agent. Flotation techniques may be applied downstream for the separation, such as (i) precipitate flotation, (ii) adsorbing colloid flotation, and (iii) sorptive flotation, which were successfully investigated in a hybrid MF cell and shown to operate promisingly. The concentrations of the remaining metals, after the suggested treatment scheme, were determined to be acceptable, according to current legislation, while the metal solution obtained after elution has sufficiently high metal concentrations (∼10 times higher), hence allowing the application of the combined process for the recovery and reuse of metals.

A comparison between biosorption and other conventional metal separation/treatment methods has been found to favor the former, in terms of removal efficiency and applicability at (more-acidic) lower pH values. The high kinetic rate of biosorption further is a particular advantage of this process. The source of the raw biomaterials for the novel sorbents preferably would be industrial wastes, including bacteria, fungi, and yeasts. The used biomass also can be regenerated and reused in subsequent treatment cycles.

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