Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Peleka, Efrosyni N. , Lazaridis, Nick K. , Mavros, Paul and Matis, Kostas A.(2006) 'A New Hybrid Flotation—Microfiltration Cell', Separation Science and Technology, 41: 14, 3229 — 3243

To link to this Article: DOI: 10.1080/01496390600786218

URL: http://dx.doi.org/10.1080/01496390600786218

Separation Science and Technology, 41: 3229–3243, 2006

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390600786218

A New Hybrid Flotation—Microfiltration Cell

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Abstract: The investigated hybrid cell combines the advantages of both flotation and membrane separation, while overcoming their limitations and having as an outcome clean water from a industrial wastewater. Hence, metals recovery from dilute aqueous solutions was a promising application of this innovative process, further to solid/liquid separation. The specific objective was to apply the process for the efficient separation of effluents containing metals (here, zinc). The main examined parameters were the following: the metal initial concentration, flotation surfactant applied, and air flowrate. The successful contribution of precipitate flotation was highlighted, while the observed metal removals were of the order of ~100%.

Keywords: Heavy/toxic metals, industrial wastewaters, separation, removal

INTRODUCTION

Membrane processes have been used in water and industrial wastewater treatment applications for volume reduction of aqueous wastes, recovery of chemicals from liquid industrial wastes, desalination, drinking water purification, removal of suspended solids, micro organisms, and dissolved organic and inorganic substances. On the other hand, flotation is a well-known process in effluent treatment that selectively separates surface-active compounds from a solution, collecting them at the gas-liquid interface and

Received 3 March 2006, Accepted 20 April 2006
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thereby concentrating them towards the surface (1, 2). The process is applied to the removal of organics from water, the removal of toxic metal ions, oils, powders, and residual reagents from wastewater etc., apart of course from the beneficiation of mineral particles in minerals technology. For the removal of heavy metals from different metal-containing effluents, a commonly applied method is that of metals precipitation, in the form of their hydroxides or the co-precipitation by ferric hydroxide.

An alternative option for the heavy metals removal is the use of synthetic or natural polymeric precipitant–coagulant reagents, such as polymerized ethylene-dichloride ammonia or polydialkylamine-dithiocarbamates (3–5); however, the downstream application of a coagulant, in order perhaps to flocculate the fine precipitates produced, was avoided being possibly detrimental to the microfilters. Secondary treatment (for example, with sand filters) is often required as the separation of precipitates is not completely achievable by simple settling. Precipitate flotation was applied in the present, a quite old separation technique but known mostly at laboratory scale. The main parameters affecting the process were analysed in depth (6).

Membrane filtration processes are nowadays used as an alternative to conventional industrial separation methods such as distillation, centrifugation, solvent extraction, decanting (7), since they potentially offer the advantages of highly selective separation, separation without any auxiliary materials, continuous and automatic operation, economical operation also in small units, ambient temperature operation, usually no phase changes, as well as relatively low capital and running costs. 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 (8), feed-pre-treatment (9), surface modification of membrane (10), and gas sparging (11, 12).

Both flotation and membrane filtration are separation processes studied extensively in literature, but their combination in a hybrid flotation-membrane filtration system is an innovative idea. Various hybrid systems include membrane separation processes which have been presented in literature in recent years, except the known membrane bioreactors—see, for example, ref. (13). Thus, a hybrid distillation-reverse osmosis system was studied (14), a hybrid distillation-membrane pervaporation system (15), and also a hybrid membrane-ozonation system (16).

The hybrid flotation-membrane filtration system combines the advantages of both these processes while overcoming the limitations (17). During its operation a suspension of fine-sized adsorbent was fed into the hybrid cell, where the solid particles were partially removed by flotation, while clean water was obtained from the membrane module. Some of the solid particles remaining in the dispersion were deposited on the surface and the pores of the membrane, forming a cake that gradually blocked the pores and caused membrane fouling. The rising gas bubbles were used for the flotation process, while at the same time acting as membrane-surface scrubbers, effectively removing the deposited cake and countering the fouling problem. It has been already reported that dispersed-air flotation was the more appropriate technique in effluent treatment for bubbles generation, when compared with dissolved-air flotation (1).

The Present Hybrid Cell

In this section we discuss the conclusions of our work on this innovative system: Microfiltration submerged membrane separation was investigated by means of which low residual metal concentration in the treated water, at maximum water yield and higher concentration of metal bonding agent in the concentrates could be accomplished (17). During the experimental series of continuous flow separation all the collected samples showed an efficient separation; the application investigated mainly was the separation of metal loaded zeolites—i.e. following the mechanism of sorptive flotation (6).

It has been also found that the crosscurrent flow of air improved the membranes operation. The finer the air bubbles used, the lower was the pressure drop through the membranes. Air sparging under the applied experimental conditions was shown to assist zeolites microfiltration, reducing fouling. The feasibility of the hybrid process was proven (18); stable fluxes of up to 80 L/m^2 h were achieved with the ceramic flat-sheet multichannel membranes applied at low transmembrane pressure (<100 mbar). Cake resistance was generally of the same magnitude as membrane resistance and thus, quite low so that it could be attributed to the formation of highly permeable zeolites cake layers. No energy, in addition to that needed for flotation, was necessary for fouling control of the membranes, leading to low operation costs of the process.

Elsewhere it was noted that there was an influence of solids concentration, as expected (17). Frothing, with the appropriate dosage of surfactant and/or frother, should be controlled. Backflushing (gentle) contribution had no important influence and rather improved the operation. The results for loaded zeolites were better at natural pH, where flotation should be operated. The cell's efficiency, expressed as flotation recovery, was found better than the respective batch flotation results.

EXPERIMENTAL

The hybrid cell, shown in Fig. 1, consisted of a cylindrical flotation column, with an i.d. of 100 mm, made from plexiglas, with a cylindrical ceramic porous gas sparger (diameter 10 mm, height 20 mm, average porosity

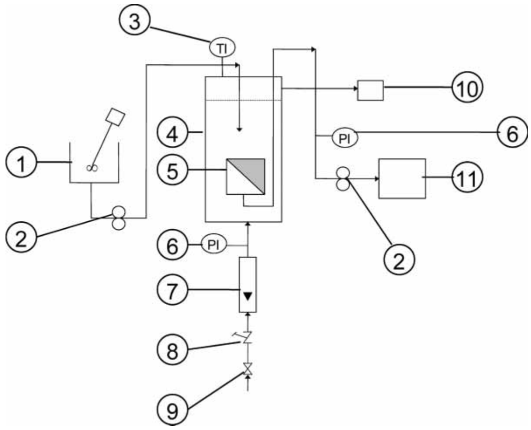

Figure 1. Laboratory arrangement for the hybrid cell; 1: Mixing tank, 2: Peristaltic pump, 3: Thermometer, 4: Flotation column, 5: Membrane microfiltration, 6: Manometer, 7: Air flowmeter, 8: Non-return valve, 9: Slide valve, 10: Foam collection tank, 11: Permeate collection tank.

40–100 μm) located close to the bottom of the cell. A membrane module was fixed at a height of 60 mm above the gas sparger. Hence, for the microfiltration (denoted as MF) arrangement a module was inserted inside the flotation column; it consisted of a twin set of parallel, double-sided ceramic membranes, with a flat sheet multi-channel geometry, having a mean pore size of 0.3 μm, a total surface area of 0.021 m^2, hydrophilic surface properties and an expected pure water flow rate of ~2 L/h.

Clean water was drawn from the membrane module through a peristaltic pump, and the membrane pressure drop due to the gradual fouling was measured close to the membrane exit. From the recorded transmembrane pressure (TMP) the following values were calculated: the permeability (expressed as L/h m^2 bar) of the module from the feed flowrate divided by the membranes area and the difference of TMP (here in bar) from atmospheric pressure; and also, the total hydraulic resistance (m^{-1}) from the Darcy-Poiseuille equation.

Air was introduced into the cell through the air diffuser, at different superficial velocities, U_G, of 0.265, 0.447 and 0.647 cm/s (where is used). The liquid superficial velocity, U_L, was kept at 0.0168 cm/s, being the higher rate earlier tested. Increasing it also the membranes resistance was increased. The solution (effluent) height was kept constant for all experiments at 400 mm. In certain experimental runs, backflush was tested using various duration and also intermediate period, as noted.

The treated solution had zinc dissolved at a concentration of 50 mg/L (unless otherwise stated). Metal precipitation as hydroxide was conducted by pH adjustment, at the pH value of 9. The main flotation collector applied was hexadecyl-trimethyl ammonium bromide (HDTMA-Br), with concentration 10 mg/L; other surfactants, cationic or anionic, were tested, too. No frother was added.

Preliminary batchwise tests preceded the continuous flow experiments and gave the necessary information for optimum flotation conditions. Zinc total removals in the membranes retentate were typically expressed as percentage. In the present paper, comparison of the obtained results was also effectively attempted, at similar conditions, with a previous work, where a sorbent—i.e. zeolite—was also added, in order to remove the metal ion. In the hybrid process developed, most of the sorbent particles were removed by flotation and the membranes were subjected to only a small part of the initial concentration. As a consequence, the flux can be established at a high level and the energy requirements for membrane operation were minimized.

RESULTS AND DISCUSSION

Separate Experiments

Typical batch flotation experiments were conducted in order to certify the process (unpublished data). It was observed that at pH 9 precipitate flotation of zinc ions (initially 50 mg/L) was more effective than at pH 8, reaching almost 99% recoveries in only 5 min by the quaternary ammonium salt HDTMA as flotation collector of the precipitate. The obtained results were worse using a primary amine, dodecylamine; while no flotation was achieved with sodium dodecyl-sulfate (and 0.1% v/v ethanol as frother). The latter could be efficient at lower pH values where $Zn(OH)_2$ has a positive surface charge.

It is known, as can be calculated from thermodynamics (i.e. the Mineql+ programme), that for the above conditions, zinc precipitates out as hydroxide around the pH value of 8.3, which decreases at higher zinc concentrations. Nevertheless, zinc redissolves at a pH of about 11. It should be also noted that between a hydrolyzed metal ion and its undissolved hydroxide, an intermediate stage exists where the cation starts to polymerize and gradually as this proceeds, the corresponding hydroxide appears, the oxygen atom playing the role of a bridge.

A good agreement was reported between the experimental data curve and the optimum precipitation area of zinc hydroxide, as obtained from theoretical solubility data; the precipitate was said to be quite hydrophobic (19). The solubility product of zinc hydroxide is 4.5×10^{-17}, i.e. low enough compared with other metals. Certainly, a dissolved metal may be precipitated by other means than the modification of solution pH, such as sulphide or by the application of a specific chemical reagent. For instance, copper ion was successfully precipitated and floated using xanthates (20).

Therefore, for a variety of reasons (including the aqueous speciation of surfactant applied and its ionization) the metal removal process is particularly susceptible to variations of solution pH. The knowledge of how pH affects each system is obviously a prerequisite to flotation. For example, moving to the alkaline region of pH, usually with the addition of lime (which has low cost) many metals precipitate as hydroxides leading to a change in the nature of the process; hence, having precipitate flotation instead of ion flotation. Advantage of the former is usually the lower requirement (non stoichiometric) for the necessary surfactant. A disadvantage of flotation was reported to be that sometimes its removal efficiency is limited due to the fact that some substances either are not retained in the froth/foam or are not sufficiently hydrophobic, thus remaining in the bulk dispersion or needing a surfactant to be added.

Microfiltration experiments were then carried out with this system and similar results were seen as earlier with the loaded zeolites separation; however, another mechanism (ion exchange) was followed there than precipitation (17). In Fig. 2 the beneficial effect of air sparging is shown. Transmembrane pressure and total resistance were decreased, while the permeability was apparently increased. Meanwhile, zinc removals (not shown) were high throughout the investigation except from the preliminary period (of one hour approximately), operating unsteadily.

The used air superficial velocity was about ten times lower than that usually applied to conventional immersed systems, resulting equally in lower energy consumption (18). It was further demonstrated that the notion of cake deposit is no more available with a gas/liquid flow (11)—the cake here being zinc hydroxide precipitates.

Various problems that appear during the application of metals precipitation as hydroxides were discussed: the presence of complexing agents, no common pH value for all the toxic metals, need for flocculation, voluminous produced sludges, metal redissolution, disposal disadvantages, etc. So, may be the application of flotation could be an alternative.

The Flotation—MF Process For Metal Ions Removal

It is common knowledge that total solids removal is not possible in a single flotation stage because some substances may not be retained in the froth or fail to become permanently attached to the bubbles remaining in the bulk. Therefore, the combination of flotation with membranes separation might be reasonable. The addition of MF could be made either downstream or in the same unit, as recently there is a trend for compact systems; however, industry has been avoiding any additional plant complexity required. In general, in the lab cell used, it seemed that flotation was a faster process than membranes filtration. It was further reported that the membranes were

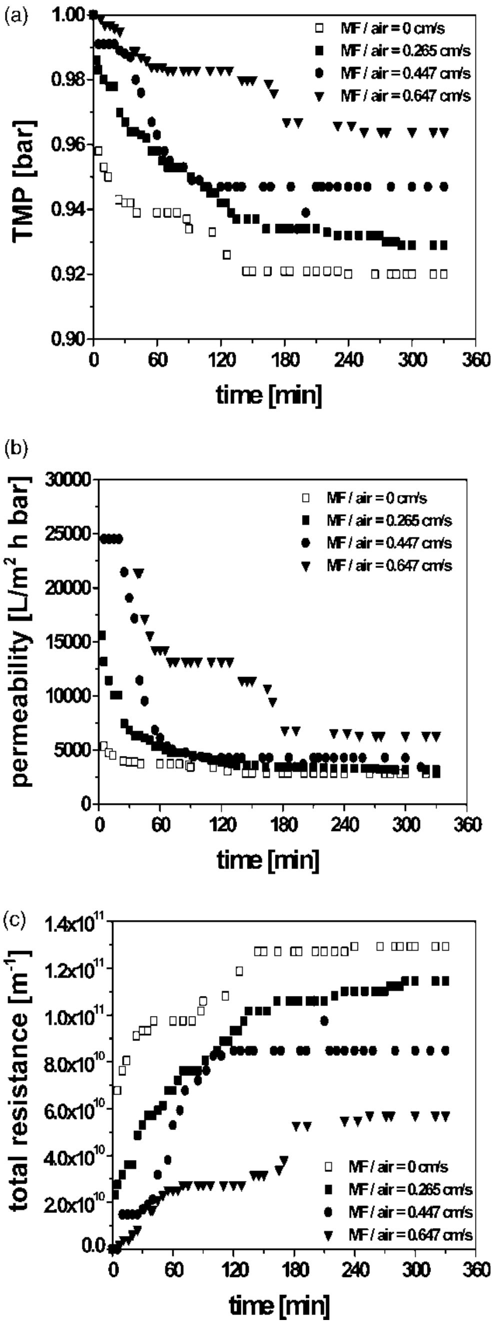

Figure 2. Microfiltration experiments alone: influence of air sparging; results expressed as (a) transmembrane pressure, (b) permeability and (c) total resistance against the time of operation ($U_L = 0.0168$ cm/s).

sensitive to small changes in flotation efficiency (18). Certainly, flotation is known for its reliability, being well established as a S/L separation technique.

Figure 3 presents the results expressed for permeability for the hybrid system; Examining the influence of air superficial velocity it was observed that this time, due to flotation, the medium value used of 0.447 cm/s was giving the higher permeability, i.e. a minimum was reached. For membrane bioreactors, it was found that aeration was a significant factor governing the filtration conditions (12). Cake-removing efficiency of the uplifting air flow was affected by the turbulence of the flow; this, however, could be detrimental to flotation, in our case.

A comparison is possible with the aforementioned case of no flotation. So, after 270 min of operation with the medium air flowrate (0.447 cm/s), the transmebrane pressure was 0.982 bar for the hybrid system, compared with 0.947 bar for microfiltration alone. The respective values of permeability were 12665 for the hybrid and only 4293 L/h m^2 bar for MF; the total resistance was 2.874 × 10^{10} for the hybrid and 8.478 × 10^{10} m^{-1} for MF.

To achieve stable membrane performance with higher fluxes, backflushing proved to be necessary; it was also reported that regarding the membrane behavior at various experimental conditions the ceramic membranes showed better performance compared to polymeric membranes in terms of their permeability (18). The effect of backflushing is shown in Fig. 4 for the module permeabilities. Similarly, curves for the transmembrane pressure and/or total resistance (as in Fig. 2) are available. The use of backflushing every 5 min was seen as suitable, its duration of 15 s was slightly better (compared to a 5 s duration). With this and after 300 min operation, the transmembrane pressure was 0.989 bar and the total resistance 1.814 × 10^{10} m^{-1}.

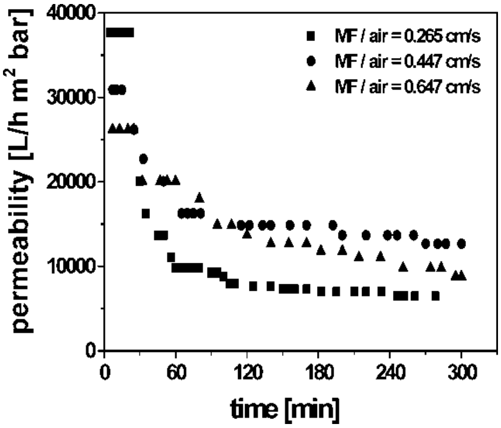

Figure 3. Hybrid system: varying the air superficial velocity; results expressed as permeability ($U_L = 0.0168$ cm/s).

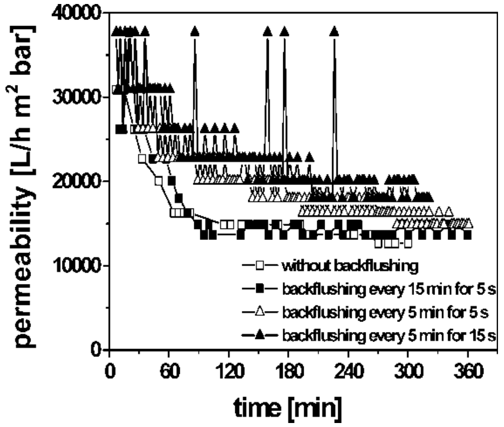

Figure 4. Influence of backflushing ($U_G = 0.447$ cm/s, the rest as in Fig. 3).

The influence of flotation collector concentration was also examined, increasing it from 10 to 50 mg/L HDTMA (see Fig. 5); meanwhile, paying attention to undesirable extensive foaming. The main differences were observed during the initial stages. After 300 min of operation, with the higher surfactant concentration (50 mg/L) applied the transmembrane pressure was 0.812 bar, the permeability 1205 L/h m^2 bar and the total membranes resistance 3.022×10^{11} m^{-1}; for the lower concentration (10 mg/L), the values were 0.735 bar, 852 L/h m^2 bar, and 4.272×10^{11} m^{-1}, respectively.

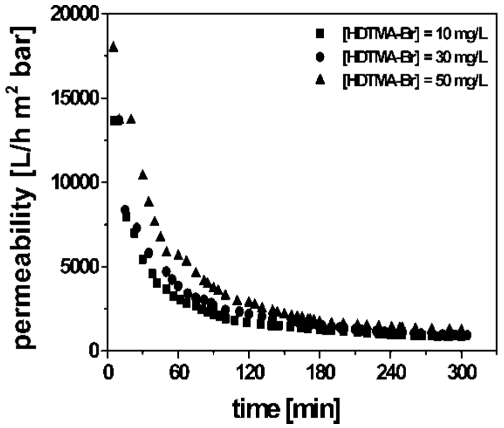

Figure 5. Influence of surfactant concentration to the hybrid system (500 mg/L Zn^{2+}).

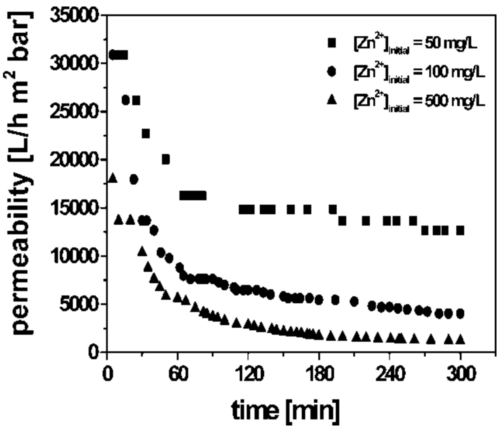

Figure 6. Influence of initial zinc concentration.

When varying the feed, i.e. metal, from 50 to 500 mg/L and hence, varying the zinc precipitate concentration, the permeabilities were reduced increasing the concentration, as possibly expected—see Fig. 6. For example, after 300 min operation with initial 50 mg/L Zn^{2+}, the permeability was 12665 L/h m^2 bar; with 100 mg/L, permeability was 4035 L/h m^2 bar and with 500 mg/L permeability was 1205 L/h m^2 bar. Analogous were the calculated values for TMP and total resistance.

The corresponding results of dissolved metal removal for these runs are presented in Fig. 7, with the scale increased in the vertical axes for better illustration. When plotting as remaining metal in solution, with the higher feed

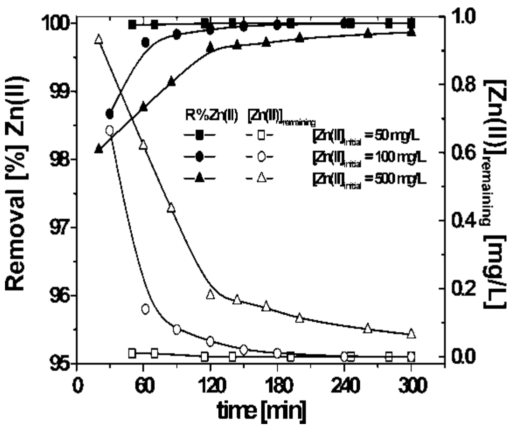

Figure 7. Obtained zinc removals in the retentate; results expressed in two ways (respective to Fig. 6).

concentration used the obtained results are not as good (although the removals were over 99.5%), due possibly to problems with the precipitation in the feed tank of the rig or the pH monitoring (perhaps, zinc redissolution). The recorded remaining zinc was chemically found undissolved in the membranes retentate.

The zeolites are a typical example of sorbents capable of bonding fast and effectively toxic metal cations from contaminated wastewater. However, due to their ultrafine size, separation downstream is generally required. As a target, ~90% solid particles recovery was set for the flotation process alone, used as the pretreatment stage for microfiltration downstream. (17). The metal removal in this case depended mainly on the amount of used sorbent, which is economically costly.

Table 1 gives the main outcome of the comparison with the previous published case of zeolites separation, expressed only for membranes permeability. All the figures found for the present case are well greater, as less solids are present inside the hybrid cell and so the pressure drops are much lower. In this way, comparing the two hybrid processes (the first of precipitate flotation with the second one using sorptive flotation):

1. after 170 min operation for air superficial velocity of 0.447 cm/s, the TMP for "hybrid 1" was 0.985 and for "hybrid 2" 0.821 bar, while the total resistance 2.450×10^{10} and $2.812 \times 10^{11}\ \mathrm{m}^{-1}$, respectively.
2. after 220 min operation applying backflushing for 5 s every 15 min, the TMP for "hybrid 1" was 0.983 and for "hybrid 2" 0.813 bar, while the total resistance 2.662×10^{10} and $2.936 \times 10^{11}\ \mathrm{m}^{-1}$, respectively.

As far as the metal removals for the two hybrid cases, the differences obtained from the comparison are not significant; however, both have been working very well as shown in Table 2.

Table 1. Comparison of two hybrid systems ("hybrid 1" is the microfiltration – zinc precipitate flotation and "hybrid 2" is the microfiltration – zinc loaded zeolite flotation); $[\mathrm{Zn}^{2+}]_{\mathrm{initial}} = 50$ mg/L, pH = 9 for "hybrid 1" and pH = 10.5 for "hybrid 2", [HDTMA-Br] = 10 mg/L, [zeolite] = 5 g/L, $U_L = 0.0168$ cm/s

	$U_G = 0.265$ cm/s	$U_G = 0.447$ cm/s	$U_G = 0.647$ cm/s
(i) Effect of air superficial velocity (after 170 min of operation)			
Hybrid 1	7289	14857	12665
Hybrid 2	1588	1263	876
	Without backflushing	Backflushing every 15 min for 5 s	Backflushing every 5 min for 5 s
(ii) Effect of backflushing (after 220 min of operation, $U_G = 0.447$ cm/s)			
Hybrid 1	13674	13674	17965
Hybrid 2	987	1209	2770

Table 2. As in Table 1(i), but comparing for zinc separation

	$U_G = 0.265$ cm/s	$U_G = 0.447$ cm/s	$U_G = 0.647$ cm/s
A) Expressing the obtained results for zinc removal (%)			
Hybrid 1	99.98	100.00	99.99
Hybrid 2	99.99	99.97	99.93
B) Expressing for zinc remaining concentration [mg/L]			
Hybrid 1	0.010	0.000	0.005
Hybrid 2	0.005	0.015	0.035

CONCLUDING REMARKS

The case study examined for this process was to an effluent sample from Assarel-Medet open pit copper mine (Bulgaria), aiming particularly at metal recovery (17); the on-site experimentation near Panagyurishte (90 km south-east of Sofia), conducted by a multinational team, lasted more than two months. A rectangular cell of 3 L content with 5–10 L/h real feed was used (the automatically controlled rig was constructed by upt). Successful testing was further carried out (by VUT Brno) of a combined process of electroflotation, dissolved-air flotation, or bioflotation and membrane separation, under realistic industrial conditions using existing flotation units. Hydrophobic polypropylene and hydrophilic polyethylene hollow fiber MF membranes were used (21).

The relative costs of the process have been recently published (20). The economic comparison with the separate system MF following flotation—using the software tool SuperPro Designer for 10 m^3/h wastewater of the Assarel's type effluent—showed that the hybrid system has lower capital cost, of the order of 0.92 millions Euros and lower operating costs, about 1.42 millions Euros per year. The former also requires larger membranes.

Although at present no experimentation was devoted to scale-up, much is already done for the flotation column itself—see, among others, ref. (22). On the other hand, perhaps a useful experience was gained with the membrane bioreactors; for instance, scale-up to 1.5 m^3/h was demonstrated in a fruit juice production plant (23)—(which one of the authors has visited in the Saarbrücken area). From a recent study of the lab hybrid cell hydrodynamics applying the tank-in-series model with a non-reactive tracer pulse input (and measuring the conductivity), it was shown that the residence time distribution of the hybrid flotation–membrane cell is practically identical to the residence time distribution of a perfectly mixed vessel; therefore, the hybrid flotation–membrane cell may be simulated as a single mixed vessel (21). The design of the hybrid cell was carefully examined due to the combination of two separate operations.

However, 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. 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 also from the treated wastewater itself—i.e., solution pH, ionic strength, and the existence of other (e.g., organic) substances besides the metal ions.

In conclusion, apart from solids separation earlier investigated with the hybrid cell, promising results were obtained also for metal ions removal from dilute aqueous solutions, as the metal-containing industrial wastewaters are—such as plating liquid wastes, dilute leach solutions, hydrometallurgical residues, etc. The advantageous results from the attempted comparison perhaps explains and justifies that the investigation of this technique, by replacing sorption with precipitation, was worthwhile.

A large number of techniques have been used today to limit the membranes fouling and among them, certainly is air bubbling constituting also the transport medium in flotation, as applied in wastewater treatment; meanwhile, dispersed-air flotation is suitable as a pretreatment stage for microfiltration. Ceramic flat-sheet membrane modules were used in the laboratory in this work, of multi-channel geometry, inserted inside a typical flotation cell and combining flotation with microfiltration by submerged membranes; the latter needing also periodic backflushing.

ACKNOWLEDGEMENTS

Many thanks are due to Dr. Valko Mavrov (upt, Saarbrücken, Germany) for supplying the membranes and experience with them; also, to Dr. Tasos Zouboulis and Dr. George Gallios (AUTh) for their help, in many ways. This work was financially supported in part by the Greek Ministry of Education (Program Pythagoras).

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