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Use of membranes for heavy metal cationic wastewater treatment: flotation and membrane filtration

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Abstract A new water treatment process—membrane flotation—is presented. The hydrodynamics of air sparging with the use of microporous membranes was studied as well as the membrane flotation efficacy for cationic wastewater treatment. The performance of membrane filtration processes was evaluated. Ways of integration of flotation and membrane filtration in cationic wastewater treatment practice are discussed.

Keywords Wastewaters · Flotation · Membranes · Reverse osmosis · Nanofiltration · Heavy metals

List of symbols

Ar Archimedes number for emerging bubble
C_1 feed wastewater concentration (ppm)
C_2 treated wastewater concentration (ppm)
D pore size (diameter) (m)
G gravitational acceleration (9.81 m/s^2)
H height of bubbling bed (m)
J the functional of minimum bubbling bed energy
N natural number
R rejection in water/wastewater treatment
Re Reynolds number for emerging bubble
V_1 two-phase bubbling bed volume (m^3)
V_2 liquid bed volume (without gas) (m^3)

w bubbling rate (superficial velocity of gas flow), m/s
w_0 single bubble emersion rate (m/s)
w_1 grope emersion rate of bubbles (m/s)
x vertical coordinate (m)
ΔP pressure difference in gas sparging (Pa)
Λ Lagrange multiplier
P liquid (water) density (kg/m^3)
σ liquid–gas surface tension (J/m^2)
σ_0 coefficient of resistance
φ as content (volume fraction of gas in bubbling bed)
θ contact angle between membrane and water (°)

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Introduction

Various heavy metal cationic wastewater treatment methods have been developed in recent years because of the high environmental risks of the wastewater discharge and rising water scarcity in the world. These methods can be divided in two groups. The first group includes chemical and electrochemical precipitation techniques, coagulation, flocculation followed by separation of the sediment by clarification, filtration, flotation, microfiltration and other techniques. The second group encloses the methods of separation of soluted heavy metal cations: ion exchange, adsorption, nano- and ultrafiltration (UF), reverse osmosis (RO), electrodialysis, etc.

Flotation is one of the most cost-effective separation methods, applied with increasing frequency in wastewater treatment practice. On the other hand, membrane filtration methods [micro-, ultra-, nanofiltration (NF) and RO] are very effective and environmental

friendly methods with low-reagents consumption and low footprint of installation.

This article presents a study of hydrodynamics and heavy metal cationic wastewater treatment efficacy with so-called ''membrane flotation'' with some experimental data on membrane filtration performance for flotation effluents post-treatment or as a competing technique for heavy metal removal.

Flotation is a hetero-phase systems separation method, using gas bubble attachment. The attached particles (droplets) are floated and separated from the liquid dispersing medium (Zabel 1984; Wang et al. 2004; Matis 1995). Water and wastewater applications of flotation are metal coating wastes purification, washing and lubricating liquids treatment, surface water clarification and thickening of activated and coagulated sludge, etc.

The flotation methods are traditionally classified based on the method of gas (air) bubbles production (Zabel 1984; Kurniawan et al. 2006). The methods can be differentiated in three groups: (1) dispersed-air flotation, air bubbles are formed by flow through a diffuser (*pneumatic flotation*) or by mechanical shearing action (*mechanical flotation*); (2) dissolved-air flotation: *pressure flotation* (dissolving air in water at overpressure and flotation at atmospheric pressure) and *vacuum flotation* (dissolving air in water at atmospheric pressure and then applying a vacuum for flotation); and (3) other flotation methods: *electroflotation* using controlled mild electrolysis for production of hydrogen and oxygen bubbles, *biological flotation* using gas of biological origin (fermentation), etc.

Microporous membranes are frequently used as air diffusers (Hasanen et al. 2006; Kawamura et al. 2006); these devices have some price benefits and can product air bubbles, which are small enough to achieve a large interfacial surface area between air and water. This process is similar to the well-known membrane emulsification process, which uses microporous membranes for a stable emulsion production (Josceline and Tragardh 2000; Vladisavljević and Williams 2005; van der Graaf et al. 2005; Lambrich and Schubert 2005; Jing et al. 2006).

Flotation is used in water and wastewater pretreatment following membrane filtration (Braghetta et al. 1997; Bonnelye et al. 2004) and in integrated units combining dispersed air flotation and immersed membrane filtration (Matis et al. 2004; Mavrov et al.2003; Lazaridis et al. 2004). The examples mentioned above allow us to predict a good outcome of combining flotation with membrane-based techniques in water and wastewater treatment.

The first way of combining membranes and flotation is the use of membranes for air sparging and application of the formed bubbles for flotation. According to the traditional classification system, this type of flotation was termed *membrane flotation* (Kagramanov et al. 2004). The second way is application of membrane filtration to treat flotation effluents or use of flotation for membrane filtration concentrate treatment. The integration of flotation and membrane filtration allows us to treat industrial wastewater up to potable-grade level.

The study of membrane flotation hydrodynamics

The theory of bubbling bed energy minimum in flotation

The bubbling rate w is related with gas content and single bubble emersion rate w_0 with the equation:

$$w = \varphi f(\varphi) w_0, \tag{1}$$

where $f(\varphi)$ is a function of gas content, expressing bonding effect of emerging bubbles.

Finding of function $f(\varphi)$, that is the ratio of group emersion rate w/φ and single bubble emersion rate, appears to be a challenge, as the literature on this problem is contradictory. There is a number of empirical formulas, most frequently presented as (Deryagin et al. 1986; Chernykh 1995 and others):

$$f(\varphi) = (1 - \varphi)^n. \tag{2}$$

If the height of bubbling bed is big enough (about 1 m and more) the gas (air) is distributed along the height according to the energy minimum of gas–liquid bed. A functional of minimum of potential, kinetic, dissipation and surface tension energies could be presented as follows (Trushin et al. 2005):

$$J = \int_0^H \left[\rho g(1 - \varphi)x + \frac{\rho w^2}{2(1 - \varphi)} \right.$$
$$\left. + \frac{3}{4} \frac{\zeta_0 \rho w^2}{\varphi(1 - \varphi)^{2n}} x + \frac{6\sigma}{d}\varphi + \lambda(1 - \varphi) \right] dx. \tag{3}$$

As integration element does not include a derivative $d\varphi/dx$, the finding of an extremum of functional J comes to equating to zero of a φ derivative of integrand.

$$-\rho g x + \frac{\rho w^2}{2(1-\varphi)^2} + \frac{3}{4}\frac{\zeta_0 \rho w^2 x}{d}$$
$$\left(\frac{2n}{\varphi(1-\varphi)^{2n+1}} - \frac{1}{\varphi^2(1-\varphi)^{2n}}\right) + \frac{6\sigma}{d} - \lambda = 0. \quad (4)$$

At x = 0 the gas content signifies φ_0. Taking this into account we shall find λ:

$$\lambda = \frac{6\sigma}{d} + \frac{\rho w^2}{2(1-\varphi_0)^2}.$$

Having substituted multiplier λ in (4), we shall receive:

$$-\rho g x + \frac{\rho w^2}{2}\left(\frac{1}{(1-\varphi)^2} - \frac{1}{(1-\varphi_0)^2}\right)$$
$$+ \frac{3}{4}\frac{\zeta_0 \rho w^2 x}{d}\left(\frac{2n}{\varphi(1-\varphi)^{2n+1}} - \frac{1}{\varphi^2(1-\varphi)^{2n}}\right) = 0. \quad (5)$$

Because of low value of rate w, the second summand in Eq. 3 can be neglected. With respect to this, and also with regard to (1) and (2), we can receive:

$$\frac{3}{4}\frac{\zeta_0 w_0^2}{gd}\frac{(2n\varphi - (1-\varphi))}{1-\varphi} = 1. \quad (6)$$

From balance of forces for single bubble emersion we have:

$$\frac{3}{4}\frac{\zeta_0 w_0^2}{gd} = 1. \quad (7)$$

In consideration of (7) we can find the gas content from Eq. 6:

$$\varphi = \frac{1}{n+1} \quad \text{or} \quad n = \frac{1-\varphi}{\varphi}. \quad (8)$$

Having substituted the received n to Eq. 2, we can find the bubbling rate, taking (1) into account:

$$w = \varphi(1-\varphi)^{\frac{1-\varphi}{\varphi}} w_0. \quad (9)$$

At a known bubbling rate Eq. 9 allows us to calculate the value of gas content. For continuously working flotation machines with help of (9) it is possible to find limiting ratios of liquid and gas flows and choose an optimum value of bubbling rate.

It is necessary to note that the derived equations are applicable at mutually dependent (bonded) emersion of bubbles, causing their mutual inhibition. The interdepended emersion of bubbles is typical at a considerably high gas content when distances between single bubbles are low.

At low φ, the mutual influence of bubbles on their emersion rate is insignificant. In this case a minimum of energy complies with value of an exponent $n = 1$, that it is possible to receive from balance of the forces working on a bubble.

This value of n at a small φ proves to hold under experimental conditions, and it is usually chosen for calculation of flotation machines, functioning at low gas content (Kolesnikov and Iliyn 2004).

Experimental study of membrane flotation hydrodynamics in static mode

This study was carried out in a static mode (with no water flow) using the unit, presented in Fig. 1. The treated wastewater was periodically fed into the flotation vessel (1 m high) of transparent plastic (Plexiglas). The vessel has a square section of 5×5 cm. The porous stainless steel membrane was used for air sparging (pore size about 0.5 μm diameter).

After air sparging through the water in the vessel, the formed froth was removed with opening the valve 2, then the treated water merges with the help of valve 3. This process could be periodically repeated for treatment of necessary amount of wastewater.

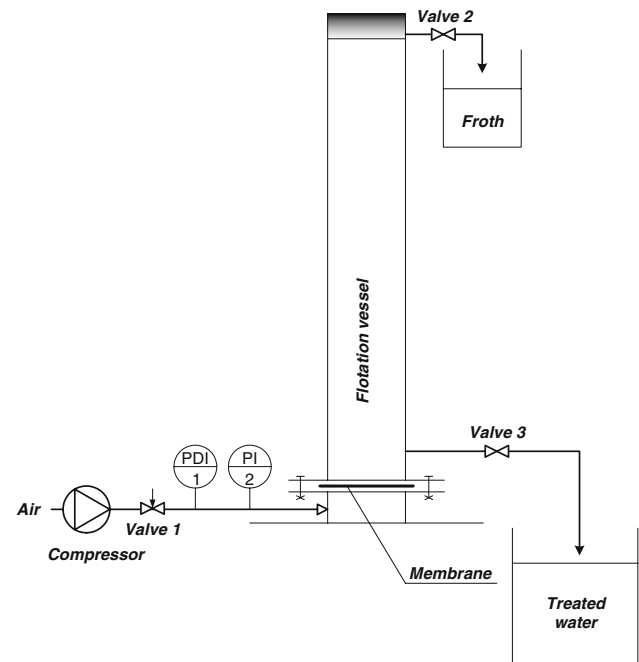The gas content was determined under the formula:

Fig. 1 A static unit for membrane flotation research

$$\varphi = \frac{V_2 - V_1}{V_2}. \tag{10}$$

Definition of bubble sizes was made with a digital video camera, which has allowed determination of the relative bubble sizes in comparison with the calibrated sample (Fig. 2).

A study of bubbling hydrodynamics was carried out with definition of bubbling rate dependence on gas content and single bubble emersion rate. The experiments were carried out with a system of air–aqueous surfactant solution sodium dodecyl sulphate (SDS) with an SDS concentration of 10 ppm. This concentration has been chosen according to literature data on "blocked" interfacial surfaces of bubbles with surfactant molecules (Chernykh 1995).

After the experiments with change of gas content from 5.5 up to 29%, the dependence of gas content on bubbling rate has been determined. As shown in Fig. 3, there are two areas of dependence—at low gas content (5–17%), area I and at higher gas content (17–29%), area II.

Calculation of single bubble emersion rate was carried out using Eq. 13 derived for single spherical particles sedimentation rate (Clift et al. 1978).

$$\text{Re} = \frac{Ar}{18} - 0.15\text{Re}^{1.687}. \tag{11}$$

Applicability of Eq. 11 for finding of single bubble emersion rate in described conditions has been tested experimentally. The fluctuations of the measured single bubble emersion rate from the calculated rate using Eq. 11 was no more than 4%.

Based on the value of single bubble emersion rate calculated for every measured bubble diameter, an average volumetric single bubble emersion rate w_0 was determined. Group emersion rate w_1 was found as the ratio of bubbling rate and gas content $w_1 = w/\varphi$.
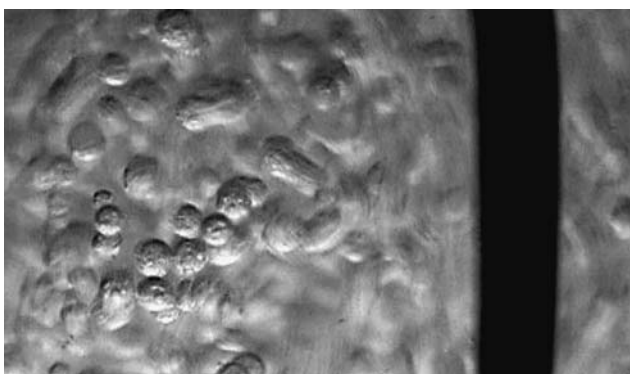
Fig. 2 A photograph of bubbles comparing to calibrated sample (*wire*)

Experimental data as well as the exponents n-values found using theoretical formula (9) are shown in Table 1.

As shown in Table 1, the experimentally obtained exponents n-values are close enough to the calculated values only for the second area (Fig. 3) at significant gas content that corresponds to the earlier conclusions. With increase of φ in the second area the divergence of theoretical and experimental values of n becomes very low. The average n-value for the second area, obtained in the experiment, is 3.4. This size is close to the reported n-value of 3 (Chernykh 1995; Tyurnikova and Naumova 1980).

Exponent n-values, obtained for the first area (Fig. 3), are strongly disordered. It suggests close values of emersion rates of single bubbles and group emersion at low gas content. Even insignificant experimental errors in definition of w_1 and w_0, results in high distortion of n-values.

The average n-value for the first bubbling area is 0.6 and differs from theoretical value for low φ ($n = 1$). Taking into account the strong disorder of experimental n-values at low gas content, further research in this bubbling area is necessary.

The study of efficacy of wastewater treatment with membrane flotation and integrated membrane-electroflotation method

Experimental study of membrane flotation treatment efficacy in static mode

One of the key issues of flotation practice is the correct use of special reagents, such as precipitants (coagulants
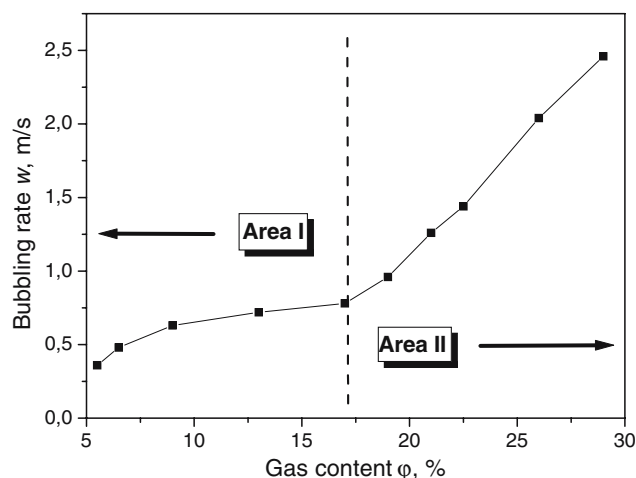
Fig. 3 Bubbling rate versus gas content during membrane flotation

Table 1 Experimental and calculated data

φ	w (cm/s)	w_1 (cm/s)	w_1/w_0	Exponent n-value in $f(\varphi)=(1-\varphi)^n$	
				Experimental	Calculated
0.055	0.36	6.55	0.9974	0.046	17.18
0.065	0.48	7.38	1.1130	−1.594	14.38
0.09	0.63	7.00	0.8630	1.562	10.11
0.13	0.72	5.54	0.7171	2.387	6.69
0.17	0.78	4.59	0.4538	*4.240*	*4.88*
0.19	0.96	5.05	0.4532	*3.756*	*4.26*
0.21	1.26	6.00	0.4173	*3.707*	*3.76*
0.225	1.44	6.40	0.4691	*3.361*	*3.44*
0.26	2.04	7.85	0.4034	*3.015*	*2.85*
0.29	2.46	8.48	0.4214	*2.523*	*2.45*

and flocculants), collectors (surfactants, adsorbents, and complexons) and acid/alkali (pH correction) (Zabel 1984; Wang et al. 2004; Matis 1995; Kurniawan et al. 2006). On the other hand, the main operation characteristics of flotation process are rejection (calculated like for membrane filtration according to formula (12)) and liquid phase (wastewater) residence time in flotation vessel that is the ratio of volumetric flow of wastewater and the vessel volume.

$$R = \frac{C_1 - C_2}{C_1} \cdot 100\%. \tag{12}$$

It is well known that the size of bubbles formed with the use of porous materials (including membranes) depends on the pore size proportionally. According to the Laplace law (13) the lower the liquid–gas surface tension the lower pressure difference needed for bubbling trough the pores. In summary, the lower the surface tension, the lower bubble size can be formed using the membrane with a given pore size applying a given pressure. Thus, the correct reagents for bubble size minimization (for interfacial surface increasing) are surfactants lowering the surface tension.

$$d = \frac{4\sigma \cos \theta}{\Delta P}. \tag{13}$$

Other important reagents for increasing flotation rejection are alkali for heavy metal hydroxides precipitation, and flocculants for formed solid phase particle aggregation resulting in an increase of the particle size from 0.1–0.2 to 0.5–2 mm. The formed flocs have a density, which is close to water so their flotation is more effective.

Original cationic wastewaters from various electrochemical processes contain 10–100 mg/l and more of Fe^{3+}, Cu^{2+}, Ni^{2+}, Cr^{2+} and other cations. Since these wastewaters are usually acidic, it is necessary to increase pH for cation hydroxides formation to make flotation applicable.

Rejection dependencies on the flotation reagents' concentration were found for experimental determination of surfactant and flocculant optimal doses. It was shown (Fig. 4) that optimal concentration of surfactant (SDS) is 7–8 ppm for treatment of water with 100 ppm concentration of each of Fe^{3+}, Cu^{3+} or Ni^{2+} cations separately. Optimal concentration of flocculant poly acryl amide (PAA) for this model of wastewater treatment is 1.5–2 ppm. As shown in Fig. 4, membrane flotation demonstrates high rejection (up to 99%), which is comparable to electroflotation rejection (Kolesnikov and Iliyn 2004).

These experimental data were obtained using the static unit presented in Fig. 1 (with no water flow, only with air bubbling trough the water). The study of rejection dependence on feed cation concentration (Fig. 5) permitted to determine the field of membrane flotation application for cationic wastewater treatment. It was shown that wastewater treatment is effective (rejection > 80%) when feed cation ($Fe^{3+}/Cu^{2+}/Ni^{2+}$) concentration is higher than 50 ppm.

On the base of reference (Kolesnikov and Iliyn 2004) and experimental electroflotation data it was cleared up that the degree of purification (rejection and selectivity) is maximal when pH-values are:

$$Fe^{3+} \rightarrow pH = 6.5, \; Cu^{2+} \rightarrow pH = 9.5, \; Ni^{2+} \rightarrow pH = 10.5.$$
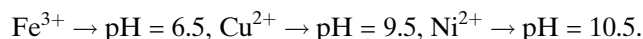
During purification of mixed solution of three cations (Fe^{3+}, Cu^{2+}, and Ni^{2+}) the flotation rejection of each cation reached a high value (more than 95%) when pH = 10.

Integrated membrane-electroflotation unit for wastewater treatment

Based on hydrodynamics and purification efficacy in static membrane flotation experiments, the integrated flotation unit combining co-current membrane flotation and counter-current electroflotation treatment was

Fig. 4 Membrane flotation rejection versus reagents concentration: **a** surfactant (*SDS*); **b** flocculant (*PAA*)
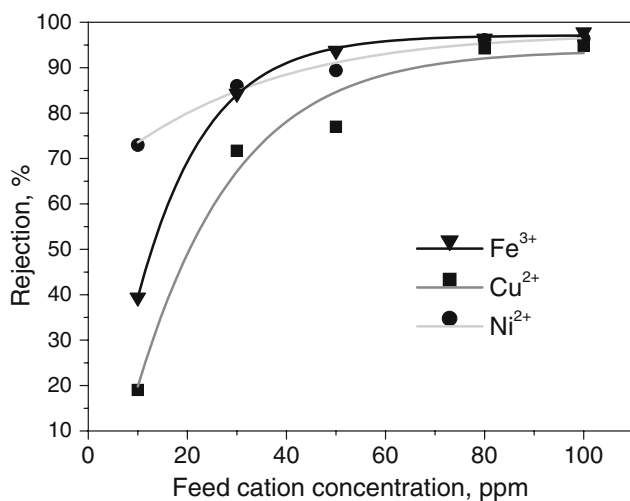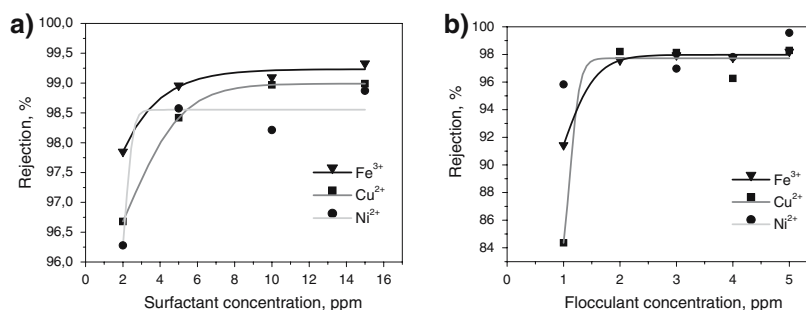
Fig. 5 Flotation rejection versus feed cation concentration

designed. Further experiments were carried out using this unit (Fig. 6).

The first step was the design of a tubular membrane diffuser with bubbling of air to the inner water flow from the outside. A tubular microfiltration (MF) membrane element with inner selective layer (0.5–1 μm pore size) was used as the diffuser for small-sized bubbles formation. Because of the turbulence of water flow in the inner space of the membrane element, the growing bubbles are "cut out" before their sizes reach the values sufficient for free detachment in the static water. The two-phase flow with gas content about 15–25% is directed to the flotation vessel.

The pilot-scale membrane-electroflotation unit (Fig. 6) consisted of a membrane diffuser and two flotation chambers: one for co-current membrane flotation (volume 5.5 l) and the other for counter-current electroflotation (volume 11 l). Electroflotation electrodes are submerged in the second chamber near the bottom. These rectangular flat electrodes are made of stainless steel (cathode) and oxidized titanium (anode). The cathode is made of a wire net and the anode is a plate with drilled bores.

The bulk quantities of impurities are rejected in the first chamber due to the high gas content and the predominant bubble size closer to the predominant particle size of flocculated impurities. The second (electroflotation) chamber is for polishing. Bubble size in the electroflotation chamber is three to five times smaller than in the first chamber, but the gas content is only 1–3% max.

Since the piping of electroplating and other heavy metal industries is usually made of carbon steel and the acidity of process water and wastewater is high (pH < 5), the corrosion of piping is a problem. As a result, the wastewater contains not only heavy metals (Cu^{2+}, Ni^{2+}, Cr^{3+}, etc.), but a considerable amount of Fe^{3+} (rust), up to 100 ppm and higher. On the other hand, coagulating properties of Fe^{3+} in the presence of sulfate anions are well known. Taking these facts into account, the model wastewater containing 10–100 ppm of Fe^{3+} was chosen for study of wastewater treatment efficacy with membrane-electroflotation unit.

Fe^{3+} rejection dependences on the feed cation concentration during wastewater treatment in integrated membrane-electroflotation unit were found (Fig. 7). The rejection stabilizes at a relatively high level when feed cation concentration exceeds 40 ppm. Furthermore, the value of electrical current $I = 1.2$ A is sufficient for effective membrane-electroflotation treatment, whereas electroflotation alone requires $I = 1.6$ A at least (Kolesnikov and Iliyn 2004).

The relationship between membrane-electroflotation rejection and wastewater residence time in the flotation unit also was determined (Fig. 8). It can be stated that 10 min residence time is sufficient for 95% rejection of each cation (Fe^{3+}; Cu^{2+}; and Ni^{2+}). Thus, the footprint of membrane-electroflotation unit is about 0.167 m^2 for each m^3/h of wastewater (height of the unit is about 1 m).

All the data were obtained at optimal pH (6.5 for Fe^{3+}; 9.5 for Cu^{2+}; 10.5 for Ni^{2+}), and optimal flocculant (PAA) and surfactant (SDS) concentration (2 and 7 ppm, respectively).
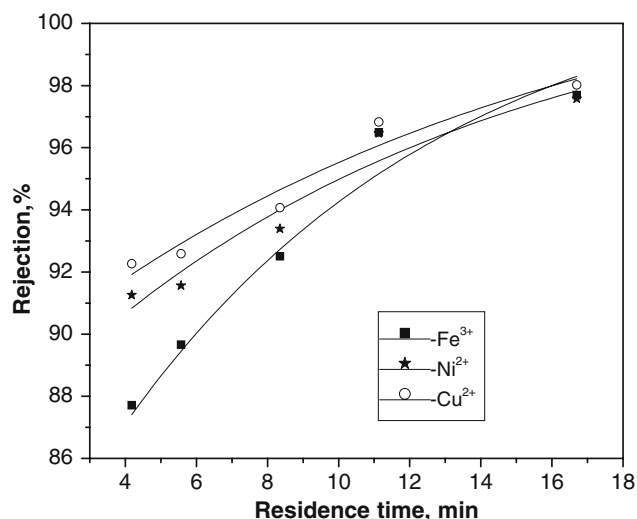
Fig. 6 A membrane-electroflotation unit

Fig. 8 Membrane-electroflotation rejection versus wastewater residence time. Feed cation concentration 50 ppm
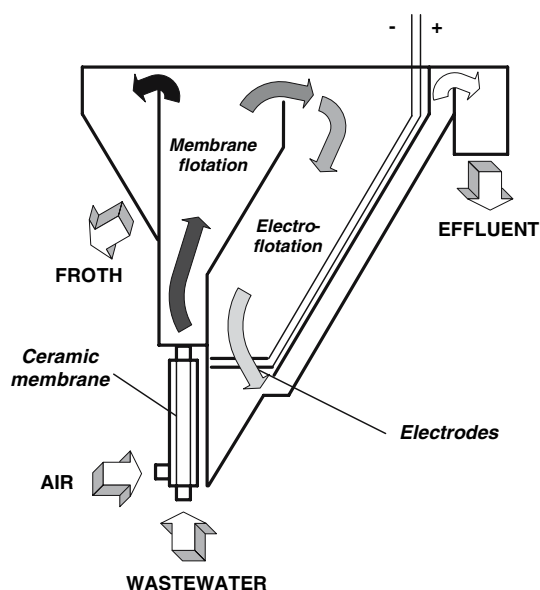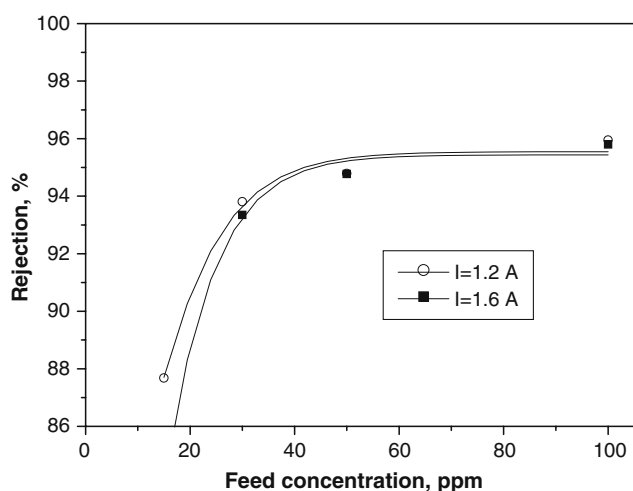
Fig. 7 Membrane-electroflotation rejection versus feed Fe^{3+} concentration. Residence time 10 min

Membrane filtration treatment as a post-treatment of flotation effluents and as a competing wastewater treatment technique

Membrane filtration processes are prevailing methods in cationic wastewater treatment (Kurniawan et al. 2006) because of their high rejection, low footprint of equipment and low reagent consumption. The membrane filtration processes are divided in four groups, depending on retaining particle size: MF, UF, NF and RO (Wagner 2001).

Microfiltration is based on particle and pore sizes (a sieving mechanism). Particles with a higher size than the membrane pore size are retained whereas smaller particles are passed through the membrane. MF can be applied for removal of precipitated heavy metal hydroxides from the wastewater (Kagramanov et al. 2001) or for separation of adsorbent powder with adsorbed cations (Matis et al. 2004; Mavrov et al. 2003; Lazaridis et al. 2004).

Ultrafiltration utilizes separation on the base of the pore size and molecular weight of the solution ingredients (adsorption-sieving mechanism). The most common technique of UF for heavy metal wastewater treatment is chemically enhanced UF with the use of some chemicals (chitosan, Juang and Shiau 2000, mono-alkylphenol polyetoxilate, Yurlova et al. 2002, etc.) as complexation agents.

Nanofiltration is akin to both UF and RO processes. It is based on the steric and Donnan effects because of membrane porosity and charged membrane surface (sieving-electrical mechanism). NF rejection for heavy metal removal is not as high (90–98%) as the one obtained with RO (97–99.5%), but the former requires a lower pressure making NF a more energy saving technique (Yurlova et al. 2002; Mohammad et al. 2004; Tanninen et al. 2006).

In the RO process a pressure is applied that is greater than the osmotic pressure of the feed solution (wastewater in our case), resulting in solvent (water) permeation and retention of all ionic compounds. RO demonstrates a high heavy metal rejection, compared to ion exchange, but it is operated in a continuous flow mode and has a lower reagent consumption (Ozaki et al. 2002; Qin et al. 2002). RO technique of heavy metal cationic wastewater treatment can provide

Fig. 9 An experimental membrane filtration unit

potable-grade water or high purity water for techno-logical operations.

Experiments on membrane filtration were carried out using commercial MF ceramic membranes (Al_2O_3, 0.5 μm pore size), NF spiral-wound ERN-B-45-300 Vladipor PA membrane element, and GE Osmonics spiral-wound RO thin film PA membrane element TFM-75 (Fig. 9).

In the experiments on MF of wastewater the mem-brane flux was decreasing and rejection was increasing during the first 4–8 h of filtration followed by further stabilization (Figs. 10, 11). This suggests that a dy-namic membrane is formed on the surface of the MF membrane.

As presented in Figs. 12 and 13, NF rejection is slightly smaller than RO rejection at pH 2–8 and it increases when pH < 2. The trend of the NF flux to increase corresponds to the temperature increase dur-ing the experiment (pH was decreased step-by-step with addition of sulfuric acid; concentrate and perme-ate were fully recycled to feedwater tank). RO flux was drastically decreased at pH < 3 due to the increase in feedwater osmotic pressure, which means that RO cannot be applied to acidic cationic wastewater with high-osmotic pressure.

Generally, membrane filtration methods can be ap-plied in combination with flotation to achieve a high rejection and a low-liquid discharge. There are at least two basic schemes:

1. Flotation pretreatment and membrane filtration post-treatment with recirculation of concentrate. The permeate is a high-grade water to be used for technology and/or potable water supply. The only discharge is the flotation froth which can be de-watered with a filter press. The formed sludge is a solid waste with 60–70% humidity.

2. Membrane filtration (NF, RO) of high-acidic cat-ionic wastewater and flotation for concentrate treatment. Similarly, the only discharge here is the flotation froth. The permeate can be discharged to lakes and rivers after pH-correction or recycled (returned to main technological process).
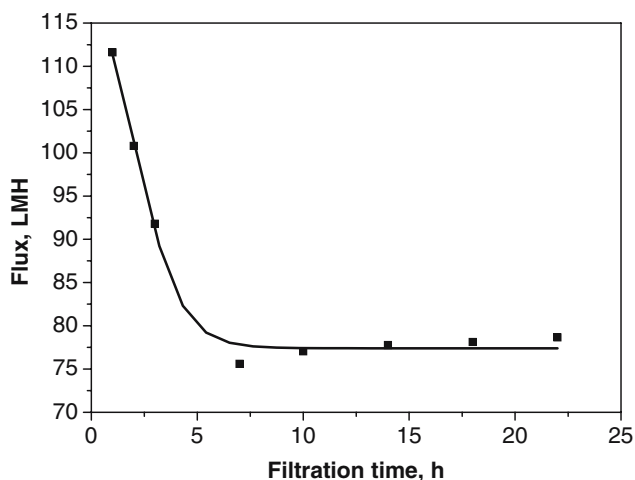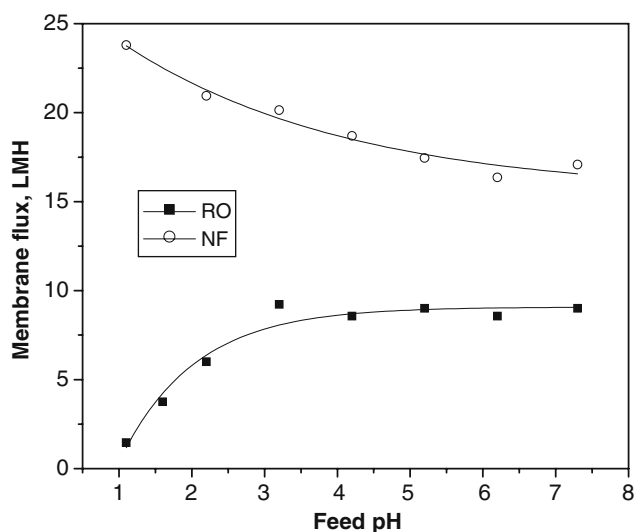

Fig. 10 MF flux versus filtration time. Ceramic membrane with pore size 0.2–0.4 μm; pH = 6.5
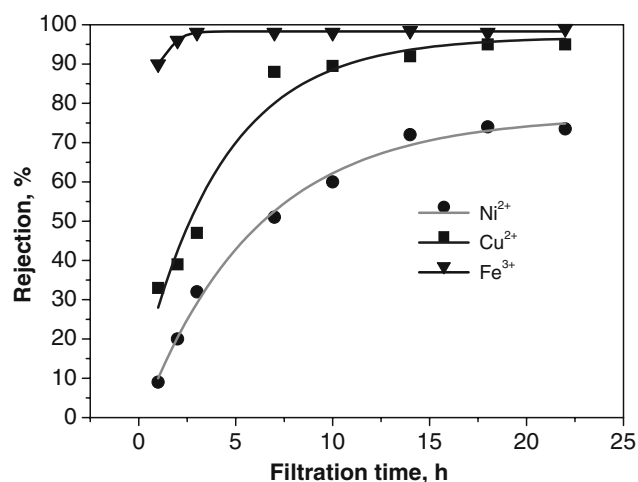
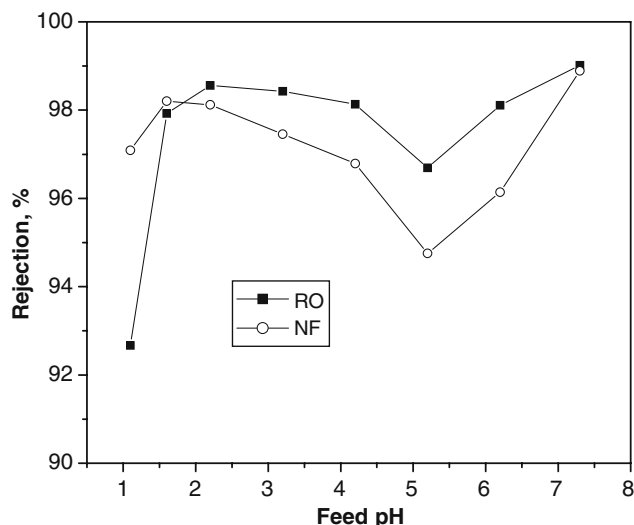**Fig. 11** MF cation rejection **1** Fe^{3+}; **2** Cu^+; **3** Ni^{2+}. Ceramic membrane with pore size 0.2–0.4 μm; pH = 6.5

Fig. 12 NF and RO flux versus pH of feedwater. Feed Cu^{2+} concentration 15 ppm. $P = 4$ bar

Fig. 13 NF and RO Cu^{2+} rejection versus pH of feedwater. Feed Cu^{2+} concentration 15 ppm. $P = 4$ bar

The choice of an optimal technology may be made based on comparison of capital and operating costs with respect to the treated water requirements.

Conclusions

Inorganic microporous membranes are eligible for air sparging in application to flotation. This method is rather effective (rejection 80–98%) for removal of precipitated and flocculated heavy metal hydroxides when the initial concentration of metal cations is higher than 50 ppm, including membrane filtration pretreatment.

Flotation units are to be designed using the theoretical equation relating bubbling rate with gas content in the flotation unit and the experimental data of rejection dependence on wastewater residence time. The volume of membrane flotation chamber as well as pump and compressor performance can be calculated with use of these data.

Membrane filtration use is prospective in combination with flotation for post-treatment or as a first stage of an integrated process of wastewater treatment.

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