

# Use of RO and NF for treatment of copper containing wastewaters in combination with flotation

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## Abstract

The process of so-called *membrane flotation* can be used in combination with NF/RO techniques for treatment of wastewaters containing copper and other heavy metals to decrease the environmental risks. Microporous inorganic membranes are used in *membrane flotation* process as diffusers for air sparging. Various ways of combination of flotation and membrane filtration in cationic wastewater treatment practice are discussed. With these combined membrane/flotation solutions wastewaters can be treated with high rejection and high pure water recovery. High performance of integrated *membrane-electroflotation* equipment as well as RO and NF spiral-wound systems allows to achieve great economy of freshwater and to diminish wastewater discharge fees.

*Keywords:* Nanofiltration; Reverse osmosis; Flotation; Wastewater treatment; Heavy metals

## 1. Introduction

Environmental friendly technological processes and full cycles are embedding more frequently all around the world. Nevertheless, uncontrolled discharge of wastewaters containing toxic heavy metals is still taking place in metal-working, electronics, electrochemical and other industries. The result is an increase of concentration of heavy metal cations (including  $\text{Cu}^{2+}$ ) in surface and well waters that can be used as sources of potable and process waters. Such pollution of hydrosphere has an extremely negative effect

on people's health and environmental safety as well.

Use of effective technologies for treatment of wastewaters containing heavy metals will allow creating water recycling systems for the industrial facilities. That will help to save wastewater discharge fees and freshwater supply payments. There are two groups of cationic wastewater treatment methods. The first group includes chemical and electrochemical precipitation methods, coagulation and flocculation followed by separation of the sediment by clarification, filtration, flotation, microfiltration (MF) and other techniques. The second group encloses such methods of separation of soluted heavy metal cations as ion

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exchange, adsorption, nano- and ultrafiltration, reverse osmosis, electrodialysis, etc.

This article presents a study of wastewater treatment efficacy with flotation and membrane filtration for copper cations removal. Since ceramic membranes were used as air diffusers this method of flotation treatment was called “*membrane flotation*” [1]. Commercial reverse osmosis (RO) and nanofiltration (NF) spiral-wound membrane modules were used to find rejection and flux dependences on feed water temperature and  $\text{Cu}^{2+}$  initial concentration. A combination of integrated membrane-electroflotation and NF/RO for copper containing wastewater treatment is discussed.

Flotation is a separation method of hetero-phase systems (suspensions and liquid emulsions), using gas bubbles attachment to dispersed phase. The formed aggregates are floated and separated from the dispersing medium [2–5]. 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.

Flotation is widely used for water and wastewater pretreatment before desalination and/or ultrapure water production, including NF/RO [6,7], and in integrated units combining dispersed air flotation and immersed MF [8–10]. These examples demonstrate good outcome of combining flotation with membrane-based techniques in water and wastewater treatment.

NF is used for  $\text{Cu}^{2+}$  and other heavy metal cations removal more and more often in laboratory studies [11–13] and in industrial practice as well [11,14–15]. T. Chaabane et al. [11] studied a removal of copper by a negatively charged microporous NF membrane. The treatment of the synthetic solutions and the wastewater of electric cable factory was studied.  $\text{CuCl}_2$  rejection of about 47–66% depending on transmembrane pressure (1–3 bar) is reported. Tanninen et al. [12] reported 60–95%  $\text{Cu}^{2+}$  rejection of various flat-sheet NF membranes. The experiments were

held in very acidic conditions (8 wt.%  $\text{H}_2\text{SO}_4$ ) at high temperature (40°C) and high pressure (20–40 bar). Castelblanque and Salimbeni [14] reported the on-site pilot testing of 2 m<sup>3</sup>/h NF unit at the electro deposition plant to increase the recovery of 99.8% of copper sulfate comparing to 55% recovery with traditional ion exchange. Qdaisa and Moussab [13] investigated synthetic wastewater treatment containing  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  ions by spiral-wound RO and NF membrane modules. Good removal efficiency of the heavy metals was reached by RO process (97–99.4% for copper). NF rejection of about 82–97% was demonstrated for copper ions depending on concentration in feed water. GE Water and Process Technologies [15] reported about the results of 4 years experience of NF unit use for 1.3 m<sup>3</sup>/h circuit board manufacturer rinse stream with a pH ranging from 1.5 to 3.9. This system concentrates the soluble copper sulfate at 50–90% recovery. The purified water (permeate) is reused for rinsing again. This system demonstrated 98.7% rejection of copper during treatment of solution with pH = 3.9 (recovery 50%).

High performance, low footprint of installations and low reagents consumption make flotation and membrane filtration methods very attractive for use in heavy metal wastewaters treatment. Therefore, a combination of these economically effective methods is very promising for solving problems of wastewater treatment with recovery of pure water and low environment influence.

## 2. Materials and methods

### 2.1. Membrane filtration

Experiments on membrane filtration were carried out using NF spiral-wound ERN-B-45-300 Vladipor PA membrane element, and GE Osmonics spiral-wound RO thin film PA membrane element TFM-75. The modules were placed in standard PP housings, which can be used at 0–5 bar pressure.

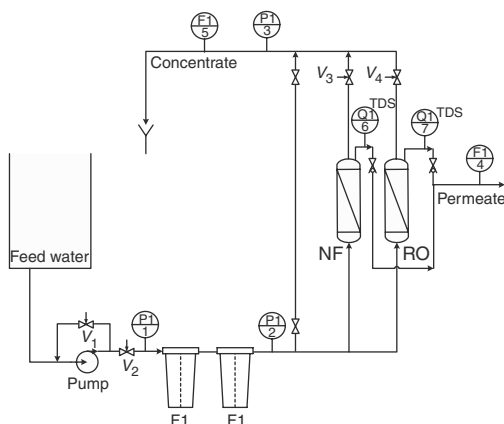


Fig. 1. Process and instrumentation diagram of NF/RO unit.

The membrane filtration unit presented on Figs. 1–2 consists of feed water tank, rotary pump, two cartridge filters (activated carbon for tap water chlorine removal and 5  $\mu\text{m}$  microfilter



Fig. 2. Spiral-wound membrane modules of NF/RO unit.

for fine particles retention), two parallel membrane modules, valves and instruments. Valves V1–4 were used for feed pressure adjustment; pressure gauges 1–2 were used to measure pressure drop on cartridge filters, and gauges 2–3 were used to measure transmembrane pressure; two flowmeters (rotameters) 4–5 were used for concentrate and permeate flow measurement.

Some NF/RO experiments were carried out with the use of this membrane filtration unit beforehand [16–17]. Dependences of membrane flux and rejection on  $\text{Cu}^{2+}$  concentration in feed water and pH of feed water were found. It was cleared that NF rejection is slightly smaller than RO rejection at pH 2–8 and it exceeded the last when pH < 2. RO flux decreased at pH < 3 due to the increase of feed water osmotic pressure.

## 2.2. Flotation

The reagents used in flotation treatment for process performance improvement are surfactants for lowering the water/air surface tension (for bubble size minimization and increase of interfacial surface); alkali for heavy metal hydroxides precipitation; and flocculants for formed solid phase particle aggregation resulted in increase of the particle size from 0.1–0.2 mm to 0.5–2 mm. The formed flocs have a density which is close to water one, so their flotation is more effective.

Rejection dependencies on the surfactant and flocculant concentration as well as feed pH were found earlier with static *membrane flotation* unit (with no continuous water flow) [16–17]. The optimal doses of the flotation reagents are 7–8 ppm of surfactant (sodium dodecyl sulfate, SDS); 1.5–2 ppm of flocculant (poly acryl amide, PAA) and pH = 9.5 for copper containing wastewater treatment. Static *membrane flotation* demonstrates high rejection (up to 99%), which is comparable to electroflotation rejection.

Based on hydrodynamics and purification efficacy in static *membrane flotation* experiments, the integrated flotation unit combining

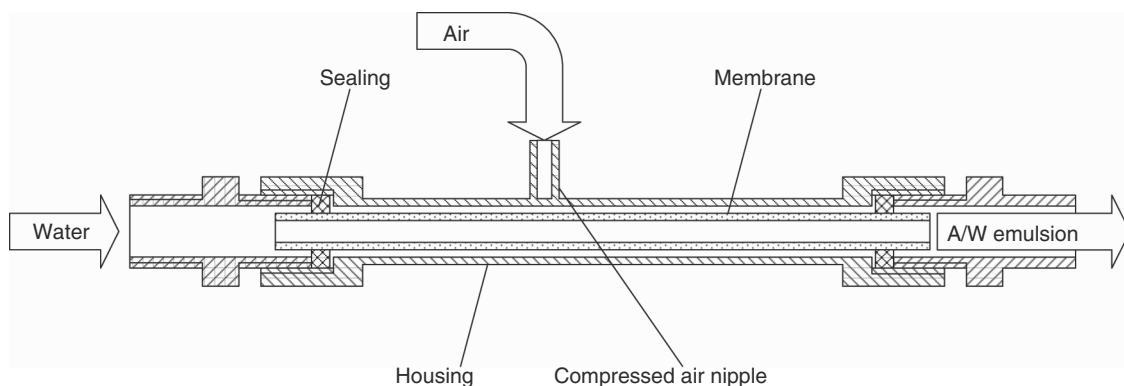


Fig. 3. Membrane sparger used for air/water emulsion production.

co-current *membrane flotation* and countercurrent electroflotation treatment was designed. Further experiments were carried out using this unit. The unit presented on Figs. 3–4 and includes two tanks for feed water and flotation effluent (purified water) storage; pump and compressor for water and air supply, membrane sparger,

flotation vessel, valves and instruments. Valves V1-2 are used for feed pressure adjustment; pressure gauge 1 was used to measure air pressure, rotameter 2 was used for feed water flow measurement. Flotation vessel consists of two chambers: the first one for *membrane flotation* and the second one for electroflotation. The electrodes

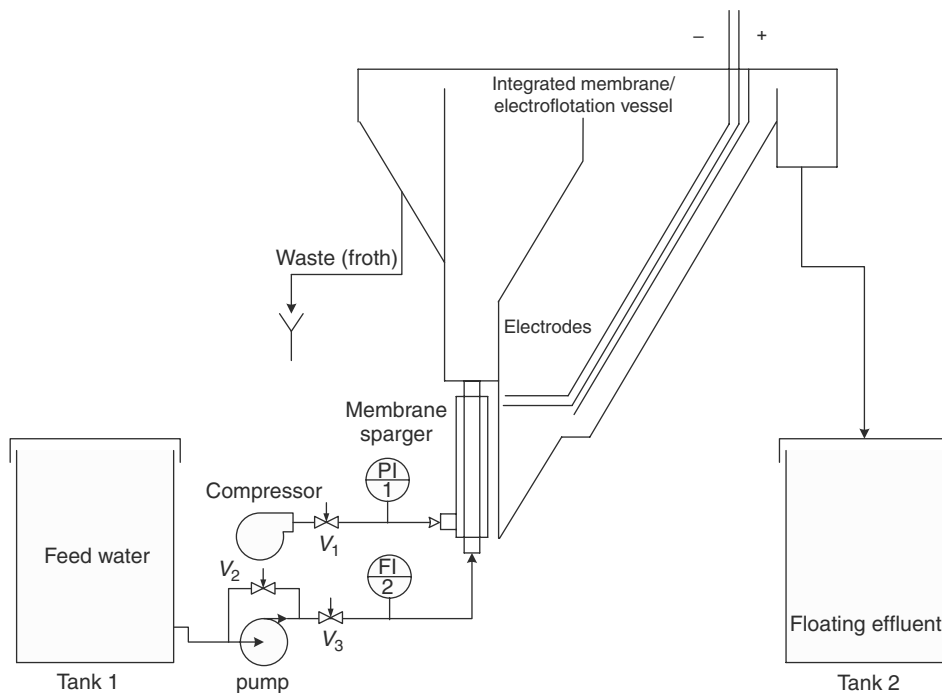


Fig. 4. Process and instrumentation diagram of flotation unit.

are submerged in the second chamber near the bottom. The cathode is made of stainless steel and the anode of oxidized titanium.

The first step in development of flotation unit was the designing of a tubular membrane diffuser with bubbling of air to the inner water flow from the outside (Fig. 5). A tubular MF membrane element with inner selective layer (0.5–1  $\mu\text{m}$  pore size) was used as the diffuser. The turbulence of water flow in the inner space of the membrane element results in “cutting out” the growing bubbles with shear-stress. The bubbles are detached before their sizes reach the values sufficient for free detachment in the static water. The two-phase flow with gas content about 15–29% is directed to the flotation vessel.

### 2.3. Chemicals and analysis

Portion of  $\text{CuSO}_4$  (weighting was carried out by electronic scales) was being dissolved in tap water obtaining the solution with 10 g/L concentration needed for making solutions with required concentration; pH of the obtained solutions was being adjusted by NaOH addition, being measured by portable pH-meter pH600, which was being calibrated by buffer solution. Then required amount of coagulant and flocculant was being added to the solution.



Fig. 5. Integrated membrane-electroflotation vessel.

Selected sample analysis was being carried out by atomic absorptive spectrometer “Kvant AFA” with plasmic sprayer. Wavelength for copper is 224.8 nm.

## 3. Results and discussion

### 3.1. NF and RO

Influence of feed water temperature on membrane flux is widely known and for PA membranes is usually presented as linear dependence. The phenomenon of temperature influence on membrane flux is explained with change of viscosity depending on temperature. We have carried out experiments on determination of flux and temperature relationship for NF and RO spiral-wound modules in equal conditions (feed water contains 15 ppm of  $\text{Cu}^{2+}$ , pH = 5, feed pressure is 3.8 bar). The results of the experiments are presented on Fig. 6 as linear function:

$$F = a + bT, \quad (1)$$

where  $F$  is membrane flux ( $\text{L}/\text{m}^2 \text{ h}$ , LMH) and  $T$  is feed wastewater temperature.

It was calculated that for NF module  $a = 10.81 \pm 0.78$  and  $b = 0.81 \pm 0.06$ ; similarly for RO module:  $a = 5.65 \pm 0.74$  and  $b = 0.40 \pm 0.05$ .

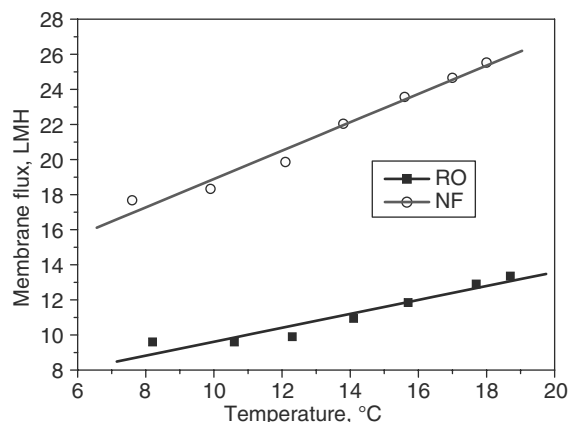


Fig. 6. NF/RO flux vs. feed temperature. Feed  $\text{Cu}^{2+}$  concentration is 15 ppm, feed pressure is 3.8 bar.

Average temperature coefficient of flux change induced with temperature change to 1°C can be calculated according to equation:

$$K_t = \frac{\Delta F_{am}}{\Delta T_{am}}, \quad (2)$$

where  $\Delta F_{am}$  and  $\Delta T_{am}$  are arithmetic means of flux and temperature changes respectively.  $K_t$  calculated for NF is 0.76; and for RO  $K_t = 0.42$ .

As realized from Fig. 6 and results of calculation with Eqs. (1) and (2) the temperature influence on membrane flux for NF is greater than that for RO. It can be explained with more contribution of frictional flow to mass transfer driving force in NF process in comparison with RO. Use of found dependences allows to design membrane equipment and to predict a change of system performance under conditions of changing temperature.

The influence of copper concentration in feed water on NF and RO rejection was analyzed too. The results of the experiments are presented on Fig. 7. As can be seen on the figure the influence of feed water concentration on NF is greater than on RO. It can be explained with lower value of concentration polarization in NF process than in RO process (in equal conditions).

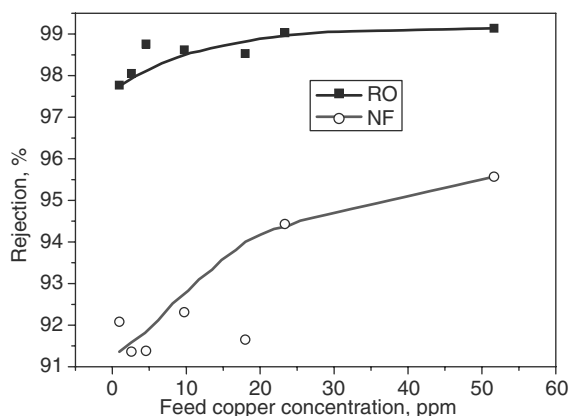


Fig. 7. NF/RO rejection vs. feed  $\text{Cu}^{2+}$  concentration, feed pressure is 3.8 bar.

### 3.2. Flotation

From the flotation practice and earlier works of the authors [18] it is known that the rejection of *membrane flotation* grows when the concentration of heavy metals in feed water is increased. This phenomenon was examined on the integrated *membrane-electroflotation* unit too. During the first run of the experiments (standard electric current for electroflotation – 1.6 A) the raise of flotation rejection in dependence on increase of feed copper concentration was realized. For feed water concentration raise from 15 to 100 ppm the rejection of integrated flotation unit was increased from 84 to 96% (Table 1).

Since electric energy consumption of electroflotation rectifier is the most in the whole *membrane-electroflotation* unit, the reduction of this expense item can affect to economical efficacy of flotation more strongly. Therefore the current of electroflotation was decreased to minimum of 1.2 A and then the second run of experiments of feed cation concentration dependence finding was realized. It was shown (Table 1) that  $I = 1.2$  A is enough for effective electroflotation of copper. Such a low value of working current is explained with the purpose of electroflotation to polish the wastewater treated by *membrane flotation* in first chamber. The second chamber works like a damper and relatively high rejection can be achieved without electroflotation, but the residence time of feed water must be increased in this case. Another way to increase a rejection of *membrane flotation* unit is the installation of lamella separator in second chamber of the vessel similar to be presented in Fig. 4.

All the flotation experiments were carried out in optimal conditions (reagents concentration and pH value) found earlier [16–17].

### 3.3. Combination of NF/RO and flotation

Two prospective ways of combination of two treatment stages (in our case NF/RO and flotation) are developed. In first case flotation is used for

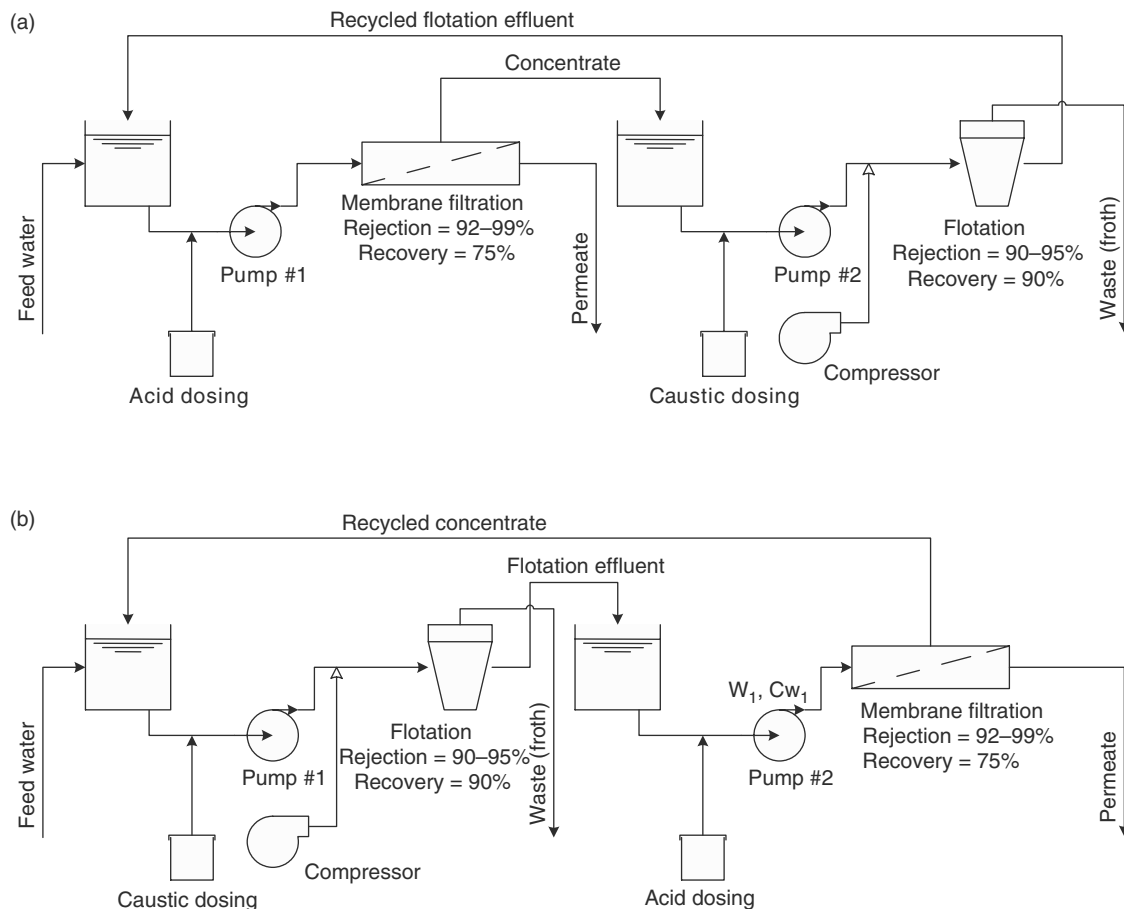


Fig. 8. Combination of NF/RO and flotation for copper-containing wastewater treatment. (a) greater recovery, lower rejection; (b) lower recovery, greater rejection.

Table 1

The influence of copper concentration in feed water on flotation rejection. Residence time 17 min, air pressure 0.6 bar

Feed $\text{Cu}^{2+}$ concentration, ppm	Electric current $I = 1.6 \text{ A}$		Electric current $I = 1.2 \text{ A}$	
	Effluent $\text{Cu}^{2+}$ concentration, ppm	$\text{Cu}^{2+}$ rejection, %	Effluent $\text{Cu}^{2+}$ concentration, ppm	$\text{Cu}^{2+}$ rejection, %
15	2.1077	83.97	1.6195	87.68
30	2.0447	93.35	1.9039	93.81
50	2.5121	94.77	2.5	94.79
100	4.2	95.8	4.05	95.95

NF/RO concentrate treatment and in the second one membrane filtration is used for flotation effluent (purified water) posttreatment. There are only two out-flows in the both cases: flotation waste (froth) and NF/RO permeate; flotation effluent and NF/RO concentrate are recycled in first and second cases, respectively. The flowcharts of two cases are presented in Fig. 8.

Comparison of two combination ways of NF/RO and flotation for copper-containing wastewater treatment can be carried out examining of overall recovery and rejection of two flowcharts and power and reagents consumption. Furthermore it is necessary to mark that NF/RO spiral-wound membrane treatment process can be used as first step of combined process (flowchart a) only if silt density index (SDI) is not more than 5. The results of comparison of the cases presented on Fig. 8 are shown in Table 2.

The ASTM Committee on Water has recommended the SDI test or “microporous membrane pluggage test” as a method of indicating the quantity of particulate matter in a water supply [19]. This method is based on determining the rate of pluggage when water is passed through a 0.45  $\mu\text{m}$  membrane filter at a constant applied pressure. The SDI is a non-dimensional number calculated

from the rate of pluggage. Spiral-wound membrane elements manufacturers use SDI as a means of specifying the maximum level of suspended solids allowable in the feed water to membrane systems in order to maintain membrane performance warranties. Some companies require daily measurement and reporting of SDI. Feed water SDI levels of less than 5 are recommended for water purification systems to minimize membrane fouling and extend required cleaning intervals.

The procedure of SDI measurement can be manual [20] or automatic [21]. It is recommended to measure SDI at least 1 time a week and it is a must before the design of water/wastewater treatment system with NF/RO membranes. Recently continuous in-line SDI monitors were developed [22]. Use of these devices helps to predict membrane fouling earlier than it can be made analyzing flux and rejection normalization.

As a result of comparison of two flowcharts it can be stated that the flowchart *a* is more energy efficient, low reagent consumptive and produces less waste (higher recovery) than flowchart *b*, but it can be used only when not very high rejection of copper or other heavy metal is enough and if *SDI* is not more than 5. The flowchart *b* is more universal (not depends on SDI), rejection is higher (this is two-pass process), but these properties are accompanied with higher power and reagents consumption and lower recovery.

Table 2

The comparison of two ways of combination of NF/RO and flotation

Parameter	Greater recovery, lower rejection	Lower recovery, greater rejection
Overall recovery, %	96.8	87.1
Overall rejection, %	95+	99+
Power consumption, kW h/m <sup>3</sup> , of feed water	1–1.1	1.1–1.3
Reagents consumption	Lower	Higher

#### 4. Conclusions

Membrane filtration techniques as well as flotation allow to achieve high performance, low reagents consumptive treatment of heavy metal containing wastewaters. Treatment of wastewater containing  $\text{Cu}^{2+}$  with NF, RO and integrated *membrane-electroflotation* was studied. Dependencies of feed water concentration on flotation and NF/RO rejection were found.

Generally, membrane filtration methods can be applied in combination with flotation to achieve a high rejection and a low liquid discharge.

There are two ways of combination of NF/RO and flotation: the first one can be characterized by greater recovery, but lower rejection, energy and reagents consumption; the second one, on the contrary, shows lower recovery, but higher rejection, energy and reagents consumption. The choice of an optimal technology may be made based on comparison of capital and operating costs with respect to the treated water requirements.

First of all an SDI of feed wastewater must be measured to estimate applicability of the first combination flowchart. If the SDI is lower than 5 this method is applicable. The second step is a calculation of concentration of copper (or another heavy metal) in treated water and comparison of it with requirements to pure water. If the rejection of the first flowchart is sufficiently high and feed water  $SDI \leq 5$ , then the first flowchart is optimal. Otherwise, the second one will be best decision.

Use of circumscribed method of comparison is universal and can be used not only for membrane filtration and flotation methods and copper containing wastewaters. With the accumulation of experimental data for other wastes and treatment techniques, an estimation of use of the combination ways for these techniques can be made automatically using spreadsheet or especially designed software.

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