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Membranes for the Treatment of the Industrial Waters: Quo Vadis?

Claude Gilles Dussap*, Lazar Avram**,
Julien Troquet***, Sorin Alexandru Avram****

* Polytech, Clermont-Ferrand, France
e-mail: mtroquet@polytech.univ-bpclermont
** Universitatea Petrol - Gaze din Ploieşti, Bd. Bucuresti 39, Ploieşti
e-mail: avram_lazar55@yahoo.com
*** Biobasic Environnement, France
e-mail: jtroquet@biobasicenvironnement.com
****Romgaz S.A., Sucursala Ploieşti
e-mail: sorinel_ap@yahoo.com

Abstract

From economic and environmental reasons there is permanently trying to find new and new possibilities for the recycling of the process waters. A part of these will be treated at the end of the chain before rejection in the natural environment. It is about the residual waters. Another part will be recycled in the internal circuit. In these processes, the membranes are in fierce competition with other processes such as: evapo – concentration, ozonolysis, centrifugation, absorption on active carbon etc. The present paper tries to present pro and against aspects, in other words advantages and disadvantages concerning the utilization at an industrial scale of the membranes for the treatment of the industrial waters.

Introduction

The membranes are all over the place. From many years, theses filters based on polymers and ceramic products *invaded* all the stages of the water treatment in the industrial environment, not only ttechniques, conceived initially for the production of the potable water, developed subsehe finishing ones. These quently and there were adapted in the industry, especially to the processes of process water recycling. With high performances and steadily decreasing prices, there became more tempting in the effluent recycling practice.

Paradoxically or not, the main inconvenient of the membranes techniques is related to their high-tech level. That is why it is crucial at this moment the transfer of the competences from the higher education institution to the company. Youth, in which we all hope will not leave, we are sure, this field with certain future unexplored. For example, the French company *Technomembranes* from Montpellier has developed a wastewater recycling equipments that suppose the coupling of different membranes techniques (nano-filtration and the reverse osmosis) with the chemical treatments that will guarantee the water bacteriological qualities.

In general, for the water part that will be recycled in the internal circuit, the basics idea consists in investigating all the possibilities of the *looping* water in order to achieve a *maximum* from the economic point of view and also from the environmental protection one.. Once treated, the aqueous effluent may return to its initial destination or may be used in other purposes as cooling, heating or re-utilization in other industrial procedure (fig. 1).

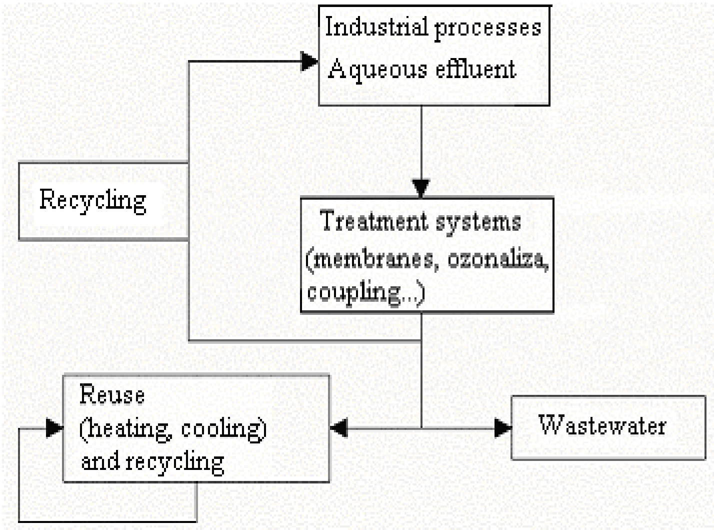

Fig. 1. Different ways of the aqueous effluent re-utilization

In the case of the vapors generators with condensate steam and cooling in semi – loop, the water is recycled without any transformation. This utilization is clean and the same water may be efficiently used with an appropriate supplement for the compensation of the loses due to leakage and evaporation involvement. In figure 2 the is presented the water cucle in the vapors generator.

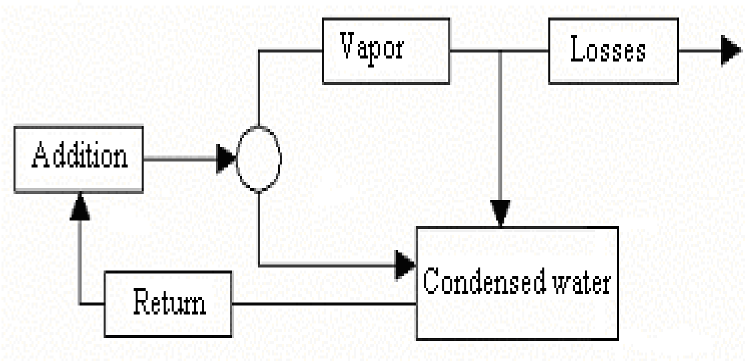

Fig. 2. The water cycle in a vapors generator

The device receives, therefore, the water supply that consists of recovered condensed water (return water) and new water more or less purified (added water). Vapors circulate a great part of salts trough their real training. The remaining water has to be decentralized by purging and a fraction of this water from the generator will be sent to the drain. Of course, the water that enters in the vapors generator has to correspond to certain criteria concerning the content in oils, phosphates, total iron, copper, suspended materials, all different depending on the type of the generator. But, in all cases, these pollutants has to be limited in order to avoid the incrustations due to the calcium salts deposits on the walls, the corrosion due to the dissolved oxygen or the attack of the iron by water and also the primary (the entrainment of the liquid vesicles in vapors in close relation with the viscosity and the foaming that depend also on the presence of certain organic and salinity substances).

For the cooling waters, the most used at present is the semi-opened circuit (fig. 3).

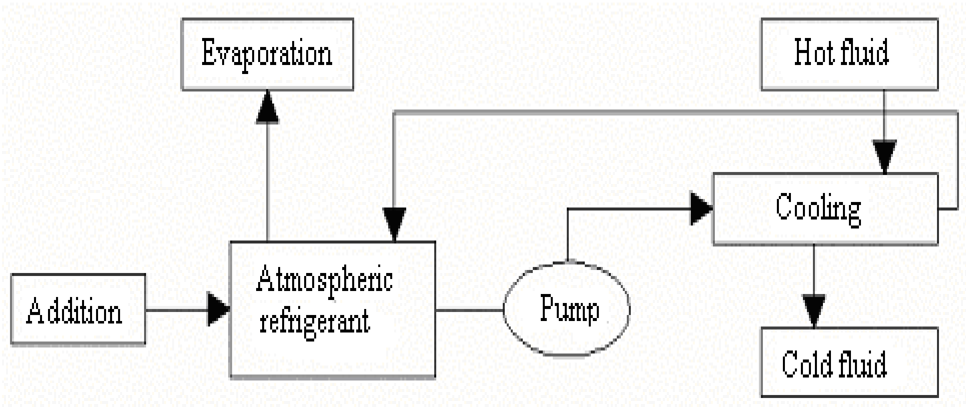

Fig. 3. The semi – opened circuit of the cooling waters

Membranes' procedures

The membranes' procedures used at industrial scale, at this moment, are diverse: reverse osmosis, nanofiltration, ultrafiltration, tangential microfiltration etc. [1, 2, 3].

The reverse osmosis is a current natural phenomenon that uses dense membranes especially cellular ones that allow water to pass and stop all the salts. The semi – permeable membranes allow the solvent to pass (but not the products from the solution) in order to balance the concentration. Thus, the reverse osmosis realizes the water purification till the monovalent salts level (NaCl).

In the *ultrafiltration* process there are used micro-porous membranes with pore diameters between 1 and 100 nm. This technique allows the separation of a stage reach in oil (concentrate) from the aqueous stage (fig. 4).

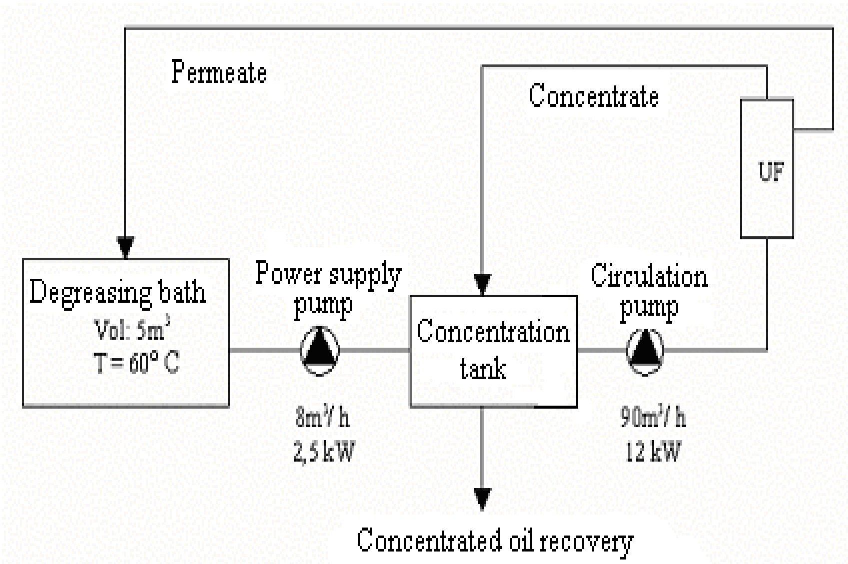

Fig. 4. The scheme of an installation used in the ultrafiltration process

This latter phase contains a large number of active constituents, soluble in water (dissolvent agents, surfactants, emulsifiers) and thus may be reused. In order to compensate the inevitable losses of active products it is necessary to readjust at regular intervals the treated bath.

The *nanofiltration* technique is between the reverse osmosis and the ultrafiltration. It allows the separation of the components that has a size, in solution, neighbor to nanometer (10 Å), from where it comes the name. The organic unionized compounds and the monovalent ionized salts with molar mass inferior to the value of 200 - 250 g/mol are not retained by this type of membranes. On the contrary, the multivalent ionized salts (calcium, magnesium, aluminum, sulfates etc.) and also the organic unionized compounds with molar mass superior to the value of 250 g/mol are strongly held.

The tangential microfiltration realizes the separation of type solid – liquid for the membranes whose pore diameters are between 0,1 and 10 µm. It, thus, enables the retention of the particles in suspension, of the bacteria and indirectly of the colloids of certain ions, after their fixation from the largest particles obtained by complexing, precipitation and flocculation. Theoretically, the difference between the ultrafiltration and microfiltration is very clear: the ultrafiltration functions in homogenous liquid phase, while the microfiltration objective is the separation type solid-liquid. However, from the technological point of view the two phases may be complementary. Thus, in order to minimize the clogging phenomenon and to avoid the penetration of the solid particles in the membranes' pores, the immediate interest consists in the utilization of the ultrafiltration membranes to carry out a microfiltration.

As immediate *advantages* of the membranes technology utilization it may be mentioned the water demineralization without a massive consummation of chemical products and the fact that the membranes may have a separating function, in particular the electro-dialysis. Currently, it is set up a treatment by electro – dialysis of the sodium sulphate effluents that allow the recovering, among others, of the caustic and, separately, of the hydrochloric acid. [3] (fig. 5).

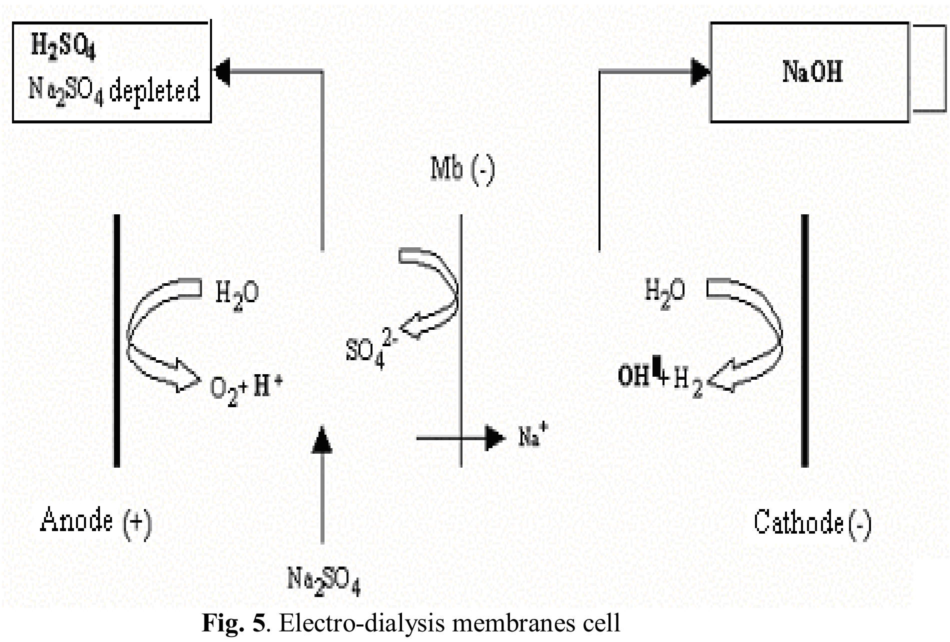

Fig. 5. Electro-dialysis membranes cell

In a cell with active surface of 42 m^2, there were separated two compartments through a cationic membrane. The only technical problem that arose was that the used anode (titanium coated with iridium oxide) was rapidly degraded, degradation due, in part, to the functioning in group.

This technique of basis and acids recovering may be improved by using a cell with three compartments coupling the bipolar membranes (cationic and anionic) with bipolar ones whose specificity consist in the water dissociation in the presence of a salt. The sulphuric acid may be then recovered separately by the saline solution. The problem is, however, that the bipolar membranes cost more than those homopolar, the conventional ones and use a stack of membranes that change alternatively the cations and the anions. The most promising application for the electro-dialysis with bipolar membranes remains the synthesis of the acids and organic basis for which there are still needed multiple technical studies.

Among the *disadvantages* may be mentioned, firstly, the fact that the membranes' procedres are rarely used alone (more often downstream the physical and chemical procedure). Then, the membranes has to be adapted to the effluents, respectively has to be decolmatated regularly and chemical washed. However, currently there are various dispersed on the market that allow the decreasing of the cleaning frequency and volume retention (that does not cross the membrane in the reverse osmosis process). In addition, it may be noticed the development of these techniques for the production of the ultrapure water.

Competing processes

The main competing processes of the membranes are evapo – concentration, ozonolysis, centrifugation and adsorption on active carbon.

The *evapo-concentration* technique is simple: there is brought the effluent to the boiling stage and it is recovered a concentrate (contains more than 99 % of heavy metals present in the effluent) and a capacitor. The recovered condensed water (condensate or distillate) may be thus reused. On the market profile there are many specific materials based on varied thermal processes. Their choice, from the technical point of view, depends on firstly the evaporation solution physical characteristics and on quantity that has to be treated each hour. Among the advantages of this process it may be mentioned the fact that it competes primarily the ultrafiltration and the direct osmosis being less sensible to the clogging phenomena than the membranes' processes. In addition, the treatment cost is more reliable because the fact that in order to realize the vapors' mechanical compression the unique energetic dependence is the electrical one. Finally, it should not be added any reactive and, moreover, it does not consume water. There are also two major inconvenient: the method is limited due to the presence of the azetropic water in the effluent and the cost of the concentrate elimination, generally by incineration, is not negligible (the initial investment is superior to a membranes' process).

The *ozonolysis* principle is based on high oxidation – reduction of O_3 (strong oxidizer). This ozone molecule is attached to carbon molecule involved in a double bond carbon-carbon in order to give a molozonid or a primary onozonid. This molozonid, very instable, splits in two molecules that react one on the other in order to give a secondary ozonoid. So, in summary, the ozonolysis serves to convert CN^- in CO_2 şi NO_3^- to precipitate iron and magnesium and to transform the organic molecules with multiple bonds in biodegradable molecules. The main advantage of this technique derives from the fact that the released oxygen is recycled in the effluent biological treatment. In addition, the ozone is a powerful disinfectant that does not give rise to chlorine products. As an immediate inconvenient: this method can not be used complementary with other process.

The c*entrifugation* is a very strong purification technique that supposes a centrifuge device that will produce very important accelerations on the cells, fact that determines the sedimentation speed increasing. In the case of the waste, it is used for the separation of different phases in order to apply specific treatments. For example, from the humid mud thus treated it will result a liquid phase, respectively dry mud that will be directed to a treatment particular chain (epuration for the aqueous phase and valorization for mud). One of the important advantages of this technique consists in its utilization in the case of great materials quantity manipulation. In other words, it is one of the rarest techniques used in industry. There are also disadvantages, particularly technical, as the rotor unbalance or the heat release as a result of the high friction with the air (sensitive problems due to the fact that the molecules are sensitive to heat).

The *adsorption on active carbon* is very simple. The active carbon is an adsorbent product obtained from carbon rich materials physically and chemically activated. Its structure is porous.

Thanks to its adsorption properties in vapor phase, it is always use as a catalyst in certain separation processes. Among the advantages it may be mentioned: the active carbon eliminates efficiently the dissolved organic matters and the chlorine; the carbon filter has a large holding capacity; the exploitation cost is relatively reduced etc. there are also important inconvenients. Thus, filters may generate fine carbon particles and also it represents a contamination surface and bacterial proliferation.

Membranes' choice

In order to demonstrate the superiority of the membranes compared with *competing processes*, it is necessary to do the connection between the effluent nature and the most suitable technique in terms of performance and cost.

If the effluent is dedicated for recycling, the water should have a certain cleanliness degree before its reuse in any process. From this point of view, the membranes assure a higher quality of the water than the biological, physical and chemical treatments that generate much mud. These are used especially for the treatment of the residual waters where the main purpose is to eliminate the pollution before their reject in the environment.

In the case of the salty waters, not nature, but the concentration will play a determinant role in the process choice. Indeed, treatment cost is sensitive to the salt concentration from the effluent (fig. 6).

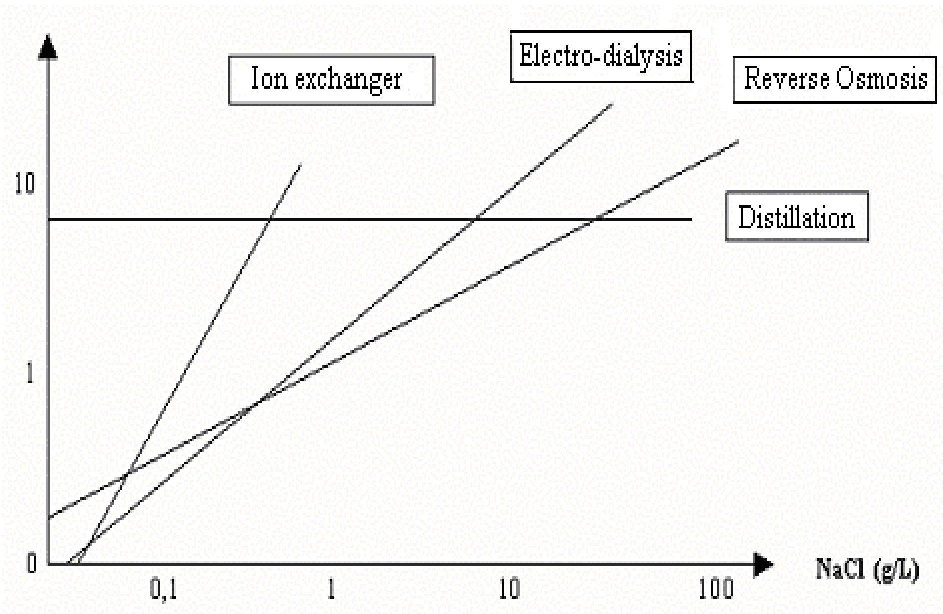

Fig. 6. The influence of the salt concentration on the water treatment cost

If it is wanted the recovery of a co-product, then the membranes are the unique efficient technical solution; as, for example, the baths regeneration in the surface treatment. In the case of the copper, the treatment generates ions of Cu^{2+} that complex by addition of CN^-. The treated surface is then washed in the demineralized water bath that is laden with salt. In order to maintain a certain quality of the bath, certain ions have to be eliminated. Thus, it is established a connection between this bath and the dilution compartment of an electro-dialyzer. The ions go back in the deposit bath and thus there are recycled in the surface treatment process. By this recycling there is avoid a demineralized water overconsumption.

The recycling scheme from the figure 1 may be a very good example concerning the important position that membranes have in the industrial water treatment.

In the same time, as it was mentioned, the industrials generally are reticent in the case of using membranes' processes. As a relatively recent technology, it has certain gaps in terms of modeling, fact translated into a miss confidence regarding the information that he daily receives. In addition, clogging the membranes is another *criticism* regularly brought. However, current preoccupations for this subject are most acute. It may be mentioned here the American company Hydranautics that uses since two years ago its LFC membranes at Singapore (at the Bedok and Knanji stations) for treating 82 000 m^3/dau of used and industrial waters and transforming then in process waters. These membranes afferent to the reverse osmosis, based on polyamide film (a negative polarized polymer) were modified in order to give a neutral surface, thus preventing any catch and development of a bacterial film (common problem in the reverse osmosis).
Although worthy in terms of efficiency, the polymers used for realizing membranes are still fragile. The most selective systems, the ultrafiltration and the reverse osmosis, suffers in what it concerns the clogging, since it does not support chemicals excess and temperature sudden changes.

But these *negative* points have to be considered simple memories in the near future. This because these materials evolutes. Thus, in the industry, the chemical membranes' utilization allowed the hard effluent treatment, because they resist to the ozone action and to high temperatures. Moreover, they resist very well also to the p*H* great variations. For example, the French company *Céramiques techniques et industrielles* (CTI) has developed at the request of the very known company Rhodia-Orelis that deals with the industrial waters treatment, a material based on doped titanium oxide. The membranes for the ultrafiltration and nanofiltration, based on this ceramic are more resistant to the acid or very basic attacks and present a great permeability to fluid (+ 20 la + 50 %).

Conclusions

1. Among so-called clean technologies, the membranes' techniques are characterized firstly by their ability to continually clear, concentrate, separate and purify. For these reasons they are adapted entirely to the effluents treatment having as main objective the permeate or the concentrate recycling.

2. Despite such issues more or less technical, research or information regarding the industrial part, to the development of the membranes in the future favors a series of factors such as: plant compactness, low operating cost (despite the high cost investment), facility of the automation processes etc.

3. The development of the technologies based on membranes amplifies also as a result of the increasing need for environmental protection (the laws more and more strict will favor the utilization of the nanofiltration membranes and reverse osmosis), respectively energetic, technical and economic performances of these processes.

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Membrane pentru tratarea apelor industriale: quo vadis?

Rezumat

Din raţiuni economice şi de mediu se încearcă, în permanenţă, găsirea de noi şi noi posibilităţi de reciclare a apelor de proces. O parte a acestora va fi tratată la capătul lanţului aferent, înainte de rejetul în mediul natural. Este vorba de apele reziduale. O altă parte va fi reciclată în circuitul intern. Ïn cadrul acestor procese, membranele sunt în competiţie acerbă cu alte procedee precum : evapo-concentraţia, ozonoliza, centrifugarea, adsorbţia pe cărbune activ etc. Lucrarea de faţă îşi propune să prezinte aspecte pro şi contra, cu alte cuvinte avantaje şi dezavantaje privind utilizarea, la scară industrială, a membranelor pentru tratarea apelor industriale.