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# Membrane engineering progresses in desalination and water reuse

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**Abstract.** The aim of this work is to analyse and discuss the use of the *Economic Evaluation* and of some new "*metrics*" for an appropriate valuation of membrane operations in the logic of Process Intensification. In particular, the proposed approach has the goal to show how the utilized indicators can drive to the choice of the most convenient process. Although in this work the planned procedure is applied, as a case study, to the membrane-based systems for boron and arsenic removal from waters, the suggested approach can be generally applied to any other process of interest.

**Keywords:** sustainability; process intensification strategy; metrics; cost.

## 1. Introduction

The keywords of our current world are *globalization*, *sustainability*, *partnership*, *innovation*, *discovery* and *development*: these are the driving forces of a world addressed towards progress and competitiveness in order to guarantee improvement and employment. Therefore, nowadays, it is become necessary to promote the research of innovative, low-cost, non-polluting, defect-free and perfectly safe industrial production processes. This leads to select processes not only on an economic basis, but also aspects such as the increased selectivity and savings linked to the process itself are important parameters to take into account. This is all that is included in the *Process Intensification,* a strategy which refers to innovative technologies aiming to replace large, expensive, energy intensive, polluting equipments and/or processes, with avant-garde versions that are smaller, less costly, more efficient, less polluting, highly safe and automatized (Charpentier 2005, 2007, Drioli and Curcio 2007, Drioli and Romano 2001). Currently, advances in nano-scale science and engineering are providing unprecedented opportunities to develop more cost effective and environmentally acceptable processes. Membrane operations respond efficiently to the requirement of Process Intensification because they have the potential to replace conventional energy-intensive techniques (such as distillation and evaporation), to realize the selective and efficient transport of specific components, to reach advanced levels of automatisation and remote control. In the last decades, in many occasions, commercial *conventional* separation processes in industry were converted to *membrane* separation processes. This is what happened in water purification and water desalination.

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In the present paper, for evaluating how much a membrane-base water treatment system is a *reliable* and *sustainable* process, the use of some *Metrics* are presented and utilized. As cases study, the application of these parameters to membrane systems for water purification is discussed and analysed.

## 2. Boron and arsenic problem

In the wide spectrum of the harmful substances contained in the polluted waters, in the present work the attention has been focused on the analysis of different membrane systems for the reduction or the elimination of boron (B) and arsenic (As) from waters due to their adverse effects both on human/animal health and on agriculture, and to their growing consumption in the current industry.

In the case of arsenic, for example, only in Massachusetts its consumption increased 13% between 1990 and 1996 driven by the electronics industry, where arsenic serves a variety of functions: it is used in the manufacture of microchips, as a doping agent in silicon wafers, to produce arsine gas (which is used to make superlattice materials, lightwave devices and high performance integrated circuits), to increase corrosion resistance and tensile strength in copper alloys, etc. Often the refuse from discarded electronics products, also known as e-waste, ends up in landfills or incinerators instead of being recycled. That means toxic substances like lead, cadmium, mercury and arsenic that are commonly used in these products, can contaminate water. As a consequence, nowadays, the number of water treatment plants equipped with arsenic removal facilities is growing but it is difficult to bring its content down to WHO levels (10 μg/L) due to its size and charge.

A similar situation happens in the case of boron. The latter is usually present in water as boric acid ($H_3BO_3$). In order to obtain waters with boron concentrations below the maximum recommended values (0.3 mg/L), currently the most parts of water treatment plants use RO systems with several pass-stages: at the first pass-stage, the salt in the seawater is removed along with most of the boron; by treating the resulting product water with other boron removal RO membrane elements at ultra-low pressure working at high pH and, eventually, with boron selective resins, the boron concentration is brought to below the regulation value. In the alkali region, ionization of boron proceeds as shown by the following formulas (Tomi, *et al*. 2005):

$$H_3BO_3 \Leftrightarrow H^+ + H_2BO_3^- \qquad pKa=9.14 \tag{1}$$

$$H_2BO_3^- \Leftrightarrow H^+ + HBO_3^{2-} \qquad pKa=12.74 \tag{2}$$

$$HBO_3^{2-} \Leftrightarrow H^+ + BO_3^{3-} \qquad pKa=13.8 \tag{3}$$

a hydration radius is achieved which is greater than that of the boron molecule. Moreover, the dissociation causes a negative charge and, since the RO membrane has also a negative charge, the two repel each other and the rejection performance of the RO membrane therefore improves.

For what concerns arsenic, dissolved As(V) and As (III) have been found to simultaneously exist in drinking water and in many contaminated groundwaters. Both As(III) and As(V) can occur in several forms; at near-neutral pH, the predominant species are $H_3AsO_3$ for As(III), and $H_2AsO_4^-$ and $HAsO_4^{2-}$ for As(V). It means that at typical pH in natural water (pH 5 ÷ 8), As(V) exists as an anion, while As(III) remains as a neutral molecule. Two types of membrane processes have been

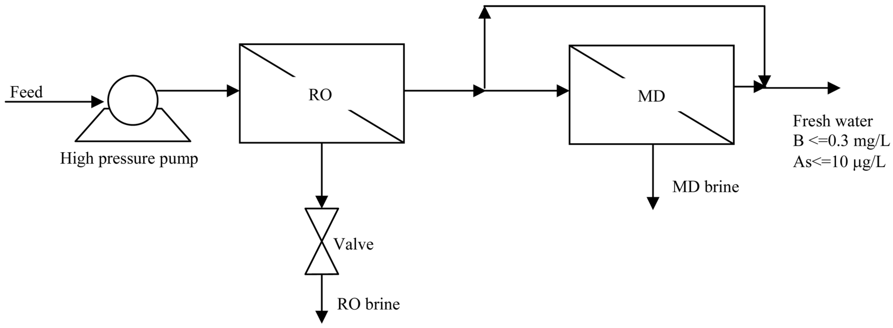


Fig. 1 An integrated RO+MD membrane system.

demonstrated to be effective in removing arsenic from water: RO and NF. Moreover in literature many examples show that both of these processes are more effective in removing As(V) than As(III) (Brandhuber and Amy 1998, Urase, *et al*. 1998, Vrijenhoek and Waypa 2000, Sato, *et al.* 2002). Thus, to achieve the best results, the feed water must be treated with an oxidizing agent to convert As(III) to As(V) in order to obtain substantial arsenic reduction in the permeate, that is the water produced by membrane process.

In a precedent work (Macedonio and Drioli 2008) it was proved that also membrane distillation (MD) technology can be used for boron and arsenic removal from polluted water. Moreover, it was showed that an integrated membrane system, constituted by a reverse osmosis step followed by a membrane distillation one, allows to obtain fresh waters with boron and arsenic concentration equal or less than the recommended values by EPA and WHO when only 36.4% of RO permeate is treated in the MD unit.

In this work, in order to check if the coupled system RO + MD can really represent an interesting and economically advantageous alternative to conventional water treatment plants, ***four*** different flow sheets for water treatment have been analysed:

- the first one is constituted only by the RO unit;
- in the second, feed water is at first pre-treated with an oxidizing agent (1.5 mg/L of chlorine which oxidizes approximately 95% of arsenite in arsenate) and then it is sent to the RO unit in order to improve removal efficiencies;
- the third flow sheet uses RO systems with two pass-stages;
- in the forth system, a fraction of RO permeate is sent to MD operation (see Fig. 1).

In order to establish which of the analyzed flow-sheets is the most *convenient, reliable* and *sustainable* process, the use of *Economic Evaluation* and of some new *"metrics"* are utilized and discussed.

## 3. Analysis and comparison of the systems through the use of economical evaluation and metrics

In all the analyzed flow sheets the same feed flow rate and composition was used (see Table 1). All the details for what concerns membrane modules rejection values, recovery factors and operative conditions can be found in Macedonio and Drioli (2008). The achieved results in terms of energy consumption, product characteristics and water cost are reported in Table 2.

Table 1 Feed water composition

| | |
|---|---|
| Chloride | 19,345 mg/L |
| Sodium | 10,752 mg/L |
| Sulphate | 2,701 mg/L |
| Magnesium | 1,295 mg/L |
| Calcium | 416 mg/L |
| Potassium | 390 mg/L |
| Bicarbonate | 145 mg/L |
| Boron | 4.5 mg/L |
| Arsenic | 0.400 mg/L |
| TDS | 35,000 mg/L - pH: 8.1 |

Table 2 Product characteristics, energy consumption and desalted water cost for four different flow sheets

| Flow Sheet | RO | RO-OX (RO with pre-oxidation step) | RO-RO | RO-MD |
|---|---|---|---|---|
| Feed flow rate [$m^3$/h] | 1048E+03 | 1048E+03 | 1048E+03 | 1048E+03 |
| Brine flow rate [$m^3$/h] | 628 | 628 | 654 | 666 |
| Brine concentration [g/L] | 57.6 | 57.6 | 55.4 | 54.4 |
| Fresh water flow rate [$m^3$/h] | 421 | 421 | 395 | 383 |
| Fresh water concentration [g/L] | 0.339 | 0.339 | 0.211 | 0.226 |
| Recovery rate [%] | 40.1 | 40.1 | 37.6 | 36.4 |
| As concentration in fresh water [g/L] | 1.400E−05 | 1.020E−05 | 6.417E−06 | 9.333E−06 |
| B concentration in fresh water [g/L] | 4.500E−04 | 4.500E−04 | 3.000E−04 | 3.000E−04 |
| Quantity of energy required per $m^3$ of fresh water produced [KWh/$m^3$] | 5.24 | 5.24 | 6.53 | 28.4/5.76[b] |
| Quantity of energy required per $m^3$ of fresh water produced [KWh/$m^3$][(a)] | 2.69 | 2.69 | 3.70 | 25.6/2.96[b] |
| Unit cost [\$/$m^3$] | 0.614 | 0.616 | 0.740 | 0.967/0.797[b] |
| Unit cost [a] [\$/$m^3$] | 0.398 | 0.399 | 0.50 | 0.729/0.559[b] |

(a) If Pelton turbine is used as energy recovery device
(b) If thermal energy is available in the plant or the stream is already at the operating temperature of the MD unit

The values reported in Table 2 show that only the two integrated systems RO-RO and RO-MD have allowed to obtain fresh water with boron and arsenic concentration below the maximum recommended values. Moreover, the achieved water cost for the third flow-sheet with Pelton turbine like energy recovery system (0.50 \$/$m^3$) is in good agreement with the corresponding values (0.45-0.55 \$/$m^3$) found in literature (Redondo, *et al.* 2003). The higher water cost of the system with MD unit (the fourth) is caused by its higher energy demand due to the retentate flow rate which has to be heated. However, in membrane distillation the required operating temperature (50°C) is much lower than that of the conventional distillation columns because it is not necessary to heat the process liquids above their boiling temperatures. Therefore, low-grade, waste and/or alternative energy sources, such as solar and geothermal energy, can be coupled with MD systems for a cost and energy efficient liquid separation system. As a consequence, if the water streams are already available at the temperature needed for carrying out the MD operation or thermal energy is available in the plant, the energy requirements and the desalted unit water cost of the RO-MD process decrease (0.56 $/m$^3$) reaching competitive values with those of the other processes.

The proposed flow-sheets have been also analyzed through the use of the following *"metrics"* (Curzons, *et al.* 2001, Constable, *et al.* 2002, Jiménez-Gonzàlez, *et al.* 2002) in the attempt to show how the suggested indicators can drive to the choice of the most convenient process:

$$\text{Mass Intensity} = \frac{\text{Total mass (seawater+reagents)}}{\text{Mass of product (fresh water)}} \tag{1}$$

$$\text{Waste Intensity} = \frac{\text{Total waste}}{\text{Mass of product (fresh water)}} \tag{2}$$

$$\text{Energy Efficiency} = \frac{\text{Total process energy (electrical+thermal)}}{\text{Mass of product (fresh water)}} \tag{3}$$

*Mass Intensity* takes into account everything that is used in a process or process step and expresses this on a weight/weight basis rather than a percentage. In the ideal situation, Mass Intensity index would approach 1. *Waste Intensity* draws attention to the quantity of waste that is produced for a given mass of product. This metric may certainly be used by industry and can, if used properly, spur innovation that results in a reduction of waste.

The mass indicators define both environmental impacts and raw material utilization (e.g., emissions and mass intensity), while the energy indicator (*Energy Efficiency*) evaluates energy consumption of the alternatives. Clearly, wasted resources and energy consumption may have significant cost implications.

Table 3 shows the value of the quantitative indicators for the proposed membrane systems.

The achieved results show that the processes possessing high Mass Intensity and, then, Waste Intensity, have also high environmental impact because their plant efficiency is low. Moreover, the

Table 3 Metrics for the three proposed flow-sheets

| | RO | RO-OX | RO-RO | RO-MD |
|---|---|---|---|---|
| Mass Intensity [kg/kg] | 2.495 | 2.495 | 2.663 | 2.744 |
| Waste Intensity [kg/kg] | 0.0861 | 0.0861 | 0.0921 | 0.0949 |
| Energy Efficiency [MJ/kg] | 0.0189 | 0.0189 | 0.0236 | 0.1026 |
| Energy Efficiency (a) [MJ/kg] | | | | 0.0208 |
| Energy Efficiency with Pelton turbine [MJ/kg] | 0.0097 | 0.0097 | 0.0133 | 0.0925 |
| Energy Efficiency with Pelton turbine (a) [MJ/kg] | | | | 0.0107 |
| Cost [$/m$^3$ fresh water] | 0.6143 | 0.6157 | 0.7396 | 0.9670 |
| Cost (a) [$/m$^3$ fresh water] | | | | 0.7969 |
| Cost with Pelton turbine [$/m$^3$ fresh water] | 0.398 | 0.399 | 0.499 | 0.729 |
| Cost with Pelton turbine (a) [$/m$^3$ fresh water] | | | | 0.559 |

(a) if thermal energy is available in the plant or the stream is already at the operating temperature of the MD unit obtained results agree with those obtained through the economic analysis. In fact they confirm that energy consumption is one of the items that more influences water cost: in the flow sheets without MD unit, the presence of the Pelton wheel, as Electrical Energy Recovery Device, is sufficient to reduce energy consumption and, then, water cost; in the system with MD, instead, thermal energy is the term that more influences energy cost; in fact the introduction of a Pelton wheel leads to a low reduction of the plant Energy Efficiency and unit water cost. In order to observe a substantial reduction in plant Energy Efficiency and cost, thermal energy has to be already available in the plant.

## 4. Conclusions

In this work a variety of membrane processes have been analysed for their ability to reject both boron and arsenic from waters. They have been compared in term of energy consumption, fresh water cost and through the recourse of some new *"metrics"* (*Mass Intensity*, *Waste Intensity* and *Energy Efficiency*). The latter are indicators useful to quantify the progress of industrial processes towards *sustainability*, and to measure their impact on environment, economy and society.

The achieved results have showed that, among the analysed processes, only the RO-RO and RO-MD systems allow to obtain fresh water with boron and arsenic concentration below the maximum recommended values. For what concerns the cost, fresh water produced from the proposed RO-RO process with Pelton turbine like energy recovery system has the lowest cost (0.50 $\$/m^3$). The higher water cost of the RO-MD integrated membrane system is due to the thermal energy demand of the MD unit. In fact, if thermal energy is available in the plant the energy consumption and unit water cost of the RO-MD process decrease reaching competitive values with those of the other processes.

The results achieved with energetic and economic analyses are in concordance with those obtained through the use of the *"metrics"*. As a matter of fact, these have confirmed that thermal energy consumption is the item that more influences water cost in the MD-RO system and that, if thermal energy is available in the plant, a substantial reduction in plant Energy Efficiency and water cost can be observed.

Moreover, processes with high Mass Intensity and Waste Intensity indices have also high environmental impact due to their low plant efficiency.

As a consequence, the recourse to the principles of Sustainable Development can help to the choice of the best alternative for two reasons:

1) they allow to avoid risks from unsustainable business practices (such as high energy consumption, low recovery factor, pollutants and toxic releases),
2) the process that reduces costs by decreasing Energy Efficiency parameter will be more economic profitable and with less environmental impact.

Other new metrics, such as the *PS (productivity/size ratio)*, *M (modularity)* (Criscuoli and Drioli 2007) and *the* eco-environmental factor, might be calculated in order to complete the analysis of the systems.

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