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Prospects for high water recovery membrane desalination

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HIGHLIGHTS

• Higher water recovery means less waste, higher energy efficiency, and lower costs.

• The scaling risk during membrane desalination is discussed.

· Possible methods for increasing water recovery are reviewed.

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1. Introduction

ABSTRACT

Water recovery is an important aspect of the work of the desalination plant. In this paper, we discuss the prospects for high water recovery in two commonly used membrane desalination methods, reverse osmosis (RO) and electrodialysis (ED). Achieving high water recovery is limited, mainly because of the risk of sparingly soluble salts precipitation and, in the case of reverse osmosis, the osmotic pressure of the retentate. We discuss the scaling risk during membrane desalination and review the possible methods for increasing water recovery, such as application of antiscalants, integration of various separation methods, and modifications in the operation of membrane processes.

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The growing human population simultaneously requires increasing amounts of fresh, clean water and produces vast amounts of waste water, often of high salinity. Hence, there is a need for more effective and less expensive desalination methods. Membrane technologies have brought important improvements to desalination technology, as they tend to be more energy efficient and easier to scale-up than thermal methods.

One of the most important parameters of any desalination process is water recovery. It describes how much of the treated water can be obtained from the given volume of a contaminated feed. Higher water recovery means a lower amount of generated waste, higher energy efficiency thanks to less energy spent on pretreatment, and lower costs. Increasing the water recovery is especially crucial for inland applications, where the concentrate disposal options are limited. Currently, 27% of desalination plants discharge the concentrate to the sewers, 45% discharge to the surface water [1]. Both options are not optimal: the sewer treatment plant may reject large amount of salinated water,

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http://dx.doi.org/10.1016/j.desal.2016.07.047 0011-9164/© 2016 Elsevier B.V. All rights reserved. disposal to the surface water carries environmental risk and may subsequently lead to the desalination plants paying high environmental fees. Moreover, inland plants have access only to finite water resources, whereas in the case of seawater treatment, the plant may intake as much feed water as needed.

This paper is a short review of the various approaches towards increasing water recovery in two membrane processes: reverse osmosis, which is nowadays the most important technology for seawater desalination; and electrodialysis, which is widely applied for brackish water desalination. For the purpose of this paper, we define "high water recovery" as above 40% in the case of seawater treatment. In the case of brack-ish water treatment, which is highly dependent on the feed water salinity, we define high water salinity as the value higher than the water recovery obtained with an unmodified, single-stage brackish water reverse osmosis (BWRO) module treating the feed water in question.

2. Scaling risk assessment

Increase in the water recovery of a membrane process is inherently connected with the operation at the highest possible discharge (usually called retentate or concentrate depending on the desalination method)

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M. Turek et al. / Desalination xxx (2016) xxx-xxx

salinity [2,3]. This results in a serious risk of membrane scaling related to the solubility limits of a number of sparingly soluble compounds present in the feed water. The salt concentration in the retentate/concentrate increases along the membrane. Exceeding the solubility limit (K) can be interpreted as the supersaturation increase. Taking into account crystallization or precipitation mechanisms, it should be recognized that a natural recovery-limiting barrier for the retentate/concentrate in a membrane desalination system is the occurrence of spontaneous nucleation in the module.

Inorganic scaling can be divided into three classes: alkaline, non-alkaline and uncharged molecule scaling. Alkaline (basic) salts increase the solution pH through hydrolysis where hydroxide ions are formed. An example can be CaCO₃, which scaling muddles processing of brackish, groundwater and seawater [4]. Presence of magnesium, sodium, sulphate and humic acid inhibits CaCO₃ precipitation [4]. Different humic substances, like humin or fulvic acid, inhibit the calcite growth. Co-precipitation of CaCO₃ with iron oxides makes the scale more porous, thus affecting the flow conditions. Non-alkaline salts cover charged ions dissolving in water, but with no pH modifications [4]. Example can be CaSO₄, NaCl, MgCl₂ and MgSO₄. Uncharged molecules with scaling tendency (e.g. clay, silt, particulate humic substances, debris and silica) are less soluble than the salts since no significant interactions with highly polar water molecules can be observed [4]. Smaller particles can be responsible for fouling. Especially scaling-active is silica - in a colloidal, particulate and dissolved (monosilic acid, after supersaturation silica starts the surface polymerization) forms. Similar scaling tendency demonstrate also iron oxides, iron hydroxides, iron oxide-hydroxides - maghemite, lepidocrocite, akaganéite, hematite.

Generally, one should keep in mind that supersaturation can be discharged in two ways. Firstly, by direct contribution to the existing scale layer (terrace) formed on the membrane surface (external scaling/fouling – heterogeneous (surface) crystallization [5-7], closely depending on hydrodynamics resulting from the spacer's geometrical configuration and the cross-flow velocity, integrated with aging phenomena involving: dissolution, redeposition, regrowth of crystals, phase change - hydration or dehydration, etc.). Secondly, indirectly via spontaneous homogeneous nucleation in the bulk of retentate/concentrate following by subsequent particle deposition on the already existing membrane scale layer (internal scaling/fouling [5–7], like attachment, aggregation or agglomeration with the existing crystalline surface layer). Depending on the specific membrane configuration, form, morphology and exposition towards retentate/concentrate additional mechanisms in respect to internal fouling, can be further distinguished. It may involve some individual or integrated mechanisms and processes depending on the foulant size (size distribution), membrane pore diameter distribution, convection intensity and structure (micro-, mezo- and macro- whirls), adsorption (up till internal pore clogging), etc.

Depending on the specific process conditions observed in high water recovery desalination (e.g. in RO hydraulic pressure compaction of the foulant structure will occur) and membrane configuration (structure) combined external and internal fouling (scaling) is usually identified, of various contribution of both fouling/scaling components – see Fig. 1 [5].

The nuclei, formed in the bulk or on the membrane, grow rapidly and cause severe membrane blockage or flow restriction. Spontaneous nucleation can be the result of concentration (supersaturation) of the compound in question exceeding the upper limits of the so-called metastable zone and operation in a labile region. Primary homo- or heterogeneous nuclei can be created both in the bulk of the retentate/ concentrate or can be deposited right on the membrane surface, thus causing scaling.

Main problems resulting from the membranes exploitation in the high water recovery mode generating scaling can be [5,6,8]:

- increase in hydraulic resistance (by systematically growing scaling/ fouling layer contribution) influencing water permeation intensity directly,
- growth of operational costs of membrane plant (higher energy demand, additional labor for cleaning),
- change in heat transfer efficiency (by low thermal conductivity of the increasing scales),
- appearance of fouling/scaling-enhanced concentration polarization and temperature polarization, affecting the effective osmotic driving force, influencing in turn the resulting water flux,
- change in membrane rejection property (through e.g. sealing pores/ defects in membrane which take essential part in diffusional processes),
- decrease of active membrane surface (blockage), lowering total water flux – necessary of adequate plant size and economical costs growth for current compensating,
- shortening of membrane lifetime by sometimes irreversible microstructural changes (chemical degradation of sensitive polymeric material(s)),
- modification of the net hydrophobicity and non-wetting properties of the membrane pore system (loosing of predefined selectivity),
- alteration of membrane surface chemistry (like formation of surface hydrophilic groups (hydroxyl and carbonyl),chemical interaction of membrane polymer(s) with the salts – e.g. stiffening of polymer, prevention of chain disentanglement, chain scission [8]),
- changes in membrane pore structure, especially some shifts in its pore size distribution,
- lowering mechanical strength of the membrane system, generation of cracks and other structural defects, morphological changes, fibril damage,
- scaling in membrane distillation processes is responsible for appearance of "negative flux".



Fig. 1. The possible theoretical mechanisms of scaling (heterogeneous nucleation) and deposition/fouling/scaling (induced by homogeneous nucleation in the bulk of retentate/ concentrate) [5].

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