Newsletter Science and Technology March 2023

Editorial

Jan Post, program director

What would a water technology institute be without a desalination research portfolio. From the start of Wetsus until today, I think we found a successful niche in the research and development of electrochemical systems. These systems containing electrodes and ion-selective membranes are an essential hotspot in our research program, especially for applications that are hard to cover with other membrane technologies. Meanwhile, with the knowledge we developed with our academic partners and companies, we are well positioned to contribute to the more mainstream technologies like reverse osmosis (RO) and nanofiltration.

For this Science & Technology newsletter, we collected interviews with colleagues and researchers to highlight the needs and relevance of desalination. Not just for the EU, but to work on new water sources worldwide.

In the EU, water scarcity is already visible in several regions, as Pieter de Jong – our man in Brussels – mentions. With Pieter, I got the assignment from the Joint Research Centre (JRC), the European Commission's science and knowledge service, to make a sector and policy review on desalination. Even though desalination enables many of the EU agendas, the EU financial contributions over the 2014-2019 period were modest.
The European Regional Development Fund (ERDF) invested €58.2 million for infrastructure, and the Research and Innovation programme Horizon 2020 (H2020) financed €23.3 million for research and innovation.
We recommended connecting desalination better to a number of programs for the Financial Framework 2021-2027. Hopefully, we will see more granting opportunities for the sector in the near future, expanding Europe's position as a major hub for innovation in desalination.

Part of the study was to identify EU opportunities for innovation in desalination. We did our best to add some challenges on top of energy and cost reductions, but who better than Paul Buijs could shine his light on the actual innovation needs? From our conception, Paul has been actively involved in the Wetsus network. Desalination is at the core of his expertise and passion, so he can tell from practice what research and development directions we should take. With a key focus on state-of-the-art RO.

Last but not least, I am proud of the researchers explaining their research projects – showing what Wetsus has to offer in expanding the availability of cheap and clean desalination. Paulina Sosa-Fernandez finished her PhD thesis on how electrodialysis can save water and chemicals in oil and gas production. Kecen Li just started his PhD journey on a similar process that potentially enables high water recoveries of over 95% without adding anti-scaling chemicals. Edward Kimani, halfway his PhD, works on understanding of mass transfer in Reverse Osmosis membranes in order to better predict permeate qualities and energy consumption that can be expected.

Desalination aspiration: future musts for desalination research

"There are a number of big myths when it comes to desalination," says Paul Buijs, "for one, the idea that it isn't a cheap option and costs a lot of electricity when it comes to water production. Yet these are old stigmas. Big Saudi desalination plants can already do it for less than 3 kilowatt-hours per cubic meter, and the costs are relatively low (<0.50 USD/m^3), especially since the discontinuation of energy subsidies and privatization. However, there is a catch – it is all about large plants (>500,000 m^3/day). Small Dutch plants, as that's how we will envisage it, would require more innovation to be economically and ecologically attractive. And we can do so on four main fronts."

And when it comes to reverse osmosis (RO) desalination, there is more than just the membranes that can do with improvements. Buijs: "Over the past decades, membranes have already been greatly improved. To an extent where it is becoming harder and harder to improve them further." But on other fronts, there is more work to be done.

Intake

"When taking in seawater, multiple industries all face the same concern – mussel larvae. Especially large energy plants take big scoops of water to cool their processes, but anytime you take seawater, the larvae pose a problem in the system."

"Currently, chlorine is often used to stop the mussels from growing and attaching to the systems it flows through. Together with other compounds like bisulfite, amines, and chlorinated hydrocarbons, it is rereleased into the sea. That has a significant impact on the local environment. In the Netherlands, we have regulations in place on whether you are allowed to dose chlorine, depending on the height of the mussel growth. This way, impact can be limited. If we are facing colder months, growth is unlikely at its peak, and the processes can go on as they should, but you have to stop the plants during some warmer periods. But in countries like in the Middle East – with warm weather year-round – this is a much larger problem."

Prediction, Prevention and Remediation

And fouling in general poses a problem for any natural-water membrane system. "By now, dealing with particulate fouling in RO has become trivial. There are some solutions to combat biofouling, but there is much to gain in predicting fouling." Before the water even reaches the membrane, it's biofouling potential should be monitored. Buijs: "we have seen attempts in the past to draw conclusions based on metabolite concentrations that could indicate growth, but the changes are meager. Too low to measure."

"Nieuwater in Emmen has been monitoring pressure changes over the membranes. This way, they made a warning system. If too much growth is on the membranes, the pressure drop will increase and be noticed – but it isn't exactly an early warning."

Obviously, a reliable prediction tool is crucial to select and optimize pretreatment processes for seawater reverse osmosis, minimizing the fouling potential of the RO feed water. The next step is to develop more effective cleaning processes, whilst minimizing the discharge of cleaning chemicals to the environment.

When it comes to the RO membrane itself, it has become quite tough to squeeze out further improvements. It is the complex challenge that Edward Kimani faces at Wetsus.

"On biofouling prevention, a lot has been tried in the membranes, but we keep facing the same problems. You need a layered system, including a spacer. Top layer augmentations like smoothing out the polyamide have not been doing much. It is the spacer that causes problems. And although there are solutions, none are cheap enough for mass production of drinking water."

And then there is boron. Buijs: "the WHO has just adjusted boron norms – now more boron is allowed in drinking water. Depending on the culture, this is a controversial change, though. Many countries still stick to the old norm, which means it is harder to remove boron by RO. It usually takes two steps before you can get it out. That could be more efficient."

Brine
Finally, effluents from desalination have also been under the attention of the world. “The UN recently published a report about the effects of dumping brines. A lot of people worry about it. In principle, concentrated seawater should be rather harmless. It is the additives that can pose a risk”.

But besides that, reprecipitated ions can be repurposed. “Depending on the location, certain minerals can be economically interesting too. There has been talk of rare earth mining, but the concentrations are very low. Magnesium is more interesting as it is replacing aluminum in many high strength low weight apllications.” A lot still needs to be done to recrystallize the minerals to the necessary purities. The H2020 project Water Mining seems promising, and there is a global interest in mineral mining to reduce discharge and to reduce the overall cost of desalination

In the end
In the end, when saying that desalination is just too expensive of a technique, people often forget to see the process as a whole. There can be economic gain. Crystallization of valuable minerals can yield benefits instead of waste, and the RO desalination has plenty to gain from prevention and optimization.

Read more:

“Paul Buijs: Busting Four Desalination Myths.” August 2020. Aquatechtrade.com. https://www.aquatechtrade.com/news/desalination/paul-buijs-busting-desalination-myths.

Desalination in the EU

Freshwater scarcity has been striking over the summer, and with our wells drying up, little will be left for the future. Water reuse is - of course – a welcome solution, but the most predictable backup tap is desalination. That is what Brussels liaison officer for Wetsus, Pieter de Jong argues.

Already around the Mediterranean, Europeans rely on salt removal from seawater for their fresh water. With an increasing demand for hydrogen and intense agriculture, the strain on local systems will keep increasing. We must innovate for a stable and sustainable Europe.

The most predictable backup tap
The relevance of water has become all too clear over the summer. Drought became a hot topic in 2022 – but unfortunately, this will likely not be the only year. “Freshwater scarcity will only become more prominent,” says Pieter de Jong, liaison officer Europe, “according to the World Weather Attribution, droughts like these used to occur once every 400 years. With global temperatures increasing by 1.2 degrees C, we already see these extremes once every twenty years. And it’s not a linear scale. If we hit the international climate goal of no further increase than 2.8 degrees, extreme summers will occur every three out of four years.” Together – Wetsus’ Jan Post, Pieter de Jong, and Irish and Spanish colleagues – published their advice on desalination to the European Commission in a report last year.

Freshwater scarcity, the way we use water now, is increasingly becoming a problem. “There are three major solutions we see for Europe as a whole: of course, the reuse of water – which is a must – desalination and retaining increasingly extreme precipitation. And although wastewater flows are well known and relatively stable, desalination is the most-predictable backup tap.” However, current smaller-scale plants yield relatively high costs per cubic meter of water.

Strain on local sources
But it is the only way to make fresh drinking water anew. “The question is, do we really want to make and use so much drinking water? Since 2017 in the EU, there are already requirements in place that allow us to reuse water of different qualities for different agricultural sectors. You can imagine that water used for lettuce growth

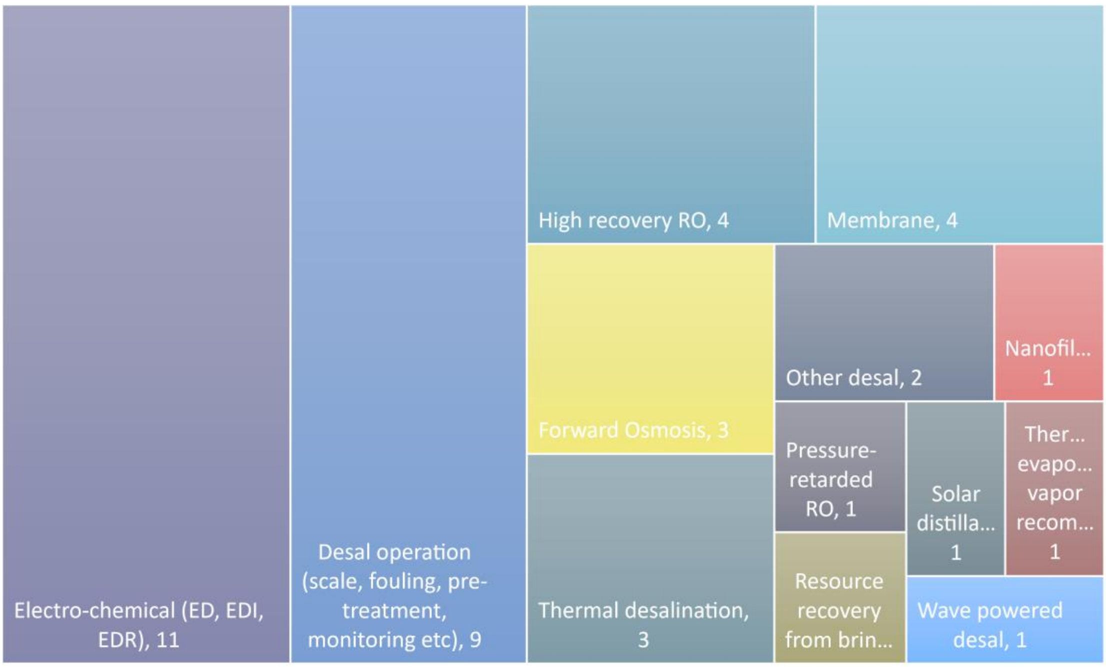
is obliged to be the cleanest, but when cultivating oranges and animal feed, the direct threat of dangerous bacteria lies a lot lower. And thus, we can use different water qualities to sustain the agricultural sectors."

The use of desalinated water can be approached similarly. "The 2030 EU agenda is focused on 100 megawatts to gigawatt-scale hydrogen plants to a total of 40 GW. Large amounts of water are needed for that – at least 150 million cubic meters a year. When we compare that to the three billion cubic meters annual desalination capacity that is expected to be in use by 2025, that does not appear to be a lot extra. But we should not forget that such intakes can put enormous strain on the local water sources, as fresh water is used as a basis.
The costs of desalinated water for hydrogen-production water can be relatively more expensive. But that does not mean we are good to go already." Plenty of innovation is still required to meet such massive energy goals by 2050, but water we often forget.

Growing home market will change EU leadership in desalination
But still, some places in Europe already have little fresh water available due to their geography. Large regions with water scarcity wherein desalination can offer a solution. "We have already seen the large impact of this summer on south and east England, but also, we should consider regions like Götland Sweden that, due to Russian threats, is now more inhabited by military forces and thus needs more water. Or always dry Murcia Spain, which already relies on desalination."

We need to improve our technology for a sustainable and independent Europe. We still face plenty of challenges, but with the fantastic leaps in RO desalination that have already been made over the decades, and enough financing and competition, freshwater generation should be a problem of the past. "Desalination challenges we need to address in EU's innovation agendas include: (1) making desalination more energy efficient and cost-effective, (2) turning brine treatment and disposal from problem into opportunity, (3) enabling second use of desalted water in agriculture, and (4) taking the holistic approach and look for systemic innovation".

For the coming five-year period it is estimated that investments for new capacity will be €400 million, but reinvestments in outdated plants may count up to €1 billion and membrane replacements to another €380 million. "Our analysis of vendors of innovative and emerging desalination technologies currently in the market shows that Europe is a major hub for innovation in desalination. Regarding patent activity and licensing opportunities, however, Europe seems lacking behind. With the increasing urgency for desalination in the EU home market, it is our challenge to change this to our favor."



Two classes of technology did show high patent activity in 2020: The first being Electrochemical processes with 11 patents filed, and the other being operational efficiency offerings with 9 patents filed (BlueTech Patent Activity Scan as part of the JRC report on "Specialisation in the Context of Blue Economy – Analysis of Desalination Sector, 2021")

Read more:

Post, Jan, Pieter de Jong, Matt Mallory, Mathieu Doussineau, and Ales Gnamus. Rep. Smart Specialisation in the Context of Blue Economy – Analysis of Desalination Sector, 2021. https://s3platform.jrc.ec.europa.eu/en/w/smart-specialisation-in-the-context-of-blue-economy-analysis-of-desalination-sector

Reclaiming water and polymers

Desalination is key, not just in drinking water, but in many more processes. One of these more-unsuspected places is the oil and gas industry, as they use a lot of desalted water to extract hard-to-reach resources. 2 to 4 million cubic meters of water per day is spent to recover just a fraction of the oil. And even in times of transition from fossil resources to renewables, reusing this liquid carrier for remaining oil and gas recovery is essential but far from trivial. And to ensure a more sustainable energy transition, multi-purpose solutions have to be found here too.

Combatting sticky situations, Dr. Paulina Sosa-Fernandez has shown that a sustainable solution is possible, and long-running desalination is already feasible. Electrodialysis to reuse polymer-flooding water is a sound economic investment.

4-8 barrels of water
Depending on the method used, large volumes of water are needed for oil extraction. Given the size of the oil industry and how common extraction with water with additives – or enhanced oil recovery (EOR) – is, there is a significant gain in reusing water from both an economical and environmental view. To put it all into perspective, 12 to 24 million barrels of water are needed per day for the eighth or quarter equivalent of oil that is recovered using EOR.

But the extraordinary conditions for which this water is used and modified, makes is much more hassle to clean up and reuse. Due to the high viscosity required in oil recovery, often charged polymers are added to bulk up the water. Once the water resurfaces, it is full of oil droplets, minerals, and the mentioned polymers.

The removal of salt from the produced water is essential to get it back to the highly viscous state required to be pumped into the ground. And in some places, fresh water is not allowed to be used for these purposes anyhow.

Simple model complications
But little was known about desalination in this context. Sure, electrodialysis was thought to have potential, but it was up to Sosa-Fernandez to pioneer this field. Rather soon, she showed that various salinity grades and temperatures seemed to be no match to the method, and a proof of concept was born.

But divalent ions proved to be a challenge. “Little was written on the effects of calcium and magnesium on the other contents of the water. But a well-known problem divalent ions cause was of course, hindering us – calcium bridging,” says Sosa-Fernandez. “The two positive charges of calcium act as a crosslinker for the polymer chains. This effect reduces the viscosity of the solution drastically, which is negative for their reuse. And additionally, it causes more severe fouling on the anion exchange membranes.”

Remarkably, it was the simplified model water used that complicated the recycling. Sosa-Fernandez: “When we used a simple solution containing just polymer and calcium, there was severe fouling formation. As soon as we started adding small oil droplets to our model, we saw a reduction in calcium-polymer retention on the membranes. Like dirtying up the water, made it cleaner in the end. Presumably, the presence of oil droplets weakened the gel layer fouling.”

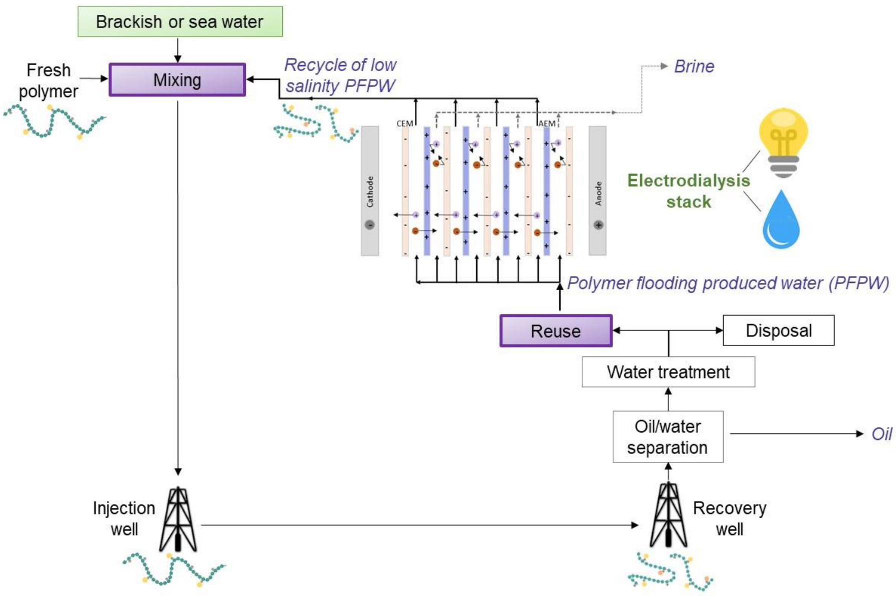
Economically viable
With those observations, the young doctor already showed a much higher feasibility for longer runtimes. “We went from six hours to ten days in some cases. So, we could you that the use for longer periods of time was technically viable.”

Economic analysis showed that desalination of produced water is already economically viable, as Sosa-Fernandez demonstrated. The technology can be of great significance in places where water is scarce, or where regulations for disposal are strict. Even though there still is room for improvement – with higher current densities, for instance. “Not only that, but we can be more sustainable by reusing some of the spent polymers. And, of course – depending on the location, the economic and environmental advantages can be a lot higher.” But as an innovative technology – it can hopefully find its way to turn more wastewaters into resources.

Read more:

Sosa-Fernandez, P. A., J. W. Post, F. A. M. Leermakers, H. Bruning, and H. H. M. Rijnaarts. 2018. “Electrodialysis-based desalination and reuse of sea and brackish Polymer-Flooding Produced Water” Desalination 447: 120-132. https://doi.org/10.1016/j.desal.2018.09.012 .

Sosa-Fernandez, P. A., J. W. Post, M. S. Ramdlan, F. A. M. Leermakers, H. Bruning, and H. H. M. Rijnaarts. 2020. “Improving the Performance of Polymer-Flooding Produced Water Electrodialysis through the Application of Pulsed Electric Field.” Desalination 484 (114424): 114424. https://doi.org/10.1016/j.desal.2020.114424.



Reclaiming water and polymers from a polymer flooding process. A viscous polymeric solution is injected through an injector well, and the mix of fluids is recovered in a production well. After the oil is separated from the water, the salts are removed by electrodialysis and the water and polymers can be recycled for injection

Chemical-free electrodialysis metathesis

A sneak peek into a scaling and chemical-free desalination technique

Less waste, no scaling, no added chemicals, and more drinking water – these are the four big expectations that PhD student Kecen Li's is trying to meet with his electrodialysis metathesis (EDM). This multi-component system of commercial membranes is to reuse its would-be discarded sodium chloride, to combat scaling, and create valuable output streams. All the while yielding more fresh water than RO systems and with just feed water and electricity as inputs.

And here is how he is doing it.

Removing RO risks

Despite years of effort, development, and progress, scaling remains one of RO desalination's big problems. Adding phosphonates, reversing flows, and closed-circuiting are solutions in the working, but they come with their own downsides – like not having a full-capacity continuous flow, and the environmental burdens that are the consequences of chemical dosing. Moreover, to operate, a relatively large amount of water is lost in concentrate streams that are yet to be valorized anyway. Researcher Kecen is about to sidestep all these problems using electrodialysis metathesis, recombining ions to solve all these problems.

Charge recombination

The problem of existing desalination systems is that all salt ions become concentrated in a single stream, and some ions start to combine and form crystals that precipitate (scaling). The idea is now to prevent these combinations by directing ions into different concentrate streams. The young researcher has just started to explore the boundaries of possible answers to this problem. Kecen: "Though there are multiple ways to tackle this, we, for now, have settled on a four-membrane system. First, to remove monovalent ions, like sodium and chloride which we then can recombine with bivalent ions in the following step."

By separating the different ions, the researchers think they can tackle scaling. "The plan is to use an electric field to separate sodium ions to one side and chloride to the other – with the feed water flowing accross monovalent-selective membranes. Next, we use these as counter-ions for the second phase. With the sodium on one side, and the chloride on the other, we can selectively draw in calcium to the chloride side, and sulfate and carbonate to sodium." That way, you create two streams of remarkably soluble salts and prevent the formation of the tenacious calcium sulfate.

More drinking water, less waste

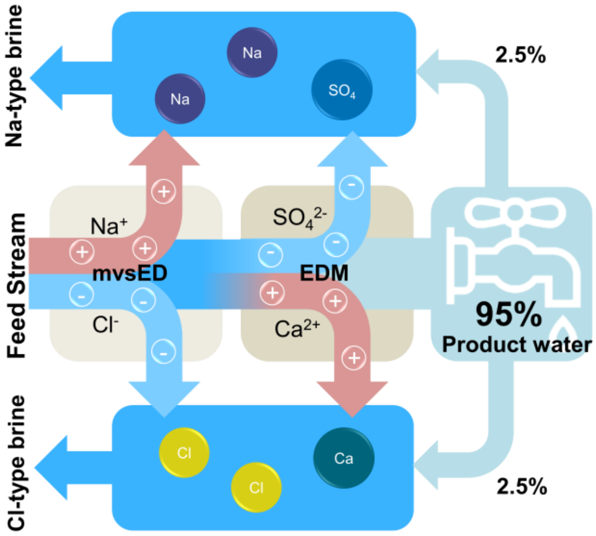
In the end, instead of a concentrated waste stream like in RO, the EDM will yield three or more outputs. Of course, a drinking water stream, which can deliver much more water than the RO variant – where too little water in the concentrate flow would risk damage to the membrane. And two or more pathways for the different combinations of discarded ions.

And the latter seem to give rise to valuable products too. Kecen: “Normally, concentrate streams are too diluted to be used, and the products that come out are too impure. With EDM we expect high purity sodium sulfate and calcium chloride upon evaporation. Probably 95% for typical brackish water desalination, but more likely even more.”

Currently

The system is one of its kind, so little is known yet. But upon preliminary models and lab tests, it seems like it might just work. But the aim is to prove its workings on a scaled-up system too. As of now, synthetic brackish water is the primary test method. "We can gradually build up the salt level to mirror real seawater. From there, we can take true seawater and see how it changes things. Lastly, we can think about upscaling."

But it will take quite some tweaking to get there. And whereas RO membranes have become cheaper and cheaper, monovalent selective membranes are on the expensive side. But it won't stop Li. "I do believe this is the way to deal with scaling issues and work toward a more sustainable desalination process. We are getting there. The benefits of EDM will have over RO could more than compensate. Moreover, the application of EDM can be a good add-on for further treatment of concentrates and thus improving the water recovery of existing RO plants".



Scheme with the two-step EDM process, firstly removing the monovalent ions and secondly recombining these as counter-ions for bivalent ions, meanwhile obtaining a high recovery of fresh water

Membrane modelling

Turning complex RO systems into virtual ion trackers

One of the largest concerns that lingers for desalination plants is their energy consumption. Despite current use of reverse osmosis (RO) as opposed to thermal plants, small-scale RO plants still require a relatively high amount of energy for portable water production. In addition, membrane retention for specific ions is poorly understood and predicted.

One researcher that is working on the solution is Edward Kimani. Through modeling and validation of ion transport theories which describe water desalination from multi-component salt mixtures using RO membrane, he hopes to find optimizations in the desalination process. But first: "We try to fundamentally understand the movement of ions in the complex structure of the membrane. First one dimensional (1D) – across the active layer, and later two dimensional (2D) – membrane module," says Kimani.

As ions move from the feed side to the permeate side of an RO membrane, little is known about the path and interactions that these charged particles take, especially when dealing with multicomponent mixtures. It's a black box on a molecular level. "Small differences in polarity can play a key role in the performance of the membrane," says Kimani. "To further optimize RO systems, we need a fundamental understanding of physical-chemical transport descriptions." Numerical models developed on a molecular level can help us simulate transport and separation process. With proper validation, these models can later be extended to a macro level.

Kimani's PhD is centered around multi-component mass transport modeling of water desalination with RO. "The approach we use involves developing and testing transport theories for RO which are based on physical principles and chemical information which result in very robust predictions. These models are then validated through experiments. Fitting and model extensions are done through a parametric studies where certain parameters are adjusted and compared to those reported in literature."

Virtual membrane

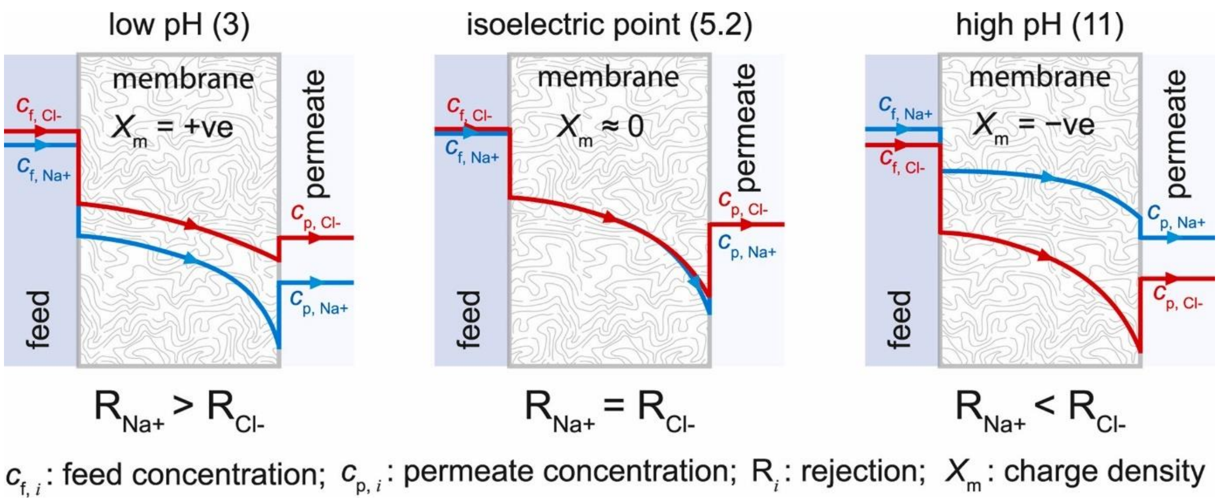
pH effect on RO membrane performance is one of the key research questions investigated. "The mostly used RO membranes are made of the polyamide (PA) active layer. Although it is only slightly charged at low and high pH ranges, it greatly influences ion transport and separation. There are so many interactions between ions and ions – such as ion pairing and acid-base reactions, and ions and the membrane matrix. Our recent paper describes how membrane charge ionization affects the overall performance of RO membranes. Our model predicts the effects of local pH on membrane rejection and is validated experimentally."

It not only shows how Kimani can virtually monitor the acidity changes, but that his physical transport theory is well described. “We track ion movements in the membrane matrix based on Nernst-Planck equation, which is already known to literature,” says the scientist. The development and extension of the model is based on the Donnan steric partitioning model for size-based calculations. This is also coupled with membrane charge ionization and interactions with protons and hydroxide ions.

Realistic simulation

Although, it is a first in combining all these theories, it means little without experimental data to back it up. Some of it is already well built into the model – like the virtual acidity of ammonium – but true validation comes from measuring the system as a whole. Kimani: “Of course, we cannot measure within the membrane itself, but there is a great value in determining the compositions of the influents and effluents. On that basis, we tweak a few parameters. We saw how the model matched our experimental data as we did that. And so, it confirms that we built a realistic simulation.”

As proof of principle, it is still 1D. “We now have proven that our model works – although we only took ion transport across the PA active layer of the RO membrane into account. It’s a robust model for a small cell. But if we want to move to a realistic geometry of an actual RO module, we will need to consider the higher dimensions. In a module, ions do move across and along the membrane, i.e., both perpendicular and parallel to the flow direction. This 2D analysis is our next goal, and so far, it is going well.”



Effect of pH on the retention of ions in a reverse osmosis membrane

Read more:

Kimani, E. M., M. Pranić, S. Porada, A. J. B. Kemperman, I. I. Ryzhkov, W. G. J. van der Meer, and P. M. Biesheuvel. 2022. “The Influence of Feedwater P.H. on Membrane Charge Ionization and Ion Rejection by Reverse Osmosis: An Experimental and Theoretical Study.” Journal of Membrane Science 660 (120800): 120800. https://doi.org/10.1016/j.memsci.2022.120800

Kimani, E. M., A. J. B. Kemperman, W. G. J. van der Meer, and P. M. Biesheuvel. 2021. “Multicomponent Mass Transport Modeling of Water Desalination by Reverse Osmosis Including Ion Pair Formation.” The Journal of Chemical Physics 154 (12): 124501. https://doi.org/10.1063/5.0039128

Wetsus Congress: Save the date!

On October 9 and 10, 2023, the next Wetsus Congress will be held.
The theme is " Environmental resilience to novel entities", and we are already busy preparing an interesting program.

We will also celebrate Wetsus 20 year anniversary!

Stay up to date via our website and socials!