NWRI GRADUATE FELLOW SEMI-ANNUAL PROGRESS REPORT

DATE:	June 2017
Project Title:	A Novel Brine Precipitation with the Aim of Higher Water Recovery
Graduate Fellow:	Mojtaba AzadiAghdam
Advisors:	Professor Shane Snyder and Professor Jim Farrell
Institution:	University of Arizona

Overview

In this research project we develop a proof-of-concept for a new pretreatment process designed to be used prior to membrane processes (nanofiltration (NF) or reverse osmosis (RO)). This new process can extend the use of bipolar membrane electrodialysis (BMED) and fluidized bed crystallization reactor (FBCR) to convert municipally treated wastewater or brackish groundwater into potable water, thereby increasing the available water supplies for drinking water by 50 percent in inland areas. The proposed process aims to remove dissolved contaminates and particulates, while the commercialized pretreatments for NF or RO remove only particles. The treatment process will nearly eliminate the production of concentrate streams, reduce the total dissolved solids (TDS) content of the treated water, and greatly decrease membrane fouling.

Motivation

Potable water scarcity has become an important issue over the last few decades due to changes in rainfall patterns and increasing population. Recent estimations demonstrate that more than 1 billion people do not have access to clean potable water, and approximately 2.3 billion people live in regions with water shortages [1]. Therefore, there is an increasing global trend toward using water more efficiently in urban and rural communities. In addition to novel water acquisition and management strategies, such as water transfers, banking and trading, municipalities are turning to water reuse to strengthen their water portfolios [2].

High pressure membrane processes, such as NF and RO, are commonly used to produce drinking water from brackish waters. The RO and NF processes are able to remove both organic and inorganic contaminants and produce clean water [3]. Two major limitations to these processes are (a) membrane fouling and (b) production of a concentrated brine stream [3, 4].

There are four main causes of membrane fouling:

1) Microorganism growth;
2) Colloidal material adsorption;
3) Mineral scale (most commonly divalent cations combined with sulfate and carbonate); and
4) Natural organic matter, such as humic and fulvic acids.

Options for concentrate disposal include: deep well injection, discharge to surface water/ocean, and evaporation [5]. Treatment of brine is a site-dependent issue, and the method usually depends on costs, which can be as high as 25% of the overall water treatment costs [6]. The high cost of brine treatment and adverse impacts of brine disposal on the environment are two variables that could be improved by using pretreatment methods that can increase the permeate water recovery and minimize brine generation.

Objective

The main goal of this research is to develop a new pretreatment technique for water treatment processes that use membranes. The proposed process consists of pretreatment techniques that will provide a cheaper water treatment option than currently used commercial processes, and aims for zero brine waste generation.

The technology to be developed here will enable large-scale inland desalination using RO and NF, which are not commonly practiced in non-coastal areas due to the high costs of brine disposal. Decreasing the volume of brine production by one order of magnitude will make inland RO and NF cost-effective [22]. This will enable both municipally treated wastewater and brackish groundwater to be used as sources of potable/industrial water. These two new sources of water may improve economic development, which was limited by water scarcity in arid regions of the country.

Background

There are numerous published research articles in the field of zero liquid discharge (ZLD) introducing different combinations treatment techniques [3, 6-10]; however, none of these methods are feasible to be commercialized. Funded by Suez Environment, we introduced a 3-step intermediate process for treating the brine solution generated in the 1st membrane stage in order to feed it to the 2nd membrane stage, with a goal of higher recoveries. As shown in **Error! Reference source not found.** on Page 3, this method was able to remove the scale-forming species (calcium, magnesium and carbonate) to a level that the secondary membrane was able to operate at 85% recovery rate without scaling (see Figure 2).

However, the overall process requires 90 minutes of mixing time, which makes it impossible to be utilized in full-scale water treatment plants due to the need for building giant mixing basins for city wastewater flowrates. On the other hand, FBCR has shown promising results in removing scale-forming compounds with much smaller (less than 10 minutes) retention times [11-14].

Therefore, in this research, we are planning to investigate the feasibility of using FBCR to remove scale-forming species from entering to the membrane process (2nd stage). FBCR, also known as pellet softening in water softening applications, have been used to promote heterogeneous crystallization of minerals (scale-forming species) on sand grains or seed particles suspended in an upflow reactor [11, 15-17]. In order to initiate the heterogeneous precipitation of minerals on the sand grains, a stream of alkaline chemical such as Na_2CO_3 or NaOH is fed to the reactor. Addition of alkaline chemicals increases the saturation index values of scale-forming species and results in their precipitation the surface of sand grains. This precipitation on the sand grains results in crystals' size growth. These crystals at sizes over 2mm can be flushed and dewatered by gravity.

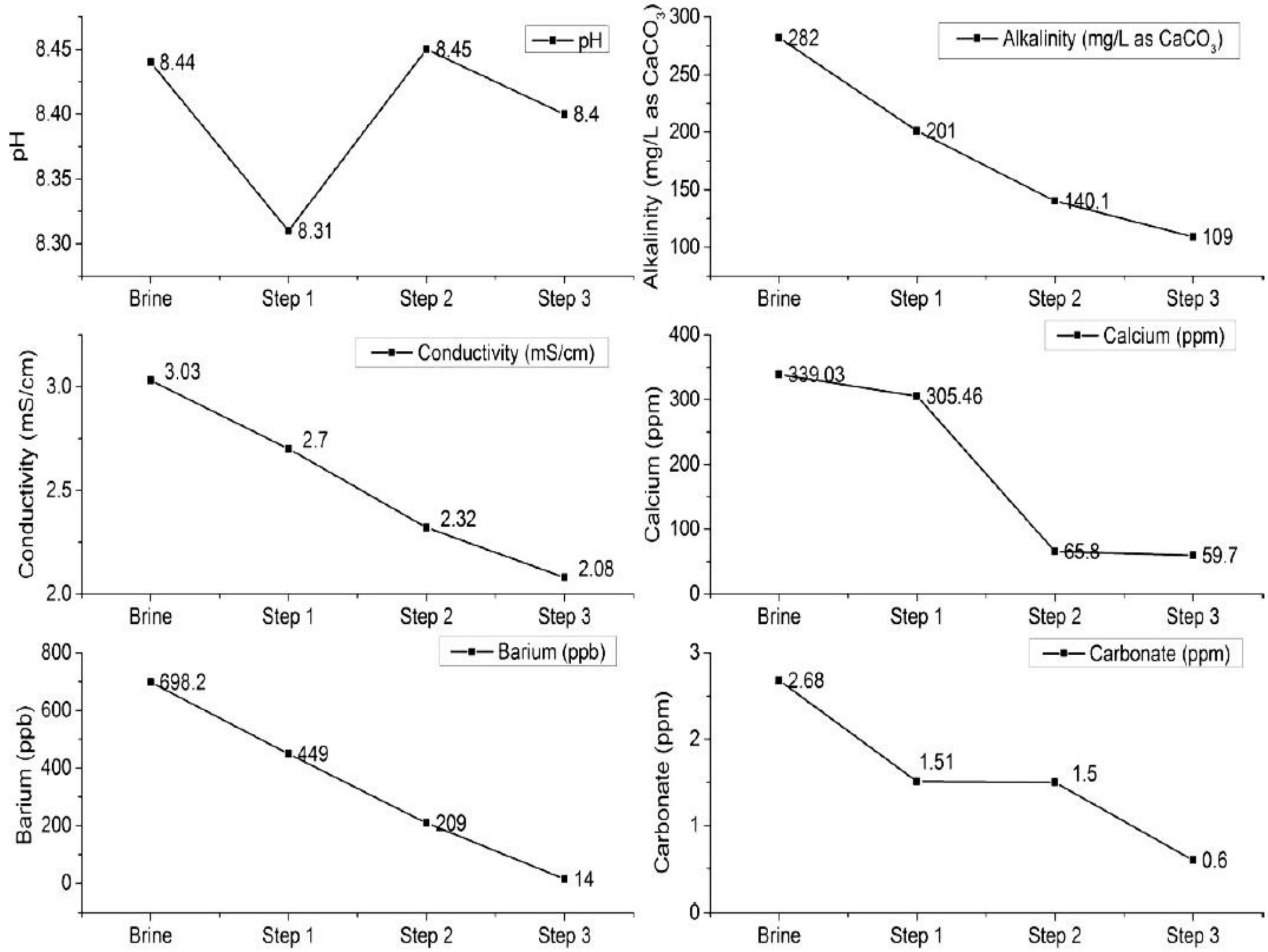

Figure 1 Changes to the composition of the brine after the 3-step treatment process [10]

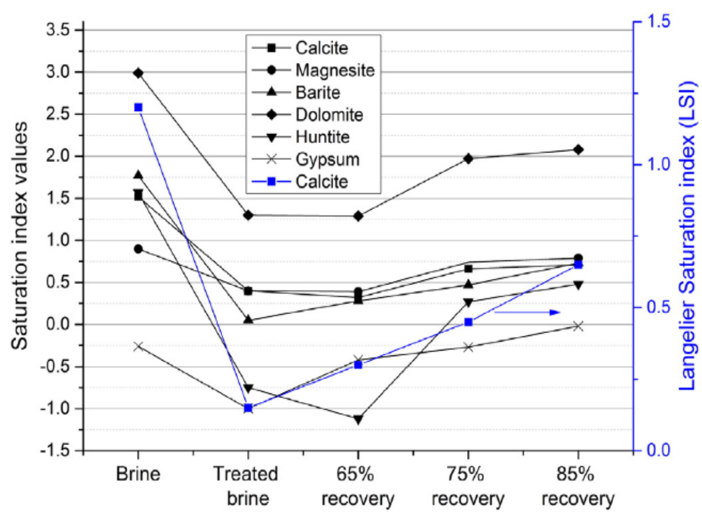

Figure 2 SI values for different recovery rates in the secondary membrane. Also shown are LSI values for $CaCO_3$ at each stage. The LSI is defined as solution pH value minus the saturation pH value.

Hypotheses and challenges

In this research, we are planning to investigate the feasibility of using FBCR to remove scale-forming species from entering to the membrane process (2nd stage). Several parameters affect the FBCR including seed particle size, retention time (reactor width and height), and pH value. Seed particle size affects the overall surface available for precipitation of scale-forming species. Retention time will affect the overall removal rate of each scale-forming species. The amount of the alkaline chemical that is added to the feed water in the FBCR step affects the pH of the solution in the FBCR. High (>12) pH values will promote homogeneous precipitation of scale-forming species; however, low pH (<9) values will not facilitate the precipitation of the minerals. The aim for this research is to optimize these parameters for highest removal of scale-forming species.

While high pH values (pH>11.5) will result in higher calcium and magnesium removal, these high pH values are also detrimental to the water quality due to introduction of nanoparticles into the water. High pH values (pH>11.5) will promote homogenous precipitation instead of heterogeneous precipitation on the seed particles, resulting in generation of nanoparticles that can rapidly clog the following membrane treatment process. This issue can be overcome by adding less base than the stoichiometric equivalent. The stoichiometric equivalent will be calculated based on the preliminary results of the feed water analysis using IC and ICP-MS instruments. However, adding less base may reduce the amount of calcium and magnesium removed by this stage of the process.

We hypothesize that the high pH (pH=11) in the FBCR will inactivate microorganisms prior to the NF process. Currently, NF and RO are only credited with a maximum of 1.5 log removal[1] of microorganism inactivation based on removal of TDS. Thus, the data from this study may allow the proposed process to claim additional disinfection credits above those for RO or NF alone. The proposed treatment process may eliminate the need for an advanced oxidation process after the NF or RO. To evaluate this hypothesis, total heterotrophic bacteria counts and total coliform bacteria counts will be measured using Hach Membrane Filtration method 8074 [24] and 8242 [25], respectively.

Membrane treatment (NF or RO) are the second treatment stage in this process. The quality of the water is crucial in determining the recovery rate for the membranes. Feed water to the membrane will have high pH value (pH=11) and this will charge the membrane negatively. Operating the membrane at high pH values will result in negative charges on any colloidal particles, dissolved organic matter, and orthosilicate species in the feed solution as well. Therefore, chances for membrane fouling will reduce as observed in high efficiency reverse osmosis (HERO) process [11]. We also hypothesize that this negative charge will result in higher organic contaminants removal for neutral compounds as well as the negatively charged compounds due to the electrostatic effects. In order to test this hypothesis, samples will be taken before and after the FBCR in different pH values of the FBCR effluent ranging from 10 to 11.5. These samples will be analyzed by gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-mass spectrometry/ mass spectrometry (LC-MS/MS) in order to quantify the removal rate of ubiquitous organic compounds in water which possess negative and neutral charges.

Progress to date

During past few months, I was able to reach a more detailed schematic of the process that can treat the secondary effluent to drinking water quality (Figure 3). I was also able to build the pilot plant and design a

[1] A log removal value (LRV) is a measure of the ability of a treatment processes to remove pathogenic microorganisms. LRVs are determined by taking the logarithm of the ratio of pathogen concentration in the influent and effluent water of a treatment process.

controlling system that eliminates any overflows and tank dry-out issues; therefore, providing a 24/7 continuous flow system.

Following is the step-by-step description of the schematics:

- Secondary effluent enters the Porex 10 µm filters, which remove large particles. Then the water is fed into a FBCR maintained at a high pH with base produced by a BMED stack.

- In the FBCR, hardness minerals are removed from solution and precipitate as $CaCO_3$ and $Mg(OH)_2$ on seed particles suspended in the fluidized bed. Effluent from the FBCR then enters the triple filters, which remove particles and precipitates larger than 5 µm.

- The filtered water containing micron and submicron particulates is then fed into a NF module. The feed to the NF is maintained at a high pH, and the NF elements are specially designed to accommodate particulates. Concentrate from the primary NF is fed into a secondary NF for further concentration.

- Permeate from the secondary NF is fed into a BMED stack and is used to produce acids and bases. The base from the BMED stack is used to maintain a high pH in the FBCR. Acid from the BMED stack is used to lower the pH of the NF feed solutions, reduce the pH of the intermediate tank, and is also used to acidify the feed solution to the BMED stack.

- The concentrate from the secondary NF is going to be treated by ferric chloride to reduce the organic contaminants' content before being fed back to the FBCR. The crystallized mineral solids in the FBCR grow over time, and replaced when the pellets' diameters are larger than 2 mm. The pellets are easily dewatered due to their large size and high density via gravity drainage to more than 99% solids, and can be sold for use in making cement [11].

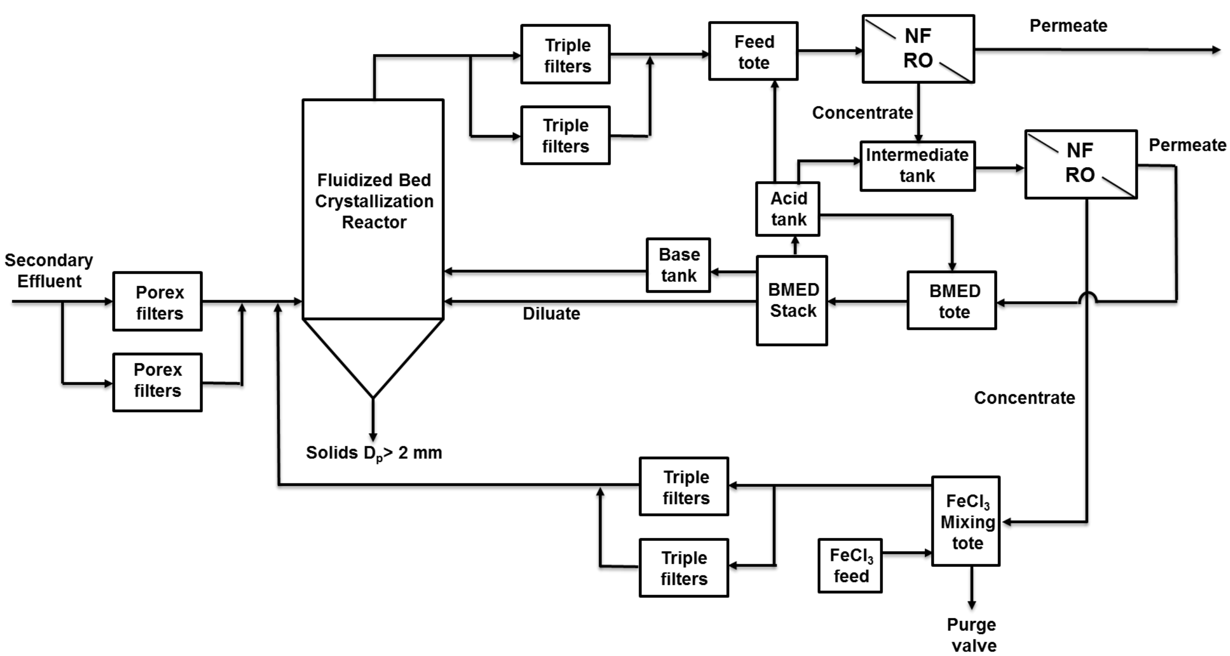

Figure 3. Schematic diagram of proposed treatment process.

Although it looks complicated, this process is smaller and less expensive compared to the current MF or UF pretreatments that are being used for NF and RO. The traditional pore sizes for MF and UF are 0.1 and 0.01 µm, respectively, while the smallest pore size filtration that is being used in this treatment is 5 µm. According to Equation 1, the flux through a MF with pore size of 5 µm will be a factor of 6.25 million greater than the MF with a pore size of 0.1 µm [23]. Therefore, the proposed process requires much smaller pretreatment filtration because our proposed system can tolerate particles up to 5 µm in size while the conventional membrane treatment systems require pre-filtrations of particles bigger than 0.1 µm. This will result in lower costs for the overall treatment process.

$$Flux = \frac{\rho_{pore}\,\pi\,r^4}{8\,\mu\,\tau}\;\frac{\Delta P}{\Delta z}$$ [Equation 1]

Conclusions

The novel aspects of this method are that it generates zero liquid waste and therefore, it increases the clean water production ratio. In addition, by eliminating expensive filtration steps, we can reduce the cost of current treatment methods. There are numerous published research articles about these treatments showing promising results for each of this treatment techniques [3,7,10,11,21,22]. Therefore, testing the combination of these treatments will be worthy.

This new technique will benefit the treatment facilities and water related companies to provide a cheaper treatment option and use a smaller land footprint to treatment the municipal wastewater. It may also reduce the water price for customers or, more importantly, provide cleaner water for low-populated areas where building a water treatment plant used to be costly and unfeasible. It will also protect the environment from the highly polluted waste line that is currently discharged to ocean or deep wells.

If successful, this process will provide a competent alternate for current treatment techniques for water treatment. This process will increase the current 85% recovery to 100%, making the overall process cheaper, producing more clean water, and minimizing the waste line that needs to be treated (or will harm the environment if discharged with no treatment). This process, if successful, will persuade water treatment plants to modify their conventional treatment train with this combination of techniques in order to benefit from abovementioned advantages.

Next steps

Several goals are set for this project. There is a treatment goal for each technique that needs to be achieved:

- FBCR: Effect of pH (10-11.5) and retention time (1-15 min) will be investigated. Higher pH will result in higher removal of inorganic and organic contaminants; however, at very high pH values, homogeneous precipitation is favored over heterogeneous precipitation, which will generate nanoparticles that can clog the next membrane treatment step. Therefore, high pH values must be avoided. If reducing the pH values to minimize the homogeneous precipitation fails, we plan to use a small ion exchange filters after the FBCR to remove magnesium.
- Staged NF/RO membranes: Membranes will be used at their highest recovery rate to produce clean water. This recovery rate is limited to the feed water quality, the level of contaminants' removal in FBCR, and the

physical limitations of the membranes. Saturation index values for the scale-forming species in the feed water will be calculated using PHREEQC software and will be used for making the changes necessary to prevent scaling and fouling of the membranes.

- BMED: Permeate water from the secondary membrane will be used as the feed water to the BMED stack. Using clean water will minimize the fouling on the BMED membranes. However, this feed water to the BMED requires to have some salt concentration (>0.1 mmol) that is necessary for BMED to produce acid with pH values less than 3 and base with pH values greater than 12. Low monovalent ions' rejection in NF membranes prior to BMED stage in the proposed treatment system will provide required salt concentration for BMED operation. Additional information about BMED process can be found in reference 21.

In the following months (summer), I am planning to start taking samples from the system and analyze the results and Based on the data achieved, I am going to optimize each step according to the parameters mentioned above.

References

[1] R.F. Service, Desalination freshens up, Science 313 (5790) (2006) 1088–1090.
[2] D. Gerrity, B. Pecson, R.S. Trussell, R.R. Trussell, Potable reuse treatment trains throughout the world, J. Water Supply Res. Technol. AQUA 62 (6) (2013) 321.
[3] A. Rahardianto, J.B. Gao, C.J. Gabelich, M.D.Williams, Y. Cohen, High recovery membrane desalting of low-salinity brackish water: integration of accelerated precipitation softening with membrane RO, J. Membr. Sci. 289 (1–2) (2007) 123–137.
[4] Hayter, S.; Tanner, S.; Urbatsch, E.; Zuboy, J. Saving energy, water, and money with efficient water treatment technologies. U.S. Department of Energy, DOE/EE-0294.
[5] P. Malmrose, J. Lozier, M. Mickley, R. Reiss, J. Russell, J. Schaefer, S. Sethi, J. Manuszak, R. Bergman, K.Z. Atasi, A.M.R. Management, Committee report: current perspectives on residuals management for desalting membranes, J. Am. Water Works Assoc. 96 (12) (2004) 73–87.
[6] L.Malaeb, G.M. Ayoub, Reverse osmosis technology for water treatment: state of the art review, Desalination 267 (1) (2011) 1–8.
[7] C.J. Gabelich, M.D. Williams, A. Rahardianto, J.C. Franklin, Y. Cohen, High-recovery reverse osmosis desalination using intermediate chemical demineralization, J. Membr. Sci. 301 (1–2) (2007) 131–141.
[8] D. Almasri, K.A. Mahmoud, A. Abdel-Wahab, Two-stage sulfate removal from reject brine in inland desalination with zero-liquid discharge, Desalination 362 (2015) 52–58.
[9] A. Subramani, J.G. Jacangelo, Treatment technologies for reverse osmosis concentrate volume minimization: a review, Sep. Purif. Technol. 122 (2014) 472–489.
[10] M. AzadiAghdam, S. A. Snyder, J. Farrell, A novel brine precipitation process for higher water recovery, Desalination 385 (2016) 69–74.
[11] Van der Veen, C.; Graveland, A. Central softening by crystallization in a fluidized bed process. J. Am. Water Works Assoc. 1988, 80, 6, 51-58.
[12] Graveland, J. C.; de Moel, P. J.; Oomen, J. H. Developments in water softening by means of pellet reactors. J. Am. Water Works Assoc. 1983, 75, 12, 619-625.
[13] van Schagen, K.; Rietveld, L.; Babuska, R.; Kramer, O. Model-based operational constraints for fluidised bed crystallisation. Water Research 2008, 42, 327–337.
[14] Sluys, J. T. M.l Verdoes, D.; Hanemaaijer, J. H. Water treatment in a membrane-assisted crystallizer (MAC). Desalination 1996, 135-139.
[15] Graveland, A.; van Dijk, J. C.; de Moel, P. J.; Oomen, J. H. C. M. Developments in water softening by means of pellet reactors. J. Am. Water Works Assoc. 1983, 75 (12), 619−625.
[16] Harms, W. D.; Robinson, R. B. Softening by fluidized bed crystallizers. J. Environ. Eng. 1992, 118, 513−529.

[17] Santa Clarita Valley Sanitation District of Los Angeles County, Santa Clara River Chloride Reduction Ordinance of 2008.
[18] van Schagen, K. M.; Rietveld, L. C.; Babuska, R.; Kramer, O. J. Model-based operational constraints for fluidised bed crystallisation. Water Res. 2008, 42, 327−337.
[19] Strathmann, H. Ion-Exchange Membrane Separation Processes, Elsevier: Amsterdam, 2004.
[20] Onsager, L. Deviations from Ohm's law in weak electrolytes. J. Chem. Phys. 1934, 2, 599-615.
[21] Davis, J.; Chen, Y.; Baygents, J. C.; Farrell, J. Production of acids and bases for ion exchange regeneration from dilute salt solutions using bipolar membrane electrodialysis. ACS Sust. Chem. Eng. 2015, 3, 2337-2342.
[22] Chen, Y.; Davis, J. R.; Nguyen, C.; Baygents, J. C.; Farrell, J. Electrochemical ion exchange regeneration and fluidized bed crystallization for zero liquid discharge water softening. Environ. Sci. Technol. 2016, in press.
[23] Davis, M. Water and Wastewater Engineering; McGraw-Hill: New York, 2010.
[24] https://www.hach.com/asset-get.download-en.jsa?code=56434
[25] https://www.hach.com/asset-get.download.jsa?id=7639984010