Chloride reduction from brackish water by hollow fiber supported liquid membranes using ionic liquids as a carrier

Tobias Slusarek, Markus Hofmeister, Rafal Madaj, William Stömbäck

Escola Politecnica Superior d’Enginerya de Vilanova I la Geltrú

Abstract- The project “Chloride reduction from brackish water by hollow fiber supported liquid membranes (HFSLM) using ionic liquids as a carrier “ is about developing an alternative and cost effective solution for the Abrera drinking water treatment plant to desalinate water from Llobregat river while accomplishing drinking water standards. With a constant increase of the world’s population, the demand for drinking water also increases. However, the supply of drinking water is limited, so desalination as one part of water treatment is of essential need. The Llobregat river water, as one of the main sources of drinking water in the Barcelona metropolitan area, has a high content of dissolved salts wherefore even already treated water does not always fulfill the quality standards set by the European Union to be classified as “drinking water”. This is why the Abrera water treatment plant currently has to clean its water using the energy – intensive technique electrodialysis reversal.

Therefore an alternative technique, called Hollow Fiber Supported Liquid Membrane (HFSLM), has been investigated. This is a specialized application of new high – tech membrane technology supplying substance transport between two separated fractions using permeable membranes filled with ionic liquids. These liquids are characterized by a high concentration of available carrier – molecules which enable these chemical systems to carry out mass transport particular selectively via ionic exchange between both the phases. Several experiments, using Aliquat® 336 as a representative phase transfer catalyst, have been conducted in order to obtain deepest understanding of the process taking place. As results, on one hand the functionality of this technique was proved and on the other hand delivered enough useful data to develop a scientific model of the transfer mechanism to predict its efficiency in a feasible up – scaled version for industrial use. Since the HFSLM technique as a concentration driven operation needs far less electricity than the common techniques electrodialysis reversal and reverse osmosis, it is already competitive in terms of running costs. The implementation costs on the other hand contain a big potential for improvement.

Index Terms- Abrera Drinking Water Treatment Plant, Desalination, Hollow Fibre Supported Liquid Membrane, ionic liquid Aliquat 336

I. INTRODUCTION

The use of water constantly increases, while supply for clean water decreases. Nowadays more than 1,3 billion people suffer from water shortage (1) and its consequences - with an upward tendency. Not only the growing world's population but also the increasing pollution and the unequally distribution of water are basic causes of the water shortage. There are three basic approaches to solve the problem of water shortage, maximizing the water supply, minimizing the use of water and optimizing techniques for water treatment. The project “Chloride Reduction” investigated the last point, trying to develop a desalination technique for the Abrera drinking water treatment plant, that is more economic than conventional ones, especially the electrodialysis reversal, since its is currently used for the desalination process. Water treatment plants have to eliminate various types of water pollution to restore the drinkability. As one type of water pollution, chlorides will make the water unpalatable, if its concentration reaches a certain level. Therefore the legislation of the European Union introduced parametric standards for drinking water and has set the limit for chlorides to 250 parts per million (ppm). The Abrera drinking water treatment plant has to treat the water from the Llobregat river Common water treatment techniques electrodialysis and reverse osmosis are accompanied by several disadvantages like inefficiency for certain concentrations or high costs of electricity and maintenance. The hollow fiber supported liquid membrane (HFSLM) on the other hand is a promising alternative technique that might be more efficient and less expensive.

The Hollow Fiber Supported Liquid Membrane technique is a specialized application of the membrane technology, which covers all procedural processes of substance transport between two fractions using permeable membranes. It is based on the solution-diffusion model which defines the transport through the membrane as an effect of diffusion. The particles which need to pass through the membrane have to get dissolved in the membrane first before they are able to be transported. The excess chloride ions from the water, which has to be treated (feed phase), are dissolved in the organic phase of the liquid.
membrane. This organic phase contains Aliquat® 336, an ionic liquid, which molecules act as the carrier to transport these ions to the other side of the membrane. Having arrived there the chloride is back – extracted to the stripping phase. The back extraction is the same process like the former extraction, just carried out vice versa.

The procedure of an ordinary ionic exchange represents the fundamental idea of our transport process through the membrane: Chloride ions are extracted from the feed and build transportable compounds with the Aliquat® 336 molecules. Due to an increasing concentration of this Aliquat® 336 – chloride complex at the feed – membrane interface the concentration gradient inside the membrane increases as well and this compound is transported to the other side of the membrane in order to establish an homogeneous concentration level over the whole membrane. In interaction with the bicarbonate anion at the stripping interface the chloride ion is set free and replaced by bicarbonate which is afterwards transported to the feed phase.

\[ \text{Aliq}^+\text{HCO}_3^-_{\text{org}} + \text{Cl}^-_{\text{aq}} \leftrightarrow \text{Aliq}^+\text{Cl}^-_{\text{org}} + \text{HCO}_3^-_{\text{aq}} \]

Generally speaking, an ion transportation circle such as seen in figure 1 gets established. To make this process useful the volume of stripping used during the process has to be much smaller than the volume of feed, otherwise the chloride contamination would just get translocated. But by transferring the chloride to a smaller volume two advantages can be achieved: The volume of polluted water decreases and, second, the concentration of chloride in the stripping phase will be much higher than in the feed what might make it useful to use this brine for salt production.

To investigate the functionality of the HFSLM technique three experiments have been carried out in the laboratory. The first experiment was the equilibrium investigation and the preparation of the phase transfer catalyst. On the one hand it helped to determine the state of chemical equilibrium of the balance extraction reactions we were looking at and on the other hand it was needed to prepare the phase transfer catalyst since Aliquat® 336 is sold in combination with chloride ions which have to be replace by bicarbonate first. The second experiment, Flat Sheet Supported Liquid Membrane, was about testing the functionality of the technique with a simple flat sheet membrane and achieving results in order to make a mathematical model of it. Lastly the third and most important experiment was about investigating the Hollow Fiber Supported Liquid Membrane technique itself. Since upscaling this technique to industrial use in the Abrera drinking water treatment plant was the main aim it had to deliver all the needed data for implementing a model in matlab.

II. MATERIAL AND METHODS

A. Phase transfer catalyst - Aliquat® 336

The Phase transfer catalysis (PTC) is a special form of heterogeneous catalysis, what means that catalyst and reactants are not present in the same phase or even not in the same state of matter. The PTC facilitates the transport of a reactant from one phase into another through a phase which could not be passed without these carrier molecules. So is chloride easily soluble in an aqueous phase but insoluble in an organic one in the absence of the phase transfer catalysts. That is the reason why an ionic carrier is needed to enable chloride to migrate through the organic SLM which separates feed and stripping phase from each other.

Aliquat® 336, known as Stark’s catalyst, is a hydrophobic anionic liquid, quaternary ammonium salt and a mixture of octyl and decyl chains which offers good attributes as a phase transfer catalyst. The choice of Aliquat 336® was imposed by our supervisors, but anyway, it is one of the the best choices for single-ion transfer carrier because of the following reasons [2]:

- It is cheap
- It is easy to be used by unqualified personnel, as:
  - It is not highly volatile, whereas the majority of another PTC’s are
  - It is chemically and thermally stable
  - It is almost solid, what supports easy handling and chemical operation
- The created salts inside are not soluble, thus they precipitate and may be easily filtered out

The transportation mechanism through the membrane is affected by two properties of the PTC: the concentration and the viscosity. The higher the concentration the more chloride molecules can be transferred at the same time. But on the other hand a higher concentration of 336 also affects a higher viscosity of the organic phase inside the membrane due to its relatively high viscosity what has a negative influence on the velocity of the Aliquat® 336. Therefore it is necessary to investigate various Aliquat® 336 mixtures with different concentrations in order to obtain the best relation between
these two contrary features in the sense of efficiency of the chloride transport.

B. The bicarbonate anion

Sodium bicarbonate (NaHCO3) is a slightly basic salt used in our experiment as an aqueous solution for replacing chloride anions (Cl-) with bicarbonate anion (HCO3-). It is able to substitute Cl- anions in the Aliquat – molecule and enforces the chloride transportation thereby.

For our project the use of NaHCO3 has numerous advantages:

- It is cheap – the price for laboratory requirements is about 20 €/kg, whereas larger amounts for industrial use – 0.2 €/kg
- It is easy to use
- It is possible to create wide range of mixture concentration due to high solubility (10.3g NaHCO3 / 100g H2O)
- As a powder it is a stable and non-toxic compound, due to which it does neither require qualified personnel nor special equipment to be used
- Instead it even has a good effect on human health: It reduces acidity of dietary components, has prevention effects on dental cavities, reduces muscle fatigue and provides a more stable acid-base balance
- Unlike sodium chloride, it does not increase the blood pressure

C. Equilibrium investigation and preparation of the phase transfer catalyst

This experiment helped to determine the state of chemical equilibrium of the balance extraction reactions we were looking at. On the other hand, in the condition as it is sold, contains itself a high fraction of chloride ions as it is composed of a large organic cation associated with a chloride anion as shown below.

\[
\text{Fig. 2 : Chemical structure of Aliquat® 336}
\]

Since the following FSM and HF experiments should deliver truthful data about the transportation process through the membrane, we considered it as useful to change the chloride ions in the Aliquat® 336 for bicarbonate at the beginning of all our experiments. Lowering the chloride concentrations inside the membrane minimizes the sources for experimental errors when measuring the chloride concentration evolutions in the feed and the stripping cell because the possibility of releasing additional chloride ions from the used Aliquat® 336 can almost be precluded.

First of all, the organic phase with its certain amount of the ionic liquid as carrier has to be prepared. 20 volume percentages of it poured in a decanol / kerosene mixture were used to ensure thorough impregnation of the solid organic membrane. Without these organic solvents this might lead to a problem because of Aliquat® 336’s quite polar behavior.

Furthermore a sodium bicarbonate solution was needed to wash out chloride anions from Stark’s catalyst. To prepare the Aliquat® 336 solution, following reagents were mixed:

- 100 ml of aliquat 336
- 50 ml of Decanol
- 350 ml of kerosene

The obtained mixture was a viscous, yellow fluid. In order to prepare the solution of NaHCO3, 2 liters of bidistilled water were mixed with 151.2g of solid sodium bicarbonate. The solution was heated in order to obtain better solubility of the solvent. Afterwards the whole Aliquat® 336 mixture was put into a separator together with 500ml of bicarbonate solution. After that, the separator has been put into a mechanical shaker for 20 minutes in order to perform the ion exchange, which reaction is as follows:

\[
\text{Aliq}^+\text{Cl}_{\text{org}}^- + \text{HCO}_3^-_{\text{aq}} \leftrightarrow \text{Aliq}^+\text{HCO}_3^-_{\text{org}} + \text{Cl}_{\text{aq}}^-
\]

The next step was to separate the two phases again in order to remove the aqueous phase and to measure its amount of out washes chloride ions. These two steps have been repeated several times to gain enough data to evaluate the equilibrium constant of the chemical reaction shown above. The phrase “washing” is used to illustrate the procedure we were using, but actually a real chemical reaction has taken place all the time.
Fig. 3: Separator filled with organic phase after shaking, aqueous phase already withdrawn into the beaker

In order to determine the chloride concentration in the aqueous phase the common method of potentiometric measuring was used: Into a beaker filled with approximately 50ml of specifically bidistilled water (free of chloride anions) a small volume sample of aqueous phase was poured. Then, 2ml of concentrated nitric acid was added to acidify the environment. Afterwards the potentiometric measurements accompanying titration with silver nitrate has been conducted.

Silver chloride is almost not soluble in water and flocculates. By measuring the added volume of silver nitrate and knowing its concentration the present concentration of chloride in the aqueous phase can be obtained.

D. Flat Sheet Supported Liquid Membrane (FSSLM)

In the next stage of our experimental investigation numerous experiments with FSSLM were conducted. This was necessary due to two main reasons: On the one hand this approach lead on to a first overall impression of the desired transport process and on the other hand the mathematical model of such a dead-end membrane geometry appliance is much easier to obtain than an appropriate one for cross-flow arrangements.

Fig. 4: Silver nitrate titration apparatus

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Fig. 5.: Schematic structure of a flat sheet membrane cell, feed phase left (3)

The flat sheet supported liquid membrane is the simplest form of the liquid membrane. The solid support is impregnated with the organic phase containing phase transfer catalysts and is clamped between two half cells using gaskets thus forming two compartments as shown above. One compartment is for feed solution and the other compartment contains the stripping phase. Both the phases are stirred by mechanical stirrers (Fig. 6).

Corresponding to the value Keq the chloride ions from the feed phase interact with the organic phase of the membrane and are partly removed from the aqueous phase. Because of this an imbalance of the chloride concentration in the membrane occurs which leads to diffusional movement of $[\text{Aq} - \text{Cl}]$ – particles to the other site of the membrane in order to recondition homogeneity. Arrived at the other site these molecules start to react with the aqueous phase in the stripping cell get back extracted. The extraction processes on both sites of the membrane can be modeled by using Keq from the former experiments. The only remaining unknown value is the constant of transport according to Fick’s law of diffusion inside the membrane.

$$ Cl^-_{\text{Aq}} + Ag^+_{\text{Aq}} \rightarrow AgCl $$
In comparison to similar balance processes, such as known from heat transfer, this procedure does not stop when equal concentration levels are reached in both cells: The main driving force of this transport mechanism is the high initial concentration of bicarbonate (adjusted to 0.9 M in our experiments) in the stripping solution which is almost 50 times as high as the initial concentration used for chloride (round about 0.02 M, which is an appropriate value to simulate the current contamination of brackish water here in the El Llobregat region). The high gradient in the bicarbonate concentration causes that almost all the chloride ions are extracted from the feed and transported to the membrane-stripping phase interface where they are back-extracted almost completely according to the local chemical equilibrium. This results in an continuous chloride concentration gradient inside the membrane accompanied by ongoing diffusion to the stripping phase far beyond an equal concentration level in both cells.

The experiments consisted of two cells and a flat membrane impregnated with different Aliquat ® 336 mixtures in between. The used flat sheet membranes are composed of polyethylene supported by a Teflon mesh. One of the cells, the so called stripping cell, was filled with an aqueous solution of sodium bicarbonate and the other one, the feed cell, with a mixture of sodium chloride. By filling the second cell, the chemical process of chloride reduction from the feed cell was initiated. Subsequently the evolution of the chloride concentration was determined. Therefore the feed phase was sampled and measured at certain times. In order to avoid unnecessary experimental errors, a solution of approximately the same volume and concentration as the taken sample was given back to the feed cell all the time after measuring each sample.

These experiments were conducted with a volume of 210 ml both for feed and stripping phase. As feed phase a solution of 1 g sodium chloride per liter of bidistilled water was used. The stirring apparatuses were adjusted to round about 1100 turns per minute to ensure thorough mixing in the cells. This procedure helps to find a relation between the velocity of the chloride reduction and the amount of phase transfer carrier molecules in the organic phase.

E. Hollow Fiber Supported Liquid Membrane

The third and most important experiment of the project was the investigation of the chloride concentration reduction in a HFSLM module in lab scale. Since the membranes in such modules are arranged in cross-flow position they are able to extract chloride from the flushed through feed phase continuously. By the help of continuous flows through the module the settling of particles at the membrane surface is reduced what extends both the lifetime and the efficiency of these membranes. These advantages make this technique particular interesting for industrial use and underline the necessity of a precisely investigation of its transport phenomenon.

The outer cell of the module is made out of a single nonporous material through which the solution, present inside, cannot be transported. Inside the shell, many thin fibers are packed in neat rows. In the present case the stripping phase passed through the fibers and the feed phase through the shell side by the help of gear pumps.

Fig. 7: Experimental setup of HFSLM process (4)
The pressure in the apparatus has been reduced to its minimum what stirring system so as to produce a thorough emulsion the remaining 150 ml of organic mixture and starting the bicarbonate solution in the feed and 150 ml of sodium bicarbonate solution. Afterwards the apparatus has been started with 300 ml for the proper measurements due to reasons mentioned further below. In comparison to the FSSSLM process the volumes of feed and stripping were not equal any more but chosen with a relation of 10 : 1 to approach our measurements to the finally required conditions: 5l of bidistilled water in the feed phase were washed with 0.5l of sodium bicarbonate stripping solution. Considering the hold – up volumes in the module, 400 ml of bicarbonate solution and 4720 ml of water were put in the apparatus. Due to fact that as a result of the steady flow small volumes of organic phase might get pulled out of the membrane the restrained 50 ml of organic mixture were added to the stripping so as to replace these possibly losses which import for supplying membrane stability.

The feed phase was carried shell – side with an adjusted pressure difference of 0.2 bar compared to the stripping shell – side. This supports the chloride transport and prevents that organic particles might get pushed into the to cleaned water. Both the flows were set to 51 l/h. After the stabilization of the process, the measurements of chloride concentration were done by sampling at different times using titration with AgNO3, like in case of previous experiments with flat sheet membranes. After taking each sample a proper amount of membrane. Therefore the replacement of the organic phase from the former experiment was essential and done like this: According to the desired volume percentage of PTC in the liquid membrane (25 %v, 50 %v, 75 %v and 100 %v) an appropriate volume of the very initial washed out Aliquat ® 336 mixture was given to a corresponding amount of a 10 %v decanol – 90 %v kerosene mixture in order to obtain 200 ml organic phase in general.

The experimental investigation itself proceeded quite similar: 5x

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![Fig. 8:Experimental setup of the HFSLM experiment](image)

50 ml of this mixture were withdrawn afterwards and saved for the proper measurements due to reasons mentioned further below. After adding the remaining 150 ml of organic mixture and starting the stirring system so as to produce a thorough emulsion the pressure in the apparatus has been reduced to its minimum what leads to a pressure difference of about 0.3 bar between the stripping tube – and the feed shell – side. Subsequently this pressure gradient forces the organic liquid through the hollow fibers. Having received at least 100 ml of organic phase in the feed beaker the replacement of “old” liquid can be seen as completed due to the empirically obtained volume of organic liquid which sticks inside the fibers of about 50 ml.

The last step was washing the module several times with bicarbonate solution and bidistilled water to ensure the module being free of chloride residues and organic phase which is not stuck in membrane.
1000 ppm chloride and distilled water was added to maintain volume and concentration equilibrium.

Sampling has been conducted every several minutes or hours, dependently on the process. Under the terms of its chemical fundamentals and as visualized by the flat sheet experiments, the difference between the concentration is getting smaller with increasing time. The experiment was stopped when this difference reached a value near zero as the equilibrium of the process was established. Besides the chloride measurement also the pH value and the temperature of the feed phase were observed in order to obtain an even more comprehensive impression of the process.

III. RESULTS

The present chloride concentrations measured during all the experiments are summarized in Table 1. The last few measurements fluctuate a bit and are not constantly increasing. They might derive from small temperature changes in the feed solution during the measurements or, even more presumable, due to a lack of accuracy while taking the samples. Problems with proper mixing would have a much higher influence than temperature. Nevertheless these errors are small and do not affect the final result massively.

![Graph](image1)

**Figure XXX: Measured chloride evolution compared to the limit set by the EU standard for drinking water (250 ppm)**

Since the organic liquid is stuck inside the membrane, once filled in, it can be seen as used over the whole life – time of one hollow fiber module. Therefore the impact of its costs on the overall cost-efficiency is not that significant and can remain unassumed.

IV. UPSCALING

Since the project’s aim is to replace Abrera’s electrodialysis reversal process with the investigated Hollow Fiber Supported Liquid Membrane technique, the achieved results from the experiments have to be upscaled to match the values used by the Abrera drinking water treatment plant. That means an output of 4m³ cleaned water per second has to be realized. It is not only important the check if it is possible to apply the HFSLM process in industrial scale, but also to compare its competitiveness in terms of costs, efficiency and sustainability to the common techniques used for desalination, especially electrodialysis reversal. Currently the electrodialysis reversal used in Abrera reduces the chloride concentration to an average of 226ppm with an output of 4m³ per second.

To achieve best possible configuration for cost efficiency the following ideas have to be taken into account:

- Optimize the number of modules, since their price is very high
- Choose proper pumps in order to maintain the desired flow with the lowest power use
- Optimize the sodium bicarbonate concentration
- Find the optimum rejection percentage of bicarbonate

By using MATLAB® to model the process it was possible to estimate the optimal parameters for both possible types of modules, counter-current and concurrent flow, in order to decrease the costs for membranes and minimalize the maintenance costs deriving from washing-out chloride anions.
using sodium bicarbonate. It was assumed that the starting chloride concentration will be around 600 mg/l, targeted to be decreased up to about 200 mg/l. The results are as follows:

Counter-current flow
- Flow – 1.225*10⁻⁴ m³/s
- Initial concentration of bicarbonate for washing – 0.13 M
- Concentration of bicarbonate after washing, in stripping solution – 0.0165 M
- Final concentration of chloride anions in treated water – 197.443 ppm
- The percentage of bicarbonate to be wasted after treatment – 12.67%

Concurrent flow
- Flow – 1.888*10⁻³ m³/s
- Initial concentration of bicarbonate for washing – 0.51 M
- Concentration of bicarbonate after washing, in stripping solution – 0.3977 M
- Final concentration of chloride anions in treated water – 202.196 ppm
- The percentage of bicarbonate to be wasted after treatment – 78.00%

Based on these values one may observe significant differences between concurrent and counter-current flows. Due to the concentration of bicarbonate used and rejected counter-current flow is much more efficient and the costs were calculated only for this one. Therefore the estimated costs for the HFSLM technique with counter-current flow are as follows:

- Number of modules – 35556
- Purchase price – 533 333 333 €
- Sodium Bicarbonate price for 1st year – 30 610 944 €
- Supply for bicarbonate every year – 3 876 886 €
- Estimated energy costs per year – 599 184 €
- Treatment of solution used for stripping – 0.023 €/(1 m³ of product)
- Average price for production of 1 m³ of clean water using HFSLM – 0.2523 €

While electrodialysis reversal has a relatively high demand for electricity reverse osmosis requires high pressures and has therefore a high electricity demand as well. Since HFSLM is neither electric potential gradient driven, nor pressure driven, the required energy will be less. It only needs the pressure to maintain, in our case, 4 m³/s and electricity for pumping. The overall electricity demanded by RO for efficiency equal to desired by us is 1.41 kWh per 1 m³ of treated water. It generates cost about 0.14 € for cleaning 1 m³. All of upper estimations were done using ROSA software (5). The overall electricity demand for electrodialysis in Abrera Water Treatment Plant is equal 0.6 kWh per 1 m³ of treated water (6). The energy cost for cleaning 1 m³ is about 0.058 €. In case of HFSLM the energy demand is equal 0.1975 kWh per 1 m³ of treated water. The energy cost then is equal 0.0196 € for cleaning 1 m³.

V. Perspective

During our experiments we only have investigated the functionality of the HFSLM technique from chloride concentrations from 200 ppm to 600 ppm, because these are the values the Abrera drinking water treatment plant has to treat. The definition of brackish water implies concentrations up to 3000 ppm, so future investigations should carry out experiments to test the efficiency of this technique for higher chloride concentrations. The higher the chloride concentration, the more bicarbonate will be replacing it, this is why the HFSLM technique might be unsuitable for seawater desalination. If the technique is applicable for higher concentrations and therefore able to treat every kind of brackish water, it would open a huge market of possible clients. India for instance has the world’s biggest lake of brackish water (Chilika Lake) and a huge demand for clean water as well. In addition to this China and Turkey have a similar situation. Even if the HFSLM technique is not efficient for higher concentrations, it can be used for the concentrations it works the best in combination with other techniques as an all-in-one solution for water treatment.

The used Hollow Fiber Membranes were originally build to degas water, so the technique might be more efficient with Hollow Fiber Membranes especially designed for the purpose to desalinate water. Since the Hollow Fiber Membrane modules are one of the most important cost drivers and a large number of them is needed, developing a custom-made Hollow Fiber Membrane for desalination might enable a significant cost reduction.

During the upscaling part of the project we have figured out that our module is a bit more expensive than one of the techniques on the market (Electrodialysis), and therefore it could may be done in another way of thinking. Instead of upscale our module to clean a big amount of water it could be downscaled for just cleaning drinking water in households. According to a research made by “Vattenfall” a Swedish water production company, every person use 160L of water every day. For personal hygiene 40% of water is used, toil visits 20%, dishing 20%, laundry 13% and only 7% for drinking water. Therefore the amount of water with low chloride concentration could be reduced significantly.

The first step would be that the big water treatment plants would only do the pre cleaning of the water that is needed. Get rid of all bigger and harmful particulars. And then flow the water out to a households area where a smaller cleaning plant would be made for the drinking water. From that module it would be made pipes to every household with a freshwater output that you only connect to the kitchen. And to every other water needed facilities in the households it could just come water directly from the water treatment plan.

This could be invented to new neighborhoods where energy costs and a green thinking is important. If this would be done before the construction has taken place there would be no need for extra planning for all new pipes.

Other thing that could have been done to improve our project could be to check other anion for binding with Aliquat336®.
nitrates etc. And other liquid membrane types to clean water from other particles as sodium which is responsible for hypertension. Finally our project turned out to be pretty good compared with the other techniques on the market. With a half year more of work and research different solutions the results would have been improved significantly.

REFERENCES