THE POSSIBILITIES OF WATER REUSE FOR POTABLE WATER SUPPLY – A STUDY OF NANOFILTRATION AND OZONATION

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Abstract
The objective of this study was to evaluate if wastewater may be utilized as potable water resource using nanofiltration (NF) and NF in combination with ozonation. In a pilot plant the volume reduction factors (VRF) of 5, 10 and 20 was studied. The recovery ratio for NF is normally 50-85% which corresponds to a VRF of 2-7. This results in a large waste stream with persistent substances present that must be removed from the environment and the water cycle. At a VRF of 60 the waste stream would correspond to 1.7 % of incoming flow to the wastewater treatment plant (WWTP) which is a reasonable volume to handle in a post treatment. To evaluate the possibility to achieve an acceptable level of reduction of pharmaceuticals and simultaneously bring about a volume reduction of the waste stream a study was performed with NF in combination with ozone at VRF 60. The feed to the pilot plant was effluent from a BNR plant, with final sand filtration including chemical precipitation for phosphorous removal.

At VRFs 5-20 the reduction of pharmaceuticals with a molecular weight, MW > 300 g/mol was good, between 65-100 % based on mass flow. Substances with MW < 300 g/mol varied between 5-60% in reduction. The combined processes of NF with pre- and post-ozonation at VRF 60 had removal levels of 99%. The retention of pharmaceuticals by NF was lower than desired and the major reduction occurred in the ozonation. To achieve higher retention it might be necessary to use reverse osmosis (RO) for concentration of the waste stream.

Keywords; *nanofiltration, ozonation, pharmaceutical residuals, wastewater reuse*

Introduction

In urban areas the length of the water cycle is constantly reduced due to increasing wastewater discharge and larger extraction of fresh water. With the increasing population follows an increased use of personal hygiene products, domestic chemicals and pharmaceuticals. Since many of these substances are not easily biodegradable this results in a larger amount of substances passing through the wastewater treatment plants reaching the receiving waters. The environmental effects of these substances in the aquatic environment are still largely unknown, especially in long term aspects (Carlsson et.al 2006).

Many times these recipients are also a potable water resources, in the potable water of Stockholm, the capital of Sweden, 10 pharmaceuticals has been detected (Stockholms Läns Landsting, 2008) due to unplanned potable reuse. Even though the concentrations have been low, most of them below 1 ng/l, it indicates that the conventional wastewater treatment plants, the retention time in the recipients/reservoirs, and the water treatment plants are not enough or sufficient to eliminate trace substances to reach our potable water.

In concern of the environment and of health aspects the natural hydrologic and man-made water cycles have to be regarded as one system. Wastewater is a resource, especially in arid areas where municipal wastewater will be produced even through droughts, which can be

treated to a required level depending on planed use and local needs. To what extent the wastewater should be treated depends on possible areas of reuse, local conditions and the acceptance of the public.

Most important to protect public health is the multiple barriers concept. These barriers are designed for reducing the amount of microorganisms and chemical substances to an acceptable level, normally to adjusted drinking water standards. The multiple barriers can be described as; treatment barriers, strategic barriers and stand-by barriers (Du Pisani, 2004).

To protect public health the requirements of treatment when used as a potable resource is high. Most countries practising indirect or direct potable reuse today have based their water quality requirement on WHO (WHO, 2006, WHO, 2008) and US EPA (USEPA, 2004) guidelines and adjusted them to local requirements. The Australian guidelines are the most exhaustive today with absolute values for many micro organisms, chemicals and pharmaceuticals.

Reverse Osmosis (RO) has shown to be efficient in removing many organic trace substances and viruses, but is an expensive process, and is used today, among others in Orange County and Singapore (Lim Chiow Giap, 2005). One option to reduce costs and still maintain high removal levels would be to use nanofiltration (NF).

The recovery ratio for NF is normally 50-85% which corresponds to a volume reduction factors (VRF) of 2-7. This result in a large waste stream that is discharged to a recipient, returned to the WWTP or treated depending on regulations and possibilities. Environmentally, and in areas were water is constrained, the last option is the only sustainable one, but with volumes of 15-50% of incoming water to a treatment plant, unrealistic.

The objective of this study was to investigate NF as a possible treatment process for indirect potable reuse in concern of pharmaceuticals. To evaluate if an acceptable reduction level could be reached for augmentation to a potable water resource and simultaneously bring about a volume reduction of the waste stream suitable for further treatment a study of VRF 60 was performed. This corresponds to 1.7 % of the incoming flow to the WWTP. The results have previously been reported (Flyborg et. al, 2009). This is a reasonable volume to handle in a post treatment step as well as it provides a potential to deliver a large amount of treated wastewater for reuse purposes.

Three setup configurations were evaluated;

- ✓ nanofiltration at VRF 5, 10 and 20
- ✓ nanofiltration of treated wastewater at VRF 60 followed by ozonation
- ✓ ozonated treated wastewater followed by nanofiltration at VRF 60

Materials and methods

Selected pharmaceuticals

Stockholm Water Co runs a project with the main objective to investigate methods for reducing the loads of pharmaceuticals from the WWTPs. A pilot plant was built where additional advanced treatment techniques of degradation of pharmaceutical residuals has been studied (Wahlberg, et. al 2009). Ozonation and NF are two of the tested methods. Another objective for the project is to evaluate fluxes in the urban waters (wastewater, drinking water and receiving waters) for a broad spectrum of pharmaceutical residuals (or Active pharmaceutical ingredients, APIs) in the region of Stockholm.

The selection of pharmaceuticals for analyses was made based on the highest sales volumes within the respective ATC code (Anatomical Therapeutic Chemical Classification System), on reports of suspected adverse environmental effects and different chemical structures (table 1).

Table 1. Substances investigated,

Acetaminophen	Enalapril	Ketoprofen	Propranolol
Amiloride	Enrofloxacin	Lansoprazole	Pyrantel
Amiodarone	Erythromycin	Loratadine	Raloxifene
Amlodipine	Estradiol	Losartan	Ramipril
Atenolol	Estriol	Metoprolol	Ranitidine
Atorvastatin	Estrone	Metronidazole	Risperidone
Azithromycin	Ethinyl Estradiol	Mianserin	Salbutamol
Bendroflumethiazide	Febantel	Mirtazapine	Salmeterol
Bromhexine	Felodipine	Mometasone	Sertraline
Bromocriptine	Fentanyl	Naproxen	Simvastatin
Budesonide	Flunitrazepam	Nelfinavir	Sulfamethoxazole
Carbamazepine	Fluoxetine	Nitenpyram	Tamoxifen
Carvediol	Fluvastatin	Norethindrone	Terbutaline
Cefuroxime	Fluvoxamine	Norfloxacin	Tetracycline
Cetirizine	Furosemide	Norgestrel	Thioridazine
Ciprofloxacin	Gemfibrozil	Ofloxacin	Tramadol
Citalopram	Glibenclamide	Omeprazole	Trimethoprim
Clozapine	Hydrochlorthiazide	Oxazepam	Tylosin
Codeine	Hydrocortisone	Oxymetazoline	Warfarin
Cyclophosphamide	Ibuprofen	Oxytetracycline	Xylometazoline
Desloratadine	Ifosfamide	Paroxetine	Zolpidem
Diazepam	Ipratropium	Praziquantel	Zopiclone
Diklofenac	Isosorbide Mononitrate	Prednisolone	
Doxycycline	Ketoconazole	Propoxyphene	

Analyses

The chemical analysis was performed by a contracting laboratory (Eurofins in Lidköping, Sweden). The APIs were analyzed using concentration by SPE (solid phase extraction), elution with methanol and final detection and quantification of the analytes by LC-MS/MS (Karlsson, 2008). The analysis performance can only detect the parent substances. If the substance is in a conjugated form (an extra, small molecule added to the API in the human body) it may be transformed back and forth to a "detectable" form or not. This limitation of the analysis is evidently a (mass flow and concentration) problem at the evaluation the tests.

Calculations are based on "limit of quantification" – LOQ, which corresponds to and is defined as three times LOD (limit of detection).

$LOQ = 3 * LOD$

The Membrane Unit

In the tests two commercial nanofilter membranes from Hydranautic, ESNA1-LF-4040, spiral wound thin film with aromatic composite polyamide were used. The nominal area of each membrane is 85 ft^2 (about 7.9 m^2) and the nominal molecular weight cut-off (MWCO) of the membranes is 150 Da (Boda R, information from Hydranautic,).

The membrane pilot plant unit was designed to work in a semi-continuously mode. The two NF membranes were arranged as a two staged array system. Every 20 min the process was stopped for 20 seconds to let the membranes relax and allow for backflow diffusion.

Incoming treated wastewater was continuously pumped to a tank with an overflow arrangement from where it flowed by gravity to the work tank of 180 litres. The total volume of the membrane unit was 200 litres. The feed was pumped through a cartridge filter, with mesh 10 µm, to the membrane high pressure pump, figure 1.

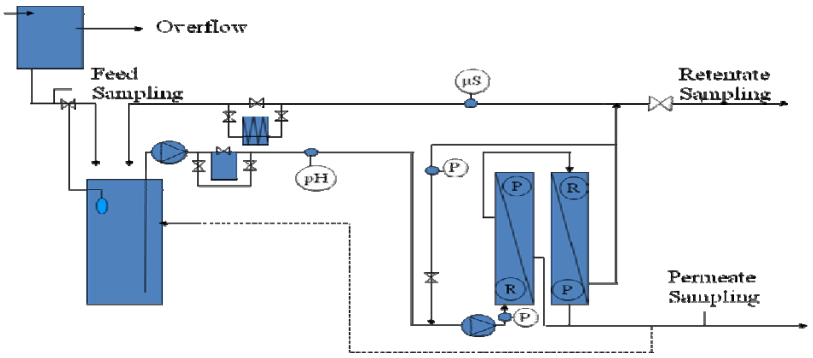

Figure 1. Outline of the membrane unit.

The Ozone Unit

Ozone was produced by a corona discharge ozonator (Ozone Tech, ICT-10) fed by oxygen from a 50L gas cylinder (Linde Gas AGA, Oxygen, approximately 99,5% purity). The gas mix of oxygen and ozone was led to an injector to be dissolved into the pretreated wastewater. The wastewater was pumped at a flow of 420 L/h and pressurized to 3 bar absolute pressure during 2 minutes, after which the wastewater passed a 5 m high column with a retention time of 25 minutes. As a final treatment the ozonated wastewater was aerated for about 20 min to remove residual ozone, figure 2.

The same ozone dosage of 5 gO_3/m^3 was used in the two different operation alternatives.

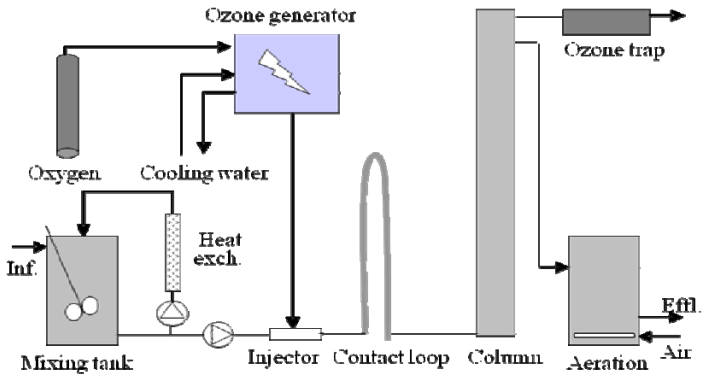

Figure 2. Outline of the ozonation process.

Pilot plant test

Three tests were performed, the first test with NF at VRF 5, 10 and 20, had a duration of 3 hours while the two following tests, NF with post- and pre-ozonation had a duration of about 2 days each. In the tests with NF and ozonation flow proportional sampling were conducted

which results in an underestimated reduction level while the first test with NF grab sampling were made.

The experiments were performed at a water temperature of the work tank between 20.7 and 24.6 ºC where the temperature was adjusted by the recycled retentate passing through a heat exchanger. To keep chemical use as low as possible no pH adjustment was made, but kept under observation. pH during the test ranged between 6.1 and 6.9.

The pilot plant feed was the effluent from Henriksdals WWTP, a BNR plant with a final process step of chemical precipitation for phosphorous removal and rapid sand filtration. The tests were performed under the normal fluctuations of temperature, pH, conductivity and loads for a WWTP effluent.

Two methods of calculation of the reduction of pharmaceuticals are presented, see figure 3. Reduction of substances considering;

a) mass flow through the membrane unit at each VRF, regardless of operational mode, in percentage of each specific substance and expressed as total sum of pharmaceuticals
b) the concentration difference over the membrane

In the calculations only substances that are over LOQ in the feed (effluent from Henriksdal WWTP) is regarded.

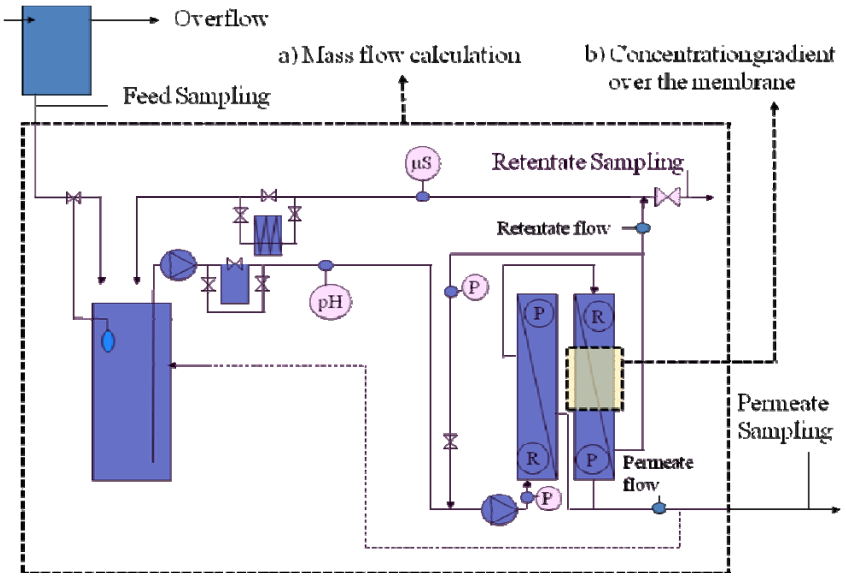

Figure 3. Definition for the calculations for a) mass flow and b) concentration gradient.

Nanofiltration of treated wastewater

Of the 94 pharmaceuticals analysed 54 were below LOD in the feed water in all tests. In total 40 substances were over LOQ, with small variation of substances for the different tests. Of the substances over LOQ 16 did at some point show an imaginary increase instead of reduction (see Analyses and table 2). These values have not been taken into account in the evaluation and are discussed under Discussions and Results.

Reduction over Nanofiltration at VRF 5, 10 and 20

To evaluate the potential of nanofiltration as a process for indirect potable reuse a test were conducted for VRF of 5, 10 and 20. This corresponds to recovery rates of 50%, 90% and 95%. Feed water temperature was between 20.6-21.1˚C, pH 6.3-6.4 and conductivity 0.59 mS/cm. In the work tank the temperature was 20.4 and pH between 6.1-6.8. The conductivity of the permeate and retentate were 0.37-0.39 mS/cm and 1.9 mS/cm (VRF 5), 3.6 mS/cm (VRF 10) and 4.0 mS/cm (VRF 20).

In the test 24 pharmaceuticals in the feed water to the NF could be detected at levels above LOQ. Of these substances, eight did at some point show an imaginary increase in the permeate (see Analysis and table 2). The overall reduction for VRF 5, 10 and 20 were 39%, 18% and 20% respectively expressed as total sum of pharmaceuticals in concentrations over LOQ. Reduction of pharmaceuticals at each VRF and molecular weight are shown in figure 4.

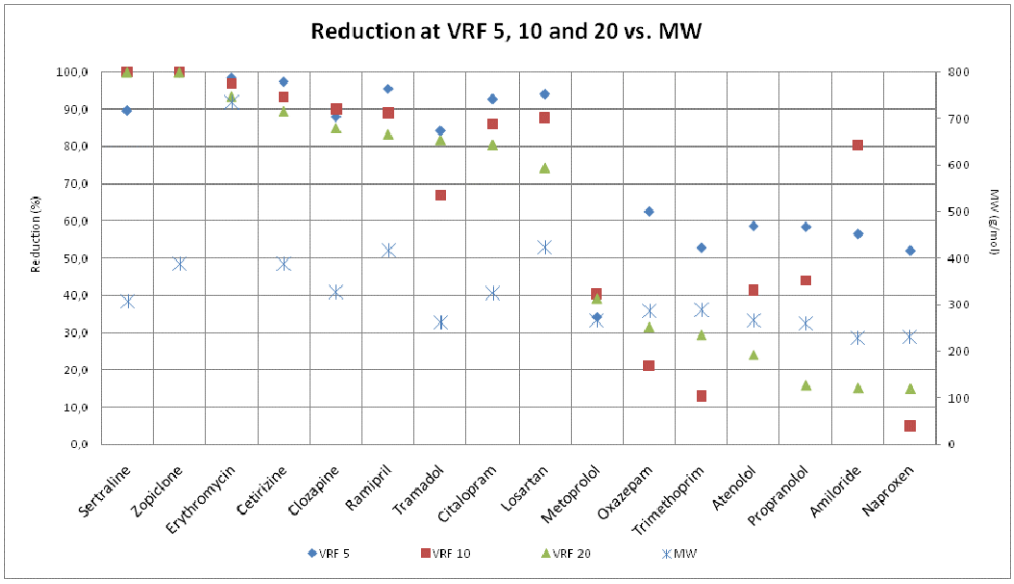

Figure 4. Reduction of pharmaceuticals calculated on mass flow.

Reduction over Nanofiltration and Ozonation

To evaluate the possibility of NF to produce an acceptable level of pharmaceuticals in the permeate and simultaneously bring about a volume reduction of the waste stream suitable for further treatment the NF was operated at VRF 60. As a second treatment step ozonation was used. Feed water to the pilot plant had a temperature of around 21.5 ºC, pH between 6.3 and 6.9 and conductivity between 0.59 and 0.74 mS/cm. In the work tank, to which the retentate was brought back and mixed with incoming water, the temperature varied between 22.5 and 24.6˚C and pH between 6.3 and 6.8. The conductivity of the permeate was between 0.50 and 0.54 mS/cm.

23 substances were over LOQ in the feed water and out eight showed an imaginary increase (see Analysis and table 2). The substances reduced are shown in figure 5. The highest retention was 89% and the average retention was 32%.

After ozonation only Oxazepam was over LOQ levels. Oxazepam was reduced with 16% over NF, 93% over ozonation and in total with 94 %. The overall reduction for the combined processes NF followed by ozonation were 99% expressed as total sum of pharmaceuticals.

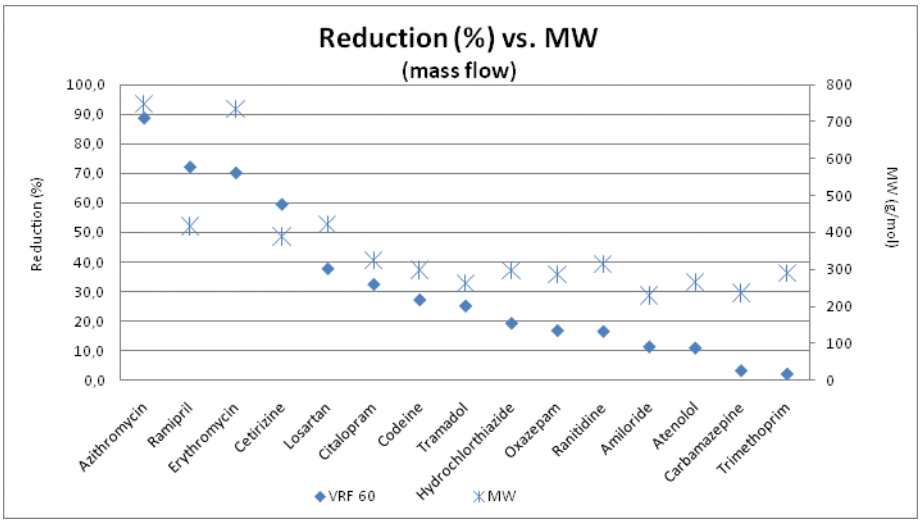

Figure 5. Reduction of pharmaceuticals calculated on mass flow at VRF 60.

Reduction over Ozonation and Nanofiltration

Of 94 pharmaceuticals 27 were over LOQ levels in incoming water. After ozonation two substances were still over LOQ levels, Glibenclamide and Ketoprofen with reduction rates of 92 % and 91 % respectively. Glibenclamide and Ketoprofen are still present in the permeate, at same concentration for Glibenclamide and with an overall reduction of 93% for Ketoprofen. The reduction of all pharmaceuticals expressed as a sum was 99%.

In the ozonated water six substances were below LOQ and were found in similar concentrations but over LOQ in the permeate (see table 2).

Results and Discussion

In this study, the total number of analysis is limited by the lack of test replicates. The results should be interpreted indicating study.

In all tests some pharmaceuticals showed an apparent production of substances. One of the reasons may be that the analysis performance only can detect the parent substances and not if it occurs in a conjugated form. Three pharmaceuticals, Ranitidine, Hydrochlorthiazide and Sulfamethoxazole, are sensitive to metal ions. Iron ions are used for chemical precipitation at Henriksdal. There is a possibility that they may have been masked in both incoming water and retentate since the iron ion is rejected by the membrane. The reason for the imaginary production could therefore be that the pharmaceuticals are conjugated to a smaller molecule or to a metal ion that do not permeating through the membrane. In the permeate the parent molecule would then be possible to measure without interference. This phenomenon naturally causes problems in evaluating the results and the substances showing negative reduction have been excluded in the calculations.

In table 2 the substances are shown and in what test they differentiated.

Table 2. Test occasions with imaginary production of substances, calculated on mass flow

	VRF 5, 10, 20	NF --> O3	O3 --> NF
Carbamazepine,	x		
Citalopram			x
Diklofenac,	x		
Furosemide,	x	x	
Hydrochlorthiazide	x		x
Ibuprofen,			x
Isosorbide Mononitrate	x		
Ketoprofen		x	
Metronidazole	x	x	
Metoprolol		x	x
Mirtazapine,		x	x
Naproxen,		x	
Oxazepam			x
Propranolol		x	
Ranitidine	x		
Sulfamethoxazole	x	x	

Reduction calculated on concentration gradient over the membrane

To evaluate the membranes actual potential to reject pharmaceuticals the concentration difference for each substance over the membranes was calculated. Due to two recirculation streams of retentate over the membranes, one that are returned and mixed with the feed in the work tank and one that are diverted directly from the outlet of the membrane to the pipe ahead of the high pressure pump. Of the water passing the membranes only about 15% was feed water. This large amount of recirculated retentate can result in a concentration polarisation at the membrane surface. The effect can be either an observed higher retention due to a second membrane of a mixture of high molecular weight substances that can reduce the possibilities for lower molecular weight substances to permeate or, an observed lower retention due to an increased solute concentration at the membrane surface.

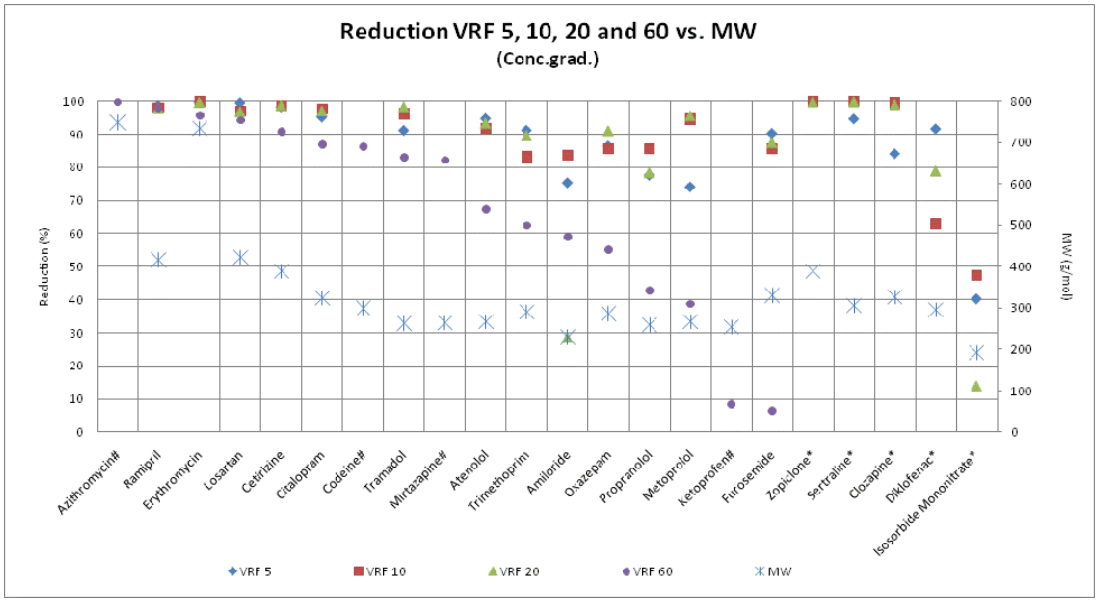

Figure 6. Reduction of pharmaceuticals over the membranes calculated on concentration gradient at VRF 5, 10, 20 and 60.

* Below LOQ at VRF 60

\# Below LOQ at VRF 5, 10 and 20

In figure 6 the reduction of substances are expressed as the concentration difference over the membrane. It should be noticed that the test for VRF 5, 10 and 20 only continued for 3 hours while the test for VRF 60 lasted for 2 days. Fouling of the membranes may result in an observed larger retention than real removal. A too short operation time may as well result in an observed false retention due to adsorption to the membrane surface. When the absorption sites are occupied the substance may start to permeate the membrane.

The retention of each single pharmaceutical is relatively similar at VRF 5, 10 and 20. The exceptions are Amiloride, Diclofenac and Isosorbide Mononitrate that indicate a false reduction at the lower VRFs.

Independent of VRF, the retention of pharmaceuticals with molecular weight over 400 is at least 90 %. The reduction rates for VRF 60 are lower but most substances show a reduction above 50%.

Water Quality

The retention of separate pharmaceuticals was 65-100% for MW > 300 g/mol and generally between 5-60 % for MW < 300 g/mol at VRFs 5-20, calculated as mass flow. At VRF 60, which is extremely high, the membrane retention is less, in general between 30-90% of substances of MW > 300 g/mol. By combining NF with ozonation a total reduction of 99% is possible to achieve at VRF 60.

In the discussion of planned indirect potable reuse of wastewater, one way of minimizing the risks with unknown organic matter, including pharmaceutical residuals, is to set high demands on the level of outgoing TOC (Water Environment Federation & American Water Works Association, 1998). For groundwater recharge of recycled water the California Department of Health Service requires that TOC must not exceed 0.5 mg/L (Bellona, et al. 2007).

In the Australian guidelines for augmentation of drinking water supplies there is drinking water guideline values for eleven of the substances investigated in this study, all in the µg/L range. The safety factor used is 1000 and each pharmaceutical is calculated from LDTD (Lowest Daily Therapeutic Dose). The eleven substances in the effluent from Henriksdal WWTP are all, except Ketoprofen, in the ng/L range and at an acceptable level for augmentation of a potable resource. Still, there is little known of the impact on the aquatic environment at low concentrations. Effects on fish living downstream WWTPs have been reported in several studies from various countries (Joblin et. al, 1998, Larsson et. al, 1999). If it is a specific substance or interaction between substances is not known (Carlsson et. al, 2006). How this may influence human health and life style in the future should be considered.

Retentate for post treatment

By operating NF at VRF 60 the possibility to reduce the volume to introduce a post treatment step was investigated. In the post-ozonation process the retention of pharmaceuticals by NF was lower than desired and in pre-ozonation the ozonation process eliminated most of the pharmaceuticals, 89% expressed as total sum of pharmaceuticals.

Conclusions

As a single process NF is not as effective as RO in pharmaceutical removal but still good. At lower VRFs the retention of pharmaceuticals with MW > 300 g/mol is 65-100%. With increasing VRF, the retention declines. At VRF 60, this was very clear.

In combination with ozone the concentration of pharmaceuticals in treated wastewater is reduced with at least 99%. Even low molecule weight substances, MW < 200 g/mol are removed for the large majority of the substances.

In concern of pharmaceuticals the concentrations in the permeates, as well as the effluent of Henriksdal WWTP, are reduced to acceptable levels for augmentation of potable water sources according to the Australian guidelines. This is the first attempt to adjust limits for discharge of pharmaceuticals. The effect on humans by normal use of pharmaceuticals is of course very well known. But, the long term effects of the mixture and/or single substances both for humans and the aquatic environment are not yet known. For each planned potable reuse facility risk assessments has to be made, both from environmental and health aspects.

From a sustainable outlook, in the long run persistent substances must be removed from the environment and the water cycle. The results show that the NF rejection to pharmaceuticals at VRF 60 was not as large as required. The tests made in this study indicate that to achieve a higher removal of pharmaceuticals it is necessary to use a tight membrane, probably RO.

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