Mitigating the Increased Risk of Toxic Chemical Composition in Desalination Outputs from Marine Outfalls

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Introduction and Problem Analysis

Multiple solutions have been considered to help solve the drought in Cape Town and its surrounding area. A solution that has also been considered and initiated by the government of Western Cape is the construction of desalination plants to produce drinking water from the sea (Simon, 2018).

However, the city's marine outfall system raises concern from the public about the quality of the water (and therefore, the desalination intake). The sewage exerted from these points goes directly into the ocean and only passes through preliminary wastewater treatment, which are metal bars, approximately 2 cm apart, filtering larger objects (Keenan, 2016). This entails that the water is still composed of blackwater, the classification of household waste that comes from urinals or toilets and any sort of water waste that is mixed with it (EPA South Australia, 2017). This type of wastewater, as further explained by EPA South Australia (2017), contains disease-causing bacteria and viruses and if exerted to the sea, can also affect the ecosystem of the marine life negatively due to nutrient-build up. It can also imperil humans if contact is made with the water or with the affected marine life. To further support this claim, the research by Petrik, et al. (2017) discovered high levels of diverse organic pollutants in marine organisms and their surrounding seawater specifically in the Northern shoreline districts of Cape Town. The chemical compounds found are not expected in seawater and moreover, the marine life (Petrik, et al., 2017). Therefore, this signifies that the quality of the intake water for the desalination process "poses a potential risk to human health" (Petrik, et al., 2017:4). Furthermore, Petrik, et al. (2017:8) also state that "it is probable that the water recovered from desalination may still be contaminated with traces of complex pollutants after the reverse osmosis process."

In their conclusion, Petrik, et al. (2017:8) advised against improving the desalination processes and instead should focus on "prevent[ing] the sewage from entering the ocean in the first place". In the former option, the waste from the process is exerted back to the sea. This will still contribute to the contamination of marine life and seawater. If the latter option is optimized, it will be more efficient and cost-effective since the problem will be taken out of the cycle completely in the initial stage. Given that desalination is an entirely separate process from wastewater treatment, a separate solution in the chain of sanitation for wastewater respectively is desirable.

Based on these statements, the following research approaches initiatives to comply to them by discussing possible filtration membranes and its application in marine outfalls which should improve the water intake of the desalination plants and its production as well. More specifically, the pollutants discussed will be constrained to phosphates and nitrates, and not other organic micropollutants since excess levels of these specific compounds negatively affect living conditions of exposed animals and plants. Although other organic micropollutants also constitute part of the problem, their specificity require different research and solutions, expanding the scope of the research excessively. Nitrates and phosphates are essential nutrients for plants and algae as they are sources of fertilizers; however, in solution, these compounds create an unstable concentration of oxygenic free radicals is created in solution. As a result of these free radicals, overgrowth of algae and marine vegetation in natural water bodies limits sunlight penetration necessary for marine life to thrive (Wheatley River Improvement Group, n.d.). In terms of impact to human health, nitrates can interfere with oxygen transport (Wheatley River Improvement Group, n.d). Due to this, elevated levels of nitrate in supposedly potable water pose a suspected increased risk of *blue baby syndrome* and miscarriage.

State of the Art

As an alternative to enhancing chemical treatment facilities, using integrated biological degradation mechanisms in combination with membrane filtration systems has become common practice, more commonly referred to as bioreactors (Cicek, 2002). These methods are usually employed in areas where conventional water treatment systems seem to function to an acceptable level, but performance could be improved, e.g. through the use of activated sludge processes (Radjenović, et al., 2008). Examples of activated sludge processes in action are aeration and anaerobic water treatment processes as will be further elaborated in the next section of this document. For instance, using bioreactors in combination with certain plant filters allows for localised [industrial] water treatment for a variety of purposes and environmental flow through (Cicek, et al., 2002). These and other options will be further explored in this document. Initially, an important distinction must be made between membrane bioreactors (MBR) and biofilters; the former is a chemical reactor based on the use of membranes, whereas the latter is a filter utilizing normal-sized plants' natural ability to filter solute contaminants from water.

Based on the 2013 review article by Shon, et al., this paper will provide a brief overview of the nanofiltration systems commonly used in wastewater treatment, hence to attempt to combine the above to create a nanofiltration (NF) membrane bioreactor with the ability to filter out toxic nitrates in addition to other contaminants. Logically, reason would lead to believe that retaining water vapor as the result of filtration will ultimately deliver the purest permeate.

The chief reason for NF being one of the promising technologies for pollutant removal is its selective removal of pollutants due to its high rejection rate for uncharged solutes, while monovalent ions (commonly found in organic solutions) are well-transmitted (Shon, et al., 2013).

According to Shon, et al. (2013), NF membranes ideally combine the relevant properties of reverse osmosis and ultrafiltration for optimal cleaning — i.e. the ability to retain ions at 1–5 nm pore size and the capacity to operate at lower pressures, e.g., 7 to 30 bar in comparison to other membranes. For the more basic methods to be explored later in this paper, pressure is no condition actively affecting the process and will hence not be elaborated on for comparison. Furthermore, in addition to the solution diffusion process as described above, NF also offers physical sieving as the dominant rejection mechanism for large molecules (Macoun, 1998).

Using NF membranes is presented with one major challenge: membrane fouling. According to Shon, et al. (2013), membrane fouling might occur as a result of inorganic particle precipitation during scaling, colloidal residue and organic absorption. The main harmful result of fouling is flux decline as filtration proceeds and internal clogging increases. Chemical pretreatment of the wastewater, e.g. using coagulation with iron, aluminum sulphate or ozonation, are amongst the most common countermeasures (Shon, et al., 2013). However, due to the nature of nitrate pollution in wastewater and its innate ability to aggravate the issue at hand, this is an approach that would preferably be avoided. Other approaches include electrolyte enhanced NF membranes and/or activated carbon in pretreatment (Levenstein, et al., 1996). Unfortunately, more research into the interactions between solutes and membranes is required before feasible measures against fouling may be considered. Given the nature of nanofiltration cleaning and its dependency on surface properties of the membrane, including surface charge affecting ion exchange across the membrane and leaving residue adhering to the membrane surface, simply sieving the solute would not suffice.

Most sanitation facilities, i.e. bioreactors, currently employed are constructed using functionalized materials based on some sort of polymeric or ceramic compounds (Han, et al., 2013). The former is preferred because of application flexibility and low-cost preparation (Han, et al., 2013). However, seen as polymeric compounds also suffer poor chemical and thermal resistance, limited half-lives and fouling, and the relative importance of sturdiness in filtration systems, the latter is often favoured because of its thermal stability, resistance to a variety of solvents, and longer half-life (Han, et al., 2013). Nevertheless, application of ceramic membranes remains limited because of complicated fabrication processes rapidly increasing the price (Han, et al., 2013). The following section will provide an adequate, yet comprehensive overview of approaches and mechanisms for water sanitation currently employed complemented with examples. Although the scope of these technologies may be limited in comparison to the proposed solution and not on the specifics of how each technology work, an accurate overview of the chemical qualities behind their techniques should suffice to provide a comprehensive list of dynamics behind water sanitation technologies currently employed.

Firstly, one of the most common membrane structures employed in water filtration systems is graphene-sheet based nanochannels, which affect filtration through confinement of water in between the graphene layers, i.e. reverse osmosis (Han, et al., 2013). Many highly selective graphene-based membranes suitable for application in water sanitation have to be completely impermeable to liquids, vapors and gases (Han, et al., 2013). The membranes, however, are permeable to water vapor by employing a mechanism referred to as thermal reduction. By splitting the water molecules into gasified H^+(g) and OH^-(g), the water is able to permeate through the pores of the selective graphene membrane (Han, et al., 2013). Unfortunately, the thermal reduction process also affects the membrane, which becomes impermeable to vaporized water ions after each thermal reduction cycle (Han, et al., 2013).

Buczek (2016) investigated the potential efficacy of potassium hydroxide (KOH)-activated carbon in different applications. As presented by Otowa, et al. (1997), KOH activated carbon might offer a potential solution. Especially compared to steam-activated carbon KOH is especially efficient in the removal of chloroform ($CHCl_3$) from water using various surface functionalized groups derived from its ions (Otowa, et al., 1997). Otowa, et al. (1997) also identified one main disadvantage to this method, i.e. KOH-functionalized carbon's lack of adhesion to non-hydrophobic particles in suspension or solution. Although today KOH-activated carbon is more commonplace e.g. in the enrichment process of carbon fuels, KOH-activated carbon has still been recognised as a widely applicable filtration technique due to its highly tuned pore size and structure (e.g., Buczek, 2016). According to Buczek (2016), KOH-activated carbon nanofiber pore sizes can be modified from anywhere between 1.001 $cm^3\ g^{-1}$ and 1.488 $cm^3\ g^{-1}$ in terms of pore volume. As a result, based on the exact circumstances chosen for KOH-activated preparation of these carbon nanofibers, selection of permeates can be tuned to a desirable degree for wastewater cleaning.

Secondly, various other methods exploiting OH^- radicals' propensity to adhere to contaminants have been explored, more commonly referred to as Phenton processes. These Phenton processes have the potential to aid in wastewater cleaning processes by facilitating permeate transfer through charged membrane surfaces by enclosing contaminants in micelles of OH^- radicals, rendering these contaminants able to cross the charge barrier. Exactly barriers might be employed to ensure ultrafiltration will be elaborated upon later in this paper. By irradiating ferrioxalate ($[Fe^{III}(C_2O_4)_3]^{3-}$) to create Fe^{2+} salts, hydrogen peroxide (H_2O_2) can be oxidized using ozone (O_3) to create OH^- radicals as shown in Equation 1 (Andreozzi, et al., 1999).

$$Fe^{2+}(aq) + H_2O_2(g) + O_3(g) \leftrightharpoons FeO_3^{\ -}(aq) + 2\ OH^-(aq) \qquad \text{(Eq. 1)}$$

The process is commonly further improved using Mn^{2+}/oxalic acid, which enhances energy release in pollutant solution upon irradiation used in H_2O_2 cleavage and hence rendering OH^- radical generation more efficient (Andreozzi, et al., 1999). The downside of this process is that hydrogen peroxide has only a small extinction rate, limiting the irradiation efficiency (Andreozzi, et al., 1999). Although the technique as described in the paragraph before is relatively old, reduction has been universally recognized as an overall efficient energy transfer method, which unsurprisingly also constitutes a logical option in wastewater cleaning processes.[1] For instance, chemistry dictates that energy is transferred in [boiling] water vapor by splitting water molecules into H_3O^+ and OH^- radicals in solution, thereby retaining the excess energy in the loose electrons orbiting the particle.

The processes as described above can be enhanced via semiconductor-driven photocatalysis. Photocatalysis is based on the principle that particles of different unoccupied energy gaps are separated using different electron transfer processes (Mills, et al., 1993). For instance, a TiO_2 semiconductor anode coupled with a Pt cathode can stimulate energy transfers in solution to such accuracy as to allow water to split into separate ions to thenceforth be filtered separately based on charge of particles (Mills, et al., 1993; Andreozzi, et al., 1999). The exact semiconductor system is displayed in Figure 1. The bottom-line of these methods is the exploitation of differences in energetic capacity between different metal ions (Andreozzi, et al., 1999).

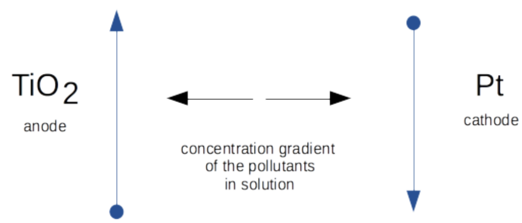

Figure 1: TiO_2-Pt anode-cathode semiconductor phase separation system (adapted from Mills, et al., 1993).

Thirdly, electrical discharges on ozone are commonly utilized to create a fast-acting oxidizer in solution, where active oxygen species are created *in situ* by electrifying ozone in close proximity to water — also preventing oxygen decay before it may enter the solution (Malik, et al., 2001). As coined by Malik, et al. (2001), a broad range of contaminants and solids in suspension can be destroyed using electrical discharge methods. Furthermore, by virtue of the energy transfer through the semiconductor in solution, this method is a lot more efficient while the electrocution of that solution also kills bacteria and spores as well as breaking down viral genetic material (Malik, et al., 2001). However, the chief disadvantage is that whatever remains of the excited oxygen species can create the effect of free radicals when introduced into circulation. This effect, more commonly referred to as oxidative stress, can cause significant damage to living cells and tissues as a result of metabolic processes; explaining the exact dynamics of this effect, however, would go beyond the scope of this paper.

Fourthly, sorbents — substances, which have the property of collecting molecules of another substance by sorption —, which have a much larger surface area for reactive species than many of their membrane counterparts, form the second approach to exploiting irradiation. For

[1] Reduction (gaining electrons) and oxidation (the loss of electrons) combine to form Redox chemistry, which contains the majority of chemical reactions. As electrons jump from atom to atom, they carry energy with them, and that transfer of energy is what makes all life on earth possible.

instance, Matthews, et al. (1987) constructed one reactor in which a woven glass mesh cylinder, coated with TiO_2, and sealed on both ends with silicone foil, positioned opposite a borosilicate glass tube with TiO_2 coiling, removed a large quantity of pollutants by attracting them to TiO_2 vapour in the coil. The exact structure of the reactor is displayed in Figure 2. More precisely, carbonaceous sorbents have proven to be highly selective to certain compounds, e.g. photochromatic particles (Matthews, et al., 1987). Common materials for membranes are benzene, toluene, p-xylene and ethylbenzene; in combination with TiO_2 as a redox-active medium, these polymers would be highly efficient at removing dyes. However, a lot more research is still required before this can become a viable option.

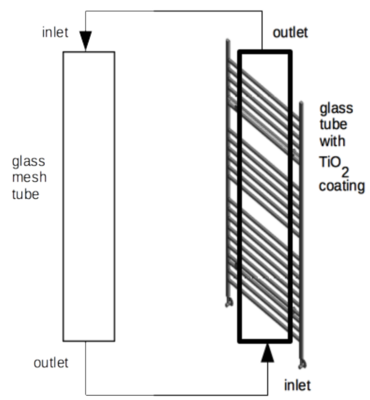

Figure 2: Sorbent reactor with TiO_2-coated coil around charged borosilicate tube (modified from Matthews, et al., 1987)..

Lastly, magnetically assisted processes represent another commonplace option. Filtration is achieved by influencing the physical properties such as surface charge, energy capacity and magnetic dependency of contaminants (Ambashta & Sillanpää, 2010). The ability to modify the particles' properties using electromagnetism depends on their size and magnetic field gradients (Ambashta & Sillanpää, 2010). The process is displayed in Figure 3. The charged pollutants in solution are collected using a wired mesh containing certain electrophile metals. Unfortunately, the principle's functionality is limited by the charge compatibility of the mesh and the pollutants.

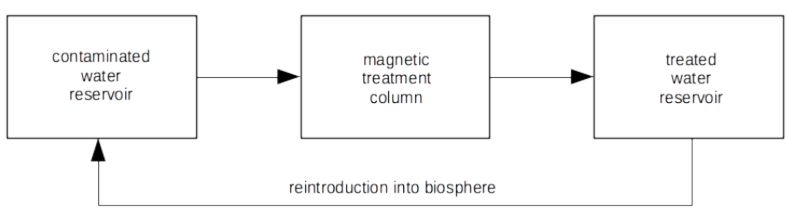

Figure 3: Magnetically assisted filtration process in bioreactor (modified from Ambashta & Sillanpää, 2010).

Mitigation Approach

Nitrates include NO_3^-, H_2N–, and HO–groups on nitrogen-compounds. From a health-related point of view, high nitrate concentrations in drinking water have been repeatedly emphasised as troublesome (e.g., Pennington, 1998; Fewtrell, 2004; Camargo & Alonso, 2006; Chiu, et al., 2007). Similarly, as noted by Canter (1997), excessive nitrate in designated potable water can also lead to a severe health issues in farming. Additionally, agricultural, industrial and household wastewater flows have already been pointed out as the major springs of nitrates (Wu, et al., 2016). As a result, the World Health Organisation (WHO) and the U.S. Environmental Protection Agency (EPA) have imposed strict nitrate concentration limits of 50 mg/L and 44 mg/L respectively. Several challenges with nitrate cleaning approaches, such as nitrate's low tendency to precipitate or dissolve, will have to be addressed as outlined by Islam, et al. (2010). The following proposal will outline an approach using nano paper structures, enhanced with active metal-oxide compounds in combination with vegetative filtration systems to guarantee optimal cleaning whilst maintaining potability of the water. Using the dynamics of various approaches outlined in this paper and a selection of novel chemical compounds, the following section proposes a concrete MBR to be used to mitigate the adverse effects of phosphoric and nitric contaminants in wastewater discharge at marine outfalls.

Firstly, a few mechanical limitations of current bioreactors will have to be addressed. For instance, due to the highly unpredictable weather circumstances in South Africa, the limited capacity of water tanks as a result of prolonged winter periods can form an excess residue before peak seasons as water reserves will implicitly be limited in summer (Ramphao, et al., 2013). On the flip side, there is also a variety of conditions during which the tank would be empty, leading to a lack of flow through, causing the tanks to start emitting an odour unless being cleansed intermittently (Ramphao, et al., 2013). Furthermore, although mechanical energy usage, i.e., hydraulic load, could be reduced through the use of more chemical parts, such as hollow fibre membranes, their application has been severely impaired by the requirement of continuous aeration to prevent extensive fouling of the membranes while maintaining optimal nitrate removal until now (Ramphao, et al., 2013).

Mannina, et al. (2017) propose a membrane reactor (MBR) using anaerobic, anoxic and aerobic chambers as outlined in Figure 4. This MBR is based on ultrafiltration hollow fibre membranes (preferably pore size ~ .3 µm) procured from nanofibrillated cellulose (CNF) "paper" sheets (Mautner, et al., 2017). To achieve optimal cleaning, wastewater is mixed with synthetic ammonium chloride before entering the cycle (Mannina, et al., 2017). Chiefly, the ammonium chloride will mitigate the consequences of the CNF sheets' chemical affinity to the chemical products generally found in wastewater, as indicated in Figure 5 (Mautner, et al., 2017). Similar to the KOH-activated carbon nanofibers, chemically charged CNF sheets also provide a wide variety of potential selective capacities based on the physical and chemical properties of the contaminant, e.g. size, charge and phase. Furthermore, trials executed by Wu, et al. (2016) already indicated that using ammonium-conjugated polymeric membranes could possibly aid in nitrate removal from wastewater by exploiting the radical tendency of ammonium to form hydrogen bonds with nitrates. The exact role of these chemicals in the filtration process will be discussed further ahead in this paper.

Classical approaches towards limiting the effects of fouling in nanofiltration membranes, e.g. activated carbon cloths, chitosan coatings, zirconium oxychloride coatings, etc. are not optimum because of a lack of recyclability of the approaches (Loganathan, et al., 2013). As a result, the first solution was to integrate a separate tank for aerobic N_2O stripping, which would also mitigate and largely prevent membrane fouling. However, using certain coatings could also enhance nitrate removal by surface modification, i.e. creating new functional groups with high affinities for nitrates on the surface of the membranes, exploiting the positive charge interactions between the particles in solution (Logathanan, et al., 2013). One of the possible approaches would be to add fibrous magnesium silicate ($Mg_4Si_8O_{15}(OH)_2.6H_2O$) to surface groups of the ammonium-conjugated CNF nanopaper sheets.

In addition to the synthetic compounds causing the nanofiltration membranes to foul, natural compounds found in water, e.g. biocarbonate, chloride and sulphate, can also clog membrane pores due to the selectivity of strong basic functional groups (Wu, et al., 2016). As the main causes of these problems are the chemical interactions between hydrogen groups and SO_4^{2-}- and HCO_3^--ions in solution, adding a biofilter to the system could alleviate these challenges. By way of membrane facilitation using OH^- radicals, these phosphates could be removed from the solute using base interactions. The following paragraphs contain a listing of potential biofilters for application in conjunction with NF MBR and *Clean-In-Place* (CIP) reservoir.

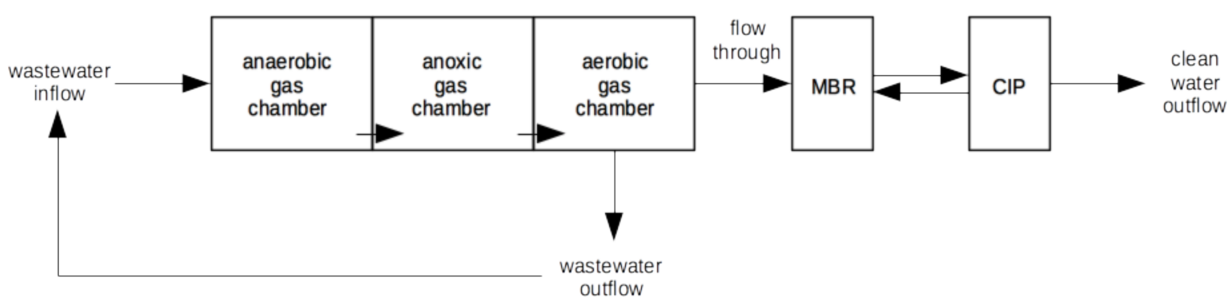

Figure 4: The filtration cycle of the CNF nanopaper-based MBRs (adapted from Mannina, et al., 2017).

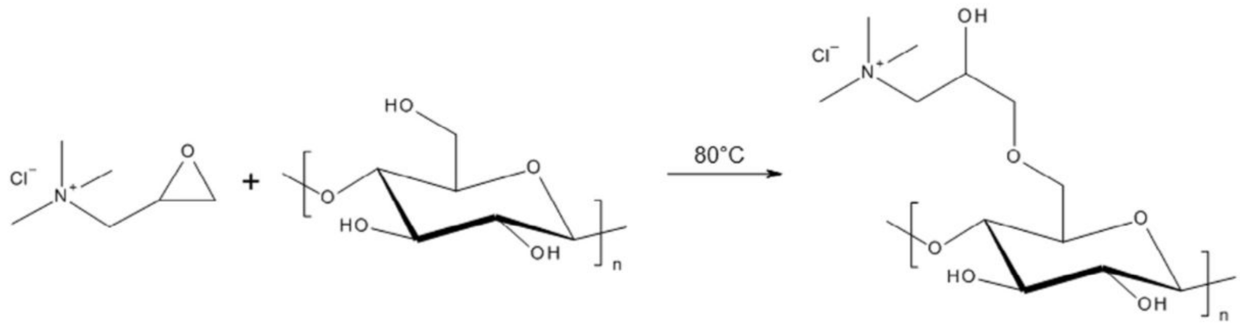

Figure 5: Attachment process of production of ammonium-CNF conjugates for MBRs (modified from Mautner, et al., 2017).

In addition to the chemical approaches to MBR construction outlined in the previous paragraphs, using vegetation could also yield benefits in reducing the unbalanced outflow of minerals in the water, improving infiltration into the soil in the environment and hence improving water quality for the environment (Milandri, et al., 2012). As previously indicated, one of the main hurdles of nitrate removal from wastewater is the excessive concentration of phosphates also adhering to the active group of ammonium-conjugated CNF nanopaper sheets.

Milandri, et al. (2012) suggested using plant species such as Agapanthus, Pennisetum, Stenotaphrum, Zantedeschia, Phragmites and Typhia for their ability to reduce the outflow phosphate (i.e. PO_4^{3-} ions) concentration by a total of 80–95% in previous stormwater treatment trials. According to Milandri, et al. (2012), the Pennisetum and Stenotaphrum species were most efficient at reduction of the outflow concentrations, consistently reducing 85% to 76% throughout cycles. Most significantly, however, it must be considered that no monolithic solution has been found as of yet, and many current results constantly indicate a need for a variety of vegetation in plant-based bioreactor designs.

Installation of the MBR will be most strategic if it is designed before water passes through the pipes of the marine outfalls yet after the already existing wastewater treatment centres. With apparent financial constrictions, the government can also consider the MBR to be constructed and attached into the treatment centres as a final process as well. By doing so, the quality of the exerted wastewater into the sea is ensured. It is also in line with the Petrik, et al.'s (2017) reasoning of stopping the pollutants before it enters the desalination water cycle

Enhancing the Efficacy of MBR

Kalyuzhnyi et al. (2000) have stressed the partially untapped potential of biomass recycling in water treatment facilities. Arguably, phosphates recovered from wastewater plants might be a viable source of fertilization materials, e.g. by using the activated sludge in fields. For instance, phosphorus removal technologies, i.e. metal-aided precipitation, enables biological removal of phosphorus, allowing for economic industrial benefit (de-Bashan & Bashan, 2004). Normally, plant biomass is won from constructed wetlands; in water treatment plants, phosphoric ions can easily be converted from solution in wastewater to solid fractions, e.g. using air stripping using CO_2 affluents (Kalyuzhnyi, et al., 2000). Using this anaerobic approach, avoiding oxygenation in the process of retrieving solids from the water, energy can be retained in these compounds' bonds.

$$O^{2+}(aq) + NO_3^{-}(aq) \rightarrow NO_4^{+}(aq) \quad \text{(Eq. 2)}$$

$$NO_4^{+}(aq) + PO_4^{3-}(aq) + 3\,H_2O(l) \leftrightharpoons NO_3^{-}(aq) + H_2PO_4^{-}(aq) + 2\,H_2O_2(g) \quad \text{(Eq. 3)}$$

Moreover, the active removal of phosphates from a solution or suspension — dephosphorization — in the presence of a small concentration of nitrates in the anaerobic phase (as indicated in the system in Figure 4) seems to actuate the active removal of nitrates — denitrification — and phosphate-accumulation processes (Ahn, et al., 2001; Ahn, et al., 2002). This effect is achieved by causing a switched oxygen atom to nitrate as electron acceptor, enhancing anoxic orthophosphate uptake, as shown in Equations 2 and 3 (e.g., Ahn, et al., 2001; Ahn, et al., 2002; Falkentoft, et al., 2002; Ostgaard, et al., 1997). In layman's terms, by subjecting the wastewater to dephosphorization in the presence of nitrates before entering the aerobic denitrification cycle could enhance the efficiency of the denitrification process.

Using this sludge and the fertilizer that may be produced from it, this biomass could also be converted to very energy-dense fuel in the form of polyphosphates and polynitrates, which in the long run, would mean that a reactor based on this system would be able to sustain itself by using this biomass fuel — alleviating one of the major factors, which impeded the widespread use of NF bioreactors for nitrate removal in the past, especially in water-scarce areas such as Cape Town as mentioned in the 1997 Water Act (Kalyuzhnyi, et al., 2000; Greencape, 2017).

Application of Biofilters in MBR

One possible approach to optimize wastewater treatment would be magnesium-phosphorus precipitation (e.g., de-Bashan & Bashan, 2004). This preferred method applies $Mg(OH)_2$ to an anaerobic sludge digester, causing a decline in the number of solids in suspension and allowing the level of biogas to reduce using the hydroxyls and oxygen in the phosphates and ammonia in solution (de-Bashan & Bashan, 2004). Conversion of phosphates using conjugation with $Mg(OH)_2$ ensures the generation of polyphosphate compounds for later energy release in the system for their high-energy storage capacity and efficient release upon hydrolysis. The anaerobic cycles required for this purpose can be obtained by allocating different spatial zones in a system of continuous flow as described in Figure 5. As pointed out by Booker, et al. (1999), Stratful, et al. (2001) and Williams (1999), magnesium ammonium phosphate hexahydrate — as mentioned in the previous section — is a promising spontaneous precipitator used for phosphate recovery from wastewater sludge.

Furthermore, trials have indicated that stimulated photosynthesis might further enhance the process, as phragmites showed significant increases in leaf number as more nutrients were removed (Milandri, et al., 2012). After the leafing increase event, phosphate (PO_4^{3-}) and nitrate (NH_3 and NO_3^-) concentrations were typically reduced by 80–94% and 85–97%/50–75% respectively. Furthermore, Pennisetum consistently removed a large percentage of each nutrient, possibly as a result of rapid growth rates (Milandri, et al., 2012). Unfortunately, however, for the time being, more research into this phenomenon is still required.

Modelling Possible Effects of Mitigation

The membrane flux describes the sum of the dynamics affecting the fluid or solute transfer across a membrane. As mentioned earlier, the flux is the most important factor when benchmarking the gravity of the effect of fouling on a specific membrane. As pointed out in the 2013 review article by Shon, et al., the Nernst-Planck equation (Equation 4) is most commonly used to describe the transport of solutes across NF membranes:

$$J = D_P \frac{dc}{dx} - \frac{zcD_p}{RT} F \frac{d\psi}{dx} + K_c c V \qquad \text{(Eq. 4)}$$

where,

- J is the ion flux across the membrane in $mol\ m^{-2}\ s^{-1}$;
- D_p is the hindered diffusivity in $m^{-2}\ s^{-1}$;
- c is the ion concentration in $mol\ m^{-3}$;
- x is the distance from the membrane in m;
- z is the valence of the solute;
- R is the gas constant of approximately 8.314 $J\ mol^{-1}\ K^{-1}$;
- T is the absolute temperature in K;
- F is the Faraday constant of approximately $9.648 \times 10^4\ C\ mol^{-1}$;
- K_c is the hindrance factor for conversion;
- ψ is the difference in ζ-potential;
- V is the solvent velocity in $m\ s^{-1}$.

Within this equation, the product of $D_P \frac{dc}{dx}$ describes the diffusivity of the solute across the entire span of the membrane. The product of $-\frac{zcD_p}{RT} F \frac{d\psi}{dx}$ describes the phase shift of the solute to permeate after diffusing across the membrane. Lastly, the product of $K_c cV$ indicates the extent of hindrance — the degree of flow obstruction due to the membrane barrier — across the thickness of the membrane.

Shon, et al. (2013) discern five steps in the filtration process. The process starts when (i) the solute diffuses from the water phase to the membrane surface, after which (ii) selective diffusion of the solute into and (iii) through the membrane occurs (e.g., Shon, et al., 2013). Once diffusion has been completed, (iv) the solute will undergo desorption on the permeate side of the membrane, after which (v) the solute will diffuse into the bulk fluid on the permeate side of the membrane (e.g., Shon, et al., 2013). To guarantee the best-case scenario, it must be considered that diffusion is the slowest step in the process and hence also exposed to the greatest risk of fouling, thereby clogging the system and wreaking a steady decline in flux.[2] As such, reliable insights may be gained using the non-equilibrium thermodynamic model as described above, granted experimental parameters will be used for the measurements. Appendix 1 presents a mathematical execution of the model based on the Nernst-Planck equation of diffusion across NF membranes, aiming to provide a benchmarking tool for production of MBR plants.[3]

Projected Outcomes

As an apparent effect of the upcoming installment of the desalination system, the water scarcity issue will be addressed by the massive production of usable water. With the MBR installed as secondary treatment to the wastewater, the eventual quality of the intake water for the desalination process will be maximized. This will ensure that the produced water from the desalinated plants will not cause harm for human and agricultural use. With regulated phosphate and nitrate in the final desalination water product, illnesses from potable drinking water are avoided.

The cleaner quality of wastewater that passes through the marine outfalls will also stop the constant contamination of the marine life, as mentioned by Petrik, et al. (2017). The reduction of excess phosphate and nitrate will balance the ecosystem and avoid the possible elimination of any species. The public that visits the shoreline for recreational purposes will also enjoy their experience and will not complain to the government any further (Keenan, 2016).

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[2] Flux is the flow rate of water applied per unit area of the membrane and has units of volume per unit area time. Filtrate is the water that has passed through the membrane per unit area of membrane.

[3] The time dependent form of the Nernst–Planck equation is a conservation of mass equation used to describe the motion of a charged chemical species in a fluid medium. The Nernst-Planck equation extends Fick's law of diffusion, when diffusing particles are also moved with respect to the fluid by electrostatic forces; Fick's first law relates the diffusive flux to the concentration by postulating that a solute will move from a region of high concentration to a region of low concentration in solution.

Like the marine life, the chances of excessive vegetation in the land will also lessen. This will be beneficial to the agricultural sector since there will be no issues with the usage of land and therefore, production. The products acquired will also strive and improve, providing healthier food and possibly expanding business opportunities. With the constant water now available from the desalination process, crop failure based on water scarcity is not to be expected.

Possible Adverse Effects

Other than expected effects already mentioned, there are possible adverse effects that might arise from this implementation. Using foreign plant species in biofilters to mitigate the consequences of micropollutants is a common approach to reducing the number of potentially adverse effects on the environment such as enhancing the biodiversity of the gene pool and introducing new organic molecules into the local biosphere. For instance, as mentioned by Le Maitre, et al. (2000), a decreased streamflow of groundwater occurs due to a greater degree of root infestation. However, fortunately, due to vegetation's integral role in the water cycle, this decrease in streamflow not necessarily causes a decline in groundwater availability and hence not automatically implies an impediment in water capacity of the region. The second aspect emphasised in the model by Le Maitre, et al. (2000) is that an increase in canopy cover may cause part of the area to be ill-adjusted due to a lack of radiation penetration. As a result, trees invading grasslands and plains may be more resistant to fires than the original vegetation (Le Maitre, et al., 2000). Unfortunately, because of the climate's essential role in determining the spread of foreign species, forecasting the exact effects becomes increasingly challenging and rather unpredictable. For instance, in the region of Western Cape, the greatest volume of runoff is lost due to mountain catchments invaded by pines. Fortunately, none of the species applied in the biofilters considered in this paper are similar to pines (e.g., *Melia azeaarach*) in characteristics (Le Maitre, et al., 2000).

In 2015, the Australian Government's Department of Industry and Sciences' Business Cooperative Research Centres Programme published a uniquely comprehensive article on the properties desirable in plants when selecting a variety of biofilters targeted towards upholding the biodiversity currently present in the region in question. One significant notion was that although plants have been universally recognised as beneficial in the urban environment, e.g. by creating greenspaces and thenceforth inadvertently enhancing the biodiversity, improving the microclimate with considerable advantages for human health and the economic health of the city, not all plant species are equally effective at biofiltration, particularly when it comes to nitrate removal and retention (*CRC for Water Sensitive Cities*, 2015). The report stated a need for having at least 50% of plant species in place with desirable traits for the removal of the pollutant compounds in question. For nitrogen removal in particular, (i) an expansive root system, (ii) a canopy with an amply large surface area, and (iii) compatibility with current biosphere are key parameters in selecting plant species for the construction of biofilters (*CRC for Water Sensitive Cities*, 2015). Unfortunately, not enough is known as of yet about the exact effects of plant species on the structural diversity around them. Although more research into local indigenous species in Cape Town's biosphere is required, one may safely state that using plants with similar microclimatological properties as the species already present is currently preferable over introducing entirely new species into the biosphere.

To provide adequate counsel on what plant species will become toxic to the currently established biosphere, two other factors must be recognised: (i) given the long residence of the species mapped in the area of Western Cape, and (ii) the ability of non-indigenous species to spread throughout their new habitat depends on their ability to disperse across different biomes (Hoveka, et al., 2016). As mentioned before, the capacity to invade depends on the availability of surface water, which is also affected by the degree of groundwater streamflow (Hoveka, et al., 2016). The spread of non-indigenous species is hence also affected by the flow rate, acidic and oxygenic degrees of the groundwater.

Discussion of Implementation and Limitations

Even though the immediate effects are to be desired, the practical implementation of an MBR facility in conjunction with the introduction of biofilters and biomass recycling as designed in this paper is intricate. The biggest issue would be the financial incentives to support it. The main concern of the government considering the drought is the production of water for various, every day means. Currently, the upcoming desalination process will achieve this, and the expected production will be on par with the minimum standards of the WHO restrictions (2011). The problems mentioned in this paper are in a lower priority due to no urgent influence to citizens. The installment of a facility proposed will already require a huge amount of money and with more important matters to take care of, the government will not take it into consideration. This is further reinforced especially with the internal issues of corruption in South Africa’s government.

A research by Judd (2017) explains the financial details more explicitly. It is specified that the total cost of the installation is based on its capital cost (CAPEX) and operating cost (OPEX). The latter is comprised mainly by the energy and chemical demand, membrane replacement (as the critical component), water supply and wastewater discharge charges, and labour; while CAPEX includes costs of “all equipment, installation services such as civil engineering, mechanical and electrical, consultancy, and land costs” (Judd, 2017:2). For MBR processes, the highest OPEX comes from its energy demand, specifically the aeration process, providing air to the biomass and scouring the membrane, which is further specified with their average value in brackets in the equation below (Judd, 2017:5):

$$E_{MBR} = E'_{A,m}SAD_p + E'_{A,bio}SAD_{bio} + E_{sludge}\Sigma R + E_{L,m} + E_{el} \quad \text{(Eq. 5)}$$

where

- $E'_{A,m}$ is the specific energy demand per unit air volume, membrane tank, kWh Nm^{-3} (*0.022*)
- $E'_{A,bio}$ is the specific energy demand per unit air volume, process tank, kWh Nm^{-3} (*23*)
- E_{sludge} is the specific energy demand, sludge pumping (power/flow), kWh m^{-3} (*0.018*)
- $E_{L,m}$ is the specific energy demand, permeate pumping (power/flow), kWh m^{-3} (*0.015*)
- E_{el} is the specific residual electrical power consumption kWh m^{-3} (*0.005*)
- ΣR is the sum of recycle ratios (*5*)
- SAD_p is the specific aeration demand for membrane scouring, air per unit permeate volume, Nm^3 m^{-3} (*0.25*)
- SAD_{bio} is the specific aeration demand for biological process, air per unit permeate volume, Nm^3 m^{-3} (*base values for analysis*)

The values in the equation described above is just a normalization, different factors such as the depth of the aerator in the tank might affect it. It goes without saying that energy efficiency decreases the OPEX value, which is also the visible trend since the original implementation (Judd, 2017). Based on the variables shown above as well, the net flux has an inverse relationship to the OPEX which is shown in the graph below.

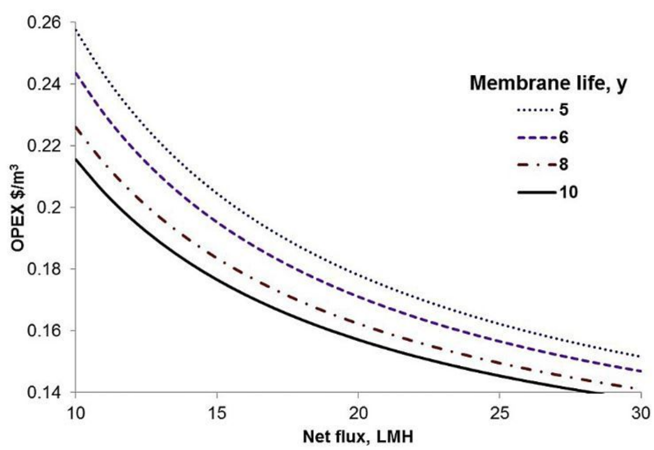

Figure 6: The net flux of a MBR to its OPEX as a function of membrane life (Judd, 2017).

Other OPEX costs that is specified in the research by Judd (2017) are the membranes that are valued around \$15-25 per m^2. In regards to CAPEX, Lo, et al. (2015) values for a 20 MLD (mega liters per day) capacity MBR plant of \$0.35-\$0.68m (2015 USD) per MLD. However, Judd also specified that there might be "an increase considerably depending on circumstances. Young et al. (2013) determined a CAPEX of up to $2.6 m/MLD when including downstream UV disinfection and primary settling" (2017:6).

From an ethical perspective, the main concern within this proposition is the introduction of various types of chemicals to water that will be consumed by living things. Another aspect to consider will be the immense energy consumption and greenhouse gas emission a facility such as this imposes. This issue is also heavily disputed within the discussion of desalination plants in general, and is the main reason why some people have opposed the idea (Al Jazeera, 2012). However, both of these reasons can be easily argued upon the benefits that the processes provide, which, in this case, improves the health and well-being of a lot of people. Some argue that desalination should be reserved as a last resort because other incentives can also help the water scarcity issue, such as public campaigning of reducing water use. Nonetheless, in Cape Town's case, this has been an impending problem which needs extreme, effective solutions.

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Appendices

Appendix 1

MatLab model of the non-equilibrium thermodynamic model of solute diffusion across NF membranes based on the Nernst-Planck equation.

```
function[q]=ries2
clear;clc;
e=1;w=10;
opt = bvpset('RelTol',1e1);
xinit=linspace(-1,1,201);
solinit = bvpinit(xinit,@yinitfcn);
sol = bvp4c(@f,@bc,solinit);
q=sol.y;
function dydx = f(x,y)
dydx = zeros(6,1);
dydx(1)=y(4);
dydx(2)=y(5);
dydx(3)=y(6);
temp=dydx(2)*dydx(3)+y(2)*dydx(6);
temp1=dydx(1)*dydx(3)+y(1)*dydx(6);
dydx(4) = 1/e*(sqrt(-1)*w*y(1))+1*temp;
dydx(5) =1/e*(sqrt(-1)*w*y(2))+1*temp1;
dydx(6)=-1/(e^2)*y(2);
end
function res = bc(YL,YR)
res = [ YL(4)+YL(2)*YL(6)
 YL(5)+YL(1)*YL(6)
YL(3)-1/(w*w+1)
  YR(3)
YR(4)+YR(2)*YR(6)
YR(5)+YR(1)*YR(6)
];
  end
function y = yinitfcn(x)
y =1* [0;0;1/w*w;0;-0;0];
end
end
```