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INSTITUTE FOR WATER EDUCATION

Effect of SAT Pre-treatment on Performance of NF Membranes

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MSc Thesis MWI 2009/027
May 2009

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Institute for Water Education

SWITCH

Effect of SAT Pre-treatment on Performance of NF Membranes

Master of Science Thesis
by
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This research is done for the partial fulfilment of requirements for the Master of Science degree at the UNESCO-IHE Institute for Water Education, Delft, the Netherlands

Delft
May 2009

This work is dedicated to my son, Alvin

and to the memory of my parents.

Abstract

Potable reuse of municipal effluents is often indirect, by infiltration or injection of treated effluent into the subsurface. In most of the reuse systems in practice, infiltration is carried out by subjecting conventional secondary treatment effluent to tertiary filtration prior to soil aquifer treatment (SAT). For subsurface injection into the aquifer, extensive pre-treatment like microfiltration or coagulation followed by tight nanofiltration (NF) or reverse osmosis (RO) are employed.

SAT represents a natural land treatment technology that has gained acceptance as an integral part of indirect potable reuse systems. However, removal of effluent organic matter (EfOM) in SAT systems is limited. Additional pre-treatment of secondary effluent (SE) is necessary to increase organic matter removal efficiency in SAT. In particular, ozone, which is a very strong oxidant, can be used as pre-treatment to SAT to convert the refractory organic compounds into more biodegradable form. Advanced membrane treatment such as RO and tight NF membranes are technologies prominently mentioned in the field of wastewater reclamation for potable reuse. However, the high organic matter content and suspended solids present in the effluent of conventional activated sludge necessitate the need for expensive pre-treatment to avoid excessive fouling rates.

SAT can play an important role as an effective pre-treatment for membrane filtration to reduce considerably the problem of membrane fouling and thereby minimize the cost of pre-treatment for RO/NF membranes. This study, therefore, focused on the analysis of SAT pre-treatment on the performance of the NF membranes by investigating DOC removal and reduction in flux decline.

Laboratory-scale soil column studies were conducted using secondary effluent from a full-scale wastewater treatment plant and NF membrane setup was used. Different pre-treatment were applied to secondary effluent before SAT and performance of two different types of NF membranes were analysed.

Soil column study showed that SAT can remove 24% of DOC in secondary effluent. With pre-ozonation dose of 1 mg O_3 to 1 mg DOC of SE, DOC removal improved to 26% by increasing the easily biodegradable fraction of DOC from 8% to 20%.

Two types of nanofiltration membranes (NF-270 and NF-90 from DOW FilmTec) were tested with four types of feed water (secondary effluent, SAT pre-treated secondary effluent, pre-ozonated SE, and SAT pre-treated and ozonated SE). Rejection of DOC, TDS, and UVA_{254} were influenced more by the type of membrane rather than by the type of feed water. No significant change in DOC removal by NF membranes was observed with or without SAT pre-treatment of wastewater treatment plant effluents. However, in terms of flux decline, the NF membrane, regardless of type, consistently performed better with SAT pre-treated feed water. The flux decline of NF-270 and NF-90 at equal delivered DOC were reduced by 2% and 18% respectively for SE as feed water and by 5% and 14% respectively for SE+O_3 as feed water, due to SAT pre-treatment. The tighter NF-90 exhibited more flux decline compared with NF-270 with any type of feed water. In summary, this study showed that SAT followed by NF could be an effective technology for water reuse applications.

Keywords:
dissolved organic carbon, effluent organic matter, flux decline,
nanofiltration, ozonation, , soil aquifer treatment, wastewater reuse

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ASR	Aquifer Storage and Recovery
BDOC	Biodegradable Organic Carbon
BMP	Biomass-associated Product
BOD	Biochemical Oxygen Demand
BTSE	Biologically Treated Secondary Effluent
CAS	Conventional Activated Sludge
DBP	Disinfection Byproduct
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
E-BDOC	Easily Biodegradable Organic Carbon
EC	Electrical Conductivity
ED	Electrodialysis
EDC	Endocrine Disrupting Compound
EfOM	Effluent Organic Matter
FEEM	Fluorescence Excitation and Emission Matrix
HPI	Hydrophilic
HPO	Hydrophobic
MD	Membrane Distillation
MF	Microfiltration
MFI	Modified Fouling Index
MPFI	Mini Plugging Fouling Index
MWCO	Molecular Weight Cut-off
NOM	Natural Organic Matter
NF	Nanofiltration
POC	Particulate Organic Carbon
PPCP	Pharmaceutical and Personal Care Product
PV	Pervaporation
RO	Reverse Osmosis
SAT	Soil Aquifer Treatment
S-BDOC	Slowly Biodegradable Organic Carbon
SDI	Silt Density Index
SE	Secondary Effluent
SMP	Soluble Microbial Product
SOC	Synthetic Organic Compound
SUVA	Specific Ultraviolet Absorbance
TDS	Total Dissolved Solids
THM	Trihalomethane
TMP	Transmembrane Pressure
TPI	Transphilic
TOC	Total Organic Carbon
UAP	Utilization Associated Product
UF	Ultrafiltration
UVA	Ultraviolet Absorbance
WWTP	Wastewater Treatment Plant

1 Introduction

1.1 Background

Water scarcity affects a lot of regions in the world. There are limited options that these communities can take to supplement their current water needs for different uses, often forcing people to rely on unsafe sources of drinking water resulting into serious health effects. The factors that contribute to the problem of water scarcity are population growth, rapid urbanization, increased domestic and industrial water use, pollution of fresh water sources and extreme weather patterns.

One method to alleviate water scarcity is to recycle water. Significant interest worldwide in water reuse is emerging to conserve freshwater resources. Reclaimed wastewater after appropriate treatment can be used for a variety of purposes in agriculture, landscape, industry, environment and recreation. Another set of applications include groundwater recharge, non-potable urban uses and potable reuse. Each application requires a minimum quality of water. This can vary from conventional secondary effluent without further treatment to water that approaches the highest quality achievable.

Municipal wastewater treatment and reuse is technically attractive because the available effluent quantity is abundant near highly populated areas and the composition is predictable throughout the year for separate sewer systems. Direct potable reuse involves advanced treatment methods in a water reclamation plant after conventional biological wastewater treatment. Indirect potable reuse comes in the form of blending with public water supplies, which can be planned or unplanned. Unplanned potable reuse is incidental reuse of wastewater. Planned indirect water reuse, however is a deliberate use without losing control over the water during its delivery (Asano et al., 2007).

Indirect potable reuse of municipal effluents is often by infiltration, or direct injection of treated effluent into the subsurface. Established projects currently are using conventional secondary treatment followed by tertiary filtration prior to soil aquifer treatment. For subsurface injection into the aquifer, extensive pre-treatment followed by tight nanofiltration (NF) or reverse osmosis (RO) are required (Drewes et al., 2003).

Soil Aquifer Treatment (SAT) represents a wastewater reclamation/reuse technology that has been gaining acceptance as an integral component in indirect potable reuse systems. SAT is a natural land treatment technology that uses soil infiltration and percolation through the unsaturated zone as treatment of the wastewater effluent before subsequent recharge to the underlying groundwater aquifer. Treatment by physical, chemical, and biological means continue as the percolate passes through the unsaturated zone. SAT, when combined with other available water treatment technology can produce an effluent quality appropriate for potable reuse.

An important technology in the field of wastewater reclamation for potable reuse involves the use of advanced polishing treatment such as reverse osmosis (RO) and nanofiltration (NF) membranes. RO/NF systems can polish any type of water to highest standards.

However, the effluent of a conventional activated sludge is still high in suspended solids and cannot be treated directly by RO/NF process without excessive fouling of the membranes. High fouling rates can be observed for typical systems using RO/NF membranes when treating conventionally filtered municipal wastewater. Fouling of membrane elements can cause operational problems such as increase of pressure required or results to a decrease of permeate flux. The secondary effluent (SE) requires pre-treatment such as sand filtration, lime clarification, microfiltration or ultrafiltration to avoid the problem of excessive fouling of the RO/NF membranes. These pre-treatment methods employ the use of costly chemicals. Furthermore, high concentration of organic pollutants and particles present in secondary effluent can influence the performance of the membrane and further increase costs.

SAT can play an important role as an effective pre-treatment for membrane filtration to reduce considerably the problem of membrane fouling. SAT before RO/NF membrane treatment can minimize the level of, if not eliminate, pre-treatment required and thereby reduce the amount of chemicals used in the treatment process.

1.2 Problem description

Effluents from primary and secondary wastewater treatment plants contain a number of pollutants including pathogens (harmful bacteria and viruses), nutrients, heavy metals and residual organic compounds. These pollutants may pose potential health hazard when present in reclaimed water for indirect potable use, resulting in immediate diseases or after years of accumulation in the body. Pathogens and heavy metals are easily removed during SAT. Biologically treated sewage effluent (BTSE) contains high levels of effluent organic matter (EfOM). Three groups of residual organic matter are identified requiring attention in water reuse systems: natural organic matter (NOM), synthetic organic compounds (SOC) and disinfection byproducts (DBP's), and soluble microbial products (SMP) (Drewes & Fox, 1999). NOM is already present in drinking water. SOC is added by consumers while DBP's are formed during chlorine disinfection of water and wastewater. SMPs are formed during decomposition of organic compounds in the wastewater treatment steps.

Some organic compounds such as carbohydrates, proteins, fat, etc. are biodegradable and hence decompose in the soil. The main concern is with the refractory residual organic compounds that are still present in the water after SAT which can easily foul the RO/NF membranes during post-treatment. The complex and heterogeneous nature of the EfOM contribute to the different physical and chemical behaviours in membrane fouling, making it difficult to understand and explain membrane fouling mechanisms. Therefore, while SAT can remove a significant amount of EfOM, additional advanced treatment process is needed to improve biodegradability of the residual organic compounds. Providing pre-treatment to the secondary effluent before soil passage may require less rigorous and less expensive polishing post treatment. In particular, Ozone, which is a very strong oxidant, can be used as pre-treatment to SAT to convert the refractory organic compounds into more biodegradable form. The role of ozonation as a pre-treatment for SAT lies in the potential to increase the biodegradability and effective removal of organic matter from wastewater. The effect of ozonation on secondary effluent before SAT and the effect of SAT pre-treatment on NF membranes have not been fully investigated.

To ascertain the effects of pre-ozonation and SAT on the performance of NF membranes, analyses of the fate of organic matter present in the secondary effluent during ozonation, SAT and nanofiltration, as well as the analyses of flux decline during nanofiltration are required.

1.3 Goal and objectives

The main goal of this research is to assess the effectiveness of SAT pre-treatment on the performance of NF membranes. The specific objectives of the study are:

1. To analyse the effect of pre-ozonation on the efficiency of organic matter removal from secondary effluent of a conventional wastewater treatment plant during SAT.
2. To analyse the effect of SAT pre-treatment on efficiency of organic matter removal from secondary effluent during nanofiltration.
3. To analyse the effect of pre-ozonation and/or SAT pre-treatment on fouling or flux decline of NF membranes.

2 Literature Review

2.1 Characteristics of a conventional wastewater treatment

2.1.1 Wastewater characterisation

Municipal wastewater generally refers to all liquid wastes collected from residential, commercial, and industrial areas conveyed by means of a sewerage system to a central treatment plant. It consists of over 99.9% water and the remaining materials include suspended, dissolved organic and inorganic matter and micro-organisms. These materials characterise the physical, chemical and biological qualities of residential and industrial wastewaters (Qasim, 1999).

The physical quality of municipal wastewater is represented by temperature, color, odour, and turbidity.

The chemical quality of wastewater is expressed in terms of organic and inorganic constituents. Domestic wastewater typically contains 50% volatile and 50% fixed materials. The main constituents of organic matter in domestic wastewater are carbohydrates, proteins, fats, oils and grease. Carbohydrates and proteins are highly biodegradable compared to fats, oils and grease which are more stable and decompose slowly when acted by micro-organisms. Wastewater may also contain fractions of synthetic detergents, phenolic compounds, pesticides and herbicides coming from industrial wastes and surface run-off. Although the concentrations of these toxic compounds in municipal wastewater are small; nevertheless, these compounds introduce problems of non-biodegradability, foaming, and carcinogenicity (Qasim, 1999).

Microorganisms contained in municipal wastewater play an important role in biological treatment. The main groups of microorganisms that are significant in wastewater treatment include bacteria, fungi, protozoa and algae. The typical microbiological composition of domestic wastewater consists of 10^5–10^8 colony-forming unit (CFU)/ml of coliform organisms, 10^3–10^4 CFU/ml fecal streptococci, 10–10^3 protozoan cysts, and 10–10^2 virus particles (Her et al., 2008).

2.1.2 Levels of wastewater treatment

Depending upon the degree of treatment aimed and methods applied wastewater treatment processes are generally classified as primary, secondary and tertiary treatment.

Primary treatment include unit operations such as bar screens, grit removal and sedimentation facilities. The main purpose of primary treatment is the removal of coarse and settleable inorganic and organic solids.

The combination of primary treatment with biological and chemical treatment processes is termed secondary treatment whose purpose is to remove dissolved organics. Secondary treatment unit operations or processes include suspended growth bioreactor, attached growth aerobic biological reactor, sequencing batch reactor, and secondary clarifier (Qasim, 1999). Secondary treatment is employed to remove oxygen-demanding organic pollutants, which are present mostly in the dissolved form. This

process utilizes bacterial biological degradation to remove the dissolved pollutants (Her et al., 2008).

Tertiary treatment is often employed for enhancing the microbial quality of secondary treatment processes, especially if the wastewater is to be reused or recycled for irrigation of food or landscape plants, recreational purposes, and drinking water. Tertiary treatment which further reduces the amount of pathogens, may include membrane filtration, addition of chemical coagulants to enhance flocculation and filtration processes, detention ponds or reservoirs, and passage through natural systems such as wetlands and soil aquifer treatment (SAT). Most tertiary treatments are very effective in reducing the number of helminthes and protozoan parasites, which are removed by filtration and detention. Overall tertiary treatment processes will remove greater than 99% of the helminthes, and 95 to 99% of the protozoan cysts and oocysts (Gerba, 2008).

2.1.3 Major pollutants in conventionally treated wastewater effluents

Effluents from primary and secondary wastewater treatment plants contain a number of pollutants including pathogens (harmful bacteria and viruses), nutrients, heavy metals and residual organic compounds. These pollutants may pose potential health hazard when present in reclaimed water for indirect potable use, resulting in immediate diseases or after years of accumulation in the body.

In wastewater reclamation technology involving SAT and aquifer recharge, pathogens and heavy metals do not pose much problem because they are removed in the pre-treatment and during SAT itself, and water will most likely be disinfected again before potable use. Most natural organic compounds such as carbohydrates, proteins, fat, etc. are biodegradable and hence decompose in the soil. The main concern is with the trace organic compounds that are still present in the water after recharge, SAT and blending with native groundwater (Bouwer, 1996a).

2.1.4 Characteristics of conventional activated sludge effluent

For the activated sludge system, it is necessary to characterise the wastewater physically: (1) soluble, (2) non-settleable (colloidal or suspended) and (3) settleable (organic or inorganic); and biologically: (1) biodegradable and (2) nonbiodegradable.

Sludge age is the main driver that governs effluent quality and size of the activated sludge system. Generally, the higher the effluent quality required from the system, the longer the sludge age. For organic matter removal only, the sludge age of the system is short (Ekama & Wentzel, 2008).

Typical range of effluent quality after conventional activated sludge secondary treatment is given in Table 2-1.

Table 2-1. Typical range of effluent quality after conventional activated sludge treatment.

Constituent	Unit	Untreated wastewater	Conventional activated sludge
Total suspended solids (TSS)	mg/L	120 – 400	5 – 25
Colloidal solids	mg/L		5 – 25
Biochemical oxygen demand (BOD)	mg/L	110 – 350	5 – 25
Chemical oxygen demand (COD)	mg/L	250 – 800	40 – 80
Total organic carbon (TOC)	mg/L	80 – 260	10 – 40
Ammonia nitrogen	mg N/L	12 – 45	1 -5
Nitrate nitrogen	mg N/L	0 – trace	10 – 30
Nitrite nitrogen	mg N/L	0 – trace	0 – trace
Total nitrogen	mg N/L	20 – 70	15 – 35
Total phosphorous	mg P/L	4 – 12	4 – 10
Turbidity	NTU		2 – 15
Volatile organic compounds (VOCs)	µg/L	<100 - > 400	10 – 40
Metals	mg/L	1.5 – 2.5	1 – 1.5
Surfactants	mg/L	4 – 10	0.5 – 2
Total dissolved solids	mg/L	270 – 860	500 – 700
Trace constituents	µg/L	10 – 50	5 – 40
Total coliform	No/100 mL	10^8 - 10^9	10^4 – 10^5
Protozoan cysts and oocysts	No/100 mL	10^1 - 10^4	10^1 -10^2
Viruses	PFU/100 mL	10^1 - 10^4	10^1 - 10^3

(Source: Asano et al., 2007)

2.1.5 Effluent organic matter (EfOM)

One of the parameters of concern for human and environmental health is organic matter originating from wastewater treatment plant (WWTP) effluents. The organic composition of wastewater is approximately 50% proteins, 40% carbohydrates, 10% fats and oils, and trace amounts (e.g., μg/L or less) of priority pollutants, surfactants, and emerging contaminants (Her et al., 2008). Characterization of effluent organic matter (EfOM) is essential in order to find an optimum treatment method for water reuse. For the purpose of wastewater reclamation reuse, it is imperative to study the characteristics of EfOM in the biologically treated secondary effluent (BTSE) in detail in order to design effective treatment methods (Shon et al., 2006b).

Total organic carbon (TOC) is a relevant surrogate parameter for monitoring the amount of organic matter in wastewater. TOC can be classified into two groups: particulate organic carbon (POC) and dissolved organic carbon (DOC). The fraction of particulate organic material measured as suspended solids (SS) includes protozoa, algae, bacterial floc and single cells, microbial waste products, and other miscellaneous debris. Dissolved organic matter (smaller than 0.45 μm) are typically cell fragments and macromolecules. Her et al. (2008) classified EfOM into two main groups by size: 1) particulate organic carbon (POC) above 0.45 μm, and 2) dissolved organic carbon (DOC) below that limit. Figure 2-1 shows the different constituents found in BTSE.

DOC in drinking water sources has been a great concern. Not only does DOC cause color and odor in water, but it also is a precursor for a variety of carcinogenic disinfection by-products (DBPs), such as trihalomethanes (THMs) in water chlorination.

POC can easily be removed by solid-liquid separation processes. However, DOC presents a greater challenge on prevailing removal techniques and remains a focus of research in wastewater treatment. Figure 2-2 presents the important DOC components in water.

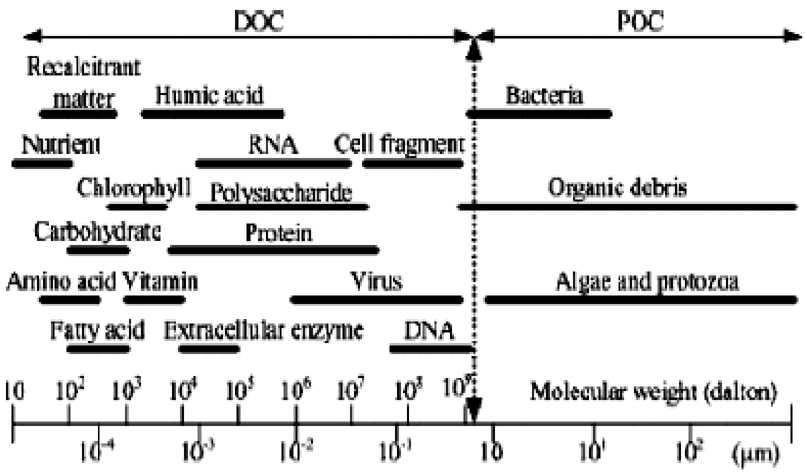


Figure 2-1. Typical organic constituents in BTSE and their size ranges
(Source: Her et al., 2008; Shon et al., 2006b)

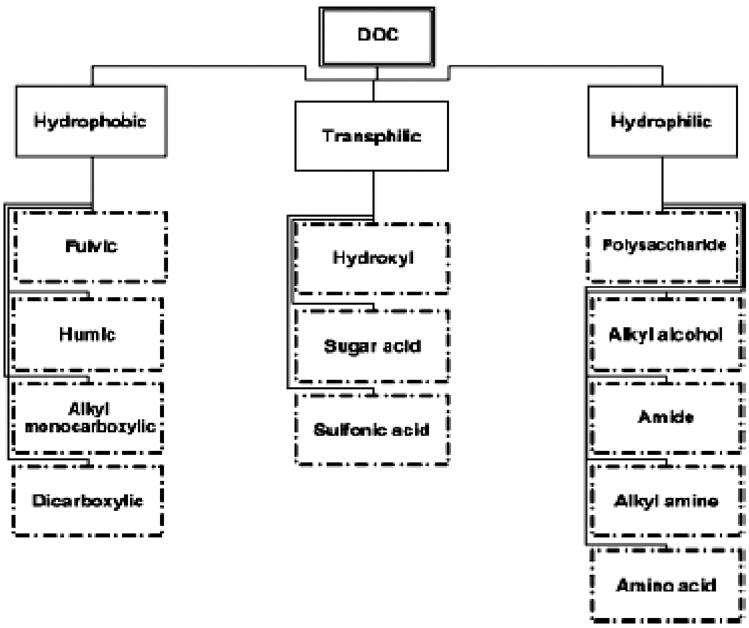


Figure 2-2. Fractions of DOC and their constituents.
(Source: Shon et al., 2006b)

EfOM in wastewater consists of both particulates and dissolved substances, and has been found to include several trace organic contaminants, including endocrine-disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs). Her et al. (2008) summarized EfOM into three general classes based on their origins:

i) Natural Organic Matter

Natural organic matter (NOM) is a mixture containing a variety of water-soluble organic components. Most of the NOM originates from drinking water, one of major components in wastewater.

ii) Soluble microbial products

Soluble microbial products (SMP) are produced during biological processes of wastewater treatment. Microbes, during the process of wastewater treatment utilizing biological degradation produce SMP and extra-cellular polymeric substances, which can be toxic.

The SMPs are found to be the majority of soluble organic matter in wastewater effluent. The SMPs that are derived during biomass growth are called utilization associated products (UAP) while those that are released from cell lysis during biomass decay are termed biomass-associated products (BMP). SMP-UAPs are more biodegradable than SMP-BMPs which results into more accumulation of SMP-BMP in most biological treatment systems. Formation of SMP was found to increase during stress condition, e.g., hydraulic shock loads, low pH, nutrient deficiency, and presence of toxic compound (Jarusutthirak et al., 2007).

Toxicity of SMP is of increasing health concern. According to Shon et al (2006b), these products may actually be more toxic than the original organic compounds present in BTSE with mutagenic response being higher in BTSE than in the primary effluent.

iii) Synthetic organic compounds and disinfection by-products

Synthetic organic compounds (SOC) are added during domestic use and disinfection by-products (DBPs) are produced during chlorination in water and wastewater treatment. Together with protein, carbohydrate, fat, oil, grease, and urea, wastewater also contains small quantities of a large number of different synthetic organic molecules consisting of surfactants, priority pollutants, volatile organic compounds, agricultural pesticides, etc. The number of such substances is expected to increase as organic molecules are continually introduced into commercial products. The presence of these substances introduces complications in wastewater treatment because of their resistance to biodegradation (Shon et al., 2006b).

2.1.6 Organic matter characterisation

A number of organic matter characterisation techniques can be employed. The amount of organic matter can be quantified through DOC concentration measurements and the character of the organic matter represented by UV absorbance at 254 nm (UVA_{254}) measurements.

UVA_{254} serves as a rough indication of the overall natural organic matter (NOM) concentration. UVA_{254} is used to identify compounds specifically for humic substances. UVA_{254} is sensitive to aromatic components and is an indicator for the presence of both humic acid and fulvic acid. UVA_{254} is proportional to the aromatic carbon content and has been used as a surrogate for DOC concentrations in natural waters (Chow et al., 2008).

The composition of organic matter is provided by specific UV absorbance (SUVA) which is defined as the sample's UV absorbance at 254 nm divided by the DOC concentration of the solution. A change in SUVA is generally accepted as an indicator of biodegradability since UVA_{254} represents relatively refractory compounds. According to Leenheer & Croue (2003), wastewater treatment plant effluents are generally enriched in hydrophobic NOM, such as humic substances. Therefore, SUVA indicates aromatic compounds in the DOC and can be used to estimate the chemical nature of the DOC at a given location. High SUVA means high aromaticity and hydrophobicity of samples. For readily biodegradable matter, the value of the SUVA will increase after a biological reaction (Cha et al., 2004)

Dissolved organic matter (DOM) has distinctive spectrophotometric properties in terms of both adsorption of light and fluorescence. As well as strong adsorption in ultra-violet light, much DOM fluoresces (Baker & Spencer, 2004). Fluorescence excitation and emission matrix (FEEM) spectra analysis has been used to characterise DOM. Finally, fluorescence index (FI), which is the ratio of the fluorescence intensity at emission wavelengths of 450 and 500 nm at excitation wavelength of 370 nm, distinguishes between autochthonous organic matter, with higher FI which are microbially derived and allochthonous organic matter, those with low FI which are from terrestrial plant origin.

Recent advances in fluorescence spectrophotometry permit the rapid determination of DOM fluorescence at a wide range of both excitation and emission wavelengths to produce an excitation-emission matrix or EEM. An EEM will typically cover a range of excitation and emission wavelengths from ~200 nm (short wavelength UV) through to ~500nm (visible blue-green light) and may contain fluorescence centers or peaks that are attributed to both natural DOM groups such as humic and fulvic-like material, as well as fluorescent proteins (Baker & Spencer, 2004). Major fluorescent components in excitation-emission matrix are given according to the range of excitation and emission of the component. Table 2-2 lists the major component types of FEEM according to the ranges of excitation and emission wavelength intensities.

Table 2-2. Major fluorescent components in excitation-emission matrix.

Range of Excitation (nm)	Range of Emission (nm)	Component Type
330 – 350	420 – 480	Humic-like primary
250 – 260	380 - 480	Humic-like secondary
310 - 320	380 - 420	Marine humic-like
270 – 280	300 - 320	Protein-like (Tyrosine-like)
270 - 280	320 - 350	Protein-like (Tryptophan-like)

Source: (Leenheer & Croue, 2003)

2.1.7 Treatment of EfOM

In a wastewater treatment process, EfOM in BTSE is reduced by physical, chemical, and biological treatment methods. Physical treatment method involves the use of physical force and includes screening, sedimentation, and filtration. Chemical treatment consists of removal or conversion of contaminants by the addition of chemicals or by indirect chemical reactions. Common chemical treatment methods are coagulation, adsorption, ion exchange, and disinfection. Biological treatment which chiefly employs microbes to perform biodegradation on organic matter is important to select an appropriate treatment to remove specific compounds found in EfOM.

However, as the use of various chemicals has increased, the pollutant component of EfOM has become of great interest but most current wastewater treatment plants (WWTP) are not designed to treat harmful compounds such as endocrine disrupting compounds (EDC), and pharmaceuticals and personal care products (PPCP). A high percentage of emerging compounds may escape elimination in WWTP and enter the surface waters or ground water via effluents. The same concern remains a big challenge to wastewater recycling and indirect potable reuse technology.

The efficiency of different treatment processes may be evaluated in terms of total organic compound (TOC/DOC) removal, EDC/PPCP removal, and molecular weight (MW) distribution for the following reasons: TOC is a surrogate for general organic contaminant removal by treatments used, EDCs and PPCPs represent removal of the low-MW compounds (about 150-500 Da) which cannot be completely removed using conventional treatment process, and MW distribution provides specific removal of different organic sizes (Shon et al., 2006b).

2.2 General overview of SAT

Accelerated increase in water demand resulted in measures that were implemented to reduce consumption and to recycle water, either for non-potable and potable uses. Non-potable uses include food crop and landscape irrigation and power plant cooling. Planned, indirect potable reuse is being accepted as an option against over-drafting of groundwater aquifer. Problems such as groundwater level decline, salt-water intrusion in coastal areas, subsidence and earth fissures are some of the detrimental effects of groundwater over-drafting. The development of rapid infiltration land treatment systems arose from the need for groundwater recharge and the desire to reuse wastewater efficiently. This artificial recharge process is referred to as soil aquifer treatment (SAT) wherein the groundwater is recharged with pre-treated wastewater effluent (Houston et al., 1999).

2.2.1 Wastewater reclamation by soil aquifer treatment

Soil aquifer treatment (SAT) embodies a wastewater reclamation/reuse technology that can refurbish wastewater effluent to drinking water levels. This technique can provide the important link as a transition step between reclaimed municipal wastewater and groundwater and offers a higher level of acceptability and attractiveness in contrast to direct potable reuse due to psychological and esthetic reasons (Asano & Cotruvo, 2004).

The SAT technology consists of infiltrating wastewater effluent through a recharge basin with eventual extraction through recovery wells. Figure 2-3 shows the schematic

diagram of SAT which embodies treatment in the unsaturated (vadose) zone and storage within the saturated (aquifer) zone. It is a natural, sustainable and advanced wastewater treatment process dominated by biodegradation which is initially aerobic and susbsequently anoxic (Amy & Drewes, 2007). A number of treatment processes operate as the wastewater flows vertically downward through the unsaturated soil of the vadose zone to the underlying aquifer. The major purification processes occurring in the soil aquifer system are: slow sand filtration, chemical precipitation, adsorption, ion exchange, biological degradation, nitrification, denitrification and disinfection (Houston et al., 1999; Kanarek & Michail, 1996). These mechanisms can be very effective in removing nitrogen, phosphorous, biochemical oxygen demand (BOD), suspended solids, organic compounds and trace metals (Kopchynski et al., 1996).

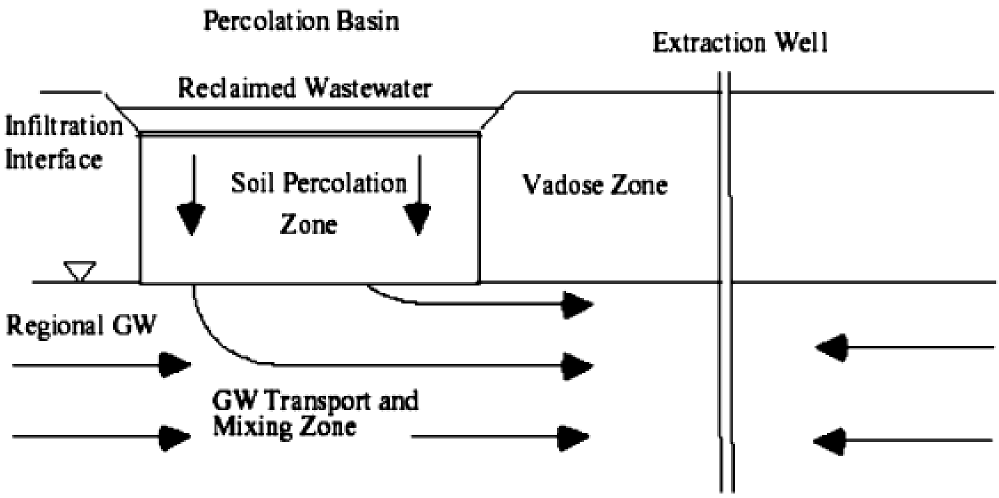


Figure 2-3. Schematic diagram of soil aquifer treatment (SAT)
(Source: Amy & Drewes, 2007; Fox et al., 2005)

Dissolved organics, nitrogen species, and pathogens present in effluent are removed (or transformed) during percolation and storage. Dissolved organic material is removed by a combination of biological, chemical, and physical processes, e.g., biodegradation and sorption, in the vadose zone and subsequently in the aquifer. Most benefits are achieved during percolation through the unsaturated zone. Removal of dissolved organics during SAT is attributed to biological activity. Removal of humic substances is due to combined mechanisms of biodegradation and sorption. Halogenated organics is removed essentially by sorption (Quanrud et al., 1996).

Direct injection of reclaimed water is possible when land is not available for spreading basins (Fox et al., 2005). Well recharge method is also practiced when there is an absence of permeable surface soils, restricting vadose zone layers and/or aquifers are confined. One method that has been gaining interest is the use of larger diameter dry wells or vadose zone wells for recharge of unconfined aquifers. Clogging around the well has been the main problem with aquifer and vadose zone wells. This is especially true for the vadose zone well because it cannot be pumped, developed, or otherwise rehabilitated after clogging. Groundwater recharge with wells is most frequently more expensive than with surface infiltration basin systems and loses some benefits of SAT where sewage effluent is used. However, well recharge still enhances the aesthetics and

reuse of sewage effluent for potable reuse because it breaks the 'pipe-to-pipe' link of direct recycling of sewage effluent with in-plant treatment only (Bouwer, 1996a).

2.2.2 Health considerations in groundwater recharge with reclaimed wastewater

The main issue in potable reuse of treated wastewater after SAT and blending with native groundwater is with the trace organic compounds that are still present in the water, although in very small concentrations. Other constituents like nitrates, pathogens and heavy metals are removed in the pre-treatment and during SAT. Most natural organic carbon compounds (carbohydrates, proteins, fats, etc.) are biodegradable and therefore decompose in soil. Also, a large number of synthetic organic compounds (SOC) that enter the water as chemicals in industrial wastewater, hospital wastes, storm runoff, and domestic wastewater are biodegradable, especially the non-halogenated compounds. The problem lies with the resistant organic compounds known as non-biodegradable, stable refractory, or recalcitrant compounds that may accumulate in the adsorbed state in the soil and aquifer and eventually may travel with the water when the adsorption sites are saturated with these chemicals (Bouwer, 1996a).

With the potable reuse of treated wastewater, a major concern is that organic pollutants known as endocrine disrupting compounds (EDCs) might survive water treatment and transport through soil-aquifer treatment (SAT) systems resulting in residual concentrations in drinking water, which might pose potential adverse human health effects [(Drewes & Shore, 2001) as cited by (Mansell et al., 2004)]. The presence of EDCs in drinking water sources is of concern because EDCs can either mimic natural hormones or inhibit the effects of a hormone causing an increase or decrease in the production of hormones. Multiple studies have shown that EDCs can survive wastewater treatment processes and are present in wastewater effluents in concentrations that can cause adverse effects on wildlife, both in nature and in a laboratory setting (Mansell et al., 2004).

2.2.3 Factors affecting SAT performance

The factors that influence infiltration rates and soil aquifer treatment are soil type, surface clogging material, pond depth and wetting/drying cycles.

i) Soil type

Results from Quanrud et al. (1996) indicate that significant differences in removal efficiencies during through-column removal of non-purgable dissolved organic carbon (NPDOC) for columns containing sandy loam (56%), sand (48%) and silty sand (44%). No significant differences in the removal of UV-absorbing organics were observed in the same experiment for columns containing sand (22%) and sandy loam (20%).

ii) Surface clogging material

The hydraulics of wastewater infiltration basins are affected by the formation of a low-conductivity clogging layer on and within the upper few millimeters of the surface soils (Bouwer, 1996b) as cited by (Houston et al., 1999). Surface clogging phenomenon is also present even in freshwater recharge basins. This clogging layer impedes wastewater infiltration (Quanrud et al., 1996).

As particulate material accumulates on the bottom of the basin to form the clogging layer it exists in a loose, compressible state. An increase in water depth translates to compression of this loose material because of the action of the seepage forces exerted by the infiltrating water, eventually resulting in the reduction of hydraulic conductivity of the clogging layer and the infiltration rate (Houston et al., 1999).

iii) Pond depth

Increased pond depth increases the hydraulic gradient across the clogging layer, which tends to increase the infiltration rate if all other factors are the same. This effect competes with that of the surface-clogging effect. The net effect depends on the relative importance of the two phenomena and increasing the pond depth may either raise or lower the infiltration rate, or maintain the same rate if the effects compensate each other (Houston et al., 1999).

iv) Wetting/drying cycles

During soil aquifer treatment, cyclic flooding/drying of the basins is necessary for improvement of infiltration rates and to control aerobic/anoxic conditions in the soil (Kopchynski et al., 1996). Recharge basins function under wet and dry cycles, alternately. A clogging layer called schmutzdecke develops at the soil surface during flooding due to the combined effects of algal growth, suspended solids deposition, and bacterial growth in soil pore spaces and slows down the infiltration rate. However, infiltration rates are restored during the drying cycles by allowing the soil surface to dry and develop cracks (Quanrud et al., 1996).

Wet-dry cycle operations consist of filling the pond to a certain depth, stopping the inflow (loading) and allowing the water to infiltrate into the ground. After all the water has infiltrated into the soil, the pond is left to dry for a period so that natural aeration can take place. During the drying period, water percolates and the infiltration potential for the next application period increases. When clogging occurs, the recharge basin can be cleaned and possibly restored to their original capacity by draining, drying and scraping. Another method of wet-dry cycle operation is to maintain a full pond, i.e., the influent water is maintained at a rate equal to the recharge rate. When the recharge rate reaches an unacceptable value, the operation is stopped so that the clogging layer can be removed (Li et al., 2000).

2.2.4 Current practices in ASR/SAT technology

Israel, United States of America and Australia are some of the countries that have successfully implemented wastewater reclamation projects featuring the aquifer recharge and recovery systems.

i) Dan Region reclamation project in Israel

The Dan Region Project is the largest water reclamation scheme in Israel, which is in operation since 1977 and provides for collection, treatment, groundwater recharge and reuse of municipal wastewater from Tel-Aviv metropolitan area and several neighboring municipalities. The special recharge-recovery method developed and practiced successfully is a SAT mainly for purification purposes as well as for seasonal and multi-annual storage. The reclaimed water was supplied for unrestricted irrigation to the

south of the country. The SAT performance for basic wastewater and irrigation water quality parameters are presented in Table 2-3.

Table 2-3. SAT performance (Dan Region Project) - basic wastewater parameters

Parameter	Units	Before SAT		After SAT		Percentage Removal, %	
		RE	MBTPE	OW54	OW17S	Soreq	Yavne
Suspended Solids	mg/l	40	17	0	0	100	100
BOD	mg/l	27	20	<0.5	<0.5	>98	>98
BOD f	mg/l	6	2	<0.5	<0.5	>98	>75
COD	mg/l	119	63	11.7	8	90	87
COD f	mg/l	71	43	11.7	8	84	81
TOC	mg/l	25	18	3.9	2.4	84	87
DOC	mg/l	17	14	3.9	2.4	77	83
UV_{254} Absorbance	$cm^{-1}x1000^{3}$	379	287	86	55	77	81
Detergents	mg/l	0.40	0.37	0.17	0.057	58	85
Phenols	mg/l	9	8	<3	<2	>67	>75
Ammonia, as N	mg/l	14.90	10.36	<0.11	<0.03	>99	>99
Kjeldahl Nitrogen	mg/l	22.6	14.0	0.83	0.57	96	96
Kjeldahl Nitrogen f	mg/l	18.9	12.9	0.83	0.57	96	96
Nitrate, as N	mg/l	<0.06	2.94	<1.28	5.33		
Nitrite, as N	mg/l	<0.097	0.94	<0.01	2.86	90	
Total N	mg/l	22.8	17.88	<2.1	8.76	>91	51
Filtered N	mg/l	19.1	16.78	<2.1	8.76	>89	48
Phosphorus	mg/l	6.1	3.3	0.02	0.01	>99	>99
Alkalinity, as $CaCO_3$	mg/l	338	288	370	310		
pH	-	7.63	7.73				

(Source: Kanarek & Michail, 1996)

ii) United States of America

In the United States of America (USA), SAT has been extensively used in wastewater reclamation systems. The list in the table below selects some of the successful SAT operations in the USA showing type of wastewater applied and typical BOD removal:

Table 2-4. Typical BOD removal for selected SAT systems in the USA

SAT Location	Pre-treatment	Applied wastewater BOD (mg/L)	Percolate BOD concentration (mg/L)	Removal efficiency (%)
Boulder, Colorado	Secondary	131	10	92
Calumet, Michigan	Untreated	228	58	75
Ft. Devens, Massachussets	Primary	112	12	89
Hollister, California	Primary	220	8	96
Lake George, New York	Secondary	38	1.2	97
Phoenix, Arizona	Secondary	15	0-1	93-100
Vineland, New Jersey	Primary	154	6.5	96

(Adapted from: Sharma & Amy, 2008)

iii) Australia

Dillon et al. (2006) presented two case studies in Australia featuring contrasting approaches for subsurface storage of reclaimed water for horticultural reuse. Table 2-5 shows some of the features of these two projects.

a) Aquifer storage and recovery (ASR) in Bolivar, South Australia

The Bolivar reclaimed water ASR project was established in 1996 to test technical, economic and environmental viability of storing reclaimed water in an aquifer in winter for recovery in summer. The product tertiary treated municipal sewage effluent is used in the ASR via a single injection and recovery well at Bolivar, South Australia. The recovered water is used for unrestricted irrigation of horticulture. A limestone aquifer at depth of 100 to 160 m confined by clay and containing brackish groundwater provides the storage zone.

b) SAT in Alice Springs

Trials are proceeding to assist in the design and establishment of a soil aquifer treatment system which will allow water derived from secondary treatment of municipal sewage effluent to be stored in an unconfined aquifer for irrigation of horticulture. Supplementary treatment is provided by intermittent infiltration.

Table 2-5. Comparisons between Bolivar ASR and Alice Springs SAT projects

	Bolivar ASR	Alice Springs SAT
Trial capacity (ML/y)	250	600
Aquifer	Extensive confined tertiary limestone	Unconfined alluvial palaeochannel
Groundwater salinity (typical) (mg/L)	2100	1900
Reclaimed water salinity (typical) (mg/L)	1200	1000
Land area required (m^2)	<200	<20,000

(Source: Dillon et al., 2006)

2.2.5 Pre-treatment and post-treatment options for SAT

SAT can only remove portions of organic matter remaining in biologically treated secondary effluent including refractory organic components, which can cause aesthetic and odour problems, as well as increase bacterial re-growth. Moreover, if the organic matter content is high, chlorine disinfection on the reclaimed water can result in the formation of mutagenic or carcinogenic compounds (Pi & Wang, 2006). Dissolved organic carbon (DOC) and other water parameters therefore must be reduced to acceptable levels using advanced treatment processes to improve the secondary effluent quality before it is used for groundwater recharge.

The degree of pre-treatment and post-treatment methods that can be combined with SAT depends on the intended use of the product water. The role of SAT in water reclamation system is schematically represented in Figure 2-4. When sewage effluent or other low quality water is used and the recharge systems are designed and operated as recharge and recovery systems, the optimum combination of pre-treatment and post-treatment for SAT must be selected.

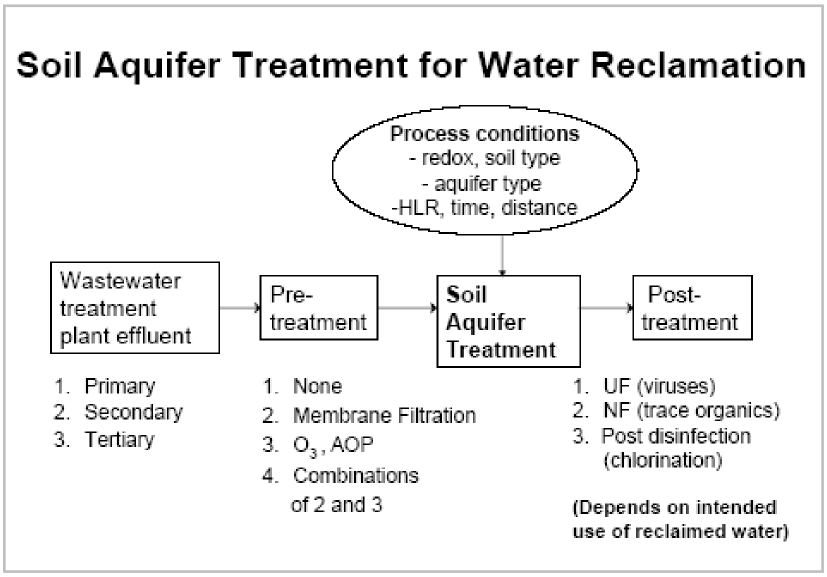


Figure 2-4. Schematic representation of SAT in water reclamation system (Source: Sharma & Amy, 2008)

2.3 Ozonation

Ozone (O_3) is a powerful oxidizing agent that can be produced by passing an electric discharge through a stream of air or oxygen. The fundamental processes involved in the formation and destruction of ozone include the presence of activated oxygen such as free radicals at the state ^3P or ^1D and also ionized oxygen species and a third element M to absorb excess energy of the reaction (Goldman & Leguiller, 1982). The principal formation/destruction reactions are represented in the following table.

Table 2-6. Principal reactions in ozone formation and decomposition

	Principal Reactions
Ozone formation	$O_2 + e \rightarrow O(^3P) + O(^1D)$ $O(^3P) + O_2 + M \rightarrow O_3 + M$ $O(^1D) + O_2 \rightarrow O_3$
Ozone decomposition	$e + O_3 \rightarrow O_2 + O^-$ $O- + O_3 \rightarrow O_2 + O^-$ $O(^3P)$ or $(^1D) + O_3 \rightarrow 2O_2$

(Source: Goldman & Leguiller, 1982)

A general reaction pathway, given by von Gunten (2003), of the reaction of ozone with inorganic and organic compounds is shown in Figure 2-5. An electrophilic addition of

ozone to the compound S leads to an intermediate adduct ($S-O_3$), which then decomposes by formation of primary products. As can be seen from the scheme, there is a wide spectrum of reactions such as oxygen atom transfer (1), electron transfer (2), formation of an oxyl radical (3), ozone insertion (4) and ring formation (5). Depending on the investigated compound, these products are stable in water or react further with compounds that will eventually be detected in drinking waters after the ozonation step. Numerous degradation products are mineralised in the biological filtration step that normally follows ozonation.

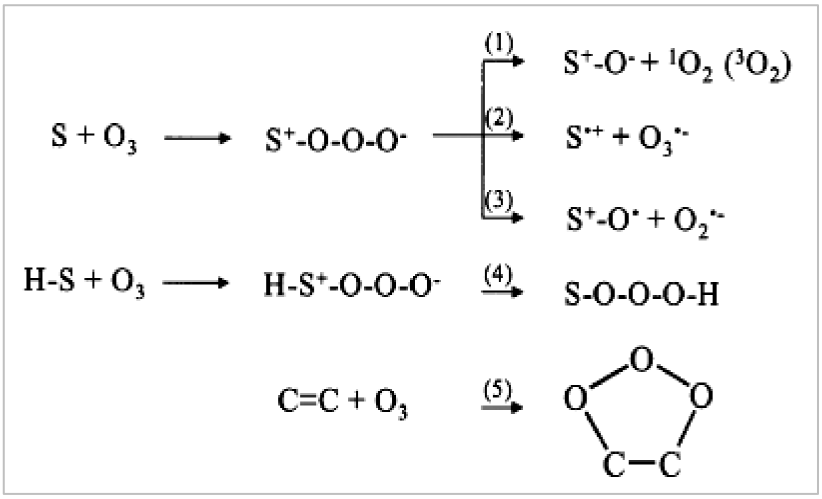


Figure 2-5. Primary reaction pathway of ozone with compound S
Source: (von Gunten, 2003)

Ozone treatment is well known for its suitability in organic matter removal from a wide range of waters. Ozone is a powerful and selective oxidant that exhibits fast reaction kinetics with compounds including functional groups such as activated aromatic rings, neutral alkylamines, double bonds and thiols. In addition, ozone may undergo self-decomposition into more powerful oxidants which are hydroxyl radicals, thus initiating an advanced oxidation process, depending on the water matrix and application conditions (Baig et al., 2008). It is more expensive than chlorination and commonly applied in drinking water treatment than in sewage treatment. Ozone as a disinfectant is not affected by pH and ammonia and does not leave residual in water (Gerba, 2008).

The use of ozone in water treatment is well established. Ozone is applied for drinking water treatment mainly because of its oxidative strength. This powerful oxidation potential facilitates the breakdown of bigger organic compounds for better biodegradability. Ozone is effective in the reduction or elimination of colour, aftertaste and odour. This same process is used to liberate organically bound heavy metals, which otherwise are not easily removed. Ozone also will oxidize heavy metals, reducing iron and manganese to very low, safe levels in water supplies.

Ozone will effectively destroy bacteria and inactivate viruses more rapidly than any other disinfectant chemical. Ozone will not lead to the formation of halogenated compounds such as Trihalomethanes (THMs), which are formed when chlorine is added to the raw water containing humic materials. Once formed, THM is very difficult to oxidise even with ozone.

Treating wastewater with ozone, again primarily for disinfection, was a key focus of its application in the United States during the late 1970s and early 1980s. This approach is again being considered as a means to avoid using chlorine as the primary disinfectant. Ozone is an effective disinfectant for treating municipal and industrial wastewater, enabling the end user to meet EPA pre-treatment standards. Ozone is effective in treating numerous complex and toxic chemicals. But for some compounds, it may be necessary to combine ozone treatment with ultraviolet light or ultrasound to increase reaction time. Quantities of ozone required to treat a specific chemical compound, and the required contact time, will vary.

In biological wastewater treatment, ozone is a strong cell-lytic agent, which can kill the microorganisms in activated sludge and further oxidize the organic substances released from the cells (Cui and Jahng, 2004; Saktaywin et al., 2005 as cited by Chu et al., 2008). Sludge disintegration by ozone can be described as sequential decomposition reactions of the cell destruction, solubilization and subsequent oxidation of the released organics into carbon dioxide (Chu et al., 2008).

Ozone is very unstable in aqueous solutions and dissociates into oxygen and hydroxyl radicals. These hydroxyl radicals have strong oxidizing properties capable of oxidising and disintegrating refractory organic matter into biodegradable simple compounds. The decay of ozone in natural waters is characterised by fast initial decrease of ozone, followed by a second phase in which ozone decreases with first order kinetics. Depending on the water quality, the half-life of ozone is in the range of seconds to hours. The major secondary oxidant formed from ozone decomposition in water is the OH radical. The stability of ozone largely depends on the water matrix, especially its pH, the type and content of natural organic matter (NOM) and its alkalinity (von Gunten, 2003).

2.4 General overview of membrane filtration

Membrane can generally be defined as a selective barrier between two phases. Membrane filtration utilizes the ability of membranes to transport the solvent, usually water, more readily than the other component because of differences in physical and chemical properties between the membrane and the solute. Transport through the membranes is accomplished by a driving force, acting on the components in the feed. The resulting permeation rate is proportional to the driving force.

As early as the middle of the eighteenth century, interest in membrane phenomena were observed and studied but the first commercial membranes for practical applications were manufactured in Germany after World War I. The first industrial use of membrane in seawater desalination using RO was introduced in the USA in 1960 (Mulder, 1996).

2.4.1 Membrane processes

A membrane process can be defined as splitting a feed stream by a membrane into a retentate (or concentrate) and a permeate fraction (van der Bruggen et al., 2003). Fane (1996) categorized the membrane processes as follows:

Pressure-driven, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) – the pore size determine the removal of contaminants by various mechanisms when the water passes through the membrane.

Solute-transfer including electrodialysis (ED) and dialysis– removal mechanism is provided by electrochemical, diffusive or preferential solubility effects.

Thermal including membrane distillation (MD) and pervaporation (PV) – the liquid water undergoes phase change as it passes through the membrane requiring heated feed.

Hybrid – one or more membrane process is combined with another unit process such as adsorption, ion exchange, coagulation, bioconversion, catalysis, and others, attaining a better performance than either of them.

Among the list, pressure-driven processes are well established and widely applied in water treatment. Pressure membrane processes use the pressure difference between the feed and permeate side as the driving force to transport the solvent (usually water) through the membrane. Retention of particles and dissolved components are dependent on the pore size of the membrane and particle properties such as size, shape and charge. This classification distinguishes among MF, UF, NF and RO as presented in Table 2-7.

Table 2-7. Membrane processes and their characteristics.

	Microfiltration (MF)	Ultrafiltration (UF)	Nanofiltration (NF)	Reverse Osmosis (RO)
Permeability ($l\text{-}h^{-1}\text{-}m^{-2}$)	>1,000	10 – 1,000	1.5 - 30	0.05 – 1.5
Pressure (bar)	0.1 - 2	0.1 - 5	3 - 20	5 - 120
Pore size (nm)	100 – 10,000	2 - 100	0.5 -2	< 0.5
Rejection				
Monovalent ions	-	-	-	+
Multivalent ions	-	-/+	+	+
Small organic compounds	-	-	-/+	+
Macromolecules	-	+	+	+
Particles	+	+	+	+
Separation mechanism	Sieving	Sieving	Sieving Charge effects	Solution-Diffusion
Applications	Clarification; pretreatment; removal of bacteria	Removal of macromolecules, bacteria and viruses	Removal of (multivalent) ions and relatively small organics	Ultrapure water; desalination

(Source: van der Bruggen et al., 2003)

MF membranes have the largest pores, ranging from 0.1 μm to 10 μm, and have the highest permeability, thereby obtaining a higher water flux at low pressure. Components larger than the pore size are removed by a sieving mechanism. Sizes corresponding to suspended solids, colloids and bacteria are retained by the membrane. On the other hand, germs and viruses are not eliminated.

UF membranes have smaller pores varying from 2 to 100 nm and lower permeability than MF; higher pressures are required. Components such as some multivalent ions and particles bigger than the pore size are retained. Typically, UF can remove large dissolved macromolecules that constitute the largest molecules on natural organic matter (NOM). The concept of molecular weight cut-off (MWCO) is often used for ultrafiltration. Ninety percent of the components larger than the MWCO are retained by the membrane. Rejection increases with molecular weight and the rejection curves (rejection versus molecular weight) have a typical S-shape. The MWCO is rough indication of the membrane's characteristic but allows comparison between different UF membrane types (van der Bruggen et al., 2003).

In nanofiltration, the pore sizes are usually around 1 nm corresponding to dissolved compounds with molecular weight of 300. NF membranes are appropriate for removal of organic micropollutants and color from surface water or groundwater and degradation products from the effluent of biologically-treated wastewater. Aside from the sieving mechanism, NF membranes allow the retention of ionic species due to the electric potential characterizing the equilibrium of the charged membrane and the bulk solution. This electric potential is termed the Donnan potential and the surface charge of the membrane results from the carboxylic or sulfonic acid groups present in the polymeric NF membrane that ionize in the presence of feed solution.

RO membranes are dense membranes without predefined pores resulting in slower permeation. Rejection is not carried out by mechanical sieving but rather from solution-diffusion mechanism. The operation requires high pressures because of the low permeability of the membranes, translating into high energy consumption. If the feed contains high concentrations of dissolved components, then this effect is even more prominent due to the high osmotic pressure that counteracts the exerted pressure.

2.4.2 Classification of membranes

Membranes are classified into two main groups: porous and nonporous membranes.

i) Porous membranes

Separation in this class of membranes is accomplished by discriminating between particle sizes. Such membranes are used in microfiltration and ultrafiltration. Porous membranes contain fixed pores in the range of 0.1 to 10 μm for MF and 2 to 100 nm for UF. Selectivity is mainly determined by the dimensions of the pores. The choice of materials does not affect flux and rejection but plays a role in the adsorption and chemical stability under condition of actual application and membrane cleaning. High selectivity can be obtained where the solute size or particle size is larger than the pore size in the membrane (Mulder, 1996).

International Union of Pure and Applied Chemistry (IUPAC, 1985) provided the following definition of pore sizes:

a) Macropores are larger than 50 nm
b) Mesopores are in the range of 2 to 50 nm
c) Micropores are smaller than 2 nm

This definition classifies NF membranes, having pore size of 0.5 to 2 nm, as porous membranes. NF can be classified in an intermediate class between porous and nonporous membranes since solution-diffusion and electrochemical effects have to be introduced in the mass transfer equations (Aptel & Buckley, 1996).

ii) Nonporous membranes

This class of membranes is capable of separating molecules of approximately the same size from each other. Nonporous membranes are used to perform separation on a molecular level. Separation is effected through differences in solubility and in diffusivity. The basic properties of the membrane material determine the extent of selectivity and permeability. The chemical nature and structure of the polymeric membrane and the degree of interaction between the polymer and the permeants are the essential factors to consider rather than the molecular weight or molecular size. The extent of selectivity and permeability is determined by the intrinsic properties of the polymeric material. Transport through nonporous membranes occurs by a solution-diffusion mechanism. Separation is achieved by differences in either solubility or diffusivity, or both. Nonporous membranes are used in gas and vapour separation and pervaporation (Mulder, 1996).

2.4.3 Concentration polarisation and membrane fouling

Membrane fouling is a major constraint on the implementation of membrane processes for use in drinking water treatment. The decrease in flux is due to an increase in the resistance of the membrane to permeation over time by the accumulation of materials (such as cake/gel formation, concentration polarization, and adsorption on the membrane surface), pore blocking and adsorption to pore walls. Fouling increases operational costs with decreasing permeate production and/or increasing transmembrane pressure (TMP) requirements. Frequent chemical cleaning deteriorates membrane performance, leading to shortenend membrane life. Therefore, the identification of foulants and their fouling mechanisms is very important to reduce or avoid membrane fouling, to optimize pre-treatment, and to decide upon optimal cleaning agents and cleaning procedures.

i) Concentration polarisation

When a driving force acts on the feed solution, the solute is partly retained by the membranes while the solvent permeates through the membrane. The membrane has a certain retentivity for the solute while the solvent can permeate more or less freely. Because the membrane retains the solutes to a certain extent, there will be accumulation of retained molecules near the membrane surface. The gradual increase of the retained solutes at the membrane surface is a phenomenon called concentration polarisation. This highly concentrated layer near the membrane exerts a resistance towards mass transfer and termed concentration polarisation resistance (R_{cp}). Other types of resistance toward mass transport are pore-blocking resistance (R_p), adsorption resistance (R_a), gel layer resistance (R_g), and the membrane resistance (R_m) itself. Total resistance (R_{tot}) of the membrane is the sum of all types of resistances and is inversely proportional to the convective flux (Mulder, 1996). The overview of membrane resistance towards mass transport in membranes is given in Figure 2-6.

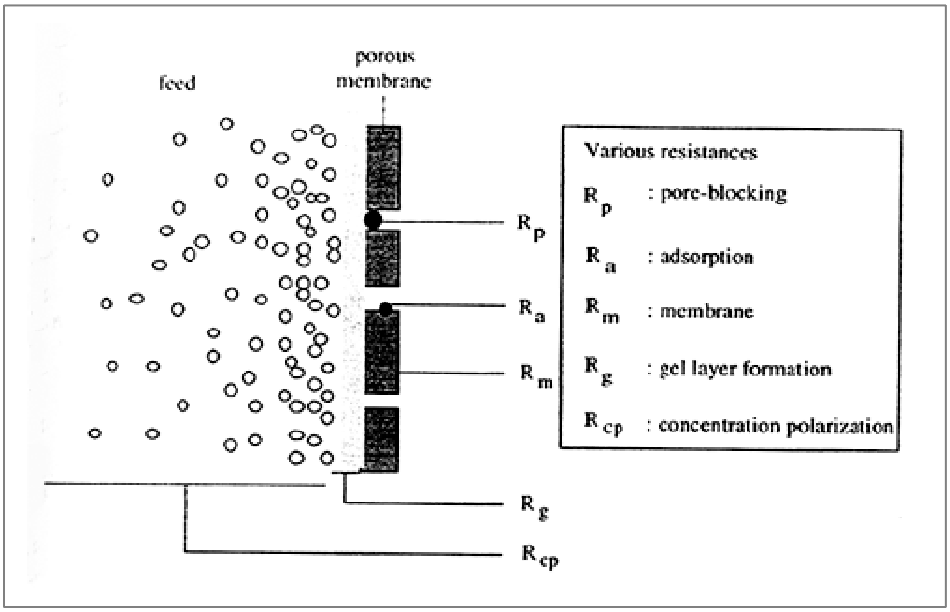


Figure 2-6. Overview of types of resistance towards mass transport in membranes (Source: Mulder, 1996)

ii) Membrane fouling

A major problem that face membrane applications is membrane fouling defined as the drop in the permeate flux with time. Fouling is due to 1) standard blocking - the deposition of small colloidal particles on the inner walls of the membrane's pores, 2) complete blocking – blocking the membrane pore openings, and 3) build up of particles in the form of a cake layer. All of the above phenomena add resistance to the flow. Fouling due to blocking and cake formation is assumed to be the predominant mechanism in UF and MF filtration whereas cake filtration is the predominant mechanism in RO and NF operation (Mousa & Al-Hitmi, 2007).

Fouling occurs mainly in MF and UF where porous membranes, which are susceptible to fouling, are used. Three types of foulants can be distinguished: 1) organic precipitates - macromolecules, biological substances, etc., 2) inorganic precipitates – metal hydroxides, calcium salts, etc. and 3) particulates (Mulder, 1996).

Membranes can be easily fouled by effluent organic matter (EfOM) present at high levels in wastewater. EfOM-fouling, defined as the accumulation and/or adsorption of organic materials on the surface, or in the pores of a membrane, affects membrane performance including permeability and EfOM rejection. The decrease of permeate flux was found to be dependent upon EfOM-fouling, occurring by the accumulation of organic materials on membrane surfaces and/or within membrane pores (Jarusutthirak & Amy, 2001).

2.4.4 Membrane fouling mechanisms

Mechanisms leading to fouling of membranes can be described by the following phenomena (Wiesner & Aptel, 1996):

i) Concentration polarisation

Although strictly not a fouling phenomenon, polarisation has the effect of the occurrence of a maximum permeate flux which can be interpreted as one of the limiting phenomena leading to fouling of a membrane. It is only the consequence of the solute being drawn toward the physical barrier of the membrane which stops this solute. This phenomenon is considered reversible, since stopping the filtration operation trigger the disappearance of the phenomena leading to existence of solute concentration gradient.

ii) Cake formation

Particle accumulation on the membrane wall leads to the formation of a cake, which may be considered as a second membrane whose hydraulic resistance adds to the initial resistance of the membrane and eventually leading to reduction of flux. This type of fouling is generally reversible by hydraulic washing techniques, e.g., flushing and backwashing.

iii) Natural organic matter (NOM) adsoption

Presence of NOM in the solvent can lead to membrane fouling either by adsorption on the particles making up the filtration cake or by adsorption in the bulk of the membrane. Both of these phenomena can be described as fouling due to adsoption and depend mainly on the affinity that the NOM have for the polymer constituting the membrane which leads to progressive saturation of adsoption sites of the membrane material. This type of fouling is difficult to reverse or is slowly reversible since it requires desorption of the organic molecules, which can be effective only when there is a sudden drop of NOM concentration occurring in the feed water, making it possible for the adsorption equilibrium to shift towards desorption. The use of oxidising shocks like chlorine during membrane backwashing or chemical washing makes it possible to limit the loss of membrane permeability.

iv) Calcium, iron and manganese precipitation

UF processes do allow sufficient dissolved salt retention, in contrast to RO or NF. This can lead to mineral precipitation on the membrane due to ion concentrations higher than the solubility products. Precipitation of certain minerals in UF processes is one of the causes of membrane fouling. Precipitation phenomena include calcium carbonate precipitation in unbalanced waters and precipitation of dissolved metals such as iron and manganese due to oxidation and hydrolysis during the filtration process. Iron and manganese precipitation on the membrane leads to fouling of the membrane on the concentrate side, when operating in filtration. This fouling is reversible by backwashing. Similarly, the membrane can be fouled on the permeate side which happens for the case of iron and manganese precipitation during the backwashing, consequently decreasing the permeability of the membrane during the backwashing phase. This decrease of the backwash flow leads to a marked decrease in the backwash efficiency resulting in a complete fouling of the membrane that needs chemical washing.

Bowen et al. (1995) presented the consecutive steps in the whole process of membrane blocking which can be explained in terms of the successive or simultaneous presence of the following stages, as illustrated in Figure 2-7:

A. The smallest pores are blocked by all particles arriving to the membrane.
B. The inner surfaces of bigger pores are covered.
C. Some particles arriving to the membrane cover other arrived particles while others block some of the pores directly.
D. Finally a cake starts to be built.

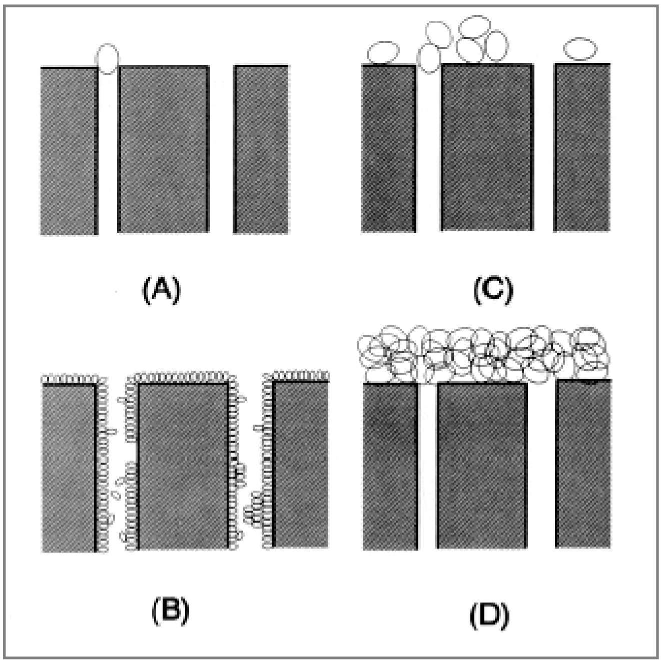


Figure 2-7. Schematic drawing of the fouling mechanisms
(Source: Bowen et al., 1995)

In practice, the four phases are superimposed, because there is a more or less wide pore size distribution. If there was only a single pore size and the pore was greater than the molecule to be deposited, blocking should start with a standard process followed by a complete blocking, an intermediate blocking, and a cake filtration. While, if the molecule was much greater than the pore, it should start with a complete blocking followed by an intermediate and a cake filtration process.

2.4.5 Role of NOM & SMPs in membrane fouling and flux decline

Certain components of NOM in natural waters (surface water and groundwater) have been found to be major membrane foulants. Typically, NOM can be separated into three fractions: hydrophobic fraction (HPO), hydrophilic fraction (HPI), and transphilic (TPI) fraction. Organic colloids and polysaccharides (hydrophilic macromolecules) are included in the hydrophilic fraction unless pre-isolation like dialysis is performed first (Lee et al., 2004).

Several studies have confirmed that NOM components of natural waters influence to a great degree the fouling of membranes.

Lee, et al. (2004) found that natural waters with a high content of hydrophilic fraction resulted in more significant flux decline in low-pressure membranes (MF and UF), explaining that this may be due to this fraction containing colloidal and

macromollecular organic matter with non-humic properties. Significant fouling was caused by adsorption of NOM around membrane pores by smaller molecules (pore construction) and/or pore blockage by larger molecules and/or colloids.

Similarly, Her et al. (2007) showed that in the case of the high DOC and hydrophobic NOM water, there was no significant flux decline indicating that the NF membrane could effectively reject hydrophobic NOM. However, for the low DOC and high hydrophilic NOM samples, these source waters exhibited a flux-decline of approximately 10% at the same operating conditions, attributing the reason to relatively high fraction of hydrophilic NOM (neutrals/bases), not expected to be readily rejected by the negatively-charged membrane due to its non-charged (or oppositely charged) properties.

In membrane filtration of wastewater effluent during wastewater reclamation, significant reduction of permeate flux caused by membrane fouling is a foremost drawback. Membrane fouling occurs instantaneously when wastewater effluent as feed water is introduced into a membrane filtration system leading to an increased resistance of the membrane and a reduction of permeate flux. Organic constituents contained in wastewater effluent collectively called effluent organic matter (EfOM) play a major role as membrane foulants. EfOM covers a range of soluble organic compounds present in biologically treated wastewater. Three different groups of complex and heterogeneous compounds can be classified: 1) refractory natural organic matter (NOM), which are already present in drinking water sources; 2) synthetic organic compounds (SOC), which are added during domestic use and disinfection by-products (DBPs) generated during disinfection of water and wastewater; and 3) soluble microbial products (SMP) derived during biological processes during wastewater treatment (Jarusutthirak et al., 2002).

Similar fractionation techniques as used in natural waters can be employed in isolating colloids, primarily consisting of large molecular weight compounds with HPI character, HPO and TPI fractions. The HPO and TPI fractions are characterised by humic and fulvic acids, with TPI fraction having smaller molecular size and more hydrophilic character than HPO fraction. However, the HPI fraction is usually found to be the most abundant fraction in the majority of biologically treated wastewater (BTSE), constituting 32-74% of total organic carbon (TOC) and HPO acids are the second most dominant portion accounting for 17-82% (Shon et al., 2006a).

Study of Shon et al. (2006a) using UF membrane on biologically treated wastewater demonstrated that the flux decline with the HPO fraction was very high compared with the TPI and HPI fractions.

Jarusutthirak et al. (2002) found that EfOM isolates exhibit different characteristics in membrane fouling and flux decline: colloids fouled the membranes by a major mechanism of pore blockage and exhibited higher flux decline than the other EfOM isolates. They postulate that the lower flux decline in the HPO and TPI fraction is likely due to the electrostatic repulsion being the major mechanism in the rejection of the two fractions. Their study also confirmed that EfOM consist of background refractory NOM associated with drinking water sources and soluble microbial products (SMP) produced from wastewater treatment plants.

Kim and Dempsey (2008) employed sequential removal of EfOM fractions using gentle techniques without using extraction and pH manipulation and tested the effects of organic materials in tertiary-treated wastewater effluent on fouling of UF membranes. The study showed that 1) removal of particle and colloids resulted in increased fouling attributed to increased contact of dissolved EfOM with the membrane; 2) HPO/HPI acids accounted for nearly all the fouling; and 3) HPO/HPI bases and neurtrals did not cause any fouling but were the dominant EfOM constituents at the surface of fouled and then hydraulically cleaned membranes.

2.4.6 Membrane fouling potential

Membrane fouling affects the cleaning frequencies, pretreatment requirements, operating conditions, cost and performance and is therefore an important consideration in the design and operation of membrane systems. Different indices have been developed to assess the treatability of a given wastewater with NF and RO membranes. The three principal indices are: i) the silt density index (SDI), ii) the modified fouling index (MFI), and iii) the mini plugging factor index (MPFI). The three fouling indices are determined using a simple laboratory dead-end membrane filter apparatus. The sample to be tested is passed through a 0.45 μm millipore filter with a 47 mm internal diameter at a constant pressure of 207 kPa (30 psi) gauge, and various measurements, depending on the index to be determined, are made (Asano et al., 2007).

i) Silt Density Index (SDI)

The SDI is the most widely used fouling index and is a static measurement of resistance which is determined by samples taken at the beginning and at the end of the test. However, SDI does not measure the rate of change of resistance during the test and is the least sensitive of the fouling indices. The equation for SDI is given by

$$SDI = 100 \times [1 - (t_1/t_f)] / t \qquad (2\text{-}1)$$

where t_1 = time to collect initial 500 mL of sample, (s)
t_f = time to collect final 500 mL of sample (s)
t = total running time of test, (s)

ii) Modified Fouling Index (MFI)

The MFI is determined using the same equipment and procedure used for the SDI except that the volume is recorded every 30 seconds over a 15-minute filtration period. The development of the MFI is consistent with Darcy's law in that the thickness of the cake layer formed on the membrane surface is assumed to be directly proportional to the filtrate volume. The total resistance is the sum of the filter and cake resistances. The following equation describes the value of MFI:

$$1 / Q = (MFI) \times V + a \qquad (2\text{-}2)$$

where Q = average flow (L/s)
MFI = modified fouling index (s/L^2)
V = volume (L)
a = constant (intercept of linear portion of curve, s/L)

iii) Mini Plugging Factor Index (MPFI)

The MPFI is defined as the ratio of flow versus time. The MPFI would seemingly be the best indicator of membrane fouling but it is rather difficult to collect flow and time data that accurately reflect fouling because of the very little flow when fouling occurs. Mathematically, MPFI is represented by

$$Q' = MPFI\,(t) + b \qquad (2\text{-}3)$$

2.4.7 Methods to reduce membrane fouling

Mulder (1996) identified several approaches as methods to reduce membrane fouling:

i) Pre-treatment of the feed solution

Fouling reduction begins with developing a proper pre-treatment method. Considerable time and effort is spent on membrane cleaning that simple yet effective pretreatment methods are often overlooked. Pretreatment methods include heat treatment, pH adjustment, addition of complexing agents (EDTA, etc.), chlorination, adsorption onto activated carbon, chemical clarification, pre-microfiltration and pre-ultrafiltration.

ii) Membrane properties

Fouling can be reduced by changing membrane properties. Porous membranes such as MF and UF produce generally much more severe fouling than dense membranes like PV and RO. Also, narrow pore size distribution can reduce fouling. Hydrophilic membranes are more resistant to fouling than hydrophobic membranes because proteins adsorb more strongly at hydrophobic surfaces and less readily removed than at hydrophilic surfaces. In the presence of negatively charged colloids in the feed, negatively charged membranes helps in reducing fouling.

iii) Module and process conditions

One example of changing a process condition having influence on fouling is by increasing the mass transfer coefficient and using lower flux membranes, concentration polarisation decreases, thereby reducing the fouling phenomena. The use of various kinds of turbulence promoters will also reduce fouling.

iv) Membrane cleaning

The methods mentioned above can reduce fouling to a certain extent. Cleaning methods will always be employed because of their deep impact on the performance and economics of membrane processes. The frequency with which membranes need to be cleaned can be estimated from process optimisation. The choice of cleaning method depends on the module configuration, the type of membranes, the chemical resistance of the membrane and the type of foulant involved. Four cleaning methods can be employed (Mulder, 1996):

Hydraulic cleaning methods include backflushing (applicable only to MF and UF), alternate pressuring and depressuring, and by changing the flow direction at a given frequency. Backflushing is performed by releasing the feed pressure after a given

period and reversing the direction of the permeate flow from the permeate side in order to remove the fouling layer within the membrane or at the membrane surface. A variant of this method is called a 'back-shock method', in which the time interval of back-flushing is reduced to seconds giving no time for cake resistance to build up, therefore maintaining a high membrane flux. The principle of back flushing is given in following diagram.

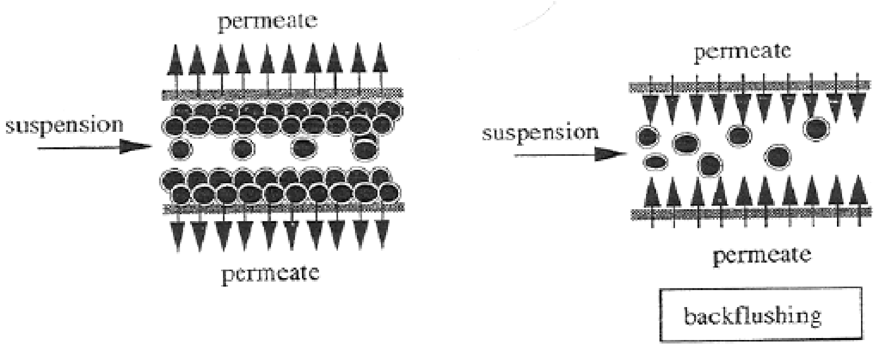


Figure 2-8. Principle of backflushing
(Source: Mulder, 1996)

Mechanical cleaning is applicable only in tubular systems using oversized sponge balls. Chemical cleaning is the most important method for reducing fouling employing a number of chemicals being used separately or in combination. The concentration of the chemical and the cleaning time are likewise very important relative to the chemical resistance of the membrane. The important classes of chemicals used are: acids (strong acids such as H_3PO_4 or weak acids such as citric acid), alkali (NaOH), detergents (alkaline, non-ionic), enzymes (proteases, amylases, glucanases), complexing agents (ethylenediaminetetraacetic acid, EDTA), polyacrylates, (sodium hexametaphosphate), disinfectants (H_2O_2 and NaOCl) and steam and gas (ethylene oxide) sterilisation.

Electric cleaning is a very special method of cleaning accomplished by applying an electric field across a membrane causing charged particles or molecules to migrate in the direction of the electric field. The electric field is applied at a certain time interval and this method of removing particles or molecules from the inter-phase can be applied without interrupting the filtration process. However, a special module arrangement with electrodes and electric conducting membranes are required.

2.5 Nanofiltration technology

Nanofiltration (NF) has always been a difficult process to define and to describe. Frequently nanofiltration and reverse osmosis (RO) are considered as one process, because of similarities of the basic principles used. The history of nanofiltration technology began in the 1970s when efforts started to develop RO membranes with reasonable water flux at relatively low pressures. The high pressures used in RO resulted in considerable energy cost but the quality of permeate was very good, and often too good (van der Bruggen & Geens, 2008). Thus a search for membranes with lower rejections of dissolved components but with higher permeability encouraged the development of NF membranes.

Tight NF membranes are in many ways similar to RO membranes, but loose NF membranes can be classified as UF membranes.

NF and RO membranes are used when low molecular weight solutes such as inorganic salts or small organic molecules such as glucose, and sucrose have to be separated from the solvent (Mulder, 1996). However, NF is distinguished from RO by lower pressure requirement with reasonable water flux.

The specific features of NF membranes are mainly the combination of very high rejections of multivalent ions (>99%) with low to moderate rejections for monovalent ions (0 to 70%), and the high rejection for organic compounds with molecular weight above the molecular weight of the membrane, which is in the range of 150 to 300 (van der Bruggen & Geens, 2008). Therefore, NF is different from RO, which has high rejection of nearly all dissolved species, and NF is different from UF, which passes nearly all low molecular weight dissolved species (Bartels, 2007).

2.5.1 Characteristics of NF membranes

Most NF membranes in commercial use are thin film composites. The membrane layer is formed in-situ by interfacial reaction and consists of a polyamide separating layer. This layer measuring as low as 0.2 microns, is supported by a porous polysulfone support and a non woven polyester fabric backing. The layered structure results in a membrane of high permeability and good mechanical strength.

The polyamide NF membranes can either be fully aromatic or a combination of aromatic and aliphatic functional groups. The fully aromatic membranes have a chlorine tolerance of around 2000 ppm-hrs while the polyamides made of combination of aromatic and aliphatic groups have much higher chlorine tolerance which is 10 to 100 times greater. Also, the polyamide membranes made with fully aromatic groups have a higher chloride rejection and are used for softening, while the aromatic/alipathic types have much higher chloride passage and are used for selective separation of charged ionic species (Bartels, 2007).

2.5.2 Applications of nanofiltration in drinking water treatment

i) Softening

The most described application of NF is softening of surface water and groundwater. NF competes with traditional water-softening processes such as inorganic and organic ion exchange systems, as well as processes such as cold and hot lime softening and pellet softening. Typical hardness removal values of NF for hardness are 70 to 99% (van der Bruggen & Geens, 2008).

When compared to lime treatment, the cost of nanofiltration is higher especially for low capacity facilities but the product water from nanofiltration is always of superior quality because of additional removal of color and turbidity. Process flexibility, smaller land requirements, absence of sludge to dispose and even site aesthetics are some other issues that are favourable for nanofiltration.

Possible problems related to the use of NF are the further treatment of the concentrate fraction and the consequent loss of water.

ii) Organics removal

The permeate quality in NF depends mainly on the type of membrane used and not primarily susceptible to changes in feed water quality. This makes NF a reliable option for surface water treatment, the focus being the removal of organic matter because surface waters have a frequently changing composition due to seasonal changes or by dilution with rain. The filtration characteristics are not affected too much by the nature of the feed water but a more extensive pre-treatment is required for surface waters compared to groundwaters (Chellam et al., 2001).

Removal of organics usually focuses on disinfection byproduct (DBP) precursors and NOM. NOM rejection is influenced by size exclusion, electrostatic repulsion, and NOM aromaticity. The use of membranes with high molecular weight cut-off (MWCO) results in sufficient but incomplete organics rejection. Thus, there is a need to use membrane with low MWCO for complete organics removal.

iii) Micropollutants

Micropollutants, also known as persitent organic pollutants (POPs), personal care products (PCPs), pharmaceutically active compounds (PhACs) and endocrine disrupting compounds (EDCs) and pesticides have become a growing concern because of the high negative impact of these substances on human health.

Many water sources are contaminated by pesticides due to the extensive use of the same in industry and agriculture. Removal of pesticides in drinking water production traditionally involves activated carbon filtration. The treatment is effective but the cost is high due to the frequent regeneration of the carbon columns. One cause of the decreased run time is the presence of NOM molecules, which compete with the pesticides for the adsorption sites on the activated carbon. Nanofiltration offers an alternative for the removal of pesticides. Because the NF membrane works as a charged sieve that retains molecules larger than the pore opening, capacity is not a limiting factor when compared to activated carbon adsorption. Large organic molecules such as humic and fulvic substances are retained together with the pesticides.

2.5.3 Performance of NF membranes

Similar to other membrane processes, the three parameters crucial for the operation of a nanofiltration unit are solvent permeability or flux through the membrane, rejection of solutes, and yield or recovery.

The flux is defined as the flow of solvent per unit area of the membrane. Permeability is the flux per unit of applied pressure. Flux, J (if the Hagen-Poisuille equation can be assumed) can be expressed as

$$J = (\varepsilon * r^2 * \Delta P) / (8 * \eta * \tau * \Delta x) \qquad (2\text{-}4)$$

Where ε = porosity of the membrane (%)
r = pore radii (mm)
ΔP = applied pressure (Pa)

	η	=	viscosity (Pa-s)
	τ	=	tortuosity (mm/mm)
and	Δx	=	membrane thickness (mm)

For concentrated solutions or solutions with high salinity, the osmotic pressure ($\Delta\pi$) should be subtracted from the applied pressure (ΔP). Equation 2-4 becomes

$$J = Lp * (\Delta P - \sigma * \Delta\pi) \qquad (2\text{-}5)$$

Where	Lp	=	solvent permeability (mm/s-Pa)
	σ	=	maximal rejection of solute (%)

Rejection of a contaminant is defined as

$$R\,(\%) = (1 - c_p / c_f) \times 100 \qquad (2\text{-}6)$$

Where	c_p	=	concentration of the contaminant in permeate
	c_f	=	concentration of the contaminant in feed water

Recovery, r is the third important parameter in nanofiltration process. It is defined as the ratio of the permeate stream (Qp) to the feed stream (Qf). This parameter is important in the design of an industrial application. The plant recovery value ranges from 40 to 90 %.

$$r\,(\%) = Qp / Qf \times 100 \qquad (2\text{-}7)$$

2.5.4 Fouling and flux decline of NF membranes

Membrane fouling is a major constraint on the implementation of nanofiltration membrane process for use in drinking water treatment. The decrease in flux is due to an increase in the resistance of the membrane to permeation over time by the accumulation of materials (such as cake/gel formation, concentration polarization, and adsorption on the membrane surface), pore blocking and adsorption to pore walls. Fouling increases operational costs with decreasing permeate production and/or increasing transmembrane pressure (TMP) requirements. Frequent chemical cleaning deteriorates membrane performance, leading to shortened membrane life. Therefore, the identification of foulants and their fouling mechanisms is very important to reduce or avoid membrane fouling, to optimize pre-treatment, and to decide upon optimal cleaning agents and cleaning procedures (Her et al., 2007).

It is well established that membrane and feed characteristics are very important to understand the phenomenon of fouling in nanofiltration, as it is the interplay between membrane and feed that determines the fouling tendency (Boussu et al., 2006). Crucial characteristics of the top layer of the membrane such as molecular weight cut-off (MWCO), hydrophobicity, surface charge and surface roughness can help explain the fouling of NF membranes. The MWCO represents the molecular weight of the compound with 90% retention. The zeta potential is the electrical potential at the shear plane between the solution and the membrane.

Flux decline is a serious problem in nanofiltration of aqueous solutions containing organic compounds. Flux decline is related to adsorption of organic compounds on the membrane material and possibly enhanced by pore blocking (Braeken et al., 2006).

Possible parameters to describe adsorption are:

i) Dipole moment – lack of data prevents use of this parameter
ii) Natural octanol-water partition coefficient – suitable parameter to describe adsorption and reflects hydrophobic interactions between membrane and solute.
iii) Water solubility – unlimited for several components and thus not applicable.

The octanol-water partition coefficient appeared to be the best parameter to describe flux decline in nanofiltration: components with a higher partition coefficient show more hydrophobic interactions and cause more flux decline.

The factors that affect and determine the extent of flux decline are:

i) Molecular size – molecules with a size that is comparable to the pore size have the most significant effect on flux decline.
ii) Hydrophobicity
iii) Charge interactions

2.6 Case study on membrane and SAT combination

The reclamation facilities in Orange County Water District's Water Factory 21 illustrates an application of water reclamation from biologically treated secondary effluent using microfiltration and reverse osmosis followed by either injection into the aquifers through wells to provide pressurized barrier against seawater intrusion or percolation through the soil to replenish groundwater supply.

The first step after conventional activated sludge treatment of secondary effluent, is to add sodium hypochlorite to disinfect the water. The hypochlorite reacts with ammonia to produce chloramines as disinfectant and antifouling agent. The stream is sent through microfiltration filters to remove any remaining suspended solids and microorganism such as bacteria. The pore size of the membrane is about 0.2 µm.

After microfiltration comes reverse osmosis to remove dissolved contaminants. The main goal is to remove minerals or salts in the water, but ammonia and viruses are also targets. The reverse osmosis membranes are made of polyamide material with molecular weight cut-off of 150 Dalton. Anything above the MWCO is likely to be removed. Sneaking through the membrane might be low-molecular-weight organics from pharmaceuticals, personal care products and industrial solvents.

The final treatment step at the reclamation plant removes low-molecular-weight organics by adding hydrogen peroxide and irradiating with ultraviolet light. Hydroxyl radicals or hydroxide anions will oxidise at least some of the remaining organic contaminants.

When water exits the membrane treatment plant, it goes to one of two places. About half is pumped to the coast, where it is injected through wells to form a hydraulic barrier to prevent seawater intrusion into groundwater. The other half is destined for a percolation pond set in permeable soil that allows water to percolate down to blend with the groundwater table. During this soil aquifer treatment, additional filtering occurs in the soil through biodegradation; naturally occurring bacteria may breakdown any remaining contaminants. Field studies done for the reclamation plant demonstrated that it takes more than six months for water to travel from injection wells or percolation ponds to drinking water well intakes (Kemsley, 2008).

3 Materials and Methods

This chapter summarises the materials, experimental setups and procedures, and analytical methods that were employed during the research. The study consisted of two principal parts. First, bulk organic matter removal during SAT was investigated using soil columns and two types of feed water: secondary effluent (SE) of a conventional activated sludge wastewater treatment plant and ozonated secondary effluent (SE+O_3). The second part consisted of nanofiltration experiments using two types of membranes (NF-270 and NF-90) and the two types of feedwater mentioned above, with and without SAT simulation pre-treatment. All experiments were conducted at the UNESCO-IHE laboratory.

3.1 Materials

3.1.1 Source water

The source of the secondary effluent used in the study was a conventional activated sludge wastewater treatment plant of Hoek van Holland in the Netherlands. This treatment plant has primary and secondary treatment steps and the sludge treatment utilises gravity thickener and digester. The schematic layout of the treatment plant including the location of the sampling point is shown in Figure 3-1. The samples used in the experiments were taken at the discharge point of the secondary clarifier. To get water samples of fairly consistent quality, collection were scheduled at the same hour and day of the week with an average frequency of one week depending on the need of the particular experiments being conducted at the time. The water samples collected from the treatment plant were stored at 4 ^{o}C to minimise microbial activity before usage.

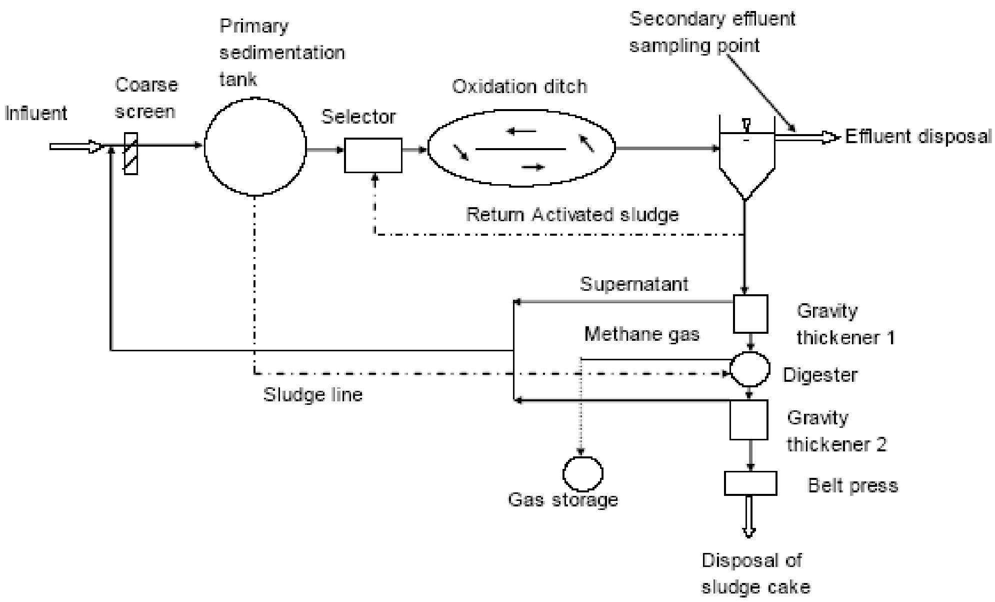


Figure 3-1. Schematic representation of Hoek van Holland wastewater treatment plant
Source: (Musabe, 2007)

3.1.2 NF membranes

The two types of membrane used in the nanofiltration experiments were supplied by DOW/FilmTec, namely NF-270 and NF-90. Both membranes consist of very thin polyamide active layer, which determines the membrane separation properties. The characteristics of the two membranes are summarised in Table 3-1. NF-270 has larger pores, is more hydrophilic, has a smoother surface and a higher surface charge than NF-90. Commercial NF-270 and NF-90 membranes have the following characteristics as shown in Table 3-2.

Table 3-1. Summary of the characteristics of the membranes, NF-270 and NF-90

Membrane Characteristic	**NF-270**	**NF-90**
MWCO (Da)	155	100
Water permeability (L/m^2-h-bar)	8.5	5.2
Contact angle (degrees)	27	54
Roughness (Angstrom)		
0.5 µm x 0.5 µm	21	108
1 µm x 1 µm	28	219
3 µm x 3 µm	42	331
5 µm x 5 µm	46	388
Zeta potential (mV)		
pH 3	4.9	3.7
pH 12	-25.6	-19.4

Source: (Boussu et al., 2006)

Table 3-2. Properties of NF-270 and NF-90 membranes.

Membrane Property	**NF-270**	**NF-90**
Membrane type	Polyamide	Polyamide
Nominal salt rejection (%)	97	98
Nominal flow (m^3/day)	47.5	36.1
Element area (m^2)	37.2	37.2
Test solution/concentration (ppm)	2000 $MgSO_4$	2000 $MgSO_4$
Test pressure (bar)	4.8	4.8

Source (Bartels, 2007)

The flat sheet membranes (NF-270 and NF-90) provided by the manufacturer (DOW-FilmTec) were delivered dry and in large sizes (1.55 m^2). After being cut into appropriately small pieces that would fit the membrane cell, the membranes were immersed in 1% sodium bisulfphite (Na_2SO_3) solution and stored at 4 ^oC for preservation (to prevent bacterial growth on the surface) until use in the experiments.

3.2 Experimental set-ups

3.2.1 Ozonation set-up

Ozonation of the secondary effluent were conducted to explore the bulk organic matter removal optimization prospects of the SAT process. The required ozone was generated in the laboratory on a semi-batch basis. The ozone generation setup is depicted schematically in Figure 3-2. The set-up consisted of ozone generator, flow board, ozone detection and ozone contactor. Ozone was produced by a laboratory-scale ozone generator (Trailigaz Ozonizer, LABO LO Type) which uses the corona discharge method with dehumidified atmospheric air as the source of oxygen. The produced ozone was applied directly in gaseous form to the sample contained in an eight-litre volume glass container (C). Glass bubble diffuser was employed to disperse the ozone and allow efficient gas-liquid contact and mass transfer of ozone to the aqueous phase. The liquid was continuously stirred at 400 rpm to help dissipate the bubbles more effectively. The ozone to DOC concentration ratio used in the experiments was 1 mg O_3/mg DOC.

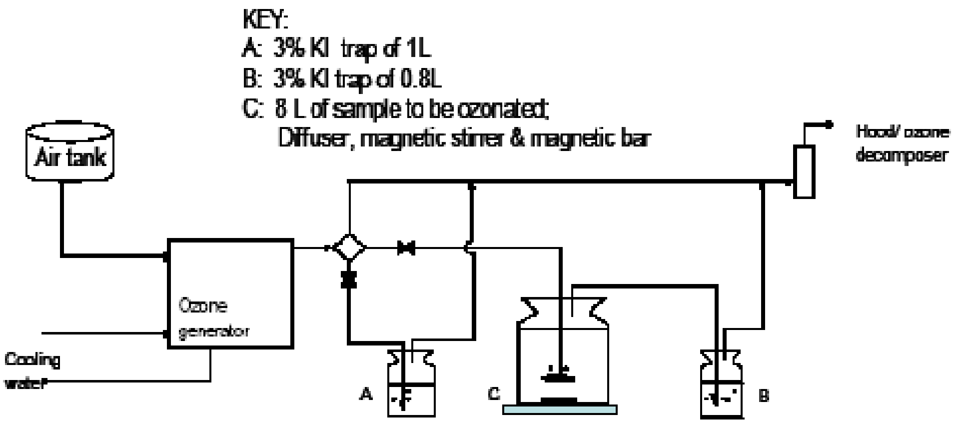


Figure 3-2. Schematic diagram and photograph of the ozone generator set-up.
Source of schematic diagram: (Musabe, 2007)

3.2.2 Soil column set-up

Two sets of laboratory-scale soil column experimental set up as shown in Figure 3-3 were used to conduct the SAT simulation study. The two soil columns were constructed from two uPVC pipes and internal diameter of 100 mm connected in series. Volumetric displacement flow pump was used to pump water from plastic vessels into the reactor bottles. The flow rates were set by controlling the speed of the pump. From the reactor bottles, the system operated by gravity to the two columns in series; downward flow in the first column and upward flow in the second column. Air was introduced by diffusing compressed dry air in the reactor bottles to insure that the SAT simulation system worked under aerobic conditions. The minimum dissolved oxygen (DO) level in the reactor was maintained at 8.0 mg/L. The media used in the soil column was pre-washed silica sand sized from 0.8 to 1.25 mm. Graded gravel of 20 cm thick was used as filter media support. A total 16 sampling points were placed along the column pipes. The sampling points as indicated on the schematic diagram are SP0, SP1, SP2, SP3, SP4, SP5, SP6, SP7, SP8, SP9, SP10, SP11 and SP12, SP13, SP14 and SP15.

Hydraulic loading rate of 1.25 +/- 0.05 m/day was maintained throughout the duration of the experiments.

The secondary effluent from the wastewater treatment plant was first filtered through a stainless steel micro-sieve of size 54 µm to prevent particulate matter present in the SE from clogging the soil columns, and allowed to stand for a few hours to let the water reach room temperature before feeding into the soil columns.

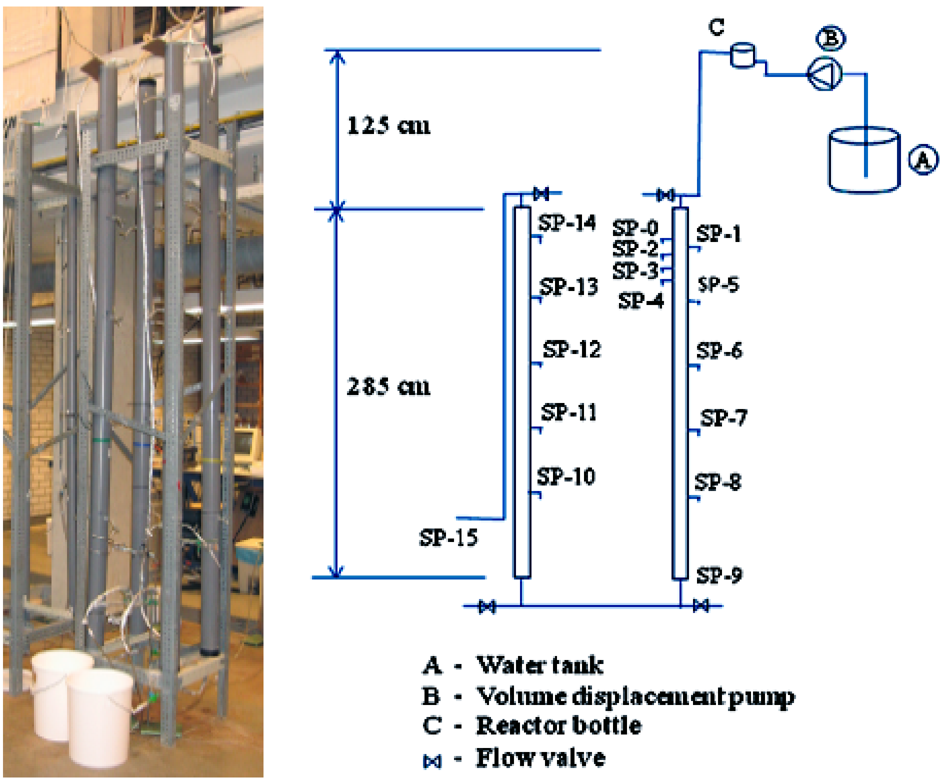


Figure 3-3. Photograph and schematic diagram of the soil column experimental setup.

3.2.3 Nanofiltration set-up

Schematic representation and photograph of the NF-membrane experimental setup shown in Figure 3-4 consists of a membrane cell and a cell holder, one hydraulic pump, stainless steel tank, a variable speed pump, a frequency driver, a chiller/heater, control needle valves, pressure gauges, flow meters and stainless steel tubings. A digital balance collecting the permeate water is connected to the computer that used WinWedge software to monitor the flow rate.

The membrane cell is made of stainless steel and has a channel space of 14.6 x 9.5 x 0.86 cm with an effective surface area of 139 cm^2. Plastic spacers were used in-between the membrane and the cell walls.

The feed flow rate, corresponding cross-flow velocity, and the trans-membrane pressure were regulated either by varying the pump head speed, controlling the needle valves in the retentate stream, or controlling the pressure relief valve on bypass stream.

The system flow configuration has three possible modes of circulation:

1. One pass – feed is applied to the membrane, retentate and permeate are not recycled and are collected separately.
2. Partial recycling – there is recirculation of retentate to the feed reservoir and permeate is collected separately.
3. Complete recycling – recirculation of retentate and permeate into the feed reservoir.

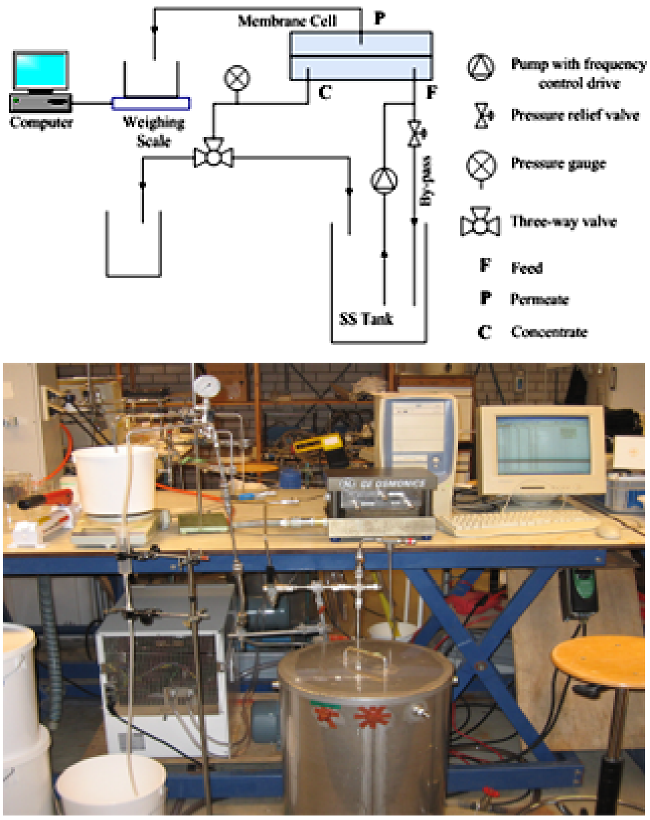


Figure 3-4. Schematic diagram and photograph of the nanofiltration experimental setup

3.3 Experimental procedures

3.3.1 Ozonation

Ozone was generated using the LABO LO type Trailigaz ozonizer in the laboratory. The ozone generator uses dehumidified air as the source of oxygen.

Strict compliance to the start-up procedure given in the operation manual was followed. Special precaution was observed to ensure that ozone was not leaking from the joints and connection along the flow lines, the lid of the reactor, and from the trap bottles. These places, which are particularly susceptible to leaks, were regularly monitored using a portable ozone detector. A fixed ozone detector was also installed with the set-up.

The three main steps of the ozonation procedure are:

1. Calibration of ozone generator
2. Calculation of ozone transfer efficiency
3. Ozonation of the samples

(1) The first step deals with the determination of ozone production rate before application of ozone to the sample.

a) To determine the strength of the ozone generated by the equipment, a trap bottle (A) with 200 mL of potassium iodide solution (2% KI by weight) was employed. During the calibration test, a fraction of the ozone produced was diverted through the bypass flow line and ozone was allowed to bubble through the KI in the trap bottle (A) for 10 minutes. KI was used because in alkaline or neutral environment, O_3 reacts with KI to release free Iodine, I_2.

$$O_3 + 2\,KI + H_2O \longrightarrow I_2 + 2\,KOH + O_2 \qquad (3\text{-}1)$$

b) To determine the mass of ozone captured in the trap bottle (A) $m_{ozone(A),}$ the KI-Iodine solution was titrated with 0.025N sodium thiosulfate ($Na_2S_3O_2$), which in acidic environment reacts with I_2.

$$I_2 + 2\,Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2\,NaI \qquad (3\text{-}2)$$

c) This mass of ozone equals the mass of ozone contained in the volume of gas that passed through the bypass flow line. The total volume of the gas that passed through the bypass line (V_{bypass}) can be read from the bypass flow meter. The concentration of ozone produced, in mg/L, can be calculated by dividing the mass of ozone in trap bottle (A) by the volume of gas that passed through the bypass line.

$$c_{ozone}\,(mg/L) = m_{ozone(A)} / V_{bypass} \qquad (3\text{-}3)$$

(2) The second step is the calculation of ozone transfer efficiency.

a) Ozonation of a control sample (3 L of secondary effluent at ambient temperature placed in a 5 L reactor vessel) was performed for 30 minutes. Throughout the

ozone generation, the flow rate of dehumidified air was maintained at 350 L/h and the power supplied was kept constant at 0.7 Ampere. Ozone was applied to the secondary effluent through a glass bubble diffuser while the sample was continuously mixed by a magnetic stirrer at 400 rpm. During the test run, ozone was directed through both the bypass and off-gas flow lines. The flow rates along the two lines can be adjusted by controlling the flow valves on the flow board. The flow rate that passed through the sample was maintained at 12 L/h. Another trap bottle (B) with 200 mL of 2% KI solution was placed after the reactor bottle to capture the un-reacted ozone.

b) The readings of the by-pass and off-gas flow meters were taken before the test and again, after 30 minutes of ozonation time. Thereafter, ozone generation was stopped and compressed dry air was blown through the flow lines for about 5 seconds to remove any remaining ozone. Compressed air was introduced through a separate flow line in the lid of the reactor to remove any un-reacted ozone present in the volume above the water surface of the reactor bottle. About 2 L of dry air was blown through this line to push the remaining ozone to be captured in the off-gas KI trap bottle.

c) The KI-iodine solutions in both trap bottles were titrated with 0.025 N $Na_2S_3O_2$ to determine the mass of ozone captured in respective trap bottles, $m_{ozone(A)}$ and $m_{ozone\ (B)}$. The quantity $m_{ozone(A)}$ represents ozone which did not react with the wastewater contaminants.

d) The concentration of ozone produced during the control sample run can be calculated with the help of Equation 3-3. The strength of ozone produced during the control sample ozonation run was compared with that of the calibration run and the average of the two values was taken.

e) Gas, with the same concentration of O_3, passed through the sample vessel. The total amount of ozone applied to the sample can be calculated by multiplying the concentration of ozone in the gas produced (c_{ozone}) by the volume of gas that passed through the sample ($V_{off\text{-}gas}$).

f) The amount of ozone used in the reaction ($m_{ozone\ used}$) can be calculated from the difference of the total O_3 passing the sample vessel and the amount of O_3 captured in trap-bottle (B).

$$m_{ozone\ used}\ (mg) = c_{ozone} \times V_{off\text{-}gas} - m_{ozone(B)} \qquad (3\text{-}4)$$

g) The transfer efficiency of ozonation is thus the mass of ozone used by the sample divided by the total mass of ozone applied to the sample.

$$\text{Transfer efficiency (\%)} = m_{ozone\ used} / (c_{ozone} \times V_{off\text{-}gas}) \times 100 \qquad (3\text{-}5)$$

(3) The third step is the ozonation of the wastewater sample. Ozonation of secondary effluent were done in batches of 8 L samples.

a) Once the concentration of ozone in the product gas of the ozone generator and the transfer efficiency of the system were known, an estimate of the required

volume of off-gas to produce the desired ozone concentration in the water sample can be calculated. The required mass of ozone (m_{reqd}) to be consumed by the sample depends on the initial DOC concentration of the sample, the required ozone to DOC ratio, and volume of the sample to be ozonated. The product of the three quantities gives the required mass of ozone to be consumed. The transfer rate (mg/L) of ozone to the water sample is equal to the transfer efficiency given by Equation 3-5 multiplied by concentration of ozone in the product gas (c_{ozone}). The required volume of off-gas, $V_{off\text{-}gas\ reqd}$ is then equal to

$$V_{off\text{-}gas\ reqd}\ (L) = m_{reqd} / (\text{Transfer efficiency} \times c_{ozone}) \qquad (3\text{-}6)$$

b) The temperature and mixing speed of the aqueous media to be ozonated can affect the transfer efficiency of ozone; care was taken to keep these conditions constant.

c) Once the required volume of off-gas was reached, ozone generation was terminated and the procedure for blowing off excess ozone was again followed. With the same procedures described in steps 1 and 2, the actual mass of ozone used ($m_{ozone\ used}$) by the sample can be established. To get the actual dosage of ozone consumed by the sample, $m_{ozone\ used}$ is divided by the volume of sample (V_{ww}). If the ratio of the ozone concentration to initial DOC concentration was within 5% of the desired ozone to DOC ratio, the ozonation process for the batch was deemed successful.

A sample calculation of the ozonation of secondary effluent can be found in Appendix-C.

3.3.2 Soil columns

Ripening of the sand media within the two sets soil columns was performed with the following procedure:

1. The secondary effluent collected from Hoek van Holland WWTP and stored at 4 ^oC was first filtered by 53 μm micro-sieve and allowed to reach room temperature before filling into the feed tanks.
2. The volumetric displacement pump speed was adjusted to obtain a desired filtration rate of 1.25 +/- 0.5 m/day. The effluent flow was measured everyday by using a 50 mL glass cylinder and a stop watch.
3. Water samples were collected at sampling point SP-1 at the top of the first column (influent) and sampling point SP-14 at the top of the second column (effluent) every other day for the of dissolved organic carbon (DOC) and dissolved oxygen (DO) levels.
4. Aerobic conditions were maintained throughout the ripening period by continuous introduction of compressed dry air into the intermediate one-litre reactor bottles. If the DO level in the influent was less than 8 mg/L, the flow rate of compressed air into the reactor bottle was increased.
5. The ripening process for the soil columns was continued until a steady state removal rate of DOC was reached.

Stability of the DOC removal rate was taken as the indicator that bio-film had fully developed on the sand media before proceeding to the next step of taking measurements of water quality parameters such as DO, pH, EC, temperature, and UVA_{254}/SUVA on all sampling points to obtain the profile along the soil column. The procedure for collecting water samples at different sampling points were as follows:

1. Stagnant water within the sampling points was flushed out by discarding the first few drops.
2. The sample collection was performed iso-kinetically (at a flow rate equal to the hydraulic loading rate) to ensure that adjacent layers were prevented from being collected.
3. About 70 mL volume was collected from each sampling point for the different water quality analyses.

After completion of the experiments for soil column 1 with SE alone, the feed water was replaced with pre-ozonated secondary effluent with this procedure:

1. The system was first cleaned to prevent contamination from the previous type of feed water. The effluent flow valve was closed and the pump was turned off. The feed tank, the intermediate reactor bottle and the connecting tubes (delivery pipes and overflow pipes) were all emptied of the remaining secondary effluent and thoroughly cleaned with tap water.
2. The feed tank then was filled with pre-ozonated SE with ozone to DOC ratio of 1 mg O_3/mg DOC. The pump was switched on and again adjusted to obtain the desired hydraulic loading rate of 1.25 m/day. Any entrapped air within the column pipes and tubings was released by opening the top valves of the first column.
3. After 4 days of flushing out the remaining secondary effluent from the previous experiment in soil column 1, influent and effluent samples were taken every day for analysis of DO and DOC removal. The DO level of the influent is kept at a minimum of 8 mg/L by adjusting the flow rate of compressed air in the reactor bottle as necessary.
4. Filtration rate was monitored daily and adjustment of the pump speed was carried out accordingly.
5. The soil column system was run using SE+O_3 as feed water until the DOC removal efficiency became stable. After the steady state was reached, samples were taken on all the sampling points isokinetically, along the column depth to obtain the profile of water quality parameters such as DO, pH, DOC, EC, temperature, UVA_{254}/SUVA and FEEM.

3.3.3 Nanofiltration

The first series of experiments involved the use of NF-270 membrane and one-pass configuration flow. The following types of feed water were used in the tests:

1. SE without pre-treatment
2. SE with SAT pre-treatment
3. SE+O_3
4. SE+O_3 with SAT pre-treatment

All experiments were conducted with feed pressure, p_f of 50 psi (3.6 bar), recovery, r of 8% and temperature of 20 ^oC.

The following procedures were followed in performing the nanofiltration experiments with NF-270:

1. Before the introduction of any of the four types of feed water, the system was run with demineralised water for about two hours. The compaction with clean water was performed to stabilise membrane permeability. After switching the pump on, care was exercised to prevent sudden increase of feed pressure. The feed pressure was gradually increased to 70 psi (5 bar) and maintained at this pressure for 30 minutes of filtration.
2. The feed pressure was then gradually reduced to the target pressure of 50 psi (3.6 bar) for another 90 minutes.
3. After two hours of filtration of demineralised water, or until the flux had become stable, the pressure was then gradually reduced to less than 10 psi before switching the pump off. Abrupt changes in the feed pressure may cause damage to the membrane.
4. After quickly draining the clean water from the feed tank by opening the drain valve, the feed tank was filled with 50 L of the appropriate type of water sample.
5. The pump was switched on again and the feed pressure was gradually increased to 50 psi (3.6 bar). The feed pressure, which was also equal to the retentate pressure, can be adjusted by manipulating the pressure relief valve on the bypass line and the needle valve on the retentate flow line.
6. During filtration, permeate was collected in a vessel on top of a weighing scale. The weight of permeate was being recorded automatically every 30 seconds through a computer with a software interface (WinWedge). The permeate flow rate, Qp (in mL/min) was at the same time computed and registered automatically on the computer. The retentate flow rate (Qc) was measured manually by using 50 mL cylinder and stop watch. The system recovery, r (%) is the ratio of the permeate flow to feed flow, Qf. But Qf is the sum of the sum of Qp and Qc, therefore,

   $$r\ (\%) = Qp / (Qp + Qc) \qquad (3\text{-}7)$$

   If the recovery is not equal to the desired value of 8%, the retentate flow rate was modified by adjusting the needle valve on the retentate stream and the pressure relief valve on the bypass flow line if necessary. These two valves were used to keep the feed pressure and the retentate flow at desired levels.
7. The filtration was done continuously for six hours under the conditions specified for these experiments. A descriptive timeline graph showing the flux against time for these experiments is shown in Figure 3-5.
8. Samples were collected from the feed tank, permeate stream and concentrate stream at regular intervals (at least three times) to monitor the removal rates during filtration of water quality parameters such as DOC, TDS, and UVA_{254}/SUVA. Flux during filtration was recorded in the computer.

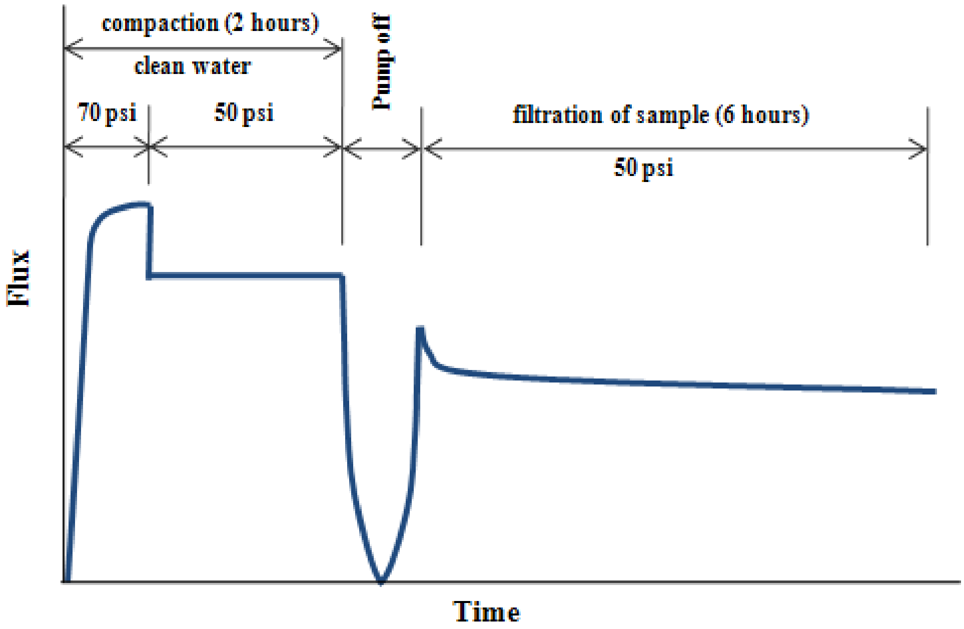


Figure 3-5. Descriptive flux behaviour vs. time during filtration tests using one-pass mode

The preceding procedures were repeated for the second series of experiments using a different type of membrane with lower MWCO, NF-90. The process conditions ($p_f = 50$ psi, r = 8%, temperature = 20°C, one-pass mode) were maintained for nanofiltration of the following types of feed water:

1. SE without pre-treatment
2. SE with SAT pre-treatment
3. SE+O_3
4. SE+O_3 with SAT pre-treatment

The last series of experiments for nanofiltration involved the use of NF-90 membrane with flow configuration mode of recirculating the concentrate back into the feed water tank. Feed pressure of 50 psi, recovery of 8% and temperature of 20°C were maintained for this batch of experiments.

The same aforementioned compaction procedure was done prior to the filtration of the following types of feed water:

1. SE without pre-treatment
2. SE with SAT pre-treatment
3. SE+O_3
4. SE+O_3 with SAT pre-treatment

Filtration was carried out for at least 20 hours for each experiment. Water samples were collected from the feed tank, permeate stream and concentrate stream at regular intervals except during night time when the laboratory was closed. The flux decline was monitored using the computer and software interface.

3.4 Analytical Methods and Equipment

3.4.1 pH, EC/TDS, temperature, dissolved oxygen

The pH of a water sample was measured using a calibrated Metrohm 691 pH-meter fitted with a WTW SenTix 61 pH electrode. When measuring the pH, the electrode was continuously stirred into the water sample until the reading became steady. Before taking pH measurements, the temperature on the pH was set to the sample temperature and the electrode of the pH meter was rinsed with demineralised water to prevent contamination from the previous sample.

The electrical conductivity, TDS and temperature was measured by a WTW cond 330i portable conductivity meter fitted with WTW Tetracon 325 electrode.

Dissolved oxygen (DO) of a sample was measured with WTW Oxi 340 portable DO meter. The WTW CellOx 325 electrode was immersed in the sample until steady reading is obtained. To obtain accurate readings for the dissolved oxygen profile of the soil columns, measurements were done simultaneously with the collection of the samples from the sampling points.

Figure 3-6. Portable pH, EC and DO meters

3.4.2 DOC/TOC

The total organic carbon (TOC) and dissolved organic carbon (DOC) were measured by TOC-VCPN, a total organic carbon analyser (Shimadzu). The machine is operated by the 680^{o}C combustion catalytic oxidation/NDIR (non dispersive infrared sensor) method. For the DOC measurement, the samples were first filtered with clean 0.45 μm cellulose acetate filters. The filter papers were soaked in Milli-Q water for 24 hours before usage since these cellulose acetate filters contribute to the reading by leaching DOC. All samples were analysed at room temperature. Samples of Milli-Q water were put in between two samples in case the first sample contained much higher DOC than the second one. Whenever the DOC of a sample was expected to be over 20 mg/L the sample was diluted with Milli-Q water.

Figure 3-7. TOC-VCPN (Shimadzu) total organic carbon analyser

3.4.3 Measurement of UVA_{254} nm/SUVA

A Perkin Elmer (Lambda 20 1.11) spectrophotometer (Figure 3-8) was used to measure the UV absorbance at a wavelength of 254 nm. The samples were first filtered through a 0.45µm filter before taking of measurements. Milli-Q water was used as the blank sample. The samples and the blank were placed in quartz cuvettes during the measurement. Before taking a reading, the cuvette used for the samples was rinsed with Milli-Q water and the outside walls of the cuvette were wiped dry with soft laboratory tissue paper to eliminate dust or water that might have affected the result.

Specific UV absorbance (SUVA or $SUVA_{254}$) is defined as the sample's UV absorbance at 254 nm divided by the DOC concentration of the sample.

Figure 3-8. Perkin Elmer (Lambda 20 1.11) spectrophotometer

3.4.4 Fluorescence EEM

The fluorescence excitation-emission matrix (FEEM) spectra for the different samples were measured by a Horiba Jobin Yvon FluoroMax-3 spectrofluorometer with xenon lamp as the excitation source. The samples were first filtered with 0.45 µm cellulose acetate filter and diluted to approximately 1.0 mg/L DOC concentration using Milli-Q water. The samples were brought to room temperature before analysis.

The ranges of wavelengths used in the analysis were: Excitation at 240 to 450 nm with 10 nm intervals and Emission at 290 to 500 nm with 2 nm intervals. Milli-Q water was employed as the blank sample. EEM of the blank was subtracted from each sample to remove raman scatter peaks and correction steps were applied to each blank-subtracted EEM using excitation and emission correction factors provided by the manufacturer. The EEM contours of the samples were plotted in MatLab software utilizing a previously prepared code for this purpose.

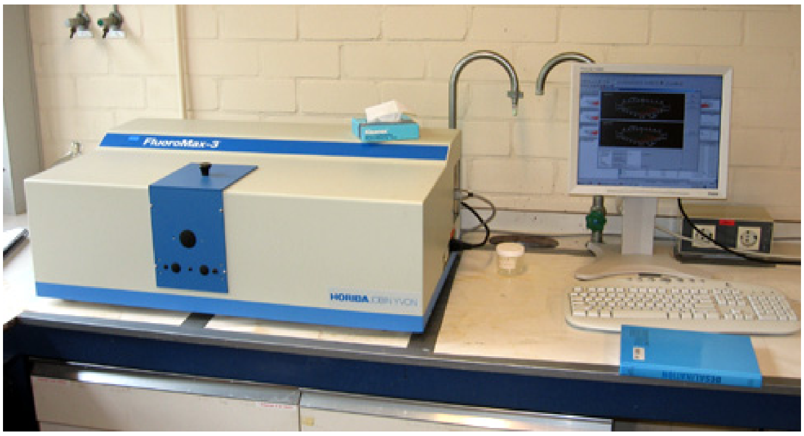


Figure 3-9. Horiba Jobin Yvon FluoroMax-3 spectrofluorometer

4 Results and Discussion

The results of the experiments carried out in the study are presented and discussed in this chapter. The first part deals with the results of the laboratory-scale soil column experiments simulating soil aquifer treatment. The second part presents the results of the nanofiltration experiments to investigate the effect of SAT pre-treatment on NF membranes.

4.1 Source water characterisation

The secondary effluent collected from Hoek van Holland wastewater treatment plant (WWTP) was characterised by measuring relevant physical and chemical water quality parameters. The results are presented in Table 4-1. The frequency of collection from the treatment plant was once per week. The trips were scheduled, preferably on the same time and day of the week, for a more consistent water quality. The wastewater samples collected were stored in a cold storage room, at temperature of 4 ^oC to retard microbial activity before use in the experiments. The SE samples were taken out of the cold storage room and allowed to reach room temperature for several hours before being used in the different experiments.

Table 4-1. Characterisation of SE from Hoek van Holland WWTP

Parameter	Unit	Value
Temperature	deg C	20
DO	mg/L	7
pH		7.66
Alkalinity	mg/L HCO_3^-	344
EC	µS/cm	960
TOC	mg/L	53.85
DOC	mg/L	12.14
UVA_{254}	Ab/cm	0.35
SUVA	L/m-mg	2.88
Cl^-	mg/L	105
F^-	mg/L	0.2
NO_3^-	mg/L	2.98
PO_4^{-3}	mg/L	3.18
SO_4^{-2}	mg/L	61.57

4.2 Evaluation of SAT performance using soil columns

The secondary effluent from Hoek van Holland WWTP was filtered through stainless steel sieve of 53 µm size before feeding into two sets of soil columns to minimize the effects of clogging by suspended matter present in the secondary effluent. The SE was fed at hydraulic loading rate (HLR) of 1.25 +/- 0.05 m/day under aerobic conditions. Aeration was introduced by diffusing air through an intermediate one-litre volume reactor.

Ripening of the sand within the soil columns took 63 days after the initial feeding of the secondary effluent. Dissolved oxygen consumption during the ripening period averaged 61.3% for soil column 1 (SC-1) and 70.8% for soil column 2 (SC-2). Dissolved oxygen consumption for SC-1 and SC-2 are presented graphically below.

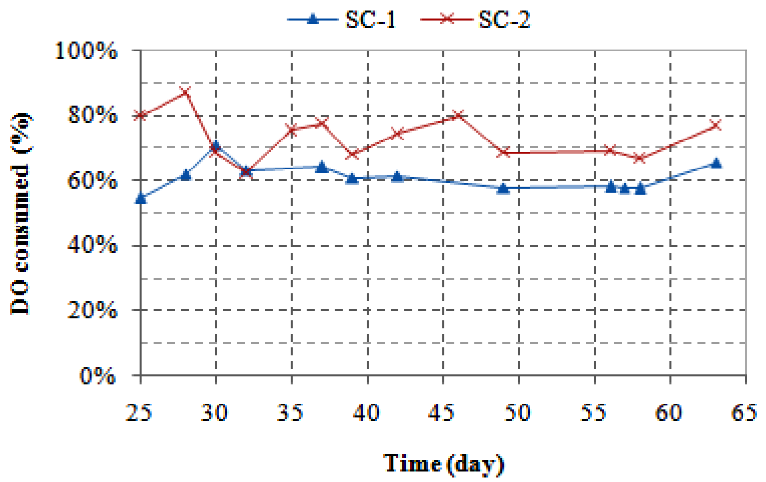


Figure 4-1. DO consumption in SAT using SE alone during ripening period (HLR = 1.25 m/day; under aerobic conditions; media=0.8-1.25 mm sand, 5 m depth; 2 columns each 100 mm diameter in series)

DOC removal was used as a gauge for measuring the level of ripening of the sand grains in the soil columns. Previous studies of similar nature found good correlation of DOC removal along the depth of the columns with biomass at the particular depth. During these studies, the soil columns reached steady state with respect to DOC removal after 40 days (Musabe, 2007), and 70 days (Kahawita, 2008). It is expected that biomass is fully developed when steady state of DOC removal is achieved.

The average DOC value of the SE used for ripening of sand grains in SC-1 was 12.11 mg/L with values ranging from as low as 5.42 mg/L to as high as 17.64 mg/L. For SC-2, the average value of DOC used for ripening was 10.24 mg/L with a range of values from 4.34 to 17.76 mg/L. After 63 days of ripening, removal efficiencies for SC-1 and SC-2 were stable at 15% and 11%, respectively. The influent sample was taken at sampling point SP-1, and effluent sample at sampling point SP-14. Another 8 days of monitoring of DOC removal for both columns were done to ensure stable removal had been attained, which suggested that the biofilm in the sand media has fully developed.

DOC removal efficiency curves for the two soil column systems are shown in Figure 4-2. The initial fluctuation of DOC removal was likely due to changes in influent DOC concentration. The introduction of secondary effluent from a new batch with considerably higher or lower DOC than that of the secondary effluent already in the soil columns resulted into peaks and troughs evident in the ripening curve until the new secondary effluent flushed out the old effluent that was present in the columns.

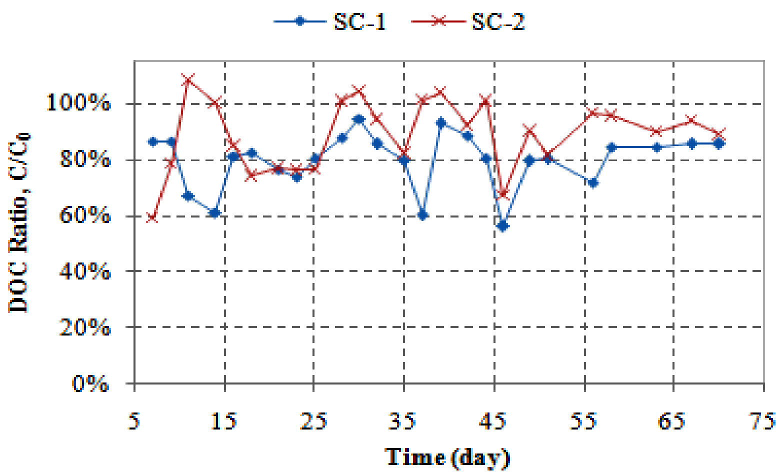


Figure 4-2. DOC removal in SAT using SE alone during ripening period (HLR = 1.25 m/day; under aerobic conditions; media=0.8-1.25 mm sand, 5 m depth; 2 columns each 100 mm diameter in series)

4.2.1 DOC removal and UVA_{254} measurements for SAT using SE alone

After the ripening of the sand in the soil columns, DOC and UVA_{254} removal along the soil column depth were investigated by taking measurements from the sampling points strategically located to represent the over-all profile of the two columns. SUVA which is the ratio of UVA_{254} to DOC was computed from the measured values. For SC-1, two profile measurements were taken on the 67th day and 73rd day, respectively, after the initial feeding of SE. Three profile measurements were made for SC-2 which was each done on the 67th, 73rd and 85th day, respectively after the start of feeding SE into soil column 2. Average values of DOC, UVA_{254} and SUVA along the depth of SC-1 and SC-2 are presented in Figure 4-3. At least 80% of the DOC removal in both columns took place in the first 50 cm of the soil columns (80% for SC-1 and 84% for SC-2). Comprehensive pilot-scale and field studies on SAT showed that the most significant removal of TOC occurred within the initial phase of SAT (Drewes et al., 2003). The results confirm that the schmutzdecke layer on the top layer of the sand inside the columns was removing most of the organic matter through physical and biological processes.

There were significant decrease in UVA_{254} values in the first meter of both soil columns. At the same time, an increase in SUVA values in the same zone suggested that the sample contained readily biodegradable organic matter that underwent biological reaction (Cha et al., 2004). The decrease in UVA_{254} is attributable to the dominant removal of non-humic substances instead of the slowly biodegradable humic substances, which together with the presence of proteins and carbohydrates result to low degradation process (Amy & Drewes, 2007). The decrease in DOC and UVA_{254}, and an increase in SUVA as organics are initially removed in SAT indicate preferential removal of non-aromatic compounds which is consistent with previous research (Drewes et al., 2003; Fox et al., 2001). The secondary effluent used in the soil column experiment had an initial value of SUVA in the range of 2.5 to 3 L/mg-m.

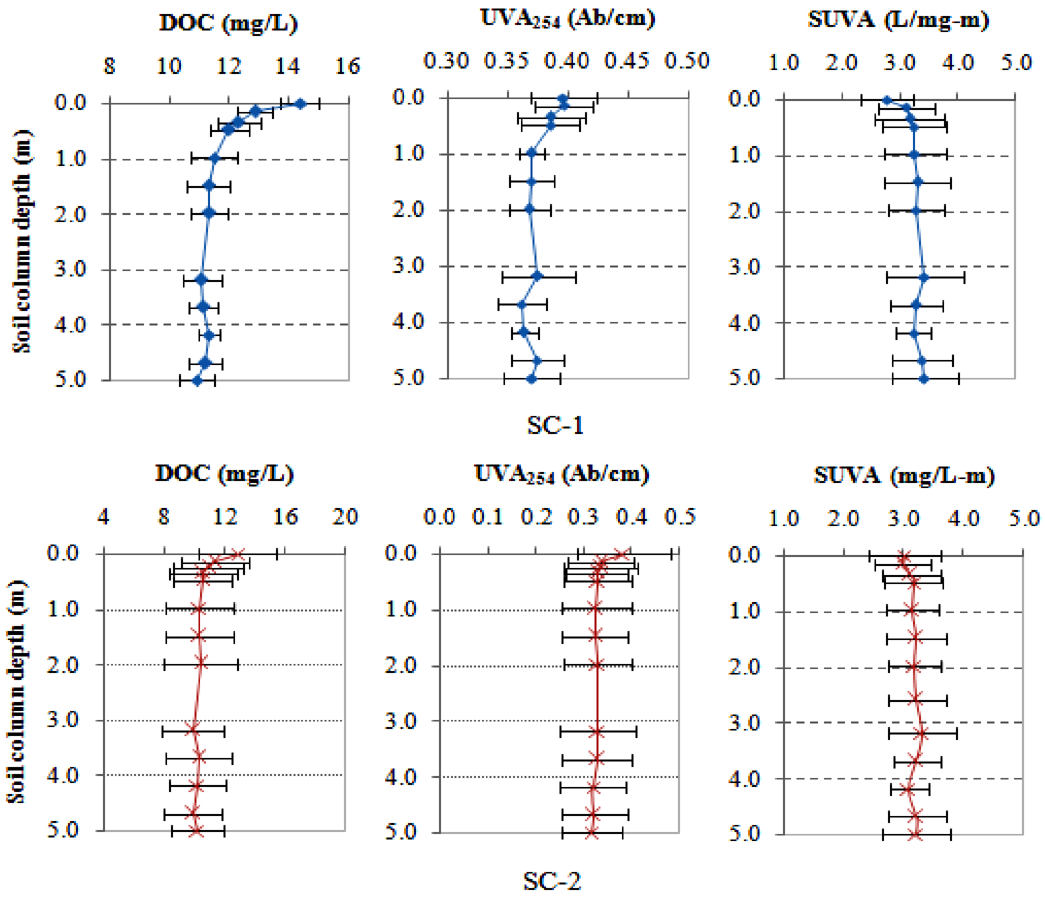


Figure 4-3. Average DOC, UVA_{254} and SUVA profile for SC-1 and SC-2 fed with SE (HLR = 1.25 m/day; under aerobic conditions; media=0.8-1.25 mm sand, 5 m depth; 2 columns each 100 mm diameter in series)

4.2.2 DOC degradation model for soil column using SE alone

The total DOC content of a water sample can be classified into two components, the biodegradable content, which is subject to microbial degradation and the non-biodegradable content. Previous studies (Kahawita, 2008; Katukiza, 2006; Musabe, 2007) used a three-term exponential decay model to explain the kinetics of DOC removal with respect to biodegradation during SAT as given below:

General equation:

$$C(t) = C_0 * e^{(-\lambda 1 * t)} + C_1 * e^{(-\lambda 2 * t)} + C_2 \qquad (4\text{-}1)$$

where: C(t) is the DOC concentration at any time t (mg/L)
C_0 is the easily biodegradable DOC fraction (mg/L)
C_1 is the slowly biodegradable DOC fraction (mg/L)
C_2 is the non-biodegradable DOC fraction (mg/L)
λ_1 and λ_2 are reaction rate constants of the biodegradation process
and t is the biodegradation process time.

The maximum DOC removal through biodegradation is the sum of the first two terms as time approaches infinity, or

$$\text{Max DOC removal} = C_o + C_1 \qquad (4\text{-}2)$$

For soil column experiments, assuming steady and laminar flow, the depth of the soil, d can be taken as the independent variable in equation 4-1, replacing the time t. The equation now becomes:

$$C(d) = C_0 * e^{(-\lambda 1 * d)} + C_1 * e^{(-\lambda 2 * d)} + C_2 \qquad (4\text{-}3)$$

The software SlideWrite Plus (Advanced Graphics Software, Inc., CA) was used to fit the equation of the model on the average DOC measurements from different sampling points along the depth of the soil column. The values of the model parameters obtained are presented in Table 4-2. The plotted curves of the average measured and modelled values for SC-1 are shown in Figure 4-4. The rate of biodegradation of easily biodegradable DOC and slowly biodegradable DOC fractions using the model are compared in Figure 4-5. From the curve, the easily biodegradable fraction of DOC was exhausted in the first few centimetres of the column. The slowly biodegradable components of DOC took a longer time or required a longer travel distance through the soil column for complete degradation. The maximum possible DOC removal in terms of biodegradation for the soil column is the sum of the first two terms in equation 4-3 which could be achieved as distance, d tends to infinity. In this particular case the maximum possible DOC removal through biodegradation was therefore 3.23 mg/L.

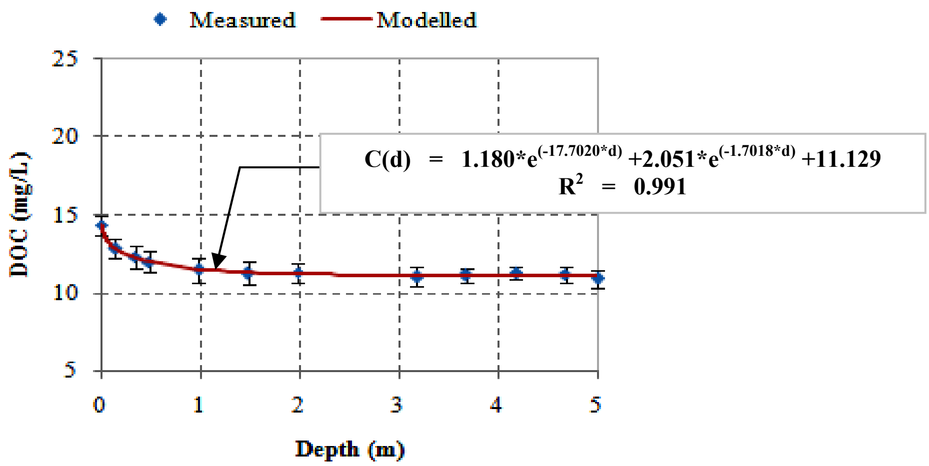


Figure 4-4. Measured values and modelled curve for DOC in SC-1 using SE alone (HLR = 1.25 m/day; under aerobic conditions; media=0.8-1.25 mm sand, 5 m depth; 2 columns each 100 mm diameter in series)

Table 4-2. Kinetic model parameters for DOC removal in SC-1 fed with SE alone (HLR = 1.25 m/day; under aerobic conditions; media=0.8-1.25 mm sand, 5 m depth; 2 columns each 100 mm diameter in series)

Model parameter	C_0	λ_1	C_1	λ_2	C_2	R^2
Unit	mg/L	m^{-1}	mg/L	m^{-1}	mg/L	-
Parameter value	1.18	17.702	2.05	1.702	11.13	0.991

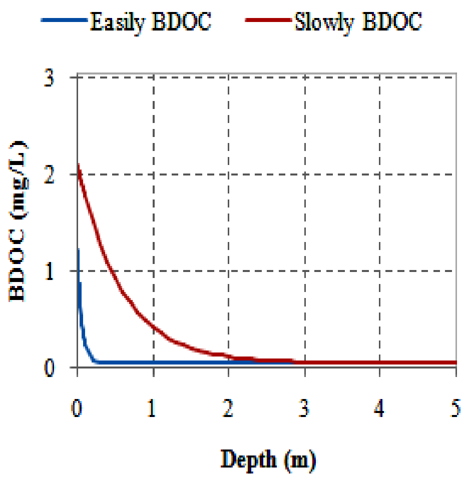


Figure 4-5. Modelled curves for removal of BDOC components in SC-1 fed with SE alone (HLR = 1.25 m/day; under aerobic conditions; media=0.8-1.25 mm sand, 5 m depth; 2 columns each 100 mm diameter in series)

It is to be noted that when most of the easily biodegradable DOC (E-BDOC) and slowly biodegradable DOC (S-BDOC) are removed quickly in the upper layer of soil column quickly, there may not be enough available carbon for biodegradation of organic micro-pollutants (OMPs) deeper in the columns. Therefore, only limited removal of OMPs would be possible in the column as long as E-BDOC or S-BDOC is available as micro-organisms which are responsible for removal of OMPs can not utilize non-biodegradable DOC.

4.2.3 FEEM analysis for SAT using SE alone

Fluorescence excitation and emission matrix (FEEM) spectra analysis were performed on the samples taken after the ripening period to investigate which fractions of DOC are removed during SAT. Figure 4-6 presents representative FEEM spectra for influent and effluent of soil column 1 showing the locations of peak intensities for the humic-like primary (A), humic-like secondary (B), and protein-like (C) fractions of DOC, taken 67 days after start of the experiment. The results of the spectral analysis (Figure 4-7 and Table 4-3) reveal average reduction in peak intensity values for the soil column fed with SE for humic-like 1, humic-like 2 and protein-like fractions of DOC were 9.3%, 7.6% and 15.8%, respectively. This shows that SAT preferentially removes protein-like fractions.

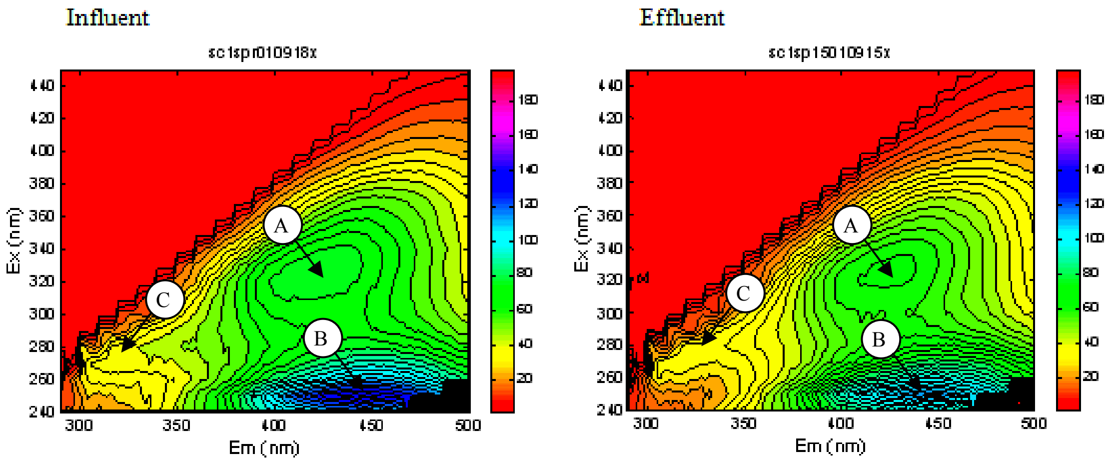


Figure 4-6. FEEM spectra for SC-1 fed with SE alone at time t = 63 days (HLR = 1.25 m/day; under aerobic conditions; media=0.8-1.25 mm sand, 5 m depth; 2 columns each 100 mm diameter in series)

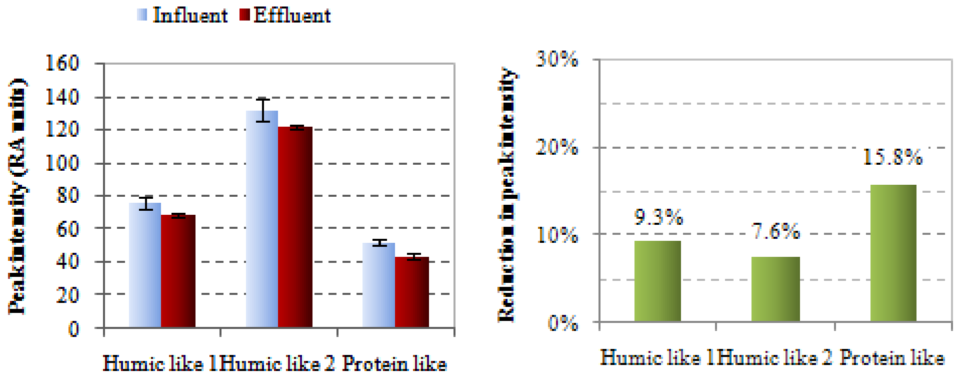


Figure 4-7. Peak intensity (ave) for influent and effluent of SC-1 & SC-2 fed with SE (HLR = 1.25 m/day; under aerobic conditions; media=0.8-1.25 mm sand, 5 m depth; 2 columns each 100 mm diameter in series)

Table 4-3. FEEM spectra results (ave) for SC-1 and SC-2 fed with SE alone (HLR = 1.25 m/day; under aerobic conditions; media=0.8-1.25 mm sand, 5 m depth; 2 columns each 100 mm diameter in series)

DOC Component		Wavelength (nm)		Peak Intensity	
		Ex	Em	(RA unit)	Reduction
Humic-like 1	Influent	330	429	76	9.3%
	Effluent	330	430	69	
Humic-like 2	Influent	250	447	132	7.6%
	Effluent	250	443	122	
Protein-like	Influent	273	319	52	15.8%
	Effluent	270	313	44	

4.2.4 Effect of ozonation on secondary effluent

To investigate the effect of ozone in terms of organic matter removal during SAT, ozone was applied to the secondary effluent from Hoek van Holland WWTP before feeding into soil column 1. Ozone was generated in the laboratory and applied to the SE using target ozone to DOC ratio of 1 mg O_3/mg DOC. This ratio was chosen because in a previous study, Siddiqui et al. (1997) found that increasing ozone doses beyond an O_3:DOC ratio of 1:1 does not result in significant reductions in DOC (in ozone-biofiltration process), suggesting that some of the organic matter is readily converted to BDOC, while the remaining organic matter is refractory and requires much more ozone to be converted to a biodegradable form.

Ozonation was done in batches of 8 litres at a time. The amount of ozone applied to or consumed by the sample were verified after each ozonation run and considered acceptable if the resulting O_3 to DOC ratio was within five percent of desired value. Transfer efficiency of the ozonation system averaged around 50% +/- 10%. A sample calculation of ozone application and transfer efficiency to SE is presented in Appendix C.

DOC, UVA_{254} and SUVA of secondary effluent and ozonated secondary effluent were first compared to examine the effect of ozone to the secondary effluent. Results are summarised in Table 4-4. DOC of the secondary effluent after application of ozone was slightly reduced by 8.3%. However, significant decrease in UVA_{254} and SUVA values were obtained, with average reductions as much as 56% and 51% respectively. Therefore, the secondary effluent contained organic matter constituents that were less humic and less aromatic after ozonation.

Table 4-4. Effect of ozone on DOC, UVA_{254}, and SUVA for SE

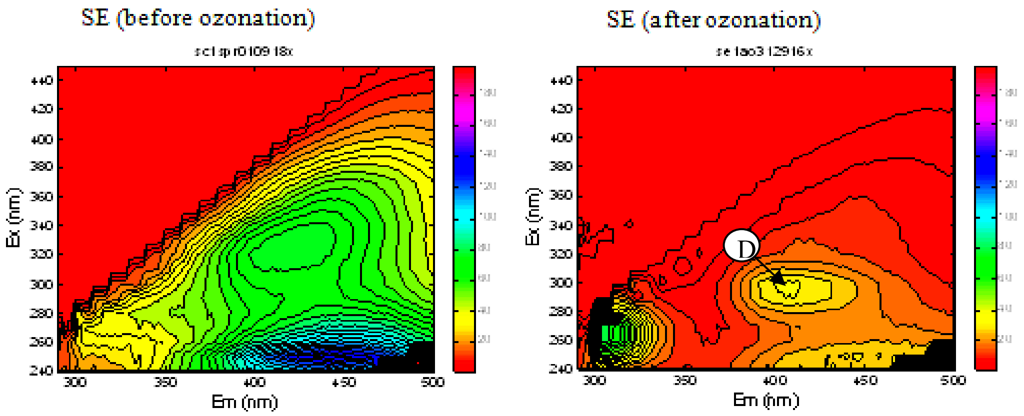
Type of water	DOC mg/L	UVA_{254} Ab/cm	SUVA L/m-mg
SE	15.78	0.42	2.61
SE+O_3	14.47	0.18	1.27
Removal	**8.3%**	**56.4%**	**51.3%**

FEEM spectra analysis results showing the effect of ozone on secondary effluent are presented in Table 4-5 and in Figure 4-8. The highest peak intensity reduction (83%) was obtained for humic-like primary component of DOC. For humic-like secondary, reduction of peak intensity amounted to 77% reduction and for protein-like fractions, a reduction of 13% was observed.

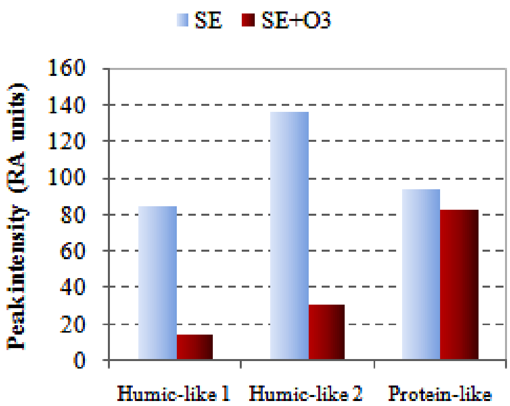
A slight shift in the location of fluorescence intensity peak was detected in the FEEM spectra after ozonation. The location of this new peak is very close to the range of marine humic-like (D) components of DOC. An intensity value of 35 arbitrary RA units was measured for this new peak at excitation and emission wavelengths of 300 and 408 nm, respectively. This value is not far from the highest intensity value in the range of humic-like 2 (30.8 RA units).

Table 4-5. Comparison of FEEM spectra analysis results for SE and SE+O_3

Type of water	DOC (mg/L)	Intensity (RA units)		
		Humic-like 1	Humic-like 2	Protein-like
SE	15.91	84.45	136.42	94.43
SE+O_3	14.86	14.18	30.81	82.39
Removal	6.6%	83.2%	77.4%	12.8%



a) FEEM spectra



b) Peak intensities

Figure 4-8. FEEM spectra and results for SE before and after ozonation

4.2.5 DOC, UVA_{254} and SUVA measurements for SAT using SE+O_3

After the initial feeding of SE+O_3 into the soil column, DOC removal was monitored by measuring the influent and effluent concentrations at regular intervals until the removal efficiency became stable. Twenty days after the initial feeding of ozonated secondary effluent into SC-1, the DOC removal was stable at 29%. Data on DOC measurements taken during the monitoring period can be found in Appendix D.

Water quality measurements at the different sampling points were taken at 21 days and 25 days after the start of experiment. Profiles of DOC removal, UVA_{254} and SUVA values for SC-1 fed with SE+O_3 are presented in Figure 4-9. The average DOC removal

was 27%. Similar to the experiments involving SE without any pre-treatment, around 80% of the total DOC removal took place in the first 50 cm of the soil column.

Summary of DOC removal and UVA_{254} values using SE and SE+O_3 as feed water in the SAT simulation experiments are presented in Table 4-6. DOC removal for SE and SE+O_3 as feed water were 23.9% and 25.6% respectively. In absolute terms, the DOC of the effluent of pre-ozonated SE+SAT was lower (9.68 mg/L) compared to SE+SAT without ozone pre-treatment (10.69 mg/L). A higher reduction in UVA_{254} was obtained for pre-ozonated SE at 21.4% when compared with the use of SE alone at 12.4%.

Effluent organic matter (EfOM) present in the DOC of wastewater typically contains high molecular weight (MW) and refractory organic matter (Jarusutthirak et al., 2007). It seems that ozone is capable of converting these larger organic molecules, including humic substances present in the secondary effluent as particulates into soluble compounds (Rivas et al., 2009). This is consistent with previous studies that showed ozone to be an effective treatment because it could convert refractory DOC, such as humic acids, into more biodegradable compounds. It has been shown that oxidative treatment improves biodegradability of specific poorly degradable organic compounds in SAT systems (Drewes & Jekel, 1998).

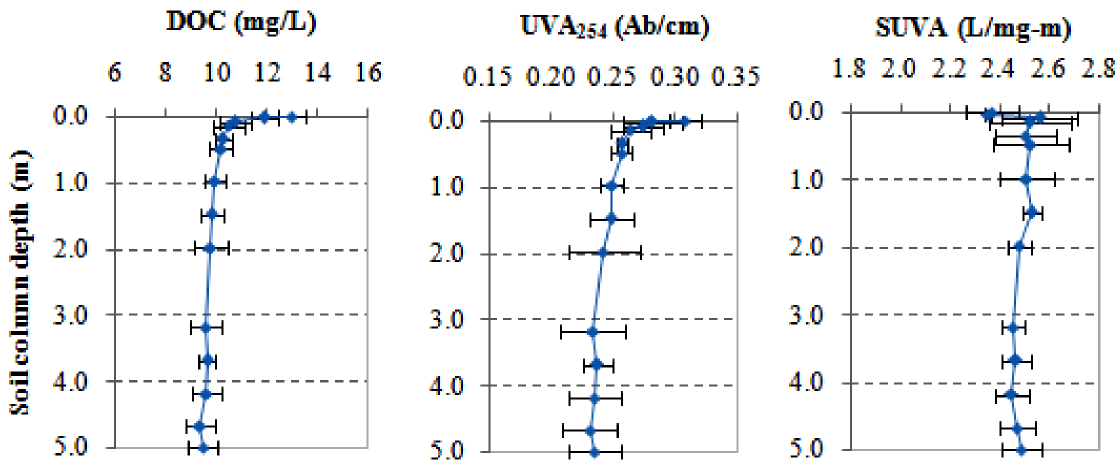


Figure 4-9. DOC, UVA_{254} and SUVA profile for SC-1 fed with SE+O_3 (HLR = 1.25 m/day; under aerobic conditions; media=0.8-1.25 mm sand, 5 m depth; 2 columns each 100 mm diameter in series)

Table 4-6. Summary of DOC, UVA_{254} for SAT with SE alone and SE+O_3 (HLR = 1.25 m/day; under aerobic conditions; media=0.8-1.25 mm sand, 5 m depth; 2 columns each 100 mm diameter in series)

Type of feed water	DOC (mg/L)			UVA254 (Ab/cm)			SUVA (L/mg-m)	
	Influent	Effluent	Removal	Influent	Effluent	Removal	Influent	Effluent
SE	14.23	10.69	23.9%	0.39	0.34	12.4%	2.82	3.23
SE+O_3	12.99	9.68	25.6%	0.31	0.24	21.4%	2.37	2.50

4.2.6 DOC degradation model for soil column using SE+O_3

Equation 4-3 is applied for the measured values of DOC of SC-1 fed with pre-ozonated SE with dosage of 1 mg O_3/mg DOC to investigate which fraction of DOC was

biodegradable. The results are presented in Table 4-7 and Figure 4-10. The degradation rates of easily biodegradable and slowly biodegradable components of DOC are shown in Figure 4-11.

Table 4-7. Kinetic model parameters for DOC removal in SC-1 fed with SE+O_3 (HLR = 1.25 m/day; under aerobic conditions; media=0.8-1.25 mm sand, 5 m depth; 2 columns each 100 mm diameter in series)

Model parameter	C_0	λ_1	C_1	λ_2	C_2	R2
Unit	mg/L	m^{-1}	mg/L	m^{-1}	mg/L	-
Parameter value	2.58	20.316	1.00	0.556	9.40	0.996

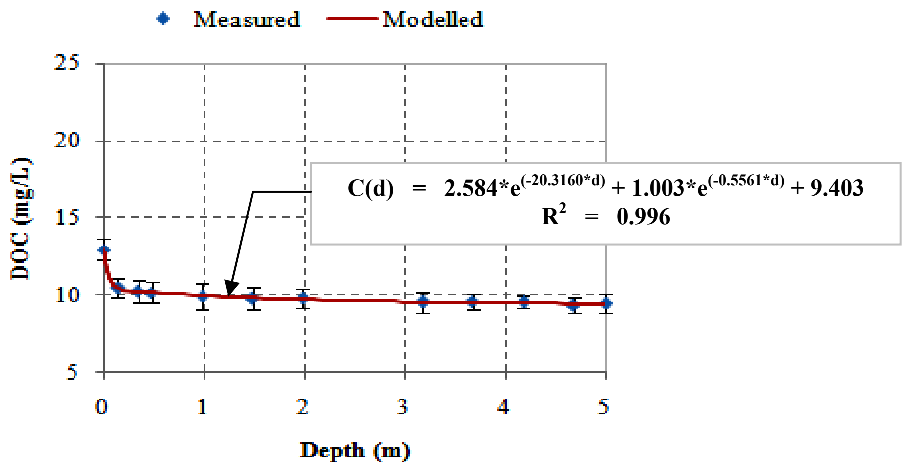


Figure 4-10. Measured values and modelled curve for DOC in SC-1 using SE+O_3 (HLR = 1.25 m/day; under aerobic conditions; media=0.8-1.25 mm sand, 5 m depth; 2 columns each 100 mm diameter in series)

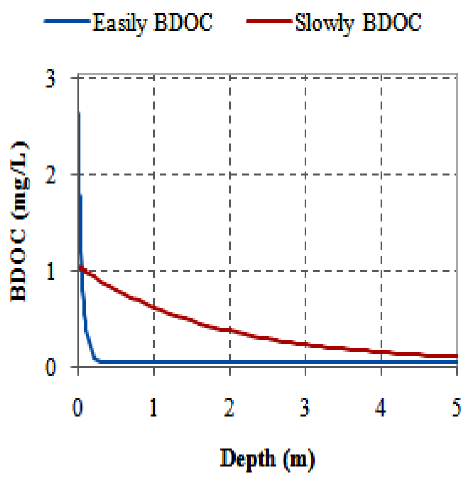


Figure 4-11. Modelled curves for removal of BDOC components in SC-1 fed with SE+O_3 (HLR = 1.25 m/day; under aerobic conditions; media=0.8-1.25 mm sand, 5 m depth; 2 columns each 100 mm diameter in series)

Based on the formulated models for biodegradation of DOC in SC-1, a maximum removal of 22.5% is achievable through biodegradation in the soil column when using

SE alone and a higher maximum removal of 27.6% for pre-ozonated secondary effluent implying that ozonation enhances the biodegradability of DOC components present in the secondary effluent. Additionally, the fraction of easily biodegradable components of DOC was higher in pre-ozonated SE at 19.9% compared to 8.8% for SE alone as illustrated in Figure 4-12. This shows that a fraction of DOC had been converted from slowly biodegradable and partly from non-biodegradable structures into easily biodegradable form by ozonation.

Table 4-8. Biodegradation of DOC in SC-1 fed with SE alone and SE+ozone

Type of water	Total DOC (mg/L)	BDOC (mg/L)			Non-BDOC (mg/L)	Max Possible Removal by (Biodegradation)
		Total	Easily BDOC	Slowly BDOC		
SE	14.36	3.23	1.18	2.05	11.13	22.5%
SE+O_3	12.99	3.59	2.58	1.00	9.40	27.6%

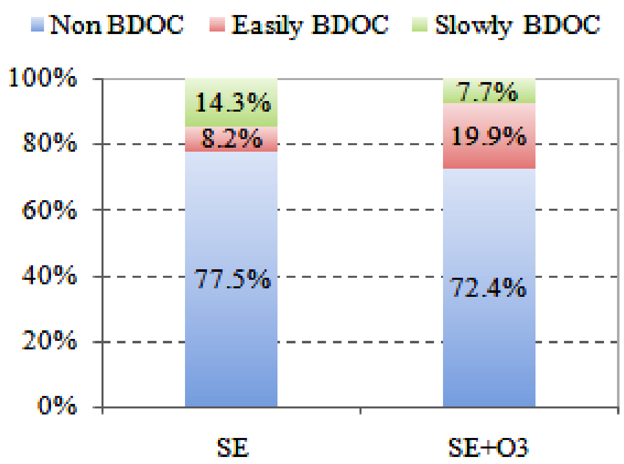


Figure 4-12. Fractions of DOC available for biodegradation for SC-1

Pre-ozonation of SE before SAT is expected to promote OMP removal. Firstly, ozone is likely to attack or breakdown some of the micro-pollutants. Secondly, ozonation increases the amount of easily biodegradable organic carbon fraction. This will help further the bio-degradation of OMPs deeper into the soil column. Ozonation also influences the redox conditions in the upper part of the column as it provides more oxic zones.

The possibility that pre-ozonation of SE before SAT will result in the destruction or disinfection of the biomass in the soil column is remote because of the following reasons: (1) Ozone is very unstable in aqueous solutions and will escape or decay quickly, (2) Most of the ozone shall have been consumed by the different contaminants present in the wastewater, and (3) A lag time of at least one day between the pre-ozonation process of SE and its application into the soil column is long enough for the remaining ozone molecules in the sample water to escape, to decay or to be consumed.

4.2.7 FEEM spectra analysis for SAT using SE+O_3

Figure 4-13 shows the FEEM spectra of the influent and effluent of SC-1 fed with pre-ozonated secondary effluent at 22 days after initial infusion into the soil column. Relatively high removal of protein-like fraction of organic matter (19.3%) was obtained for ozonated SE after SAT treatment, when compared to humic-like 1 fraction removal (only 2.3%) as shown in Figure 4-14. This again shows the preferential removal of protein-like fractions of DOC in SAT. Surprisingly, there was an increase in the peak intensity after SAT treatment for humic-like 2 fraction (5.8% increase) when SE+O_3 was used as feed water for SAT but, in terms of absolute values, the influent peak intensities for un-ozonated SE for all fractions of DOC considered were much higher than those of SE+O_3. Figure 4-15 shows peak intensity values of DOC fractions for SAT influent and effluent fed with SE and SE+O_3.

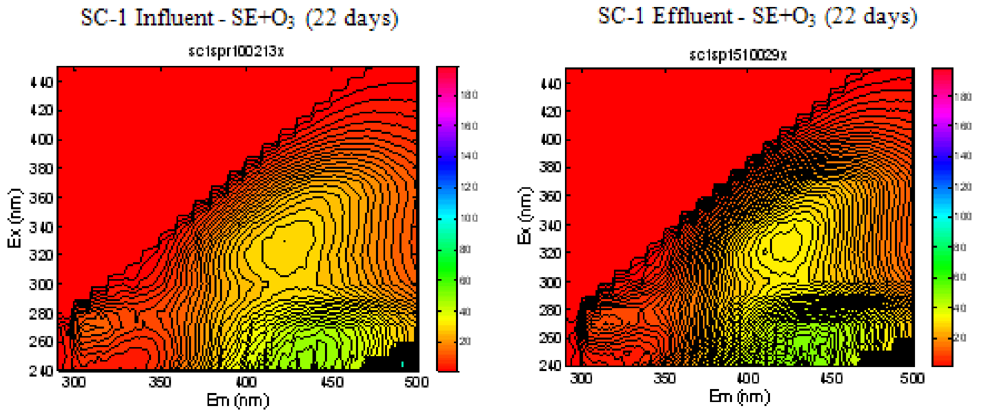


Figure 4-13. FEEM spectra for SC-1 fed with SE+O_3 at time t = 22 days (HLR = 1.25 m/day; under aerobic conditions; media=0.8-1.25 mm sand, 5 m depth; 2 columns each 100 mm diameter in series)

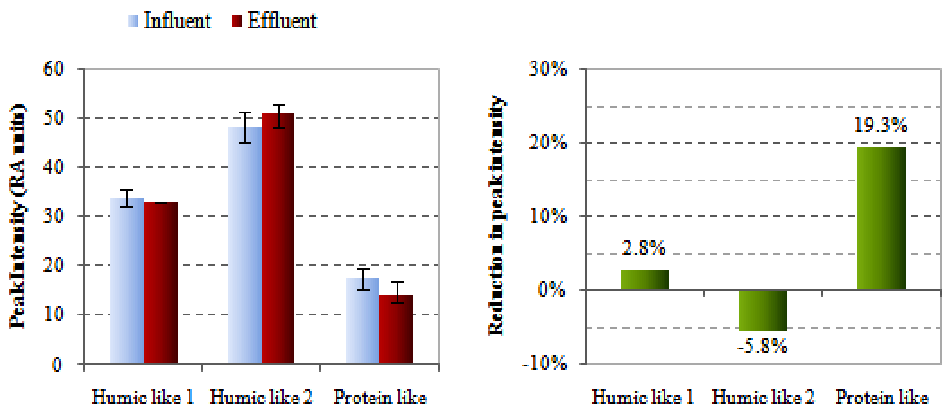


Figure 4-14. FEEM spectra results for influent and effluent of SC-1 fed with SE+O_3 (HLR = 1.25 m/day; under aerobic conditions; media=0.8-1.25 mm sand, 5 m depth; 2 columns each 100 mm diameter in series)

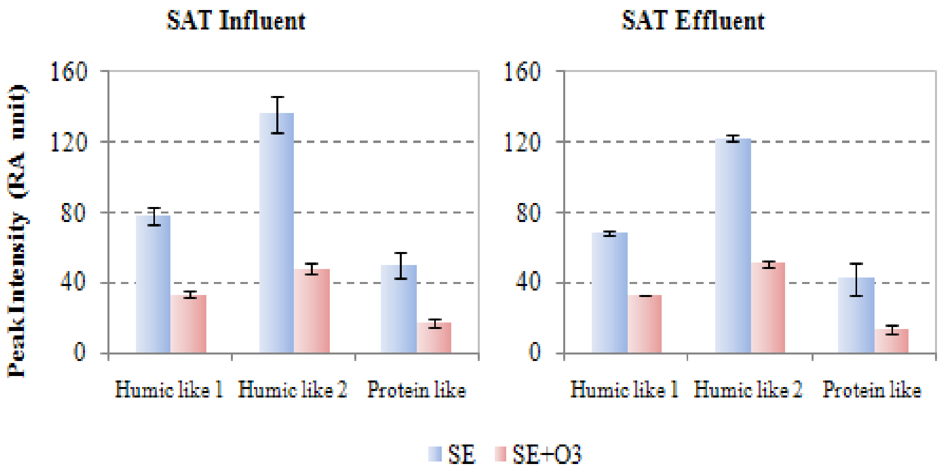


Figure 4-15. Peak intensity values of SAT influent and effluent fed with SE and SE+O_3 (HLR = 1.25 m/day; under aerobic conditions; media=0.8-1.25 mm sand, 5 m depth; 2 columns each 100 mm diameter in series)

4.3 Nanofiltration using NF-270

Nanofiltration experiments were conducted using NF-270 (DOW-FilmTec) membranes using SE, SE+SAT, SE+O_3, SE+O_3+SAT. All experiments using NF-270 were conducted under the following conditions:

Feed pressure	=	50 psi (3.6 bars)
Recovery	=	8%
Temperature	=	20 °C
Filtration mode	=	One-pass (without recirculation of concentrate)

4.3.1 DOC, TDS, UVA_{254} and SUVA for NF-270 using SE alone and SE+SAT

Rejection of a contaminant or component in membrane filtration is defined as

$$R = (1 - C_p/C_f) \times 100 \qquad (4\text{-}4)$$

Where:	R	=	rejection (%)
	C_p	=	contaminant concentration in the permeate (mg/L)
	C_f	=	contaminant concentration in the feed (mg/L)

R is a dimensionless parameter and its value normally varies between 100% for complete rejection of the solute and 0% for the case of solute and solvent passing freely through the membrane. Negative rejections can sometimes be observed when the solute passes favourably through the membrane (van der Bruggen & Geens, 2008).

The study focused mainly on the removal of DOC and TDS and the reduction of UVA_{254}, and the peak intensities in FEEM spectra analysis.

Table 4-9 and Figure 4-16 reveal that very high DOC and UVA_{254} removal rates were obtained by nanofiltration using NF-270 for both types of feed water: SE alone and SAT pre-treated SE. More than 90% of DOC and UVA_{254} were removed in either type of feed water. Moderate removal of TDS was detected at 43% for SE alone and 48% for

SE+SAT. Organic and inorganic compounds are removed by NF due to steric/size exclusion, electrostatic repulsion and hydrophobic interaction, or adsorption (Her et al., 2008). More influence is exerted by membrane characteristics in rejection of contaminants in nanofiltration than the characteristics of the feed water. Chellam (2000) showed that membrane type has a stronger influence on contaminant removal when compared to source water characteristics. However, according to Boussu et al. (2006), membrane and feed characteristics play major roles in the phenomenon of membrane fouling in nanofiltration, as it is the interplay between membrane and feed that determines the fouling tendency.

Table 4-9. DOC, TDS, UVA_{254} and SUVA for NF-270 using SE alone and SE+SAT (p=50 psi, r = 8%, without recirculation of concentrate)

Type of feed water	DOC (mg/L)			TDS (mg/L)		
	Feed	Permeate	Removal	Feed	Permeate	Removal
SE	15.62	0.91	94.2%	752	425	43.4%
SE+SAT	11.12	0.87	92.2%	737	378	48.7%
	UVA_{254} (Ab/cm)			SUVA (L/mg-m)		
	Feed	Permeate	Removal	Feed	Permeate	Removal
SE	0.389	0.014	96.3%	2.495	1.584	36.5%
SE+SAT	0.357	0.021	94.1%	3.21	2.33	27.4%

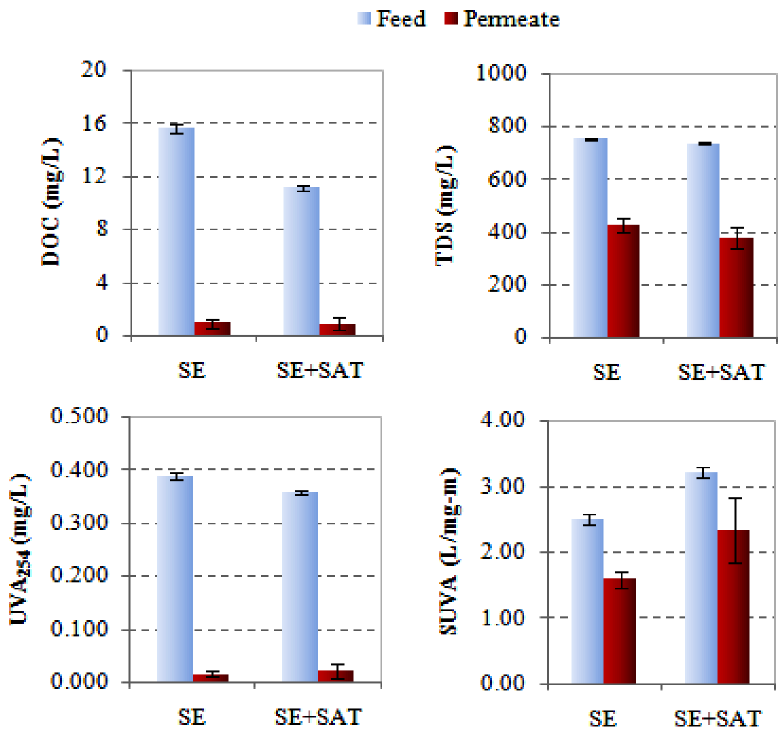


Figure 4-16. DOC, TDS, UVA_{254}, SUVA for NF-270 using SE alone and SE+SAT (p=50 psi, r = 8%, without recirculation of concentrate)

If the DOC removal from SAT is taken at 23.9% as shown in section 4.2.5, the total removal of DOC from secondary effluent in SAT-NF system was 94%, of which,

23.9% is contributed by the SAT system and 70.1% contributed by nanofiltration. The calculation is presented in Table 4-10 and shown in Figure 4-17. This means that there is no major change in overall DOC removal by SAT pre-treatment for SAT-NF system. However, with SAT pre-treatment, DOC load on NF membrane is reduced considerably.

Table 4-10. DOC removal contribution of SAT for SE in SAT-NF(NF-270) system

Type of feed water	DOC Removal						
	due to SAT			due to NF			Total Removal
	Influent	Effluent	Removal	Feed	Permeate	Removal	
SE	15.62	15.62	0	15.62	0.91	94.2%	94.2%
SE+SAT	14.62	11.12	23.9%	11.12	0.87	70.1%	94.0%

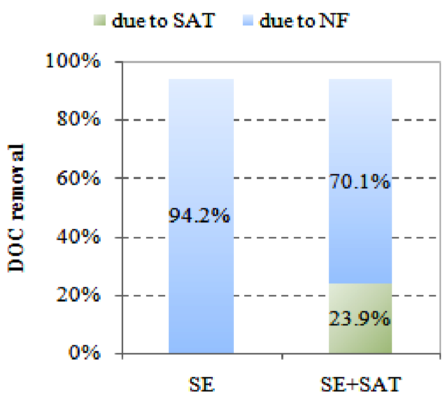


Figure 4-17. DOC removal by NF and SAT-NF (NF-270) system for SE

4.3.2 FEEM spectra analysis for NF-270 using SE alone and SE+SAT

Peak intensity values for the feed and permeate during nanofiltration of SE were higher than the feed and permeate intensities during nanofiltration with the use of SE+SAT as feed. Slightly higher rejections of different DOC fractions were obtained for nanofiltration using NF-270 with SE+SAT as feed solution than with SE alone as can be seen from Table 4-11 and Figure 4-19. However, all peak intensity reductions were over 90% in all cases. Representative feed and permeate FEEM spectra for nanofiltration of NF-270 using SE and SE+SAT are shown in Figure 4-18.

Table 4-11. FEEM spectra results for NF-270 using SE alone and SE+SAT (p=50 psi, r = 8%, without recirculation of concentrate)

Type of feed water	DOC Component		Wavelength (nm) Ex	Wavelength (nm) Em	Peak Intensity (RA unit)	Peak Intensity Reduction
SE	Humic-like 1	Feed	340	439	66.0	91.2%
		Permeate	340	422	5.8	
	Humic-like 2	Feed	255	431	138.6	92.0%
		Permeate	250	445	11.1	
	Protein-like	Feed	265	336	48.1	90.5%
		Permeate	270	308	4.6	
SE + SAT	Humic-like 1	Feed	330	428	64.3	94.5%
		Permeate	330	415	3.5	
	Humic-like 2	Feed	253	441	115.9	94.4%
		Permeate	255	437	6.5	
	Protein-like	Feed	270	306	47.6	93.1%
		Permeate	270	310	3.3	

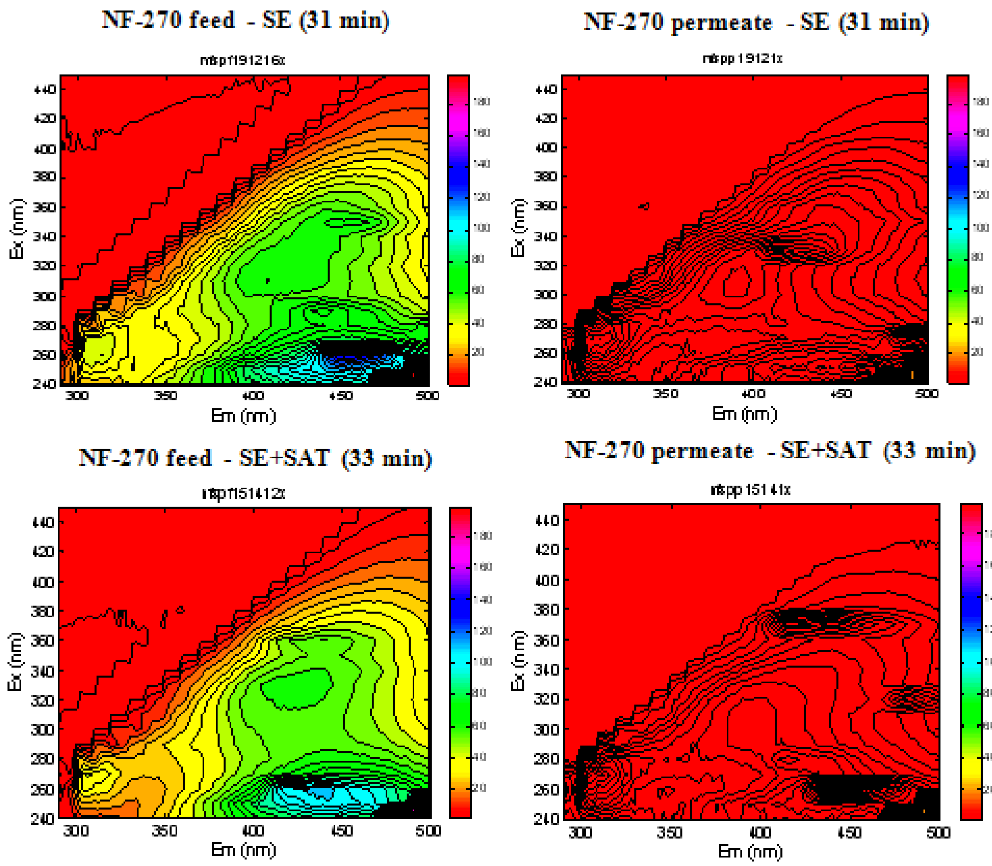


Figure 4-18. FEEM spectra for NF-270 using SE alone and SE+SAT (p=50 psi, r = 8%, without recirculation of concentrate)

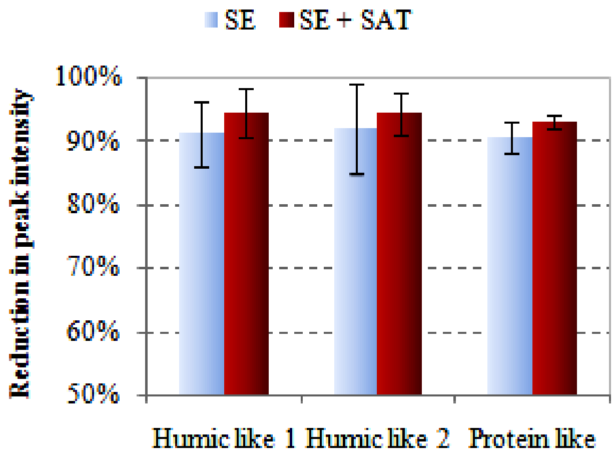


Figure 4-19. FEEM spectra analysis results for NF-270 using SE alone and SE+SAT (p=50 psi, r = 8%, without recirculation of concentrate)

4.3.3 Flux decline for NF-270 using SE alone and SE with SAT pre-treatment

To investigate the rate of fouling of the NF membranes, the flux and normalised flux are plotted against time as shown in Figure 4-20. Normalized flux represents the flux decline in membrane filtration and is defined as the ratio of permeate flux, J at any time t over the initial permeate flux, J_o.

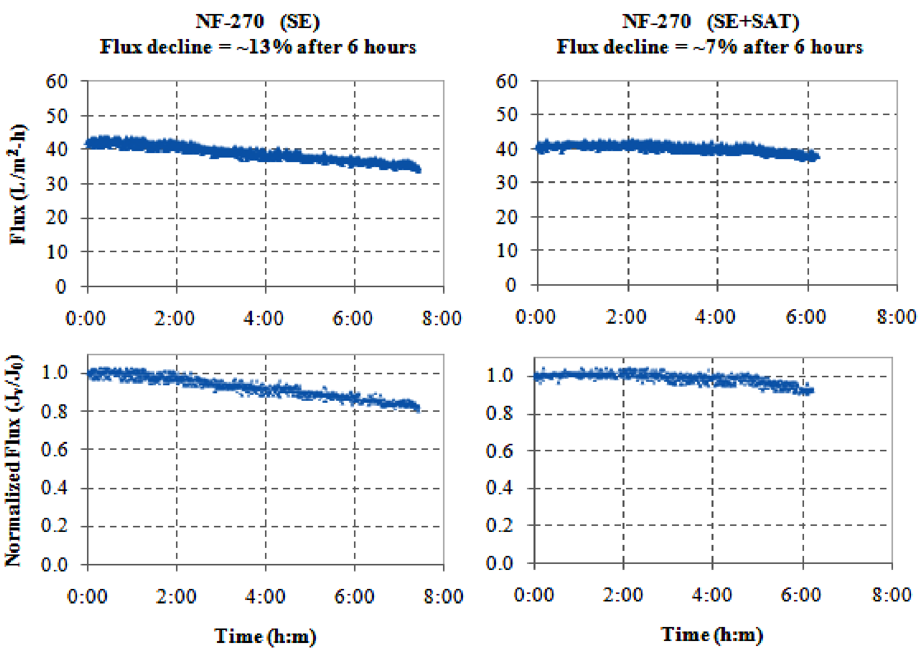


Figure 4-20 . Flux and normalised flux for NF-270 using SE alone and SE+SAT (p=50 psi, r = 8%, without recirculation of concentrate)

Delivered DOC is a measure of the amount of organic carbon per unit membrane area delivered to the membrane. Delivered DOC provides a basis for an equitable

comparison of different types of water with different DOC levels (Her et al., 2008) and can be expressed as

$$\text{Delivered DOC} = Vf * Cf / A \qquad (4\text{-}5)$$

where V_f = volume of feed at any time t (L)
C_f = DOC concentration in feed (mg/L)
A = surface area of membrane (cm^2)

Delivered DOC during nanofiltration for NF-270 using SE and SE+SAT as feed water are shown in Figure 4-21. After 6 hours of filtration, delivered DOC for NF-270 using SE as feed water was 4.7 mg/cm^2 and that for SE+SAT was 3.4 mg/cm^2.

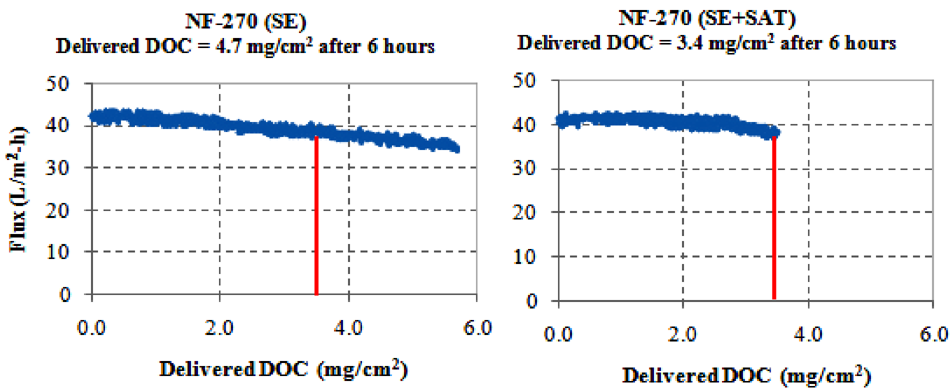


Figure 4-21. Delivered DOC for NF-270 using SE alone and SE+SAT (p=50 psi, r = 8%, without recirculation of concentrate)

A summary of flux decline at a common delivered DOC of 3.5 mg/cm^2 for NF-270 using SE and SE+SAT as feed water is presented in Table 4-12. Using feed pressure of 50 psi (3.6 bar) and 8% recovery, without recirculation of the concentrate, it was found that around 8% of flux decline was obtained at 3.5 mg/cm^2 of delivered DOC to the NF-270 membrane using SE alone. In comparison, 6% flux decline was obtained at same delivered DOC when SAT pre-treated SE was used.

Table 4-12. Flux decline at same delivered DOC for NF-270 using SE and SE+SAT (p=50 psi, r = 8%, without recirculation of concentrate)

Type of Feed	DOC of feed (mg/L)	Initial Flux (L/m^2-h)	Delivered DOC (mg/cm^2)	Time (hh:mm)	Flux Decline (%)
SE	15.62	42.3	3.5	4:24	8%
SE+SAT	11.12	41.0	3.5	6:12	6%

4.3.4 DOC, TDS, UVA and SUVA for NF-270 using SE+O_3 and SE+O_3+SAT

Removal rates of DOC, TDS, UVA_{254} and SUVA for NF-270 using SE+O_3 and SE+O_3+SAT are shown in Table 4-13 and Figure 4-22. Slightly lower removal ratios were obtained for DOC, TDS and UVA_{254} for SE+O_3 and SE+O_3+SAT when compared with those of SE and SE+SAT (section 4.3.1). However, in general, SE+O_3 and SE+O_3+SAT contained lower initial values of these parameters for the feed water compared with those of their counterparts. In particular, UVA_{254} had much lower initial values for the experiments involving SE+O_3 and SE+O_3+SAT.

Table 4-13. DOC, TDS, UVA_{254} and SUVA for NF-270 using SE+O_3 and SE+O_3+SAT (p=50 psi, r = 8%, without recirculation of concentrate)

Type of feed water	DOC (mg/L)			TDS (mg/L)		
	Feed	Permeate	Removal	Feed	Permeate	Removal
SE+O_3	9.45	1.15	87.9%	533	289	45.7%
SE+O_3+SAT	8.40	1.00	88.1%	761	426	44.1%
	UVA_{254} (Ab/cm)			SUVA (L/mg-m)		
	Feed	Permeate	Removal	Feed	Permeate	Removal
SE+O_3	0.150	0.010	93.1%	1.59	0.92	41.8%
SE+O_3+SAT	0.208	0.022	89.7%	2.47	2.09	15.4%

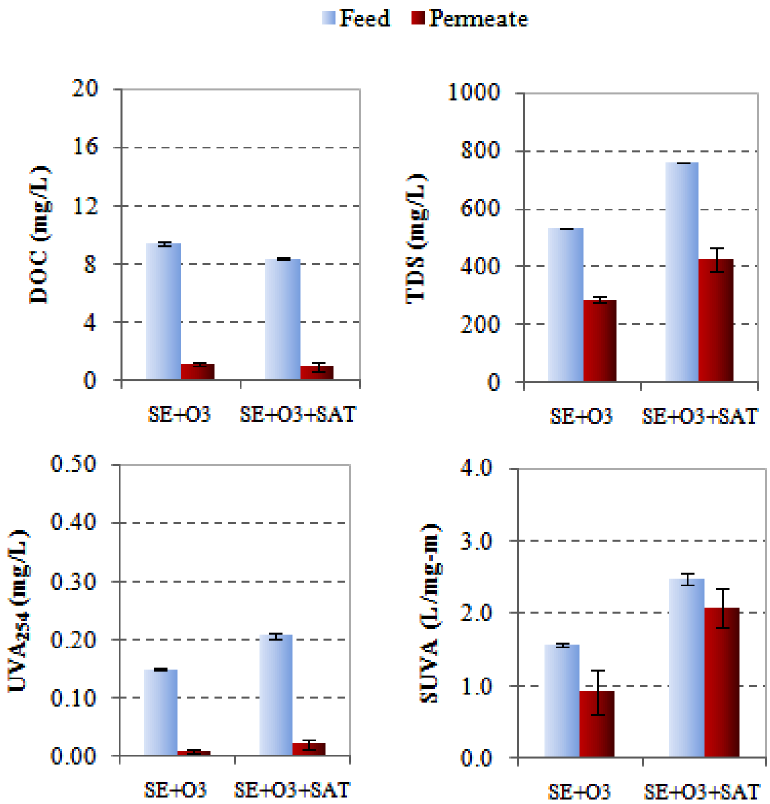


Figure 4-22. DOC, TDS, UVA_{254}, SUVA for NF-270 using SE+O_3 and SE+O_3+SAT (p=50 psi, r = 8%, without recirculation of concentrate)

If the removal efficiency of SAT in terms of DOC removal is taken at 25.6% for ozonated SE as shown in section 4.2.5, then the over-all removal efficiency for the SAT-NF system when using SE+O_3 as feed water was 91.2%. Without SAT pre-treatment the removal rate is 87.9%. This comparison is shown in Table 4-14 and Figure 4-23.

Table 4-14. DOC removal contribution of SAT for SE+O_3 in SAT-NF(NF-270) system

Type of feed water	DOC Removal						
	due to SAT			due to NF			Total Removal
	Influent	Effluent	Removal	Feed	Permeate	Removal	
SE+O_3	9.45	9.45	0	9.45	1.15	87.9%	87.9%
SE+O_3+SAT	11.29	8.40	25.6%	8.40	1.00	65.6%	91.2%

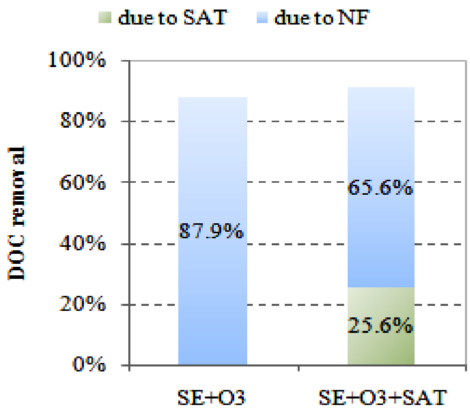


Figure 4-23. DOC removal by NF and SAT-NF (NF-270) system for SE+O_3

4.3.5 FEEM spectra analysis for NF-270 using SE+O_3 and SE+O_3+SAT

Representative FEEM spectra for NF-270 filtration using SE+O_3 and SE+O_3+SAT are presented in Figure 4-24. Peak intensity values from the FEEM spectra analysis are tabulated in Table 4-15 showing very high reductions (over 90%) of humic-like 1 and humic-like 2 for both types feed water. Removal ratios of protein-like components were 76.1% and 87.5% for SE+O_3 and SE+O_3+SAT, respectively.

Table 4-15. FEEM spectra results for NF-270 using SE+O_3 and SE+O_3+SAT
(p=50 psi, r = 8%, without recirculation of concentrate)

Type of feed water	DOC Component		Wavelength (nm)		Peak Intensity	
			Ex	Em	(RA unit)	Reduction
SE+O_3	Humic-like 1	Feed	335	442	28.11	96.9%
		Permeate	330	439	0.87	
	Humic-like 2	Feed	250	444	28.21	92.5%
		Permeate	250	437	2.11	
	Protein-like	Feed	270	311	9.11	76.1%
		Permeate	270	306	2.18	
SE+O_3+SAT	Humic-like 1	Feed	337	421	32.20	92.2%
		Permeate	330	419	2.52	
	Humic-like 2	Feed	253	432	44.43	91.4%
		Permeate	250	435	3.84	
	Protein-like	Feed	270	311	13.03	87.5%
		Permeate	277	331	1.62	

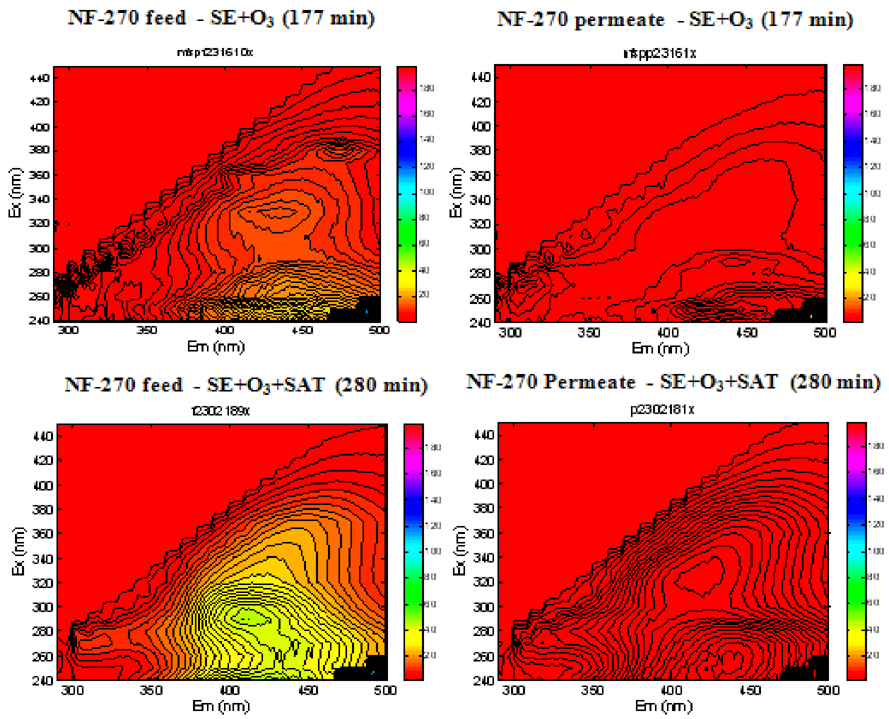


Figure 4-24. FEEM spectra for NF-270 using SE+O_3 and SE+O_3+SAT (p=50 psi, r = 8%, without recirculation of concentrate)

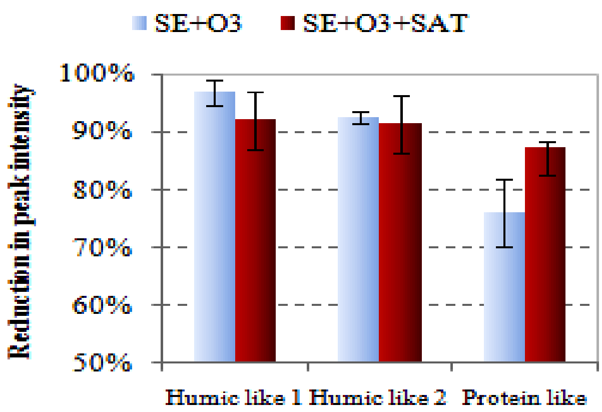


Figure 4-25. FEEM spectra analysis results for NF-270 using SE+O_3 and SE+O_3+SAT (p=50 psi, r = 8%, without recirculation of concentrate)

4.3.6 Flux decline for NF-270 using SE+O_3 and SE+O_3+SAT pre-treatment

Flux decline for NF-270 filtration using SE+O_3 was around 12% after six hours of filtration, and for SE+O_3+SAT, the flux decline for the same period was only around 6%, which are just under the values obtained in section 4.3.3 for SE and SE+SAT as feed, 13% and 7%, respectively.

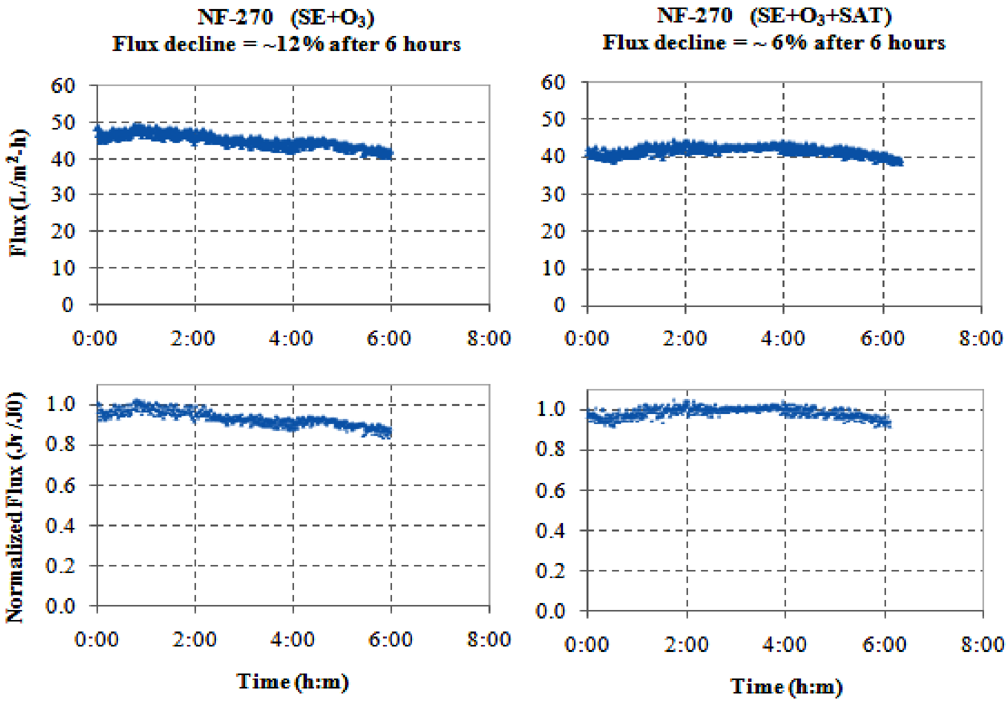


Figure 4-26. Flux and normalised flux for NF-270 using SE+O_3 and SE+O_3+SAT (p=50 psi, r = 8%, without recirculation of concentrate)

Values of flux against delivered DOC for NF-270 using SE+O_3 and SE+O_3+SAT are plotted in Figure 4-27. After six hours of filtration, delivered DOC for SE+O_3 amounted to 3.2 mg/cm^2 while for SE+O_3+SAT, it is 2.6 mg/cm^2.

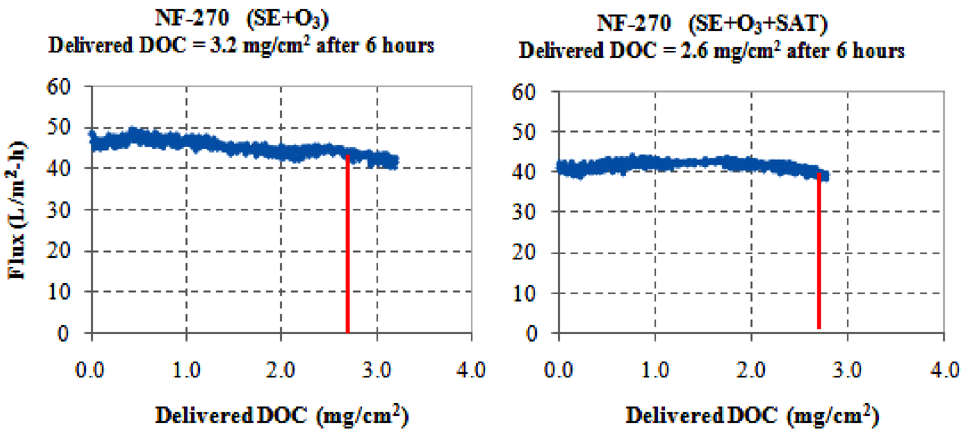


Figure 4-27. Delivered DOC for NF-270 using SE+O_3 and SE+O_3+SAT (p=50 psi, r = 8%, without recirculation of concentrate)

The comparison of flux decline at same delivered DOC of 2.7 mg/cm^2 for NF-270 with SE+O_3 and SE+O_3+SAT as feed water are summarised in Table 4-16. At the same delivered DOC of 2.7 mg/cm2, the flux decline using SE+O_3 was 10%. With SAT pre-treatment of SE+O_3, the flux decline was only 5% showing that SAT can reduce the rate of fouling of the NF membrane.

Table 4-16. Flux decline at same delivered DOC for NF-270 using SE+O_3 and SE+O_3+SAT (p=50 psi, r = 8%, without recirculation of concentrate)

Type of Feed	DOC of feed (mg/L)	Initial Flux (L/m^2-h)	Delivered DOC (mg/cm^2)	Time (hh:mm)	Flux Decline (%)
SE+O_3	9.45	48.3	2.7	5:00	10%
SE+O_3+SAT	8.40	42.3	2.7	6:09	5%

4.4 Nanofiltration using NF-90

To investigate the effect of membrane characteristics on nanofiltration, experiments were conducted using another type of membrane NF-90 (DOW-FilmTec) which has lower MWCO than NF-270. The first set of experiments involved the use of SE (with and without SAT pre-treatment) and the second set used SE+O_3 (with and without SAT pre-treatment). The experiments were conducted under the following conditions:

Feed pressure	=	50 psi (3.6 bar)
Recovery	=	8%
Temperature	=	20 ^oC
Filtration mode	=	One pass (without recirculation of concentrate)

4.4.1 DOC, TDS, UVA and SUVA for NF-90 using SE alone and SE+SAT

Removal of DOC, TDS, UVA_{254} and SUVA for NF-90 using secondary effluent, with and without SAT pre-treatment are summarised in Table 4-17 and shown in Figure 4-28. For DOC, removal efficiency was about 97% for both types of feed water. In case of TDS, NF-90 filtration using SE and SE+SAT removed 94.8% and 91.6%, respectively. These removal rates for TDS were much higher for the tight NF-90 membrane compared with NF-270 membrane (43.4% for SE and 48.7% for SE+SAT) because of pore size differences.

Table 4-17. DOC, TDS, UVA_{254} and SUVA for NF-90 using SE alone and SE+SAT (p=50 psi, r = 8%, without recirculation of concentrate)

Type of feed water	DOC (mg/L)			TDS (mg/L)		
	Feed	**Permeate**	**Removal**	**Feed**	**Permeate**	**Removal**
SE	12.34	0.32	97.4%	649	34	94.8%
SE+SAT	13.39	0.41	96.9%	799	67	91.6%
	UVA_{254} (Ab/cm)			**SUVA (L/mg-m)**		
	Feed	**Permeate**	**Removal**	**Feed**	**Permeate**	**Removal**
SE	0.396	0.003	99.3%	3.207	0.969	69.8%
SE+SAT	0.272	0.001	99.5%	2.029	0.326	84.0%

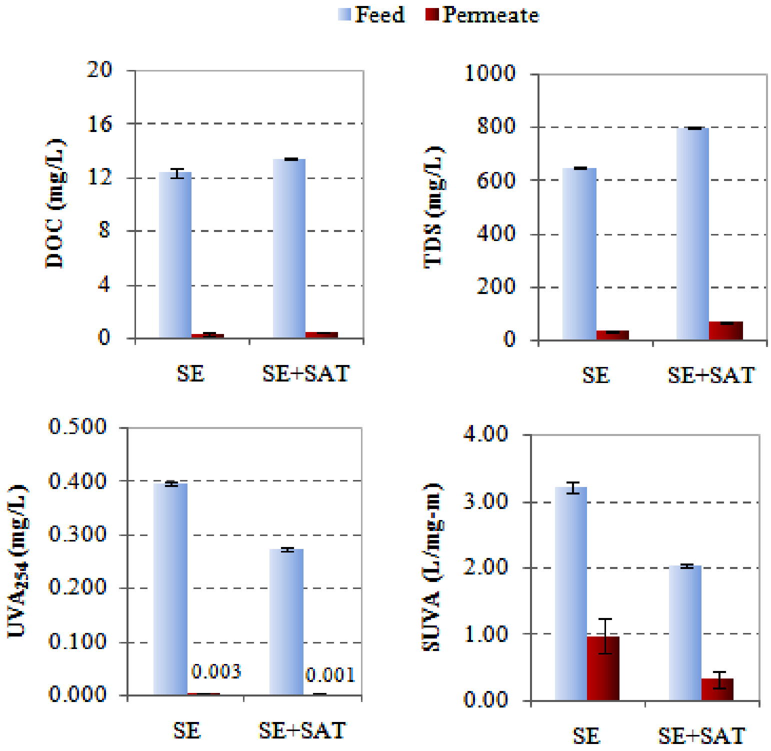


Figure 4-28. DOC, TDS, UVA_{254}, SUVA for NF-90 using SE alone and SE+SAT (p=50 psi, r = 8%, without recirculation of concentrate)

If the average DOC removal rate of 23.9% due to SAT is taken into consideration (section 4.2.5), the total removal of SAT-NF system was 97.7%, of which 73.8% was contributed by NF. The calculation is summarised in Table 4-18 and presented in Figure 4-29.

Table 4-18. DOC removal contribution of SAT for SE in SAT-NF (NF-90) system

Type of feed water	DOC Removal						
	due to SAT			due to NF			Total Removal
	Influent	Effluent	Removal	Feed	Permeate	Removal	
SE	12.34	12.34	0	12.34	0.32	97.4%	97.4%
SE+SAT	17.60	13.39	23.9%	13.39	0.41	73.8%	97.7%

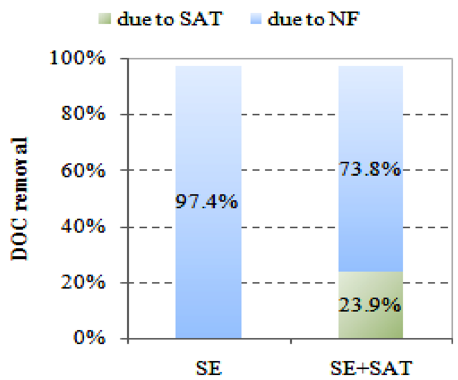


Figure 4-29. DOC removal by NF and SAT-NF (NF-90) system for SE

4.4.2 FEEM spectra analysis for NF-90 using SE alone and SE+SAT

FEEM spectra for these experiments are shown in Figure 4-30 and the analysis results are presented in Table 4-19 and Figure 4-31. Removal rates of over 99% were obtained by NF-90 for both SE and SE+SAT as feed water for humic-like primary and humic-like secondary components of DOC, and over 95% removal for protein-like fraction. In contrast NF-270 removals of humic-like primary and humic-like secondary were around 92% for SE and around 95% for SE+SAT. NF-270 can remove around 91% for SE and 93% of protein-like components for SE+SAT (section 4.3.2).

Table 4-19. FEEM spectra results for NF-90 using SE alone and SE+SAT
(p=50 psi, r = 8%, without recirculation of concentrate)

Type of feed water	DOC Component		Wavelength (nm)		Peak Intensity	
			Ex	Em	(RA unit)	Reduction
SE	Humic-like 1	Feed	333	427	69.9	99.4%
		Permeate	330	424	0.5	
	Humic-like 2	Feed	253	448	99.2	99.3%
		Permeate	250	417	0.7	
	Protein-like	Feed	270	317	16.0	95.9%
		Permeate	270	307	0.7	
SE + SAT	Humic-like 1	Feed	330	421	98.9	99.2%
		Permeate	330	405	0.8	
	Humic-like 2	Feed	250	439	133.5	99.2%
		Permeate	250	418	1.1	
	Protein-like	Feed	270	310	26.6	95.0%
		Permeate	270	310	1.3	

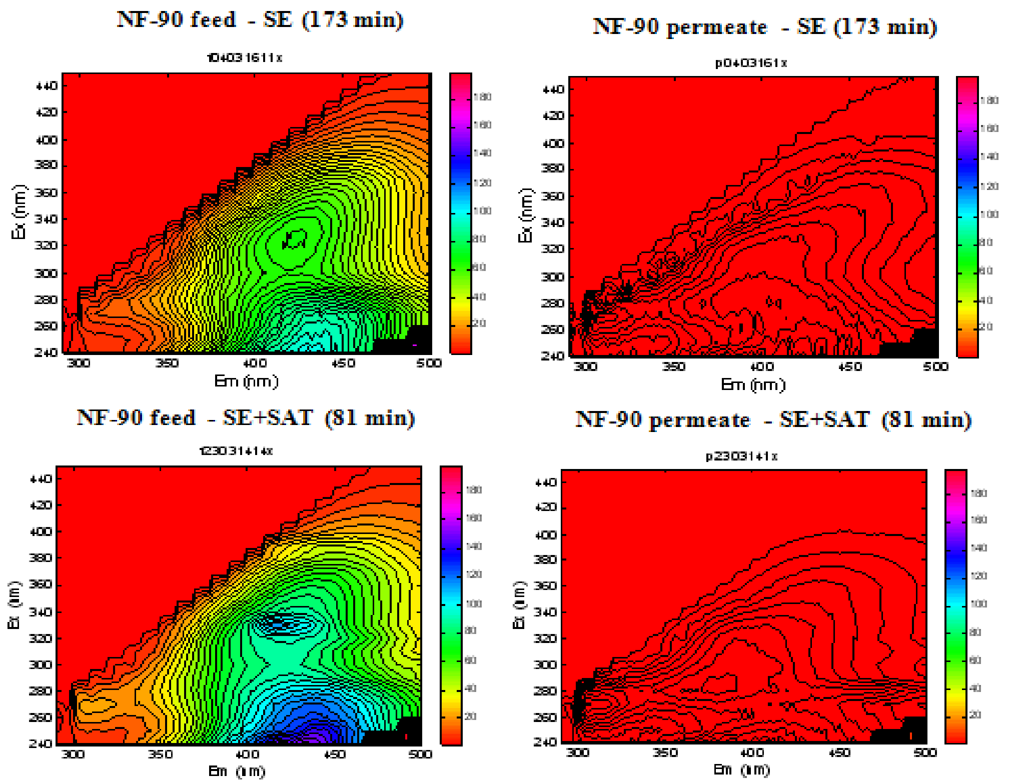


Figure 4-30. FEEM spectra for NF-270 using SE alone and SE+SAT
(p=50 psi, r = 8%, without recirculation of concentrate)

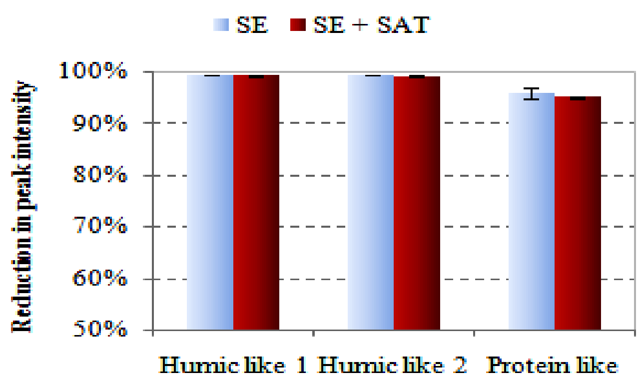


Figure 4-31. FEEM spectra analysis results for NF-90 using SE alone and SE+SAT
(p=50 psi, r = 8%, without recirculation of concentrate)

4.4.3 Flux decline for NF-90 using SE alone and SE+SAT pre-treatment

As expected, much higher flux decline were obtained for nanofiltration using the tighter NF-90 than with NF-270. Flux decline for NF-90 with SE was around 50% after six hours of filtration and around 39% for SE+SAT as feed water. The graphs of flux and normalised flux for NF-90 using SE alone and SE+SAT are shown in Figure 4-32.

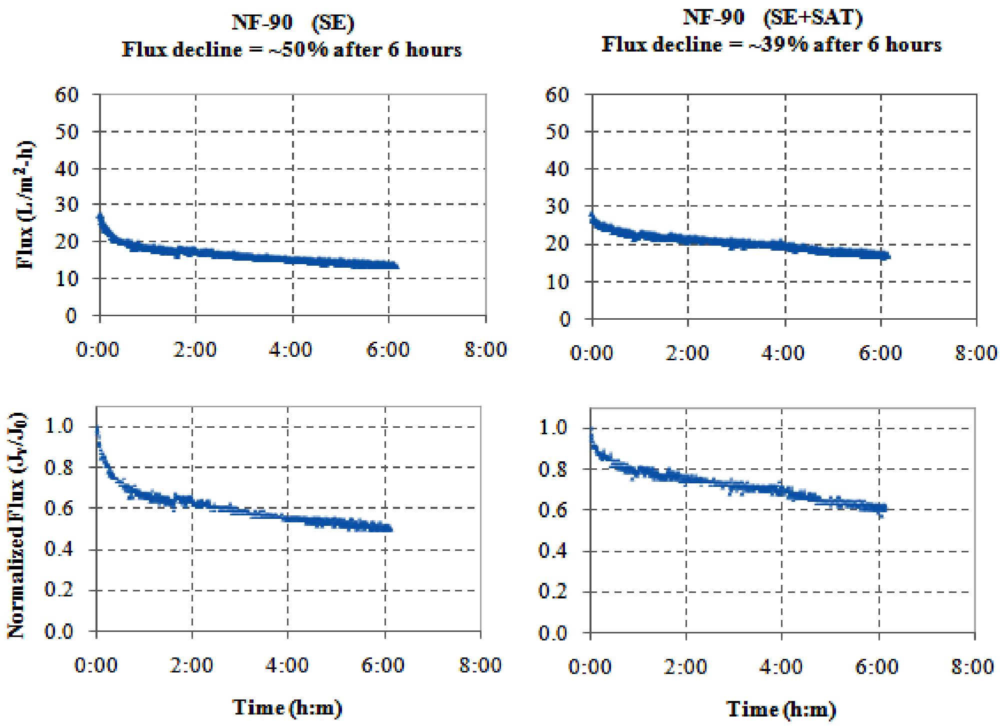


Figure 4-32. Flux and normalised flux for NF-90 using SE alone and SE+SAT (p=50 psi,, r=8%, without recirculation of concentrate)

Flux against delivered DOC during nanofiltration for NF-90 using SE and SE+SAT as feed water are plotted in Figure 4-33. Without recirculation of concentrate back into feed tank, the average of the feed DOC concentration measurements was taken for the computation of delivered DOC. After 6 hours of filtration, delivered DOC for NF-90 using SE as feed water was 1.6 mg/cm^2 and that of using SE+SAT was 2.1 mg/cm^2.

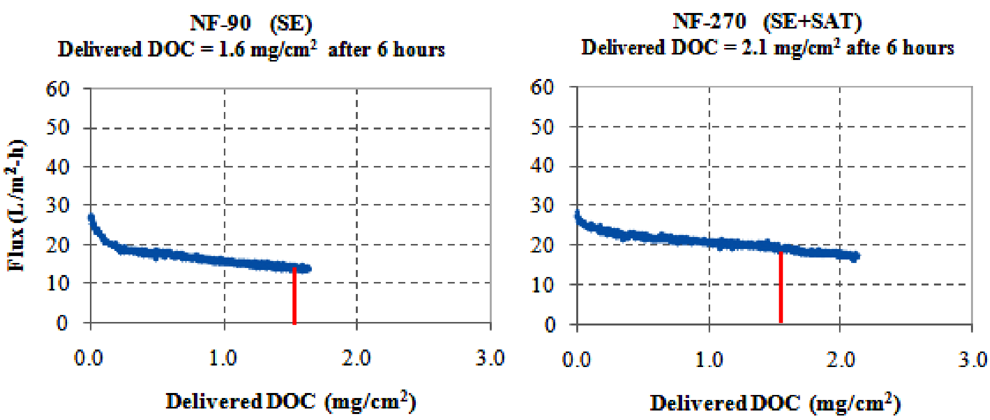


Figure 4-33. Delivered DOC for NF-90 using SE alone and SE+SAT (p=50 psi, r = 8%, without recirculation of concentrate)

Table 4-20 summarises the flux decline at same delivered DOC of 1.6 mg/cm^2 for NF-90 using SE and SE+SAT as feed water. The system performed better in terms of flux decline (32%) with SAT pre-treatment than with SE alone (50%).

Table 4-20. Flux decline at same delivered DOC for NF-90 using SE and SE+SAT (p=50 psi, r = 8%, without recirculation of concentrate)

Type of Feed	DOC of feed (mg/L)	Initial Flux (L/m^2-h)	Delivered DOC (mg/cm^2)	Time (hh:mm)	Flux Decline (%)
SE	12.34	27.6	1.6	6:13	50%
SE+SAT	11.39	28.5	1.6.	4:26	32%

4.4.4 DOC, TDS, UVA and SUVA for NF-90 using SE+O_3 and SE+O_3+SAT

Similar trends in removal rates for DOC, TDS and UVA_{254} were observed for NF-90 when using SE+O_3 and SE+O_3+SAT as feed and when using SE alone and SE+SAT as feed. Again, comparing with NF-270 the removal rates for these types of feed were higher with NF-90 especially for TDS, for which the removal rates of the latter (94% and 89.5%) were more than double that of the former (45.7% and 44.1%). These measurements are shown in Table 4-21 and Figure 4-34.

Table 4-21. DOC, TDS, UVA_{254} and SUVA for NF-90 using SE+O_3 and SE+O_3+SAT (p=50 psi, r = 8%, without recirculation of concentrate)

Type of feed water	DOC (mg/L)			TDS (mg/L)		
	Feed	**Permeate**	**Removal**	**Feed**	**Permeate**	**Removal**
SE+O_3	17.21	0.43	97.5%	830	50	94.0%
SE+O_3+SAT	7.66	0.49	93.6%	634	67	89.5%
	UVA_{254} (Ab/cm)			**SUVA (L/mg-m)**		
	Feed	**Permeate**	**Removal**	**Feed**	**Permeate**	**Removal**
SE+O_3	0.230	0.002	99.2%	1.337	0.382	71.5%
SE+O_3+SAT	0.174	0.003	98.4%	2.278	0.603	73.5%

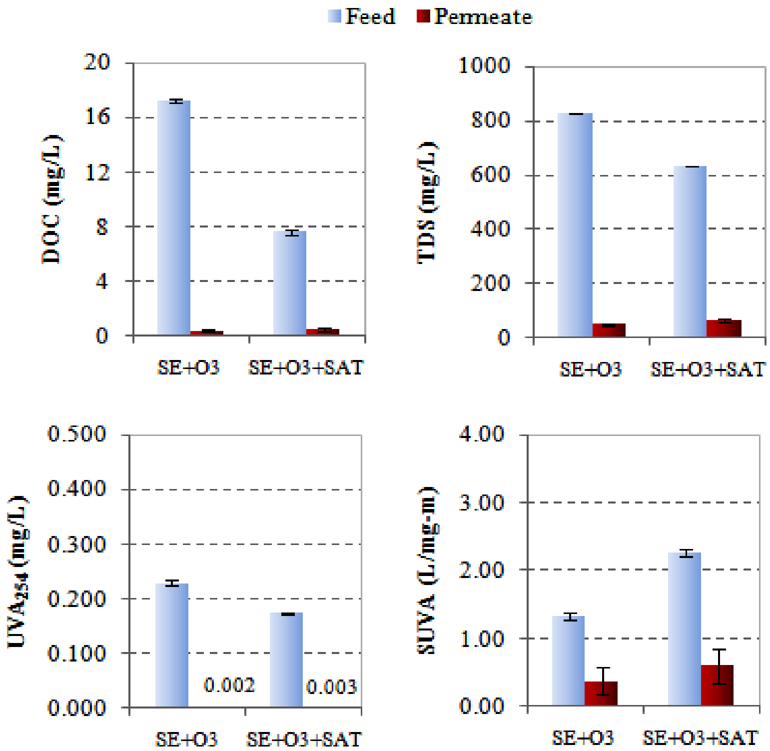


Figure 4-34. DOC, TDS, UVA_{254}, SUVA for NF-90 using $SE+O_3$ and $SE+O_3$+SAT (p=50 psi, r = 8%, without recirculation of concentrate)

Over-all DOC removal of 95.2% was calculated for SAT-NF system for $SE+O_3$ (25.6% contributed by SAT and 69.6% contributed by NF) based on 25.6% removal of DOC by SAT as presented in section 4.2.5. The values are summarised in Table 4-22 and Figure 4-35.

Table 4-22. DOC removal contribution of SAT for $SE+O_3$ in SAT-NF (NF-90) system

Type of feed water	DOC Removal						
	due to SAT			due to NF			Total Removal
	Influent	Effluent	Removal	Feed	Permeate	Removal	
$SE+O_3$	17.21	17.21	0	17.21	0.43	97.5%	97.5%
$SE+O_3$+SAT	10.29	7.66	25.6%	7.66	0.49	69.6%	95.2%

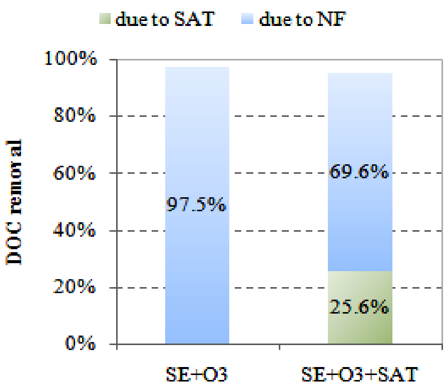


Figure 4-35. DOC removal by NF and SAT-NF (NF-90) system for $SE+O_3$

4.4.5 FEEM spectra analysis for NF-90 using SE+O_3 and SE+O_3+SAT

Figure 4-36 shows the FEEM spectra for feed and permeate of NF-90 for SE+O_3 and SE+O_3+SAT as feed water. Table 4-23 and Figure 4-37 show the peak intensities and reduction rates for the different fractions of DOC from the spectra analysis. Reductions of humic-like fraction were very high for both types of feed water. Protein-like fraction reduction rates were relatively less but still, for both types of feed, were above 90%.

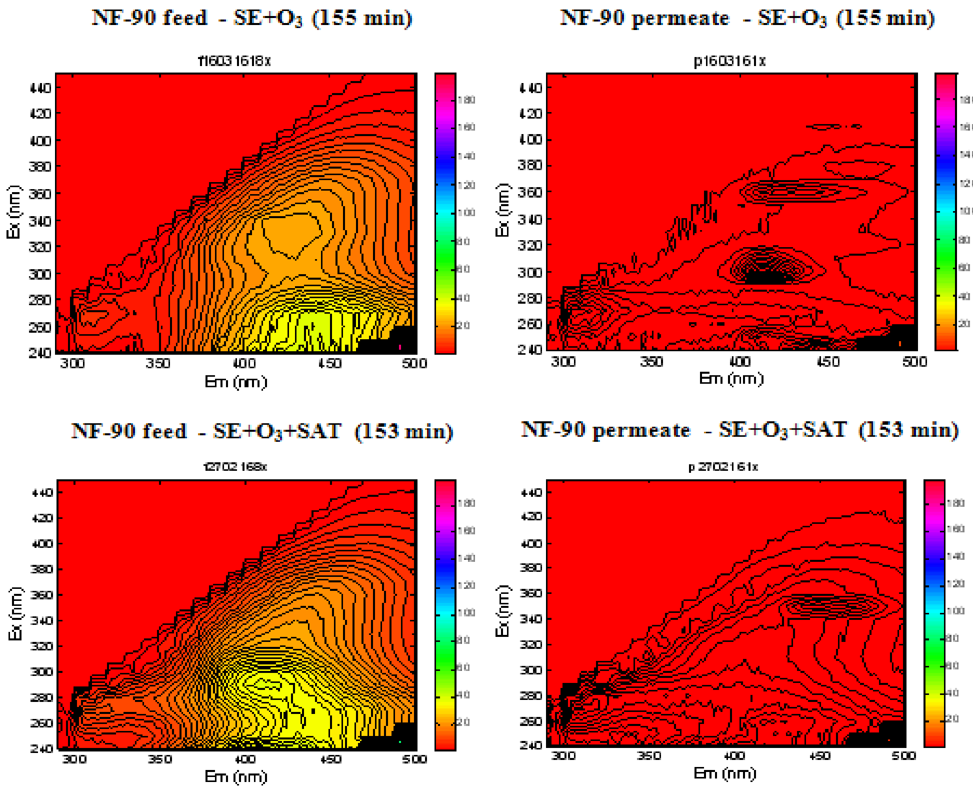


Figure 4-36. FEEM spectra for NF-90 using SE+O_3 and SE+O_3+SAT
(p=50 psi, r = 8%, without recirculation of concentrate)

Table 4-23. FEEM spectra results for NF-90 using SE+O_3 and SE+O_3+SAT
(p=50 psi, r = 8%, without recirculation of concentrate)

Type of feed water	DOC Component		Wavelength (nm)		Peak Intensity	
			Ex	Em	(RA unit)	Reduction
SE+O_3	Humic-like 1	Feed	333	430	28.2	98.2%
		Permeate	347	427	0.5	
	Humic-like 2	Feed	250	439	43.1	99.0%
		Permeate	250	423	0.4	
	Protein-like	Feed	270	309	8.8	92.4%
		Permeate	270	306	0.7	
SE+O_3+SAT	Humic-like 1	Feed	330	427	23.7	97.4%
		Permeate	350	451	0.6	
	Humic-like 2	Feed	257	431	37.8	98.0%
		Permeate	257	433	0.8	
	Protein-like	Feed	270	311	12.4	91.9%
		Permeate	270	306	1.0	

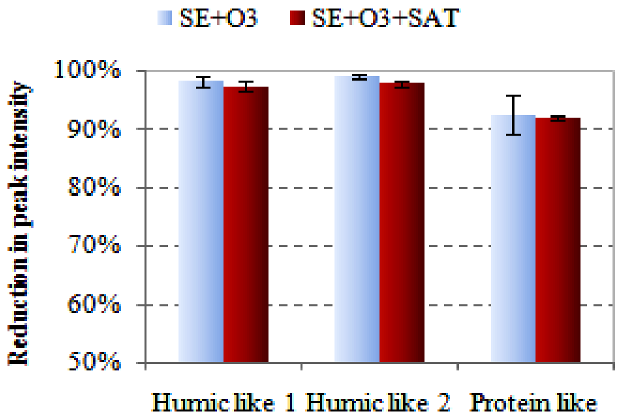


Figure 4-37. FEEM spectra analysis results for NF-90 using SE+O_3 and SE+O_3+SAT (p=50 psi, r = 8%, without recirculation of concentrate)

4.4.6 Flux decline for NF-90 using SE+O_3 and SE+O_3+SAT pre-treatment

Figure 4-38 depicts the record of flux and normalised flux against time for NF-90 filtration using SE+O_3 and SE+O_3+SAT as feed water. After six hours of filtration, SE+O_3 caused 40% flux decline for NF-90. With SAT pre-treatment, the flux decline for the same type of feed water was only 21%.

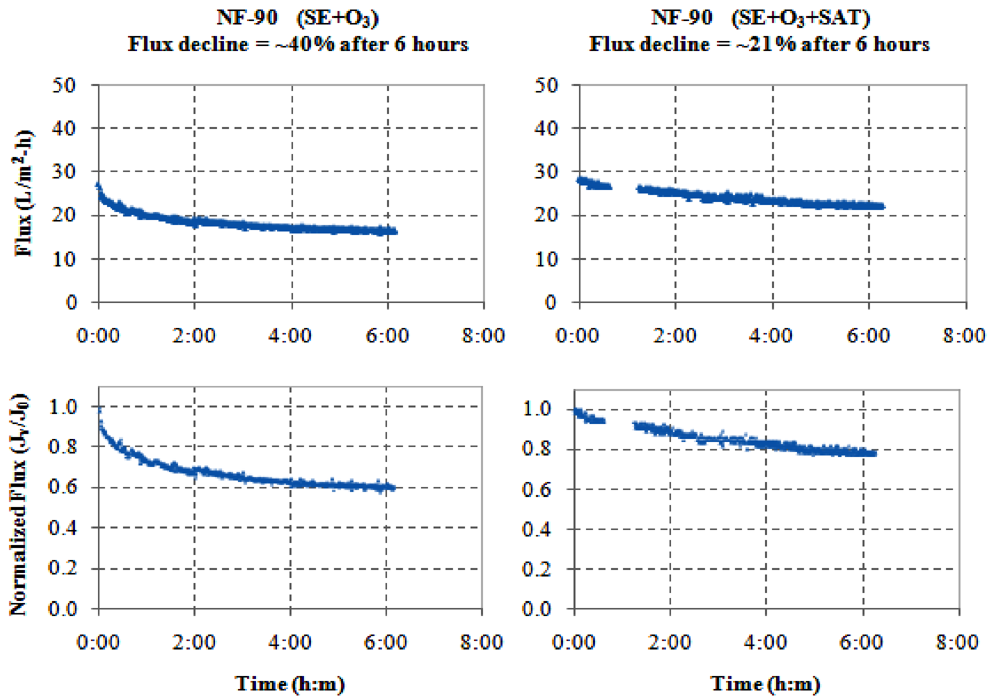


Figure 4-38. Flux and normalised flux for NF-90 using SE+O_3 and SE+O_3+SAT (p=50 psi, r = 8%, without recirculation of concentrate)

Flux against delivered DOC during nanofiltration for NF-90 using SE+O_3 and SE+O_3+SAT as feed are plotted in Figure 4-39. After 6 hours of filtration, delivered DOC for NF-90 using SE as feed water was 1.6 mg/cm^2 and that of using SE+SAT was 2.1 mg/cm^2. Again, even with higher load of DOC, the system performed better with SAT pre-treatment of SE.

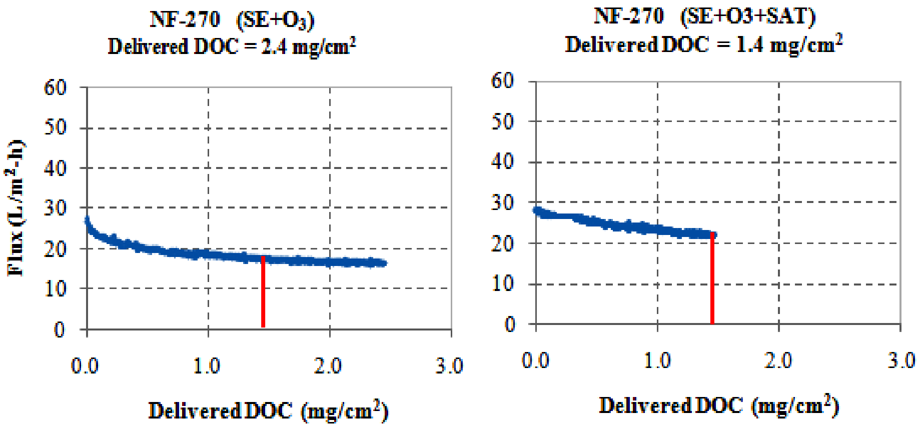


Figure 4-39. Delivered DOC for NF-90 using SE+O_3 and SE+O_3+SAT
(p=50 psi, r = 8%, without recirculation of concentrate)

Table 4-24 summarises the flux decline at the same delivered DOC of 1.4 mg/cm^2 for NF-90 using SE+O_3 and SE+O_3+SAT as feed water. The flux decline was 35% when SE+O_3 was used as feed water. The flux decline was reduced to 21% with SAT pre-treatment of SE+O_3.

Table 4-24. Flux decline at same delivered DOC for NF-90 using SE+O_3 and SE+O_3+SAT
(p=50 psi, r = 8%, without recirculation of concentrate)

Type of Feed	DOC of feed (mg/L)	Initial Flux (L/m^2-h)	Delivered DOC (mg/cm^2)	Time (hh:mm)	Flux Decline (%)
SE+O_3	17.24	27.5	1.4	3:16	35%
SE+O_3+SAT	7.66	28.5	1.4	5:56	21%

4.5 Nanofiltration using NF-90 with recirculation of concentrate

To investigate the effect of longer filtration time, experiments with NF-90 membrane were conducted by re-circulating the concentrate back into the feed water tank. A three-way valve along the concentrate line was manipulated in such a way that the concentrate would flow into the feed tank instead of being collected in a separate bucket. The first set of experiments involved the use of SE (with and without SAT pre-treatment) and the second set used SE+O_3 (with and without SAT pre-treatment). Each of the experiments was done continuously for at least 20 hours. The experiments were performed under the following conditions:

Feed pressure = 50 psi (3.6 bars)
Recovery = 8%
Temperature = 20 deg C
Filtration mode = Partial recirculation (with recirculation of concentrate)

4.5.1 DOC, TDS removal for NF-90 using SE and SE+SAT with recirculation

Measurements of water quality parameters were taken during NF-90 filtration with recirculation of concentrate for SE and SE+SAT as feed water. Graphical representation for DOC and TDS concentration values are plotted in Figure 4-40. DOC measurements for the case of SE+SAT as feed water were much lower than those of using SE. In both experiments, increase in DOC and TDS concentrations in feed were expected as the filtration progressed due to recirculation of concentrate back into feed tank. DOC and TDS removal of NF-90 using SE as feed water averaged 98.6% and 95.8% respectively. When using SE+SAT, the removals were 99.4% and 89.1%. Complete tables of water quality parameters for these experiments are included in Appendix I.

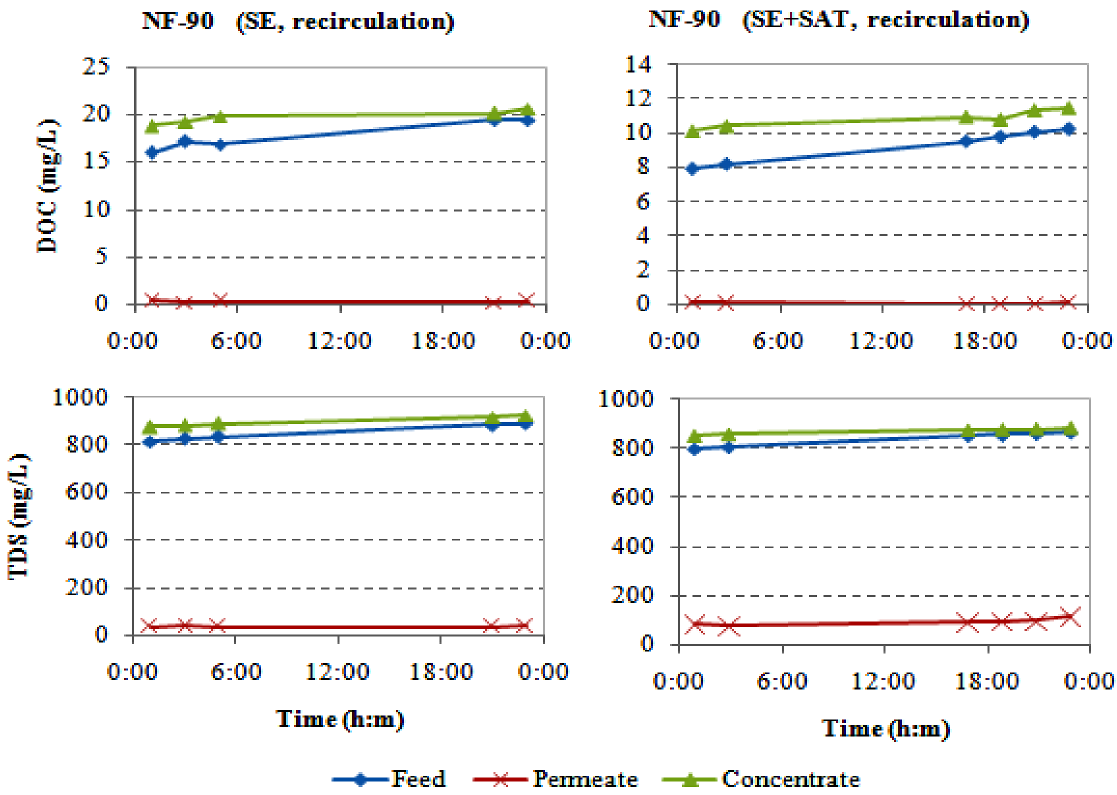


Figure 4-40. DOC, TDS values for NF-90 using SE and SE+SAT
(p=50 psi, r = 8%, with recirculation of concentrate)

4.5.2 Flux decline for NF-90 using SE and SE+SAT with recirculation

The flux decline after 20 hours of NF-90 filtration with recirculation of concentrate using SE and SE+SAT were nearly the same (75% and 74%, respectively) as shown in Figure 4-41.

Flux against delivered DOC during nanofiltration for NF-90 using SE and SE+SAT, with recirculation of concentrate as feed are plotted in Figure 4-42. With recirculation of concentrate back into feed tank, the feed DOC concentration was increasing over time during filtration, and the average of two successive measurements of the feed DOC was considered for the computation of delivered DOC.

Table 4-25 and Table 4-26 summarise the flux decline and delivered DOC, after at least twenty hours of filtration for NF-90 using SE and SE+SAT, respectively, as feed water. The values of flux and flux decline were interpolated at the same delivered DOC value of 2.5 mg/cm^2. The results revealed that at this value of delivered DOC, the flux decline was 57% for SE alone as feed water and for SE+SAT, the flux decline was 76%.

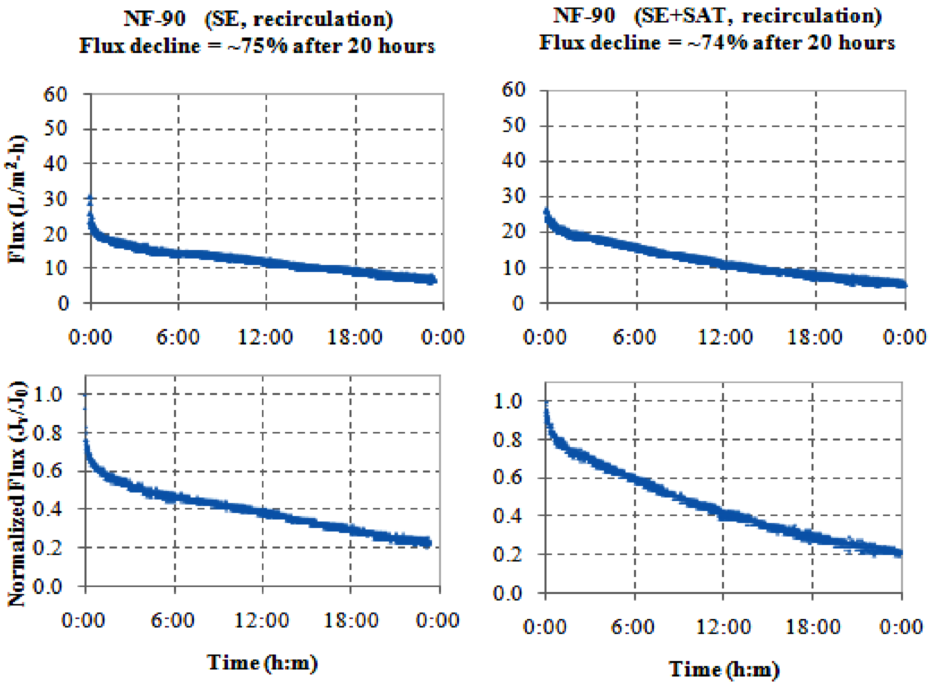


Figure 4-41. Flux and normalised flux for NF-90 using SE alone and SE+SAT (p=50 psi, r = 8%, with recirculation of concentrate)

Table 4-25. Summary of flux decline and delivered DOC for NF-90 using SE (p=50 psi, r = 8%, with recirculation of concentrate)

Time (h:m)	Flux, J (L/m^2-h)	Flow (mL/min)		Feed vol, V_f (L)	Feed DOC, C_f (mg/L)	Delivered DOC (mg/cm^2)
		Permeate, Q_p	Feed, Q_f			
0:00	31.08	7.20	90.00	0.00	15.90	0.00
0:58	18.99	4.40	55.00	3.22	15.90	0.37
2:58	17.27	4.00	50.00	9.19	16.87	1.08
4:58	15.11	3.50	43.75	14.44	17.08	1.76
20:58	8.20	1.90	23.75	37.25	19.43	4.89
22:58	7.34	1.70	21.25	39.80	19.41	5.56

Table 4-26. Summary of flux decline and delivered DOC for NF-90 using SE+SAT (p=50 psi, r = 8%, with recirculation of concentrate)

Time (h:m)	Flux, J (L/m^2-h)	Flow (mL/min)		Feed vol, V_f (L)	Feed DOC, C_f (mg/L)	Delivered DOC (mg/cm^2)
		Permeate, Q_p	Feed, Q_f			
0:00	26.33	6.10	76.25	0.00	7.94	0.00
0:51	20.72	4.80	60.00	3.06	7.94	0.17
2:51	18.56	4.30	53.75	9.51	8.21	0.55
16:51	8.20	1.90	23.75	29.48	9.51	1.88
18:51	7.77	1.80	22.50	32.16	9.76	2.23
20:51	6.47	1.50	18.75	34.42	10.05	2.45
22:51	6.04	1.40	17.50	36.53	10.22	2.66

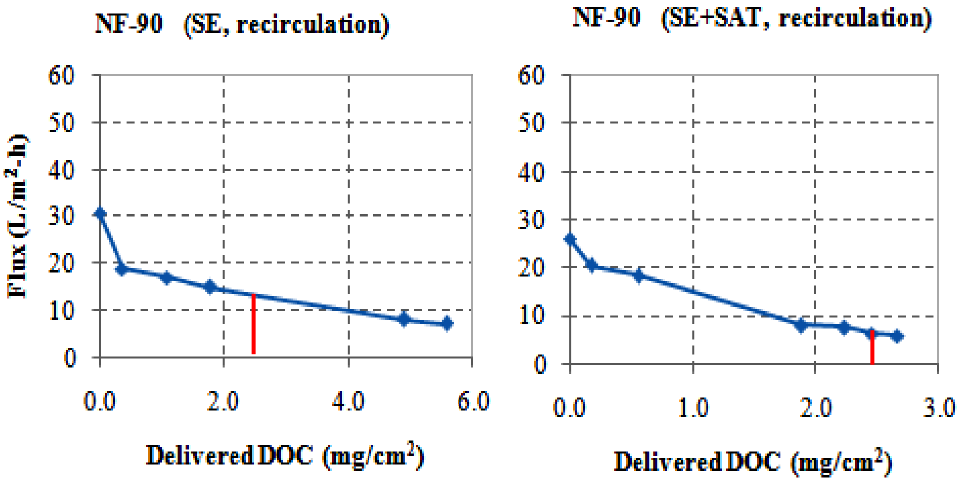


Figure 4-42. Delivered DOC for NF-90 using SE and SE+SAT (p=50 psi, r = 8%, with recirculation of concentrate)

4.5.3 DOC, TDS removal for NF-90 using SE+O_3 and SE+O_3+SAT with recirculation

DOC and TDS concentrations for the feed, permeate and concentrate for NF-90 filtration with recirculation of concentrate using SE+O_3 and SE+O_3+SAT are shown in Figure 4-43. Percentage removals of DOC and TDS for SE+O_3 as feed water were 97.0% and 93.3% respectively while the DOC and TDS removals when using SE+O_3+SAT were 97.2 and 91.7%, respectively. The table of water quality parameters for these experiments are presented in Appendix J.

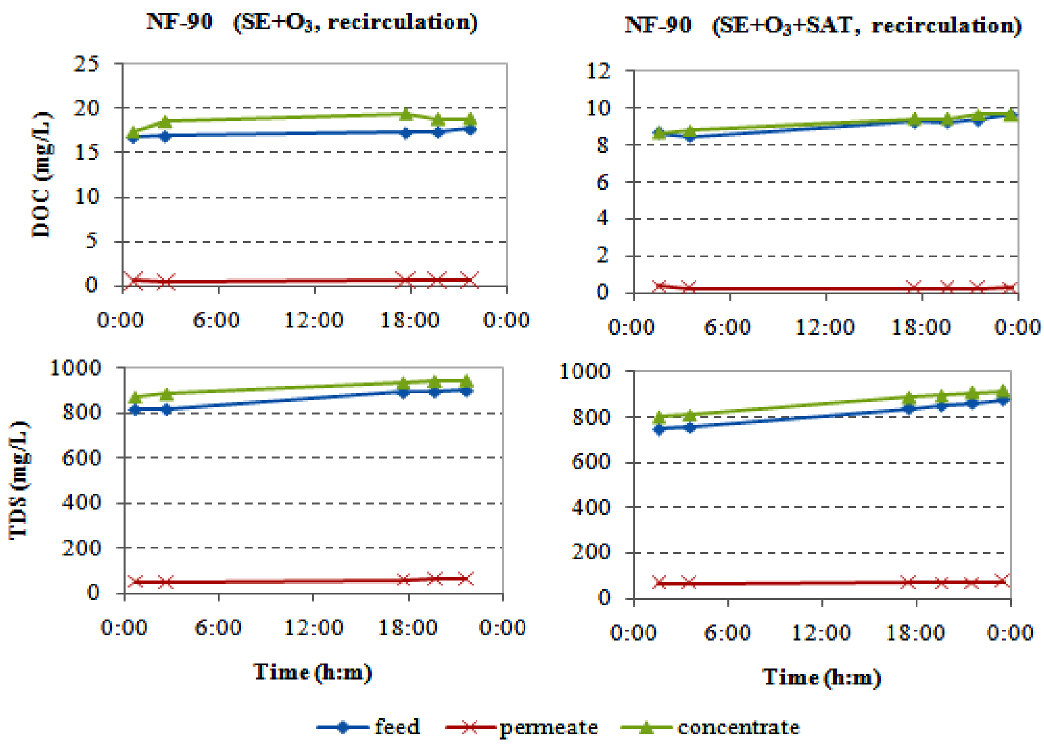


Figure 4-43. DOC, TDS values for NF-90 using $SE+O_3$ and $SE+O_3+SAT$ (p=50 psi, r = 8%, with recirculation of concentrate)

4.5.4 Flux decline for NF-90 using $SE+O_3$ and $SE+O_3+SAT$ with recirculation

In terms of flux decline, SAT pre-treated $SE+O_3$ performed better when compared to $SE+O_3$ as feed water for NF-90 filtration with recirculation of concentrate. After 20 hours of filtration, the flux declined by 58% for $SE+O_3$ and only 43% for $SE+O_3+SAT$ as shown in Figure 4-44. This is quite an improvement when compared to using SE alone or SE+SAT (75% and 74% flux decline after 20 hours)

Flux against delivered DOC during nanofiltration for NF-90 using $SE+O_3$ and $SE+O_3+SAT$, with recirculation of concentrate as feed are plotted in Figure 4-45.

With the same feed pressure, the flux with $SE+O_3+SAT$ was higher, although the DOC concentration used for this experiment was also lower than that of $SE+O_3$. The summaries of flux decline and delivered DOC for NF-90 using SE and SE+SAT as feed water, with recirculation of concentrate are presented in Table 4-27 and Table 4-28, respectively. The values of flux and flux decline were interpolated at the same delivered DOC value of 5.4 mg/cm^2. The results revealed that at this value of delivered DOC, the flux decline was 53% for SE alone as feed water and for SE+SAT, the flux decline was 52%.

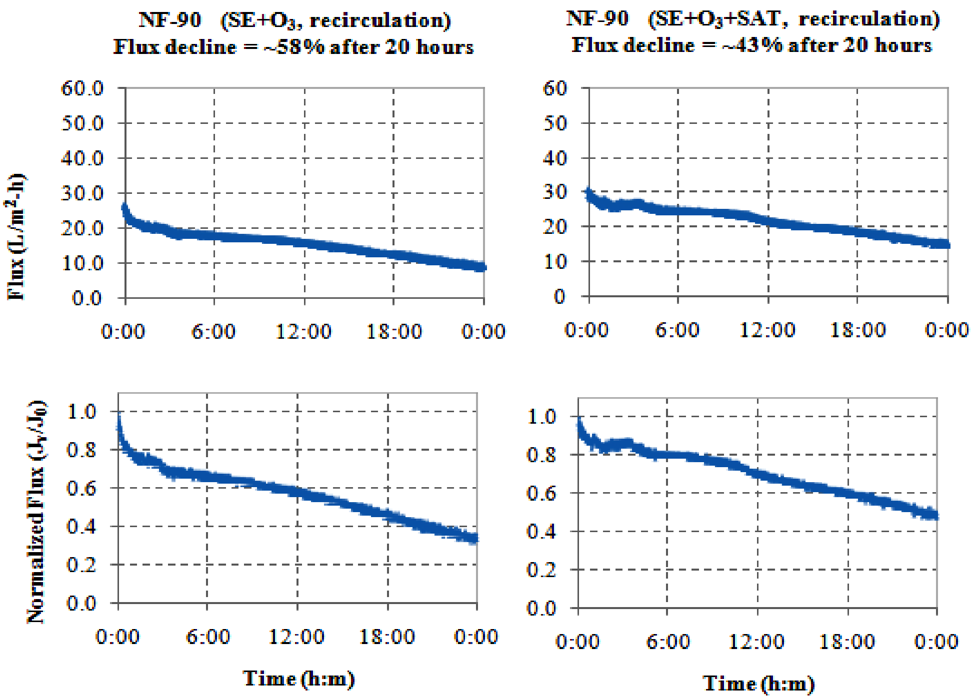


Figure 4-44. Flux and normalised flux for NF-90 using SE+O_3 and SE+O_3+SAT
(p=50 psi, r = 8%, with recirculation of concentrate)

Table 4-27. Summary of flux decline and delivered DOC for NF-90 using SE+O_3
(p=50 psi, r = 8%, with recirculation of concentrate)

Time (h:m)	Flux, J (L/m^2-h)	Flow (mL/min)		Feed vol, V_f (L)	Feed DOC, C_f (mg/L)	Delivered DOC (mg/cm^2)
		Permeate, Q_p	Feed, Q_f			
0:00	27.19	6.30	78.75	0.00	16.75	0.00
0:40	21.58	5.00	62.50	2.50	16.75	0.30
2:40	19.86	4.60	57.50	9.40	16.87	1.14
17:40	12.95	3.00	37.50	43.16	17.27	5.30
19:40	11.65	2.70	33.75	47.21	17.37	5.88
21:40	10.36	2.40	30.00	50.81	17.72	6.41

Table 4-28. Summary of flux decline and delivered DOC for NF-90 using SE+O_3+SAT (p=50 psi, r = 8%, with recirculation of concentrate)

Time (h:m)	Flux, J (L/m^2-h)	Flow (mL/min)		Feed vol, V_f (L)	Feed DOC, C_f (mg/L)	Delivered DOC (mg/cm^2)
		Permeate, Q_p	Feed, Q_f			
0:00	31.08	7.20	90.00	0.00	8.68	0.00
1:32	26.76	6.20	77.50	7.13	8.68	0.45
3:32	26.76	6.20	77.50	16.43	8.46	1.01
17:32	18.99	4.40	55.00	62.64	9.28	4.00
19:32	18.56	4.30	53.75	69.09	9.26	4.61
21:32	16.40	3.80	47.50	74.79	9.37	5.01
23:32	14.68	3.40	42.50	79.90	9.67	5.47

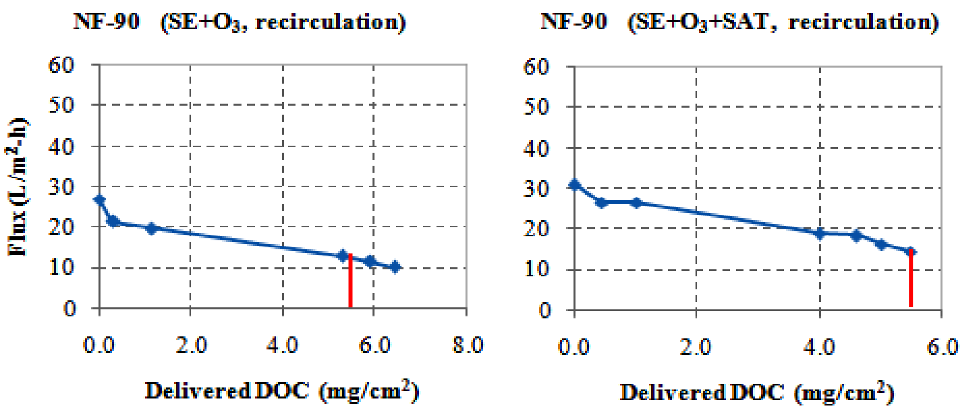


Figure 4-45. Delivered DOC for NF-90 using SE+O_3 and SE+O_3+SAT (p=50 psi, r = 8%, with recirculation of concentrate)

4.6 Practical implications of the study

SAT-NF systems for potable reuse can be applied in highly populated regions where options for new water sources are extremely limited. SAT removes some contaminants including the humic substances in wastewater with biodegradation as the dominant transformation process and the nanofiltration serves as the polishing step. SAT is envisioned to minimize pre-treatment before nanofiltration. However, because SAT pre-treated water will ultimately mix with the natural ground water utmost care should be taken to ensure that the system does not adversely affect the quality of existing ground water.

The following four treatment systems can be an appropriate wastewater treatment technology depending on cost limitation and the intended use of the product water:

1. SAT only
2. O_3 + SAT
3. SAT + NF
4. O_3 + SAT + NF

The first two technologies involving SAT and O_3+SAT to treat wastewater may be applied for irrigation purposes. SAT treatment of wastewater is the least costly among the different alternatives and can be an appropriate technology for developing countries. The treatment of O_3+SAT is more expensive because of the cost of ozonation. With post chlorination as a precautionary measure to eliminate any residual pathogenic organism associated with human excreta, the reclaimed water after the two treatment systems can be used for unrestricted irrigation of all types of food crops, including vegetables and fruits eaten uncooked. The use of SAT treatment alone of secondary effluent of municipal wastewater treatment plant with post chlorination for unrestricted irrigation of all types of food crops has been demonstrated and currently practiced in the Dan region wastewater treatment and reclamation scheme in Israel (Shelef et al., 1994).

The use of ozonation prior to SAT entails additional cost but maximizes the removal of humics during SAT by conversion of slowly biodegradable and non-biodegradable fractions of DOC into easily biodegradable component, which improves the organic matter removal in SAT. Ozonation prior to SAT also promotes sustainable long term operation of NF membrane because bio-fouling is minimized as well as organic fouling due to the removal of proteins in the SAT process. The additional cost of ozonation can be offset by less frequency of cleaning and longer operation of the NF membranes.

The cost of nanofiltration may preclude developing countries from implementing its use. Options 3 and 4 which include nanofiltration may be more appropriate for developed countries. SAT + NF can be applied in potable reuse; the product water can be injected into the aquifer or mixed with other sources of potable water and additional treatment may be required as polishing steps before distribution. If tight NF/RO is used after SAT, then direct potable reuse of wastewater is possible.

The following table summarises the relative cost and relative effectiveness in terms of DOC and organic micro-pollutant (OMP) removal of the four treatment options for wastewater reuse.

Table 4-29. Relative cost and DOC and OMP removal of different treatment options

Treatment	Cost	DOC removal	OMP removal
SAT	+ ↓	+ ↓	- ↓
O_3 + SAT	++	+	-/+
SAT + NF	+++	+++	+
O_3 + SAT + NF	++++	+++	++

Note: direction of arrow indicates increasing cost or increasing removal of contaminant

5 Conclusions and Recommendations

5.1 Conclusions

Based on the results of laboratory-scale soil column studies and nanofiltration experiments, the following conclusions can be drawn:

- In soil column studies simulating SAT, about 23.9% of DOC was removed from secondary effluent. DOC removal from secondary effluent increased to 25.6% by means of pre-ozonation (ozone to DOC ratio of 1 mg O_3 / mg DOC).

- Preferential removal or reduction in intensity of protein-like (15.8%) over humic-like primary (9.3%) and humic-like secondary (7.6%) fractions of DOC using SE alone as influent was demonstrated by the SAT simulation.

- Pre-ozonation of secondary effluent complemented SAT by reducing humic-like 1 and humic-like 2 (as much 83.2% and 77.4% reduction, respectively) and moderate reduction of protein-like (12.8% reduction) fractions of the DOC in the secondary effluent.

- Pre-ozonation converted the organic matter content of secondary effluent into less humic (reduction of UVA_{254} value from 0.42 to 0.18 Ab/cm) and less aromatic character (reduction of SUVA from 2.61 to 1.27 L/m-mg).

- Based on the DOC degradation model, ozonation increased the easily biodegradable fraction of DOC from 8.2% to 19.9%. Furthermore, ozonation increased the maximum possible removal of DOC from secondary effluent through biodegradation in the soil column from 22.5 to 27.6 %.

- Removal efficiencies of DOC, TDS and UVA_{254} during nanofiltration were less affected by feed water characteristics than membrane type. Slightly higher removals of DOC and UVA_{254} were obtained with NF-90 than with NF-270. The efficiency of TDS removal for NF-90 is around twice that of NF-270.

- Both feed water characteristics and membrane type had substantial effect on flux decline during nanofiltration. With SAT pre-treatment of SE and SE+O_3, the flux decline at same delivered DOC were lower for both NF-270 and NF-90 than those without SAT pre-treatment. For NF-270, the flux decline was reduced from 8% (SE alone) to 6% (SAT pre-treated SE) at delivered DOC of 3.5 mg/cm^2 and from 10% (SE+O_3) to 5% (SE+O_3+SAT) at delivered DOC of 2.7 mg/cm^2. Similarly for NF-90, the flux decline was lessened from 50% (SE alone) to 32% (SAT pre-treated SE) at delivered DOC of 1.6 mg/cm^2 and from 35% (SE+O_3) to 21% (SE+O_3+SAT) at delivered DOC of 1.4 mg/cm^2. From these figures, the flux decline for NF-270 was consistently lower than with the tighter NF-90 membranes with any type of feed water.

- In general, it can be concluded SAT pre-treatment before NF membrane could be an effective technology for water reuse applications as SAT pre-treatment not only reduces the fouling of NF membranes but also removes other contaminants and allows longer operation of NF system.

5.2 Recommendations

The following are recommended for further development of SAT+NF technology:

- Other pre-treatment options for SAT like advanced oxidation processes should be studied for optimization of SAT-NF systems.

- Similar study should be conducted using SAT effluent from existing or pilot plants to evaluate the performance of long term SAT and nanofiltration systems.

- A more detailed investigation on molecular weight (MW) distribution of the feed water organic matter as well as the amount of hydrophilic/hydrophobic organic fraction in different MW ranges will be helpful to describe fully the membrane fouling mechanisms of SAT-NF systems.

- Effect of SAT+NF on the removal of other contaminants namely organic micro-pollutants and pathogens should be studied in detail.

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7 Appendices

Appendix A. Ripening of Soil Columns with SE

Process conditions during ripening of SC-1 and SC-2

Feed water : Secondary effluent (SE)
HLR : 1.25 +/- 0.5 m/day
Media : Silica sand (0.8-1.25mm), total depth = 5m
Columns : 2-pvc pipes each 100 mm diameter in series

Table A-1. Dissolved oxygen for SC-1 fed with SE during ripening period

Date	Time (day)	C_0 (mg/L) at SP-R	C (mg/L) at SP-14	DO consumed
28-11-08	25	7.3	3.3	54.8%
1-12-08	28	8.2	3.1	62.2%
3-12-08	30	8.6	2.5	70.9%
5-12-08	32	8.2	3	63.4%
10-12-08	37	8.1	2.9	64.2%
12-12-08	39	8.2	3.2	61.0%
15-12-08	42	8.6	3.3	61.6%
22-12-08	49	8.6	3.6	58.1%
29-12-08	56	8.4	3.5	58.3%
30-12-08	57	8.8	3.7	58.0%
31-12-08	58	8.5	3.6	57.6%
5-01-09	63	9	3.1	65.6%
	Average	8.4	3.2	61.3%

Table A-2. Dissolved oxygen for SC-2 fed with SE during ripening period

Date	Time (day)	C_0 (mg/L) at SP-R	C (mg/L) at SP-14	DO consumed
28-11-08	25	8.1	1.6	80.2%
1-12-08	28	9.3	1.2	87.1%
3-12-08	30	9	2.8	68.9%
5-12-08	32	8.8	3.3	62.5%
8-12-08	35	9.4	2.3	75.5%
10-12-08	37	9	2	77.8%
12-12-08	39	9.1	2.9	68.1%
15-12-08	42	9.4	2.4	74.5%
19-12-08	46	9	1.8	80.0%
22-12-08	49	9	2.8	68.9%
29-12-08	56	9.1	2.8	69.2%
31-12-08	58	9.1	3	67.0%
5-01-09	63	9.2	2.1	77.2%
	Average	9.0	2.4	73.6%

Table A-3. DOC measurements for SC-1 fed with SE during ripening period

Date	Time (day)	C_0 (mg/L) at SP-1	C (mg/L) at SP-14	DOC Removal (C/C_0)
10-11-08	7	13.01	11.23	86.3%
12-11-08	9	11.27	9.75	86.5%
14-11-08	11	7.16	4.78	66.8%
17-11-08	14	9.08	5.55	61.1%
19-11-08	16	5.42	4.40	81.3%
21-11-08	18	5.44	4.48	82.4%
24-11-08	21	8.06	6.15	76.3%
26-11-08	23	13.37	9.85	73.7%
28-11-08	25	12.44	10.03	80.6%
1-12-08	28	10.85	9.54	88.0%
3-12-08	30	8.45	7.97	94.4%
5-12-08	32	9.62	8.22	85.4%
8-12-08	35	10.96	8.75	79.9%
10-12-08	37	13.67	8.20	60.0%
12-12-08	39	9.55	8.87	92.9%
15-12-08	42	9.72	8.60	88.5%
17-12-08	44	10.73	8.64	80.5%
19-12-08	46	14.92	8.36	56.0%
22-12-08	49	15.34	12.18	79.4%
24-12-08	51	17.64	14.14	80.2%
29-12-08	56	15.80	11.36	71.9%
31-12-08	58	17.24	14.53	84.3%
5-01-09	63	14.90	12.61	84.6%
9-01-09	67	11.82	10.09	85.4%
12-01-09	70	17.34	14.80	85.4%

Table A-4. DOC measurements for SC-2 fed with SE during ripening period

Date	Time (day)	C_0 (mg/L) at SP-1	C (mg/L) at SP-14	DOC Ratio (C/C_0)
10-11-08	7	12.01	7.10	59.1%
12-11-08	9	13.12	10.29	78.4%
14-11-08	11	5.78	6.25	108.1%
17-11-08	14	4.34	4.34	100.1%
19-11-08	16	5.35	4.54	84.8%
21-11-08	18	5.60	4.14	74.1%
24-11-08	21	7.82	6.00	76.8%
26-11-08	23	12.63	9.61	76.1%
28-11-08	25	13.39	10.21	76.3%
1-12-08	28	9.39	9.48	100.9%
3-12-08	30	7.58	7.90	104.2%
5-12-08	32	7.87	7.41	94.2%
8-12-08	35	9.62	7.89	82.1%
10-12-08	37	8.03	8.12	101.1%
12-12-08	39	8.84	9.20	104.0%
15-12-08	42	8.75	8.06	92.1%
17-12-08	44	8.86	8.94	100.9%
19-12-08	46	12.39	8.30	67.0%
22-12-08	49	12.92	11.64	90.1%
24-12-08	51	15.90	12.95	81.5%
29-12-08	56	17.76	17.15	96.5%
31-12-08	58	15.99	15.25	95.4%
5-01-09	63	13.68	12.27	89.7%
9-01-09	67	11.29	10.61	94.0%
12-01-09	70	16.02	14.22	88.8%

Appendix B. Soil Columns fed with SE after the ripening period

Process conditions for SC-1 and SC-2 after ripening period

Feed water	:	Secondary effluent (SE)
HLR	:	1.25 +/- 0.5 m/day
Media	:	Silica sand (0.8-1.25mm), total depth = 5m
Columns	:	2-pvc pipes each 100 mm diameter in series

Table B-1. WQ parameters measurements for SC-1 fed with SE for Profile-1

Date: 9-01-09 **Column Age:** 67 days

Sampling point	Depth (m)	O_2 mg/L	pH	EC µS/cm	Temp deg C	DOC mg/L	UVA_{254} Ab/cm	SUVA L/m-mg
SP-R	0.00	7.6	7.86	1191	19.1	13.44	0.415	3.088
SP-0	0.02	7.9	7.88	1194	18.7	13.07	0.387	2.961
SP-1	0.08	5.8	7.73	1198	18.5	11.82	0.480	4.061
SP-2	0.14	4.8	7.69	1199	18.7	11.98	0.413	3.447
SP-4	0.34	3.4	7.59	1202	19.1	11.31	0.405	3.581
SP-5	0.48	3.2	7.58	1199	18.8	11.06	0.402	3.635
SP-6	0.98	3.0	7.53	1197	19.5	10.36	0.376	3.629
SP-7	1.48	2.4	7.54	1196	19.0	10.30	0.382	3.709
SP-8	1.98	2.8	7.53	1194	19.0	10.45	0.379	3.627
SP-9	2.58	3.8	7.64	1187	18.7	10.60	0.392	3.698
SP-10	3.18	4.0	7.67	1190	18.6	10.16	0.396	3.898
SP-11	3.68	3.0	7.60	1181	18.7	10.45	0.375	3.589
SP-12	4.18	3.0	7.58	1188	19.0	10.77	0.371	3.445
SP-13	4.68	3.2	7.58	1189	18.9	10.43	0.389	3.730
SP-14	5.00	3.2	7.62	1181	19.0	10.09	0.386	3.826
SP-15	5.00	4.2	7.52	1182	18.8	10.18	0.380	3.733

Table B-2. WQ parameters measurements for SC-1 fed with SE for Profile-2

Date: 15-01-09 **Column Age:** 73 days

Sampling point	Depth (m)	O_2 mg/L	pH	EC µS/cm	Temp deg C	DOC mg/L	UVA_{254} Ab/cm	SUVA L/m-mg
SP-R	0.00	7.4	7.86	1200	21.1	15.27	0.376	2.462
SP-0	0.02	7.4	7.82	1196	21.1	14.60	0.373	2.555
SP-1	0.08	5.9	7.69	1197	21.3	14.20	0.365	2.570
SP-2	0.14	3.9	7.60	1189	21.9	13.70	0.379	2.766
SP-4	0.34	5.4	7.62	1194	21.6	13.32	0.365	2.740
SP-5	0.48	4.5	7.58	1197	21.1	12.91	0.367	2.843
SP-6	0.98	3.9	7.57	1196	21.1	12.59	0.361	2.867
SP-7	1.48	4.7	7.61	1195	22.7	12.29	0.356	2.897
SP-8	1.98	4.2	7.60	1197	21.7	12.17	0.356	2.925
SP-9	2.58	3.9	7.59	1199	20.6	12.13	0.348	2.869
SP-10	3.18	3.7	7.55	1188	22.1	11.98	0.353	2.947
SP-11	3.68	3.5	7.57	1204	21.5	11.78	0.347	2.946
SP-12	4.18	3.7	7.56	1199	21.5	11.81	0.355	3.006
SP-13	4.68	4.5	7.59	1206	20.7	11.94	0.358	2.998
SP-14	5.00	5.7	7.63	1198	20.7	11.72	0.353	3.012
SP-15	5.00	3.5	7.37	1205	20.2	12.60	0.350	2.778

Table B-3. WQ parameters measurements for SC-2 fed with SE for Profile-1

Sampling point	Depth (m)	O_2 mg/L	pH	EC µS/cm	Temp deg C	DOC mg/L	UVA_{254} Ab/cm	SUVA L/m-mg
SP-R	0.00	8.6	8.17	1190	19.0	13.45	0.487	3.621
SP-0	0.02	3.9	7.75	1191	18.6	12.14	0.407	3.353
SP-1	0.08	4.4	7.76	1197	18.8	11.29	0.394	3.490
SP-2	0.14	3.8	7.70	1197	18.9	11.47	0.404	3.522
SP-3	0.24	3.8	7.66	1199	18.6	11.82	0.415	3.511
SP-4	0.34	3.5	7.66	1196	18.5	10.98	0.386	3.515
SP-5	0.48	3.1	7.71	1197	19.3	10.77	0.390	3.621
SP-6	0.98	3.9	7.73	1201	18.6	10.98	0.394	3.588
SP-7	1.48	3.1	7.74	1198	18.9	10.67	0.381	3.571
SP-8	1.98	4.4	7.78	1193	18.9	10.78	0.389	3.609
SP-9	2.58	4.0	7.78	1182	18.5	10.73	0.381	3.551
SP-10	3.18	4.8	7.73	1188	18.7	10.30	0.408	3.961
SP-11	3.68	5.4	7.81	1196	17.8	11.01	0.396	3.597
SP-12	4.18	3.1	7.74	1187	18.6	10.54	0.377	3.577
SP-13	4.68	2.7	7.70	1186	19.3	10.06	0.389	3.867
SP-14	5.00	3.5	7.81	1188	17.7	10.61	0.376	3.544
SP-15	5.00	3.6	7.65	1185	18.8	10.69	0.378	3.536

Table B-4. WQ parameters measurements for SC-2 fed with SE for Profile-2

Date: **9-01-09** **Column Age:** **73 days**

Sampling point	Depth (m)	O_2 mg/L	pH	EC mS/cm	Temp deg C	DOC mg/L	UVA_{254} Ab/cm	SUVA L/m-mg
SP-R	0.00	8.1	8.09	1186	21.1	15.05	0.366	2.432
SP-0	0.02	5.5	7.77	1202	21.0	13.45	0.347	2.580
SP-1	0.08	4.7	7.71	1196	21.2	13.35	0.337	2.524
SP-2	0.14	4.2	7.68	1197	21.4	13.44	0.336	2.500
SP-3	0.24	4.6	7.69	1195	21.3	12.66	0.331	2.615
SP-4	0.34	4.1	7.70	1199	20.9	12.66	0.335	2.646
SP-5	0.48	5.2	7.71	1192	21.2	12.33	0.346	2.806
SP-6	0.98	2.9	7.64	1194	21.7	12.23	0.333	2.723
SP-7	1.48	3.3	7.64	1198	21.4	12.34	0.340	2.755
SP-8	1.98	3.5	7.66	1194	21.5	12.67	0.344	2.715
SP-9	2.58	2.9	7.67	1196	20.6	12.11	0.328	2.709
SP-10	3.18	4.0	7.70	1200	21.7	11.76	0.328	2.789
SP-11	3.68	4.7	7.76	1203	21.4	12.00	0.336	2.800
SP-12	4.18	4.4	7.74	1206	21.4	11.81	0.336	2.845
SP-13	4.68	5.3	7.78	1200	21.4	11.76	0.322	2.738
SP-14	5.00	5.2	7.72	1201	21.5	11.67	0.317	2.716
SP-15	5.00	5.4	7.61	1205	21.3	12.01	0.333	2.773

Table B-5. WQ parameters measurements for SC-2 fed with SE for Profile-3

Date: **9-01-09** **Column Age:** **86 days**

Sampling point	Depth (m)	O_2 mg/L	pH	EC µS/cm	Temp deg C	DOC mg/L	UVA_{254} Ab/cm	SUVA L/m-mg
SP-R	0.00	8.0	7.77	901	19.9	9.96	0.292	2.931
SP-0	0.02	7.6	7.66	896	19.8	8.59	0.287	3.341
SP-1	0.08	7.0	7.55	885	19.7	8.39	0.274	3.265
SP-2	0.14	6.7	7.53	891	19.7	8.97	0.265	2.956
SP-3	0.24	6.1	7.42	888	19.6	8.26	0.261	3.161
SP-4	0.34	6.3	7.50	884	19.6	8.12	0.259	3.189
SP-5	0.48	6.4	7.53	881	20.0	8.50	0.252	2.965
SP-6	0.98	6.4	7.58	886	19.7	7.85	0.249	3.173
SP-7	1.48	6.8	7.65	885	19.7	7.89	0.246	3.117
SP-8	1.98	5.5	7.55	887	19.7	7.76	0.250	3.220
SP-9	2.58	4.7	7.51	890	19.4	8.00	0.244	3.049
SP-10	3.18	5.9	7.64	896	19.3	7.68	0.247	3.214
SP-11	3.68	6.6	7.76	896	19.7	7.72	0.251	3.251
SP-12	4.18	6.4	7.74	902	19.3	8.12	0.241	2.969
SP-13	4.68	6.5	7.74	901	19.3	7.87	0.250	3.177
SP-14	5.00	6.5	7.76	905	19.3	8.19	0.251	3.065
SP-15	5.00	7.2	7.77	902	19.8	7.97	0.248	3.114

Table B-6. Comparison of FEEM spectra for influent and effluent of soil columns fed with SE

Time (day)	Soil column	DOC Component		Wavelength (nm) Ex	Wavelength (nm) Em	Peak Intensity (RA unit)	Peak Intensity Reduction
67	SC-1	Humic-like 1	Influent	330	428	81	17.0%
			Effluent	330	428	68	
		Humic-like 2	Influent	250	448	144	15.7%
			Effluent	250	444	121	
		Protein-like	Influent	270	316	45	20.8%
			Effluent	270	318	36	
73	SC-1	Humic-like 1	Influent	330	430	75	7.4%
			Effluent	330	432	69	
		Humic-like 2	Influent	250	442	129	4.0%
			Effluent	250	440	124	
		Protein-like	Influent	270	308	56	12.2%
			Effluent	270	312	49	
Ave-1	SC-1	Humic-like 1	Influent	330	429	78	12.4%
			Effluent	330	430	68	
		Humic-like 2	Influent	250	445	136	10.2%
			Effluent	250	442	123	
		Protein-like	Influent	270	312	51	16.1%
			Effluent	270	315	42	
67	SC-2	Humic-like 1	Influent	330	428	78	8.3%
			Effluent	330	432	72	
		Humic-like 2	Influent	250	448	134	5.9%
			Effluent	250	442	126	
		Protein-like	Influent	280	342	54	24.3%
			Effluent	270	316	41	
73	SC-2	Humic-like 1	Influent	330	430	69	3.4%
			Effluent	330	428	67	
		Humic-like 2	Influent	250	448	121	3.6%
			Effluent	250	444	116	
		Protein-like	Influent	270	310	53	6.5%
			Effluent	270	306	49	
Ave-2	SC-2	Humic-like 1	Influent	330	429	74	6.0%
			Effluent	330	430	69	
		Humic-like 2	Influent	250	448	127	4.8%
			Effluent	250	443	121	
		Protein-like	Influent	275	326	53	15.5%
			Effluent	270	311	45	
Over-all Ave	SC-1 & SC-2	Humic-like 1	Influent	330	429	76	9.3%
			Effluent	330	430	69	
		Humic-like 2	Influent	250	447	132	7.6%
			Effluent	250	443	122	
		Protein-like	Influent	273	319	52	15.8%
			Effluent	270	313	44	

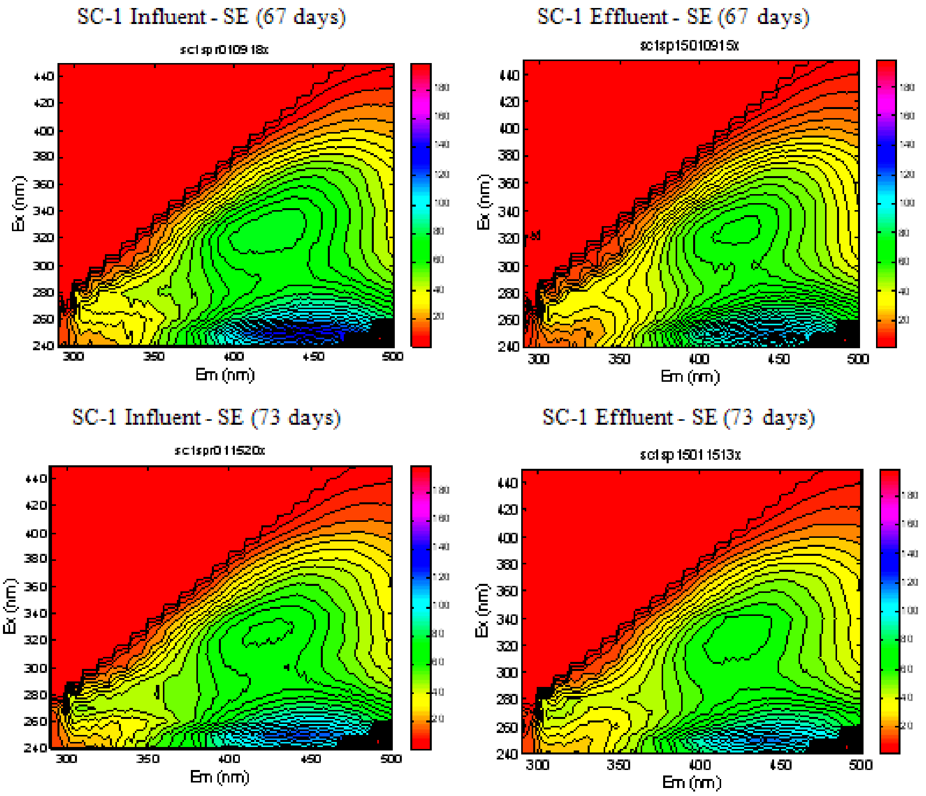

Figure B-1. FEEM spectra for influent and effluent of SC-1 fed with SE

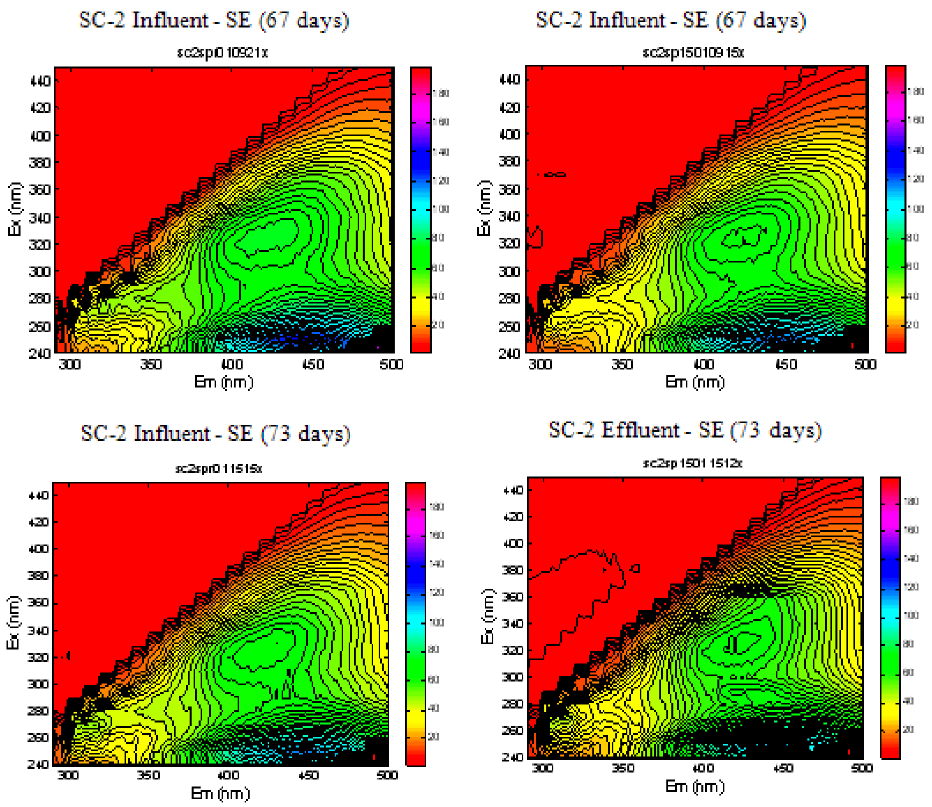

Figure B-2. FEEM spectra for influent and effluent of SC-2 fed with SE

Appendix C. Sample calculation for ozonation of SE

Ozonation of Secondary Effluent

Date	1/16/2009		
Time started =	16:45:00		
Time finished =	17:23:50		
Total Ozonation Time =	38.83	minutes	
Vww =	8	L	(volume of wastewater used in ozonation)
DOC measurement of SE sample			
$[DOC]_{initial}$	15.54	mg/L	(initial DOC in the wastewater before ozonation)
$[DOC]_{afterO3}$	14.80	mg/L	(DOC in the wastewater after ozonation)
Flow meter reading (L)			
R1 =	51935.26	L	(initial reading on the by-pass gas flow meter)
R2 =	51935.98	L	(final reading on the by-pass gas flow meter)
R3 =	3198.93	L	(initial reading on the off-gas flow meter)
R4 =	3208.29	L	(final reading on the off-gas flow meter)
Vo =	9.36	L	(volume of gas applied to reactor, Vo = R4-R3)
V1 =	0.72	L	(volume of air that passed through the by-pass line, V1 = R2 - R1)
$c(Na_2S_2O_3)$ =	0.1	M	(concentration $Na_2S_2O_3$ stock solution)
Volume =	250	mL	(volume of $Na_2S_2O_3$ stock solution used in titration)
Total volume =	1000	mL	(volume diluted $Na_2S_2O_3$ solution as titrant)
c(titrant) =	0.025	M	(concentration of titrant = $VolNa_2S_2O_3$ x $c(Na_2S_2O_3)$ / Total Vol)
$V_{KI+H2SO4}$ =	250	mL	
Vtitrated =	50	mL	
$V_{titrant}$ = Volume of $Na_2S_2O_3$ used in titration of $KI+H_2SO_4$			
$V_{titrant(A)}$ =	5.1	mL	(in wash bottle A, by-pass)
$V_{titrant(B)}$ =	25.5	mL	(in wash bottle B, off-gas)
Mi = mass of O_3 trapped in KI bottle = Vtitrant x Mtitrant * 24 * ($V_{KI+H2SO4}$ / $V_{titrated}$)			
M1 =	76.50	mg	(mass of ozone trapped in Off-gas KI bottle)
M2 =	15.30	mg	(mass of ozone trapped in By-pass KI bottle)
Co =	21.25	mg/L	(concentration of ozone gas in air = M2 / V1)
M3 =	198.90	mg	(total mass of ozone applied to ww sample = Co x Vo)
Eff =	61.54%		(transfer efficiency of ozone = ((M3 - M1)/M3) x 100%)
Ratio =	1		(Required $[O_3]$:[DOC] ratio)
M_{O-R} =	124.32	mg	(required mass of ozone = DOC x Ratio x Vww)
r =	13.08	mg/L	(Actual rate of ozone transfer = Eff x Co)
Vo_{reqd} =	9.51	L	(Actual volume of off-gas requied = M_{O-R}/r)
t =	38.83	minutes	(ozonation time)
q_{offgas} =	0.24	L/min	(flow rate of off-gas = Vo/t)
Treqd =	39.4	minutes	(Estimated time required = $Vo_{reqd}/q_{off-gas}$)
m_{O3used} =	122.40	mg	(mass of O_3 used by ww sample in reactor bottle = M3 - M1)
$[O_3]_{sample}$ =	15.30	mg/L	($[O3]_{sample} = m_{O3(used)}$ / Vww)
$[O_3]$:[DOC] =	0.98		(actual Ozone:[DOC] ratio)

Appendix D. Soil column fed with SE+O_3

Process conditions for SC-1

Feed water	:	Secondary effluent plus ozone (SE+O_3)
HLR	:	1.25 +/- 0.5 m/day
Media	:	Silica sand (0.8-1.25mm), total depth = 5m
Columns	:	2-pvc pipes each 100 mm diameter in series

Table D-1. DOC removal for SC-1 fed with SE+O_3

Date	Time (day)	C_0 (mg/L) at SP-R	C (mg/L) at SP-15	DOC Ratio (C/C_0)
23-01-09	4	13.51	9.36	69.3%
26-01-09	7	10.50	8.17	77.8%
27-01-09	8	10.54	7.55	71.7%
29-01-09	10	9.94	7.17	72.2%
30-01-09	11	10.02	6.85	68.4%
2-02-09	14	10.92	7.74	70.9%
3-02-09	15	10.31	7.41	71.9%
4-02-09	16	10.02	7.16	71.5%
8-02-09	20	12.10	8.52	70.4%

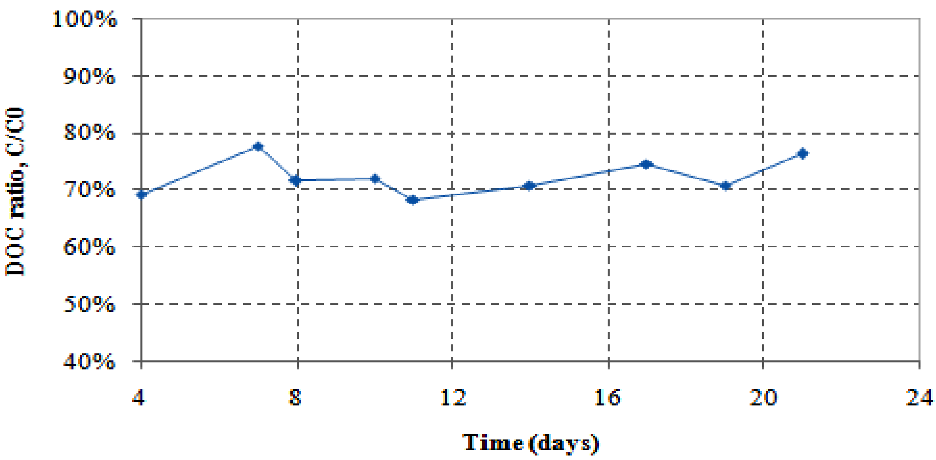

Figure D-1. DOC ratio for SC-1 fed with SE+O_3

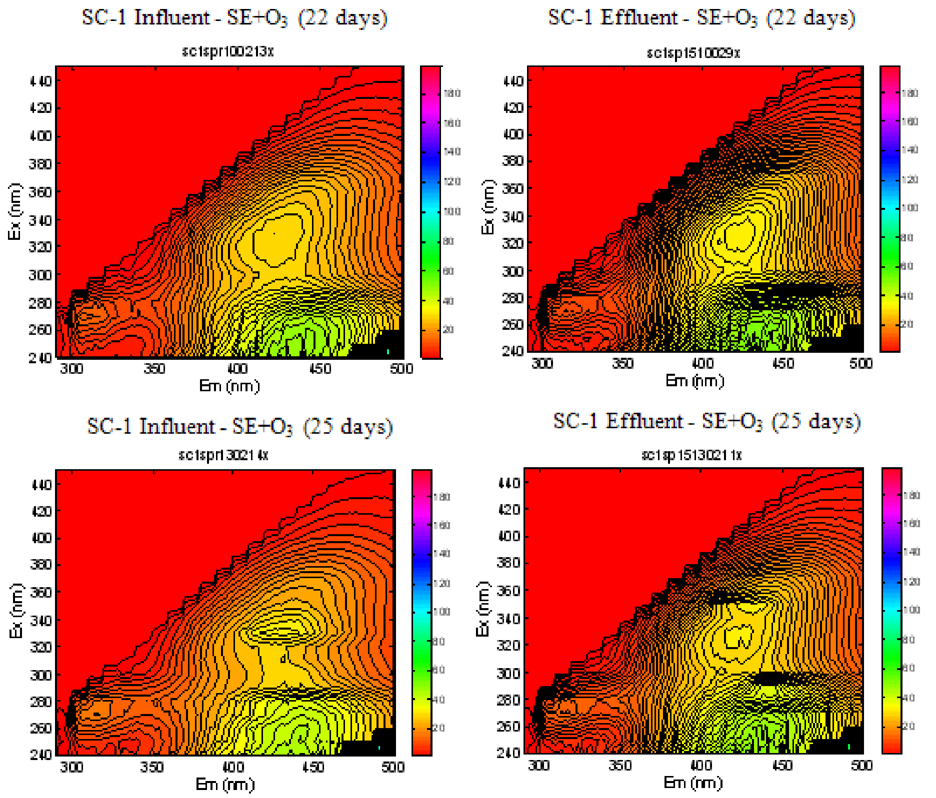

Figure D-2. FEEM spectra for influent and effluent of SC-1 fed with SE+O_3

Appendix E. NF-270 using SE alone and SE + SAT pre-treatment

Process conditions:

Membrane	=	NF-270
Feed pressure	=	50 psi (3.6 bar)
Recovery	=	8%
Temperature	=	20 ^{o}C
Filtration mode	=	One pass (without recirculation of concentrate)

Table E-1. Water quality parameters for NF-270 using SE alone

Time hh:mm	pH	EC µS/cm	Temp deg C	DOC mg/L	UVA_{254} Ab/cm	SUVA L/m-mg	TDS mg/L
Feed							
0:31	7.52	1192	19.9	16.08	0.381	2.37	751
2:31	7.69	1199	20.2	15.26	0.389	2.55	755
4:31	7.89	1192	20.5	15.49	0.394	2.54	751
6:01	8.16	1189	21.4	15.64	0.394	2.52	749
Average	**7.82**	**1193**	**20.5**	**15.62**	**0.389**	**2.49**	**752**
Permeate							
0:31	7.50	612	19.6	0.59	0.011	1.78	386
2:31	7.81	680	20.0	0.65	0.010	1.53	428
4:31	7.91	700	20.2	1.04	0.016	1.49	441
6:01	8.09	709	20.6	1.37	0.021	1.53	447
Average	**7.83**	**675**	**20.1**	**0.91**	**0.014**	**1.58**	**425**

Table E-2. Water quality parameters for NF-270 using SE with SAT pre-treatment

Time hh:mm	pH	EC µS/cm	Temp deg C	DOC mg/L	UVA_{254} Ab/cm	SUVA L/m-mg	TDS mg/L
Feed							
0:33	7.92	1173	21.1	10.78	0.359	3.33	739
2:33	8.13	1169	20.8	11.31	0.361	3.19	736
4:33	8.25	1166	21.3	11.06	0.357	3.23	735
6:03	8.32	1173	21.4	11.34	0.352	3.10	739
Average	**8.16**	**1170**	**21.2**	**11.12**	**0.357**	**3.21**	**737**
Permeate							
0:33	7.88	562	20.5	0.52	0.010	1.92	354
2:33	8.05	530	20.7	0.49	0.012	2.45	334
4:33	8.14	640	20.6	1.06	0.021	1.98	403
6:03	8.22	669	20.6	1.41	0.042	2.98	421
Average	**8.07**	**600**	**20.6**	**0.87**	**0.021**	**2.33**	**378**

Table E-3. DOC, TDS, UVA_{254} and SUVA removal for NF-270 using SE alone

Time (h:m)	DOC (mg/L)			TDS (mg/L)		
	Feed, Cf	Permeate, Cp	1-Cp/Cf	Feed, Cf	Permeate, Cp	1-Cp/Cf
0:31	16.08	0.59	96.3%	751	386	48.7%
2:31	15.26	0.65	95.7%	755	428	43.3%
4:31	15.49	1.04	93.3%	751	441	41.3%
6:01	15.64	1.37	91.2%	749	447	40.4%
Average	**15.62**	**0.91**	**94.1%**	**752**	**425**	**43.4%**
	UVA_{254} (Ab/cm)			SUVA (L/mg-m)		
	Feed, Cf	Permeate, Cp	1-Cp/Cf	Feed, Cf	Permeate, Cp	1-Cp/Cf
0:31	0.381	0.011	97.2%	2.37	1.78	25.0%
2:31	0.389	0.010	97.4%	2.55	1.53	39.8%
4:31	0.394	0.016	96.1%	2.54	1.49	41.2%
6:01	0.394	0.021	94.7%	2.52	1.53	39.2%
Average	**0.389**	**0.014**	**96.4%**	**2.49**	**1.58**	**36.3%**

Table E-4. DOC, TDS, UVA_{254} and SUVA removal for NF-270 using SE+SAT

Time (h:m)	DOC (mg/L)			TDS (mg/L)		
	Feed, Cf	Permeate, Cp	1-Cp/Cf	Feed, Cf	Permeate, Cp	1-Cp/Cf
0:33	10.78	0.52	95.2%	739	354	52.1%
2:33	11.31	0.49	95.7%	736	334	54.7%
4:33	11.06	1.06	90.4%	735	403	45.1%
6:03	11.34	1.41	87.6%	739	421	43.0%
Average	**11.12**	**0.87**	**92.2%**	**737**	**378**	**48.7%**
	UV_{A254} (Ab/cm)			SUVA (L/mg-m)		
	Feed, Cf	Permeate, Cp	1-Cp/Cf	Feed, Cf	Permeate, Cp	1-Cp/Cf
0:33	0.359	0.010	97.2%	3.33	1.92	42.3%
2:33	0.361	0.012	96.7%	3.19	2.45	23.3%
4:33	0.357	0.021	94.1%	3.23	1.98	38.6%
6:03	0.352	0.042	88.1%	3.10	2.98	4.0%
Average	**0.357**	**0.021**	**94.0%**	**3.21**	**2.33**	**27.0%**

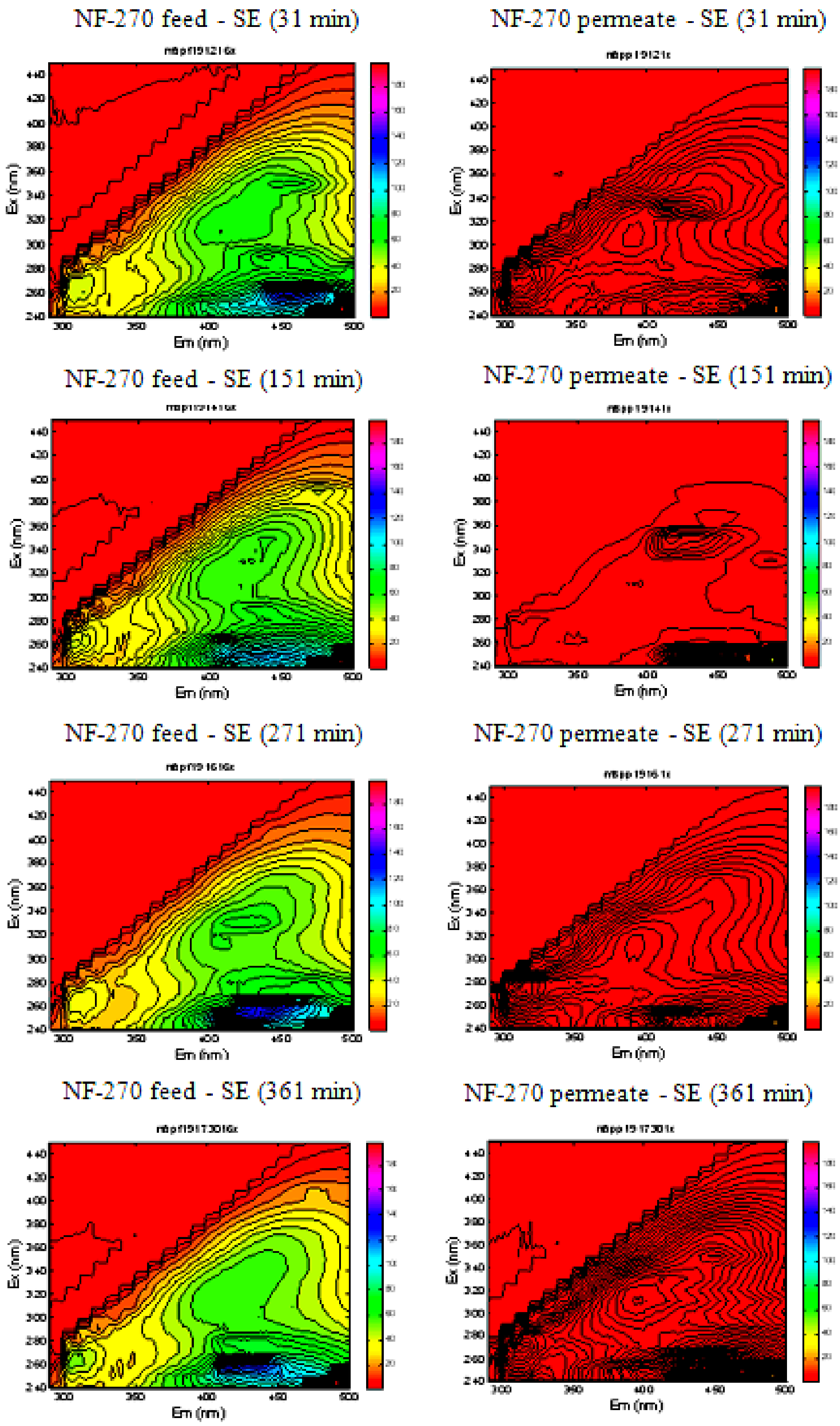

Figure E-1. FEEM spectra for feed and permeate of NF-270 with SE alone

Table E-5. Comparison of FEEM spectra results for feed and permeate using NF-270 fed with SE

Time (h:m)	DOC Component		Wavelength (nm)		Peak Intensity	
			Ex	Em	(RA unit)	Reduction
0:53	Humic-like 1	Feed	340	428	69.99	99.3%
		Permeate	330	418	0.46	
	Humic-like 2	Feed	260	464	100.23	99.3%
		Permeate	250	418	0.70	
	Protein-like	Feed	270	316	15.15	94.7%
		Permeate	270	306	0.81	
2:53	Humic-like 1	Feed	330	426	68.81	99.3%
		Permeate	330	442	0.45	
	Humic-like 2	Feed	250	442	96.64	99.3%
		Permeate	250	416	0.67	
	Protein-like	Feed	270	318	15.94	96.9%
		Permeate	270	306	0.50	
4:53	Humic-like 1	Feed	330	428	70.82	99.4%
		Permeate	330	412	0.44	
	Humic-like 2	Feed	250	438	100.68	99.4%
		Permeate	250	416	0.64	
	Protein-like	Feed	270	318	16.85	96.1%
		Permeate	270	308	0.65	
Ave	Humic-like 1	Feed	333	427	69.87	99.4%
		Permeate	330	424	0.45	
	Humic-like 2	Feed	253	448	99.18	99.3%
		Permeate	250	417	0.67	
	Protein-like	Feed	270	317	15.98	95.9%
		Permeate	270	307	0.65	

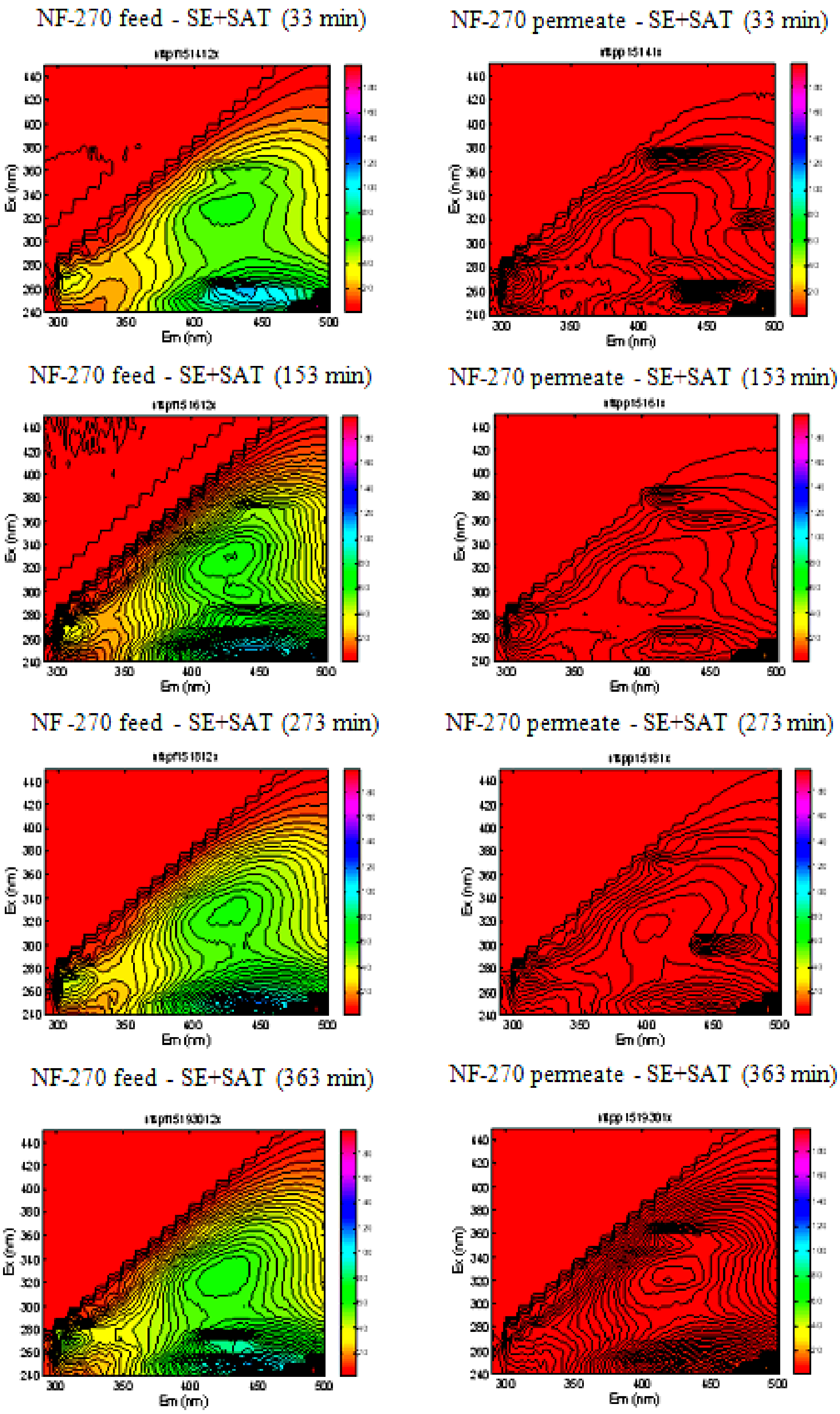

Figure E-2. FEEM spectra for feed and permeate of NF-270 with SE+SAT

Table E-6. Comparison of FEEM spectra results for feed and permeate using NF-270 fed with SE

Time (h:m)	DOC Component		Wavelength (nm)		Peak Intensity	
			Ex	Em	(RA unit)	Reduction
1:21	Humic-like 1	Feed	330	416	117.42	99.3%
		Permeate	330	408	0.83	
	Humic-like 2	Feed	250	444	146.47	99.2%
		Permeate	250	418	1.11	
	Protein-like	Feed	270	308	27.97	95.3%
		Permeate	270	306	1.32	
3:21	Humic-like 1	Feed	330	424	84.62	99.1%
		Permeate	330	398	0.74	
	Humic-like 2	Feed	250	436	120.88	99.1%
		Permeate	250	418	1.06	
	Protein-like	Feed	270	310	24.35	95.0%
		Permeate	270	308	1.21	
5:21	Humic-like 1	Feed	330	424	94.72	99.2%
		Permeate	330	408	0.74	
	Humic-like 2	Feed	250	438	133.17	99.2%
		Permeate	250	418	1.09	
	Protein-like	Feed	270	312	27.57	94.6%
		Permeate	270	316	1.48	
Ave	Humic-like 1	Feed	330	421	98.92	99.2%
		Permeate	330	405	0.77	
	Humic-like 2	Feed	250	439	133.51	99.2%
		Permeate	250	418	1.09	
	Protein-like	Feed	270	310	26.63	95.0%
		Permeate	270	310	1.33	

Appendix F. NF-270 using SE+O_3 and SE+O_3+SAT pre-treatment

Process conditions:

Membrane	=	NF-270
Feed pressure	=	50 psi (3.6 bar)
Recovery	=	8%
Temperature	=	20 ^{o}C
Filtration mode	=	One pass (without recirculation of concentrate)

Table F-1. Water quality parameters for NF-270 using SE+O_3

Time h:m	pH	EC mS/cm	Temp deg C	DOC mg/L	UVA_{254} Ab/cm	SUVA L/m-mg	TDS mg/L
Feed							
0:57	7.77	843	21.2	9.53	0.149	1.56	531
2:57	7.78	846	22.2	9.32	0.150	1.61	533
4:57	7.84	850	21.9	9.51	0.152	1.59	536
Average	**7.80**	**846**	**21.8**	**9.45**	**0.150**	**1.59**	**533**
Permeate							
0:57	7.64	437	21.2	1.05	0.012	1.09	275
2:57	7.63	470	22.2	1.09	0.012	1.10	296
4:57	7.85	471	21.1	1.30	0.008	0.58	297
Average	**7.71**	**459**	**21.5**	**1.15**	**0.010**	**0.92**	**289**

Table F-2. Water quality parameters for NF-270 using SE+O_3+SAT

Time h:m	pH	EC mS/cm	Temp deg C	DOC mg/L	UVA_{254} Ab/cm	SUVA L/m-mg	TDS mg/L
Feed							
0:40	8.02	1205	19.9	8.27	0.202	2.44	759
1:40	8.02	1207	20.1	8.41	0.209	2.49	760
2:40	8.07	1206	20.0	8.34	0.207	2.48	760
3:40	8.13	1206	20.0	8.58	0.202	2.36	760
4:40	8.16	1210	20.0	8.43	0.209	2.48	762
5:40	8.26	1213	20.1	8.38	0.218	2.60	764
Average	**8.11**	**1208**	**20.0**	**8.40**	**0.208**	**2.47**	**761**
Permeate							
0:40	7.75	554	18.9	0.58	0.010	1.74	349
1:40	7.83	651	18.9	0.64	0.012	1.86	410
2:40	7.94	686	19.0	0.99	0.021	2.12	432
3:40	7.90	720	19.0	1.27	0.028	2.20	454
4:40	8.02	721	18.9	1.31	0.028	2.14	454
5:40	8.09	721	18.9	1.20	0.030	2.50	454
Average	**7.92**	**676**	**18.9**	**1.00**	**0.022**	**2.01**	**426**

Table F-3. DOC, TDS, UVA_{254} and SUVA removal for NF-270 using SE+O_3

Time (h:m)	DOC (mg/L)			TDS (mg/L)		
	Feed, Cf	Permeate, Cp	1-Cp/Cf	Feed, Cf	Permeate, Cp	1-Cp/Cf
0:57	9.53	1.05	88.9%	531	275	48.2%
2:57	9.32	1.09	88.4%	533	296	44.4%
4:57	9.51	1.30	86.3%	536	297	44.6%
Average	**9.45**	**1.15**	**87.9%**	**533**	**289**	**45.7%**
	UVA_{254} (Ab/cm)			SUVA (L/mg-m)		
	Feed, Cf	Permeate, Cp	1-Cp/Cf	Feed, Cf	Permeate, Cp	1-Cp/Cf
0:57	0.149	0.012	92.3%	1.56	1.09	30.0%
2:57	0.150	0.012	92.0%	1.61	1.10	31.3%
4:57	0.152	0.008	95.0%	1.59	0.58	63.8%
Average	**0.150**	**0.010**	**93.1%**	**1.59**	**0.92**	**41.7%**

Table F-4. DOC, TDS, UVA_{254} and SUVA removal for NF-270 using SE+O_3+SAT

Time (h:m)	DOC (mg/L)			TDS (mg/L)		
	Feed, Cf	Permeate, Cp	(Cf-Cp)/Cf	Feed, Cf	Permeate, Cp	(Cf-Cp)/Cf
0:40	8.27	0.58	93.0%	759	349	54.0%
1:40	8.41	0.64	92.3%	760	410	46.1%
2:40	8.34	0.99	88.1%	760	432	43.1%
3:40	8.58	1.27	85.1%	760	454	40.3%
4:40	8.43	1.31	84.5%	762	454	40.4%
5:40	8.38	1.20	85.7%	764	454	40.6%
Average	**8.40**	**1.00**	**88.1%**	**761**	**426**	**44.1%**
	UVA_{254} (Ab/cm)			SUVA (L/mg-m)		
	Feed, Cf	Permeate, Cp	1-Cp/Cf	Feed, Cf	Permeate, Cp	1-Cp/Cf
0:40	0.202	0.010	95.0%	2.44	1.74	28.8%
1:40	0.209	0.012	94.3%	2.49	1.86	25.0%
2:40	0.207	0.021	89.9%	2.48	2.12	14.7%
3:40	0.202	0.028	86.1%	2.36	2.20	6.7%
4:40	0.209	0.028	86.6%	2.48	2.14	13.7%
5:40	0.218	0.030	86.2%	2.60	2.50	3.9%
Average	**0.208**	**0.022**	**89.7%**	**2.47**	**2.09**	**15.5%**

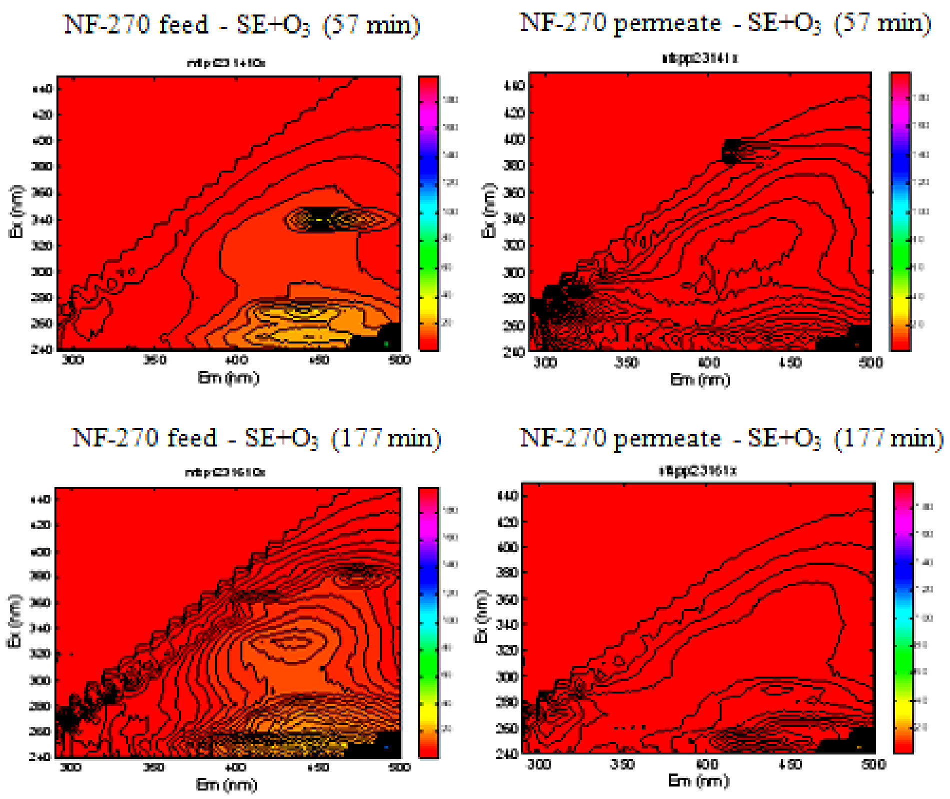

Figure F-1. FEEM spectra for feed and permeate of NF-270 with SE+O_3

Table F-5. Comparison of FEEM spectra results for feed and permeate using NF-270 fed with SE+O_3

Time (h:m)	DOC Component		Wavelength (nm)		Peak Intensity	
			Ex	Em	(RA unit)	Reduction
0:57	Humic-like 1	Feed	340	450	40.53	97.8%
		Permeate	330	436	0.89	
	Humic-like 2	Feed	250	442	27.70	93.4%
		Permeate	250	438	1.84	
	Protein-like	Feed	270	308	9.77	72.2%
		Permeate	270	306	2.72	
2:57	Humic-like 1	Feed	330	434	15.68	94.5%
		Permeate	330	442	0.86	
	Humic-like 2	Feed	250	446	28.71	91.7%
		Permeate	250	436	2.38	
	Protein-like	Feed	270	314	8.44	80.6%
		Permeate	270	306	1.64	
Ave	Humic-like 1	Feed	335	442	28.11	96.9%
		Permeate	330	439	0.87	
	Humic-like 2	Feed	250	444	28.21	92.5%
		Permeate	250	437	2.11	
	Protein-like	Feed	270	311	9.11	76.1%
		Permeate	270	306	2.18	

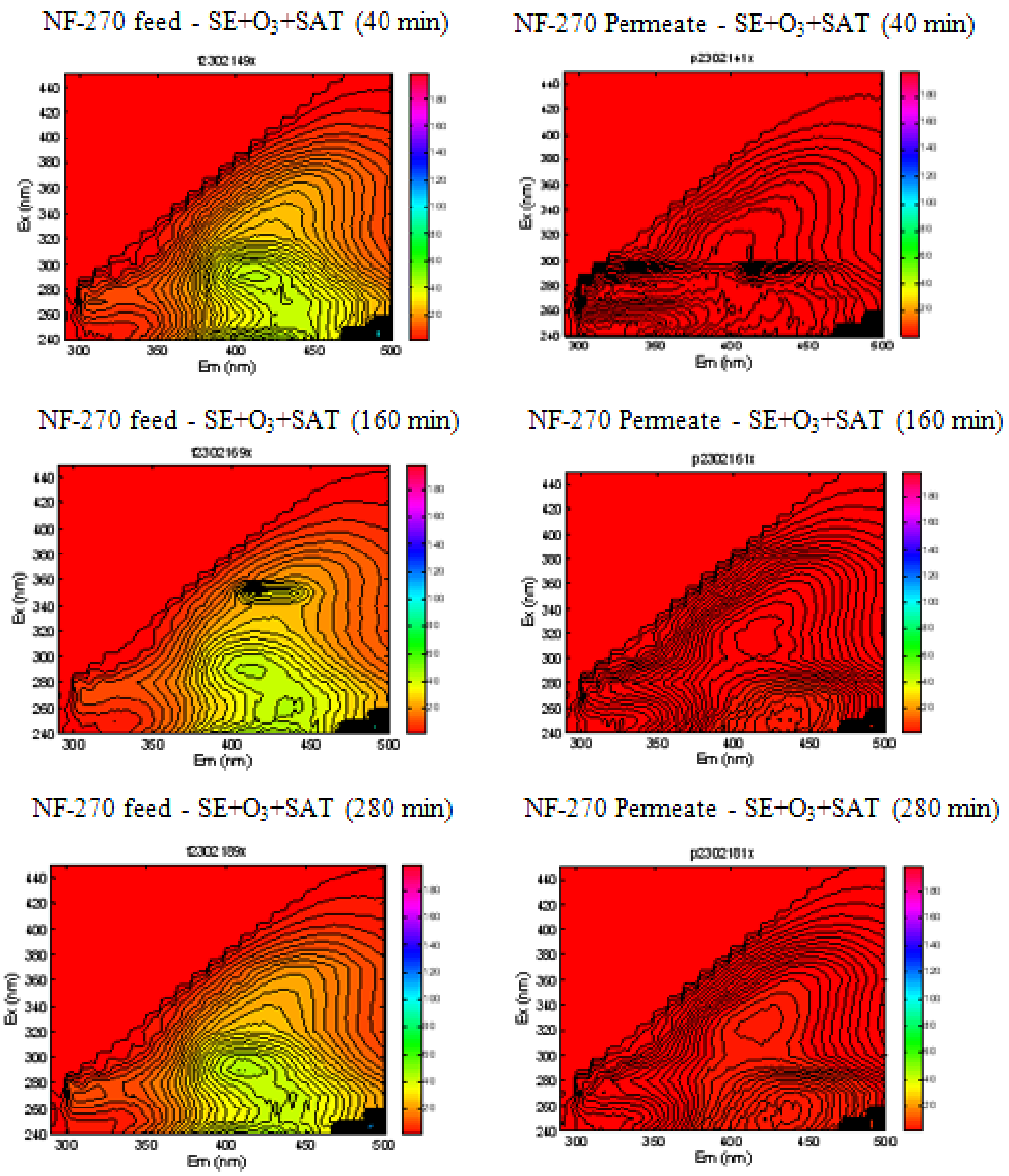

Figure F-2. FEEM spectra for feed and permeate of NF-270 with SE+O_3+SAT

Table F-6. Comparison of FEEM spectra results for feed and permeate using NF-270 fed with SE+O_3+SAT

Time (h:m)	DOC Component		Wavelength (nm)		Peak Intensity	
			Ex	Em	(RA unit)	Reduction
0:40	Humic-like 1	Feed	330	420	28.29	96.4%
		Permeate	330	418	1.01	
	Humic-like 2	Feed	250	426	44.14	96.6%
		Permeate	250	430	1.50	
	Protein-like	Feed	270	312	12.13	87.2%
		Permeate	280	336	1.55	
2:40	Humic-like 1	Feed	350	418	40.01	93.1%
		Permeate	330	420	2.76	
	Humic-like 2	Feed	260	438	45.38	90.7%
		Permeate	250	438	4.24	
	Protein-like	Feed	270	308	12.58	86.8%
		Permeate	280	336	1.66	
4:40	Humic-like 1	Feed	330	424	28.30	86.6%
		Permeate	330	420	3.78	
	Humic-like 2	Feed	250	432	43.76	86.8%
		Permeate	250	436	5.78	
	Protein-like	Feed	270	312	14.38	88.5%
		Permeate	270	320	1.66	
Ave	Humic-like 1	Feed	337	421	32.20	92.2%
		Permeate	330	419	2.52	
	Humic-like 2	Feed	253	432	44.43	91.4%
		Permeate	250	435	3.84	
	Protein-like	Feed	270	311	13.03	87.5%
		Permeate	277	331	1.62	

Appendix G. NF-90 using SE and SE+SAT pre-treatment

Process conditions:

Membrane	=	NF-90
Feed pressure	=	50 psi (3.6 bar)
Recovery	=	8%
Temperature	=	20 ^{o}C
Filtration mode	=	One pass (without recirculation of concentrate)

Table G-1. Water quality parameters for NF-90 using SE alone

Time h:m	pH	EC mS/cm	Temp deg C	DOC mg/L	UVA_{254} Ab/cm	SUVA L/m-mg	TDS mg/L
Feed							
0:53	7.44	1027	20.8	12.27	0.388	3.16	647
1:53	7.50	1030	20.9	12.82	0.398	3.10	649
2:53	7.63	1030	20.7	12.34	0.396	3.21	649
3:53	7.80	1030	20.8	12.34	0.397	3.22	649
4:53	7.89	1030	20.5	11.85	0.399	3.37	649
5:53	8.06	1030	20.4	12.44	0.396	3.18	649
Average	**7.72**	**1030**	**20.7**	**12.34**	**0.396**	**3.21**	**649**
Permeate							
0:53	7.06	65	19.6	0.33	0.004	1.06	41
1:53	7.04	56	20.4	0.19	0.002	1.05	35
2:53	7.11	52	19.9	0.23	0.003	1.10	33
3:53	7.16	51	19.9	0.50	0.003	0.60	32
4:53	7.18	49	19.9	0.42	0.003	0.72	31
5:53	7.26	48	19.9	0.24	0.003	1.28	30
Average	**7.14**	**54**	**19.9**	**0.32**	**0.003**	**0.91**	**34**
Concentrate							
0:53	7.56	1103	21.6	13.57	0.421	3.10	695
1:53	7.65	1108	21.6	13.57	0.424	3.12	698
2:53	7.75	1113	21.3	13.86	0.418	3.02	701
3:53	7.87	1114	21.4	14.87	0.441	2.97	702
4:53	7.98	1110	21.5	14.60	0.426	2.92	699
5:53	8.12	1138	21.4	14.87	0.437	2.94	717
Average	**7.82**	**1114**	**21.5**	**14.22**	**0.428**	**3.01**	**702**

Table G-2. Water quality parameters for NF-90 using SE with SAT pre-treatment

Time h:m	pH	EC mS/cm	Temp deg C	DOC mg/L	UVA_{254} Ab/cm	SUVA L/m-mg	TDS mg/L
Feed							
0:21	8.12	1268	20.1	13.32	0.268	2.012	799
1:21	8.12	1270	20.4	13.35	0.271	2.030	800
2:21	8.15	1270	20.4	13.31	0.276	2.074	800
3:21	8.21	1268	20.5	13.51	0.269	1.991	799
4:21	8.28	1269	20.5	13.44	0.272	2.024	799
5:21	8.34	1269	20.6	13.41	0.274	2.043	799
Average	**8.20**	**1269**	**20.4**	**13.39**	**0.272**	**2.029**	**799**
Permeate							
0:21	7.20	99	20.0	0.46	0.002	0.439	62
1:21	7.22	104	19.9	0.43	0.001	0.230	66
2:21	7.21	110	20.3	0.42	0.001	0.236	69
3:21	7.23	110	20.3	0.39	0.002	0.519	69
4:21	7.25	109	20.4	0.43	0.001	0.235	69
5:21	7.26	104	20.4	0.34	0.001	0.294	66
Average	**7.23**	**106**	**20.2**	**0.41**	**0.001**	**0.332**	**67**
Concentrate							
0:21	8.17	1368	21.1	14.56	0.029	0.199	862
1:21	8.16	1370	21.1	14.28	0.028	0.196	863
2:21	8.22	1367	21.1	14.38	0.028	0.195	861
3:21	8.24	1369	21.2	14.57	0.027	0.185	862
4:21	8.31	1372	21.3	14.69	0.028	0.191	864
5:21	8.37	1364	21.3	14.63	0.026	0.178	859
Average	**8.25**	**1368**	**21.2**	**14.52**	**0.028**	**0.191**	**862**

Table G-3. DOC, TDS, UVA_{254} and SUVA removal for NF-90 using SE alone

Time (h:m)	DOC (mg/L)			TDS (mg/L)		
	Feed, Cf	Permeate, Cp	1-Cp/Cf	Feed, Cf	Permeate, Cp	1-Cp/Cf
0:53	12.27	0.33	97.3%	647	41	93.7%
1:53	12.82	0.19	98.5%	649	35	94.6%
2:53	12.34	0.23	98.2%	649	33	95.0%
3:53	12.34	0.50	96.0%	649	32	95.0%
4:53	11.85	0.42	96.5%	649	31	95.2%
5:53	12.44	0.24	98.1%	649	30	95.3%
Average	**12.34**	**0.32**	**97.4%**	**649**	**34**	**94.8%**
	UVA_{254} (Ab/cm)			**SUVA (L/mg-m)**		
	Feed, Cf	Permeate, Cp	1-Cp/Cf	Feed, Cf	Permeate, Cp	1-Cp/Cf
0:53	0.388	0.004	99.1%	3.162	1.064	66.4%
1:53	0.398	0.002	99.5%	3.105	1.047	66.3%
2:53	0.396	0.003	99.4%	3.209	1.101	65.7%
3:53	0.397	0.003	99.2%	3.217	0.604	81.2%
4:53	0.399	0.003	99.2%	3.367	0.719	78.6%
5:53	0.396	0.003	99.2%	3.183	1.277	59.9%
Average	**0.396**	**0.003**	**99.3%**	**3.207**	**0.969**	**69.7%**

Table G-4. DOC, TDS, UVA_{254} and SUVA removal for NF-90 using SE+SAT

Time (h:m)	DOC (mg/L)			TDS (mg/L)		
	Feed, Cf	Permeate, Cp	1-Cp/Cf	Feed, Cf	Permeate, Cp	1-Cp/Cf
0:21	13.32	0.46	96.6%	799	62	92.2%
1:21	13.35	0.43	96.7%	800	66	91.8%
2:21	13.31	0.42	96.8%	800	69	91.3%
3:21	13.51	0.39	97.2%	799	69	91.3%
4:21	13.44	0.43	96.8%	799	69	91.4%
5:21	13.41	0.34	97.5%	799	66	91.8%
Average	**13.39**	**0.41**	**96.9%**	**799**	**67**	**91.6%**
	UVA_{254} (Ab/cm)			**SUVA (L/mg-m)**		
	Feed, Cf	Permeate, Cp	1-Cp/Cf	Feed, Cf	Permeate, Cp	1-Cp/Cf
0:21	0.268	0.002	99.3%	2.012	0.439	78.2%
1:21	0.271	0.001	99.6%	2.030	0.230	88.6%
2:21	0.276	0.001	99.6%	2.074	0.236	88.6%
3:21	0.269	0.002	99.3%	1.991	0.519	73.9%
4:21	0.272	0.001	99.6%	2.024	0.235	88.4%
5:21	0.274	0.001	99.6%	2.043	0.294	85.6%
Average	**0.272**	**0.001**	**99.5%**	**2.029**	**0.326**	**83.9%**

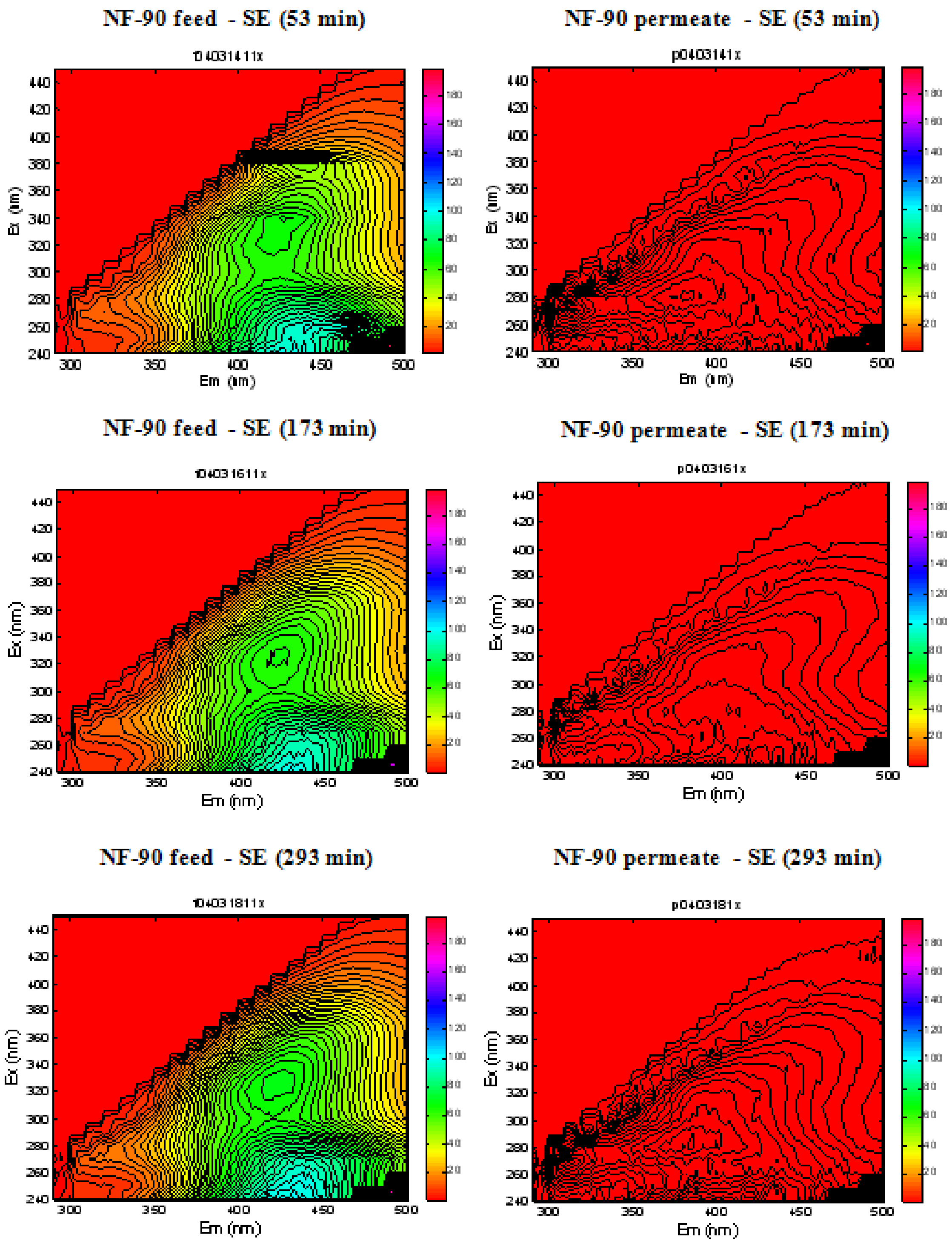

Figure G-1. FEEM spectra for feed and permeate of NF-90 with SE alone

Table G-5. Comparison of FEEM spectra results for feed and permeate using NF-90 fed with SE alone

Time (h:m)	DOC Component		Wavelength (nm)		Peak Intensity	
			Ex	Em	(RA unit)	Reduction
0:53	Humic-like 1	Feed	340	428	69.99	99.3%
		Permeate	330	418	0.46	
	Humic-like 2	Feed	260	464	100.23	99.3%
		Permeate	250	418	0.70	
	Protein-like	Feed	270	316	15.15	94.7%
		Permeate	270	306	0.81	
2:53	Humic-like 1	Feed	330	426	68.81	99.3%
		Permeate	330	442	0.45	
	Humic-like 2	Feed	250	442	96.64	99.3%
		Permeate	250	416	0.67	
	Protein-like	Feed	270	318	15.94	96.9%
		Permeate	270	306	0.50	
4:53	Humic-like 1	Feed	330	428	70.82	99.4%
		Permeate	330	412	0.44	
	Humic-like 2	Feed	250	438	100.68	99.4%
		Permeate	250	416	0.64	
	Protein-like	Feed	270	318	16.85	96.1%
		Permeate	270	308	0.65	
Ave	Humic-like 1	Feed	333	427	69.87	99.4%
		Permeate	330	424	0.45	
	Humic-like 2	Feed	253	448	99.18	99.3%
		Permeate	250	417	0.67	
	Protein-like	Feed	270	317	15.98	95.9%
		Permeate	270	307	0.65	

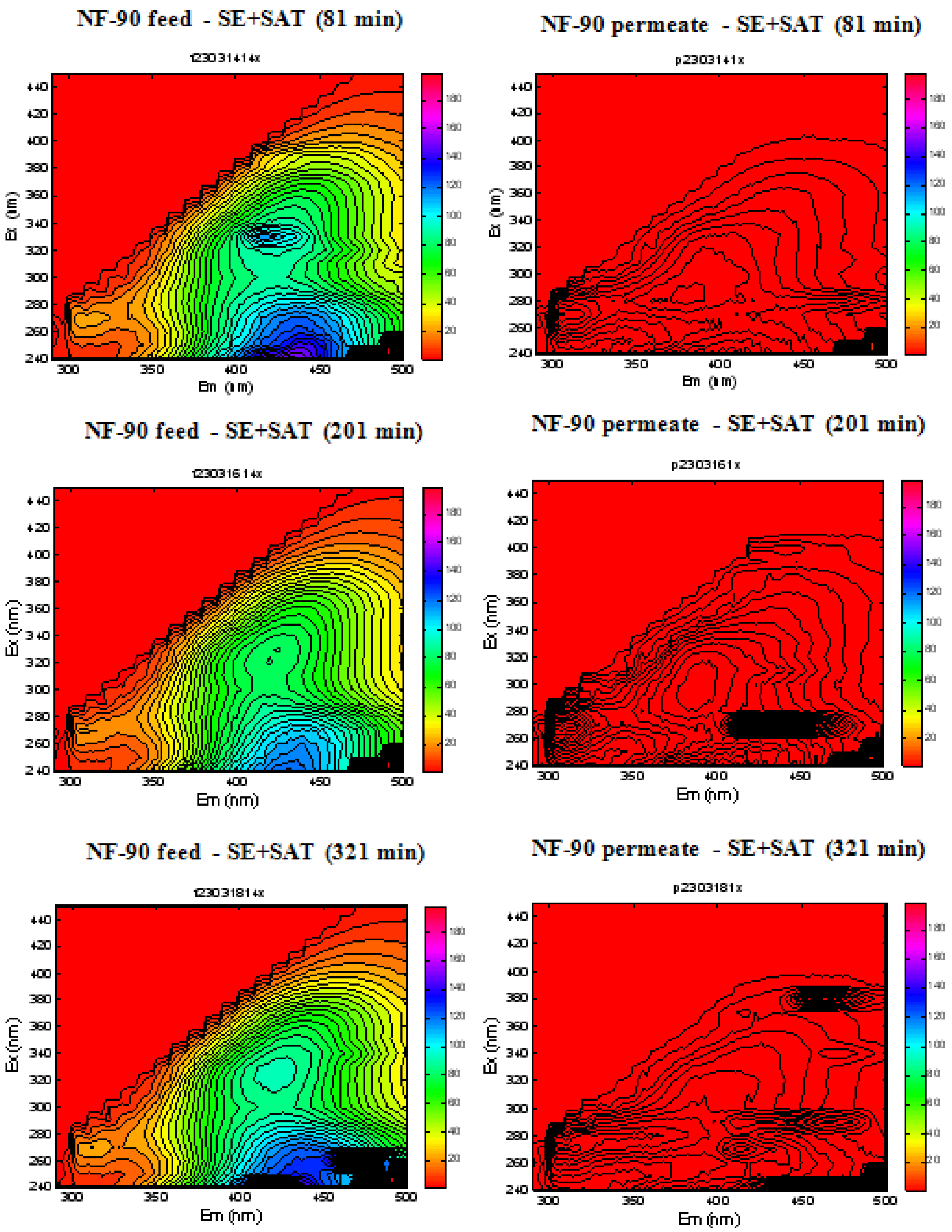

Figure G-2. FEEM spectra for feed and permeate of NF-90 with SE+SAT

Table G-6. Comparison of FEEM spectra results for feed and permeate using NF-90 fed with SE+SAT

Time (h:m)	DOC Component		Wavelength (nm)		Peak Intensity	
			Ex	Em	(RA unit)	Reduction
1:21	Humic-like 1	Feed	330	416	117.42	99.3%
		Permeate	330	408	0.83	
	Humic-like 2	Feed	250	444	146.47	99.2%
		Permeate	250	418	1.11	
	Protein-like	Feed	270	308	27.97	95.3%
		Permeate	270	306	1.32	
3:21	Humic-like 1	Feed	330	424	84.62	99.1%
		Permeate	330	398	0.74	
	Humic-like 2	Feed	250	436	120.88	99.1%
		Permeate	250	418	1.06	
	Protein-like	Feed	270	310	24.35	95.0%
		Permeate	270	308	1.21	
5:21	Humic-like 1	Feed	330	424	94.72	99.2%
		Permeate	330	408	0.74	
	Humic-like 2	Feed	250	438	133.17	99.2%
		Permeate	250	418	1.09	
	Protein-like	Feed	270	312	27.57	94.6%
		Permeate	270	316	1.48	
Ave	Humic-like 1	Feed	330	421	98.92	99.2%
		Permeate	330	405	0.77	
	Humic-like 2	Feed	250	439	133.51	99.2%
		Permeate	250	418	1.09	
	Protein-like	Feed	270	310	26.63	95.0%
		Permeate	270	310	1.33	

Appendix H. NF-90 using SE+O_3 and SE+O_3+SAT pre-treatment

Process conditions:

Membrane	=	NF-90
Feed pressure	=	50 psi (3.6 bar)
Recovery	=	8%
Temperature	=	20 ^oC
Filtration mode	=	One pass (without recirculation of concentrate)

Table H-1. Water quality parameters for NF-90 using SE+O_3

Time h:m	pH	EC µS/cm	Temp deg C	DOC mg/L	UVA_{254} Ab/cm	SUVA L/m-mg	TDS mg/L
Feed							
0:35	7.74	1318	17.3	17.35	0.225	1.30	830
1:35	7.77	1318	18.3	17.27	0.232	1.34	830
2:35	7.85	1318	18.4	17.35	0.227	1.31	830
3:35	7.90	1318	18.8	17.01	0.236	1.39	830
4:35	8.01	1316	19.3	17.15	0.231	1.35	829
5:35	8.06	1316	19.4	17.29	0.218	1.26	829
Average	**7.89**	**1317**	**18.6**	**17.24**	**0.228**	**1.32**	**830**
Permeate							
0:35	7.12	89	19.8	0.43	0.001	0.23	56
1:35	7.12	80	20.0	0.45	0.001	0.22	50
2:35	7.13	76	19.8	0.39	0.001	0.25	48
3:35	7.11	77	19.7	0.56	0.004	0.72	49
4:35	7.14	76	19.7	0.42	0.002	0.48	48
5:35	7.18	74	19.7	0.31	0.001	0.32	47
Average	**7.13**	**79**	**19.8**	**0.43**	**0.002**	**0.37**	**50**
Concentrate							
0:35	7.84	1434	20.0	19.12	0.012	0.06	903
1:35	7.87	1468	20.3	19.83	0.013	0.07	925
2:35	7.94	1472	20.2	19.50	0.012	0.06	927
3:35	7.99	1478	20.4	19.64	0.013	0.07	931
4:35	8.08	1473	20.5	19.23	0.013	0.07	928
5:35	8.12	1476	20.6	19.36	0.012	0.06	930
Average	**7.97**	**1467**	**20.3**	**19.45**	**0.013**	**0.06**	**924**

Table H-2. Water quality parameters for NF-90 using SE+O_3+SAT

Time hh:mm	pH	EC µS/cm	Temp deg C	DOC mg/L	UVA_{254} Ab/cm	SUVA L/m-mg	TDS mg/L
Feed							
0:33	8.13	1004	20.4	7.65	0.171	2.24	633
1:33	8.20	1003	20.3	7.46	0.173	2.32	632
2:33	8.23	1009	20.4	7.74	0.178	2.30	636
3:33	8.26	1008	20.5	7.38	0.173	2.35	635
4:33	8.31	1009	20.6	7.75	0.174	2.25	636
5:33	8.35	1009	20.6	7.98	0.177	2.22	636
Average	**8.25**	**1007**	**20.5**	**7.66**	**0.174**	**2.28**	**634**
Permeate							
0:33	6.36	92	20.0	0.45	0.002	0.45	58
1:33	6.56	107	20.0	0.68	0.002	0.29	67
2:33	6.59	109	20.3	0.49	0.003	0.61	69
3:33	6.70	112	20.2	0.46	0.004	0.87	71
4:33	6.78	108	20.0	0.44	0.004	0.92	68
5:33	6.86	106	20.0	0.42	0.002	0.48	67
Average	**6.64**	**106**	**20.1**	**0.49**	**0.003**	**0.63**	**67**
Concentrate							
0:33	8.18	1077	21.4	8.43	0.187	2.22	679
1:33	8.24	1081	21.5	8.27	0.188	2.27	681
2:33	8.27	1081	21.5	7.98	0.188	2.36	681
3:33	8.29	1079	21.5	8.24	0.188	2.28	680
4:33	8.34	1078	21.6	8.38	0.188	2.24	679
5:33	8.37	1079	21.7	7.89	0.187	2.37	680
Average	**8.28**	**1079**	**21.5**	**8.20**	**0.188**	**2.29**	**680**

Table H-3. DOC, TDS, UVA_{254} and SUVA removal for NF-90 using $SE+O_3$

Time (h:m)	DOC (mg/L)			TDS (mg/L)		
	Feed, Cf	Permeate, Cp	1-Cp/Cf	Feed, Cf	Permeate, Cp	1-Cp/Cf
0:35	17.35	0.43	97.5%	830	56	93.2%
1:35	17.27	0.45	97.4%	830	50	93.9%
3:35	17.01	0.56	96.7%	830	49	94.2%
4:35	17.15	0.42	97.5%	829	48	94.2%
5:35	17.29	0.31	98.2%	829	47	94.4%
Average	**17.21**	**0.43**	**97.5%**	**830**	**50**	**94.0%**
	UVA_{254} (Ab/cm)			SUVA (L/mg-m)		
	Feed, Cf	Permeate, Cp	1-Cp/Cf	Feed, Cf	Permeate, Cp	1-Cp/Cf
0:35	0.225	0.001	99.6%	1.297	0.235	81.9%
1:35	0.232	0.001	99.6%	1.343	0.223	83.4%
3:35	0.227	0.001	99.6%	1.308	0.254	80.6%
4:35	0.236	0.004	98.3%	1.387	0.721	48.1%
5:35	0.231	0.002	99.1%	1.347	0.475	64.7%
Average	**0.230**	**0.002**	**99.2%**	**1.337**	**0.382**	**71.7%**

Table H-4. DOC, TDS, UVA_{254} and SUVA removal for NF-90 using $SE+O_3+SAT$

Time (h:m)	DOC (mg/L)			TDS (mg/L)		
	Feed, Cf	Permeate, Cp	1-Cp/Cf	Feed, Cf	Permeate, Cp	1-Cp/Cf
0:33	7.65	0.45	94.1%	633	58	90.8%
1:33	7.46	0.68	90.8%	632	67	89.3%
2:33	7.74	0.49	93.7%	636	69	89.2%
3:33	7.38	0.46	93.8%	635	71	88.9%
4:33	7.75	0.44	94.4%	636	68	89.3%
5:33	7.98	0.42	94.8%	636	67	89.5%
Average	**7.66**	**0.49**	**93.6%**	**634**	**67**	**89.5%**
	UVA_{254} (Ab/cm)			SUVA (L/mg-m)		
	Feed, Cf	Permeate, Cp	1-Cp/Cf	Feed, Cf	Permeate, Cp	1-Cp/Cf
0:33	0.171	0.002	98.8%	2.236	0.445	80.1%
1:33	0.173	0.002	98.8%	2.320	0.292	87.4%
2:33	0.178	0.003	98.3%	2.301	0.615	73.3%
3:33	0.173	0.004	97.7%	2.346	0.873	62.8%
4:33	0.174	0.004	97.7%	2.247	0.915	59.3%
5:33	0.177	0.002	98.9%	2.218	0.478	78.4%
Average	**0.174**	**0.003**	**98.4%**	**2.278**	**0.603**	**73.5%**

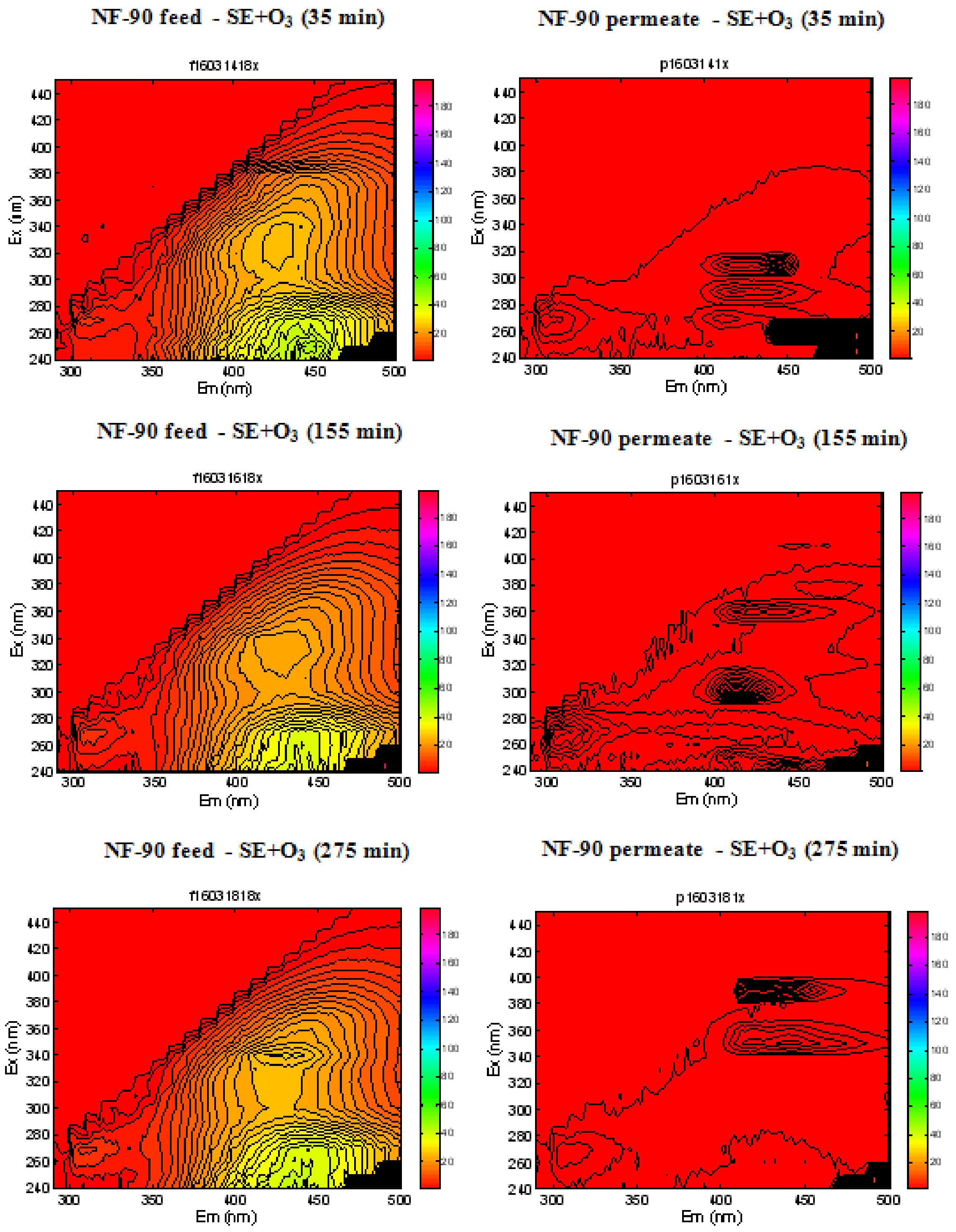

Figure H-1. FEEM spectra for feed and permeate of NF-90 with SE+O_3

Table H-5. Comparison of FEEM spectra results for feed and permeate using NF-90 fed with SE+O_3

Time (h:m)	DOC Component		Wavelength (nm)		Peak Intensity	
			Ex	Em	(RA unit)	Reduction
0:35	Humic-like 1	Feed	330	426	27.88	99.1%
		Permeate	340	422	0.25	
	Humic-like 2	Feed	250	440	46.47	99.1%
		Permeate	250	438	0.40	
	Protein-like	Feed	270	310	7.68	88.5%
		Permeate	270	306	0.89	
2:35	Humic-like 1	Feed	330	434	26.20	98.4%
		Permeate	350	418	0.41	
	Humic-like 2	Feed	250	442	39.90	98.6%
		Permeate	250	410	0.57	
	Protein-like	Feed	270	306	9.64	93.2%
		Permeate	270	306	0.66	
4:35	Humic-like 1	Feed	340	430	30.49	97.3%
		Permeate	350	440	0.83	
	Humic-like 2	Feed	250	434	42.98	99.3%
		Permeate	250	420	0.32	
	Protein-like	Feed	270	312	9.16	94.9%
		Permeate	270	306	0.46	
Ave	Humic-like 1	Feed	333	430	28.19	98.2%
		Permeate	347	427	0.50	
	Humic-like 2	Feed	250	439	43.12	99.0%
		Permeate	250	423	0.43	
	Protein-like	Feed	270	309	8.83	92.4%
		Permeate	270	306	0.67	

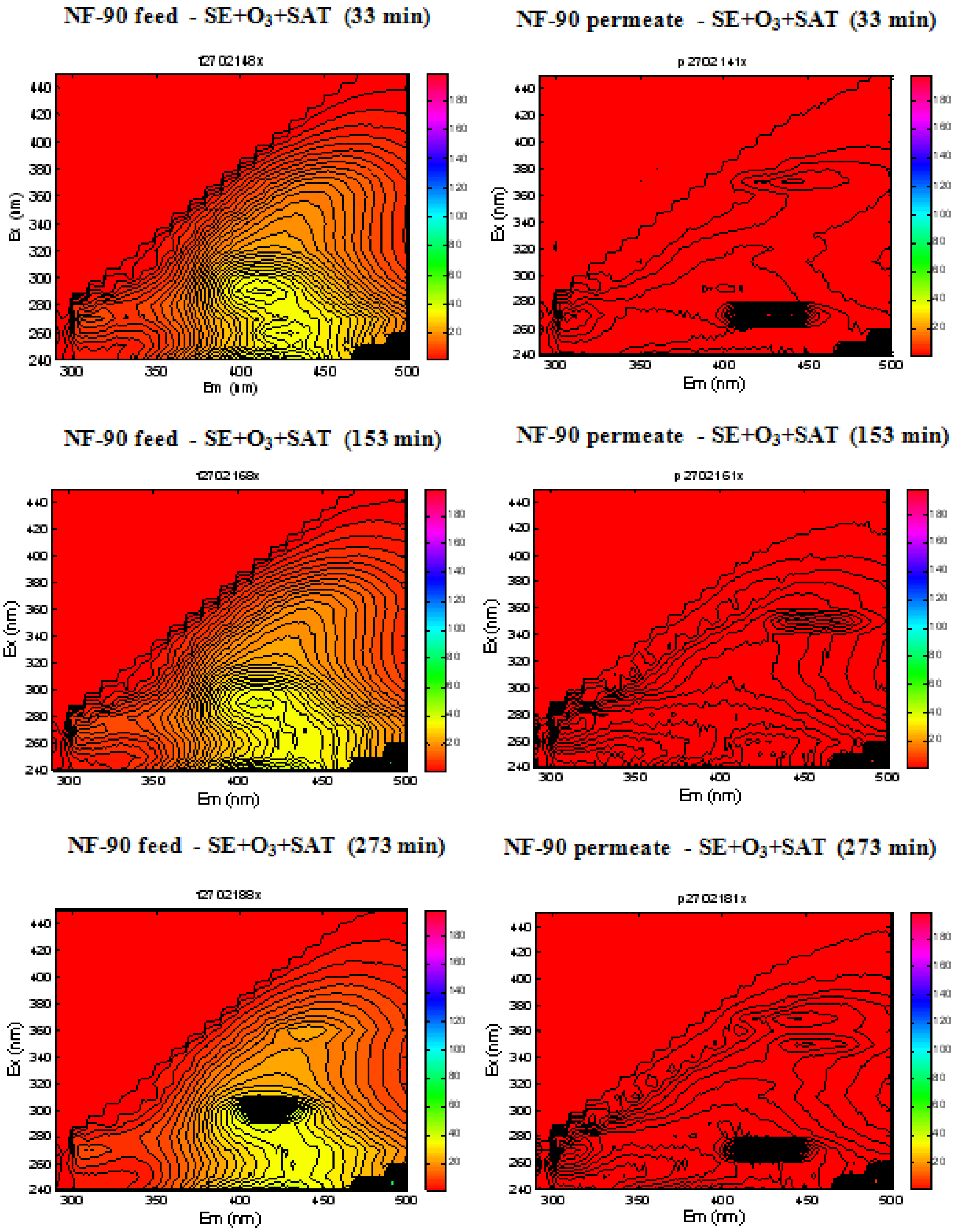

Figure H-2. FEEM spectra for feed and permeate of NF-90 with SE+O_3+SAT

Table H-6. Comparison of FEEM spectra results for feed and permeate using NF-90 fed with SE+O_3+SAT

Time (h:m)	DOC Component		Wavelength (nm)		Peak Intensity	
			Ex	Em	(RA unit)	Reduction
0:33	Humic-like 1	Feed	330	428	23.01	98.4%
		Permeate	350	462	0.37	
	Humic-like 2	Feed	260	426	37.71	98.5%
		Permeate	250	446	0.58	
	Protein-like	Feed	270	310	12.47	92.0%
		Permeate	270	306	0.99	
2:33	Humic-like 1	Feed	330	430	24.22	96.4%
		Permeate	350	444	0.87	
	Humic-like 2	Feed	250	430	37.74	97.4%
		Permeate	260	418	1.00	
	Protein-like	Feed	270	314	12.92	92.2%
		Permeate	270	306	1.01	
4:33	Humic-like 1	Feed	330	424	23.86	97.5%
		Permeate	350	448	0.60	
	Humic-like 2	Feed	260	436	37.84	98.0%
		Permeate	260	434	0.75	
	Protein-like	Feed	270	308	11.86	91.5%
		Permeate	270	306	1.00	
Ave	Humic-like 1	Feed	330	427	23.70	97.4%
		Permeate	350	451	0.61	
	Humic-like 2	Feed	257	431	37.76	98.0%
		Permeate	257	433	0.77	
	Protein-like	Feed	270	311	12.42	91.9%
		Permeate	270	306	1.00	

Appendix I. NF-90 using SE and SE+SAT with recirculation

Process conditions:

Membrane	=	NF-90
Feed pressure	=	50 psi (3.6 bar)
Recovery	=	8%
Temperature	=	20 °C
Filtration mode	=	Partial recirculation (with recirculation of concentrate)

Table I-1. Water quality parameters for NF-90 using SE with recirculation

Time h:m	pH	EC µS/cm	Temp °C	DOC mg/L	UVA_{254} Ab/cm	SUVA L/m-mg	TDS mg/L
Feed							
0:58	7.62	1296	21.0	15.90	0.515	3.24	816
2:58	7.77	1314	21.0	17.08	0.534	3.13	828
4:58	7.88	1326	21.0	16.87	0.546	3.24	835
20:58	7.38	1406	21.5	19.43	0.579	2.98	886
22:58	8.47	1413	21.2	19.41	0.567	2.92	890
Average	**7.82**	**1351**	**21.1**	**17.74**	**0.548**	**3.10**	**851**
Permeate							
0:58	7.16	55	20.2	0.33	0.006	1.84	35
2:58	7.08	59	20.2	0.21	0.003	1.44	37
4:58	7.02	56	19.6	0.22	0.004	1.79	35
20:58	7.03	56	20.5	0.18	0.004	2.20	35
22:58	7.04	59	21.2	0.24	0.006	2.50	37
Average	**7.07**	**57**	**20.3**	**0.24**	**0.005**	**1.95**	**36**
Concentrate							
0:58	7.78	1393	21.2	18.78	0.572	3.05	878
2:58	7.88	1402	21.3	19.22	0.578	3.01	883
4:58	7.94	1416	21.4	19.79	0.602	3.04	892
20:58	8.41	1458	21.7	20.06	0.601	3.00	919
22:58	8.48	1470	21.1	20.61	0.609	2.95	926
Average	**8.10**	**1428**	**21.3**	**19.69**	**0.592**	**3.01**	**900**

Table I-2. DOC and TDS removal for NF-90 using SE with recirculation

Time (h:m)	DOC (mg/L)			TDS (mg/L)		
	Feed, Cf	Permeate, Cp	1-Cp/Cf	Feed, Cf	Permeate, Cp	1-Cp/Cf
0:58	15.90	0.33	97.9%	816	35	95.8%
2:58	17.08	0.21	98.8%	828	37	95.5%
4:58	16.87	0.22	98.7%	835	35	95.8%
20:58	19.43	0.18	99.1%	886	35	96.0%
22:58	19.41	0.24	98.8%	890	37	95.8%
Average	**17.74**	**0.24**	**98.6%**	**851**	**36**	**95.8%**

Table I-3. Water quality parameters for NF-90 using SE+SAT with recirculation

Time h:m	pH	EC µS/cm	Temp °C	DOC mg/L	UVA_{254} Ab/cm	SUVA L/m-mg	TDS mg/L
Feed							
0:51	8.24	1264	19.7	7.94	0.032	0.403	796
2:51	8.28	1277	20.0	8.21	0.028	0.341	805
16:51	8.60	1353	21.2	9.51	0.031	0.326	852
18:51	8.55	1356	21.3	9.76	0.030	0.307	854
20:51	8.57	1366	21.2	10.05	0.030	0.299	861
22:51	8.58	1374	21.1	10.22	0.030	0.294	866
Average	**8.47**	**1332**	**20.8**	**9.28**	**0.030**	**0.328**	**839**
Permeate							
0:51	7.21	134	20.2	0.11	0.002	1.802	84
2:51	7.21	119	20.3	0.07	0.001	1.515	75
16:51	7.43	144	20.9	0.03	0.001	3.704	91
18:51	7.46	149	20.8	0.02	0.001	5.000	94
20:51	7.48	150	20.9	0.03	0.001	4.000	95
22:51	7.57	179	20.5	0.07	0.002	2.778	113
Average	**7.39**	**146**	**20.6**	**0.05**	**0.001**	**3.133**	**92**
Concentrate							
0:51	8.27	1350	20.6	10.11	0.030	0.297	851
2:51	8.30	1360	20.8	10.40	0.032	0.308	857
16:51	8.61	1388	21.8	10.94	0.031	0.283	874
18:51	8.56	1393	21.8	10.79	0.031	0.287	878
20:51	8.58	1398	21.9	11.33	0.031	0.274	881
22:51	8.59	1406	21.8	11.45	0.031	0.271	886
Average	**8.49**	**1383**	**21.5**	**10.84**	**0.031**	**0.287**	**871**

Table I-4. DOC and TDS removal for NF-90 using SE+SAT with recirculation

Time (h:m)	DOC (mg/L)			TDS (mg/L)		
	Feed, Cf	Permeate, Cp	1-Cp/Cf	Feed, Cf	Permeate, Cp	1-Cp/Cf
0:51	7.94	0.11	98.6%	796	84	89.4%
2:51	8.21	0.07	99.2%	805	75	90.7%
16:51	9.51	0.03	99.7%	852	91	89.4%
18:51	9.76	0.02	99.8%	854	94	89.0%
20:51	10.05	0.03	99.8%	861	95	89.0%
22:51	10.22	0.07	99.3%	866	113	87.0%
Average	**9.28**	**0.05**	**99.4%**	**839**	**92**	**89.1%**

Appendix J. NF-90 using SE+O_3 and SE+O_3+SAT with recirculation

Process conditions:

Membrane	=	NF-90
Feed pressure	=	50 psi (3.6 bar)
Recovery	=	8%
Temperature	=	20 ^oC
Filtration mode	=	Partial recirculation (with recirculation of concentrate)

Table J-1. Water quality parameters for NF-90 using SE+O_3 with recirculation

Time h:m	pH	EC µS/cm	Temp °C	DOC mg/L	UVA Ab/cm	SUVA L/m-mg	TDS mg/L
Feed							
0:40	7.62	1295	20.5	16.75	0.388	2.32	816
2:40	7.77	1297	20.6	16.87	0.398	2.36	817
17:40	7.88	1417	20.6	17.27	0.396	2.29	893
19:40	7.38	1426	20.4	17.37	0.397	2.29	898
21:40	8.47	1433	20.4	17.72	0.399	2.25	903
Average	**7.82**	**1374**	**20.5**	**17.20**	**0.396**	**2.30**	**865**
Permeate							
0:40	7.10	82	20.2	0.50	0.004	0.69	52
2:40	7.14	74	20.1	0.42	0.002	0.48	47
17:40	7.31	98	19.9	0.52	0.003	0.48	62
19:40	7.32	106	19.2	0.57	0.003	0.52	67
21:40	7.38	102	19.4	0.55	0.003	0.55	64
Average	**7.25**	**92**	**19.8**	**0.51**	**0.003**	**0.55**	**58**
Concentrate							
0:40	7.78	1387	21.1	17.35	0.421	2.43	874
2:40	7.88	1407	21.3	18.51	0.424	2.29	886
17:40	7.94	1489	21.2	19.38	0.418	2.16	938
19:40	8.41	1498	20.9	18.80	0.441	2.35	944
21:40	8.48	1503	20.8	18.87	0.426	2.26	947
Average	**8.10**	**1457**	**21.1**	**18.58**	**0.426**	**2.30**	**918**

Table J-2. DOC and TDS removal for NF-90 using SE+O_3 with recirculation

Time (h:m)	DOC (mg/L)			TDS (mg/L)		
	Feed, Cf	Permeate, Cp	1-Cp/Cf	Feed, Cf	Permeate, Cp	1-Cp/Cf
0:40	16.75	0.50	97.0%	816	52	93.7%
2:40	16.87	0.42	97.5%	817	47	94.3%
17:40	17.27	0.52	97.0%	893	62	93.1%
19:40	17.37	0.57	96.7%	898	67	92.6%
21:40	17.72	0.55	96.9%	903	64	92.9%
Average	**17.20**	**0.51**	**97.0%**	**865**	**58**	**93.3%**

Table J-3. Water quality parameters for NF-90 using $SE+O_3+SAT$ with recirculation

Time h:m	pH	EC µS/cm	Temp °C	DOC mg/L	UVA Ab/cm	SUVA L/m-mg	TDS mg/L
Feed							
1:32	8.18	1186	21.0	8.68	0.009	0.10	747
3:32	8.23	1200	20.5	8.46	0.010	0.12	756
17:32	8.55	1330	20.8	9.28	0.010	0.11	838
19:32	8.56	1350	20.8	9.26	0.010	0.11	851
21:32	8.58	1366	20.9	9.37	0.011	0.12	861
23:32	8.59	1391	20.7	9.67	0.010	0.10	876
Average	**8.45**	**1304**	**20.8**	**9.12**	**0.010**	**0.11**	**821**
Permeate							
1:32	7.15	101	20.1	0.36	0.001	0.28	64
3:32	7.20	101	20.0	0.22	0.002	0.93	64
17:32	7.27	107	20.4	0.22	0.003	1.36	67
19:32	7.30	109	20.6	0.22	0.002	0.90	69
21:32	7.32	112	20.3	0.21	0.001	0.49	71
23:32	7.36	115	19.9	0.30	0.002	0.68	72
Average	**7.27**	**108**	**20.2**	**0.25**	**0.002**	**0.77**	**68**
Concentrate							
1:32	8.22	1273	21.2	8.66	0.013	0.15	802
3:32	8.26	1289	20.9	8.83	0.011	0.12	812
17:32	8.56	1408	21.1	9.42	0.011	0.12	887
19:32	8.56	1421	21.3	9.42	0.013	0.14	895
21:32	8.60	1439	21.3	9.68	0.010	0.10	907
23:32	8.60	1452	21.0	9.66	0.011	0.11	915
Average	**8.47**	**1380**	**21.1**	**9.28**	**0.012**	**0.12**	**870**

Table J-4. DOC and TDS removal for NF-90 using $SE+O_3+SAT$ with recirculation

Time (h:m)	DOC (mg/L)			TDS (mg/L)		
	Feed, Cf	Permeate, Cp	1-Cp/Cf	Feed, Cf	Permeate, Cp	1-Cp/Cf
1:32	8.68	0.36	95.8%	747	64	91.5%
3:32	8.46	0.22	97.4%	756	64	91.6%
17:32	9.28	0.22	97.6%	838	67	92.0%
19:32	9.26	0.22	97.6%	851	69	91.9%
21:32	9.37	0.21	97.8%	861	71	91.8%
23:32	9.67	0.30	96.9%	876	72	91.7%
Average	**9.12**	**0.25**	**97.2%**	**821**	**68**	**91.7%**